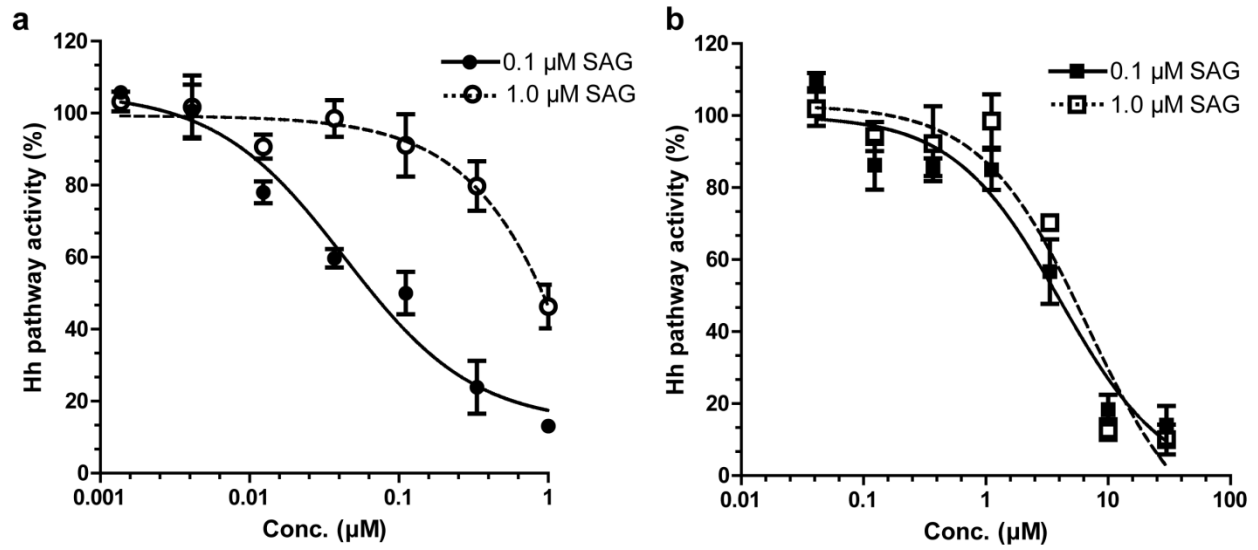
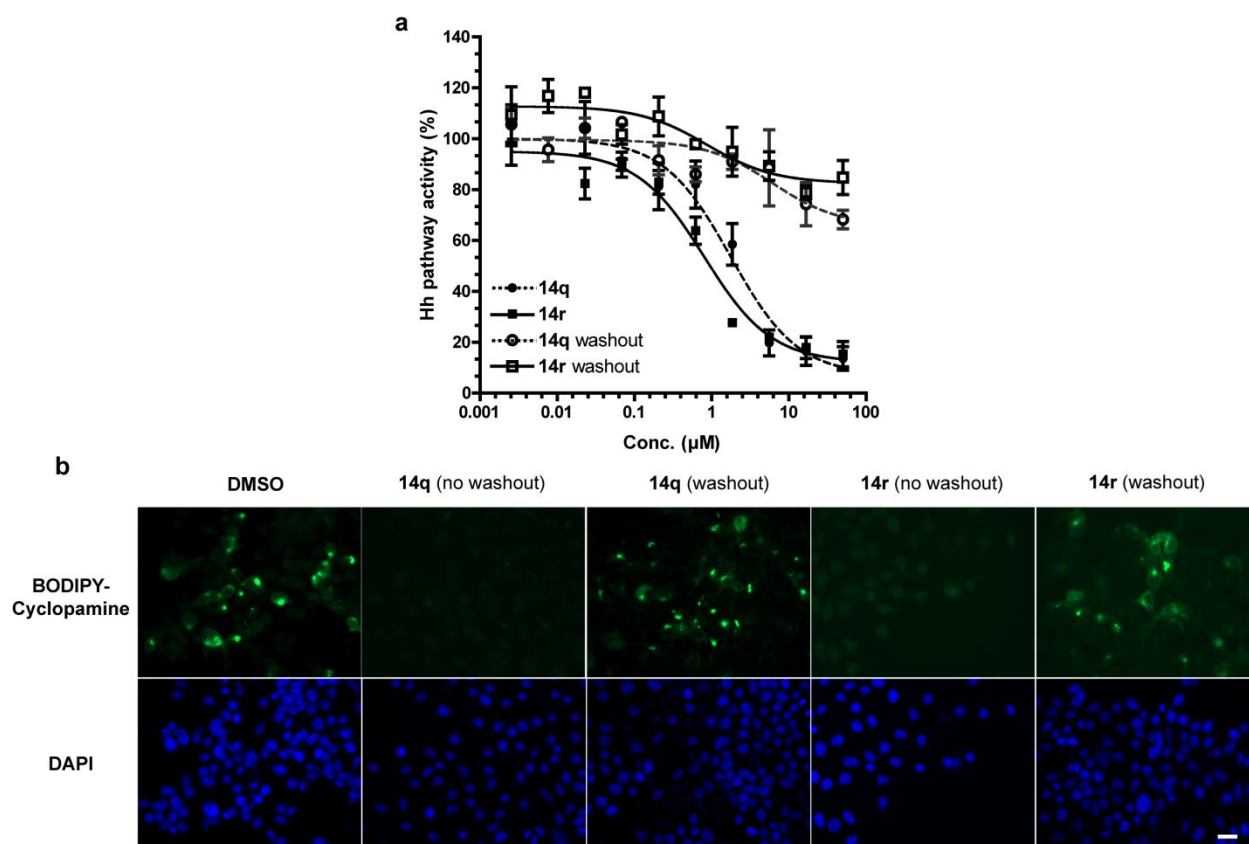
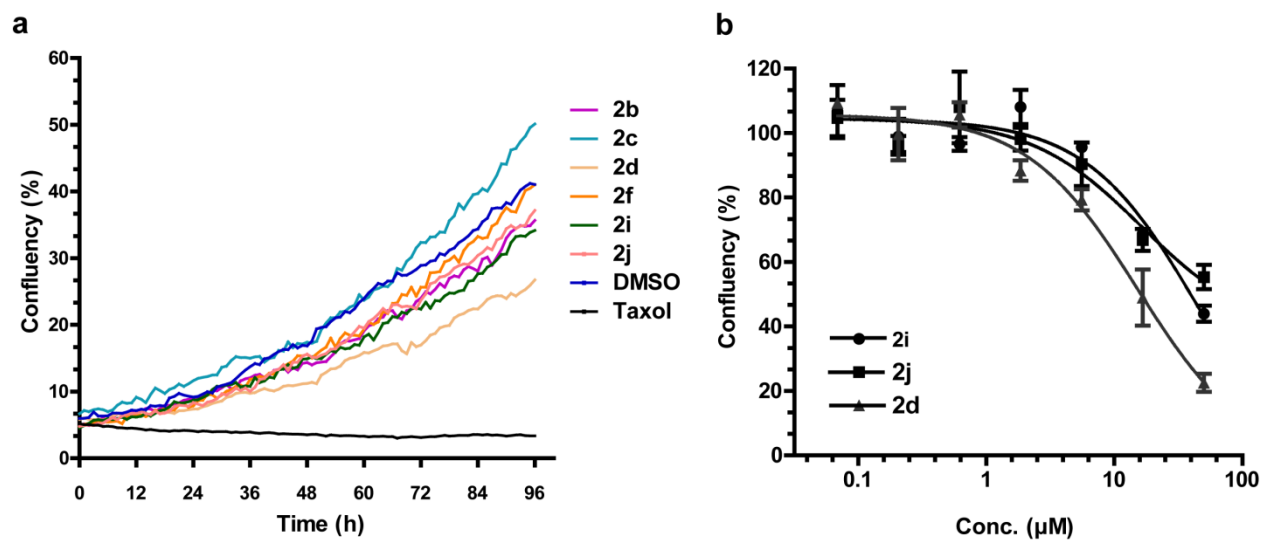




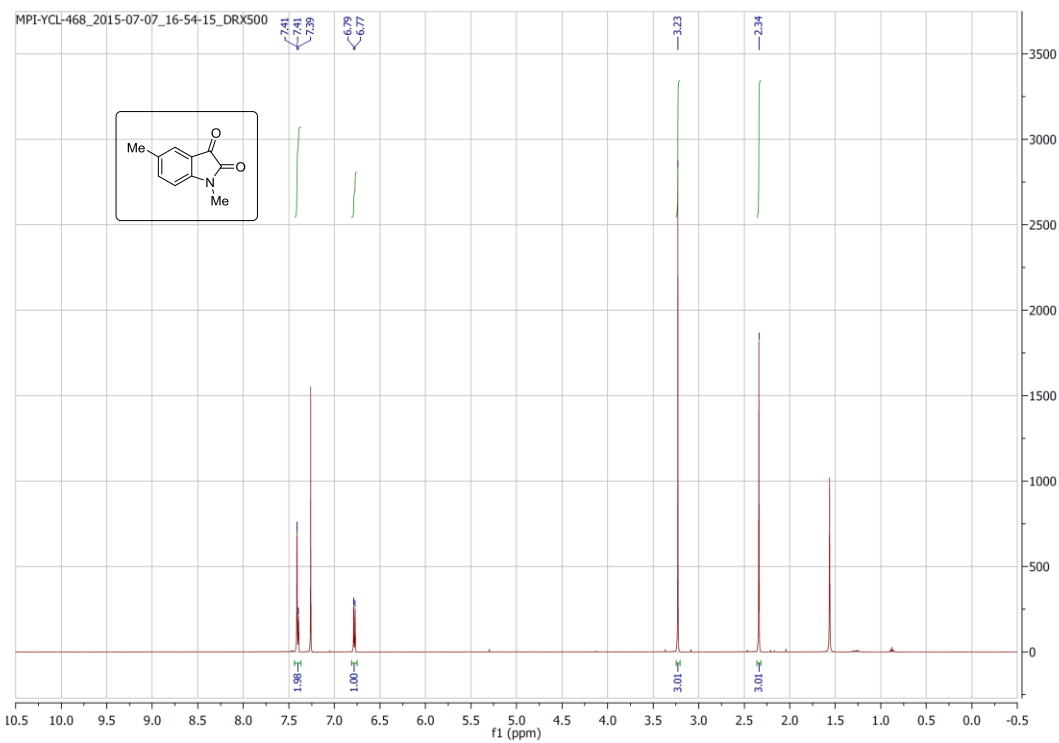
Supplementary Figure 1. SAG competition assay with vismodegib and GANT 61. Influence of vismodegib (a) and GANT-61 (b) on the Gli-mediated reporter gene expression upon Hh pathway activation in Shh Light II cells by SAG (0.1 μM and 1 μM). Nonlinear regression analysis was performed using a four parameter fit. Data are mean values of three independent experiments ($n = 3$) $\pm$ s.d. and were normalized to cells treated with the respective concentration of SAG (set to 100 %).



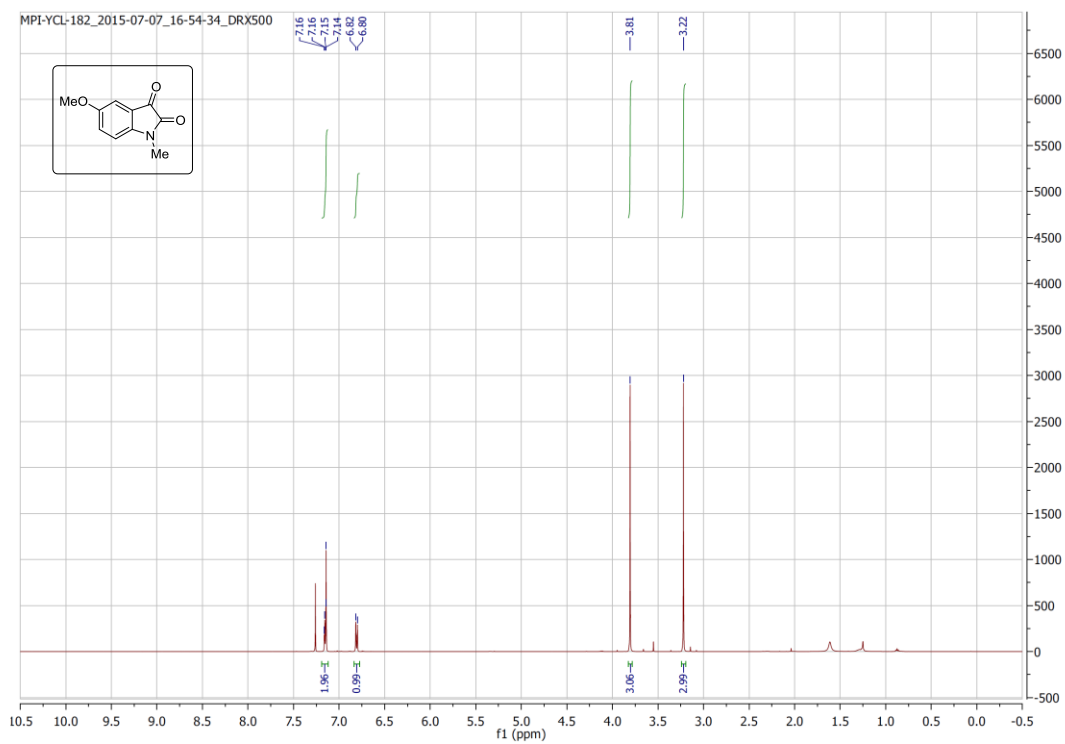
Supplementary Figure 2. Wash out experiment to access the mode of inhibition of **14q** and **14r**. **(a)** Hh signaling activity was determined using the in Gli-dependent reporter gene expression in Shh Light II cells. Cells were treated with 1.5 μM purmorphamine and different concentrations of compounds for 30 min prior to washout followed by addition of fresh media containing 1.5 μM purmorphamine or DMSO as a control and incubation for 48 h. Firefly and Renilla luciferase activities were then determined. Ratios of firefly luciferase/Renilla luciferase signals were calculated as a measure of Hedgehog pathway activity. Nonlinear regression analysis was performed using a four parameter fit. Data are mean values of three independent experiments ($n = 3$) $\pm$ s.d. **(b)** HEK293T cells were transiently transfected with Smo-expressing plasmid or empty vector. 48 h later cells were treated with 10 μM of **14q** or **14r** and DMSO as a control for one hour. Cells were then washed three times with media and supplemented with 5 nM BODIPY-cyclopamine (green) for 1 h prior to fixation and staining with DAPI to visualize the nuclei (blue). Scale bar: 20 μm .



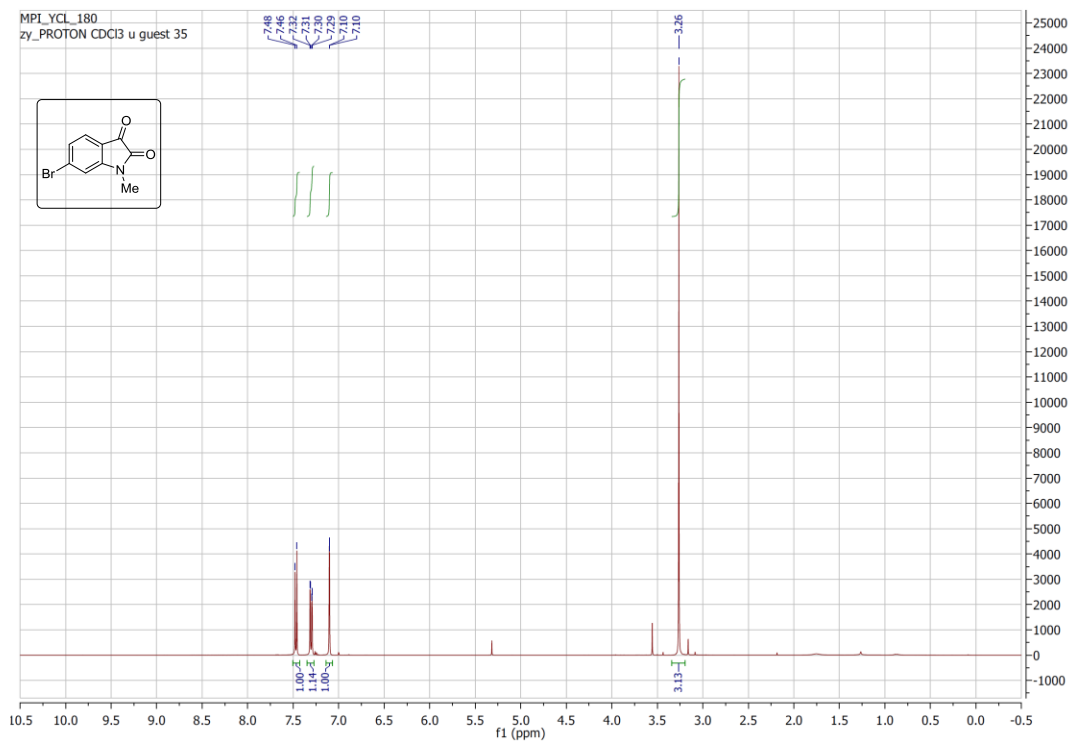
Supplementary Figure 3. Influence of selected compounds on HeLa cell proliferation. **(a)** HeLa cells were treated with the compounds and DMSO or taxol as controls for 96 h. Live-cell imaging using the IncuCyte Zoom[®] imaging system was performed to assess cell confluency. The data are representative results of three independent replicates. **(b)** Dose-dependent decrease in cell confluency by compound **2i**, **2j** and **2d** after treatment of HeLa cells for 72 h. Nonlinear regression analysis was performed using a four parameter fit. Data are mean values of three independent experiments ($n = 3$) $\pm$ s.d.



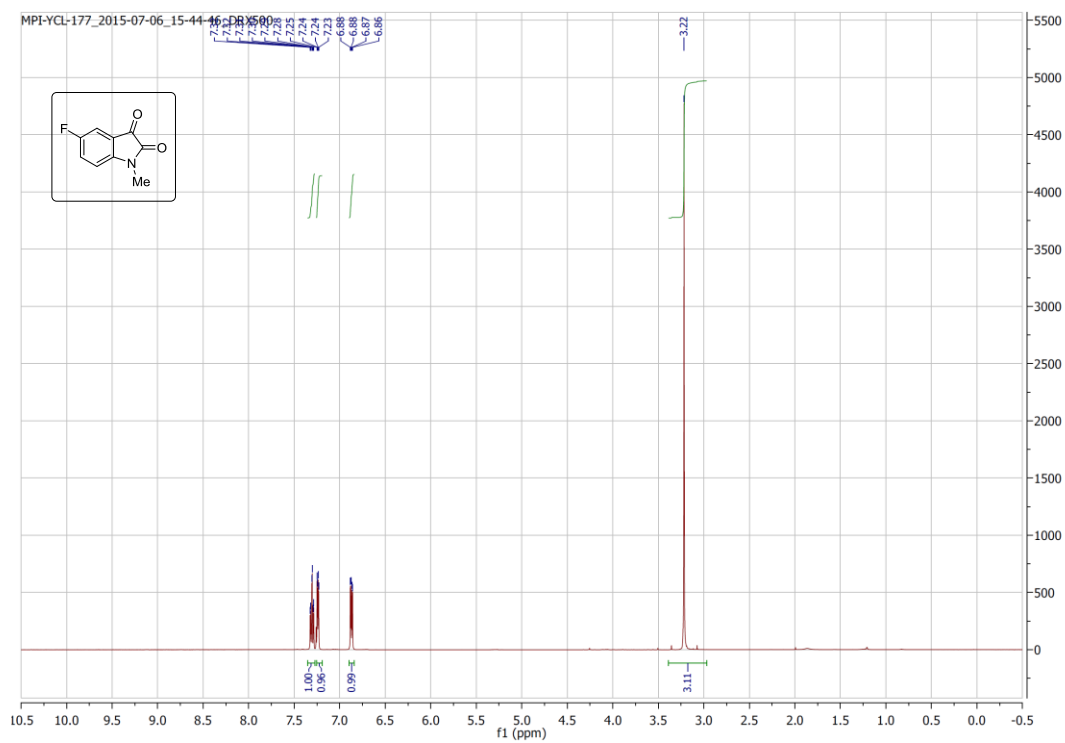
Supplementary Figure 4. ^1H NMR spectrum for S8a.



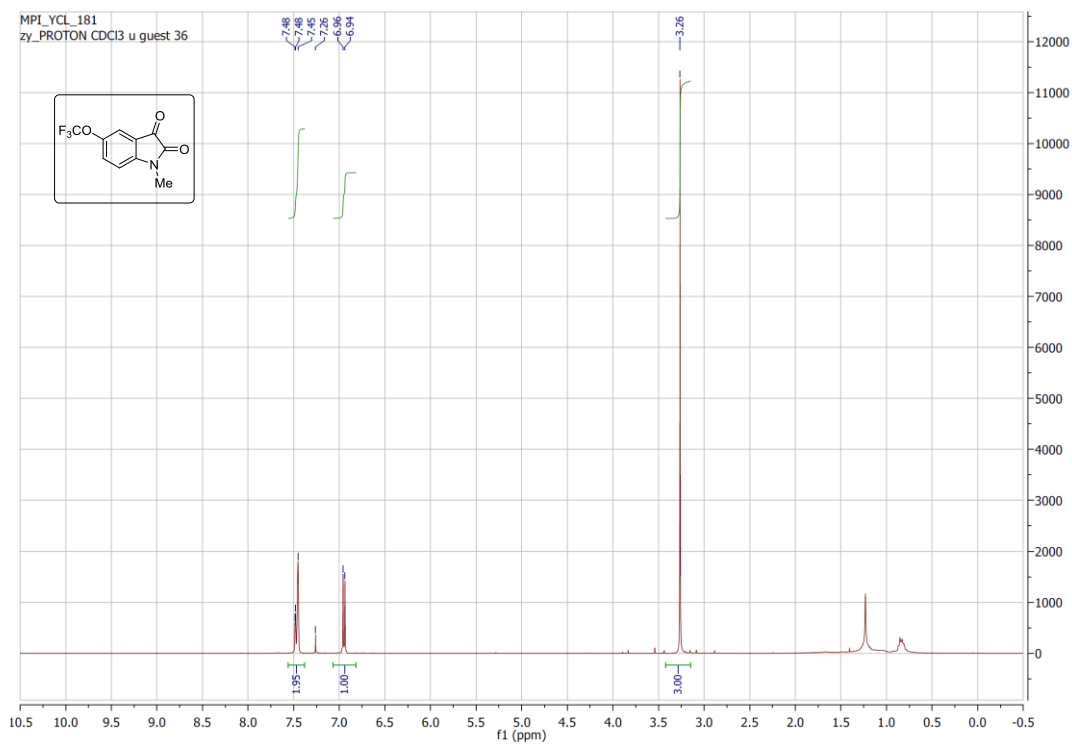
Supplementary Figure 5. ^1H NMR spectrum for S8b.



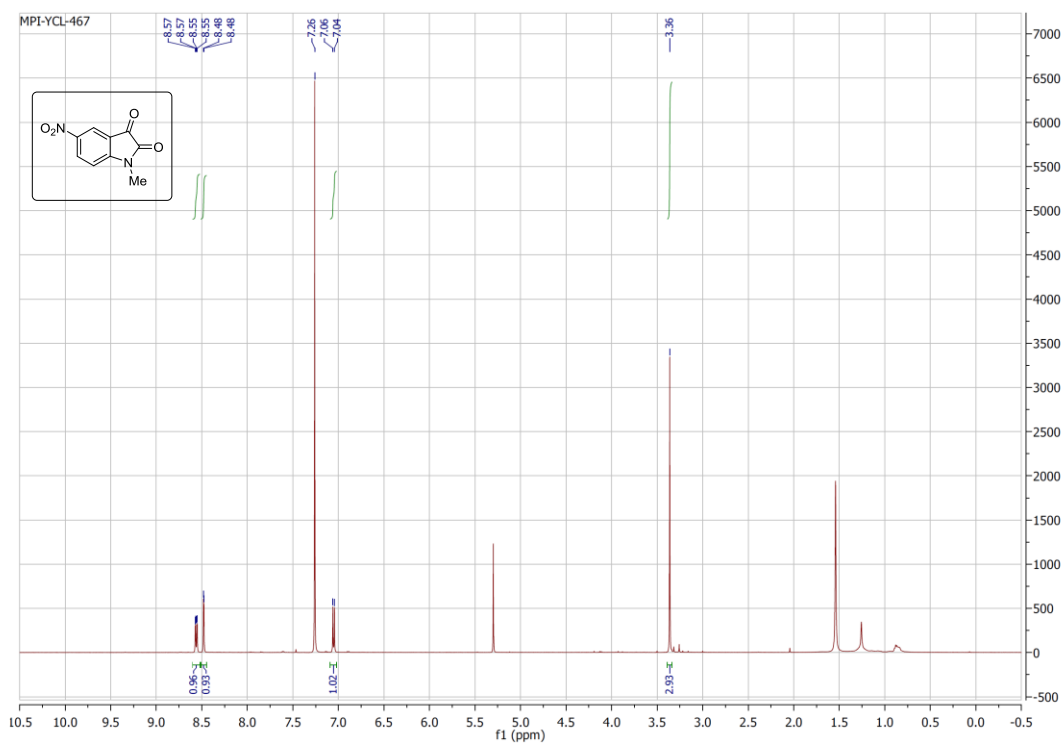
Supplementary Figure 6. ^1H NMR spectrum for **S8c**.



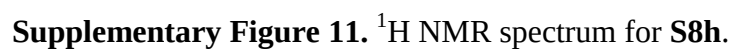
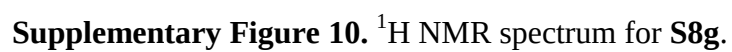
Supplementary Figure 7. ^1H NMR spectrum for **S8d**.

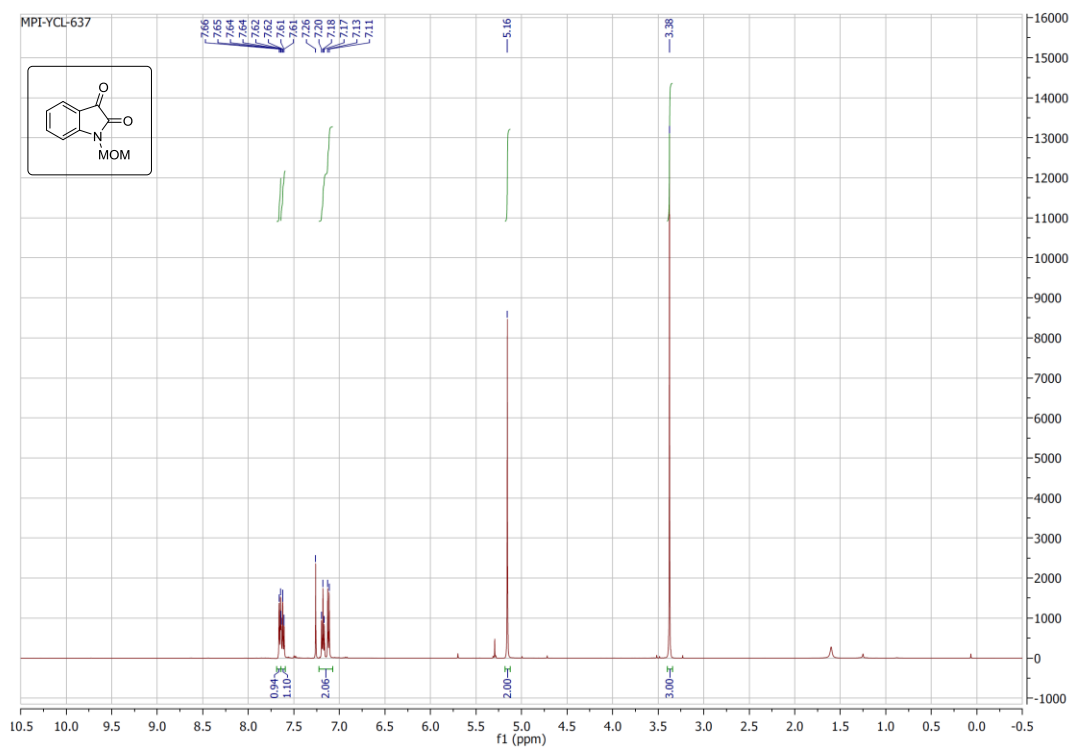


Supplementary Figure 8. ^1H NMR spectrum for **S8e**.

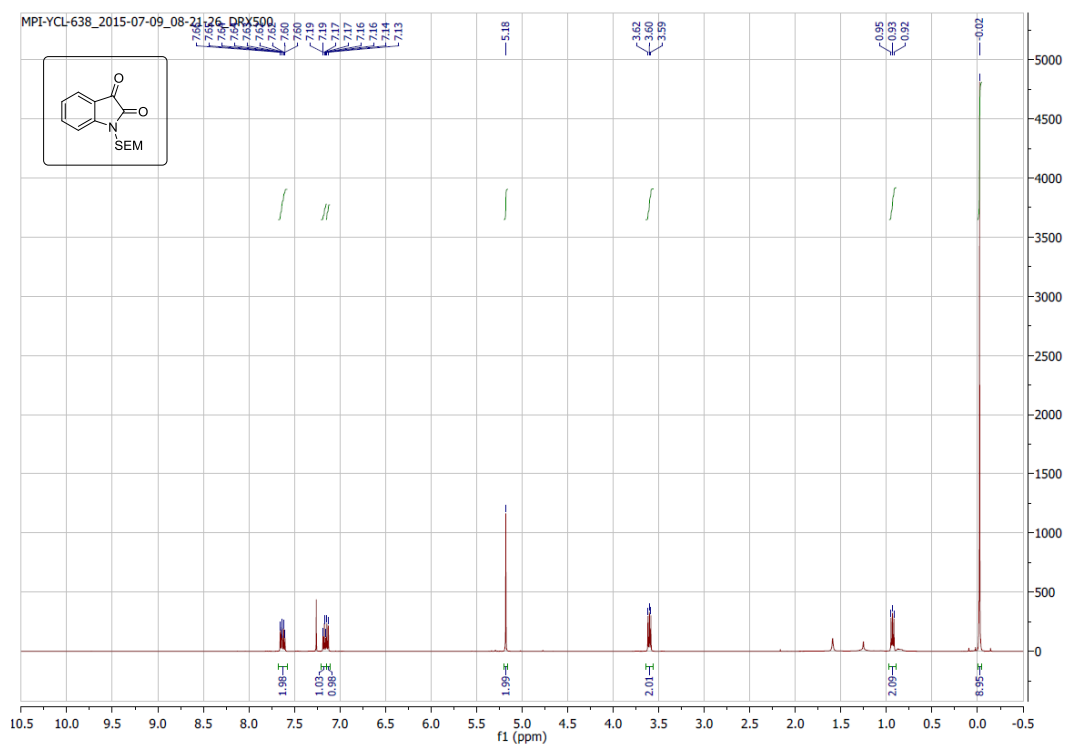


Supplementary Figure 9. ^1H NMR spectrum for **S8f**.

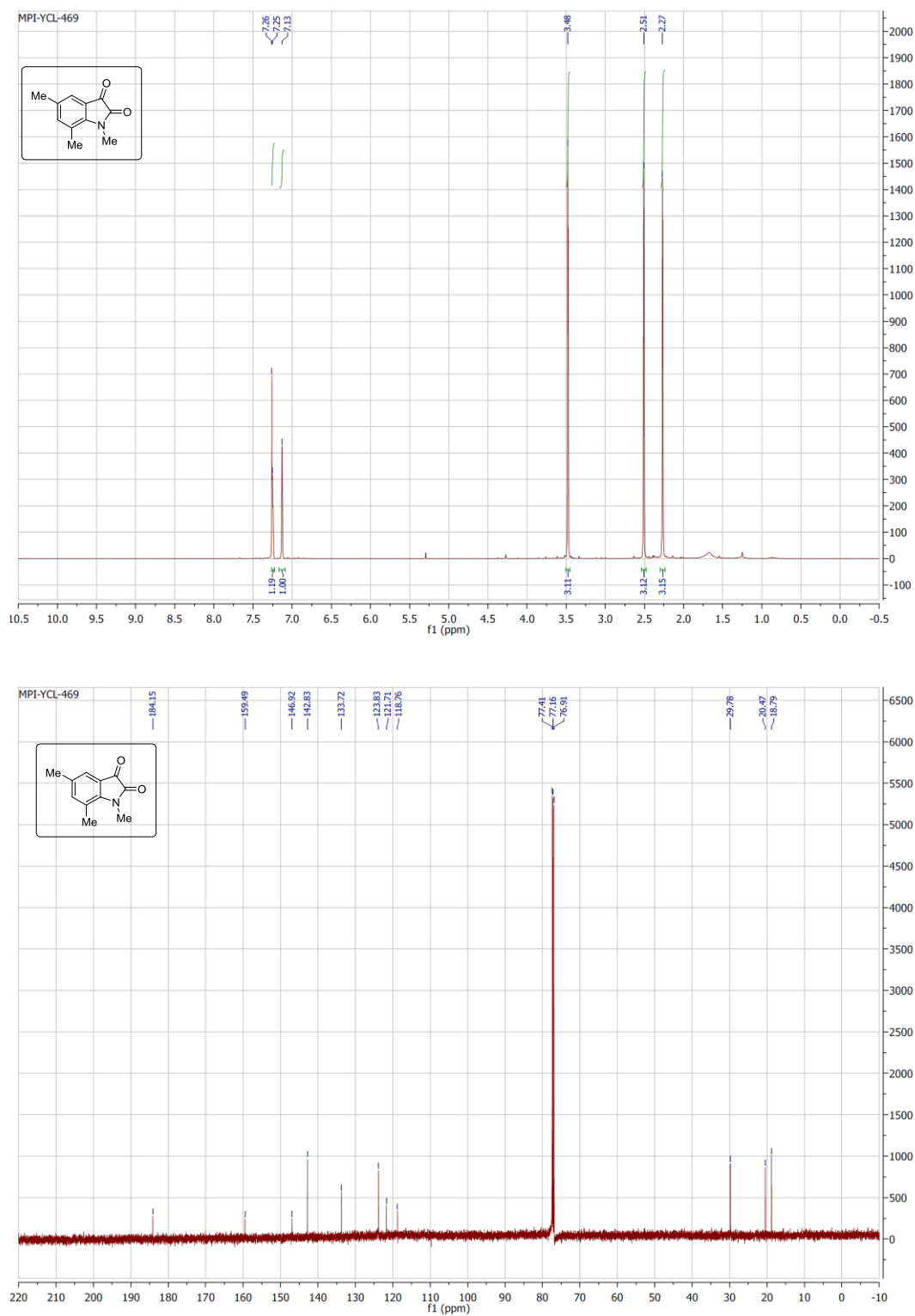




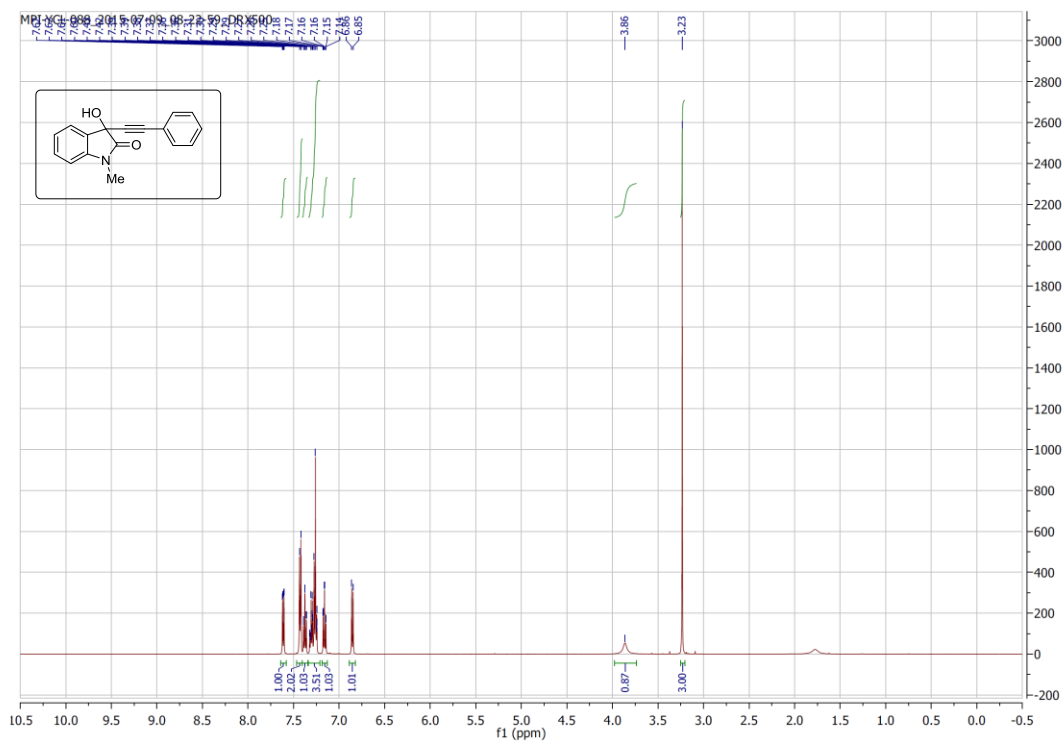
Supplementary Figure 12. ^1H NMR spectrum for **S8i**.



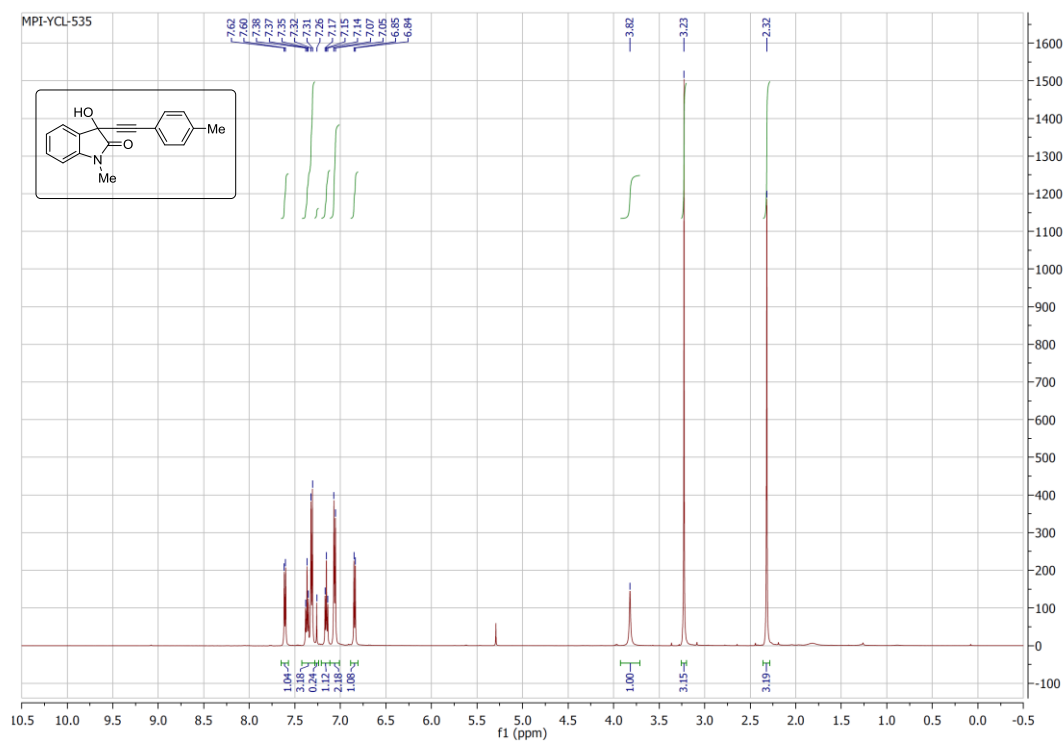
Supplementary Figure 13. ^1H NMR spectrum for **S8j**.



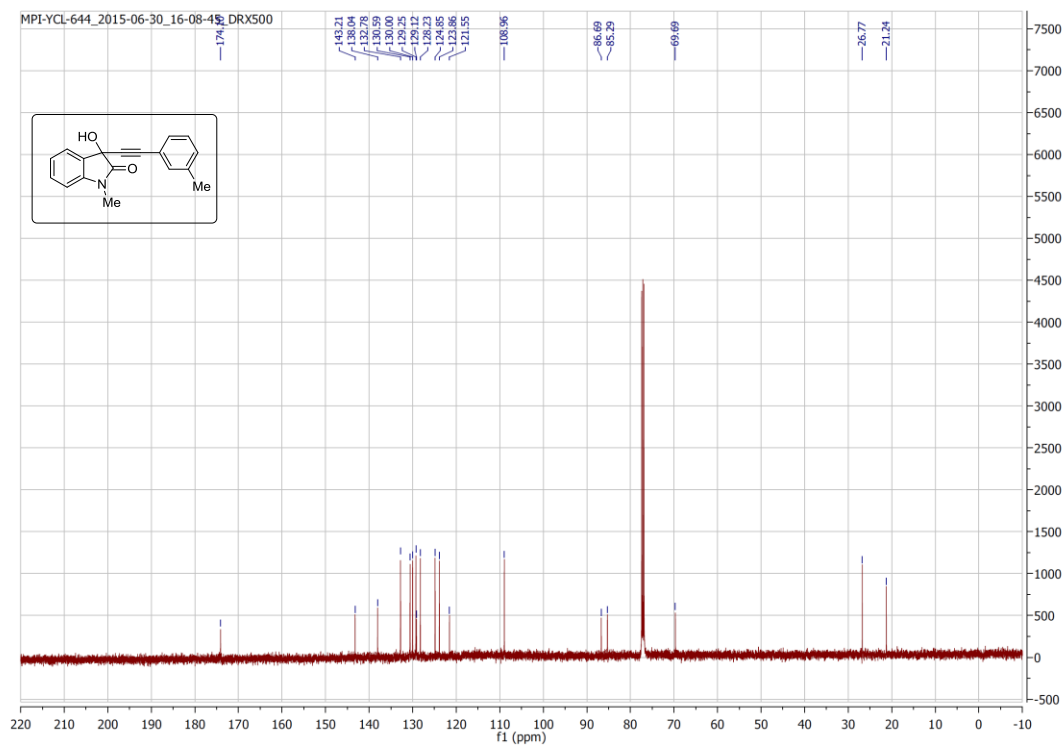
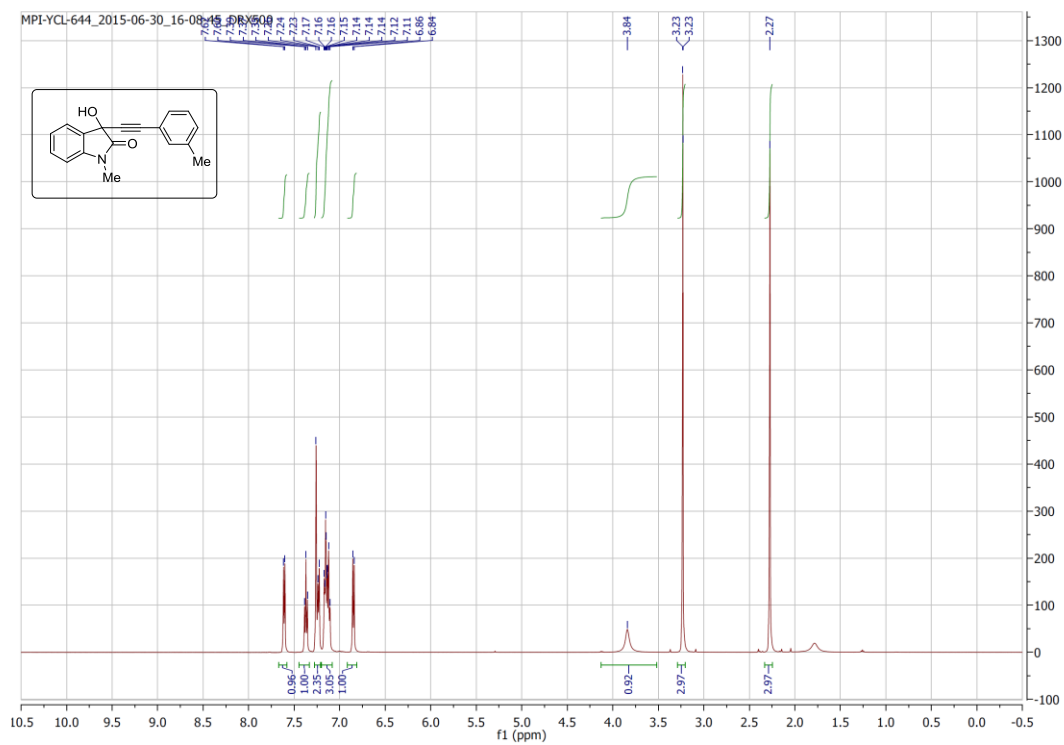
Supplementary Figure 14. ¹H and ¹³C NMR spectra for **S8k**.



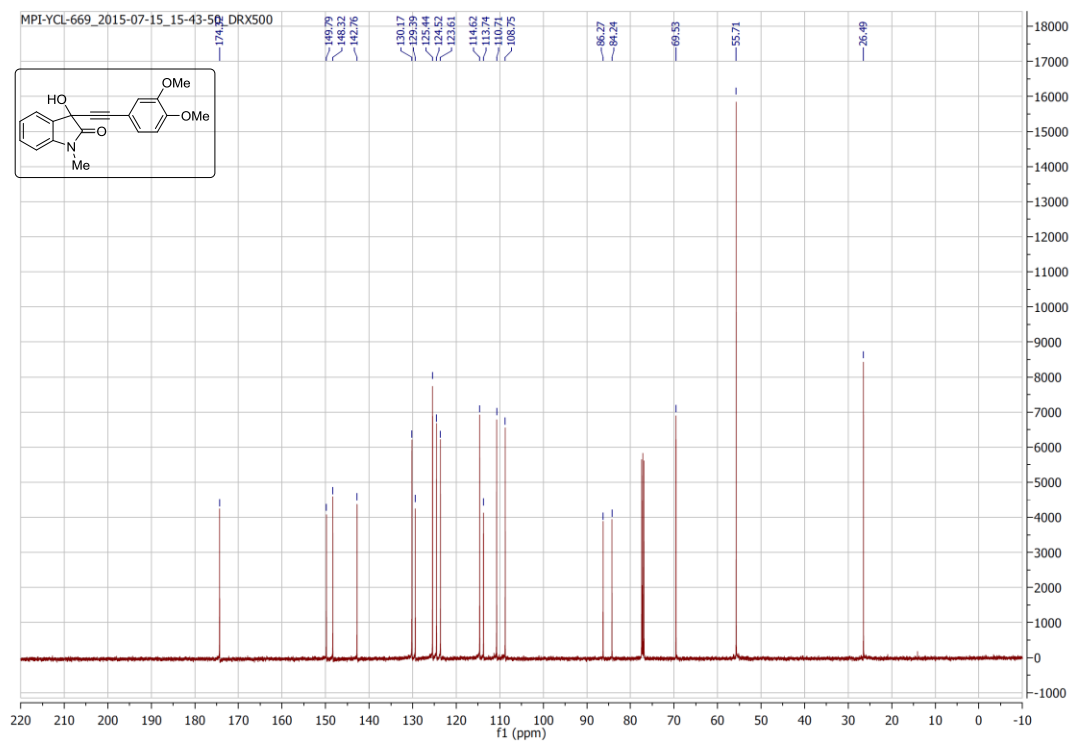
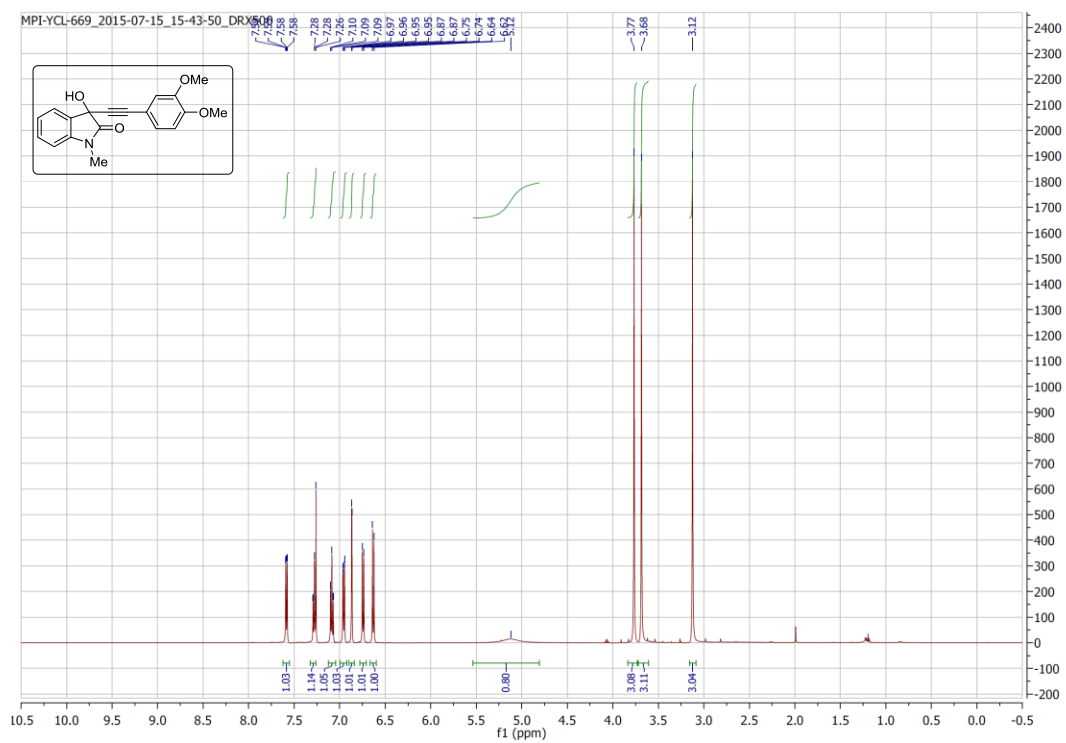
Supplementary Figure 15. ^1H NMR spectrum for **S9a**.



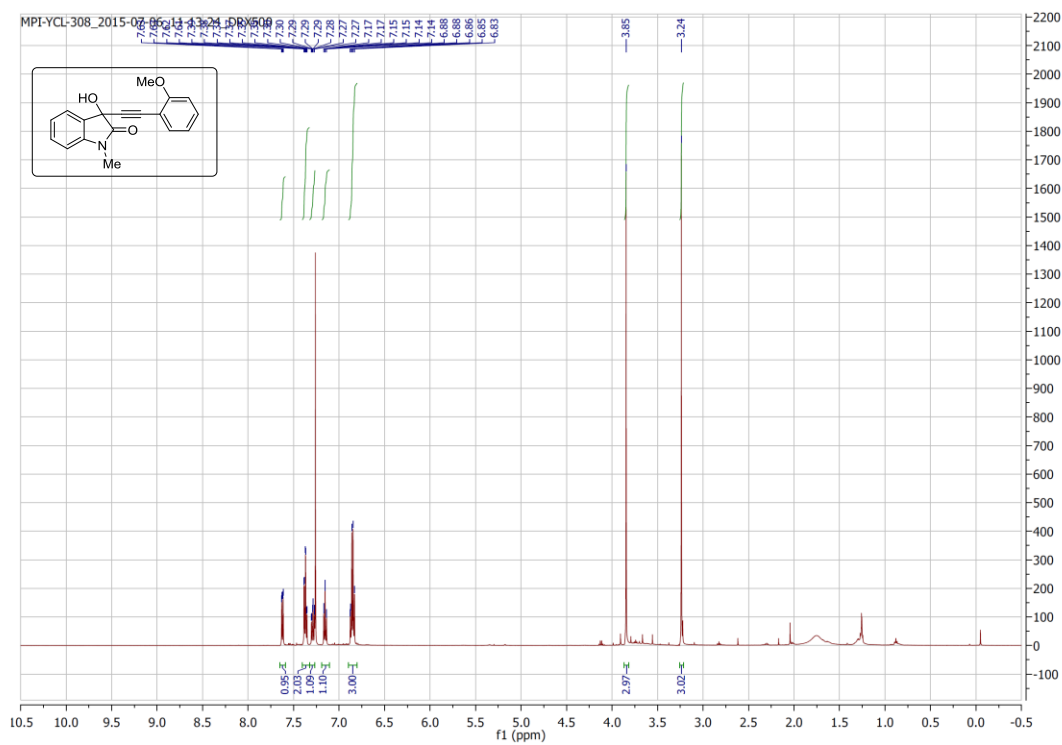
Supplementary Figure 16. ^1H NMR spectrum for **S9b**.



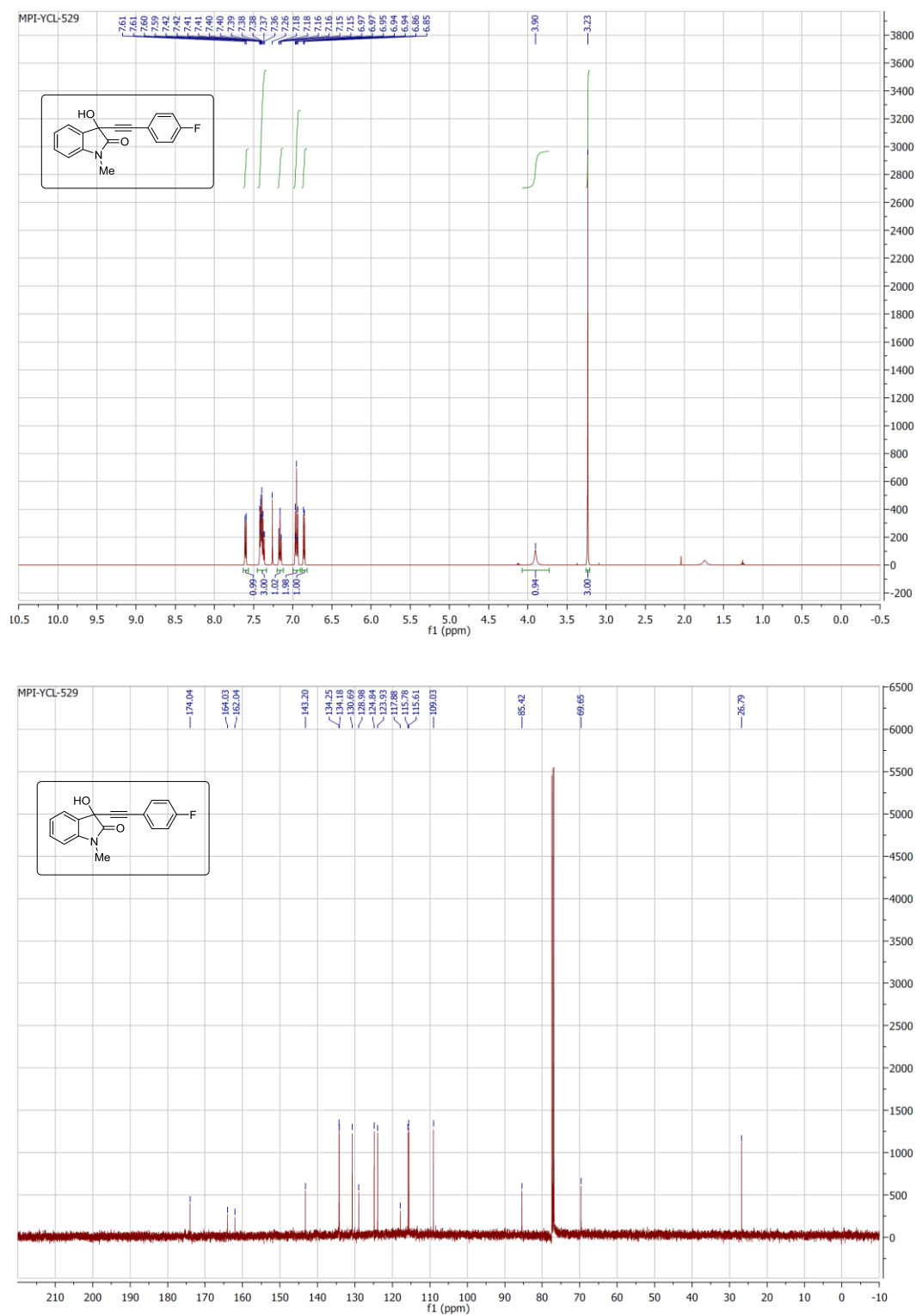
Supplementary Figure 17. ^1H and ^{13}C NMR spectra for **S9c**.



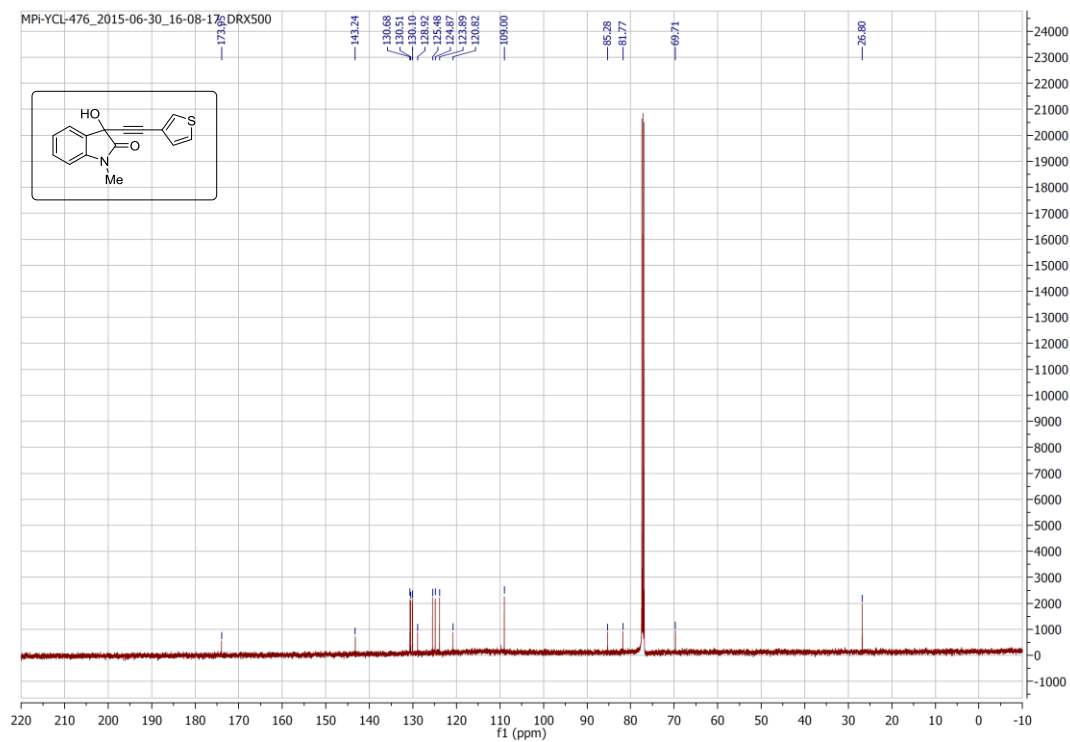
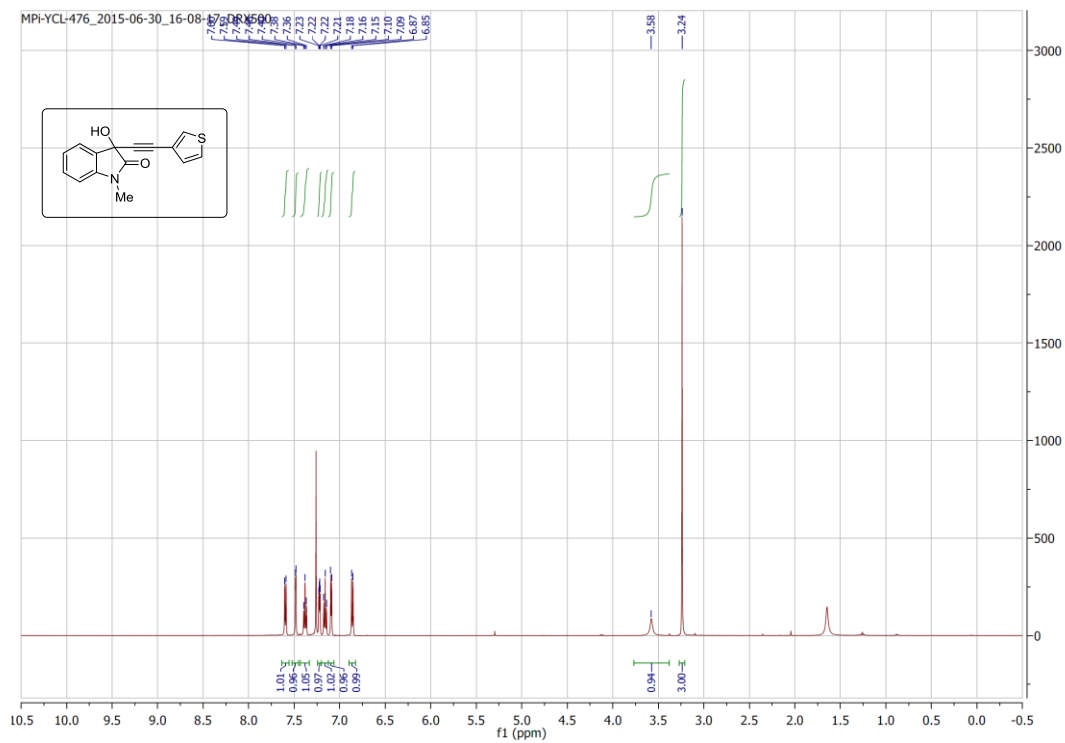
Supplementary Figure 18. ¹H and ¹³C NMR spectra for S9d.



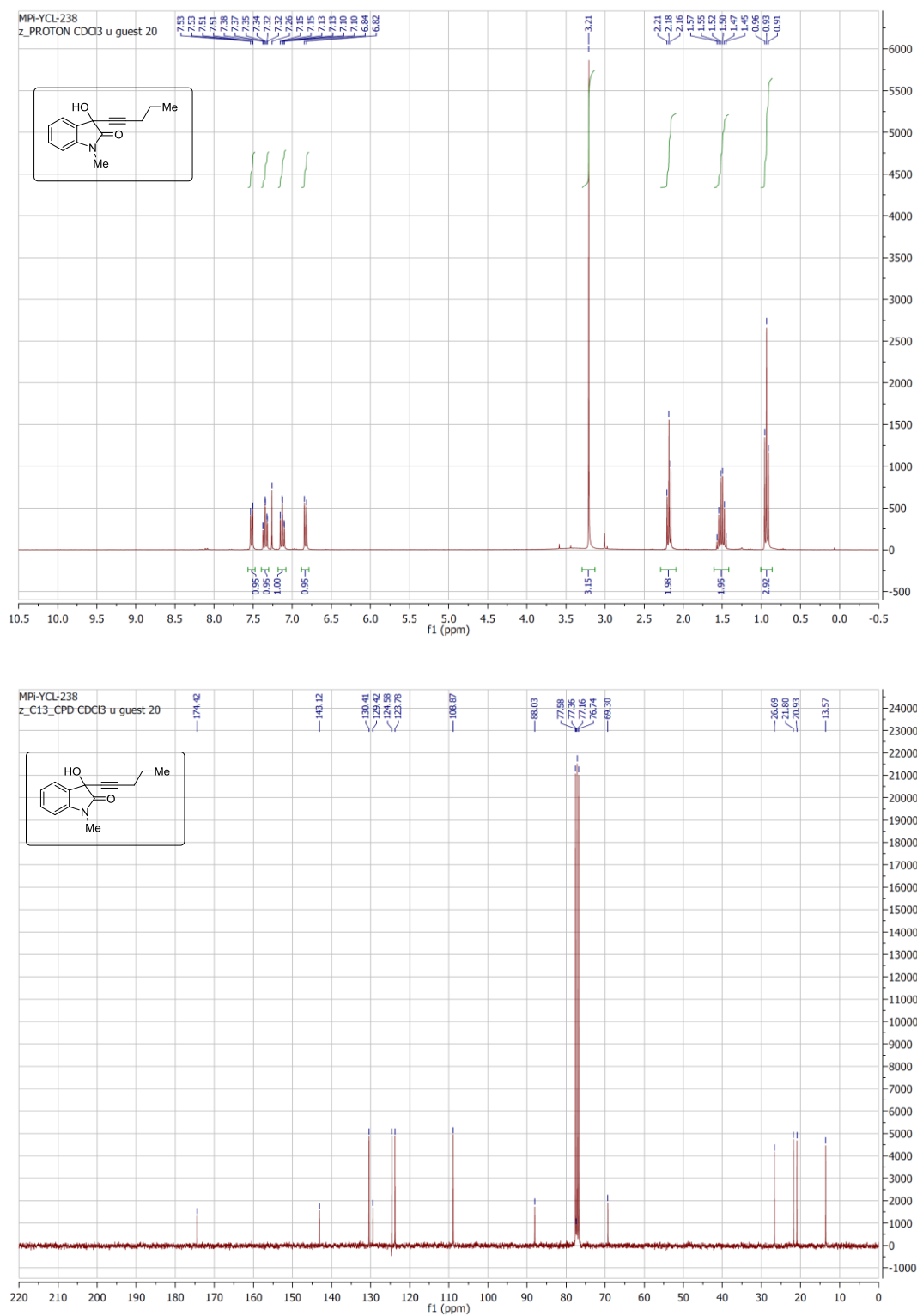
Supplementary Figure 19. ^1H NMR spectrum for **S9e**.



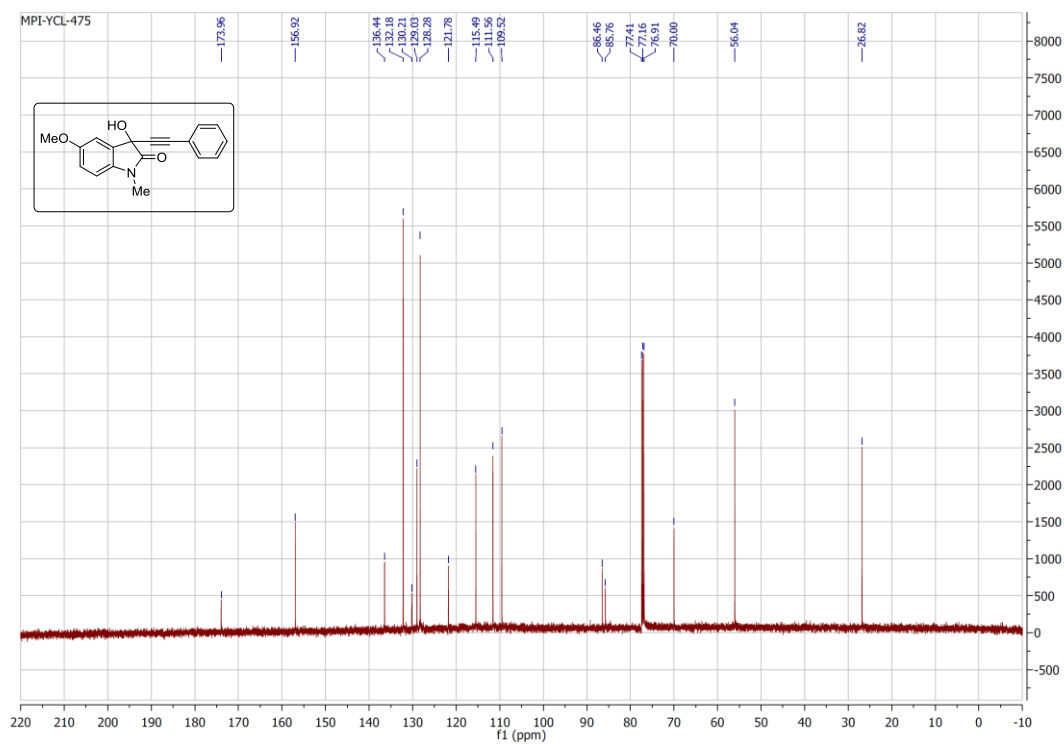
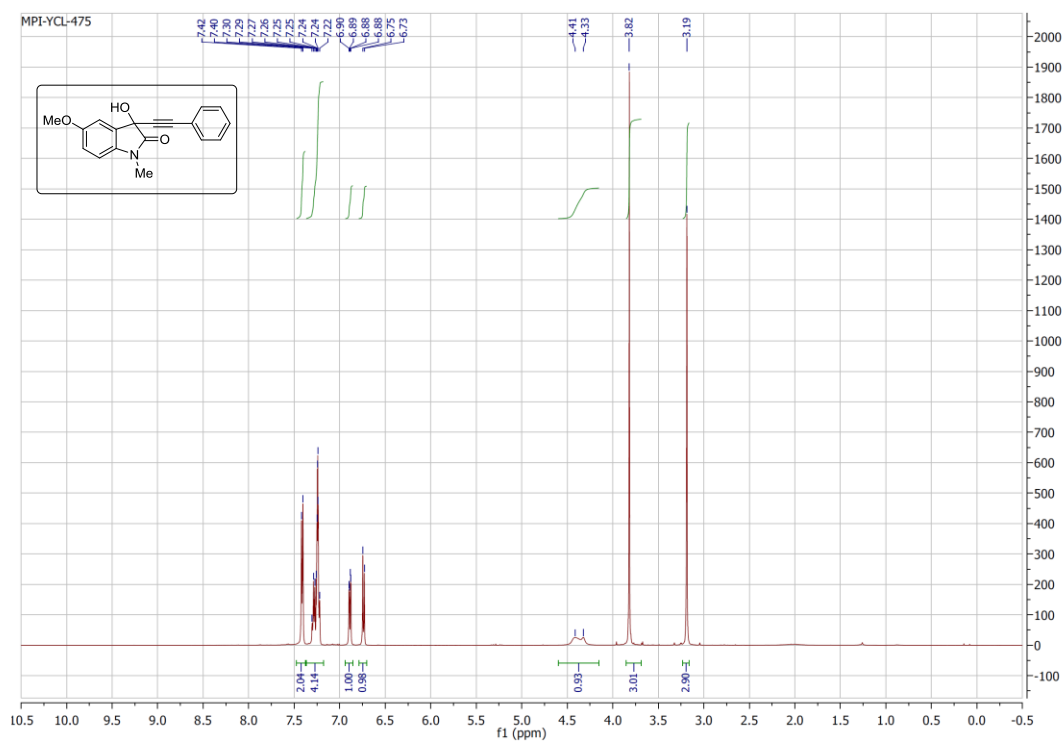
Supplementary Figure 20. ¹H and ¹³C NMR spectra for S9f.



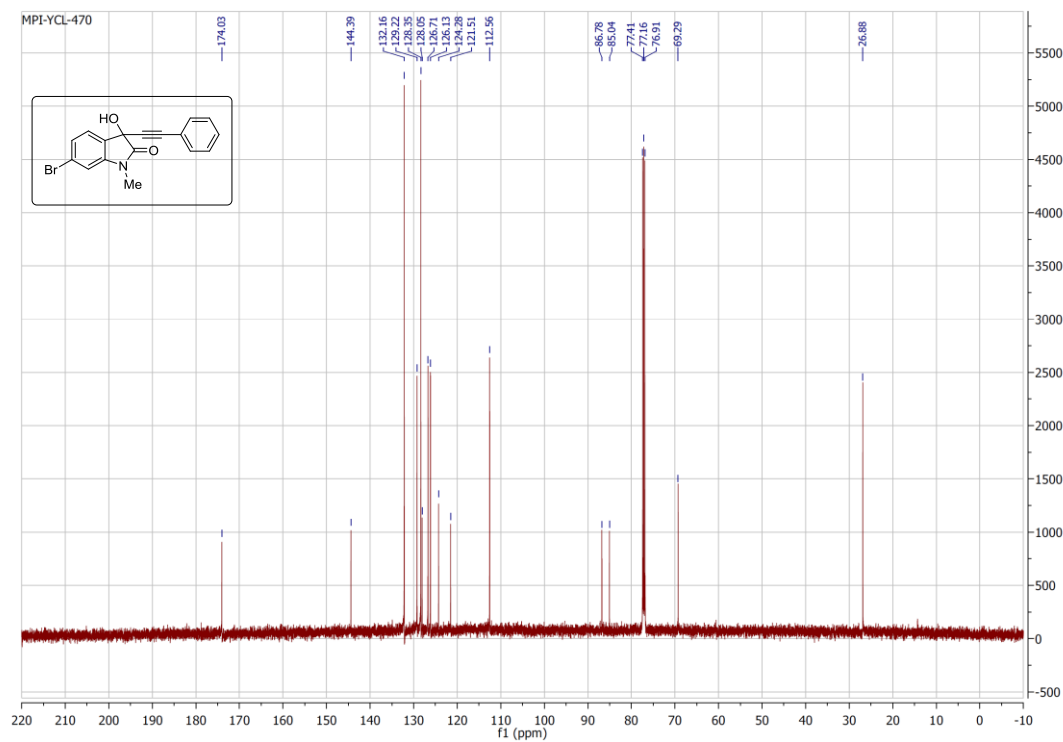
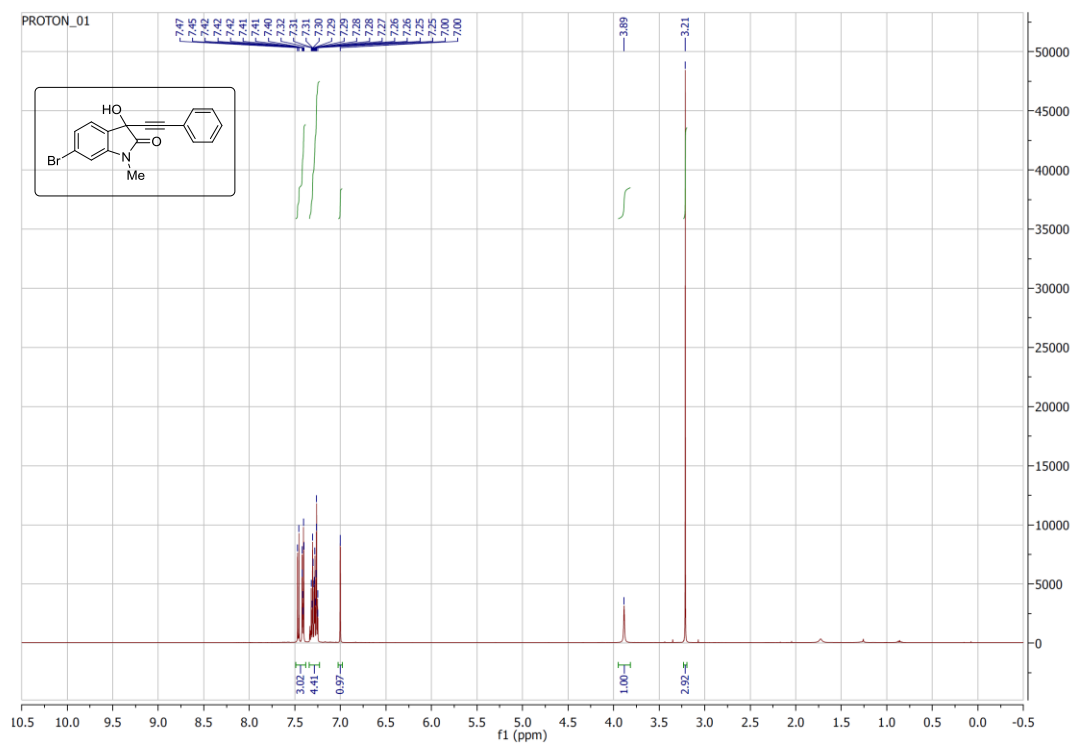
Supplementary Figure 21. ^1H and ^{13}C NMR spectra for **S9g**.



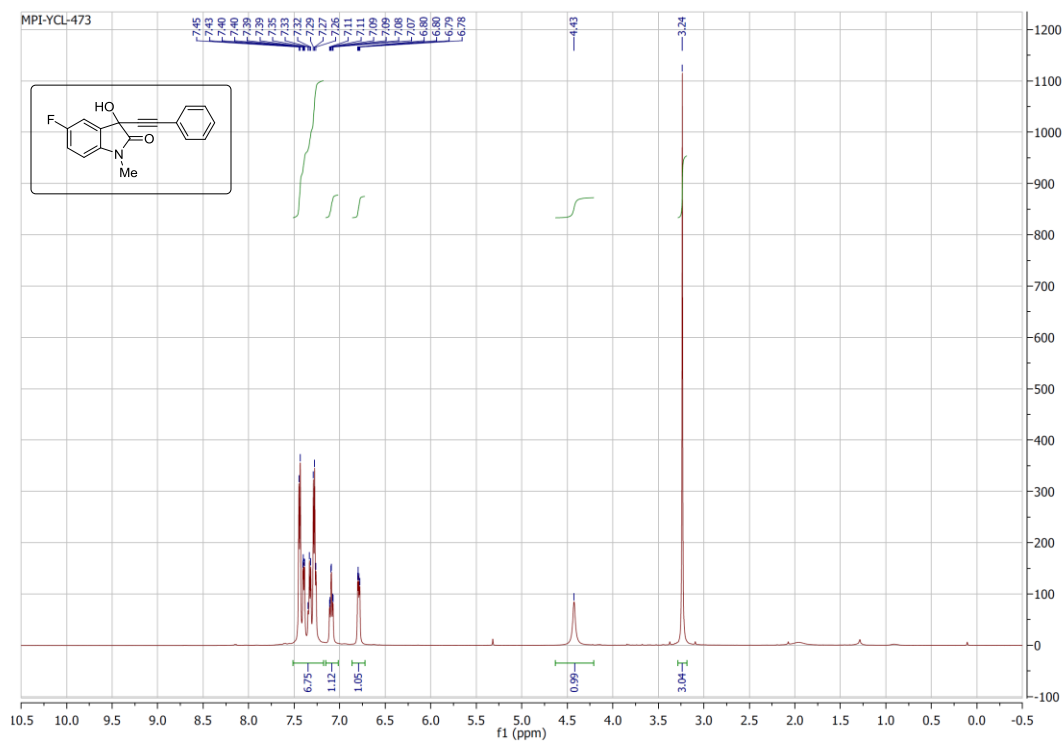
Supplementary Figure 22. ^1H and ^{13}C NMR spectra for S9h.



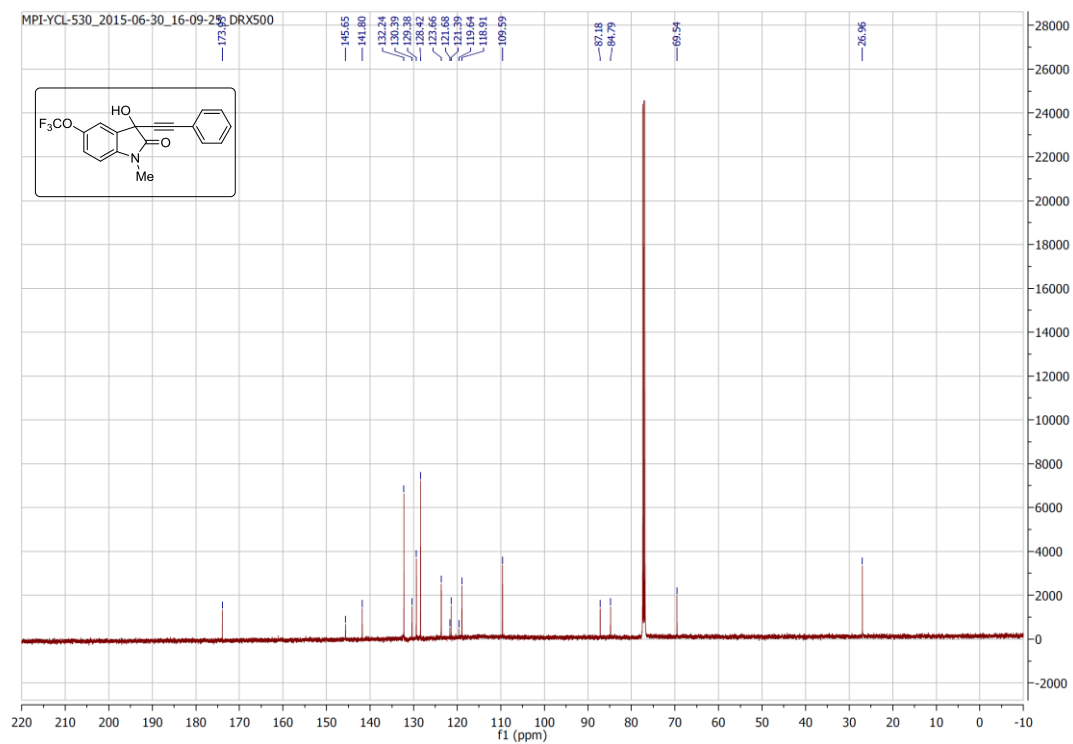
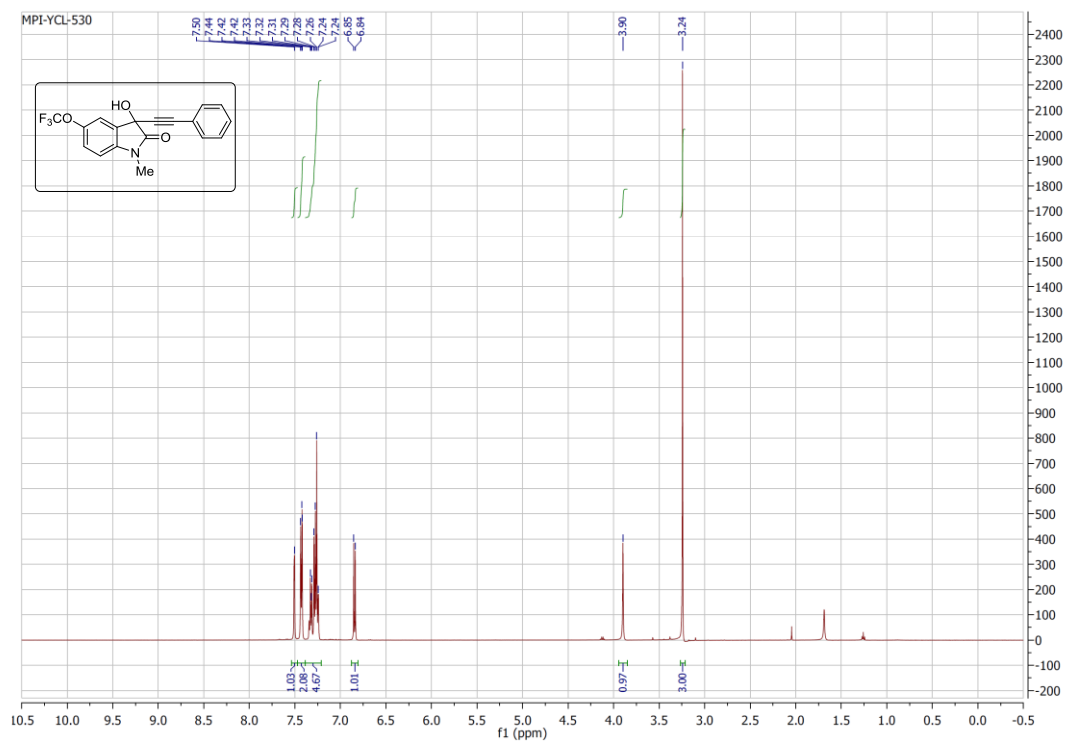
Supplementary Figure 25. ¹H and ¹³C NMR spectra for S9k.



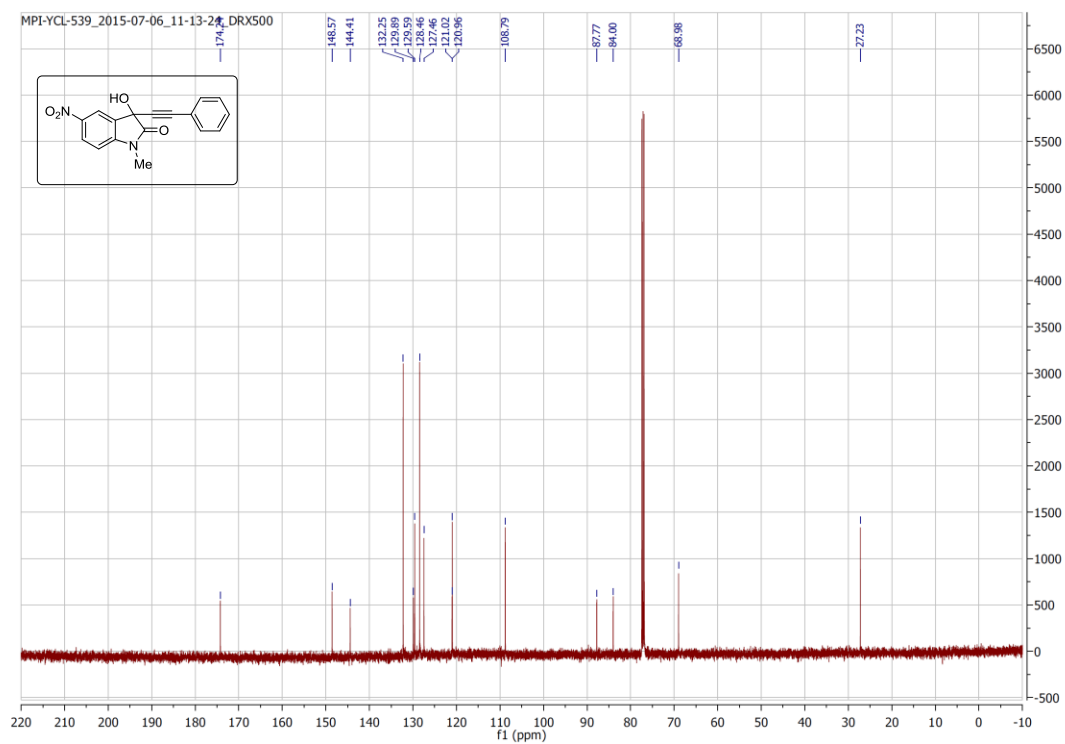
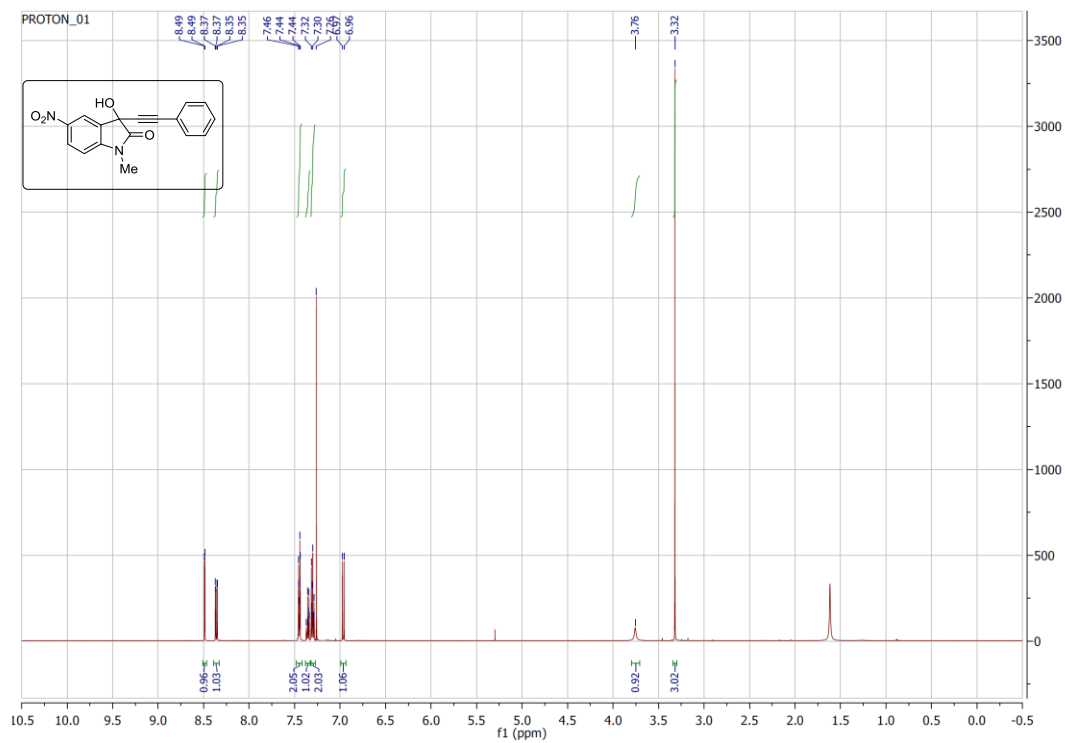
Supplementary Figure 26. ^1H and ^{13}C NMR spectra for S9I.



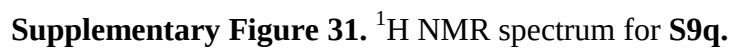
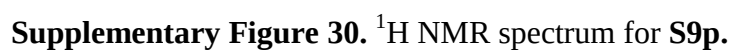
Supplementary Figure 27. ¹H NMR spectrum for **S9m**.

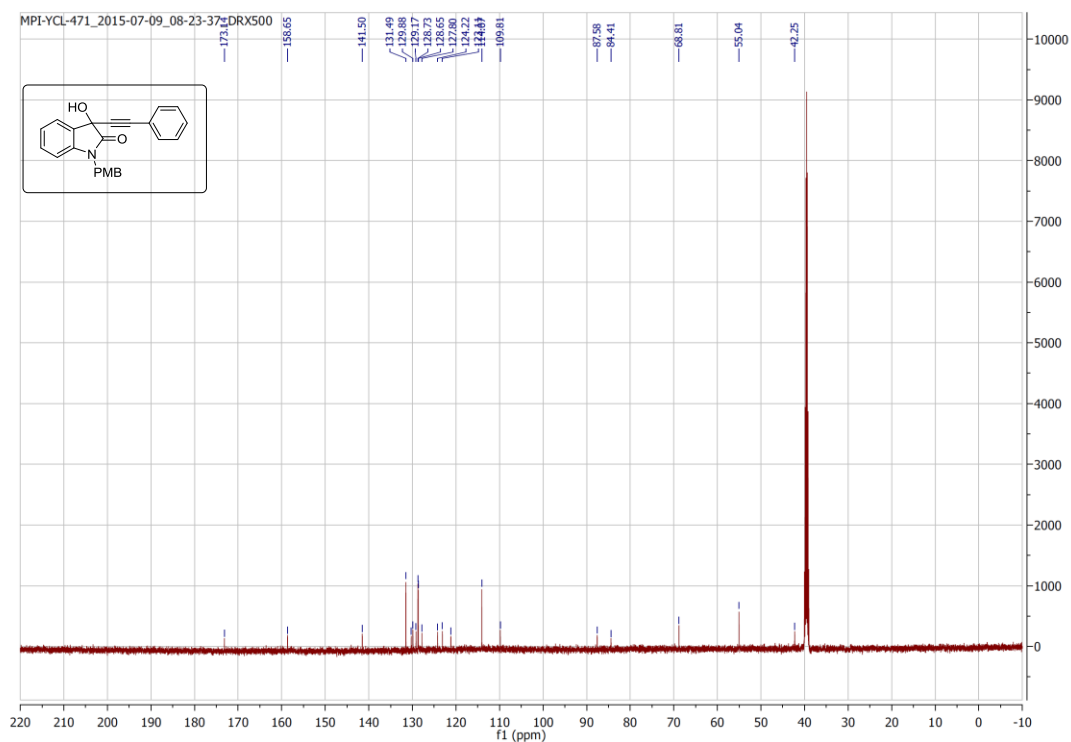
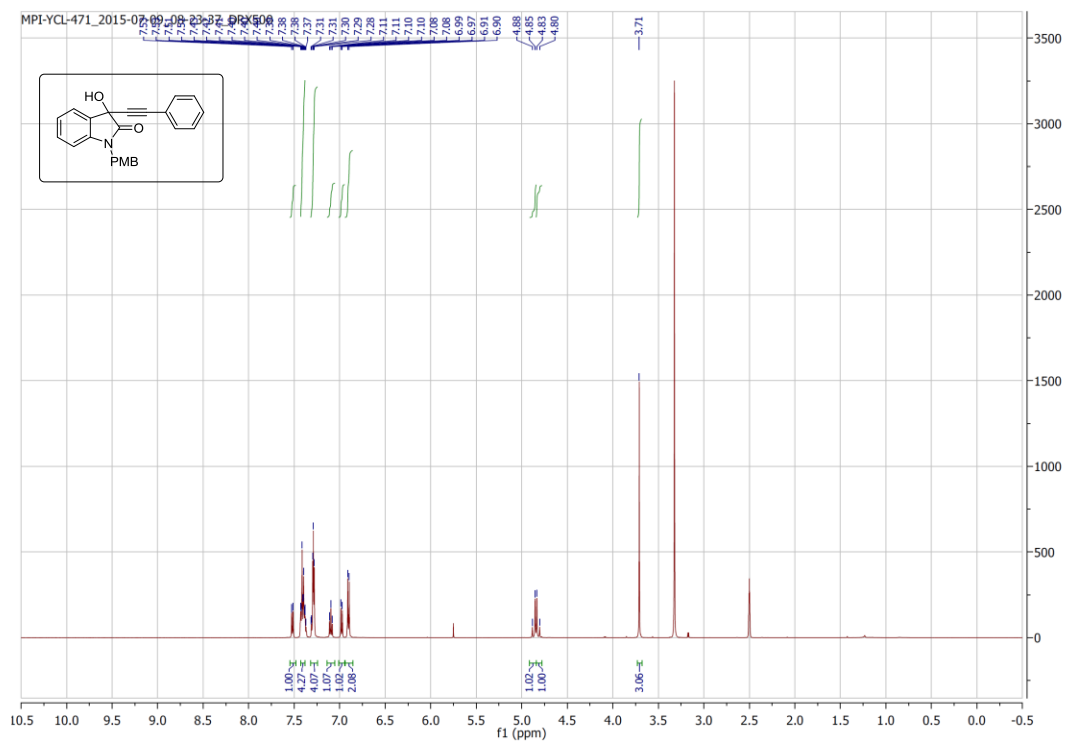


Supplementary Figure 28. ^1H and ^{13}C NMR spectra for S9n.

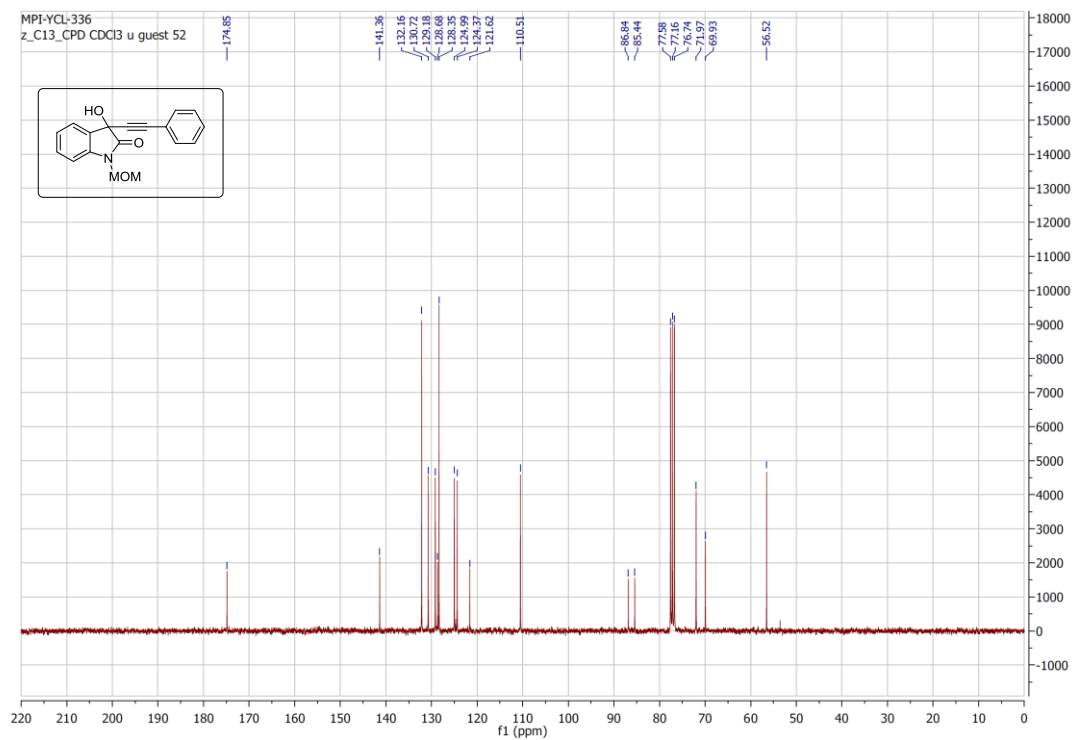
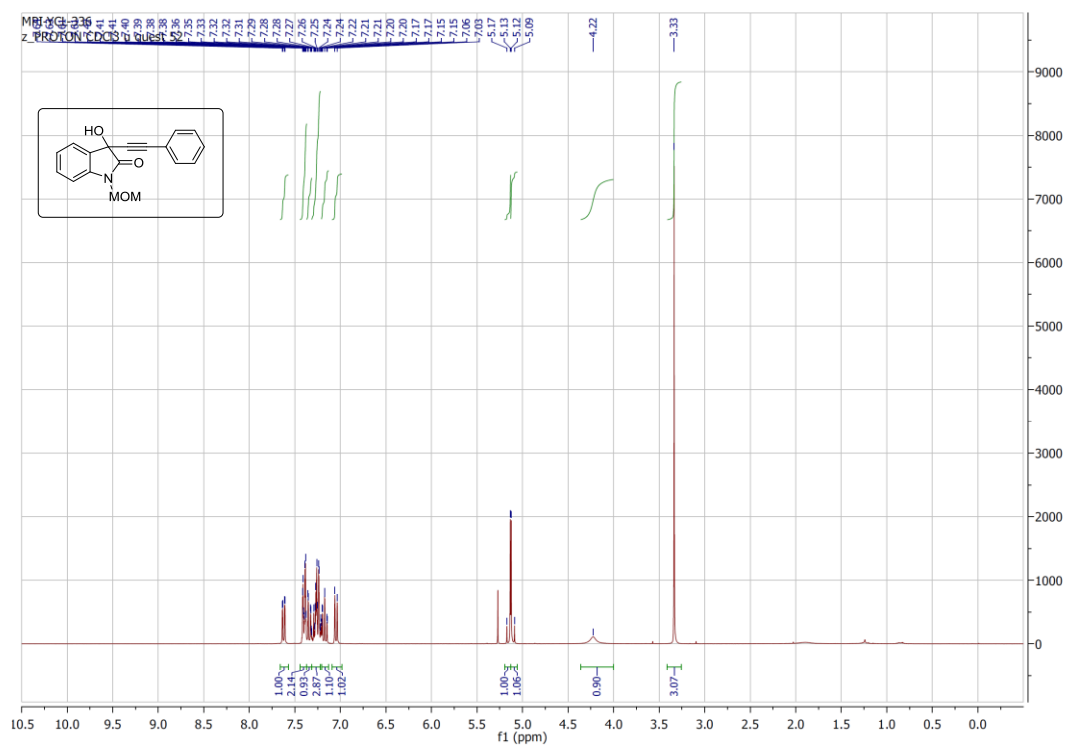


Supplementary Figure 29. ^1H and ^{13}C NMR spectra for S9o.

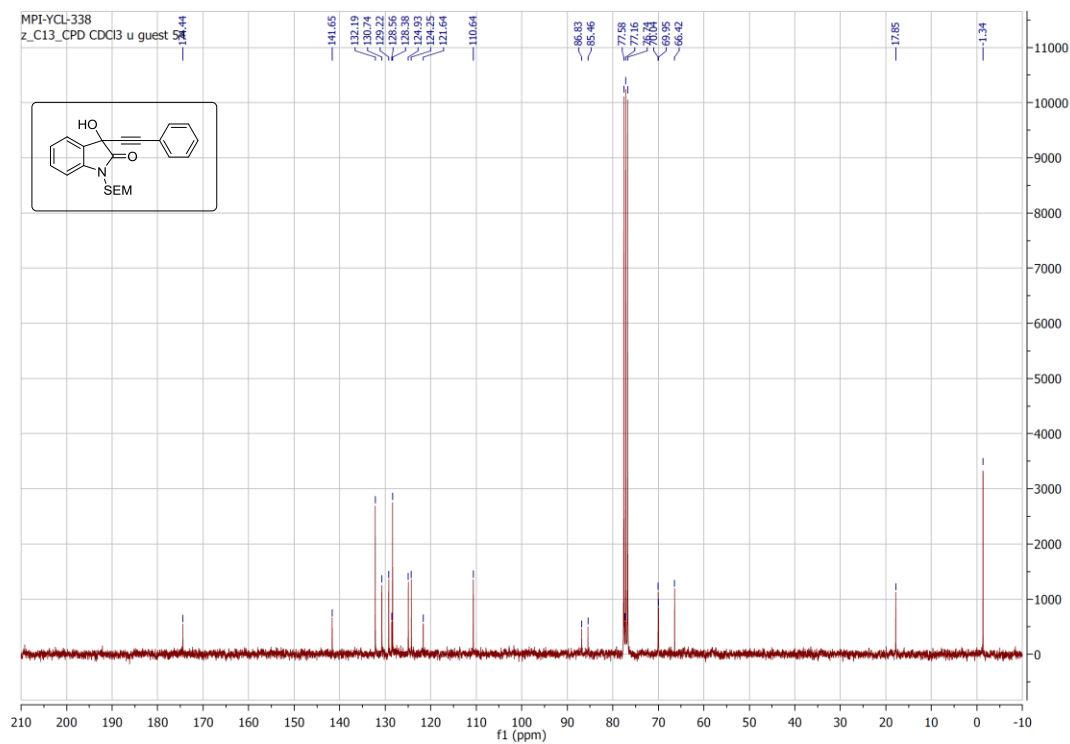
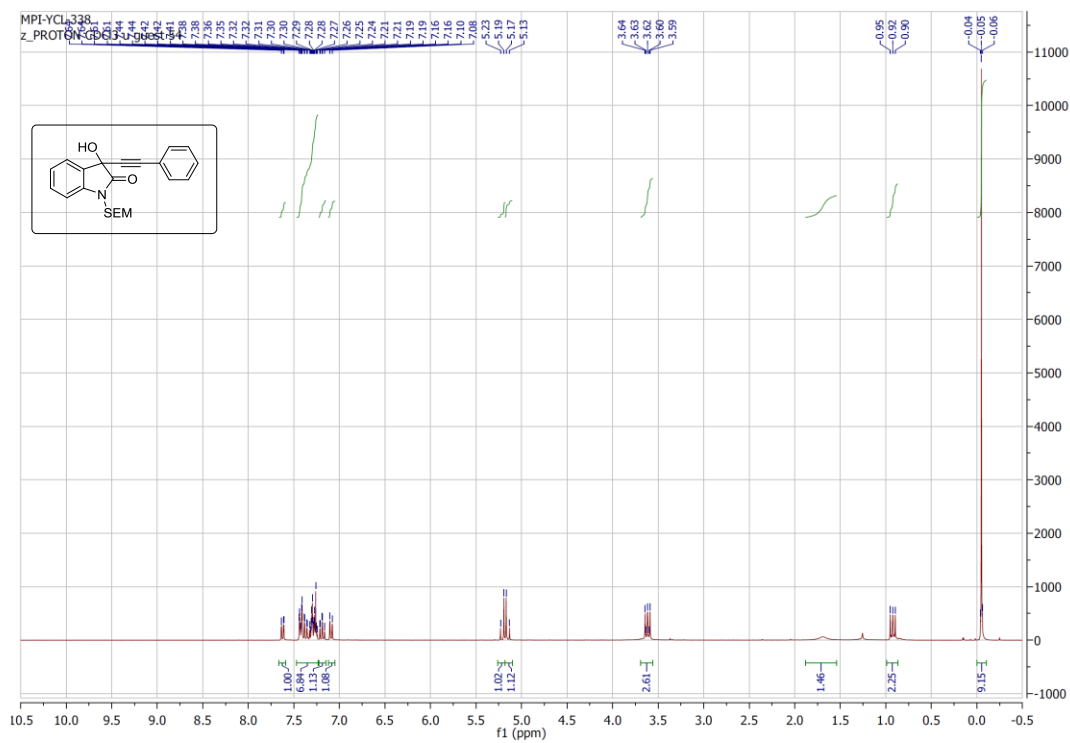




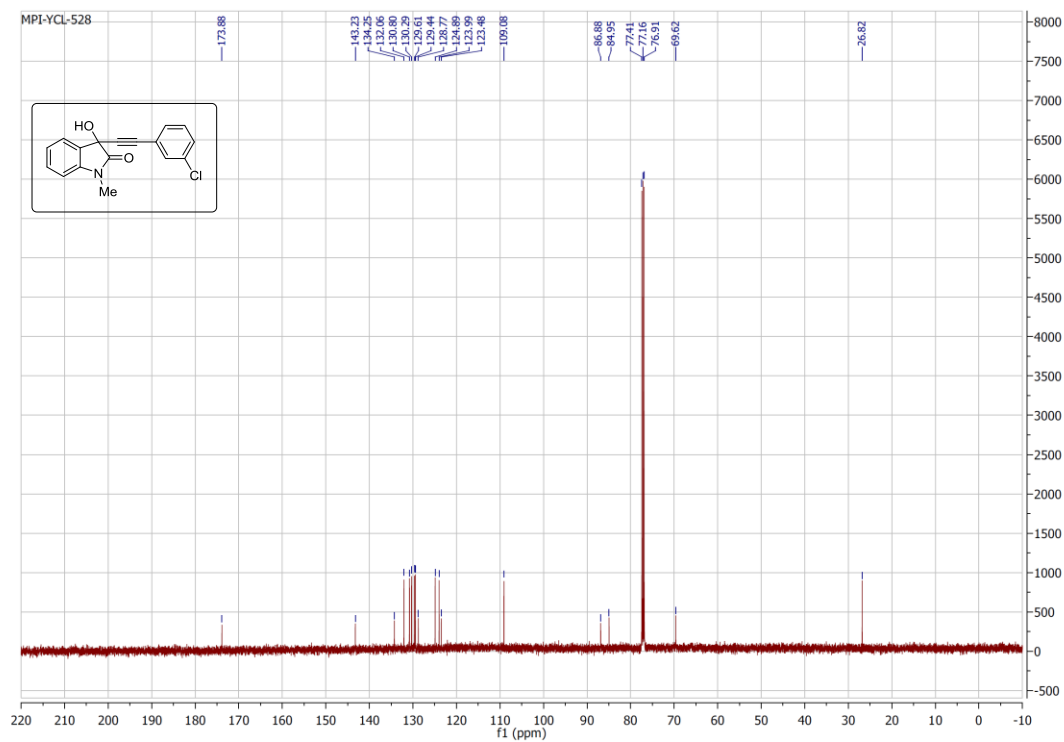
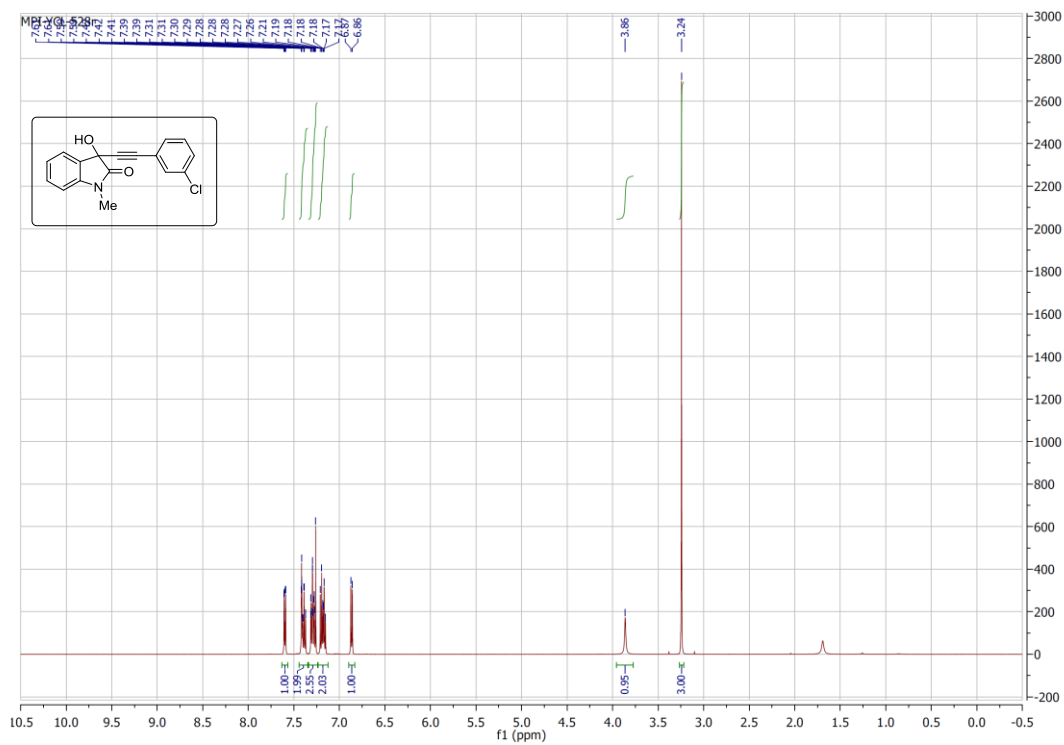
Supplementary Figure 32. ^1H and ^{13}C NMR spectra for S9r.



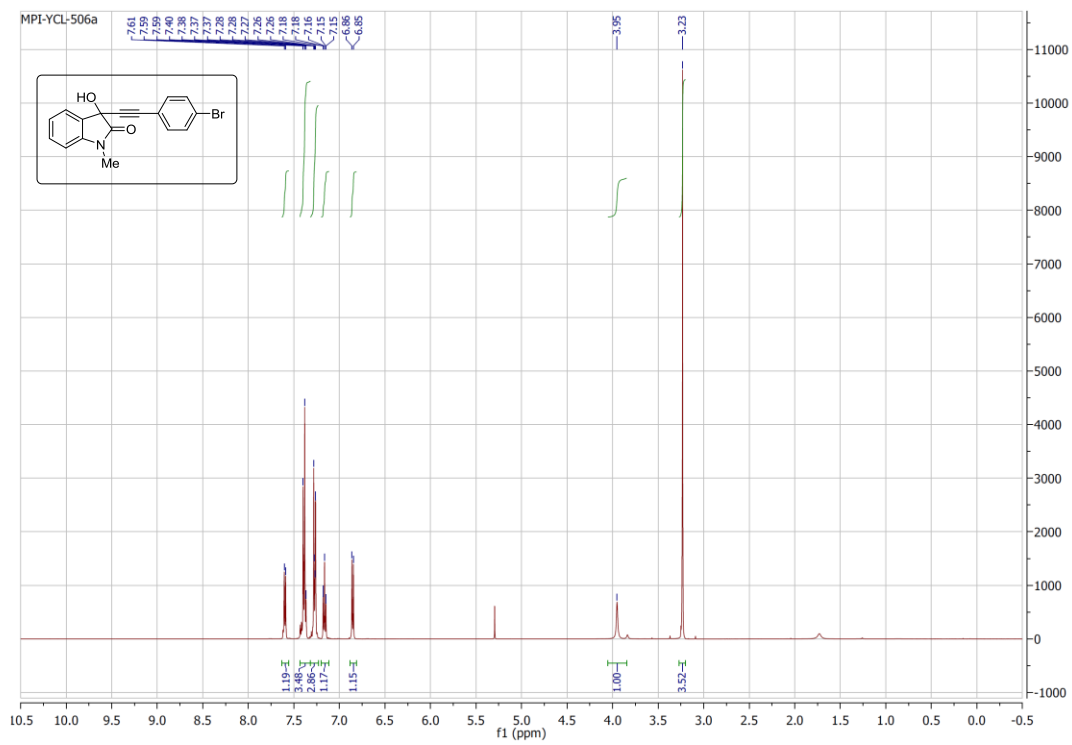
Supplementary Figure 33. ^1H and ^{13}C NMR spectra for S9s.



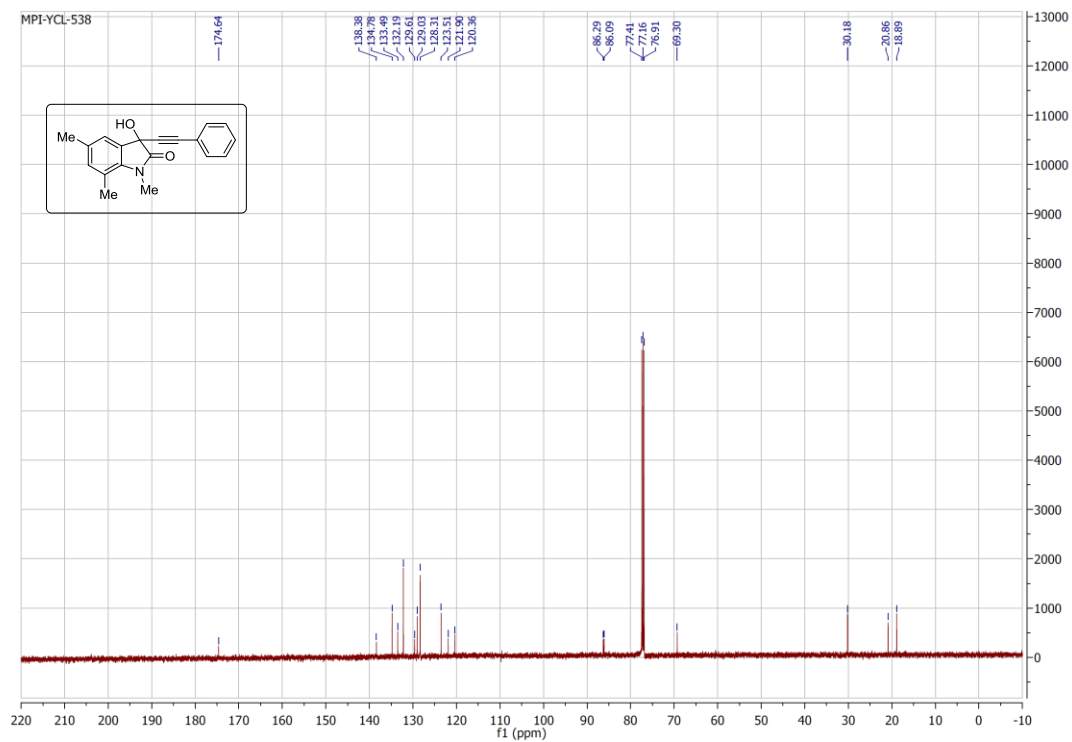
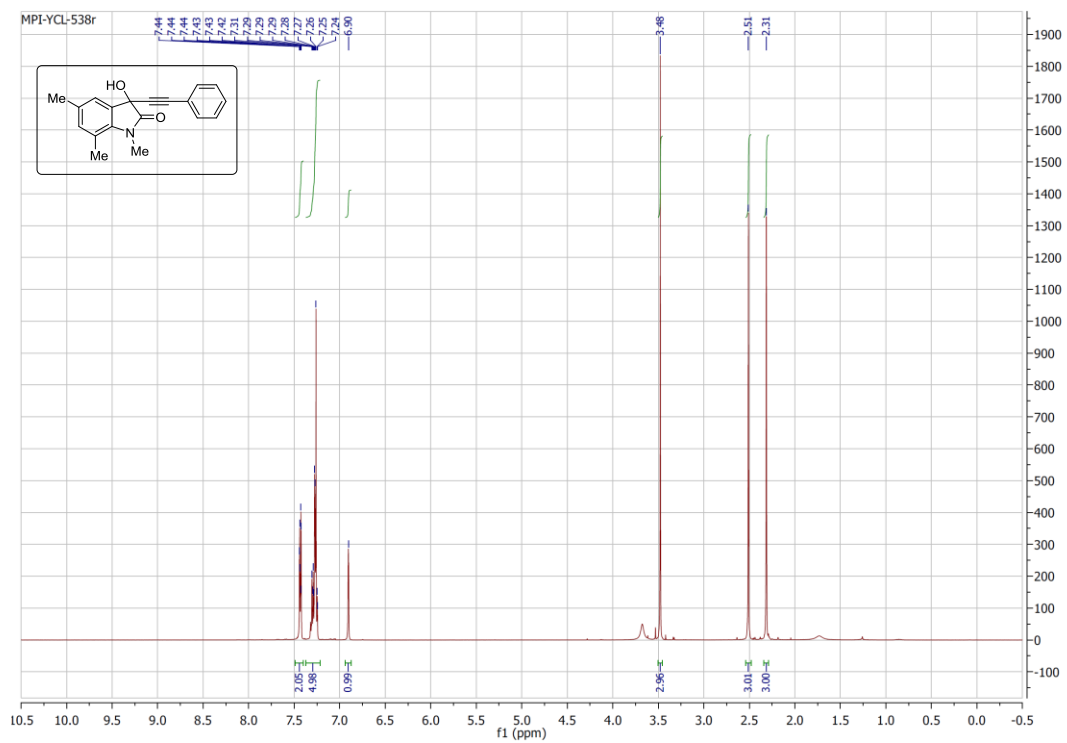
Supplementary Figure 34. ^1H and ^{13}C NMR spectra for **S9t**.



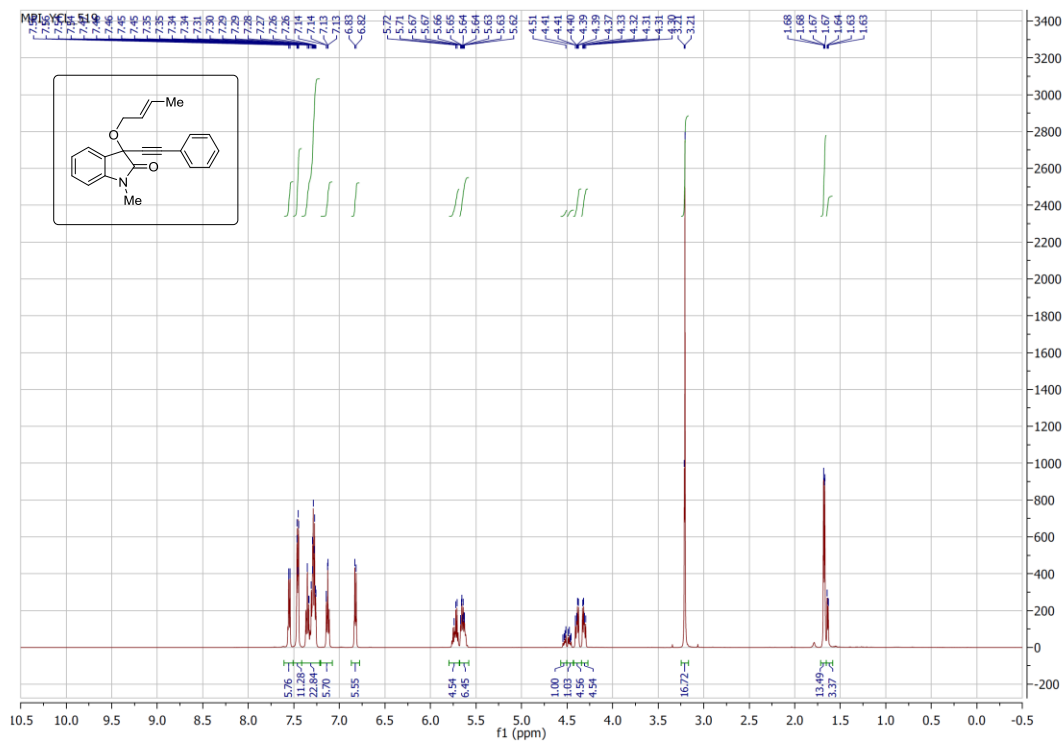
Supplementary Figure 35. ¹H and ¹³C NMR spectra for S9u.



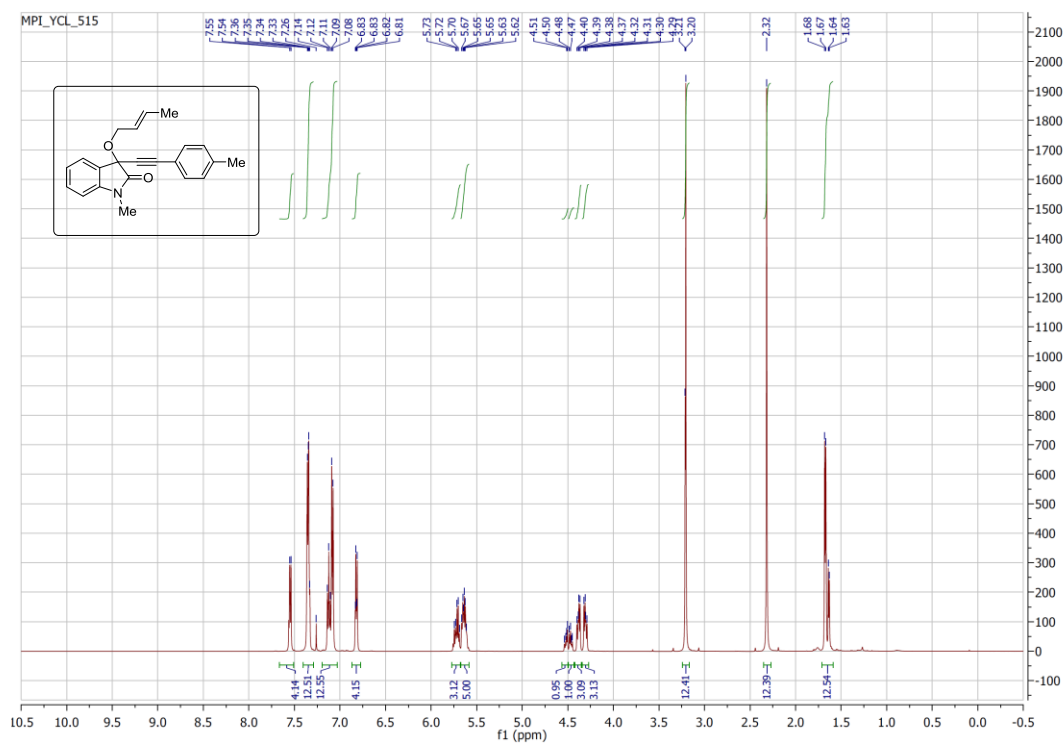
Supplementary Figure 36. ^1H NMR spectrum for **S9v**.



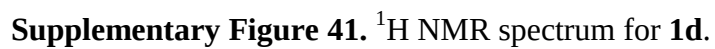
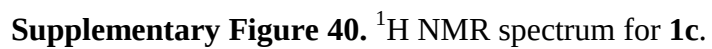
Supplementary Figure 37. ¹H and ¹³C NMR spectra for S9w.



Supplementary Figure 38. ^1H NMR spectrum for **1a**.

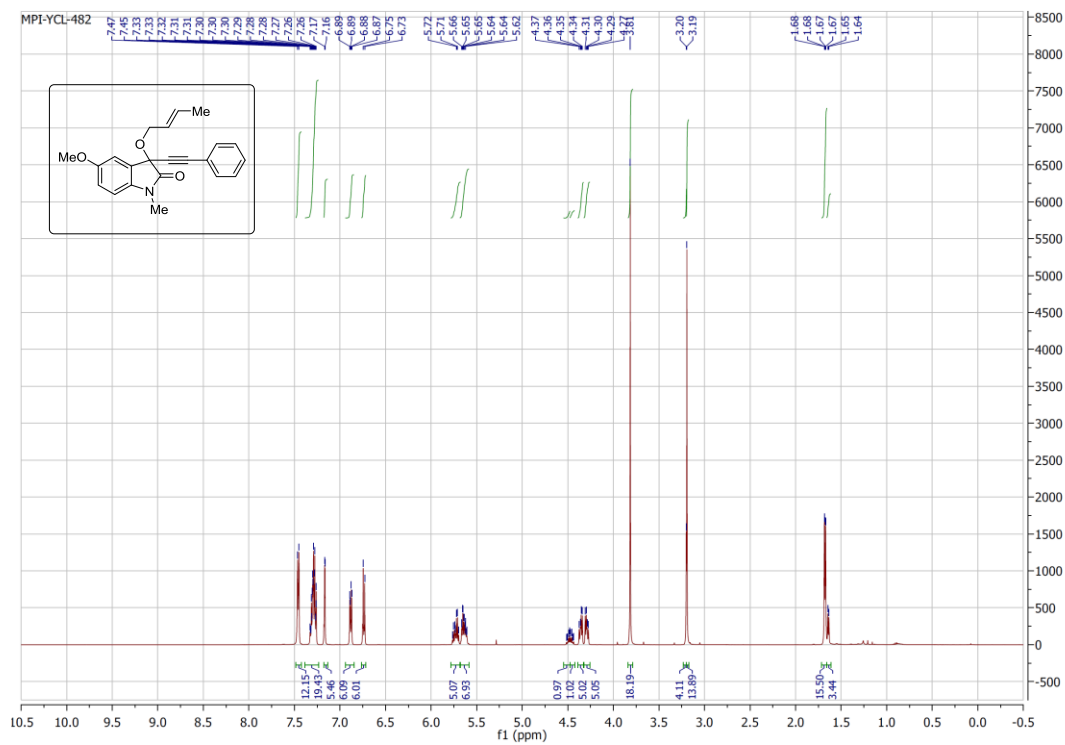


Supplementary Figure 39. ^1H NMR spectrum for **1b**.

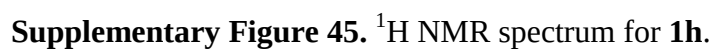
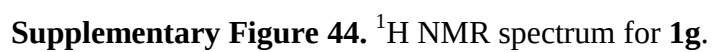


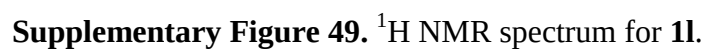
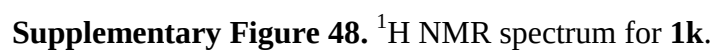


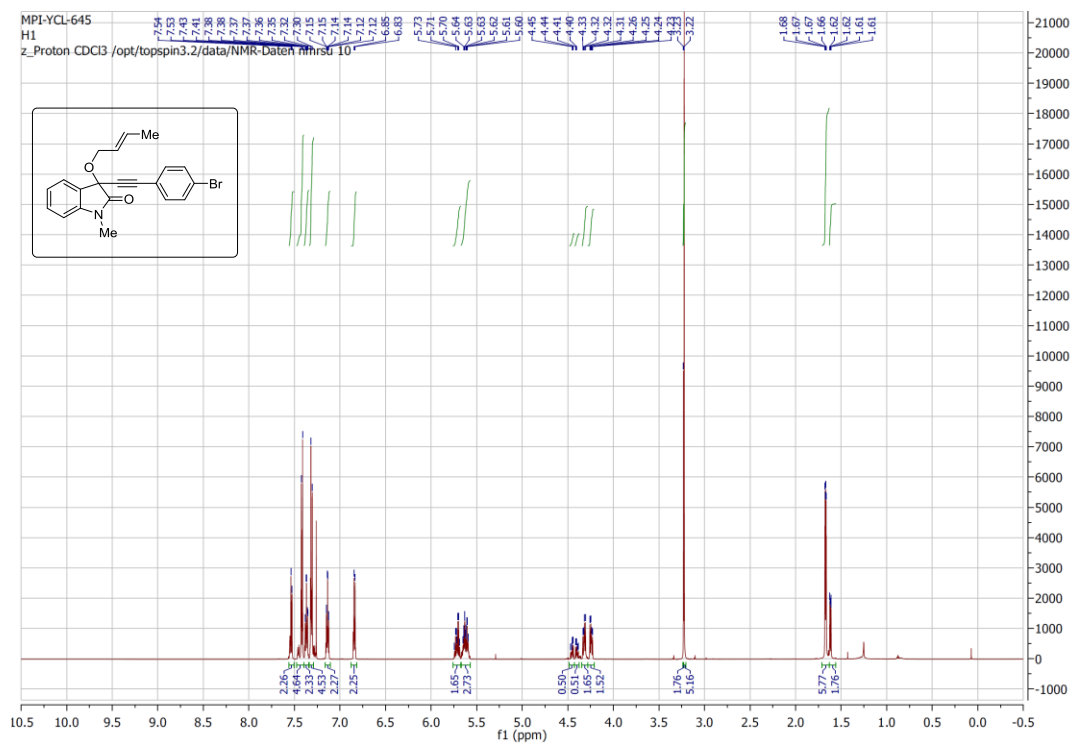
Supplementary Figure 42. ¹H NMR spectrum for **1e**.



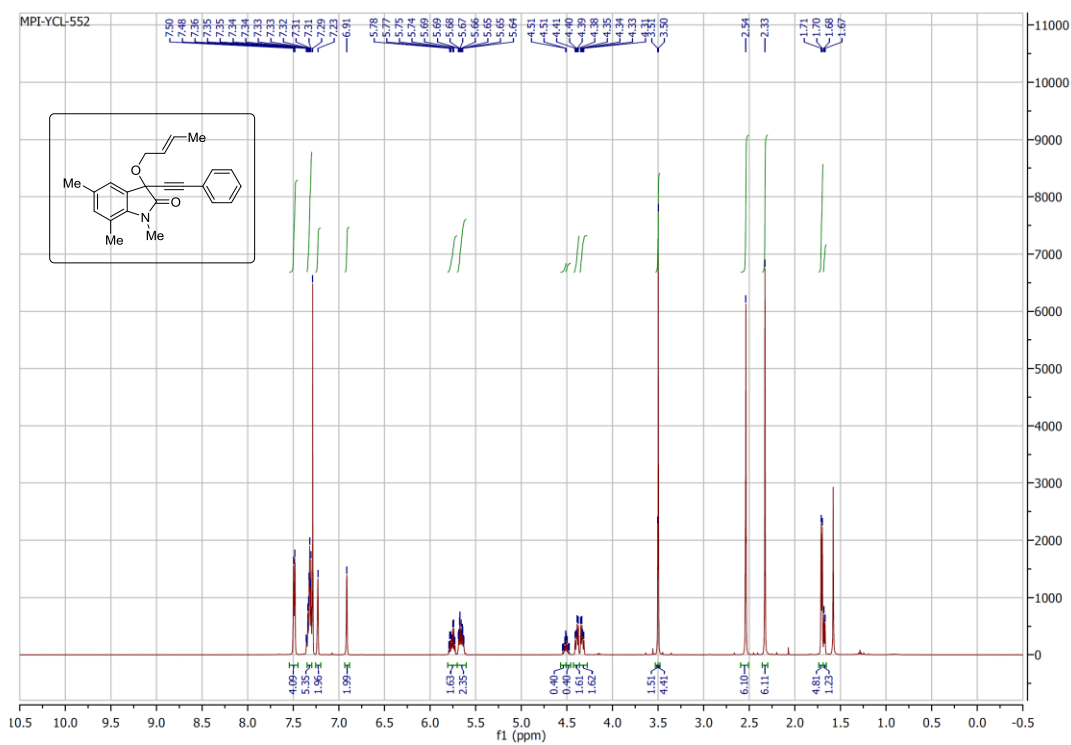
Supplementary Figure 43. ¹H NMR spectrum for **1f**.



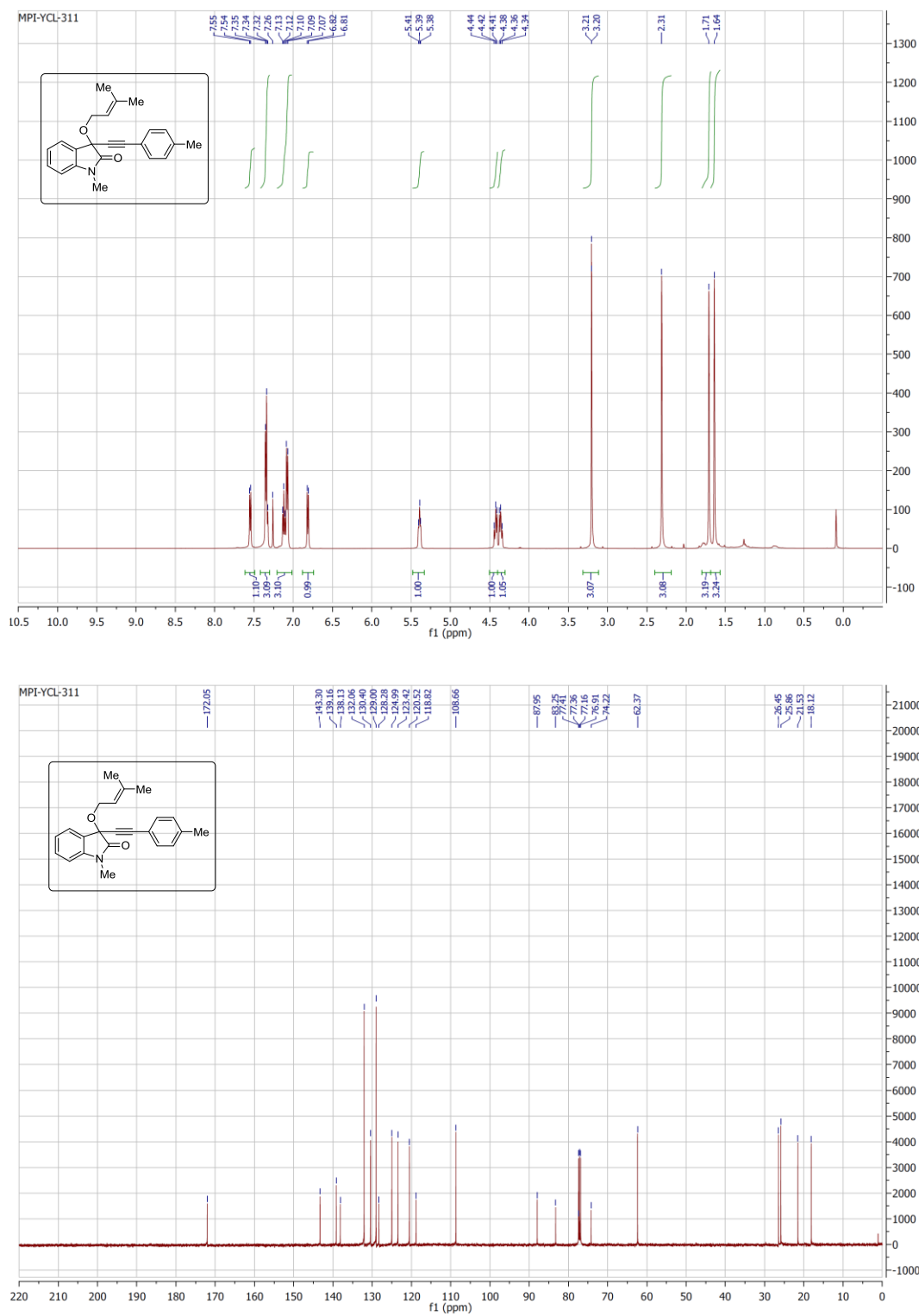




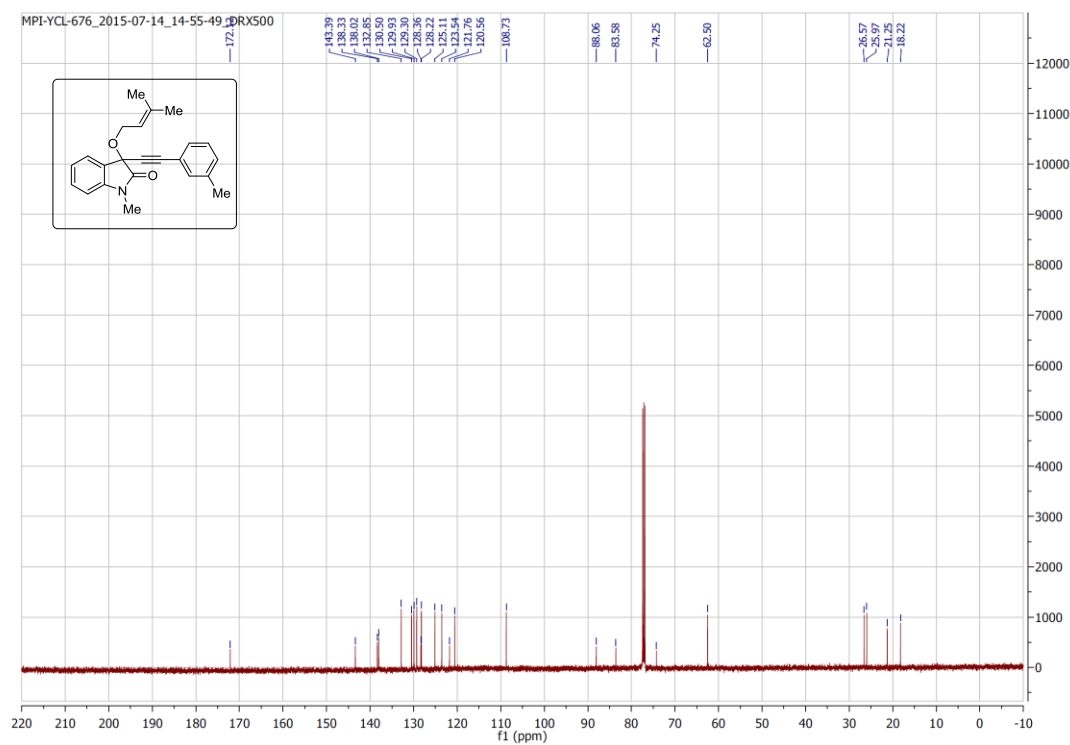
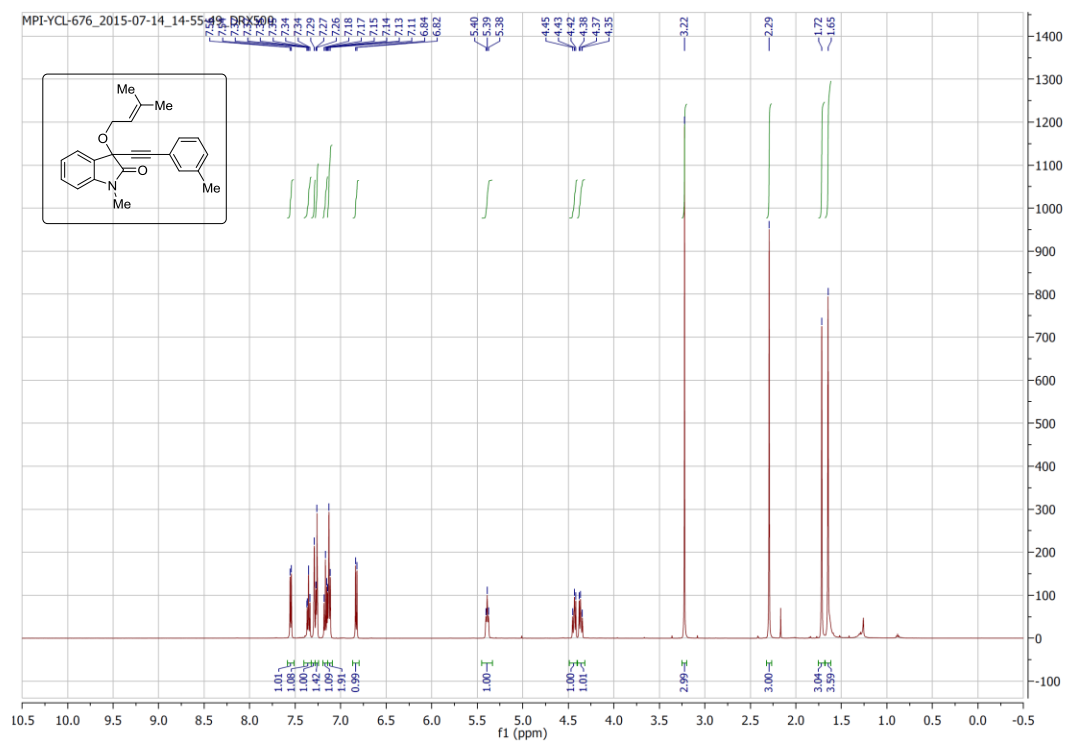
Supplementary Figure 50. ^1H NMR spectrum for **1m**.



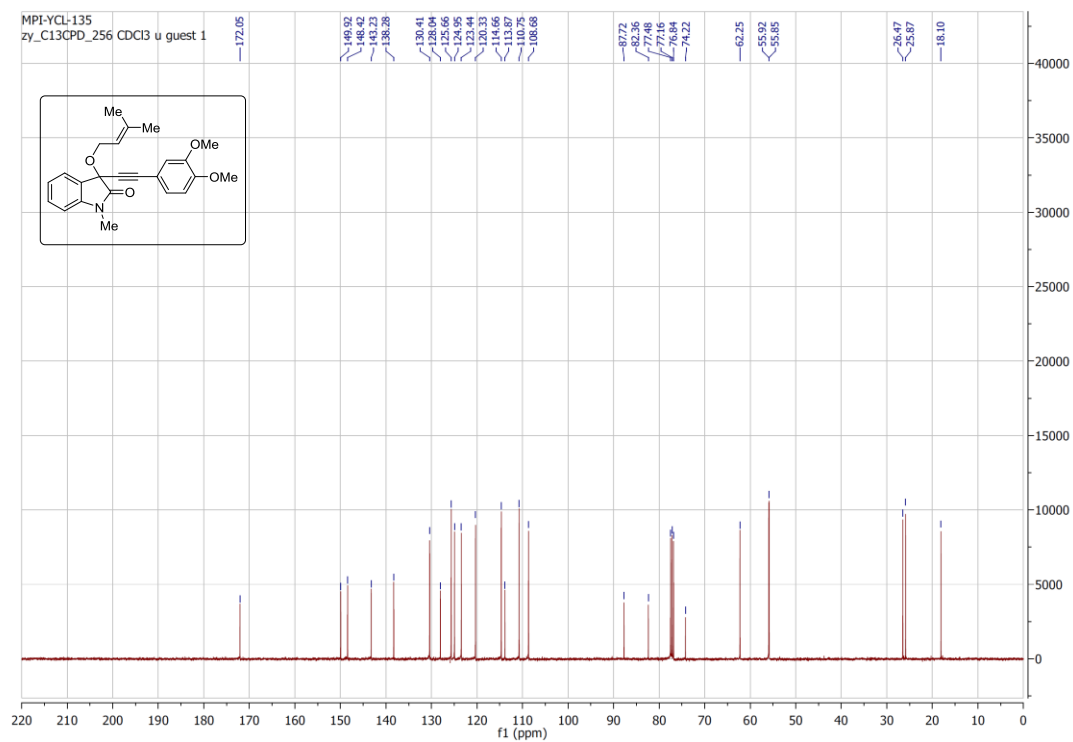
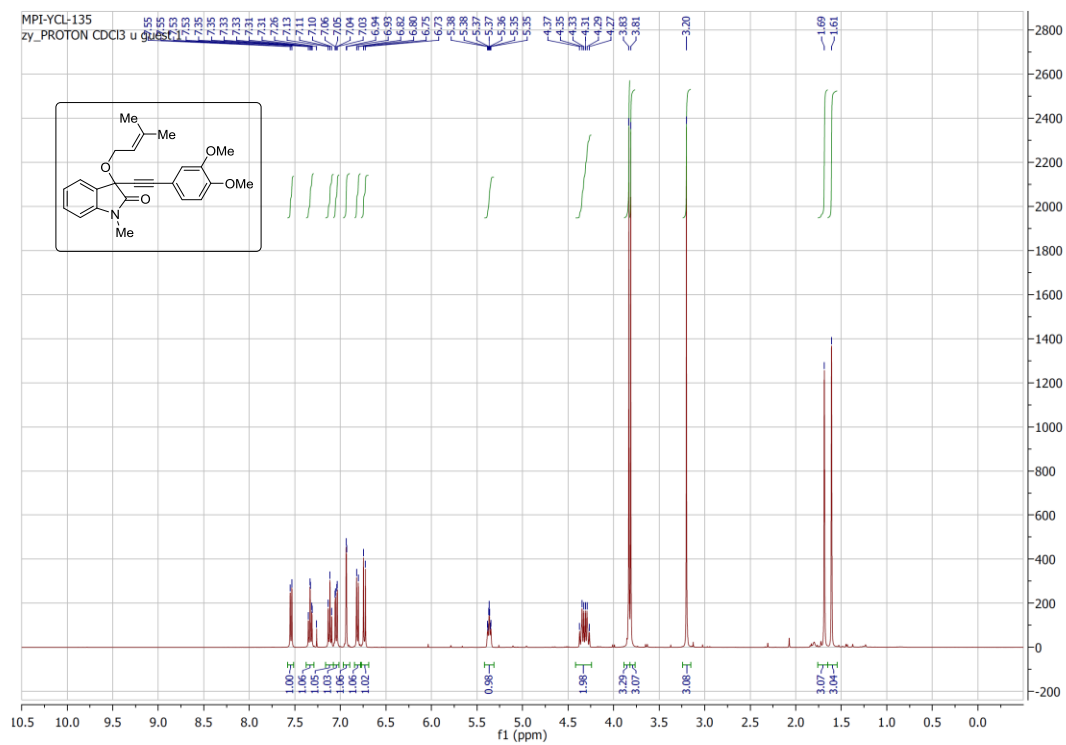
Supplementary Figure 51. ^1H NMR spectrum for **1n**.



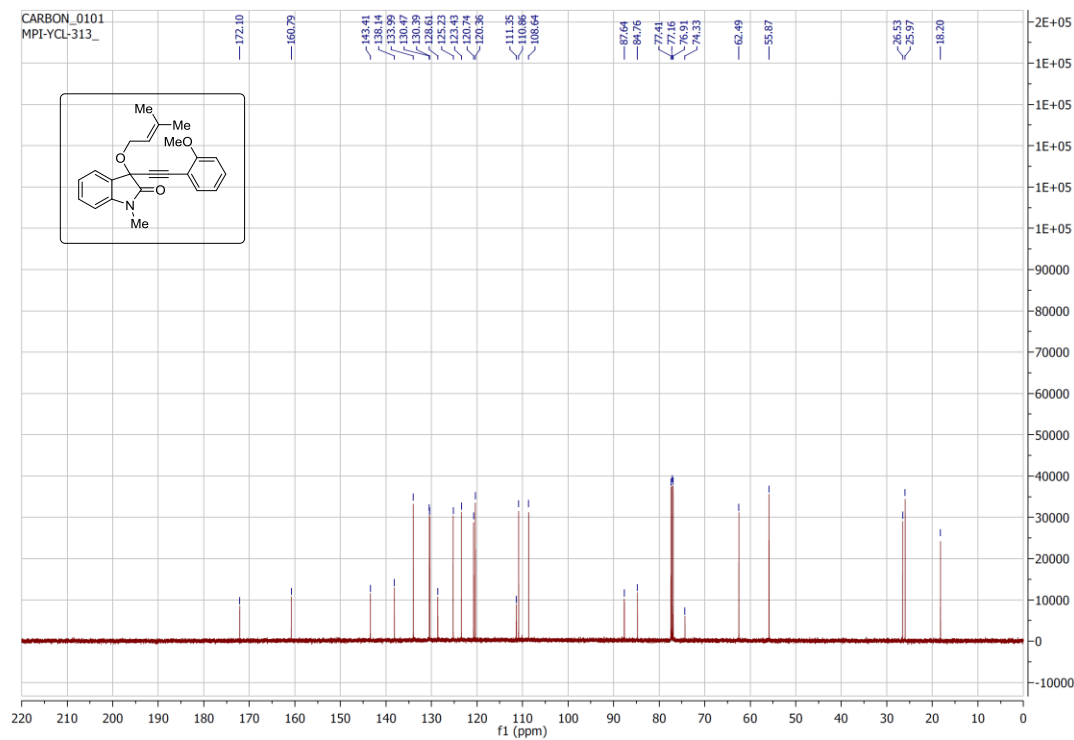
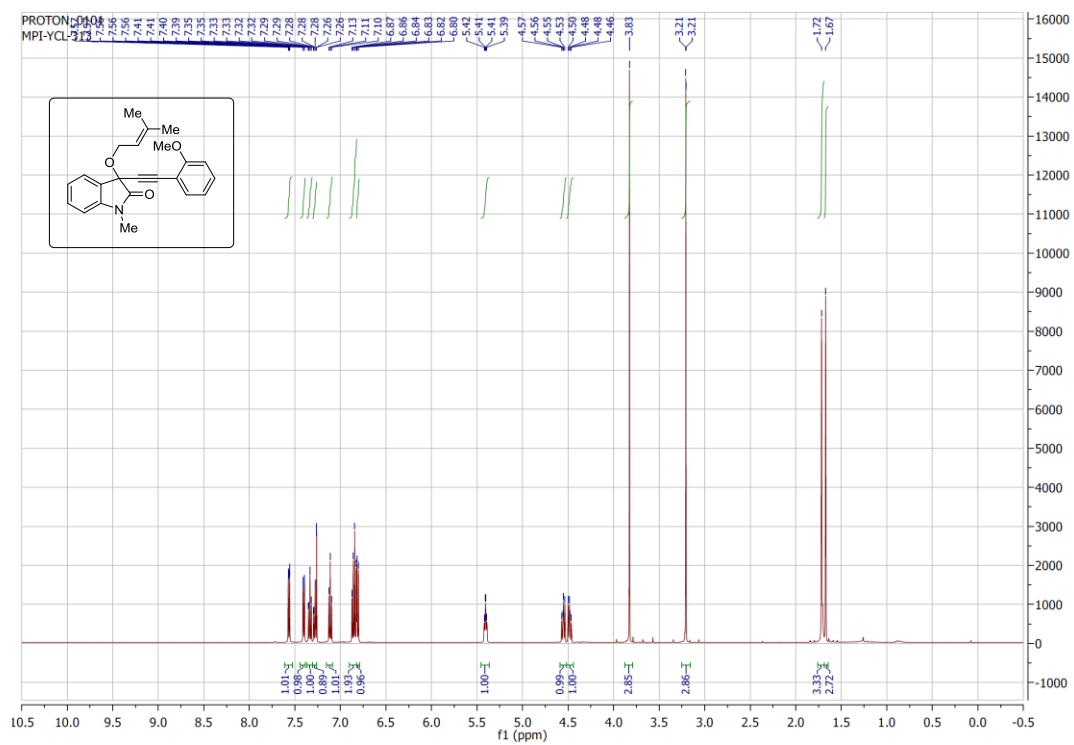
Supplementary Figure 53. ¹H and ¹³C NMR spectra for 13b.



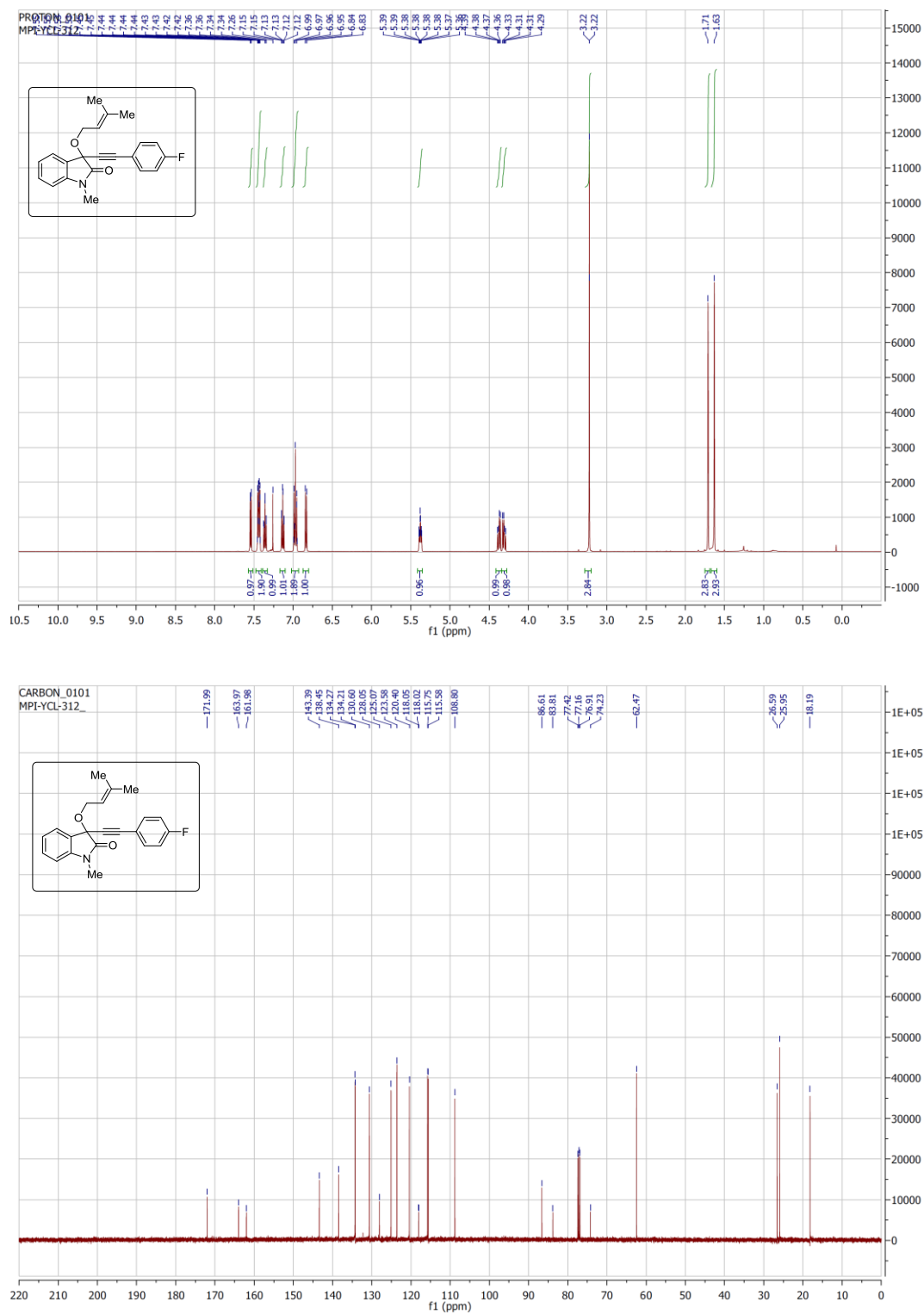
Supplementary Figure 54. ¹H and ¹³C NMR spectra for 13c.



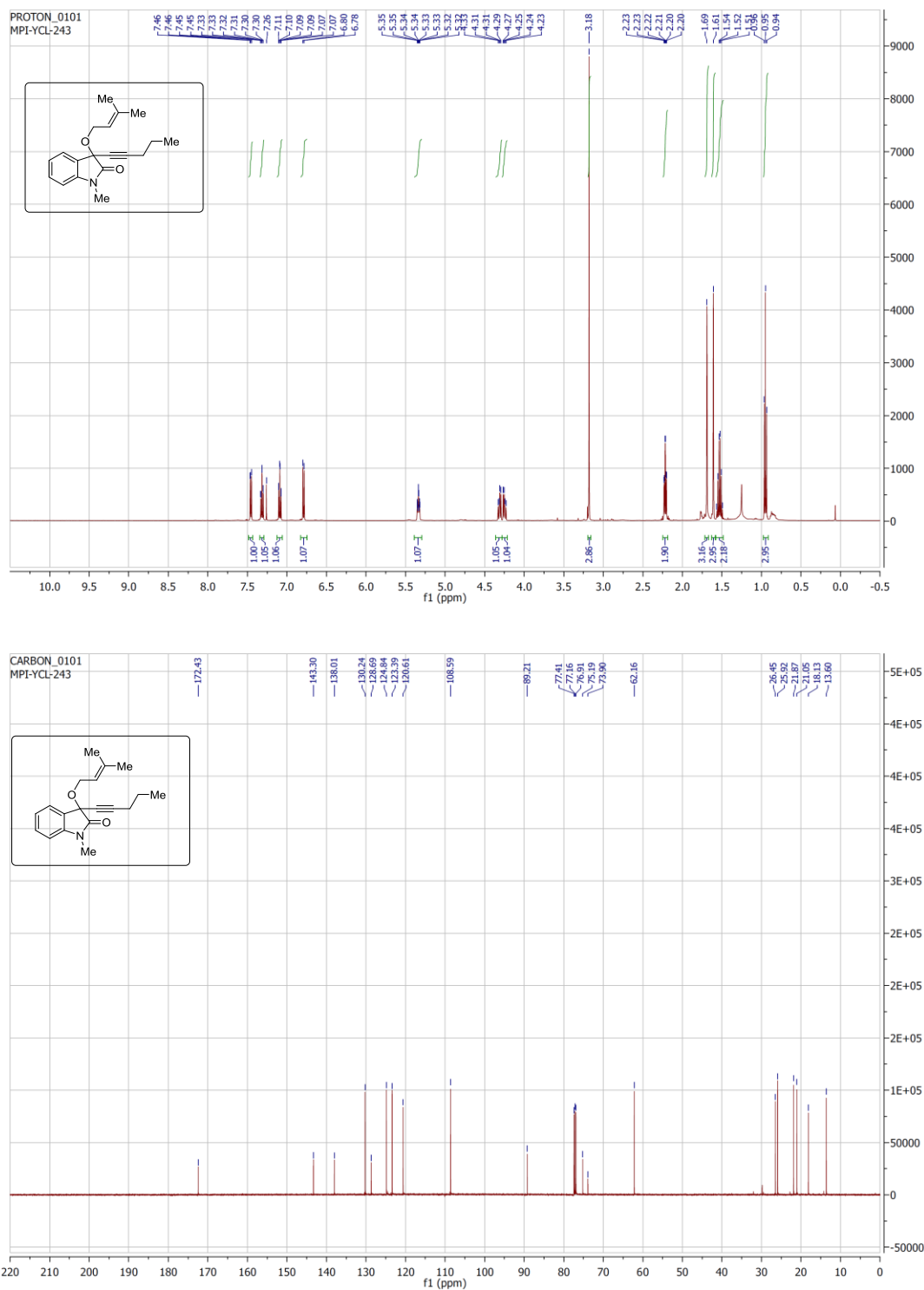
Supplementary Figure 55. ^1H and ^{13}C NMR spectra for **13d**.



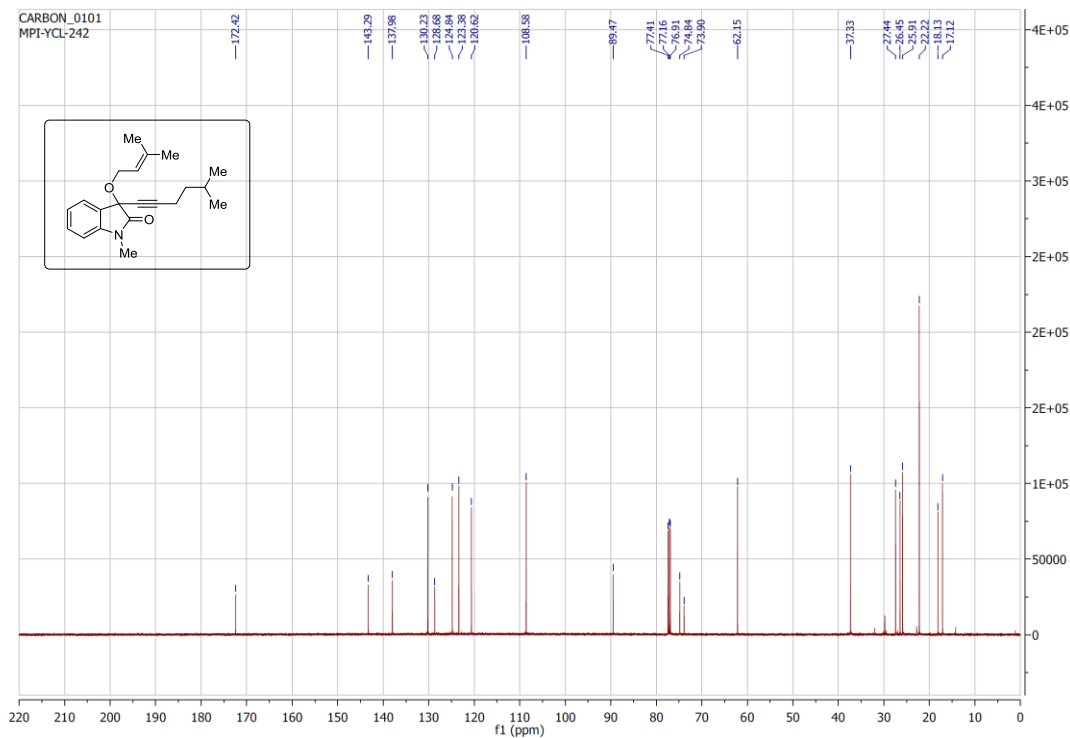
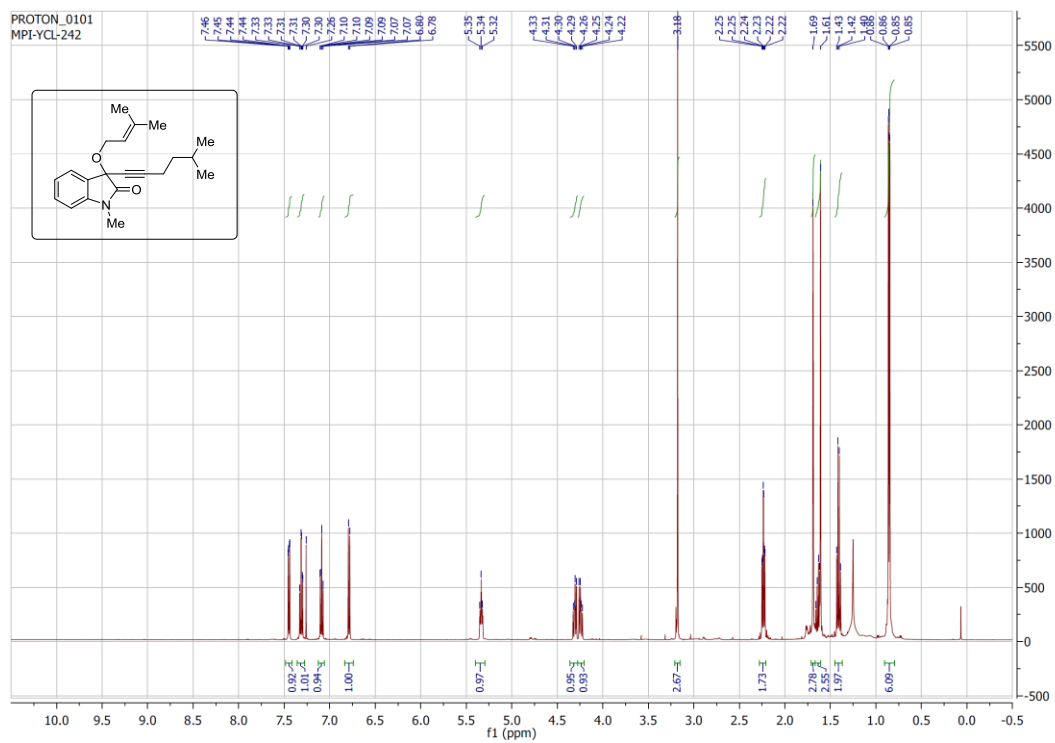
Supplementary Figure 56. ^1H and ^{13}C NMR spectra for 13e.



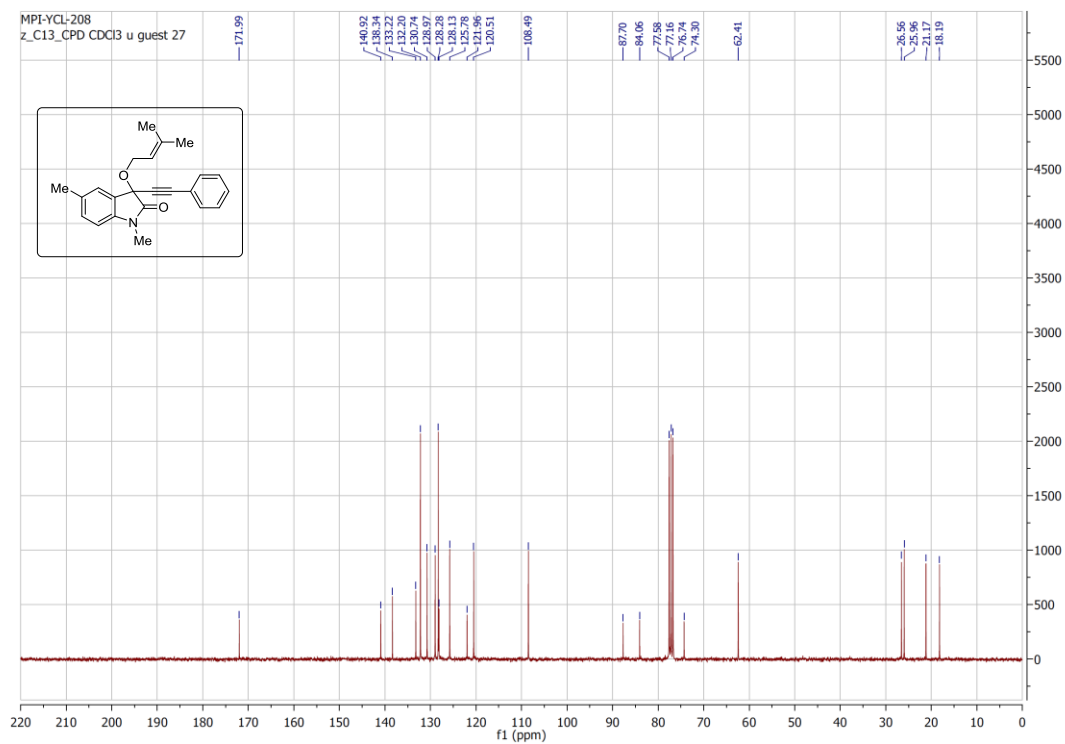
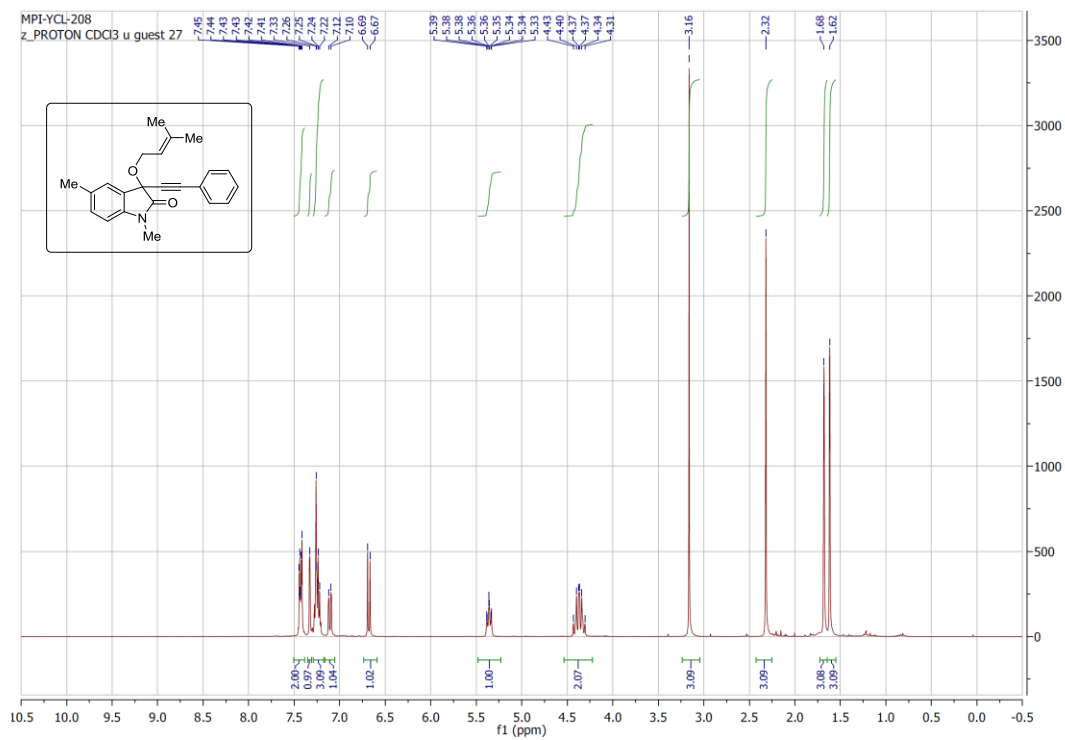
Supplementary Figure 57. ^1H and ^{13}C NMR spectra for **13f**.



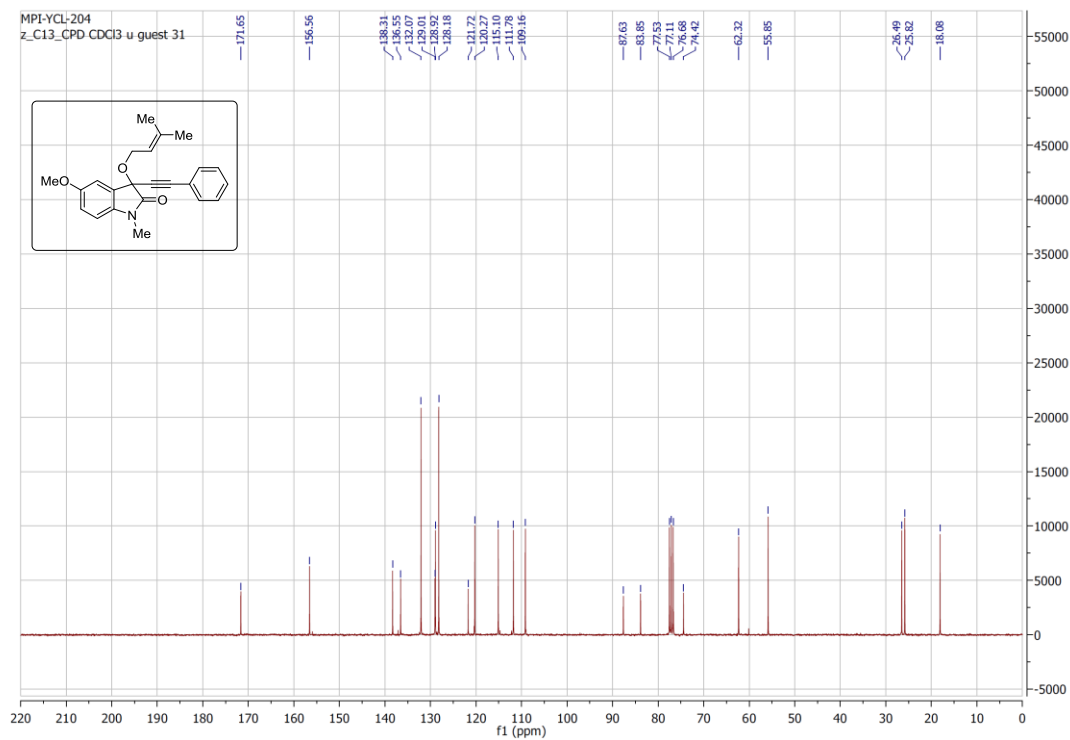
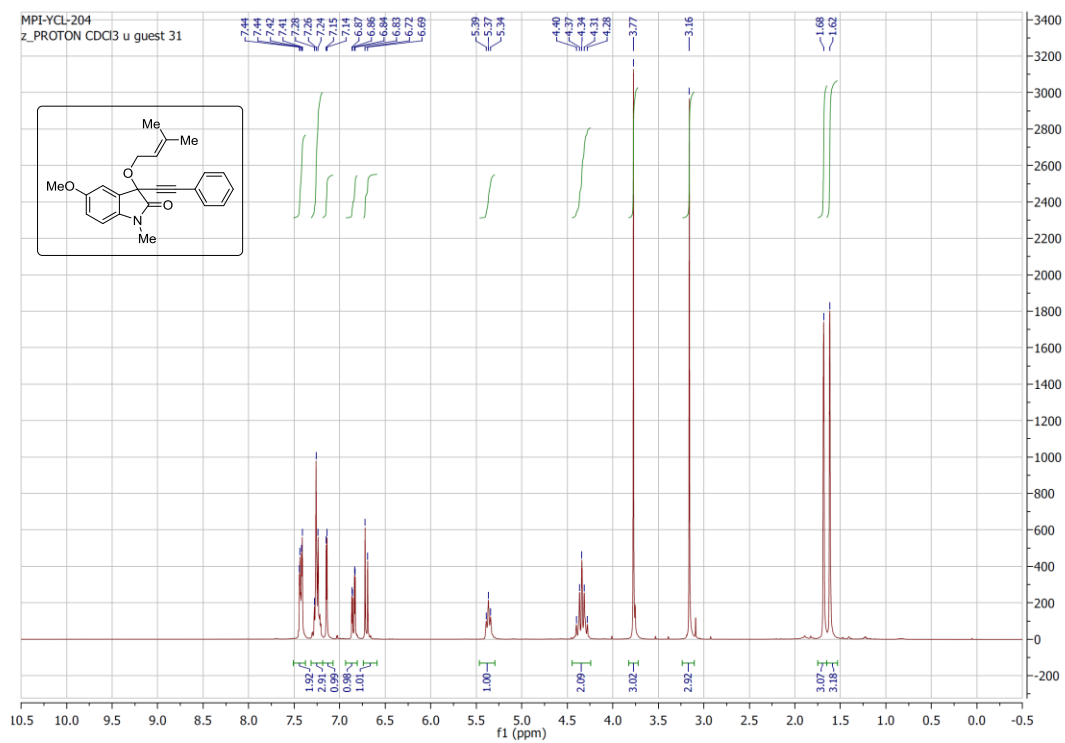
Supplementary Figure 59. ¹H and ¹³C NMR spectra for 13h.



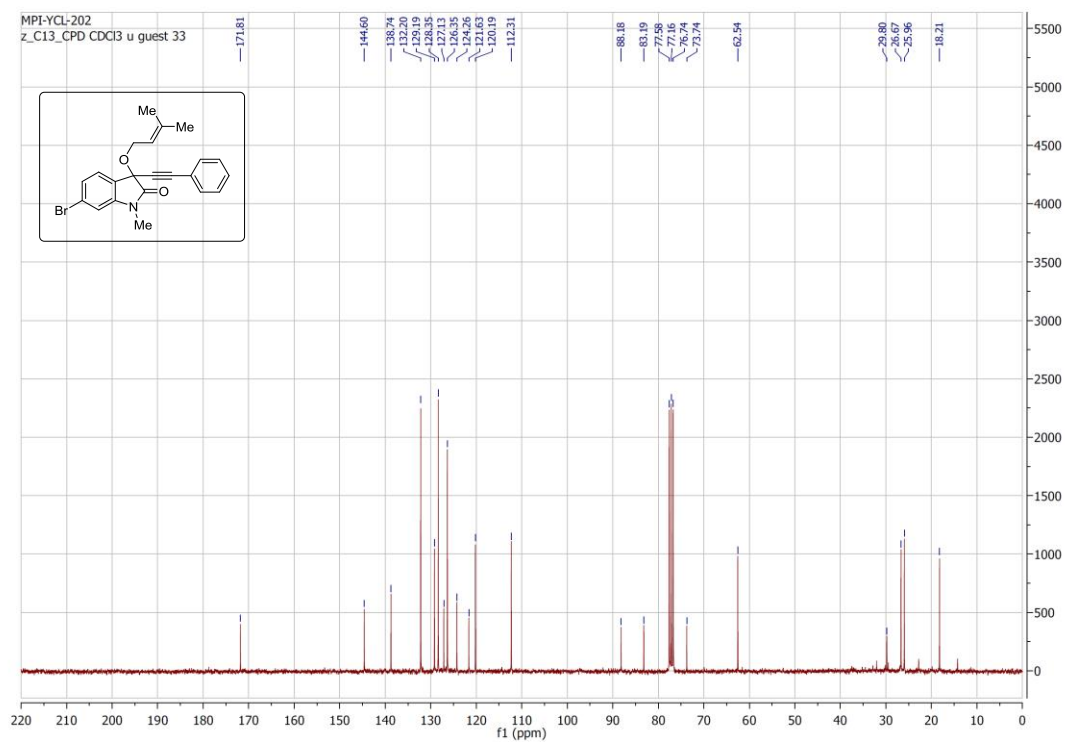
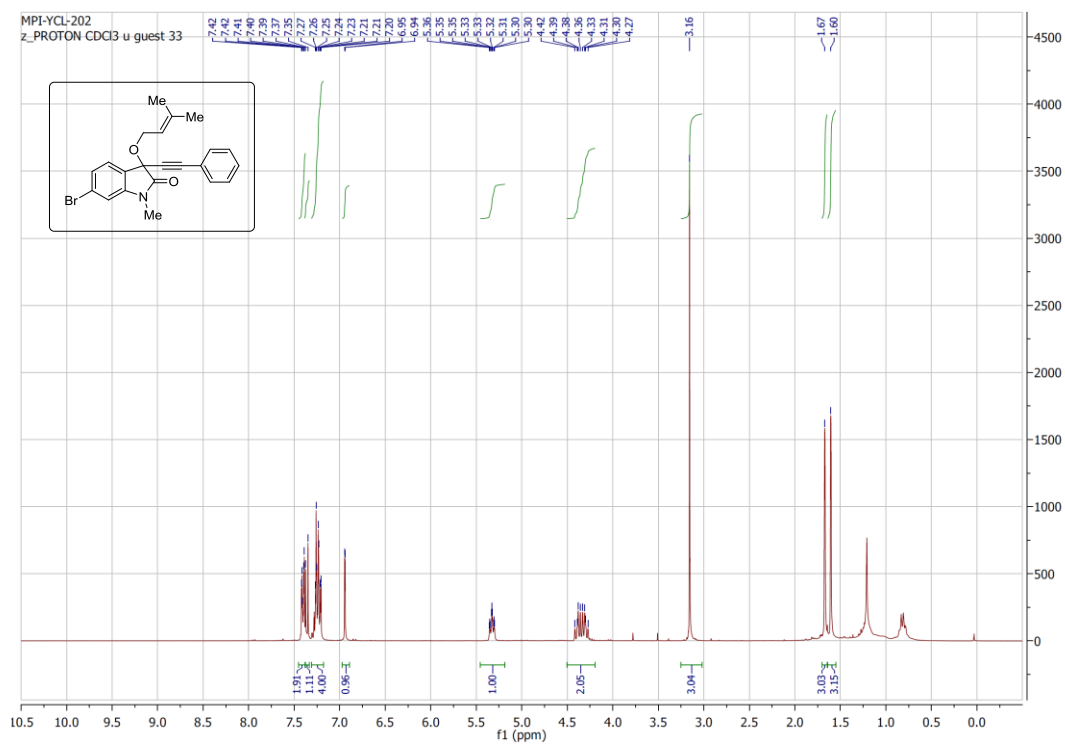
Supplementary Figure 60. ¹H and ¹³C NMR spectra for 13i.



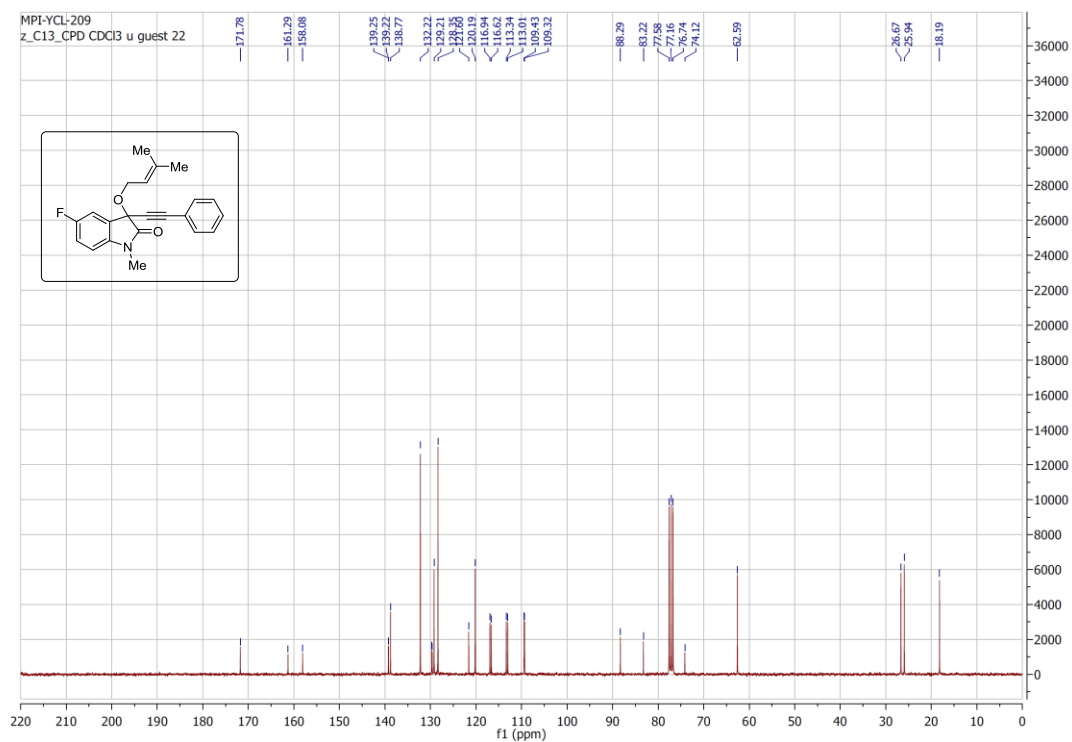
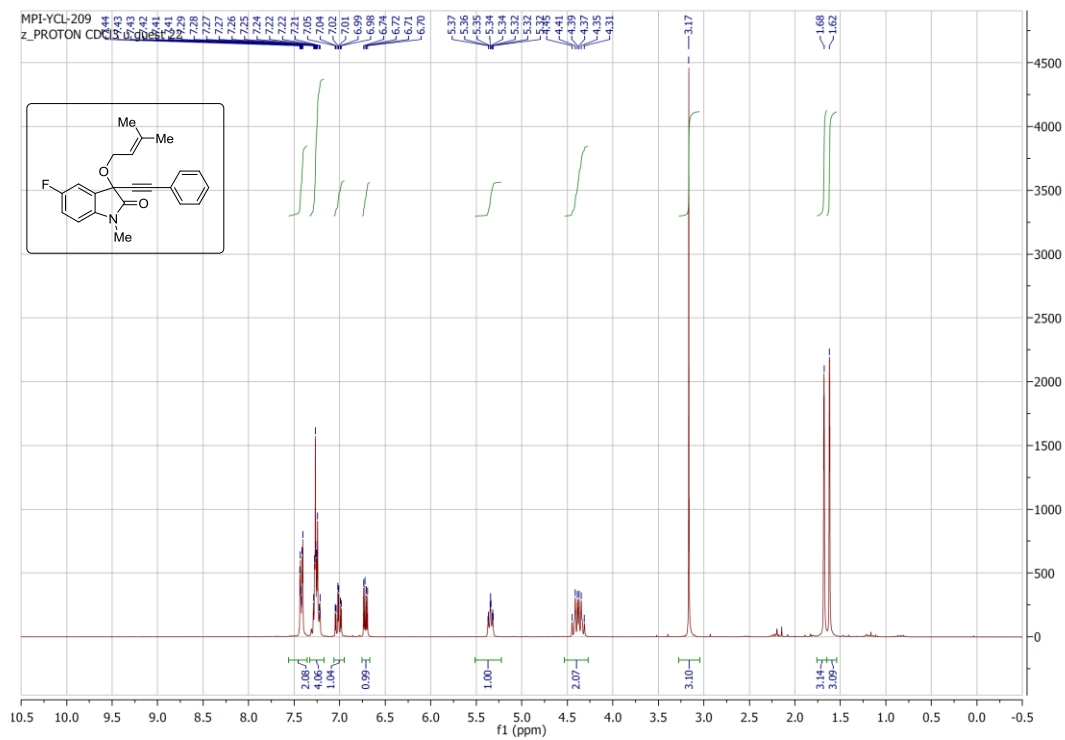
Supplementary Figure 61. ^1H and ^{13}C NMR spectra for **13j**.



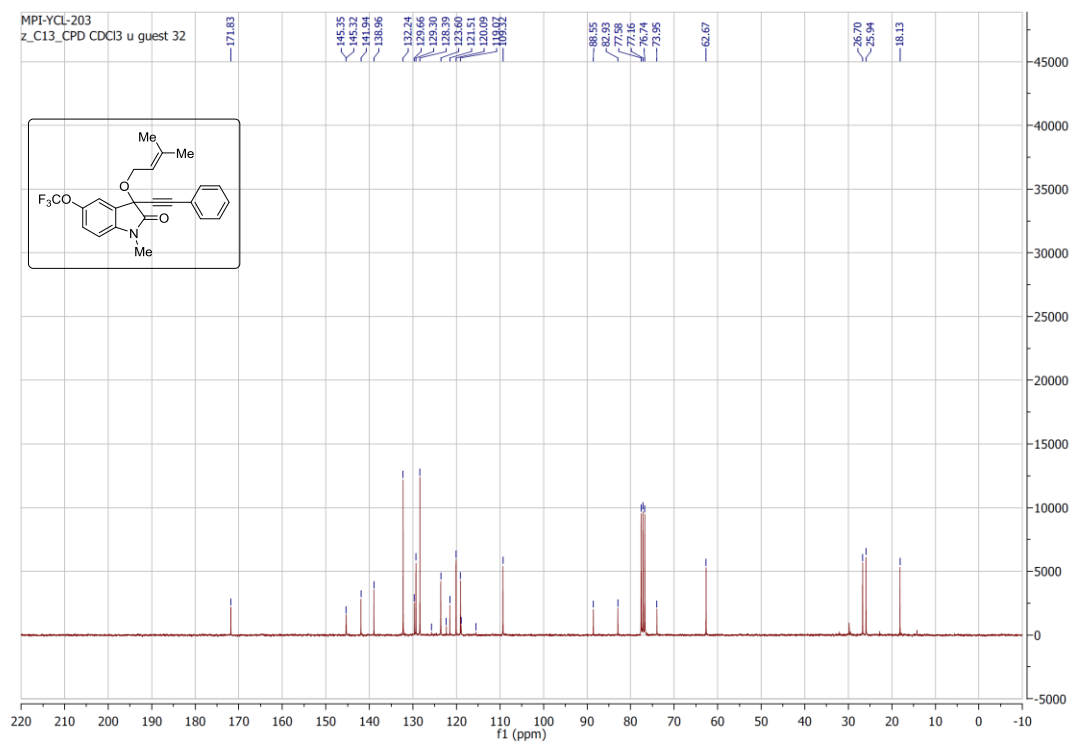
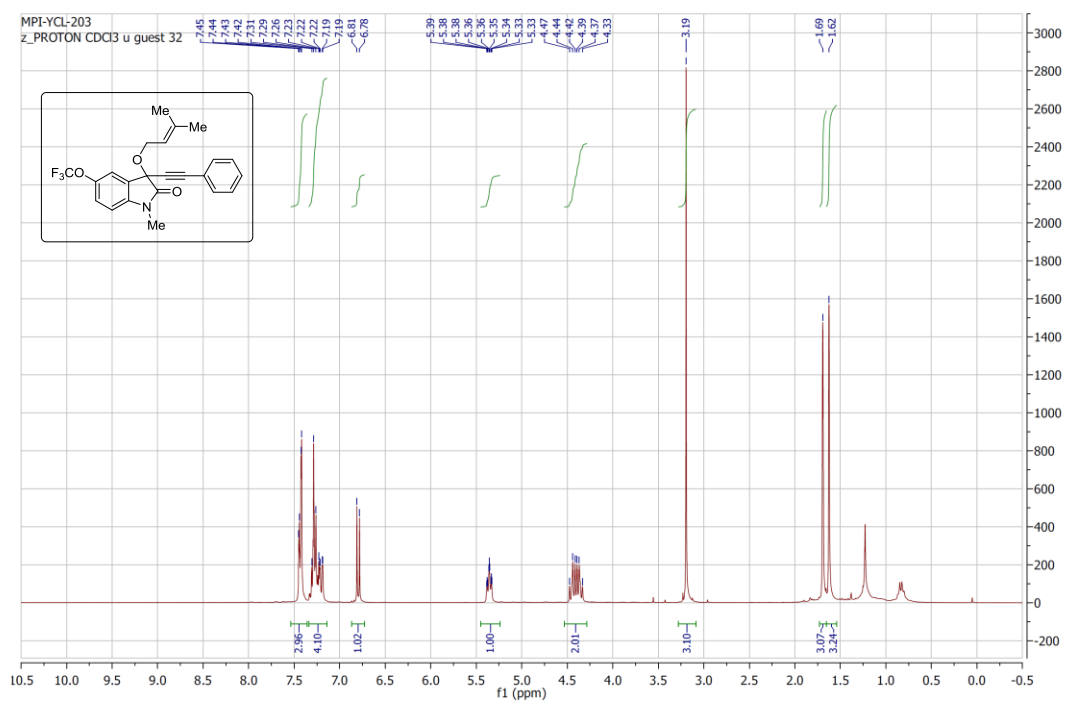
Supplementary Figure 62. ¹H and ¹³C NMR spectra for 13k.



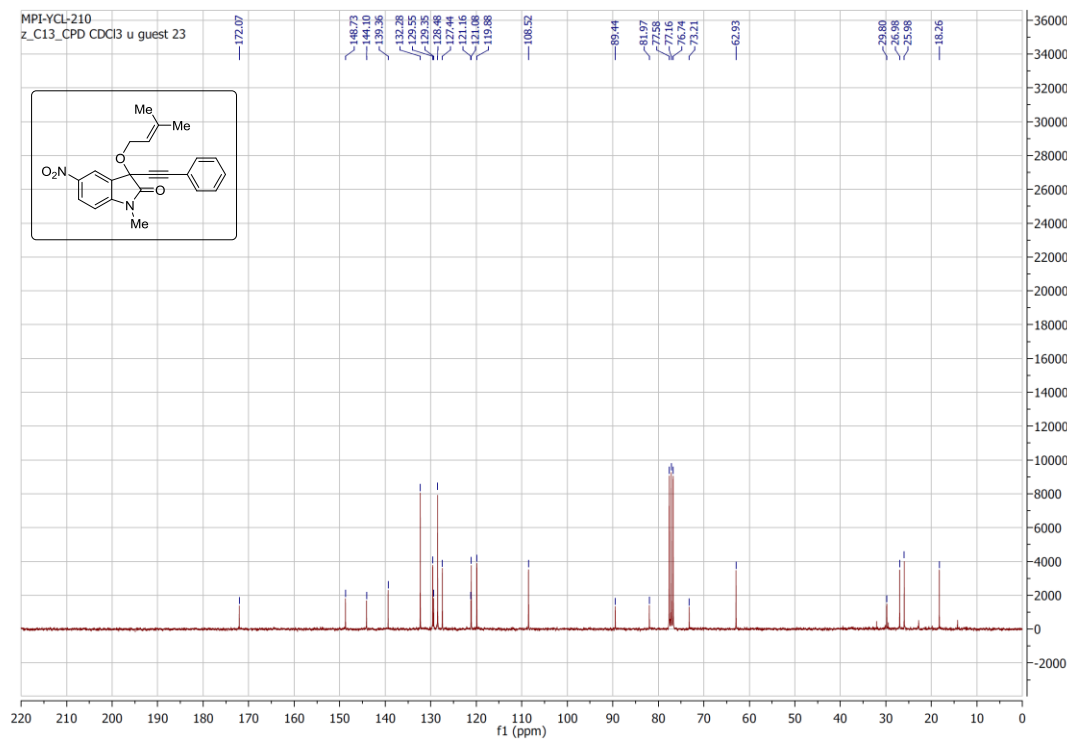
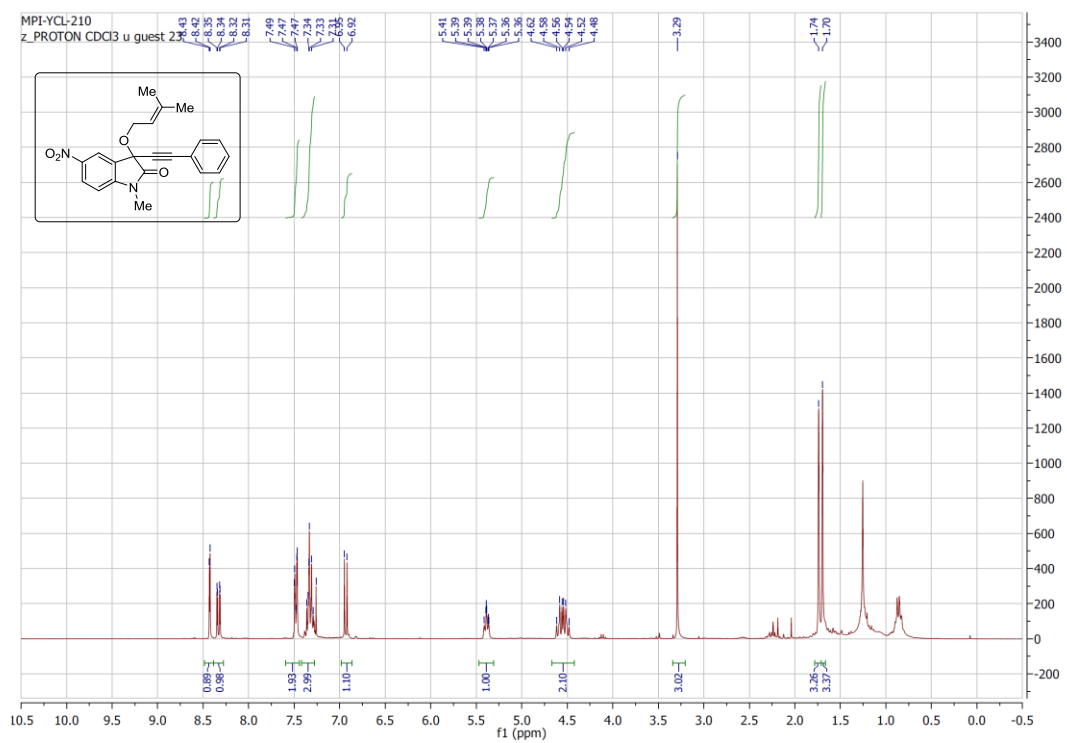
Supplementary Figure 63. ^1H and ^{13}C NMR spectra for **13l**.



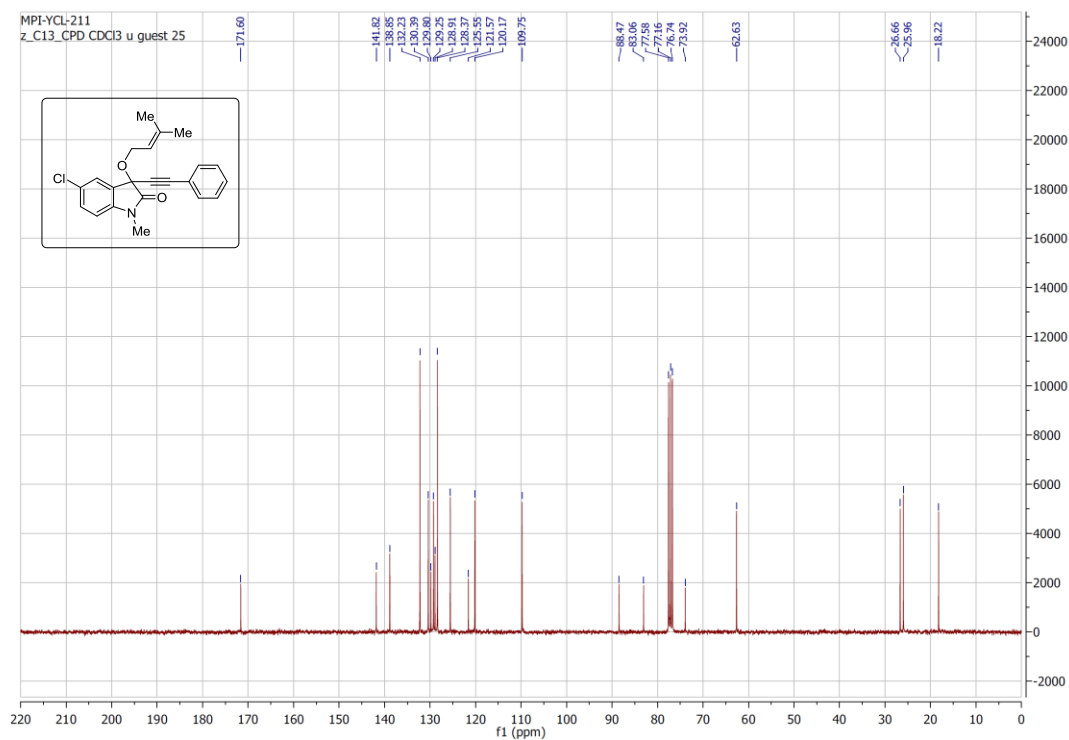
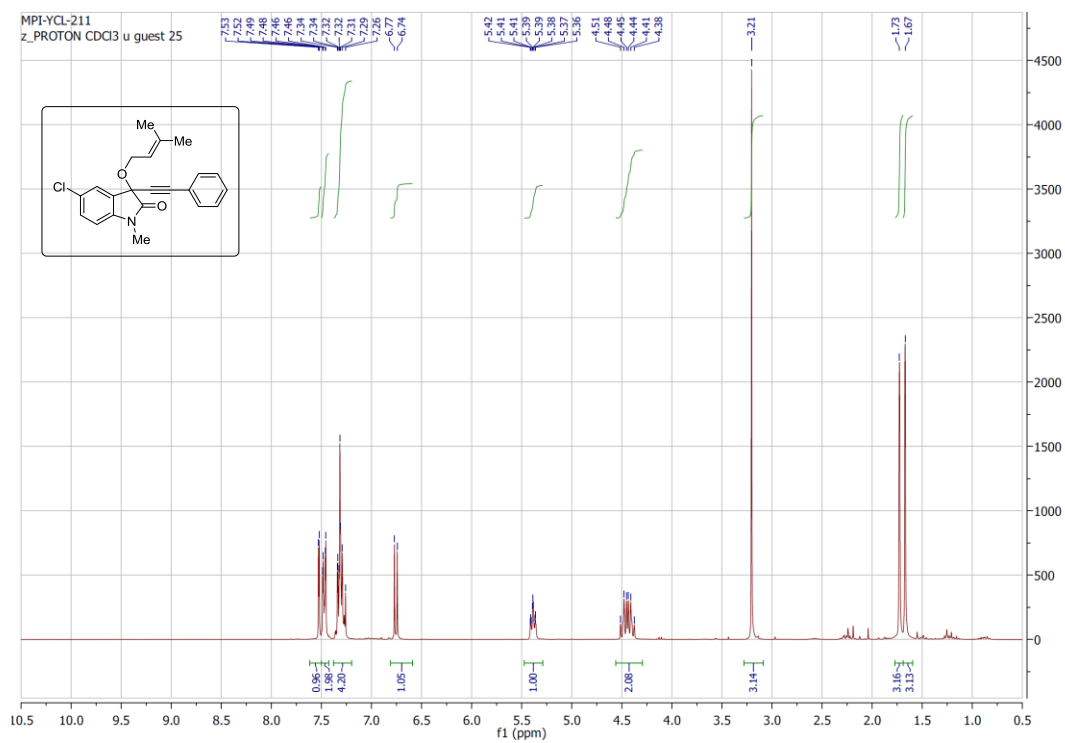
Supplementary Figure 64. ^1H and ^{13}C NMR spectra for **13m**.



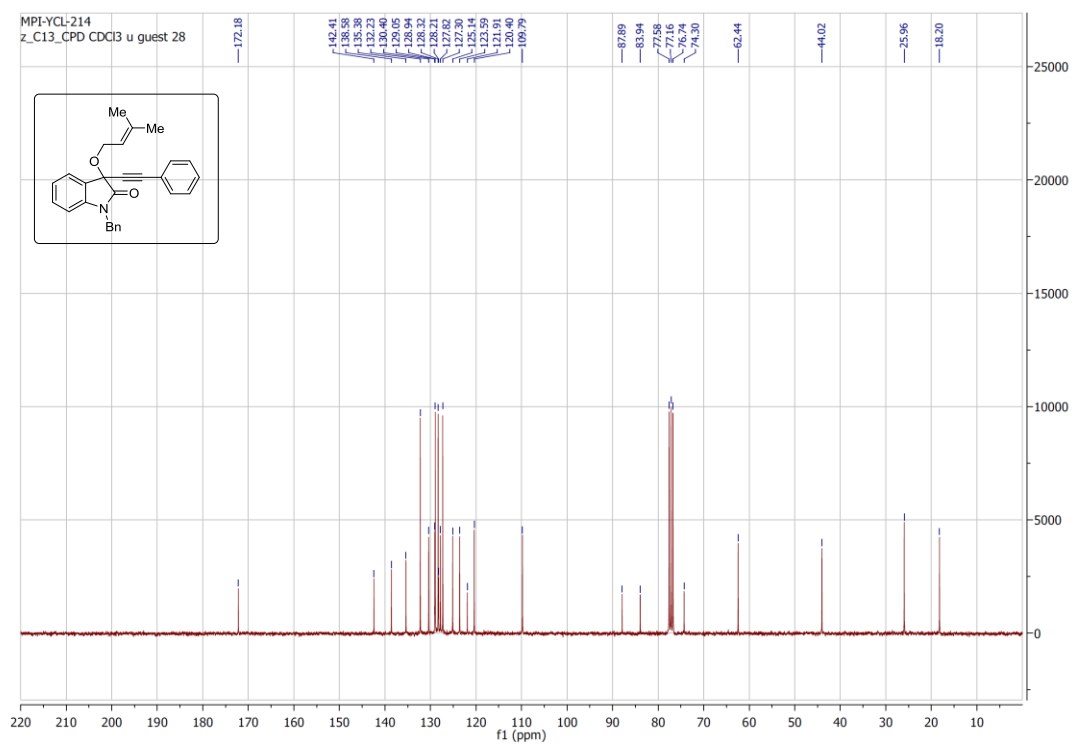
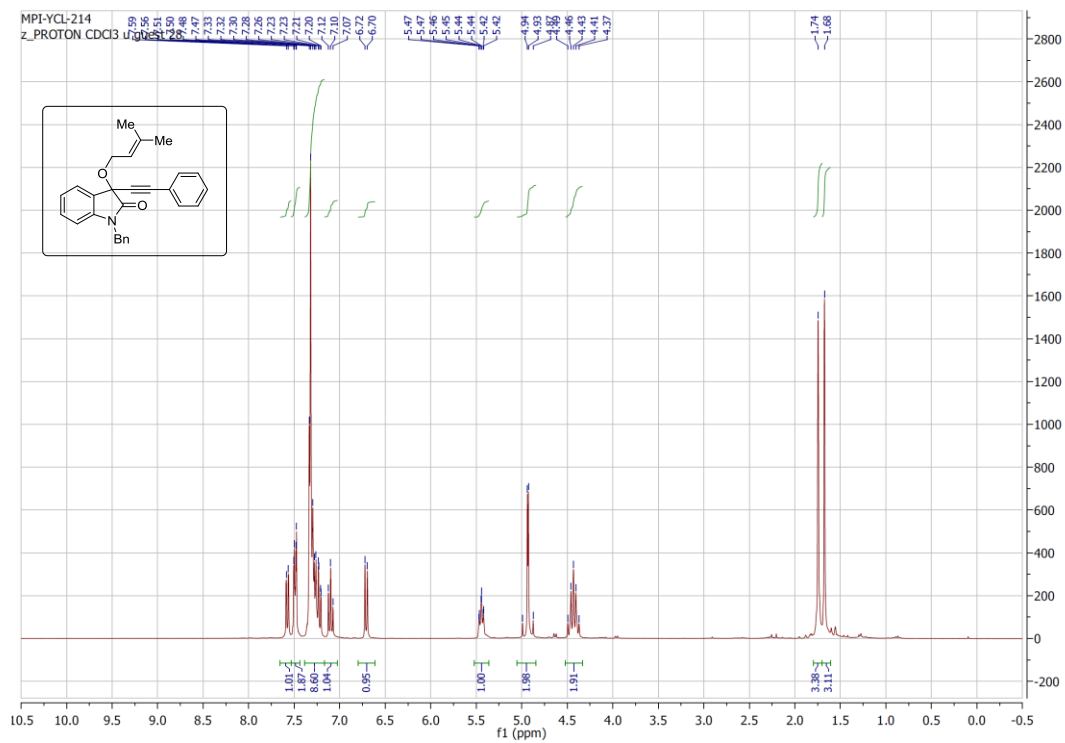
Supplementary Figure 65. ^1H and ^{13}C NMR spectra for **13n**.



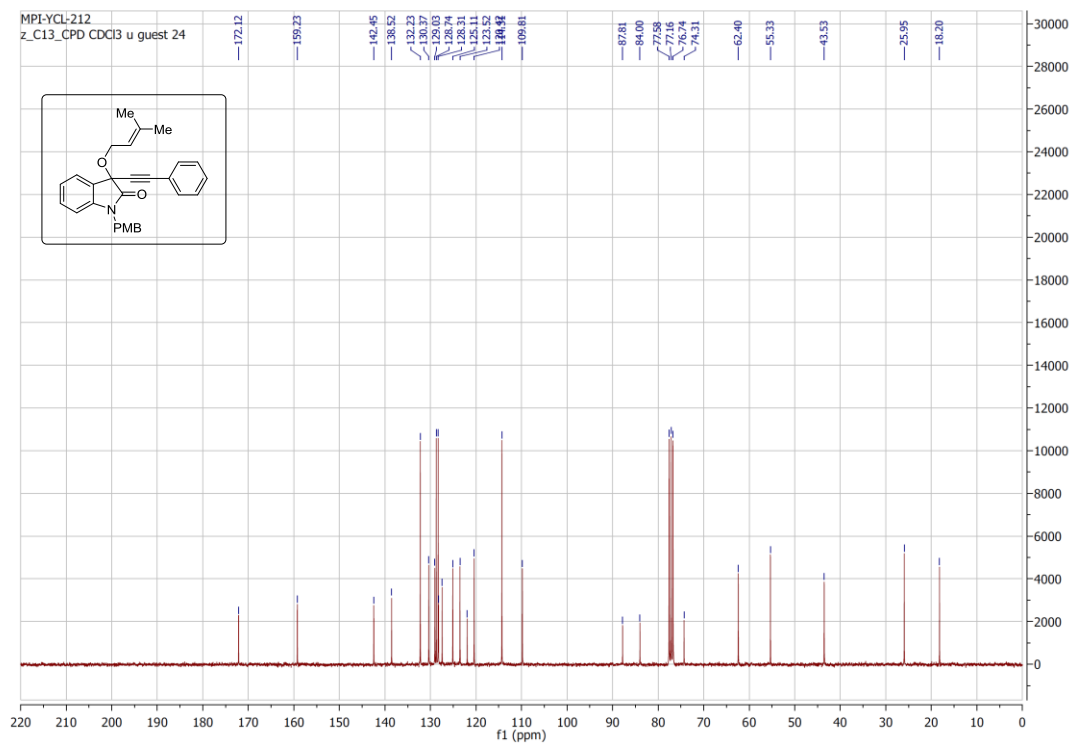
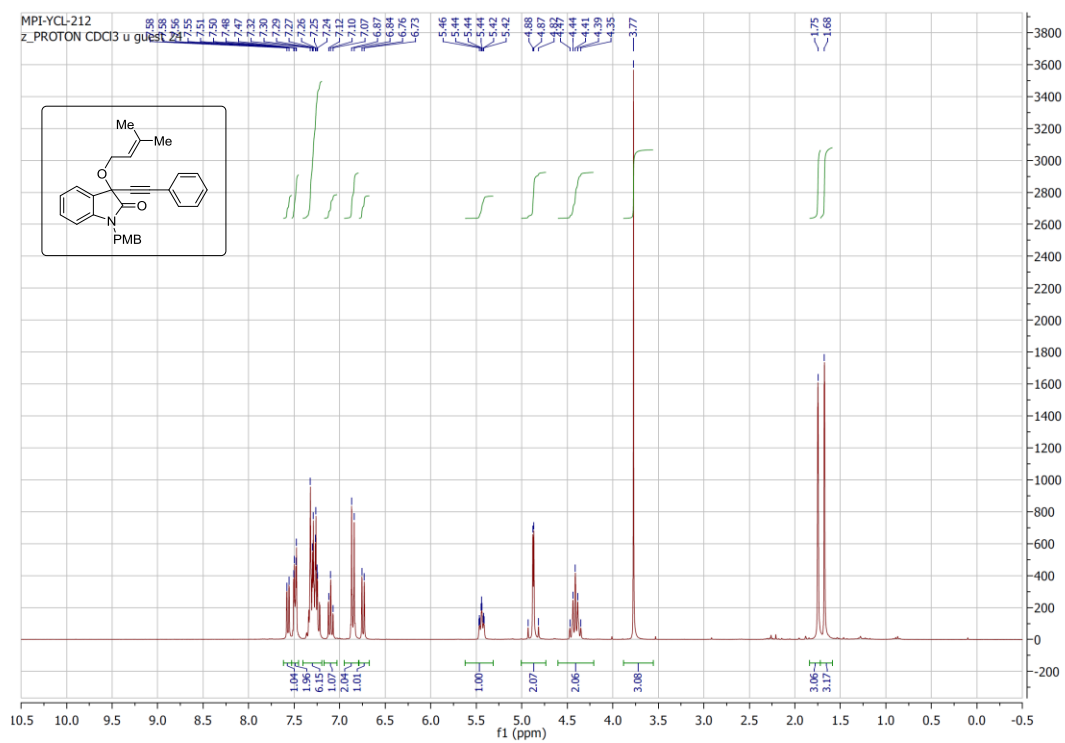
Supplementary Figure 66. ^1H and ^{13}C NMR spectra for **13o**.



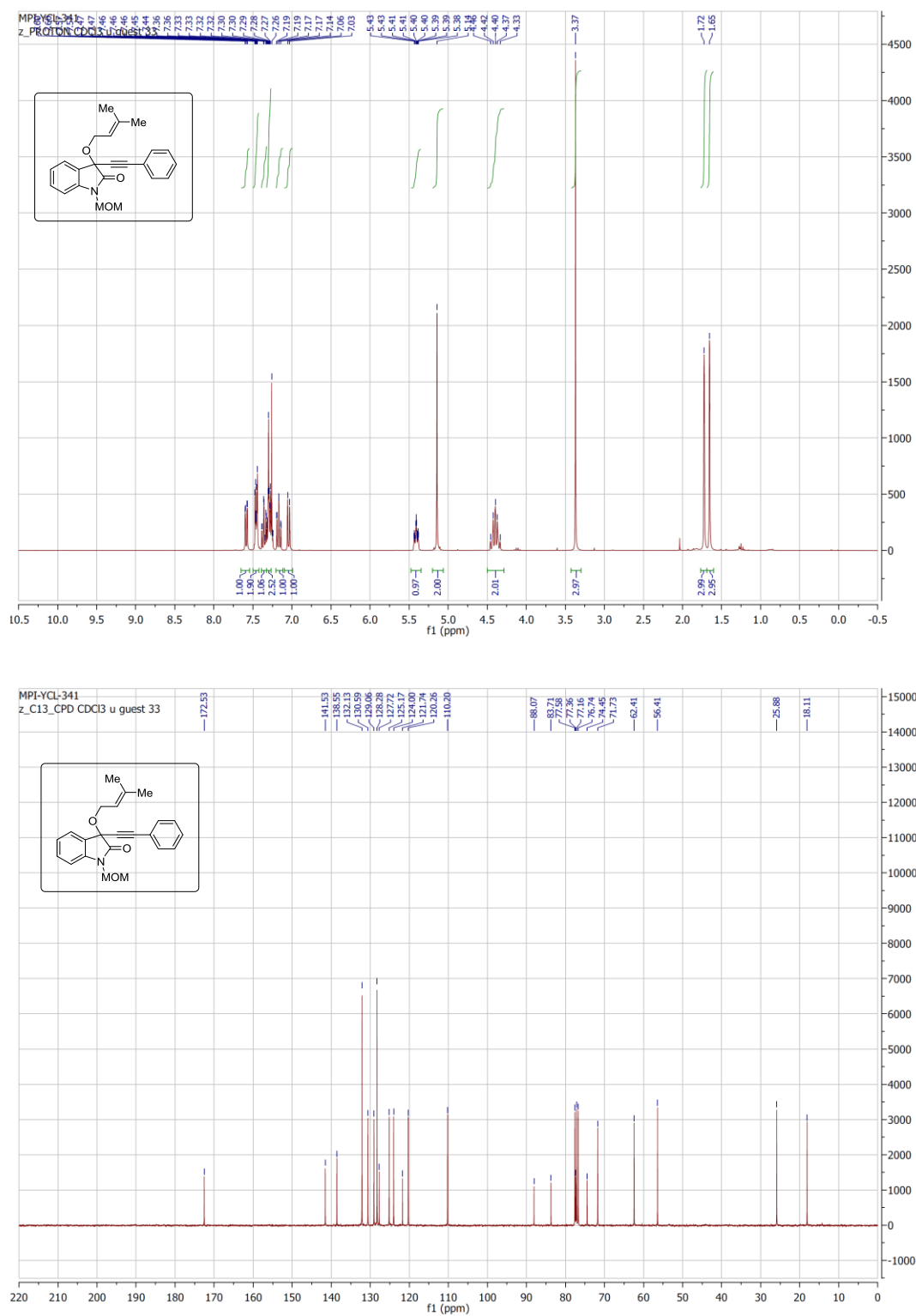
Supplementary Figure 67. ^1H and ^{13}C NMR spectra for **13p**.



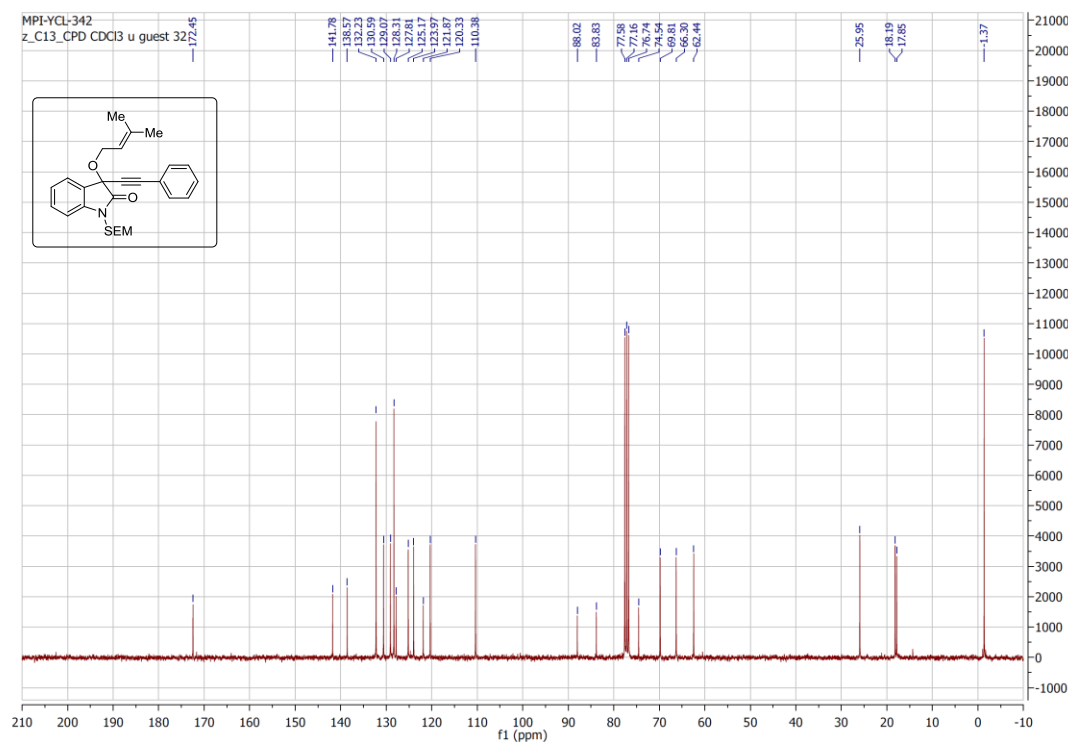
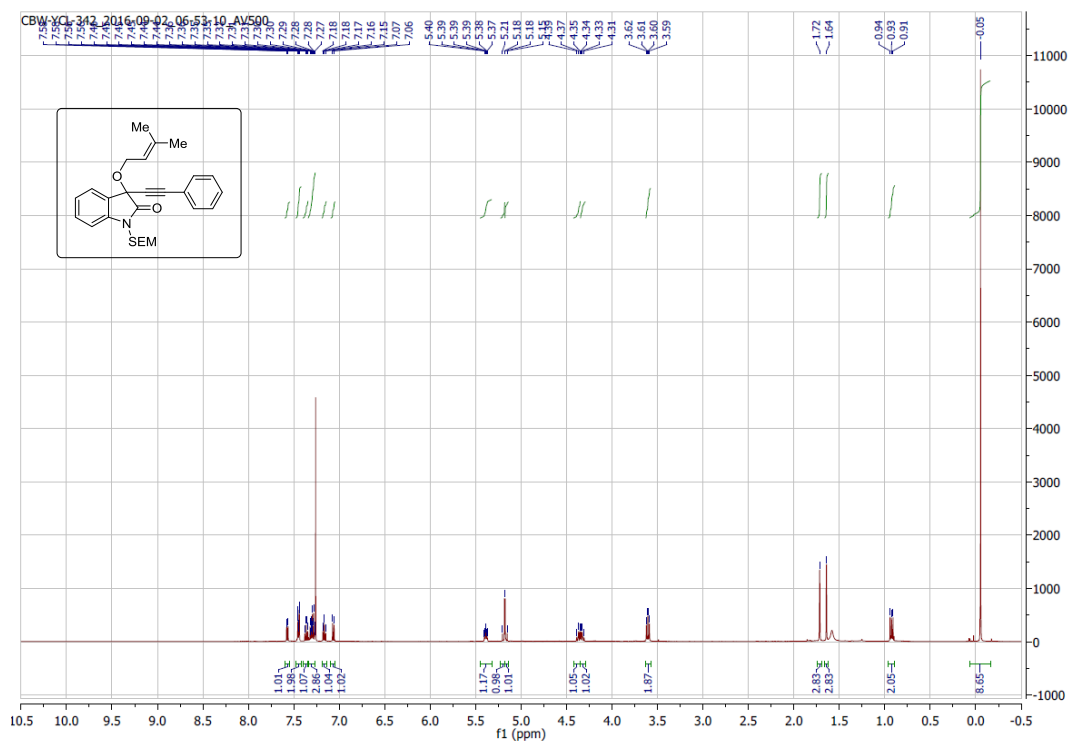
Supplementary Figure 68. ¹H and ¹³C NMR spectra for **13q**.



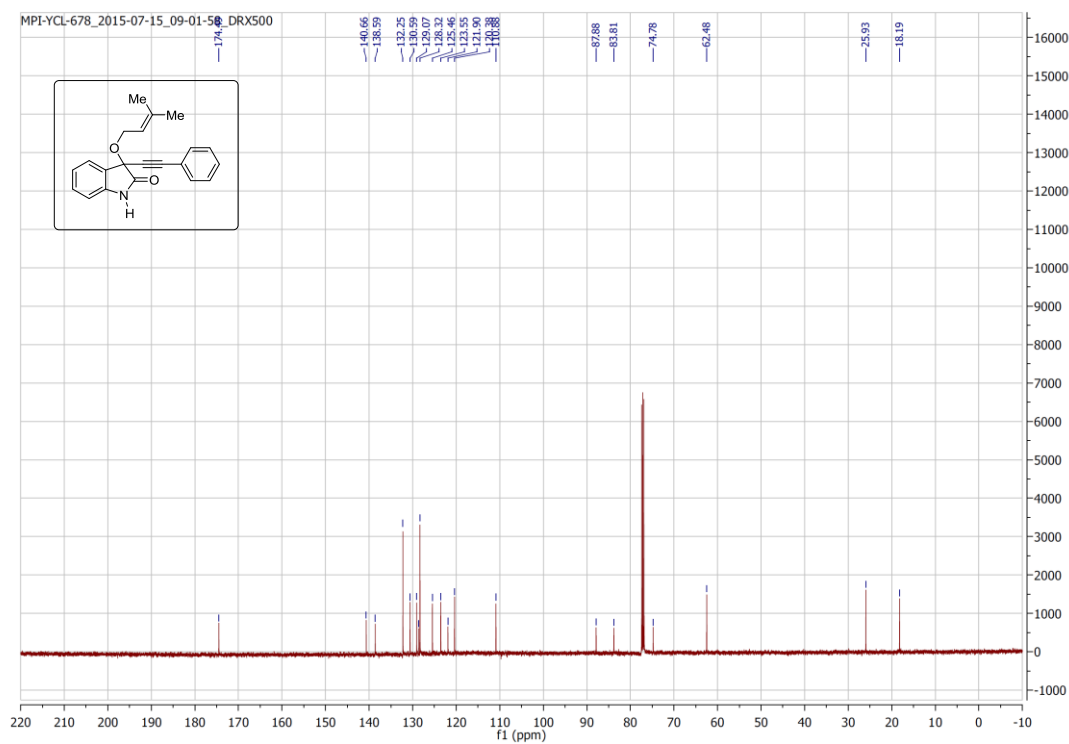
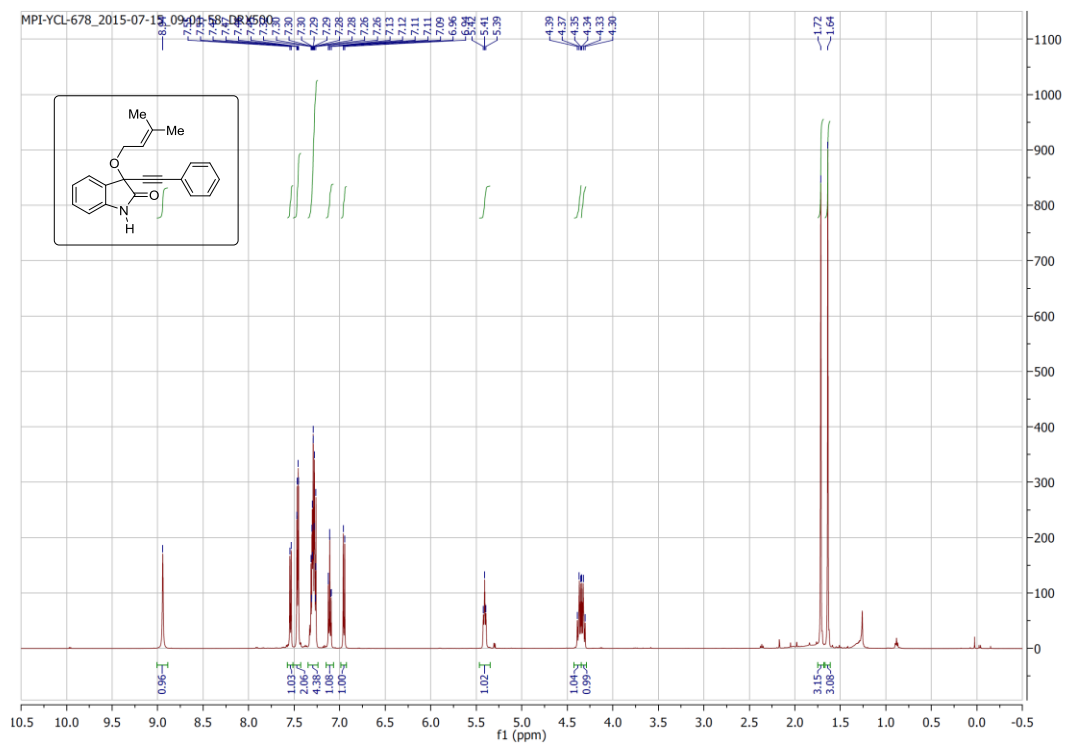
Supplementary Figure 69. ^1H and ^{13}C NMR spectra for **13r**.



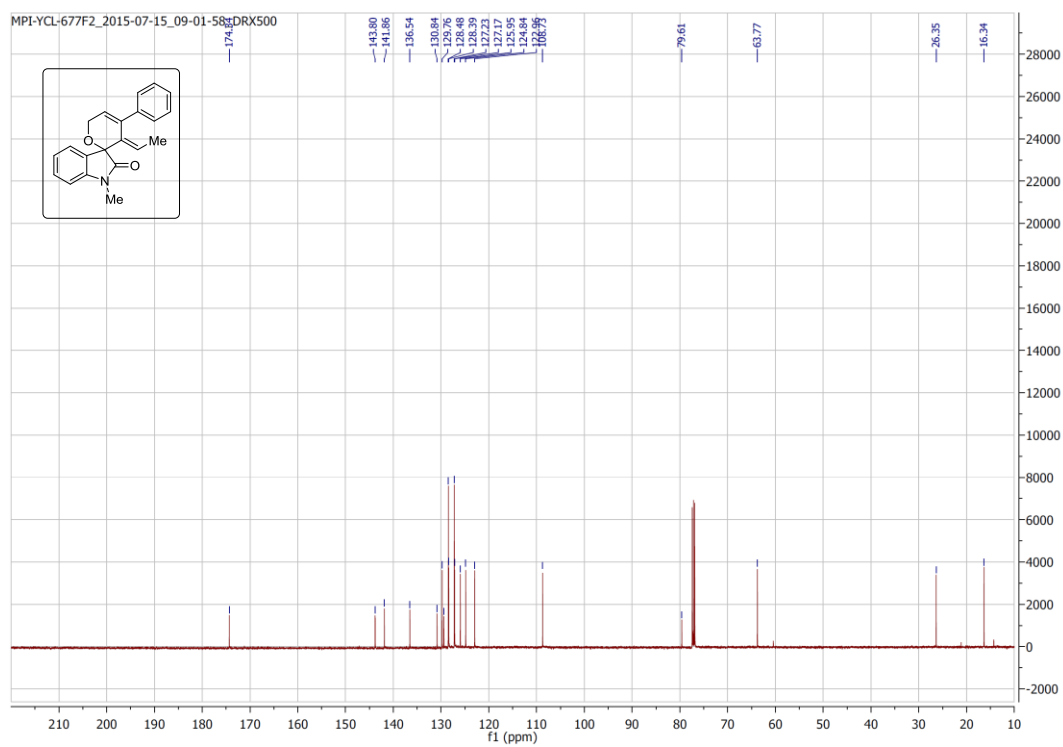
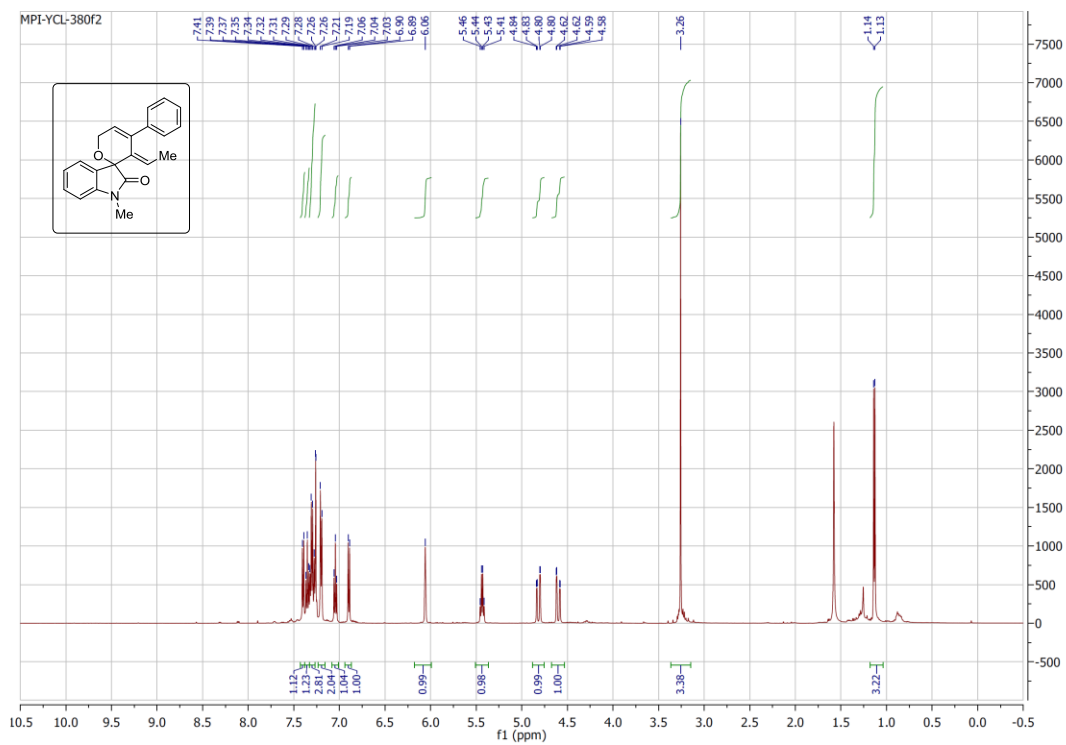
Supplementary Figure 70. ¹H and ¹³C NMR spectra for 13s.



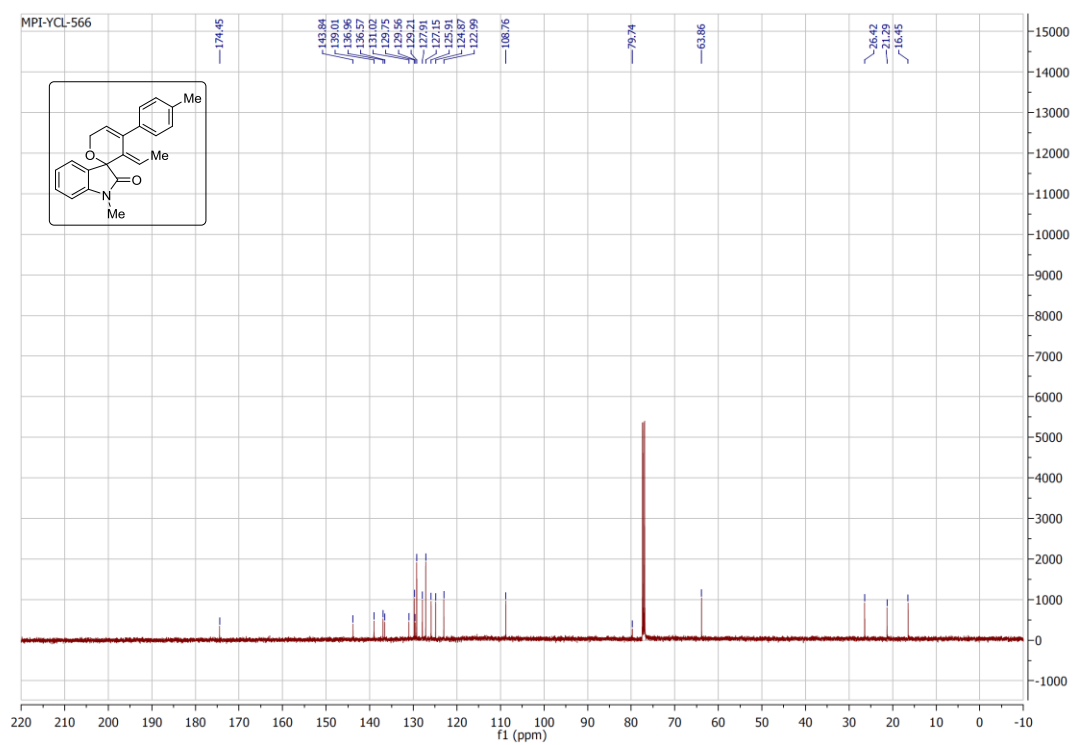
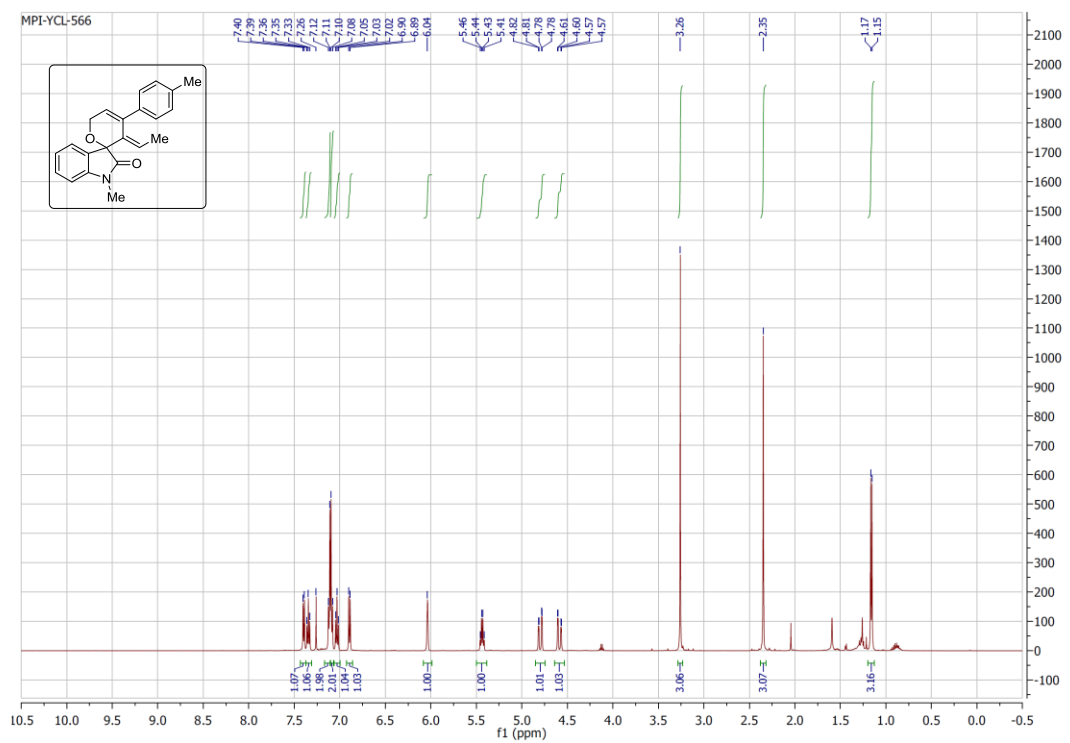
Supplementary Figure 71. ¹H and ¹³C NMR spectra for **13t**.



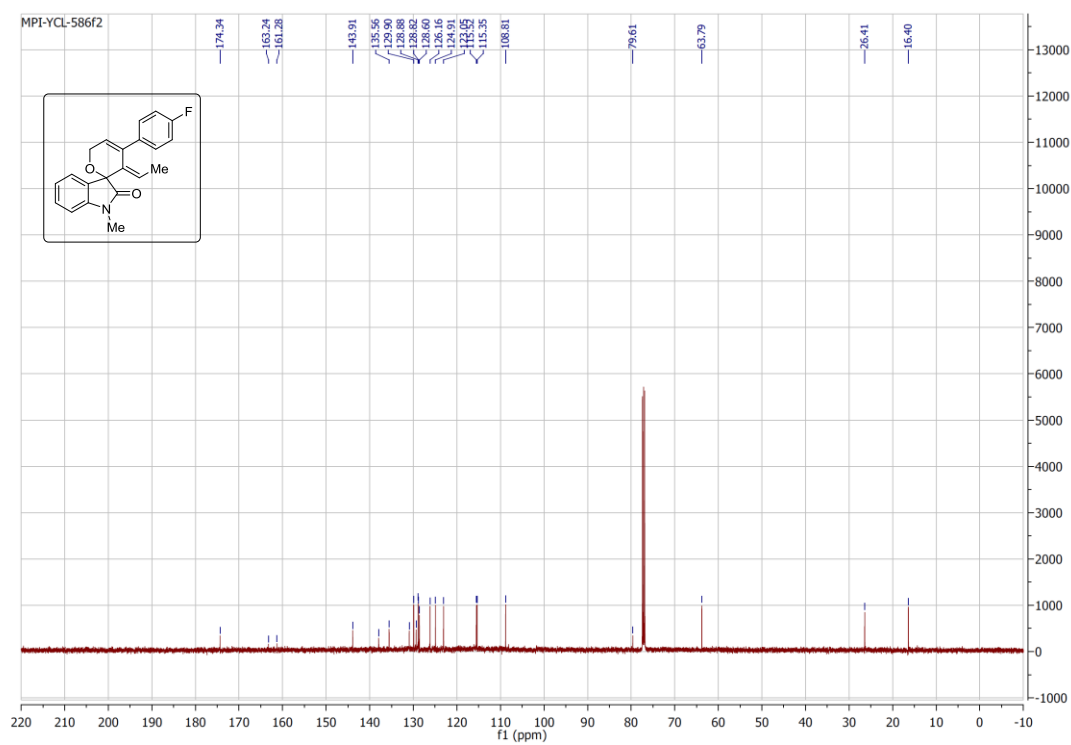
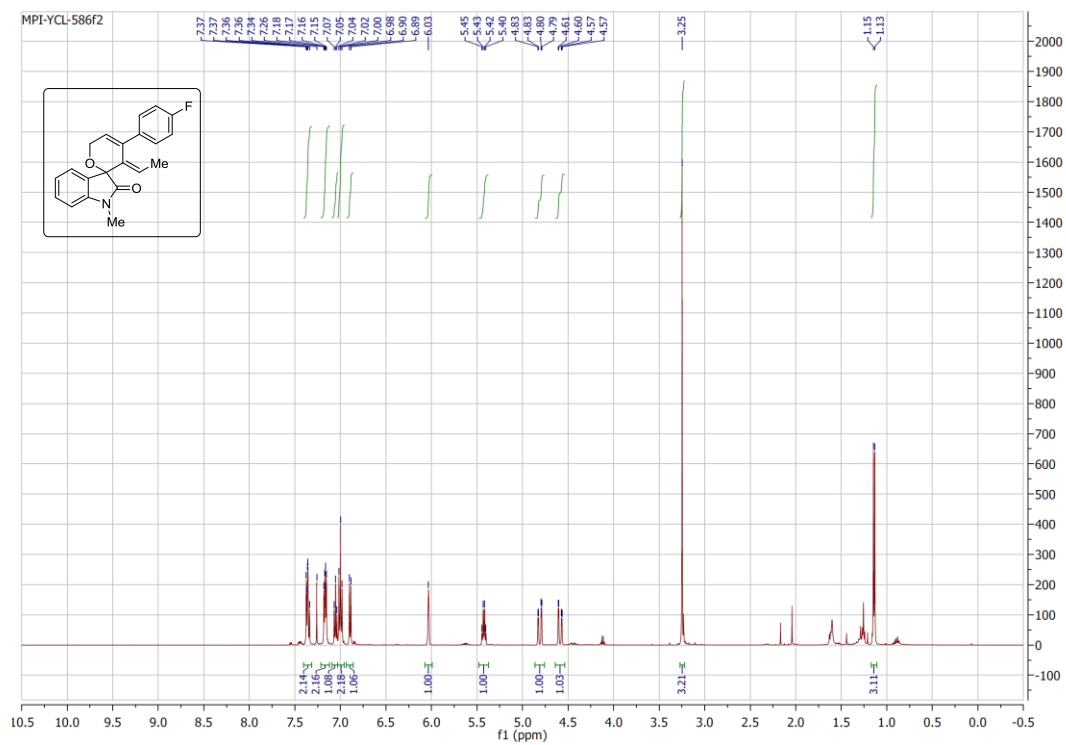
Supplementary Figure 72. ¹H and ¹³C NMR spectra for **13u**.



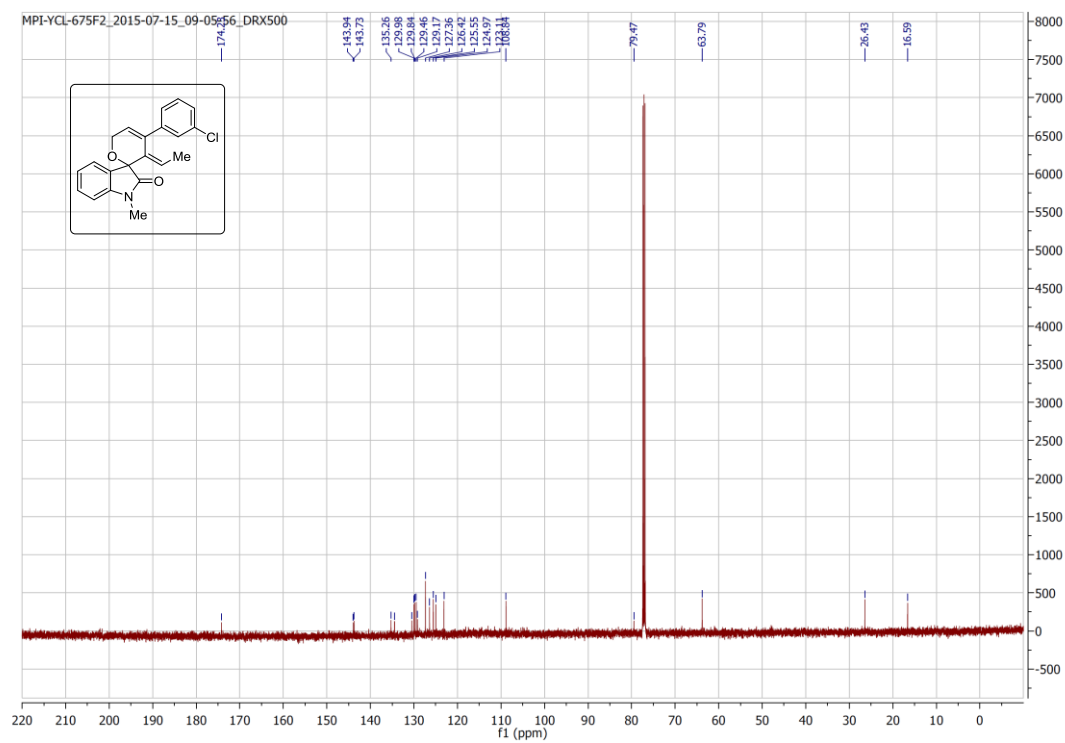
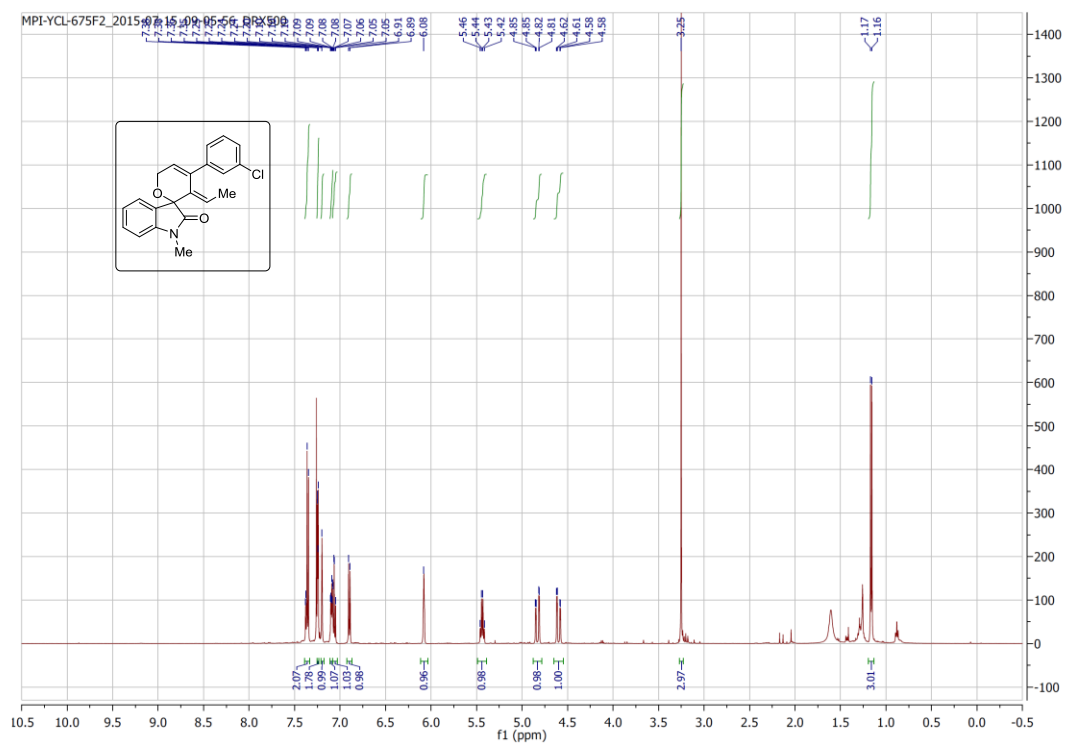
Supplementary Figure 73. ¹H and ¹³C NMR spectra for 2a.



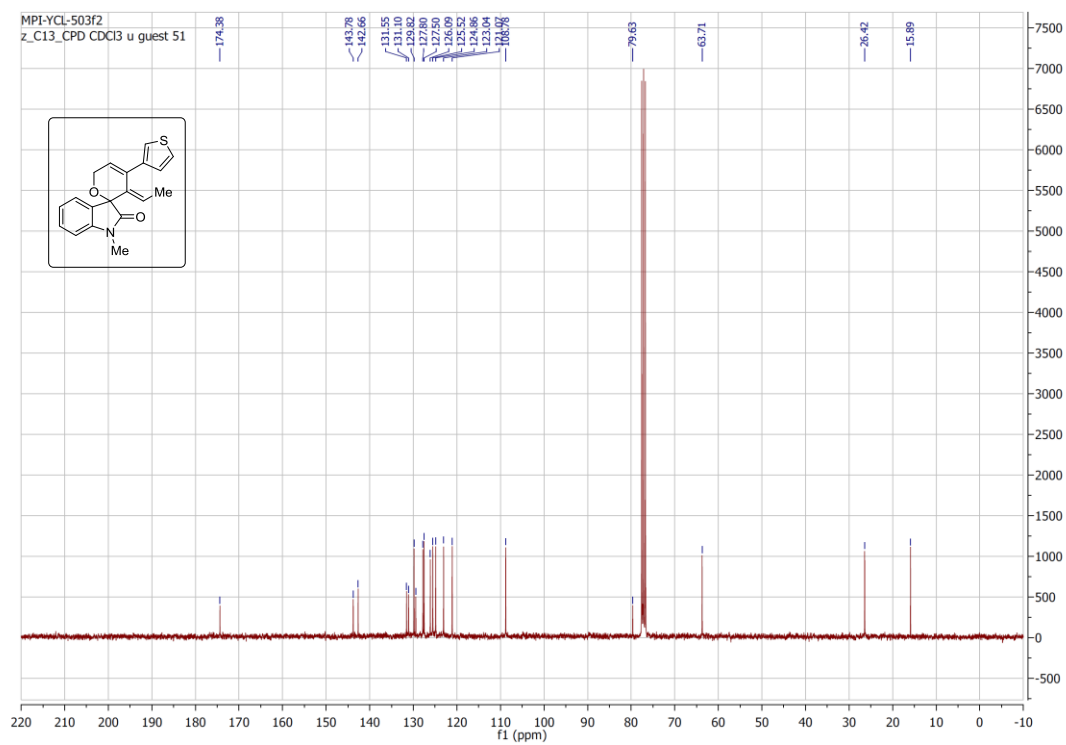
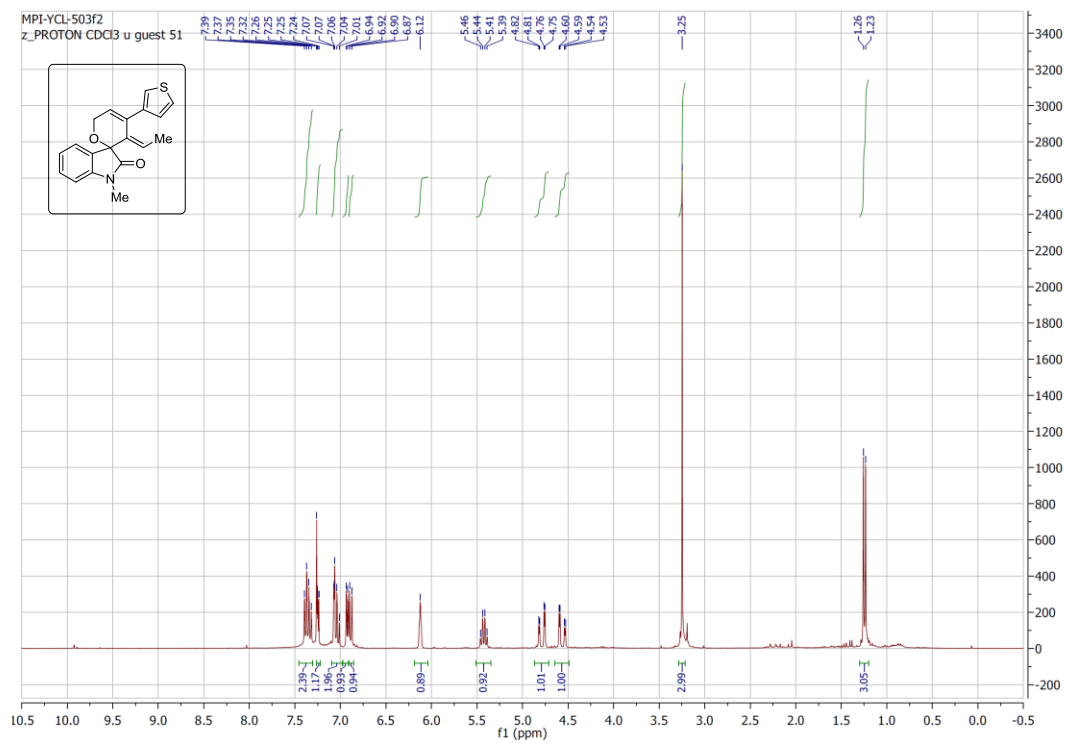
Supplementary Figure 74. ¹H and ¹³C NMR spectra for **2b**.



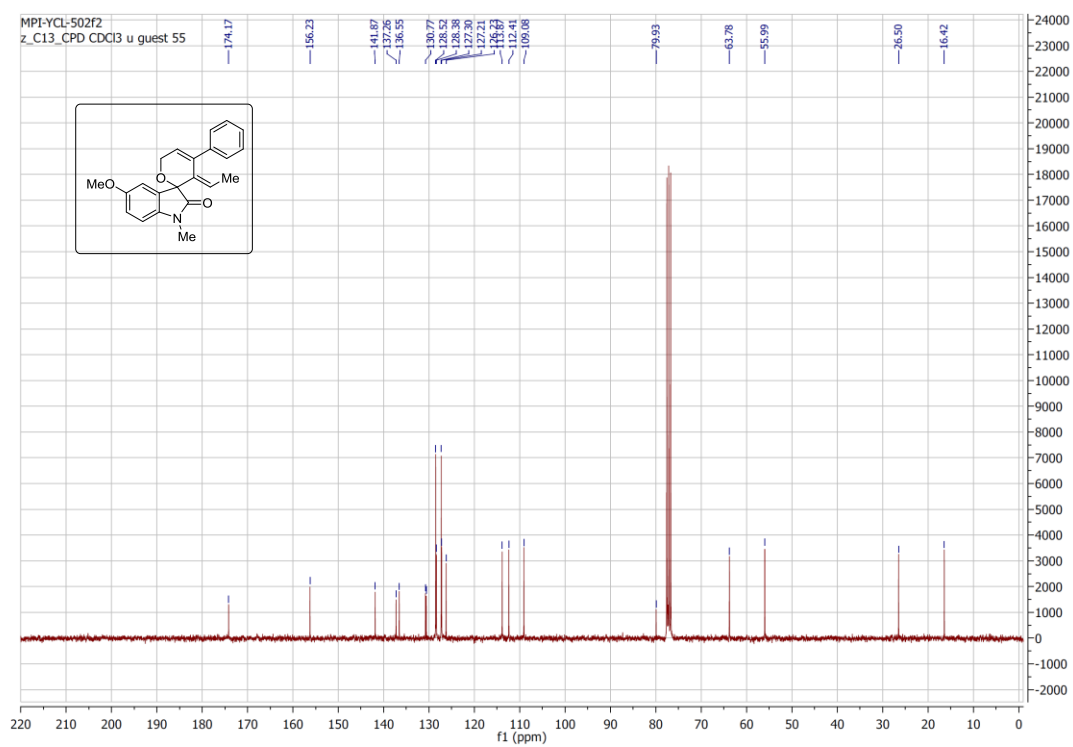
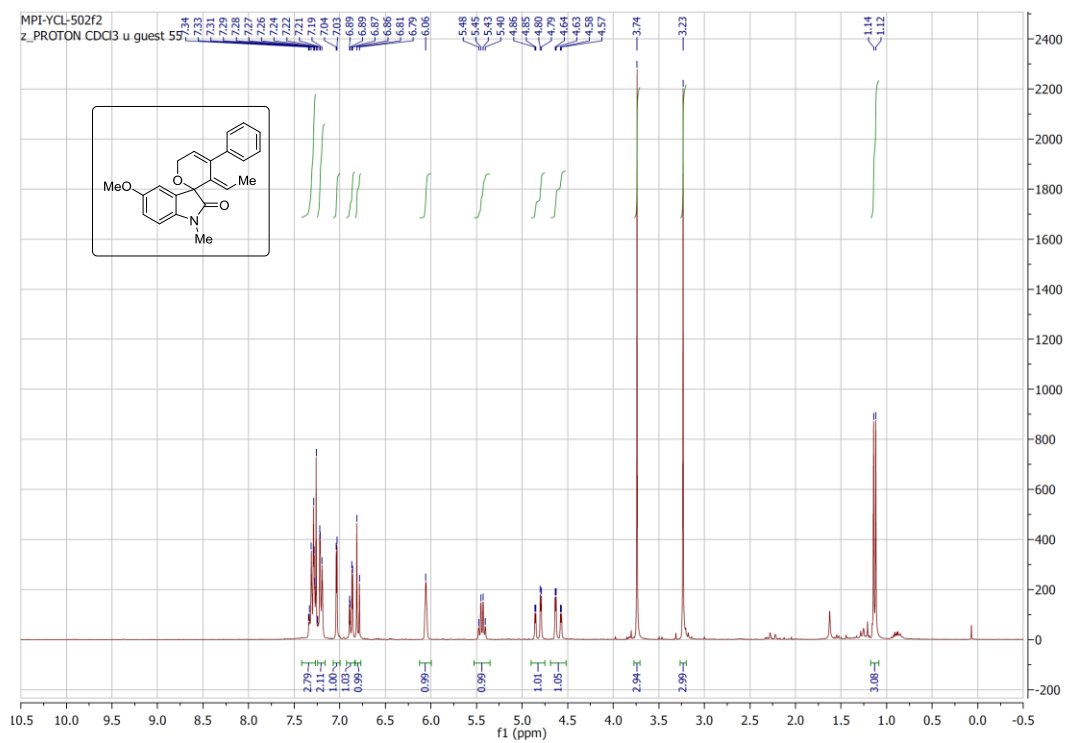
Supplementary Figure 75. ^1H and ^{13}C NMR spectra for 2c.



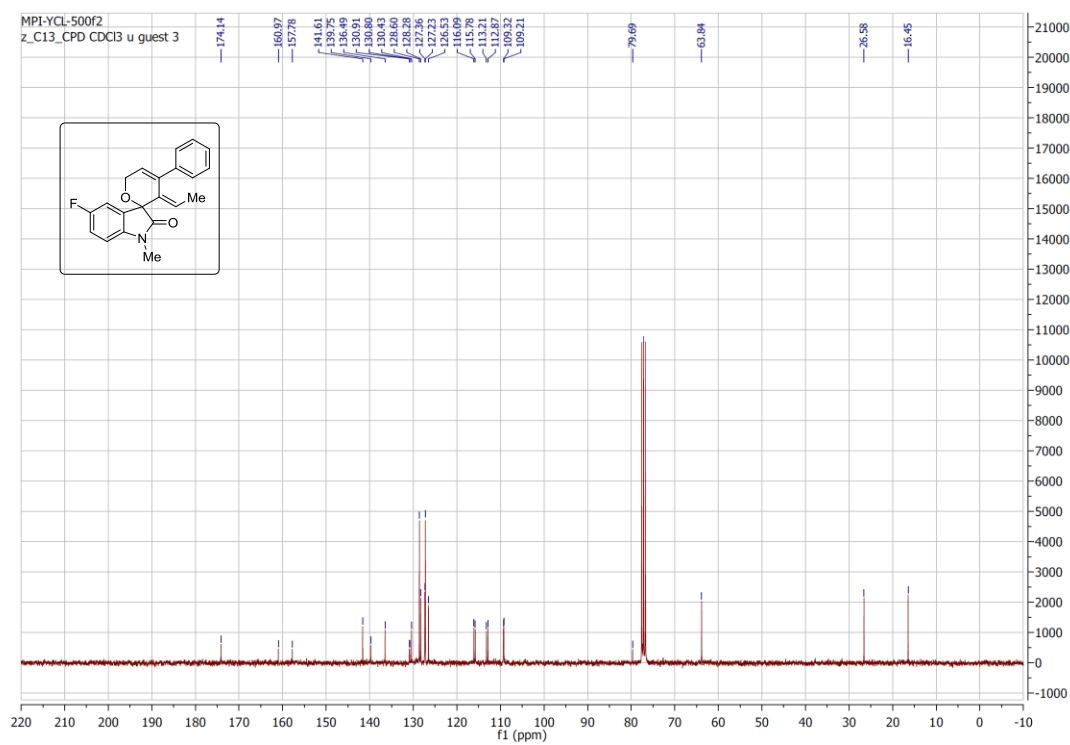
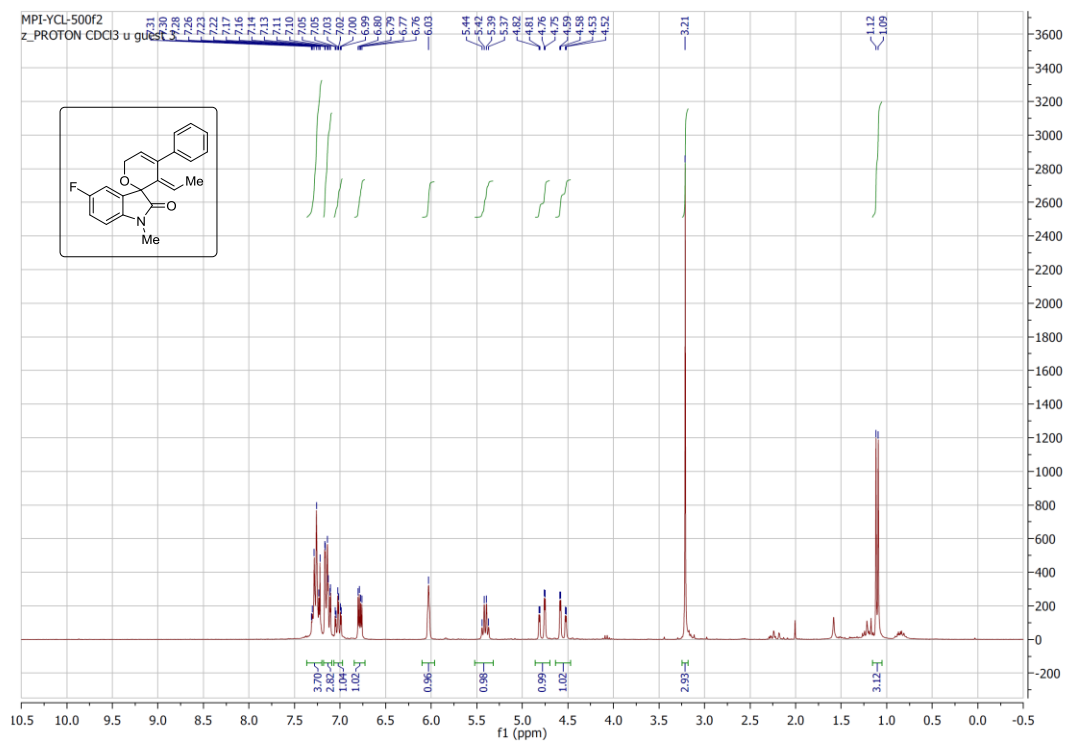
Supplementary Figure 76. ^1H and ^{13}C NMR spectra for **2d**.



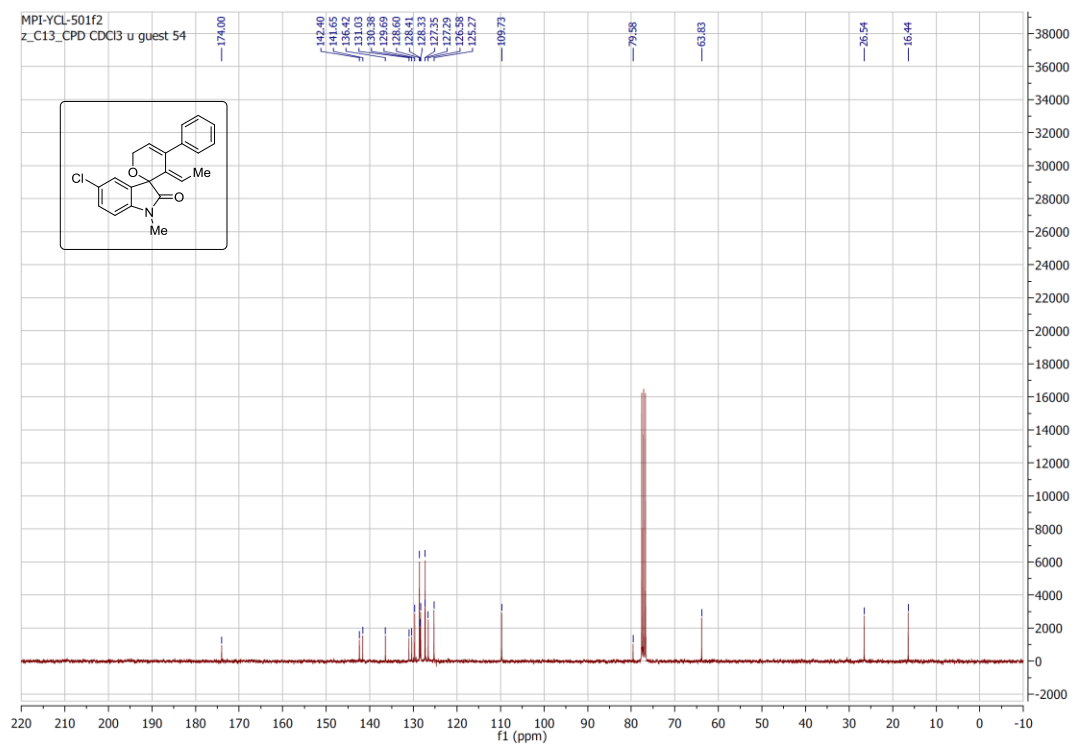
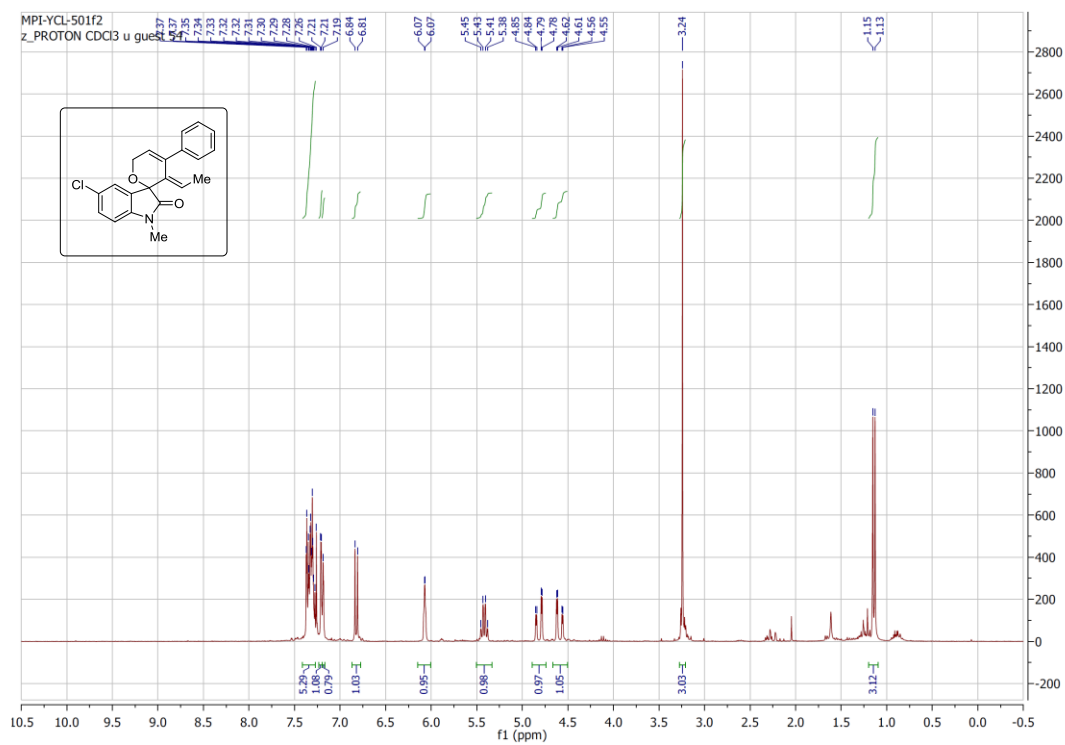
Supplementary Figure 77. ^1H and ^{13}C NMR spectra for **2e**.



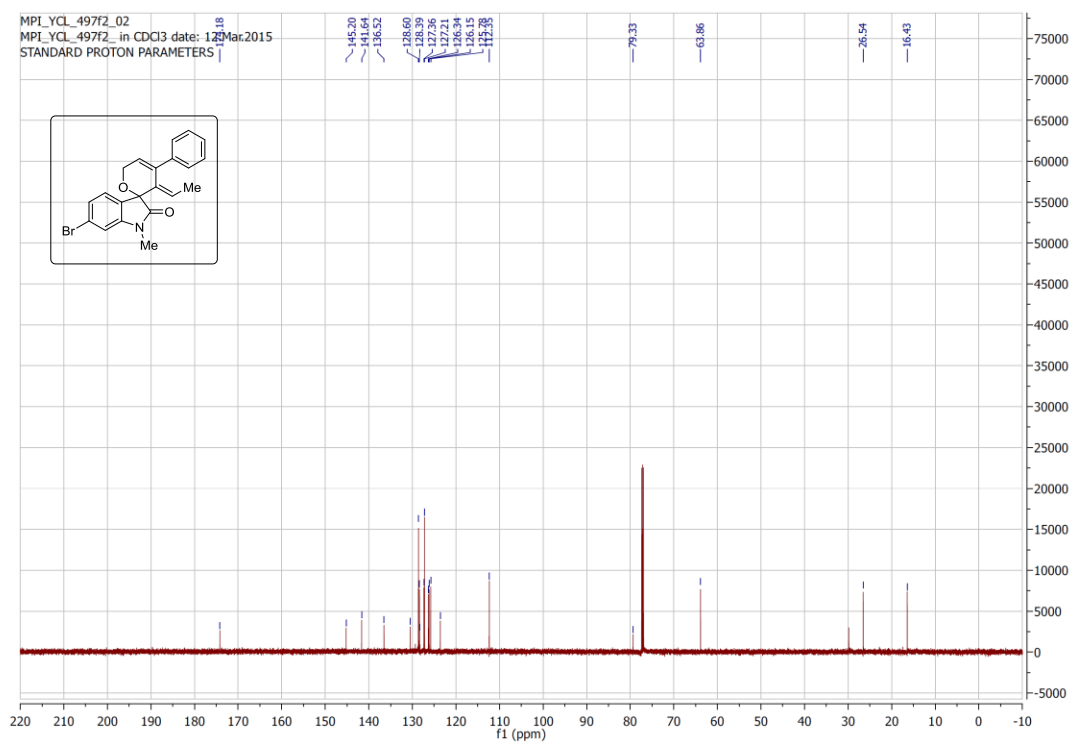
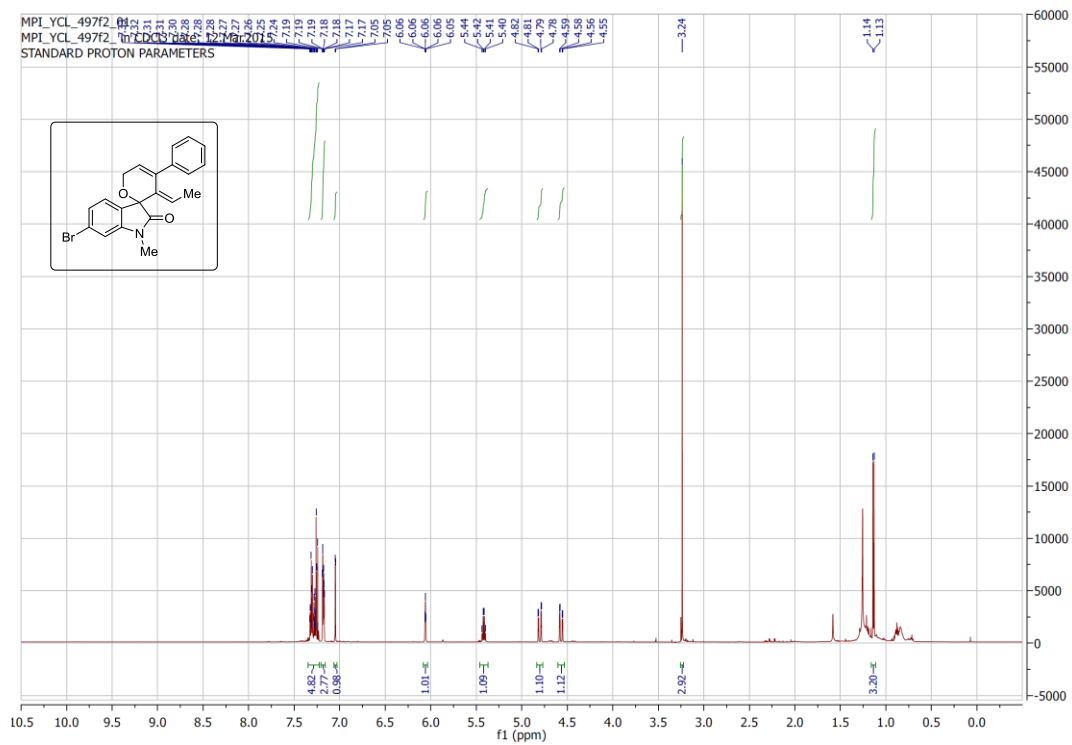
Supplementary Figure 78. ^1H and ^{13}C NMR spectra for **2f**.



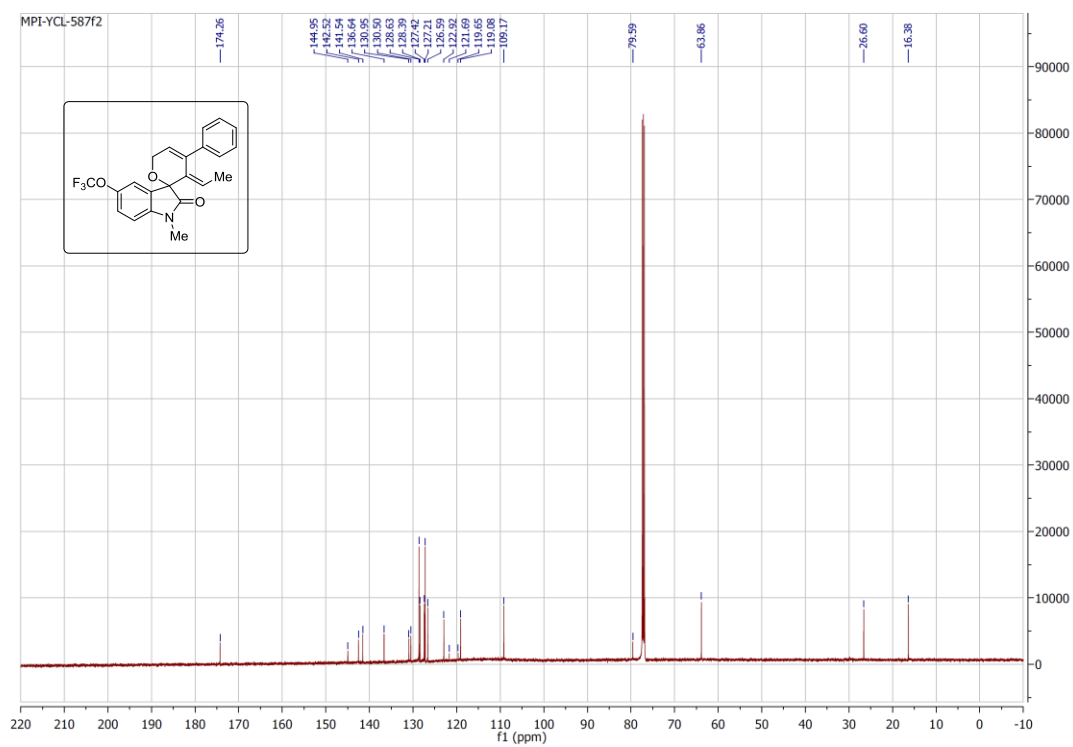
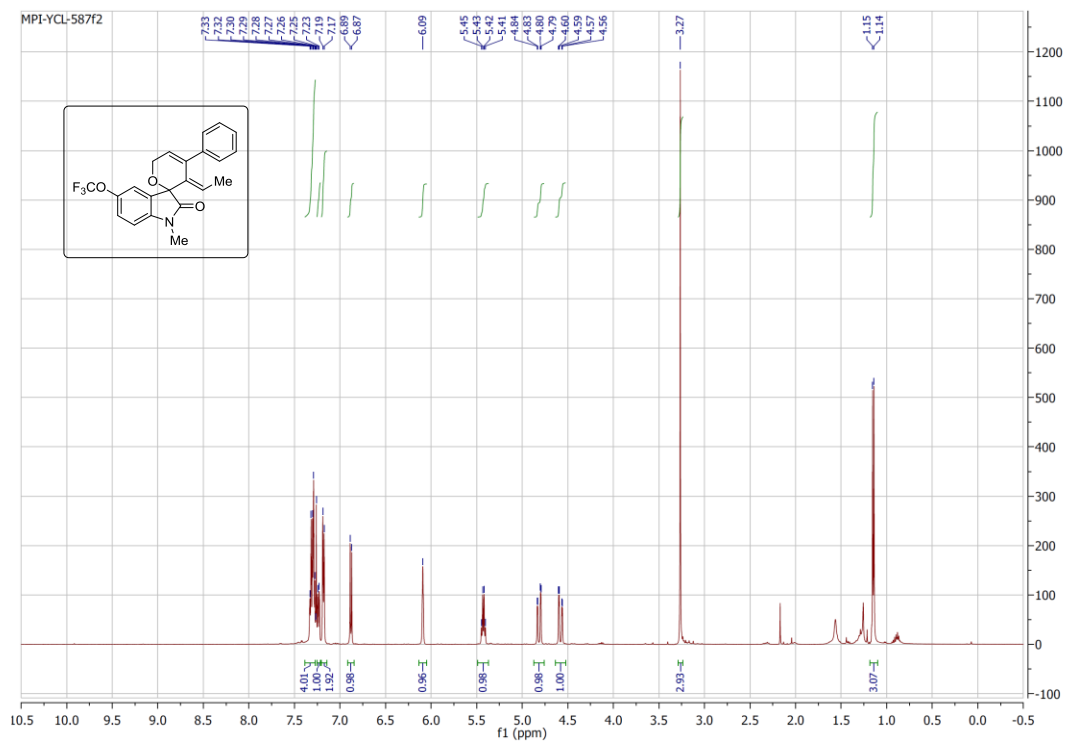
Supplementary Figure 79. ^1H and ^{13}C NMR spectra for **2g**.



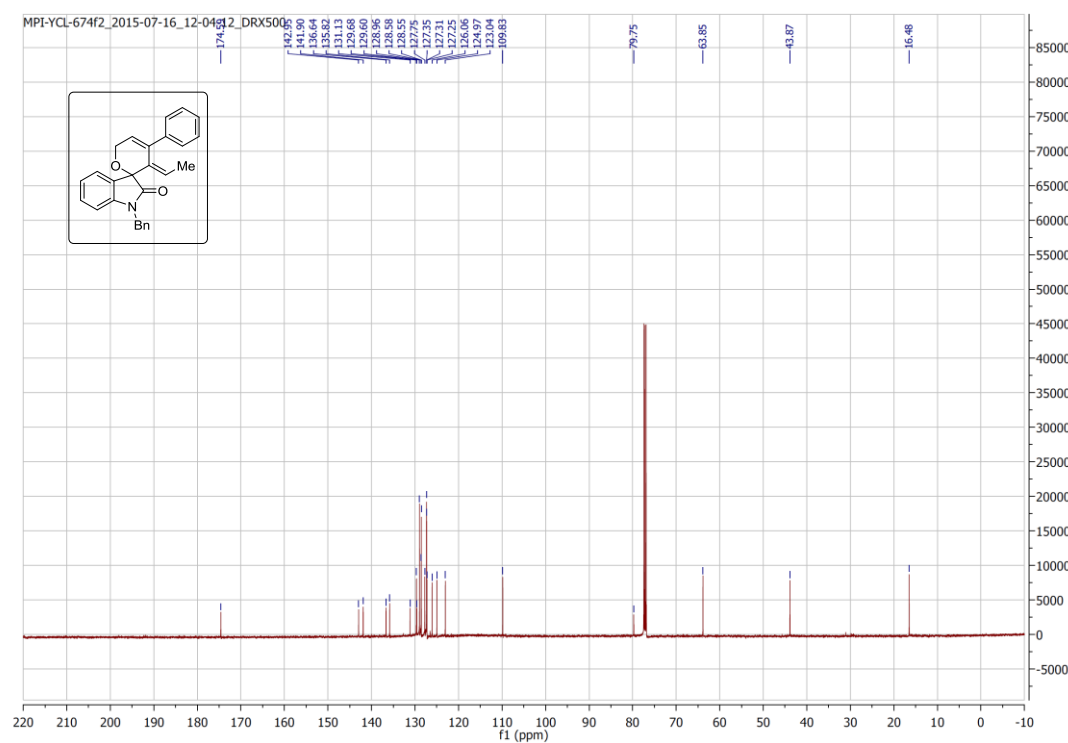
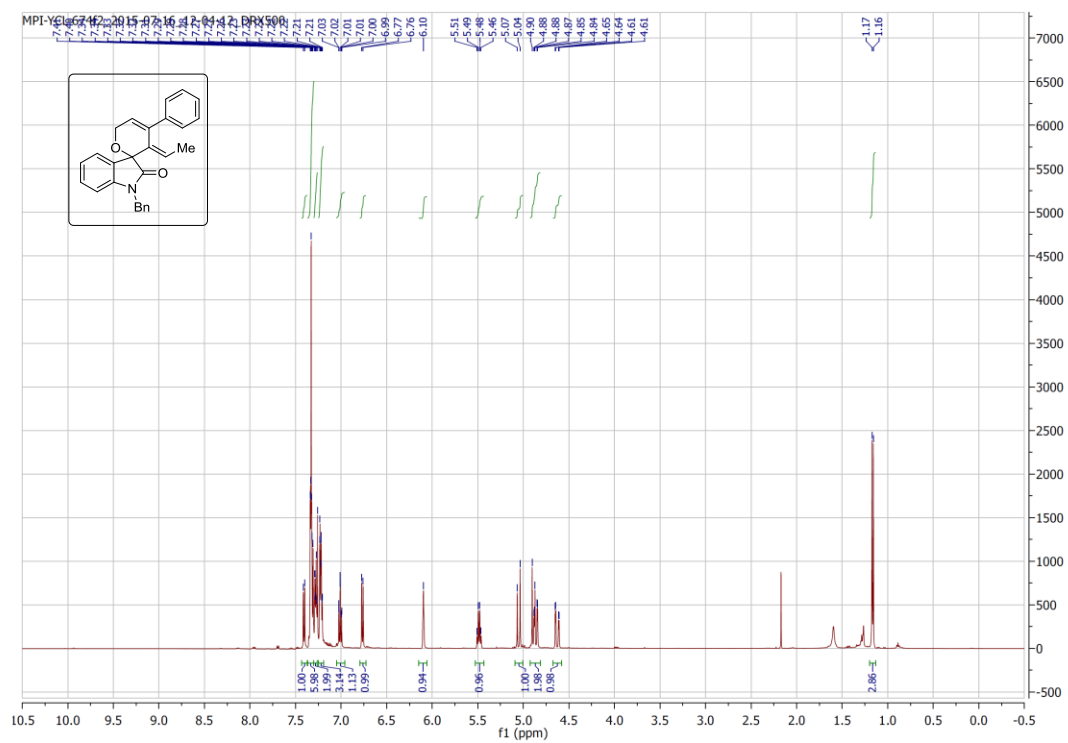
Supplementary Figure 80. ^1H and ^{13}C NMR spectra for **2h**.



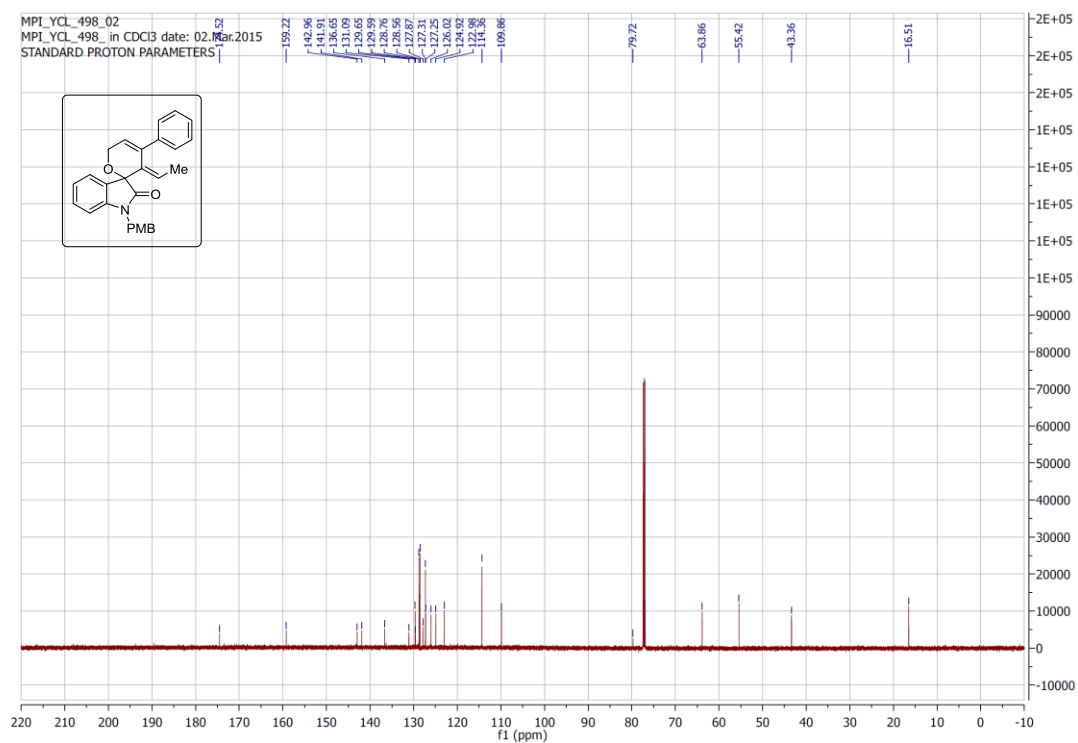
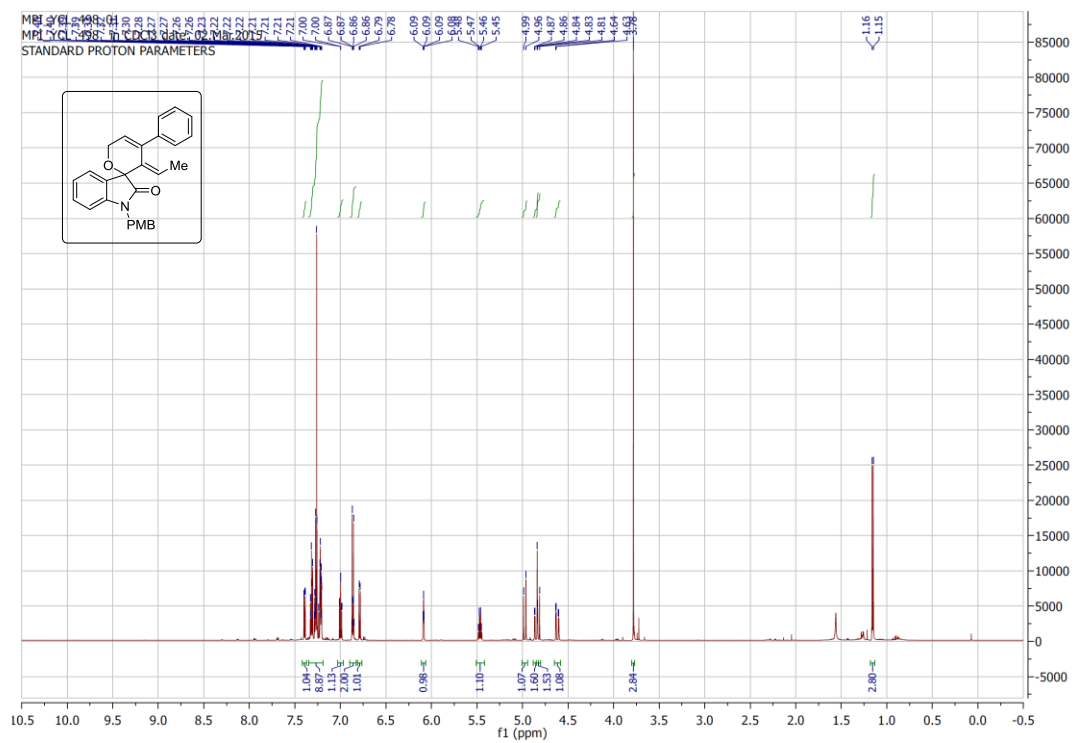
Supplementary Figure 81. ^1H and ^{13}C NMR spectra for **2i**.



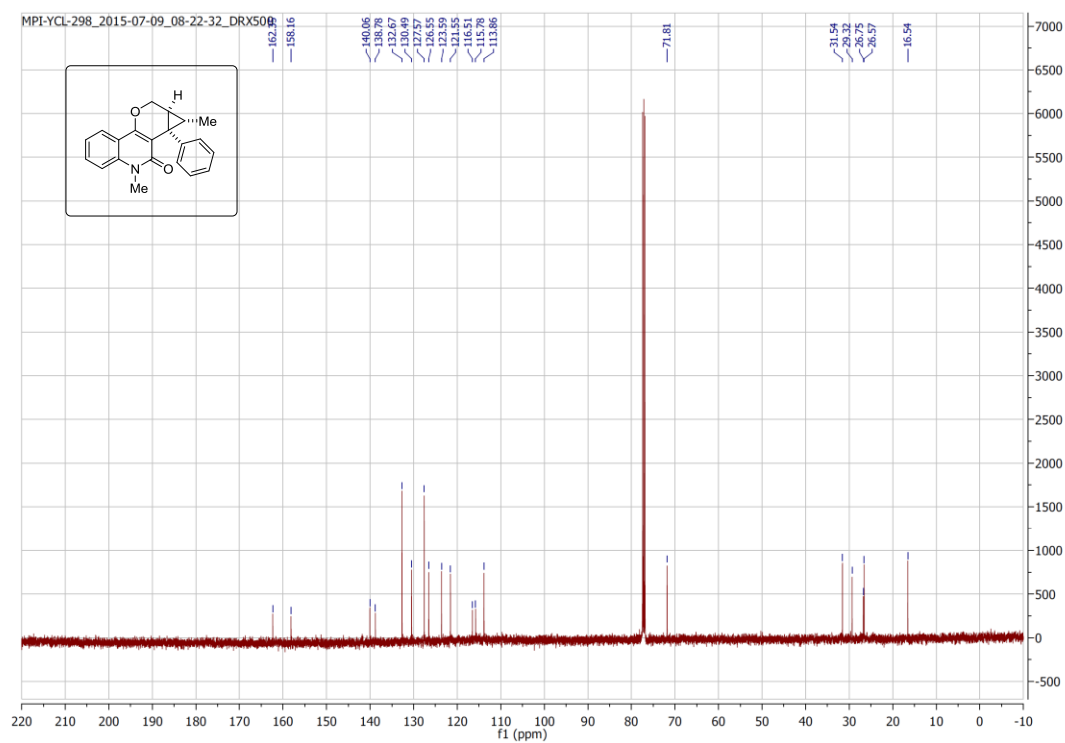
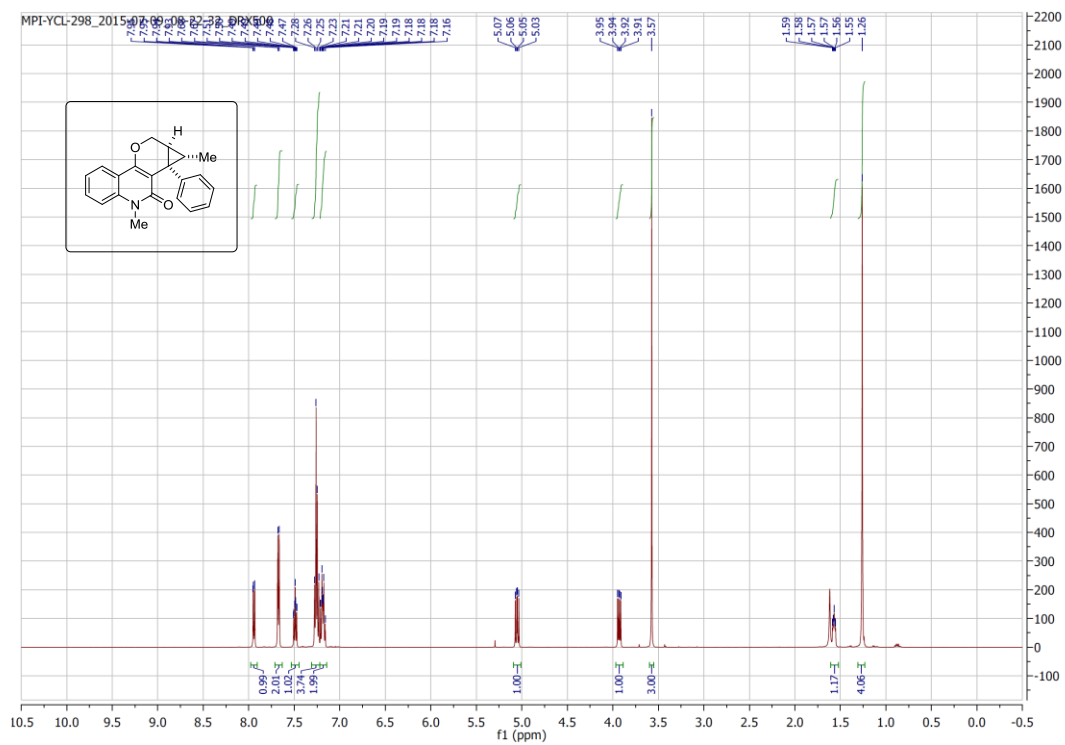
Supplementary Figure 82. ¹H and ¹³C NMR spectra for **2j**.



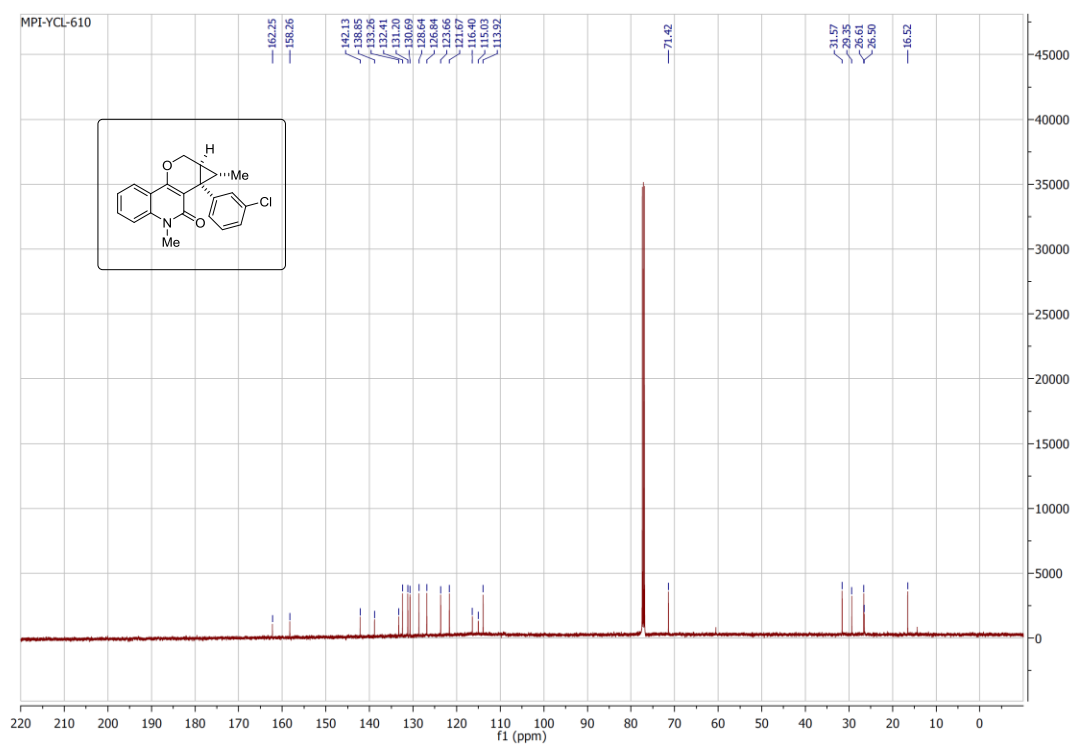
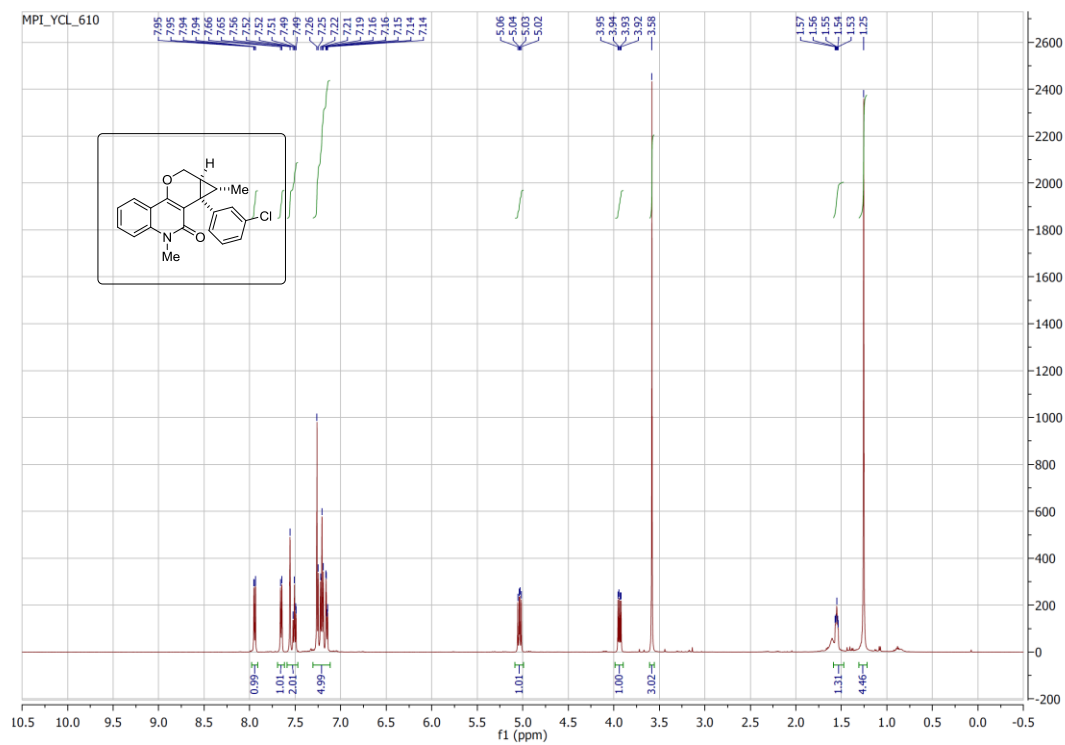
Supplementary Figure 83. ^1H and ^{13}C NMR spectra for **2k**.



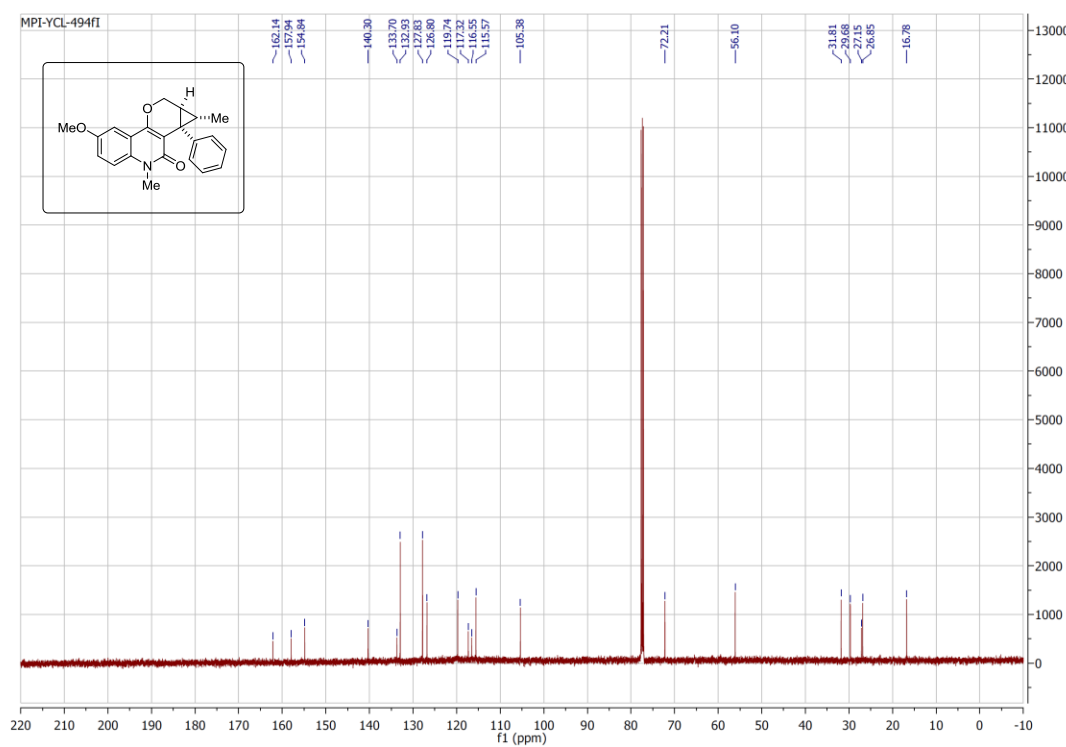
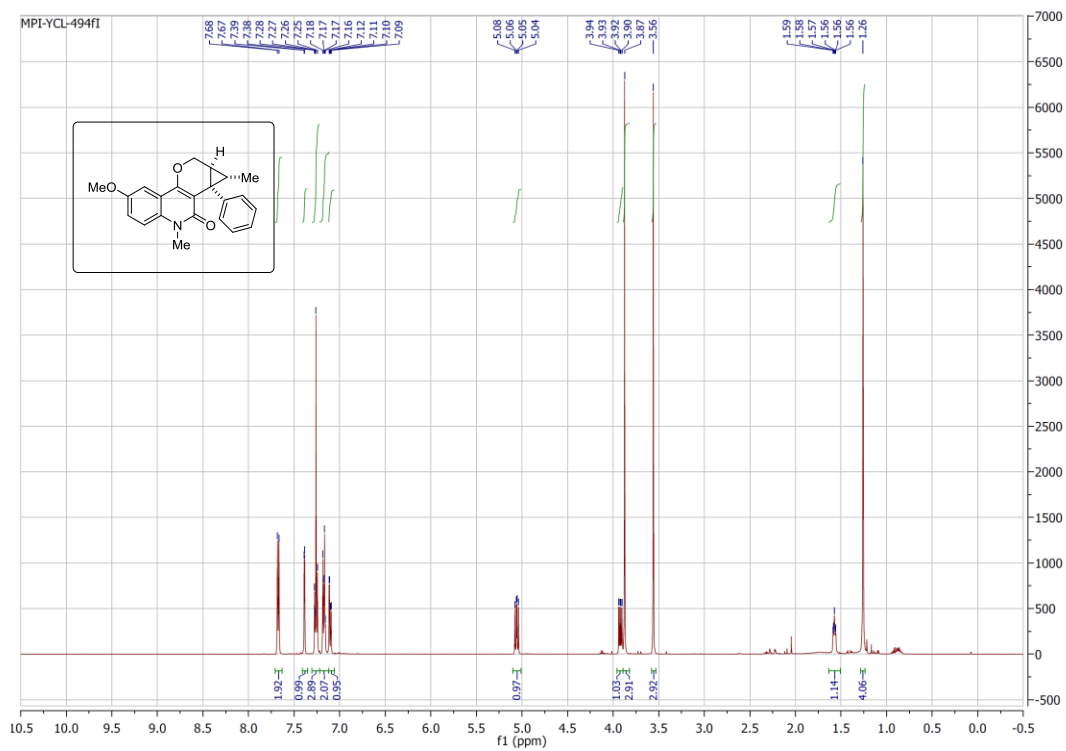
Supplementary Figure 84. ¹H and ¹³C NMR spectra for 2l.



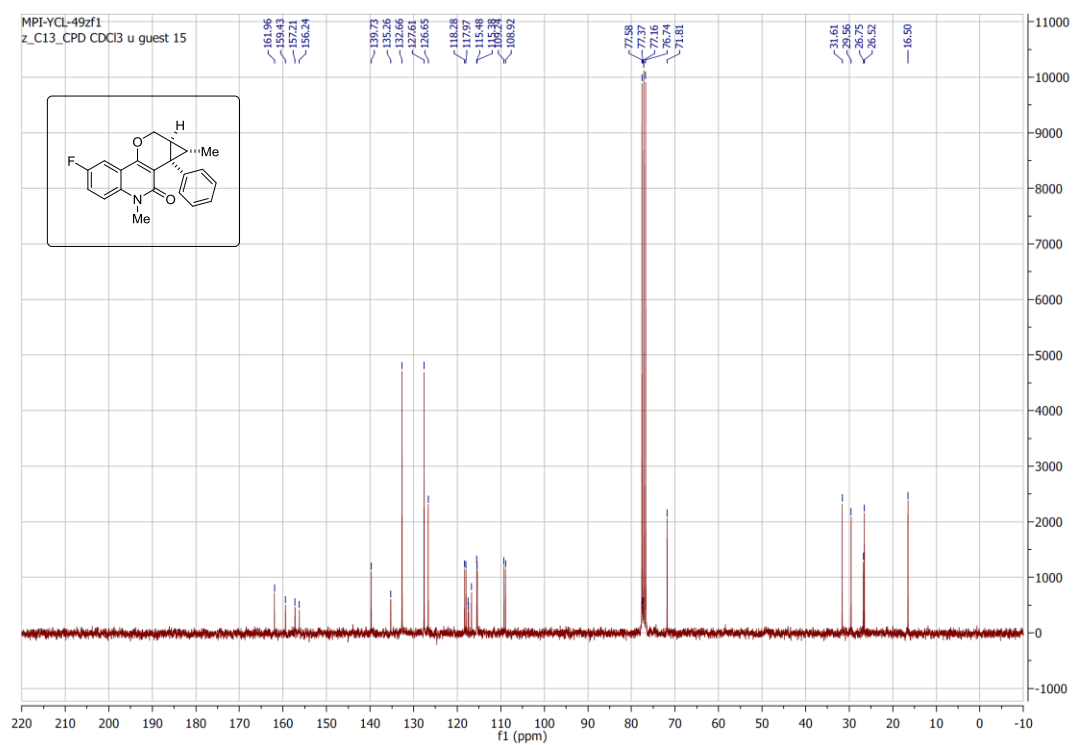
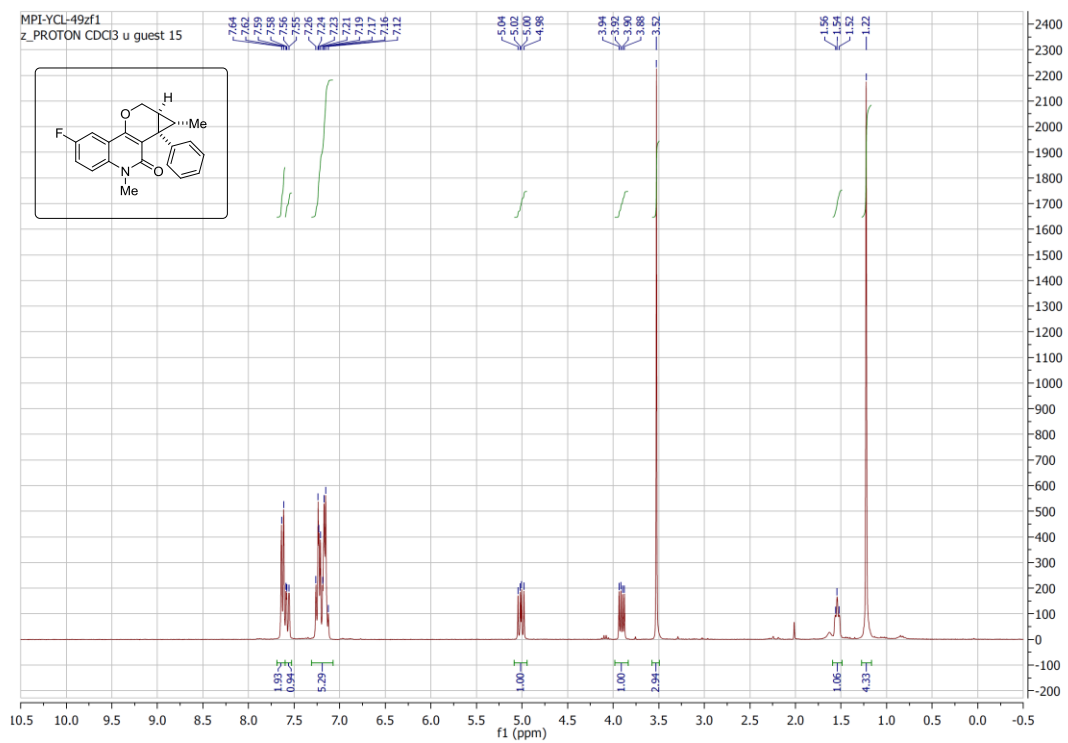
Supplementary Figure 85. ¹H and ¹³C NMR spectra for **3a**.



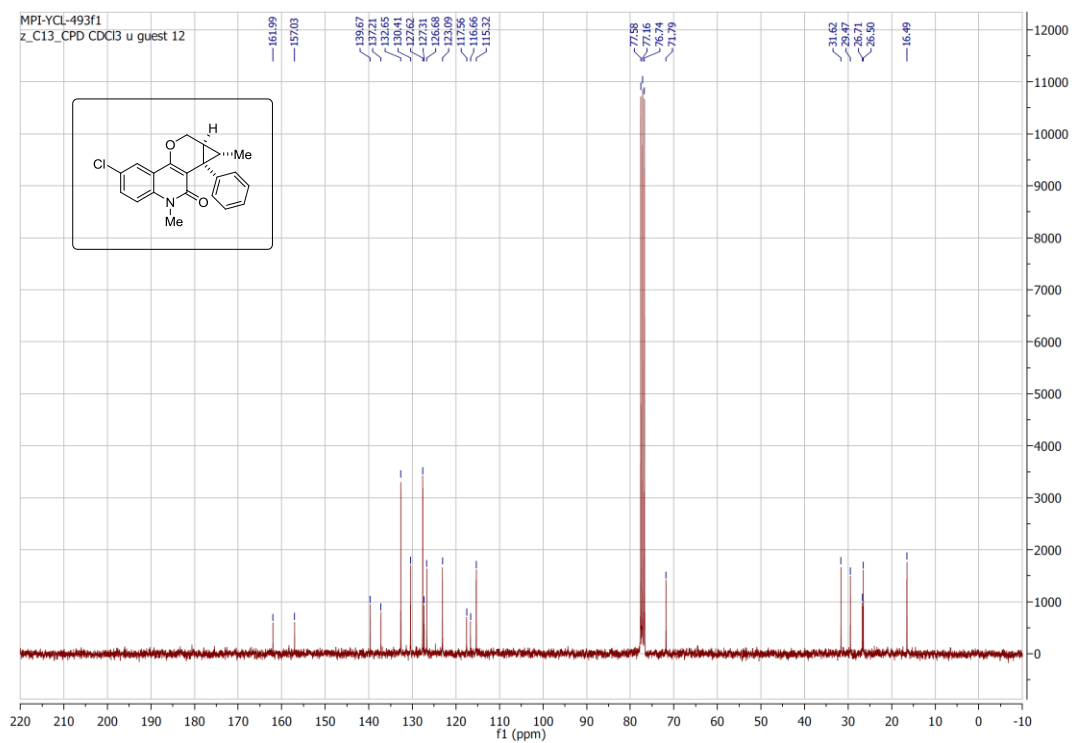
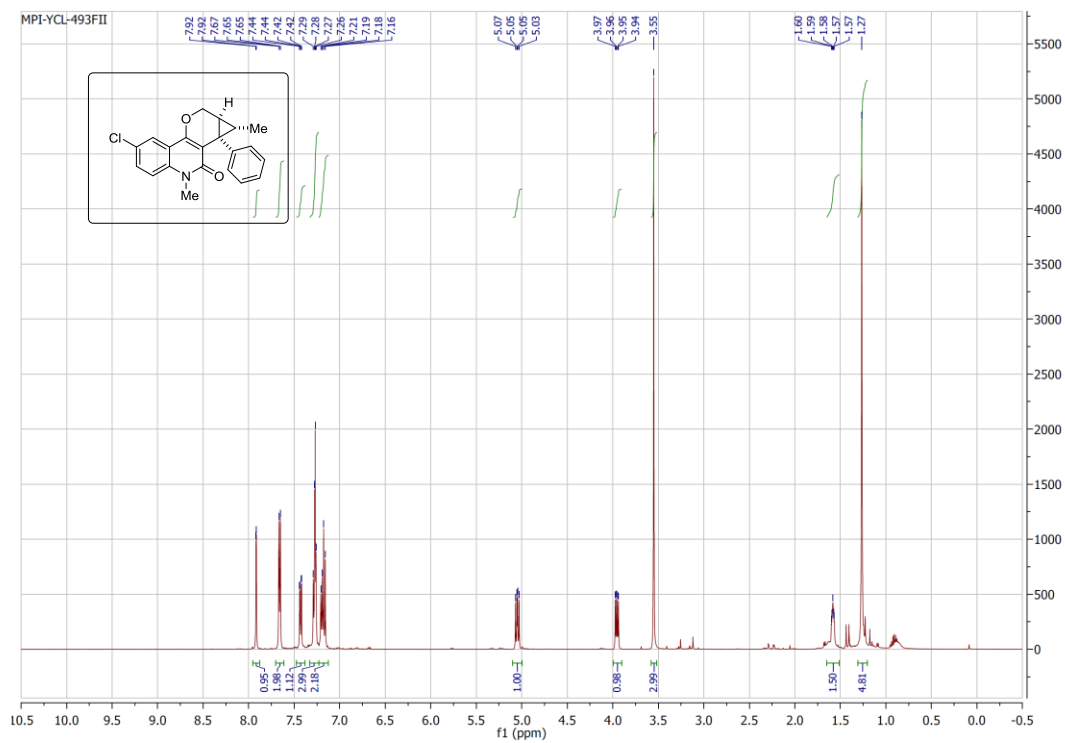
Supplementary Figure 86. ¹H and ¹³C NMR spectra for **3b**.



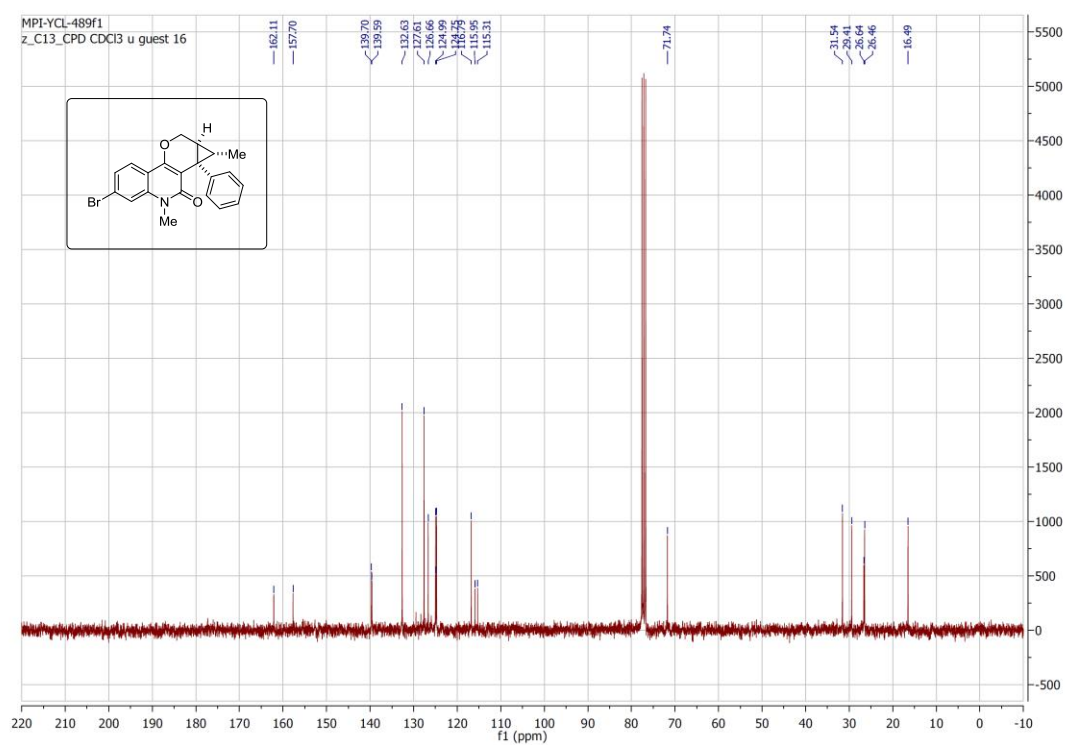
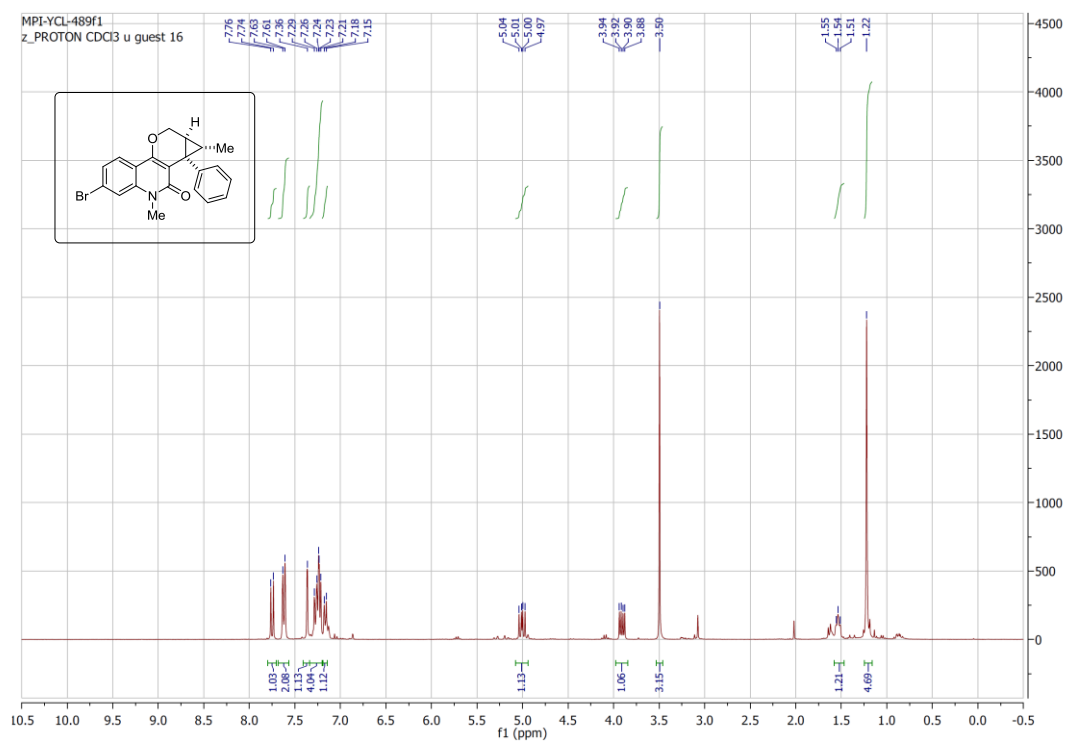
Supplementary Figure 88. ¹H and ¹³C NMR spectra for 3d.



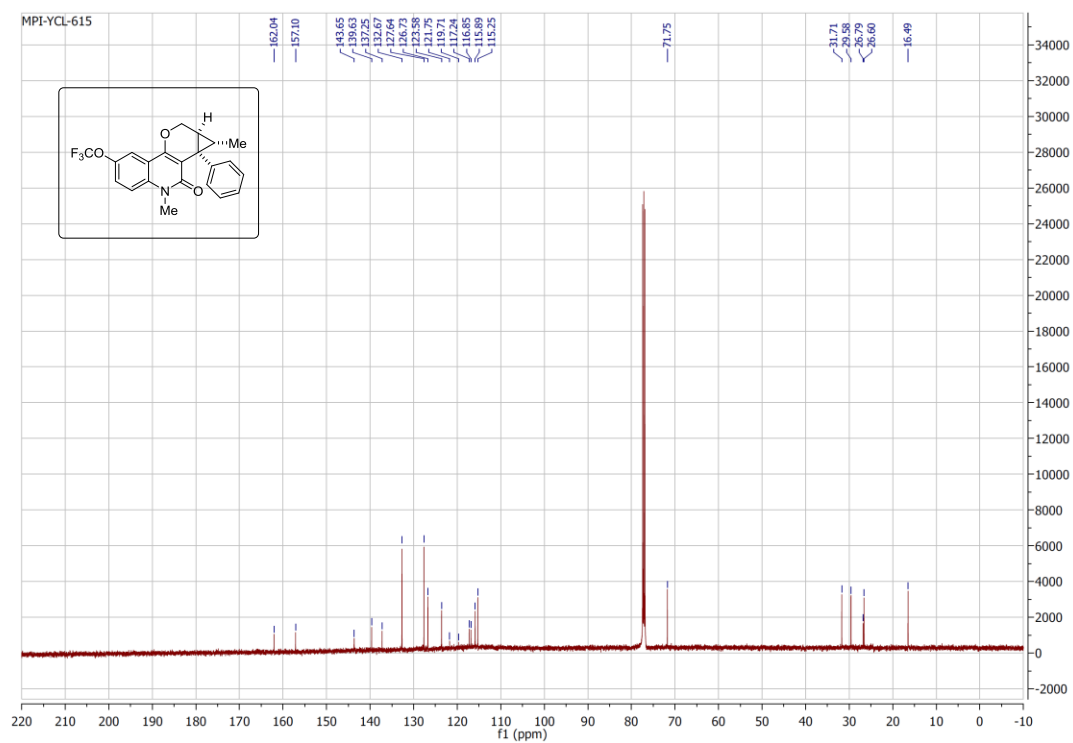
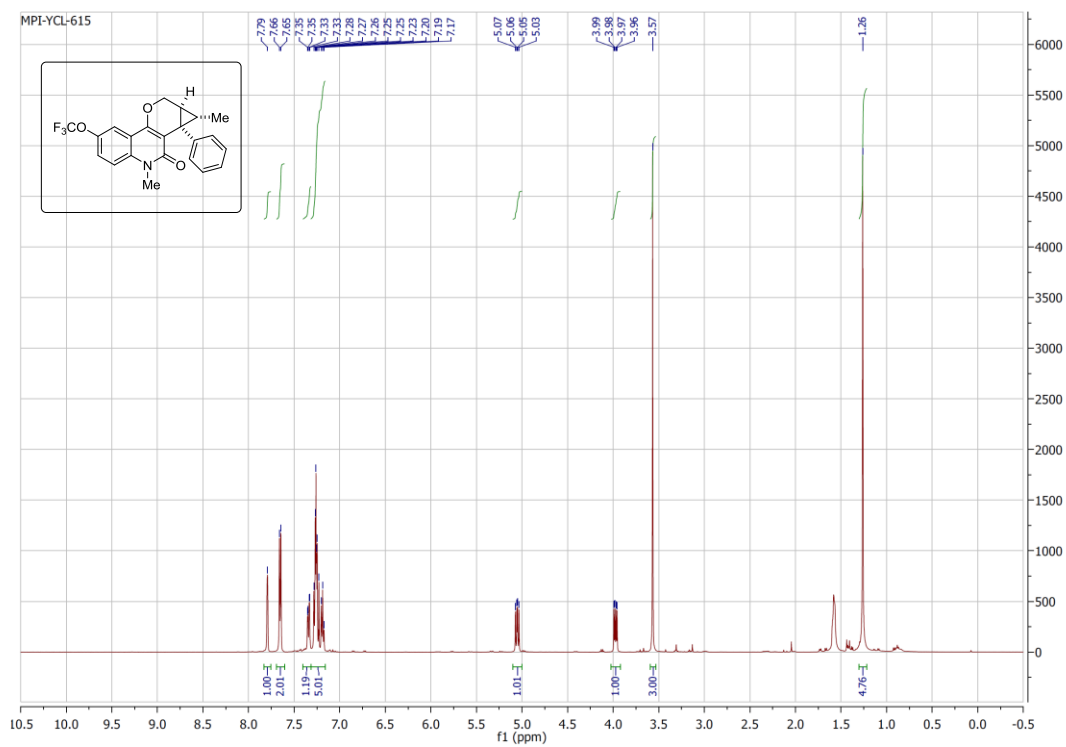
Supplementary Figure 89. ^1H and ^{13}C NMR spectra for **3e**.



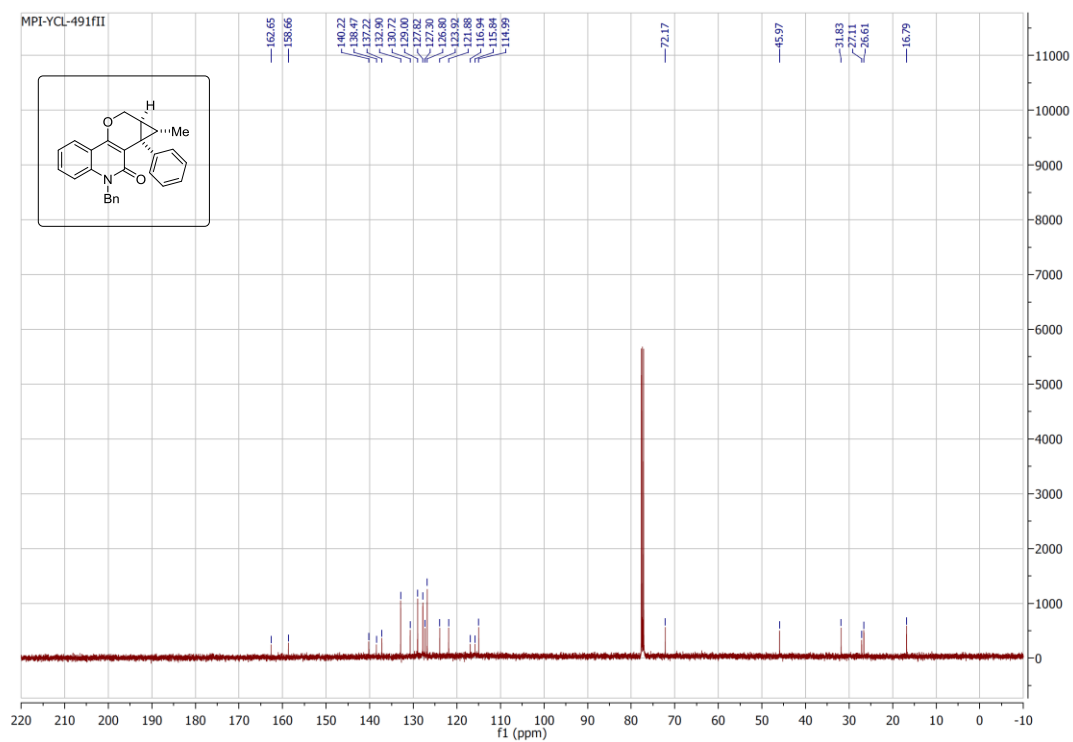
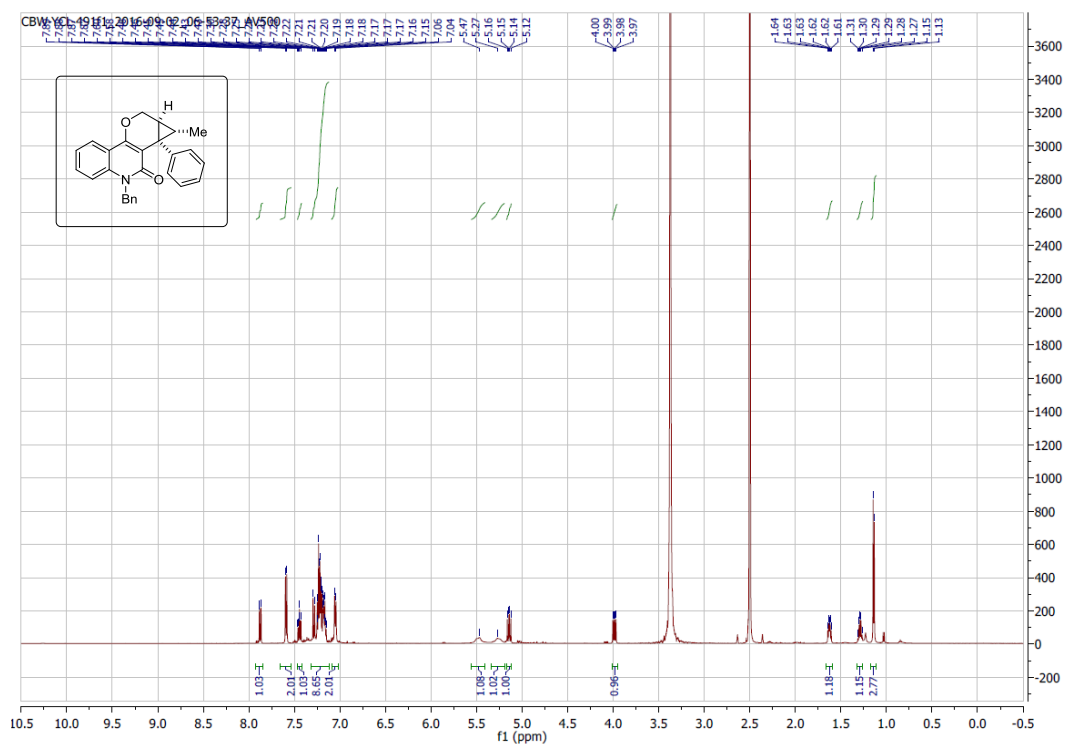
Supplementary Figure 90. ¹H and ¹³C NMR spectra for **3f**.



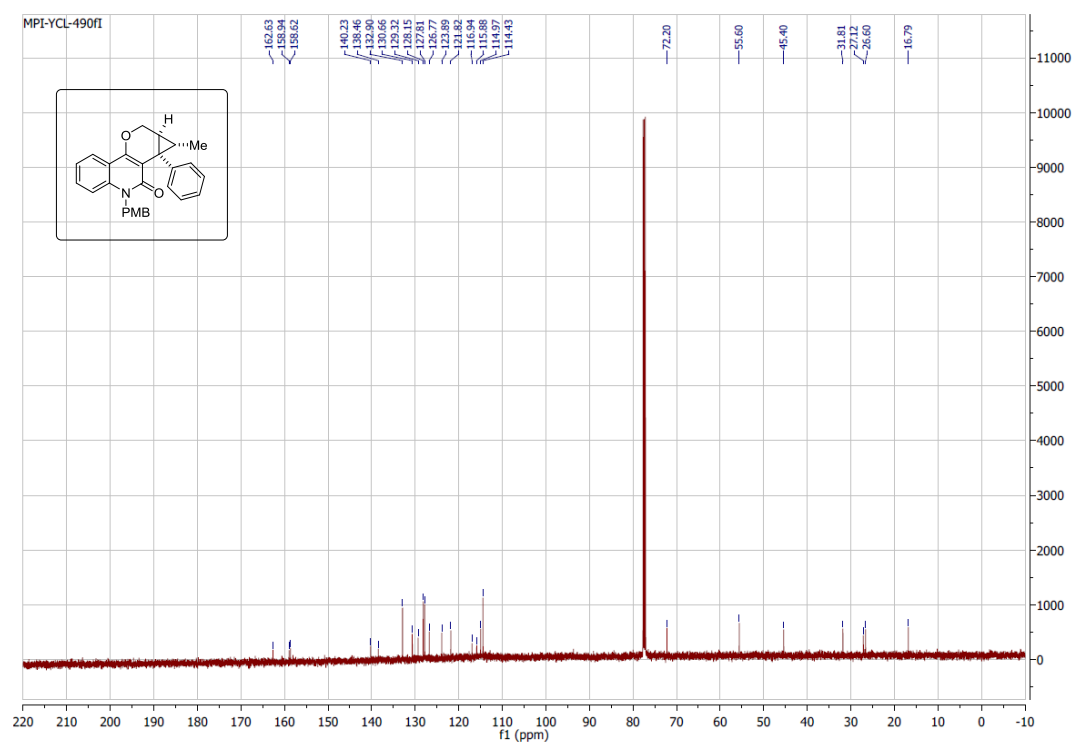
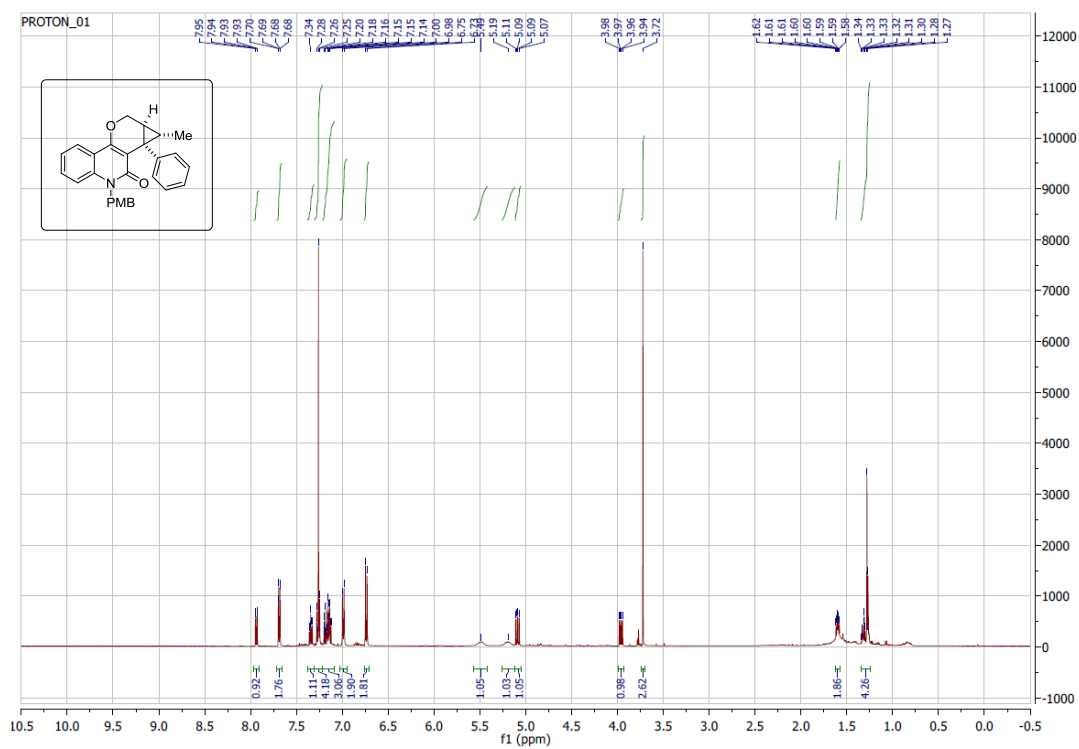
Supplementary Figure 91. ¹H and ¹³C NMR spectra for **3g**.



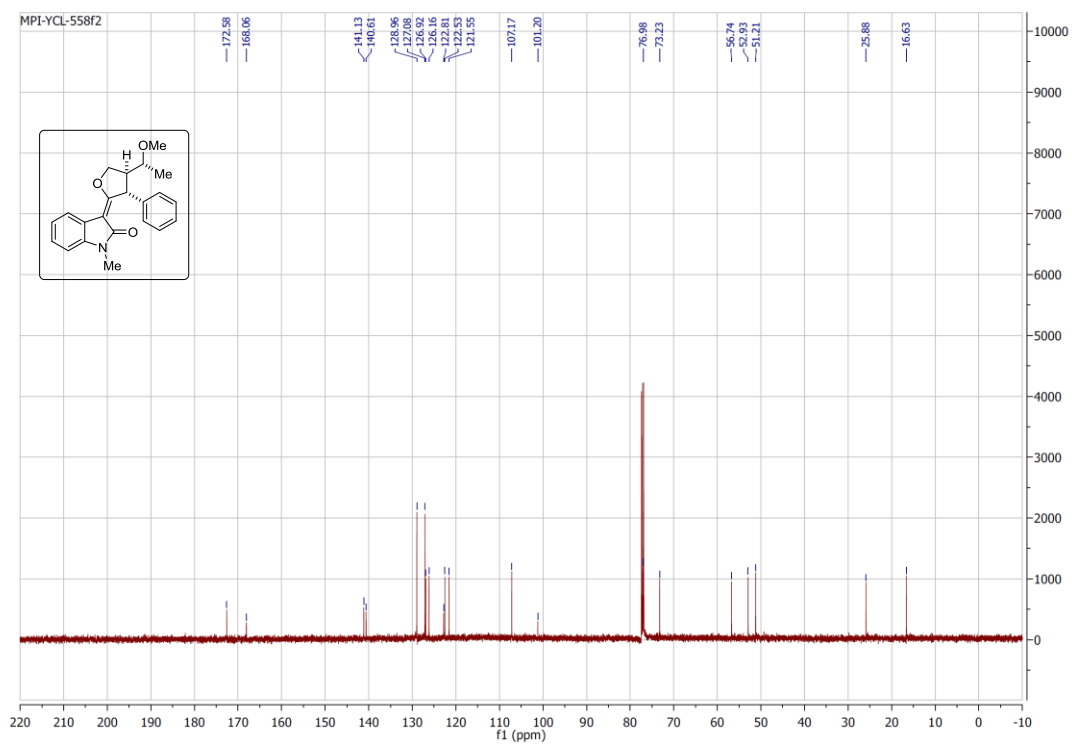
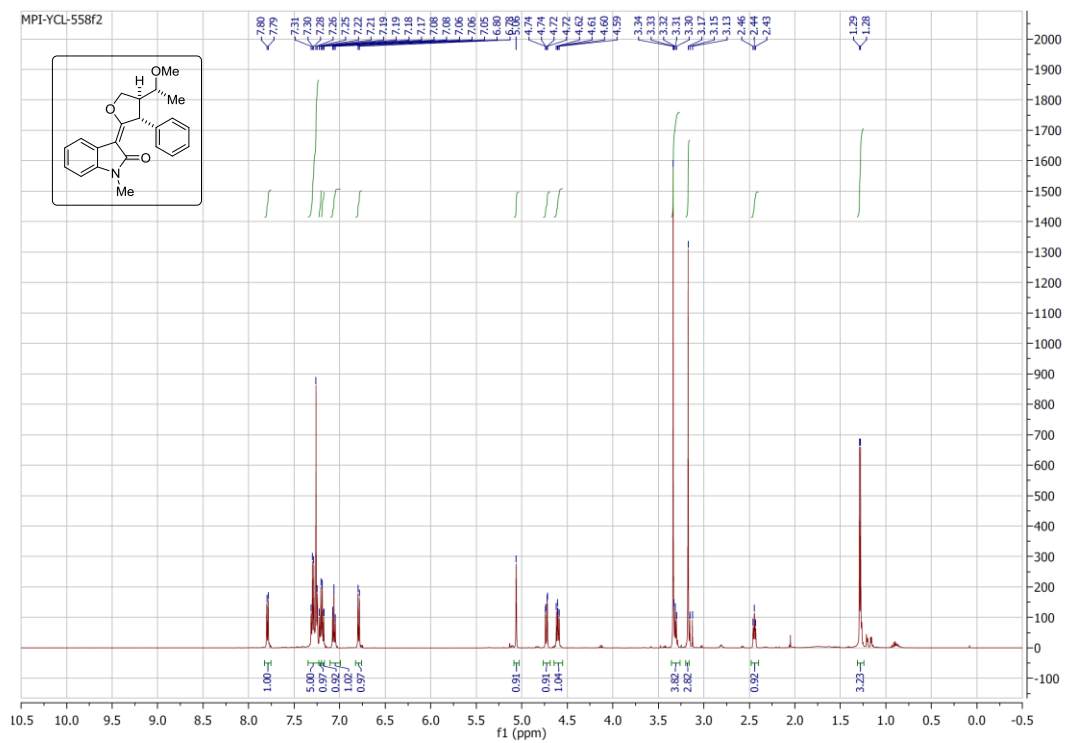
Supplementary Figure 92. ¹H and ¹³C NMR spectra for **3h**.



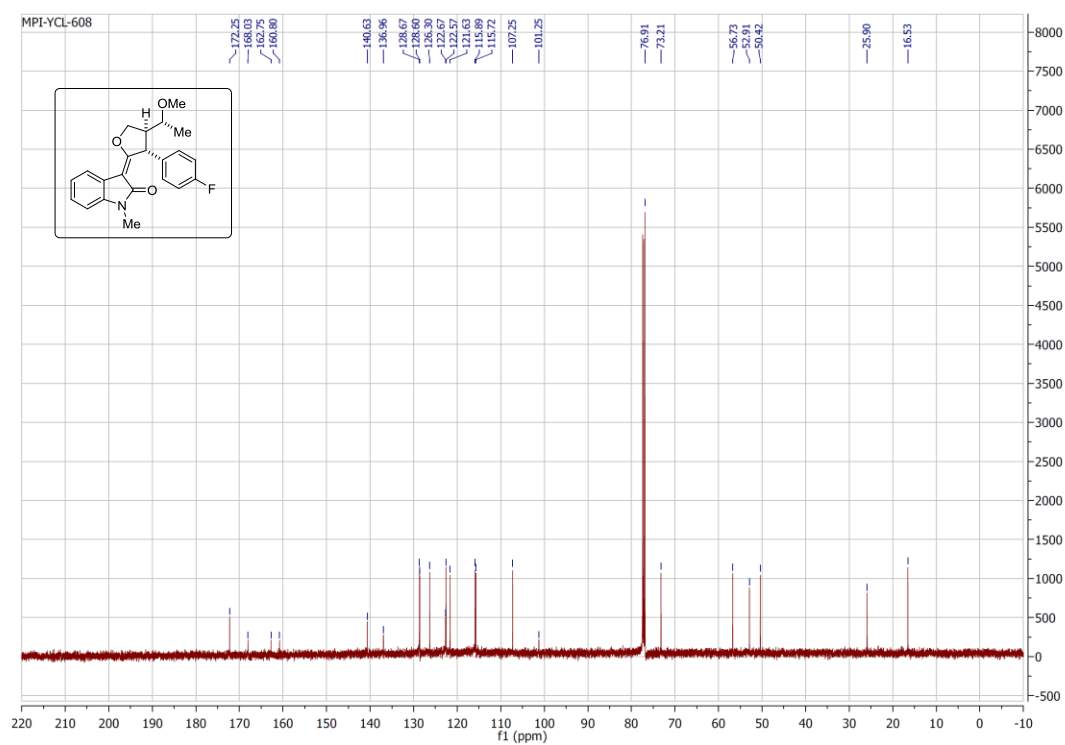
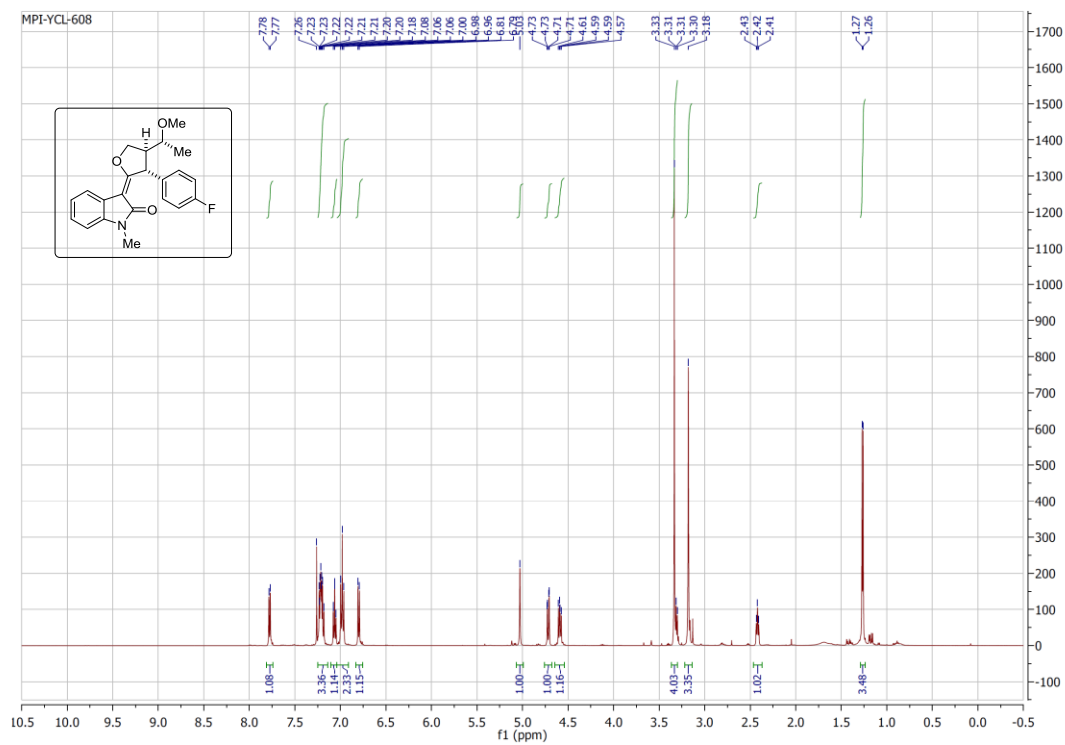
Supplementary Figure 93. ^1H and ^{13}C NMR spectra for **3i**.



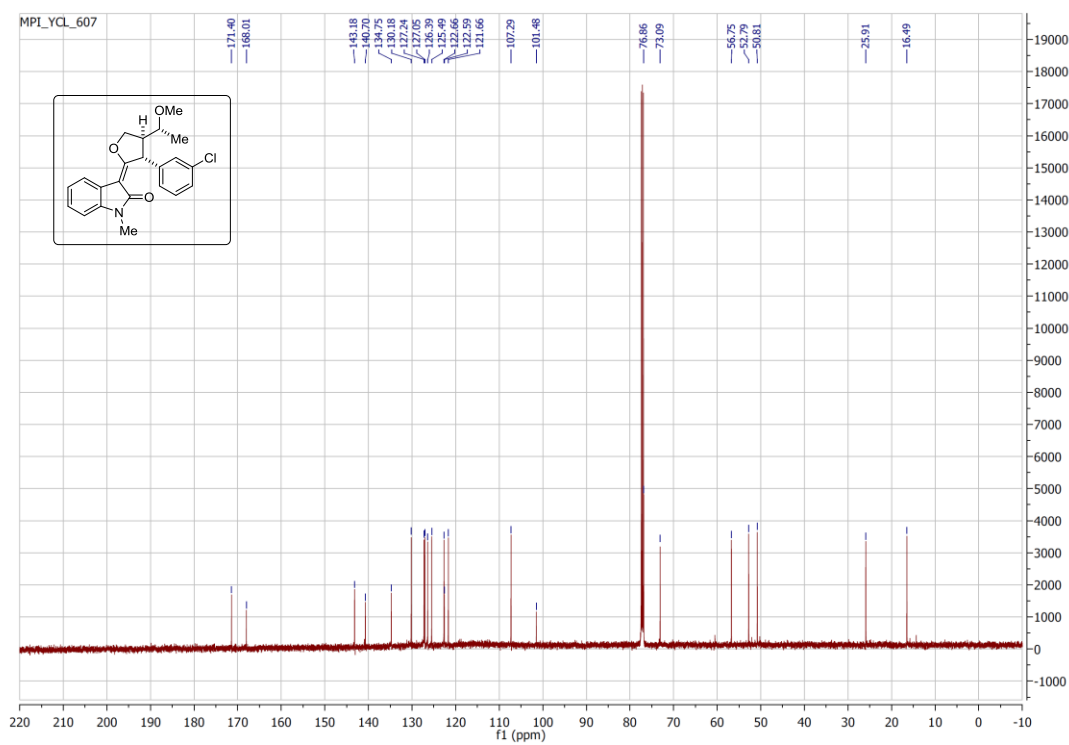
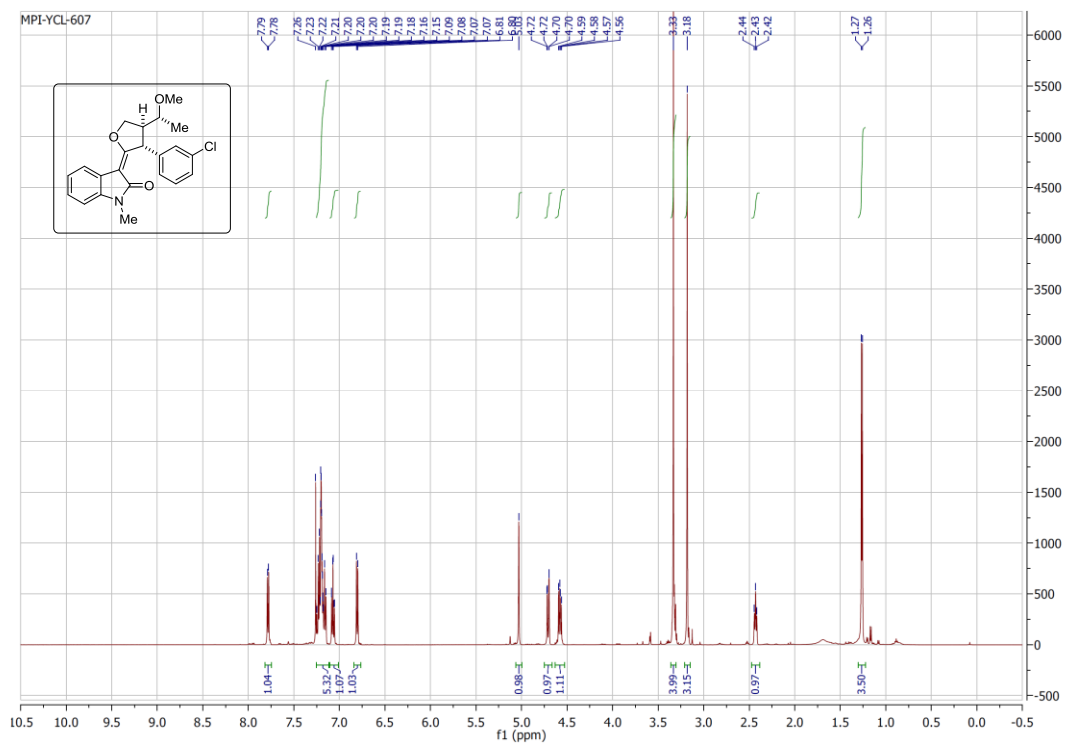
Supplementary Figure 94. ^1H and ^{13}C NMR spectra for **3j**.



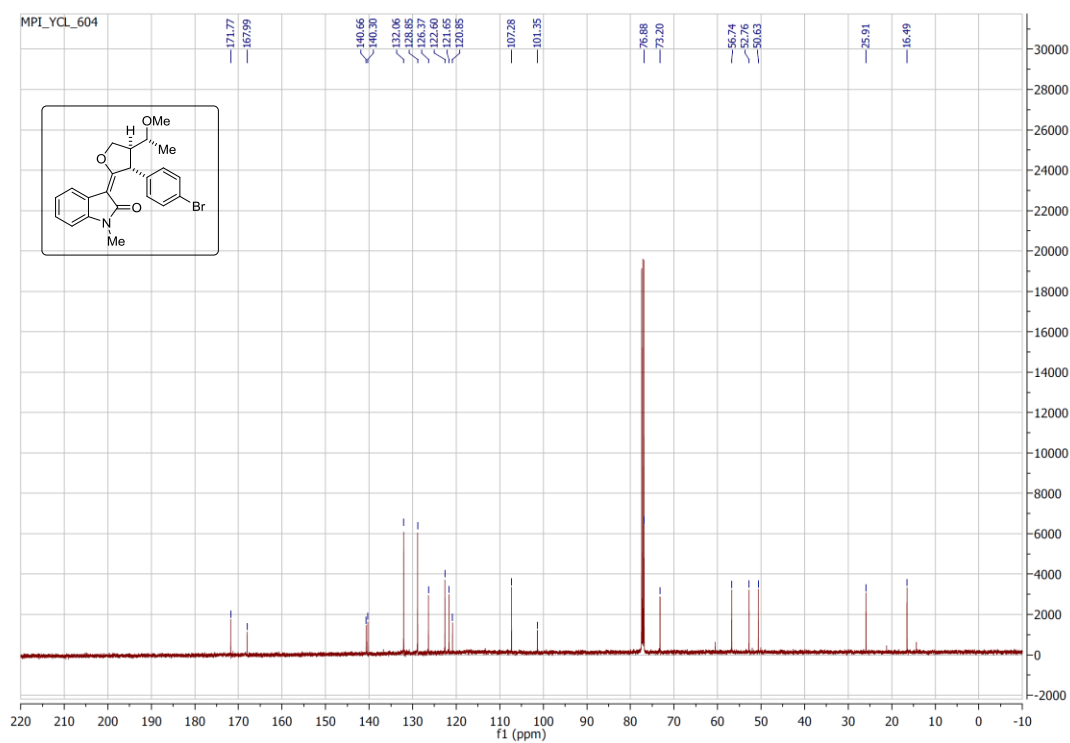
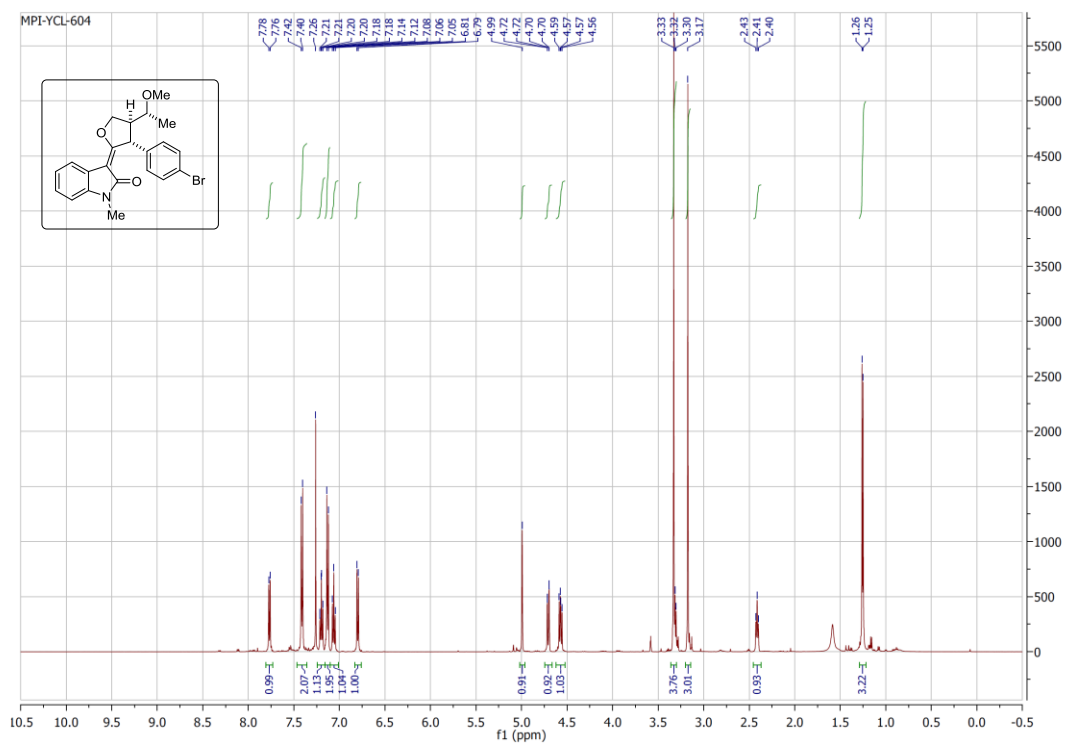
Supplementary Figure 95. ¹H and ¹³C NMR spectra for 4a.



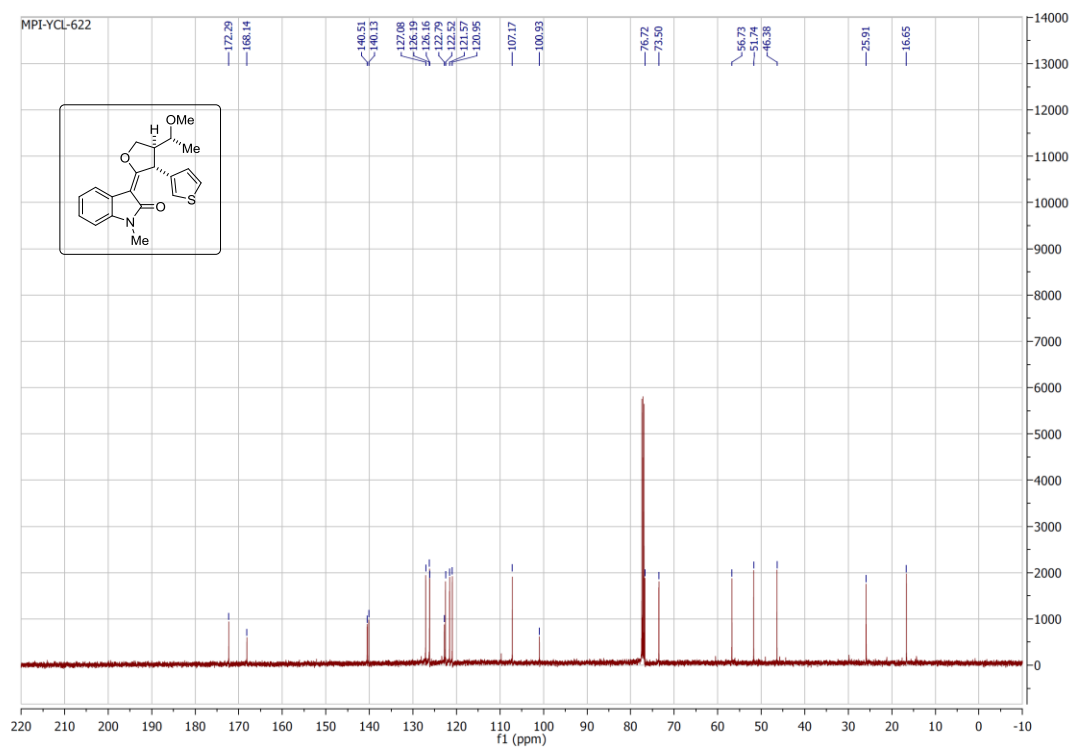
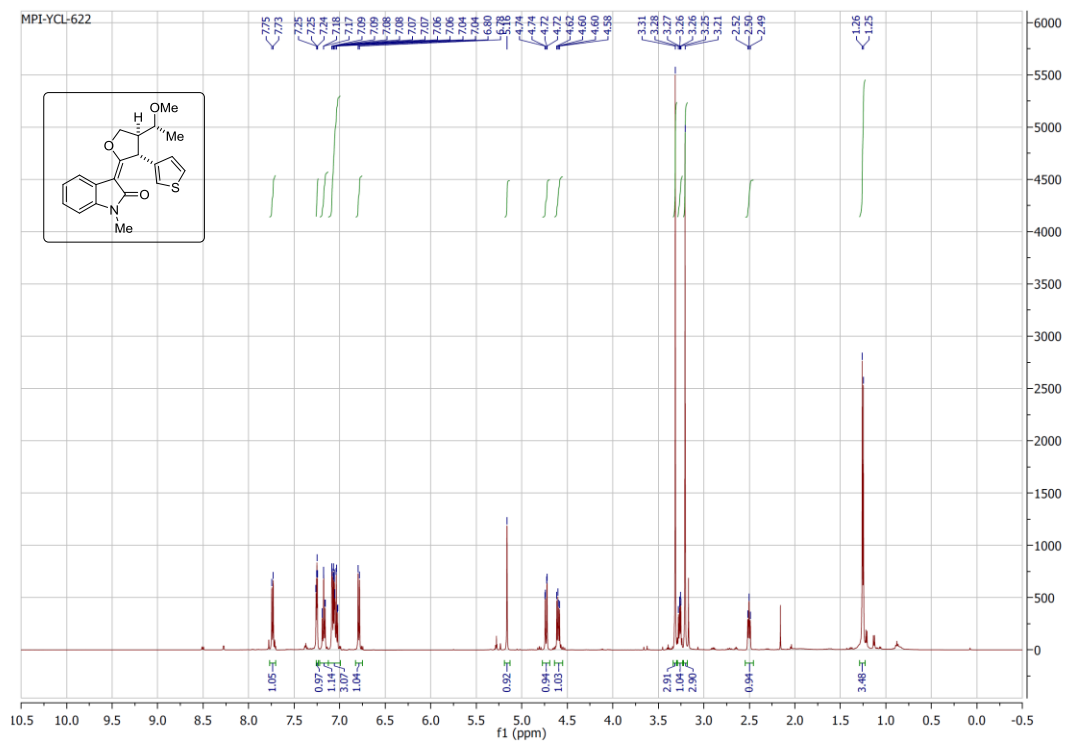
Supplementary Figure 96. ^1H and ^{13}C NMR spectra for 4b.



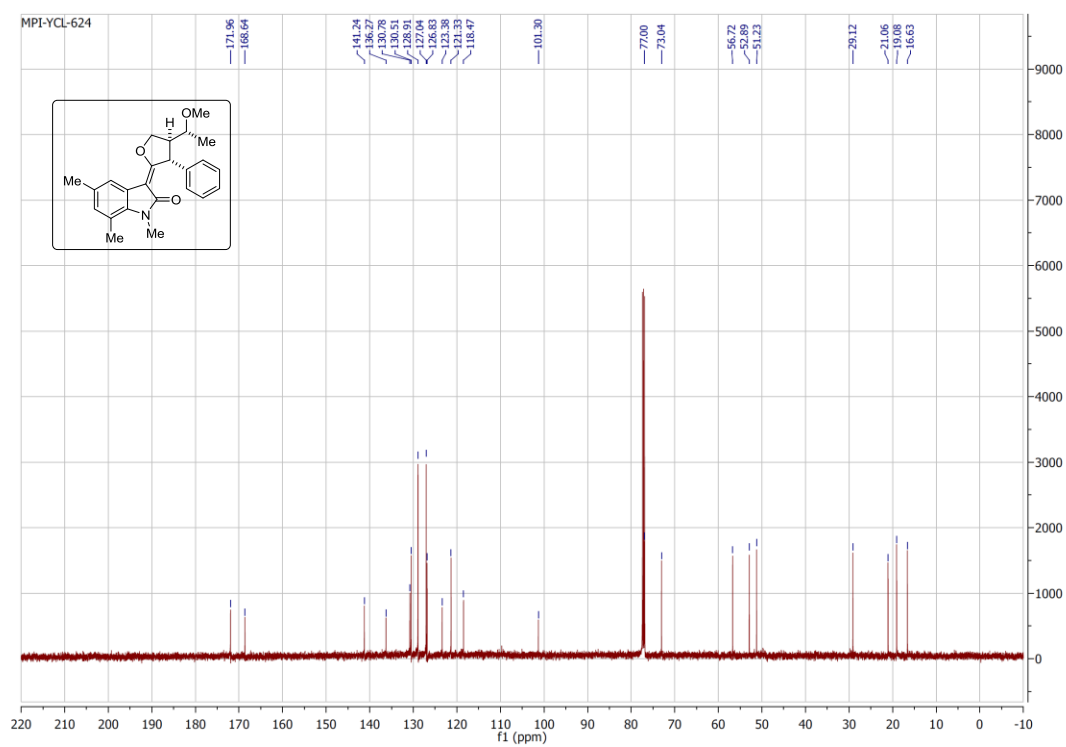
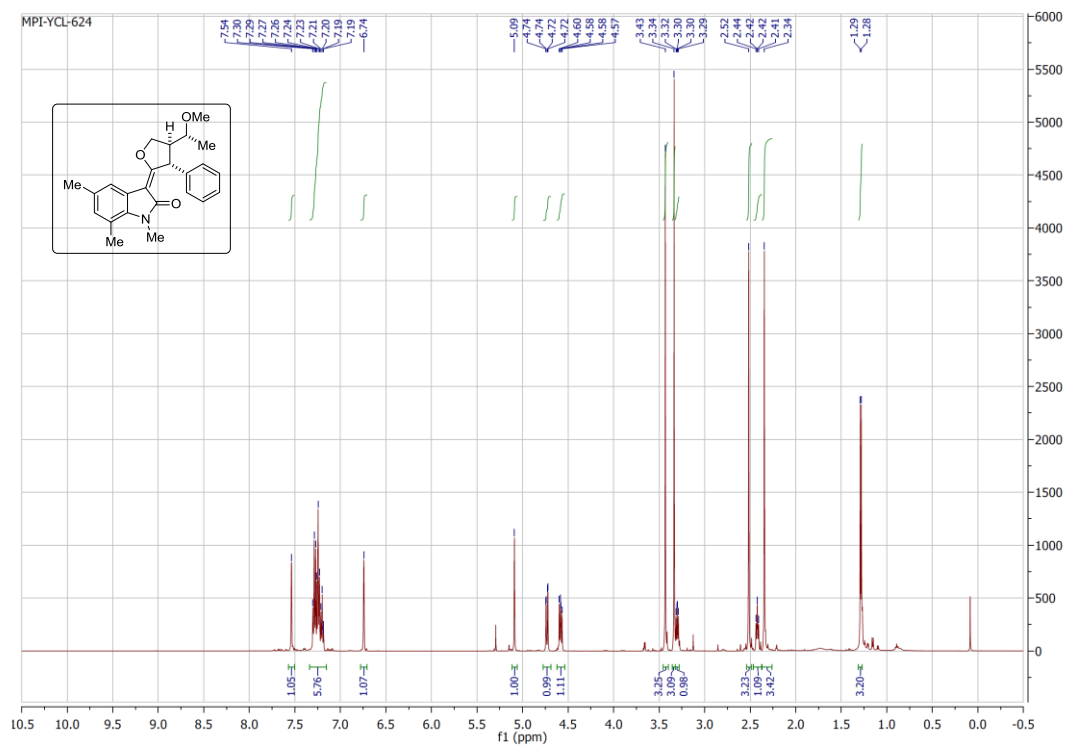
Supplementary Figure 97. ¹H and ¹³C NMR spectra for 4c.



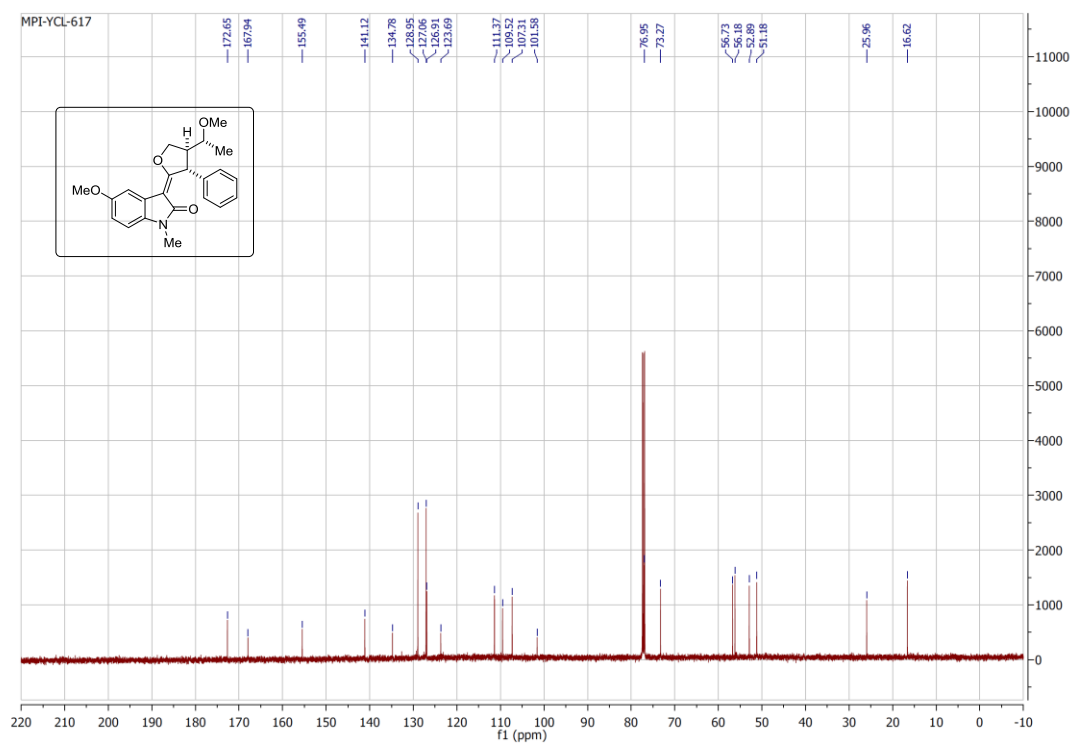
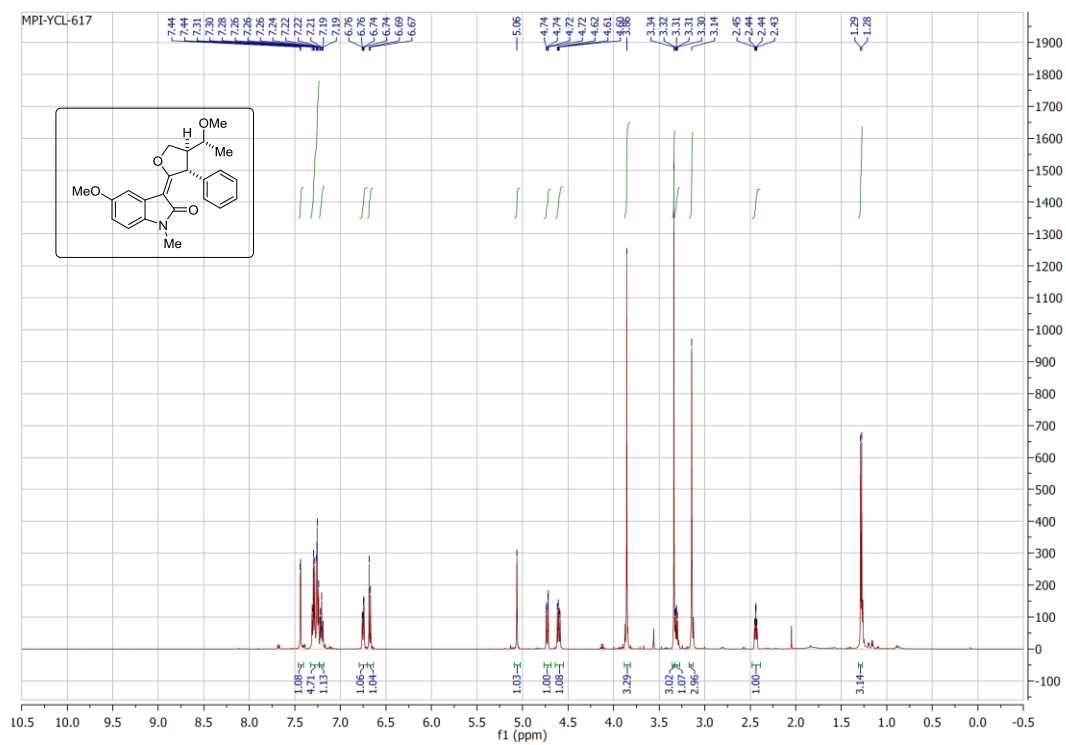
Supplementary Figure 98. ¹H and ¹³C NMR spectra for 4d.



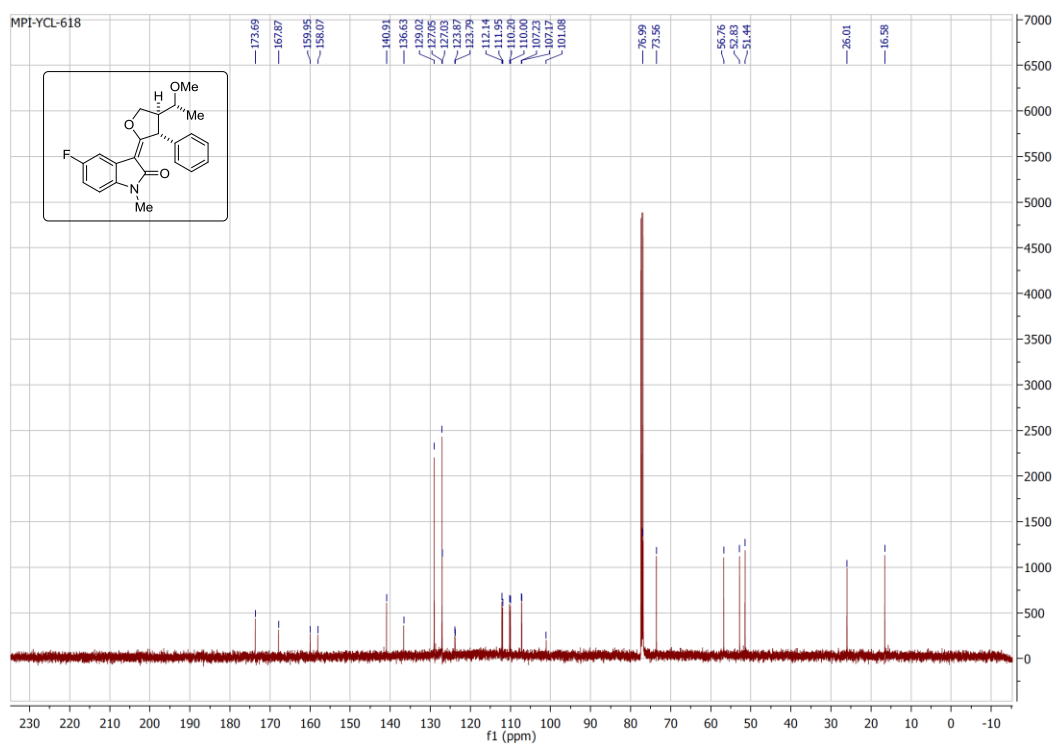
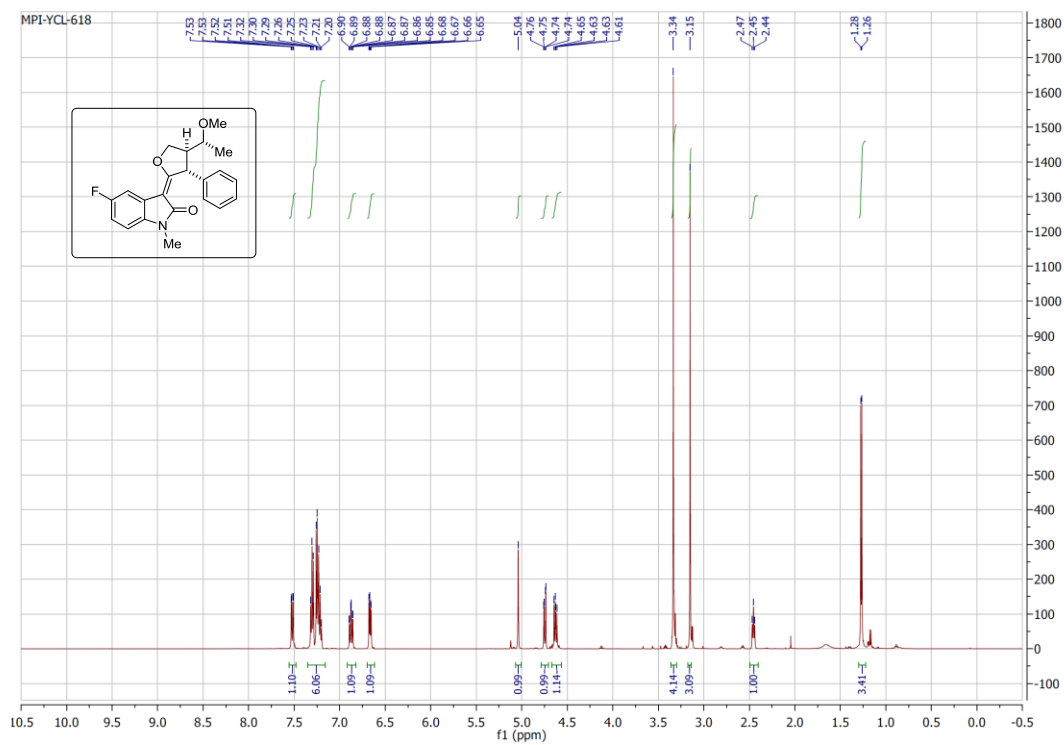
Supplementary Figure 99. ^1H and ^{13}C NMR spectra for 4e.



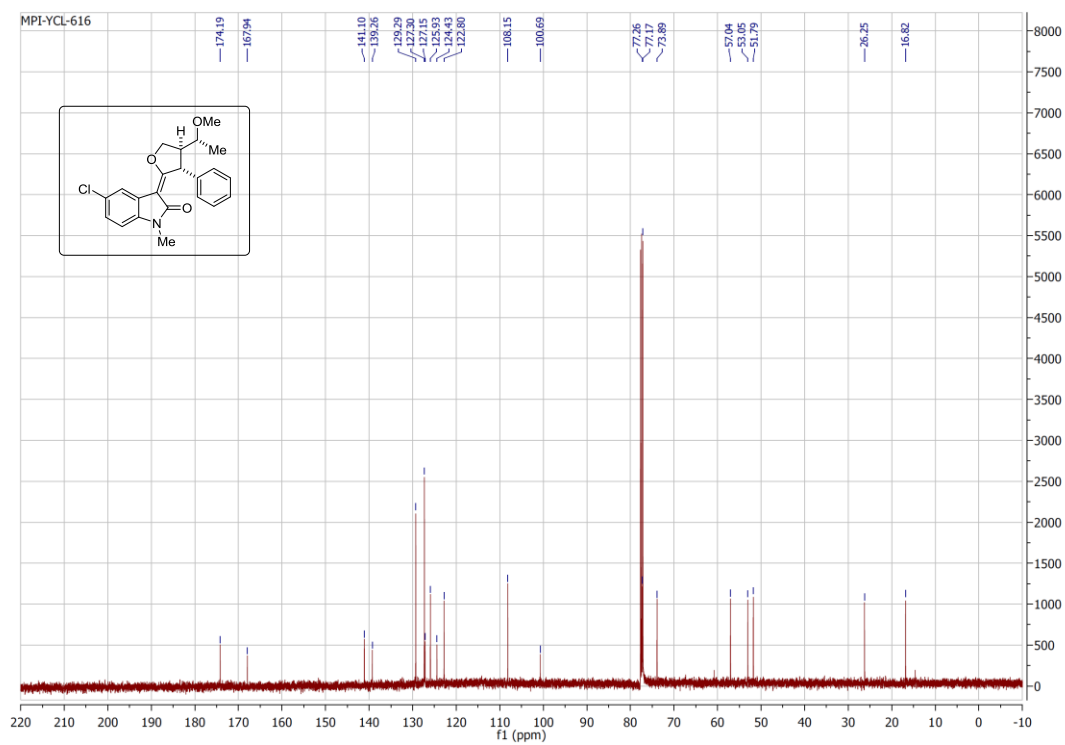
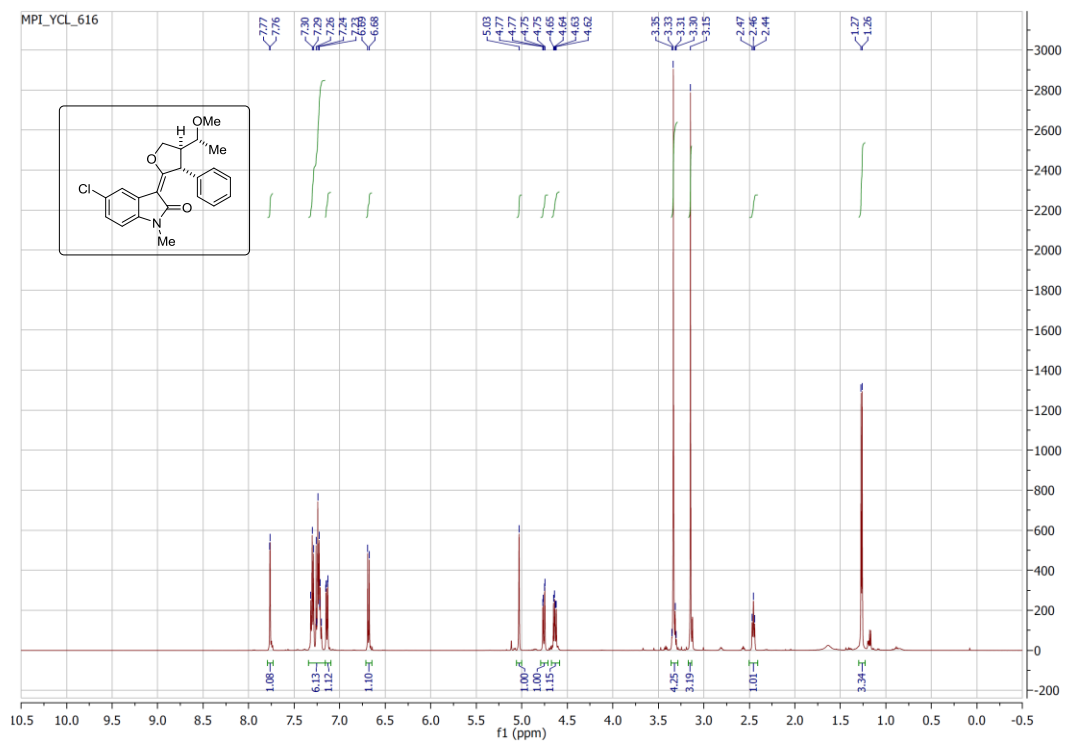
Supplementary Figure 100. ^1H and ^{13}C NMR spectra for 4f.



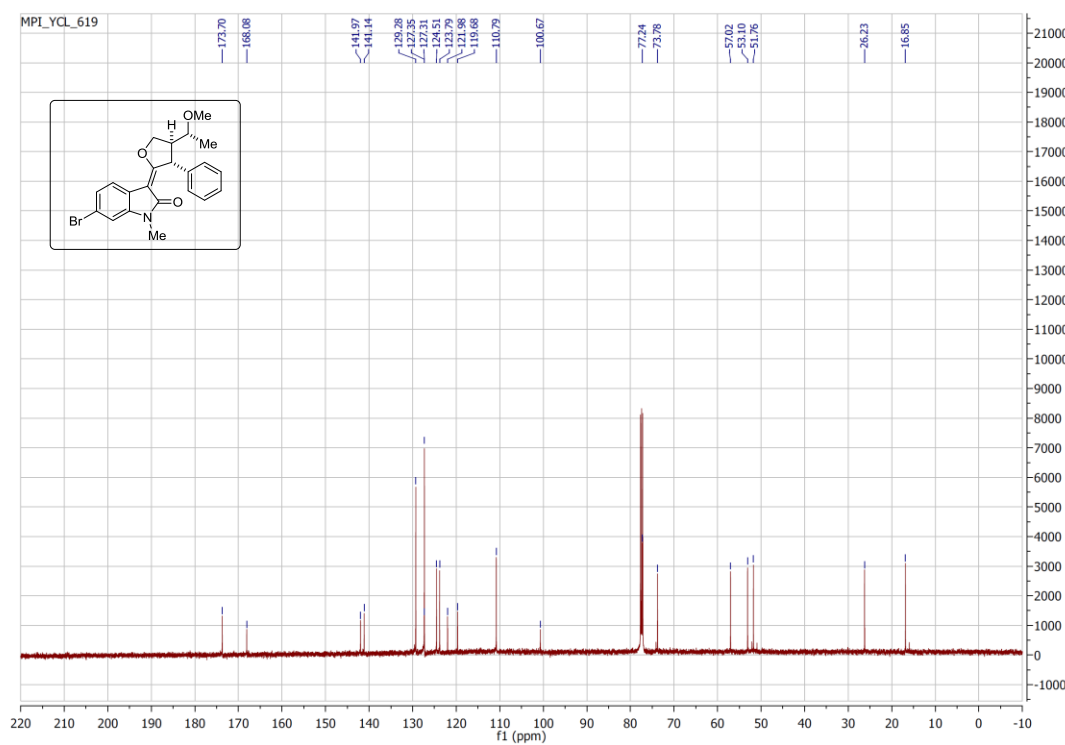
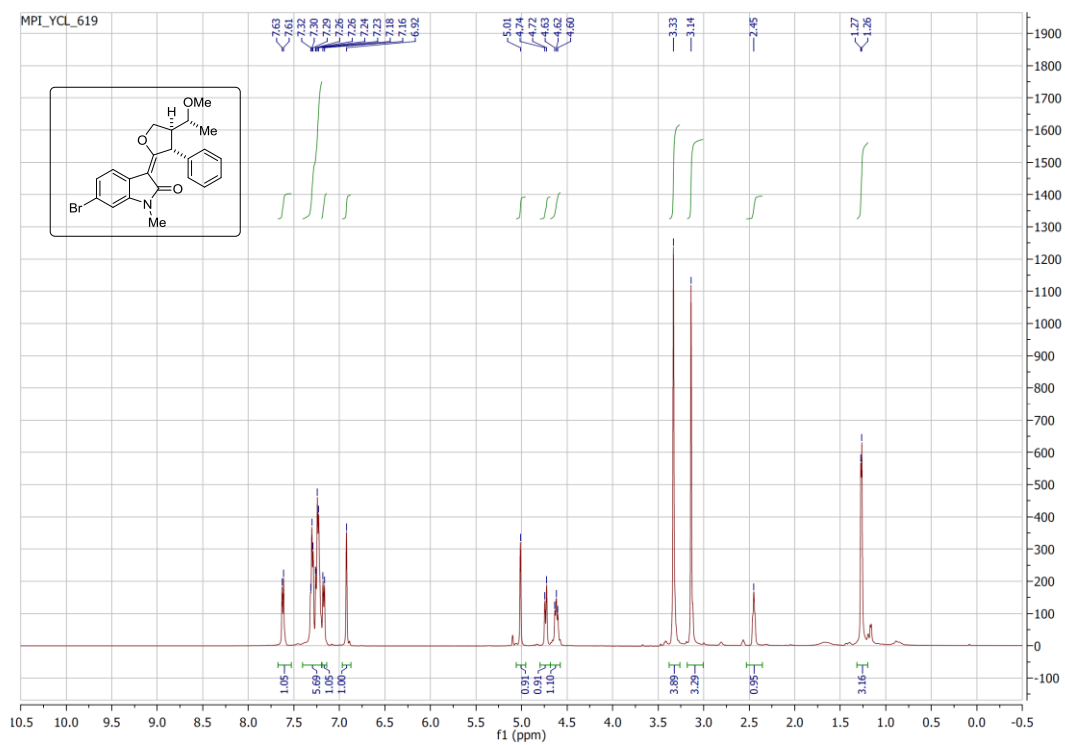
Supplementary Figure 101. ^1H and ^{13}C NMR spectra for **4g**.



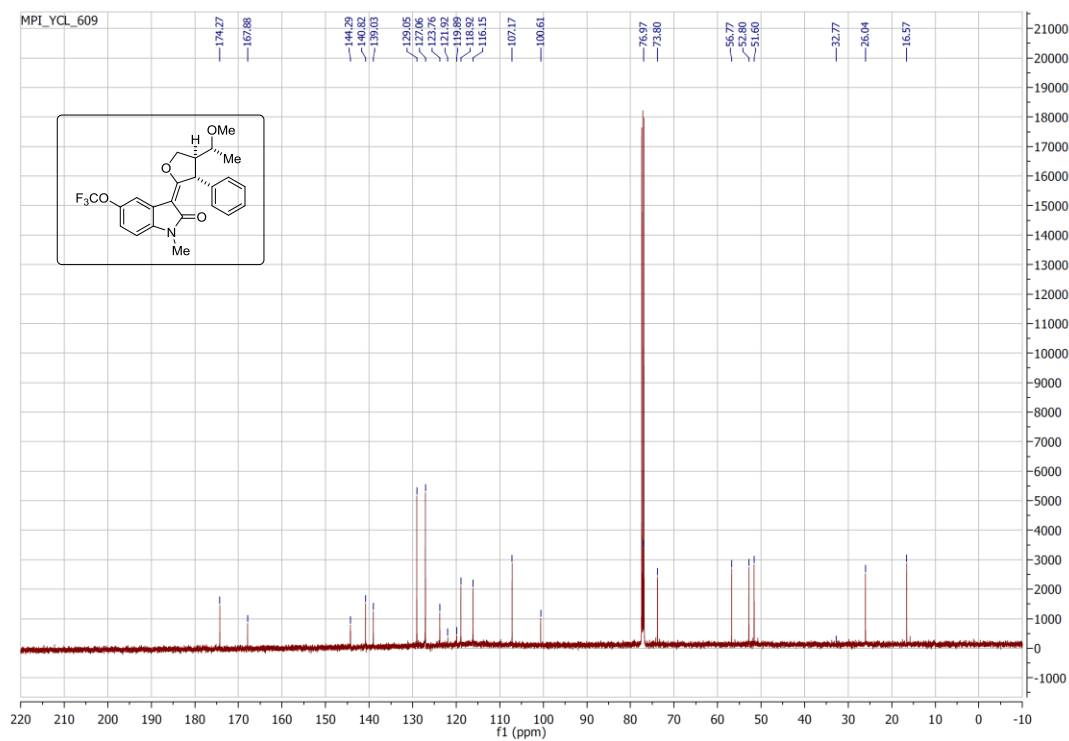
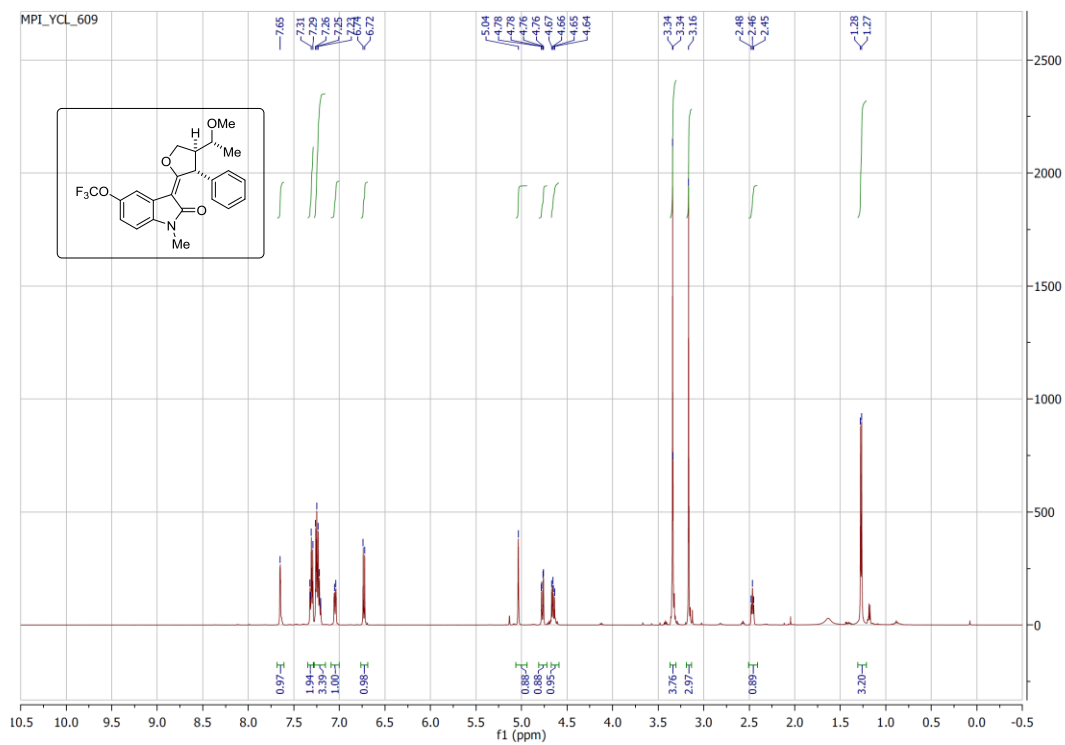
Supplementary Figure 102. ^1H and ^{13}C NMR spectra for 4h.



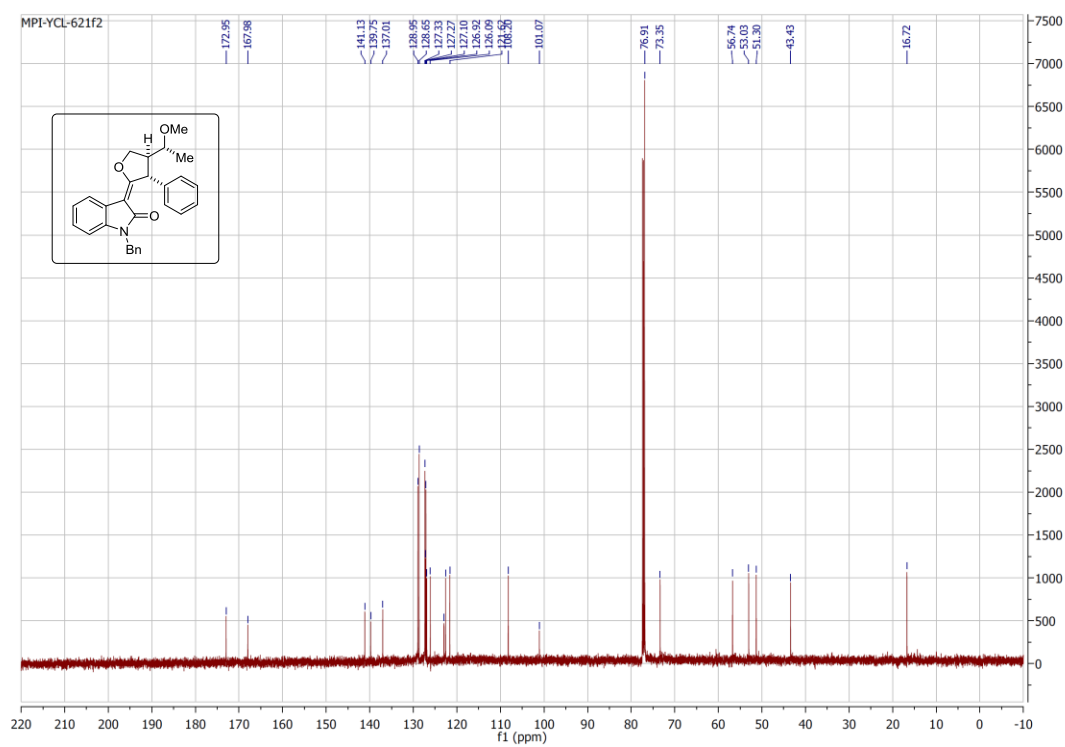
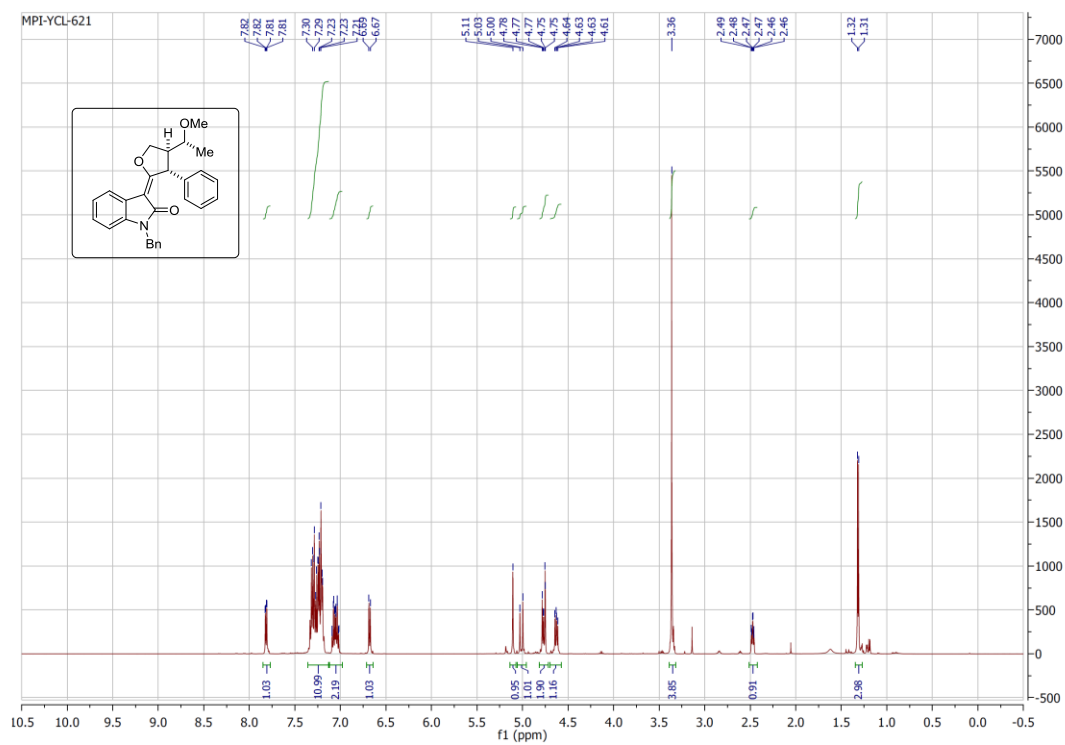
Supplementary Figure 103. ^1H and ^{13}C NMR spectra for 4i.



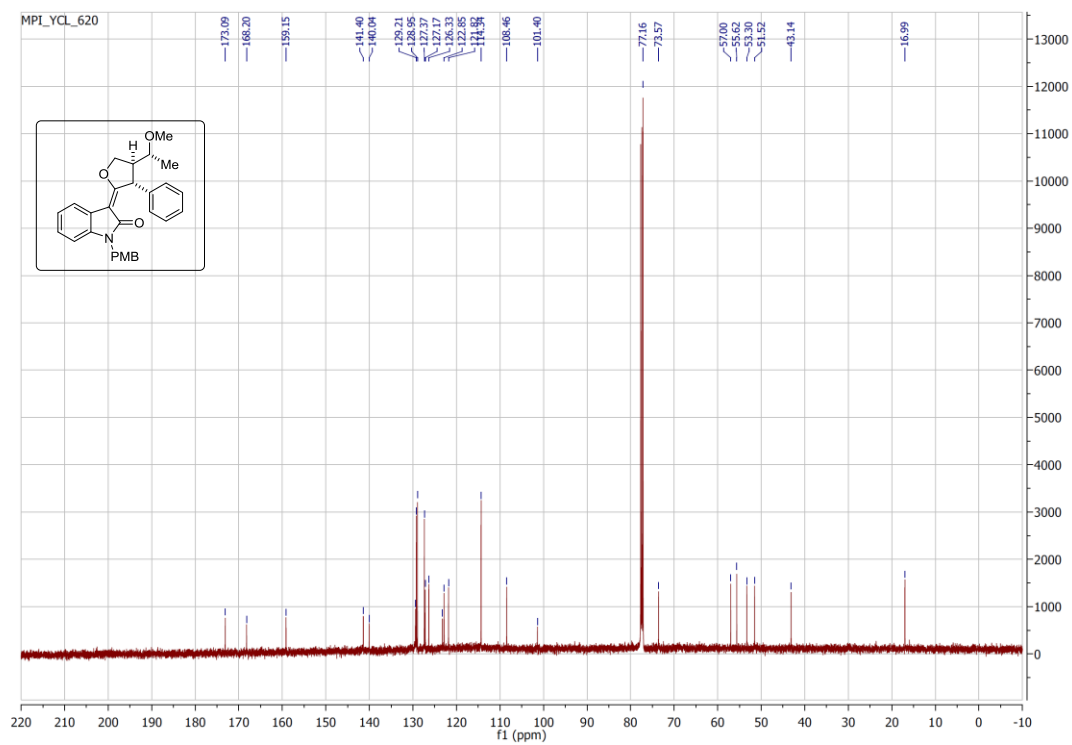
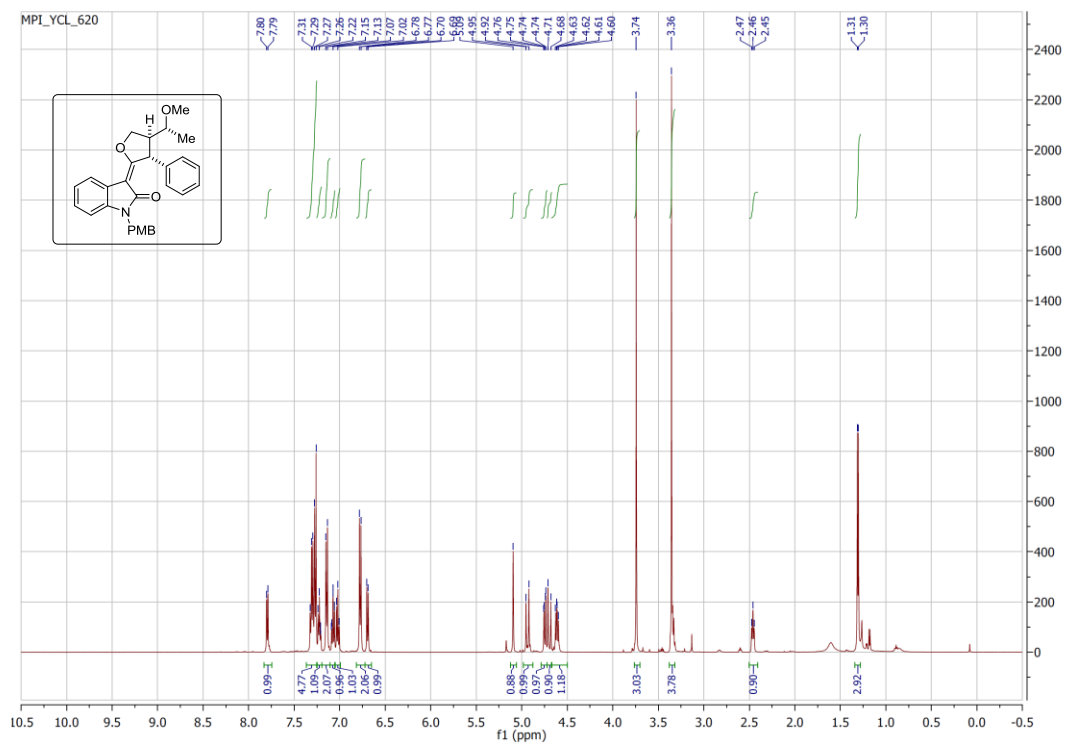
Supplementary Figure 104. ^1H and ^{13}C NMR spectra for 4j.



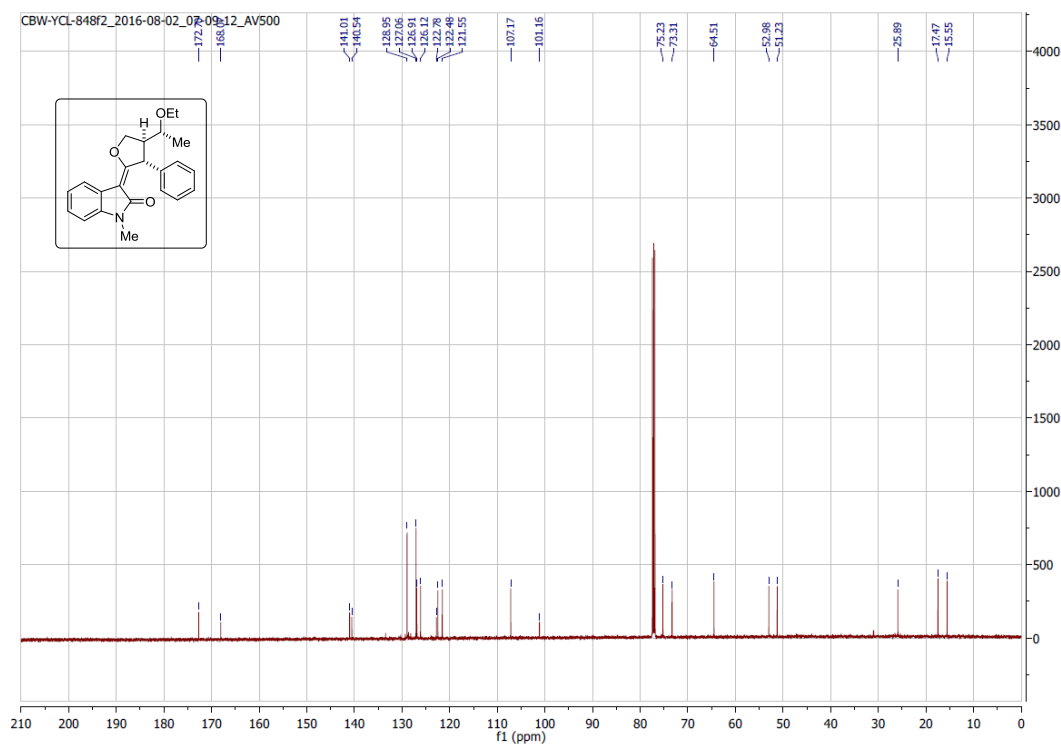
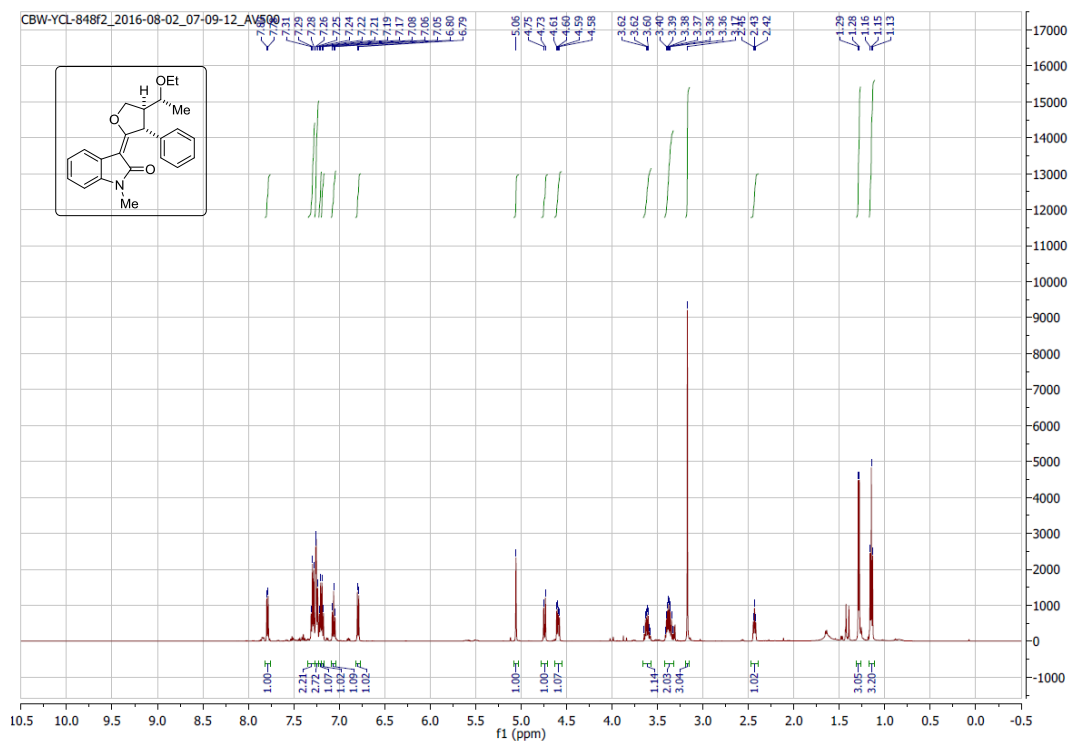
Supplementary Figure 105. ¹H and ¹³C NMR spectra for 4k.



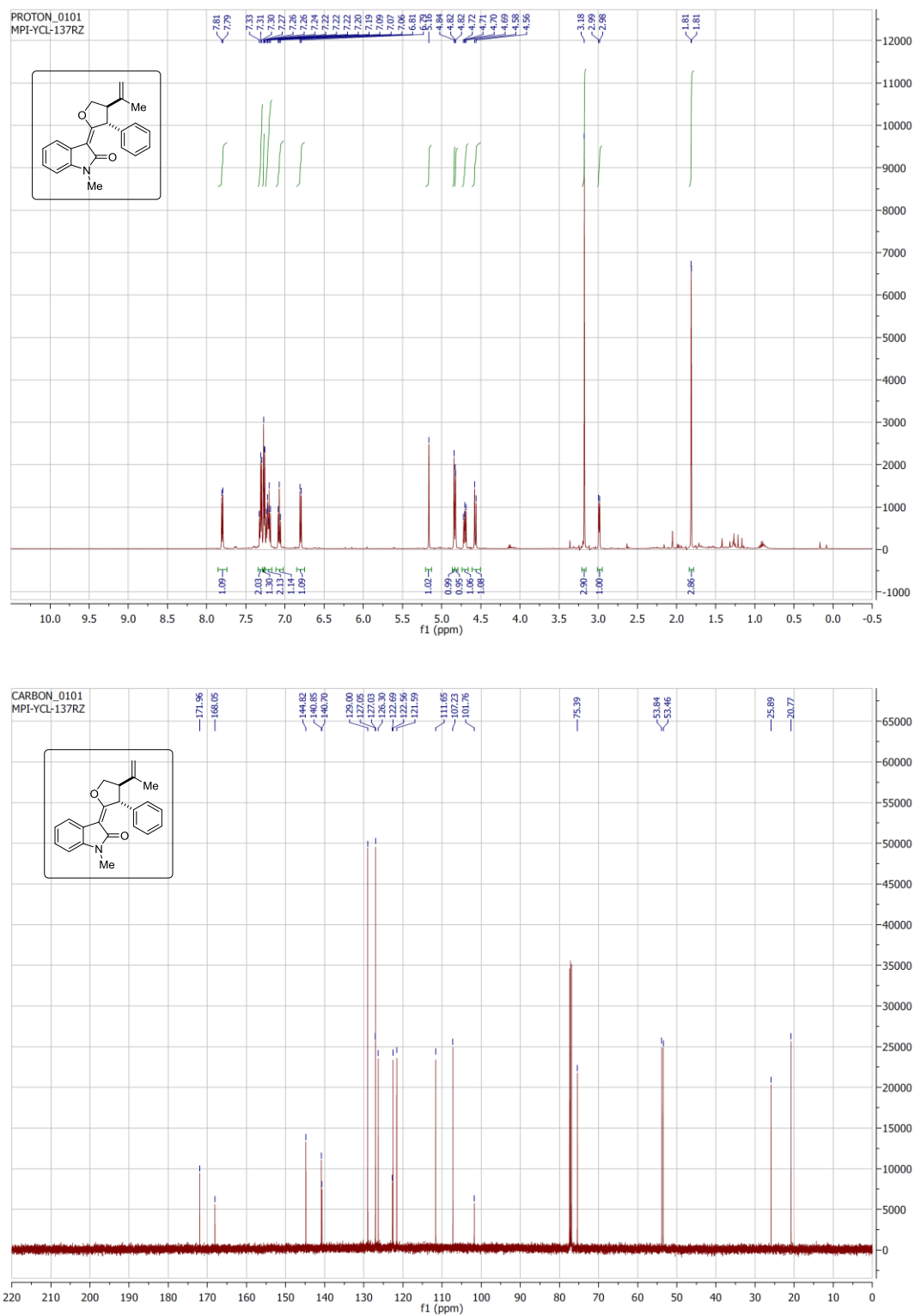
Supplementary Figure 106. ¹H and ¹³C NMR spectra for 4I.



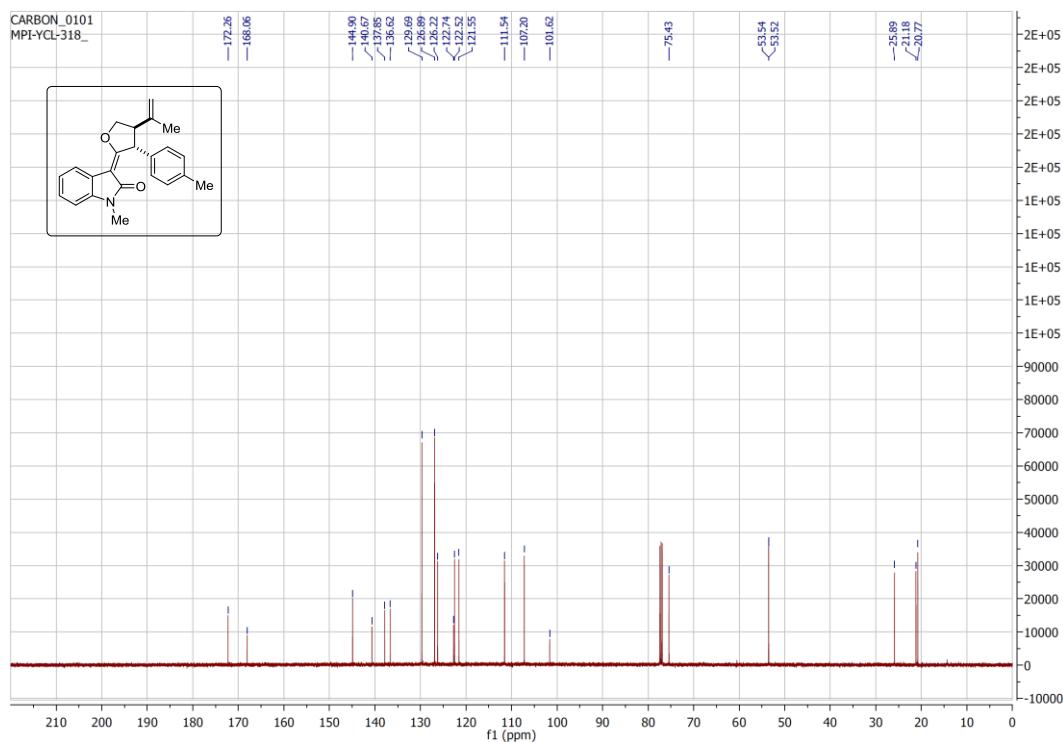
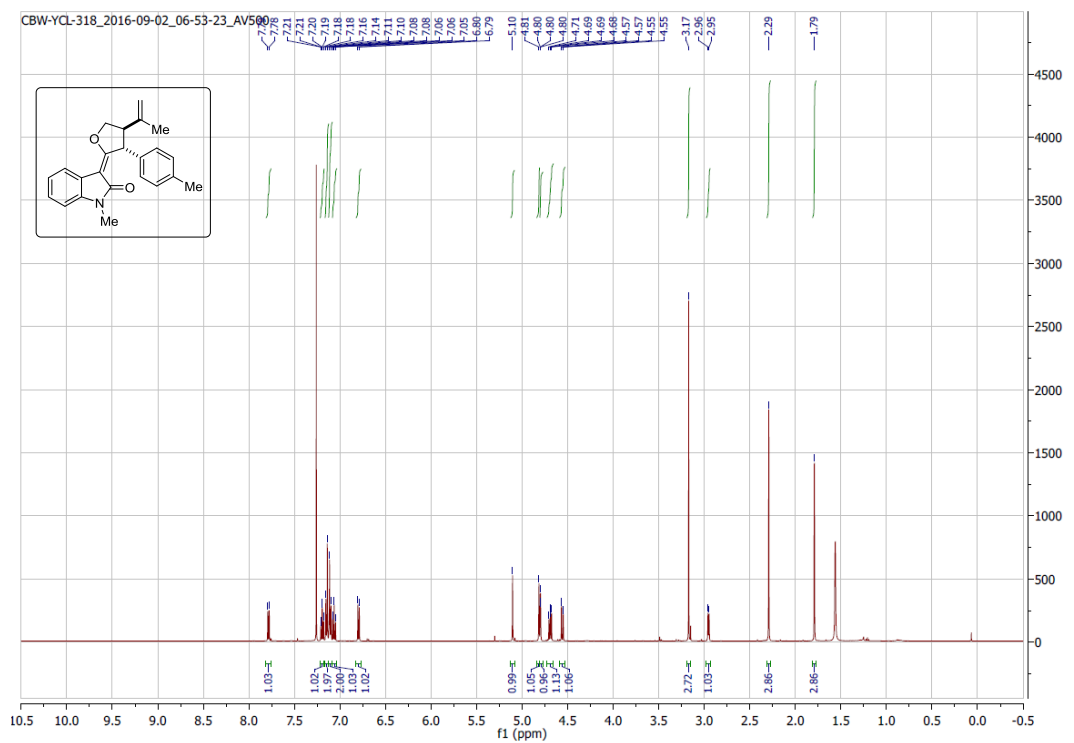
Supplementary Figure 107. ¹H and ¹³C NMR spectra for **4m**.



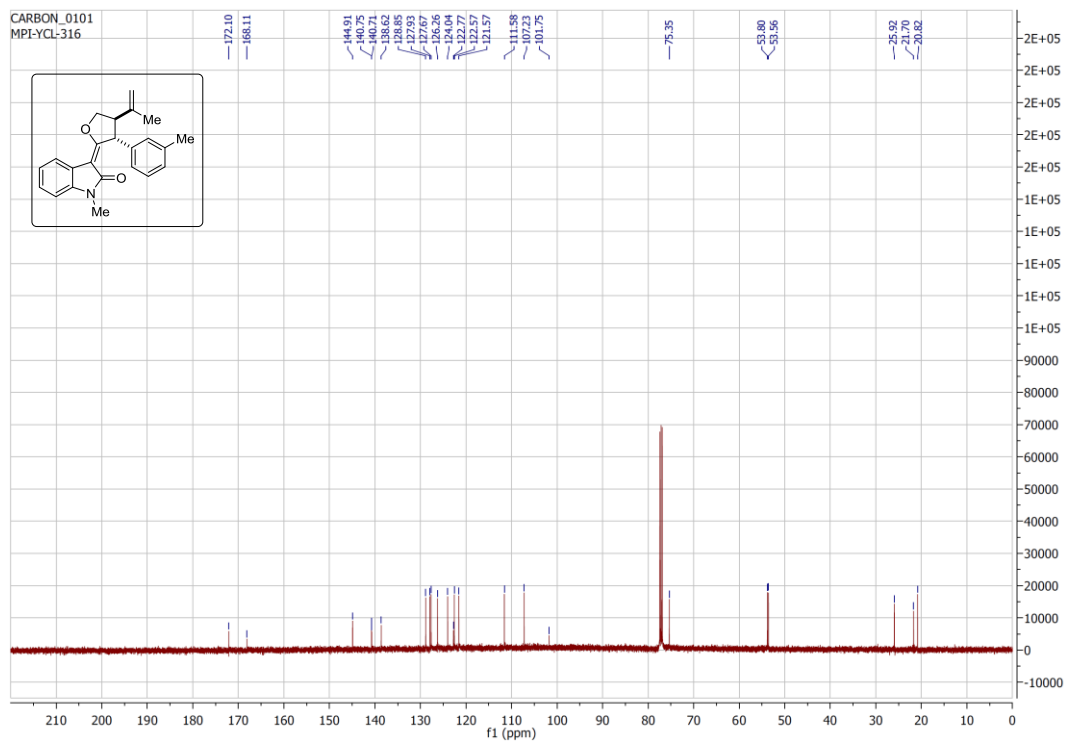
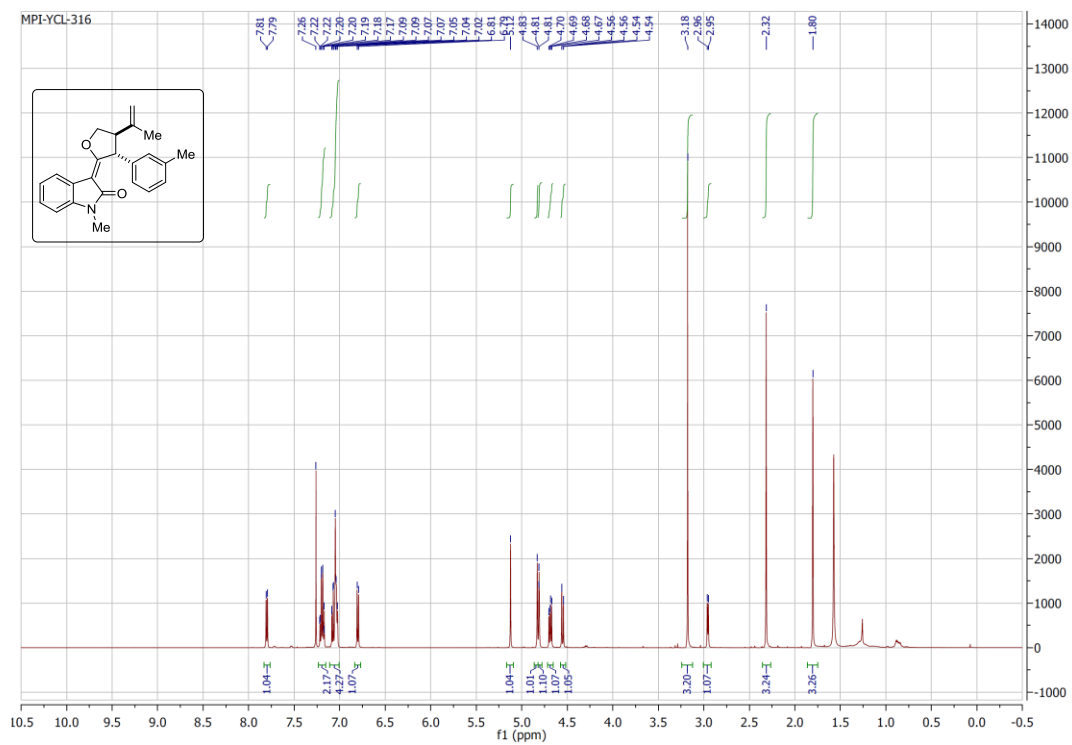
Supplementary Figure 108. ¹H and ¹³C NMR spectra for 4n.



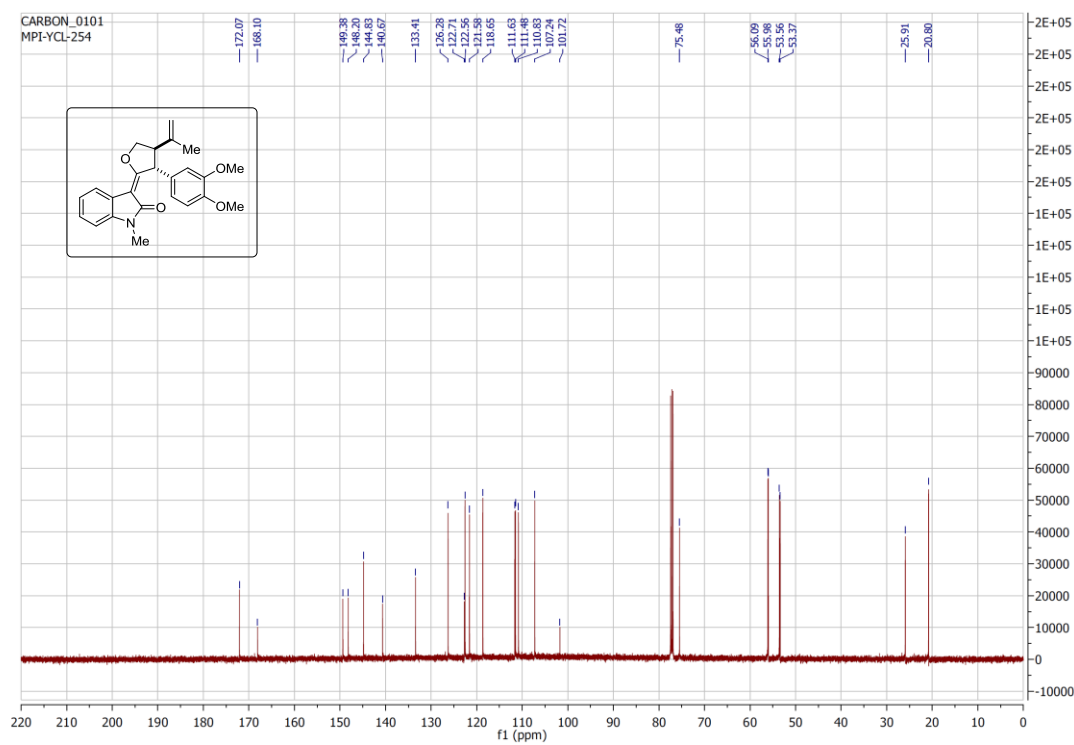
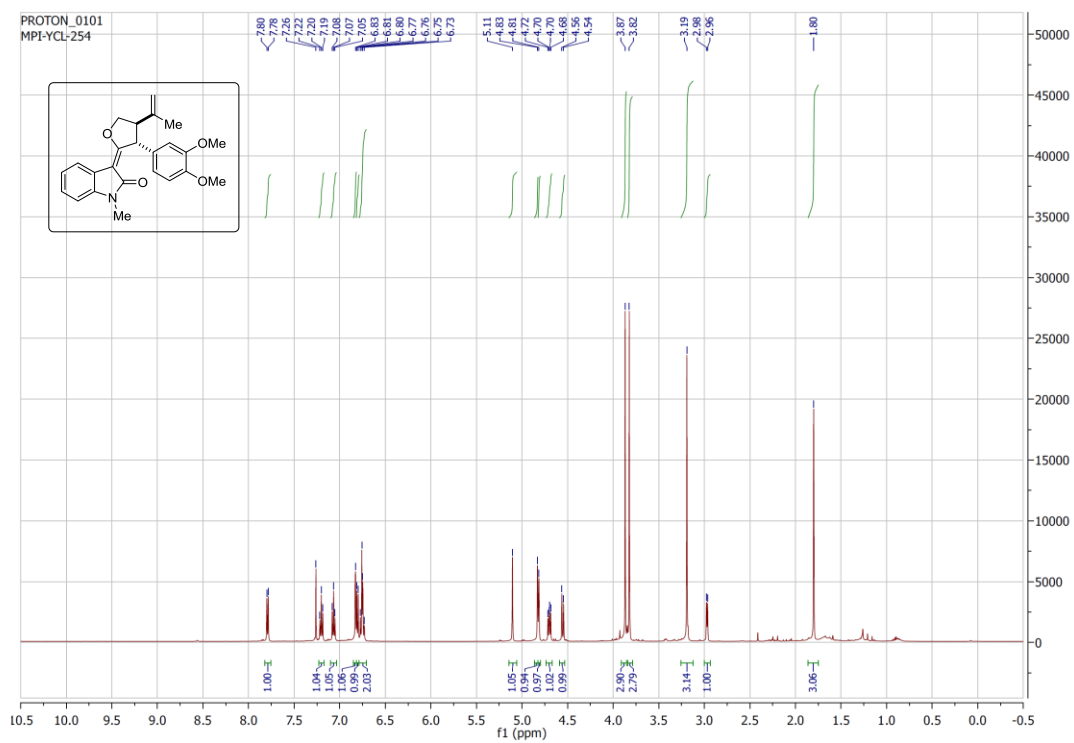
Supplementary Figure 109. ^1H and ^{13}C NMR spectra for 14a.



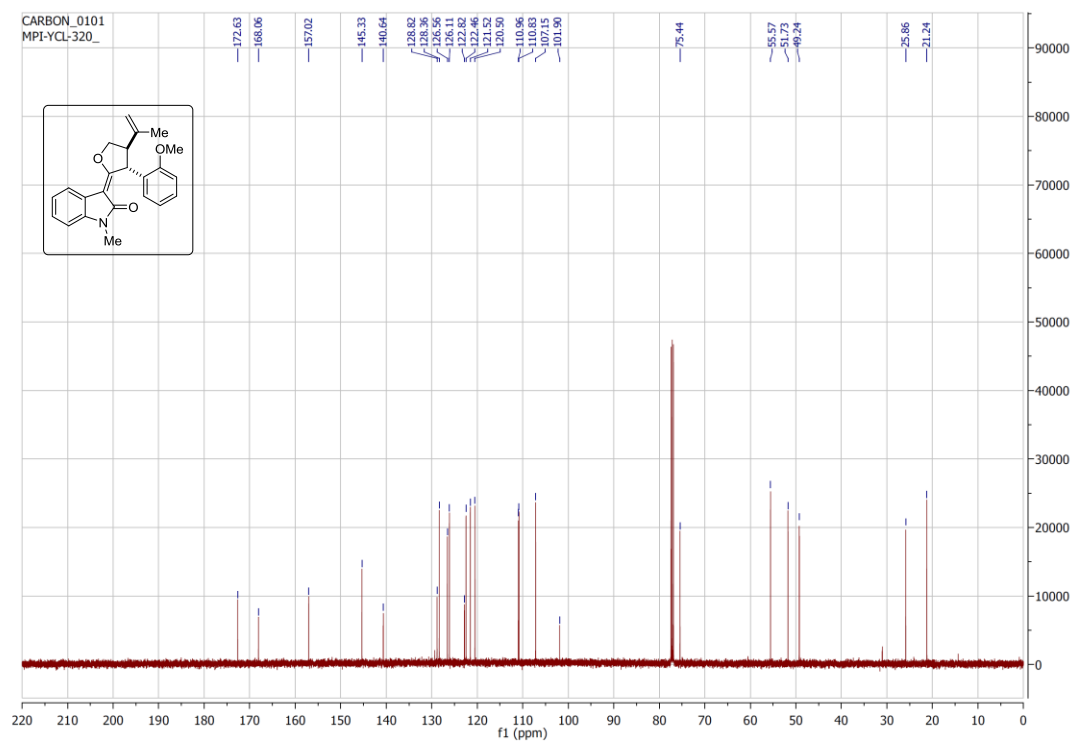
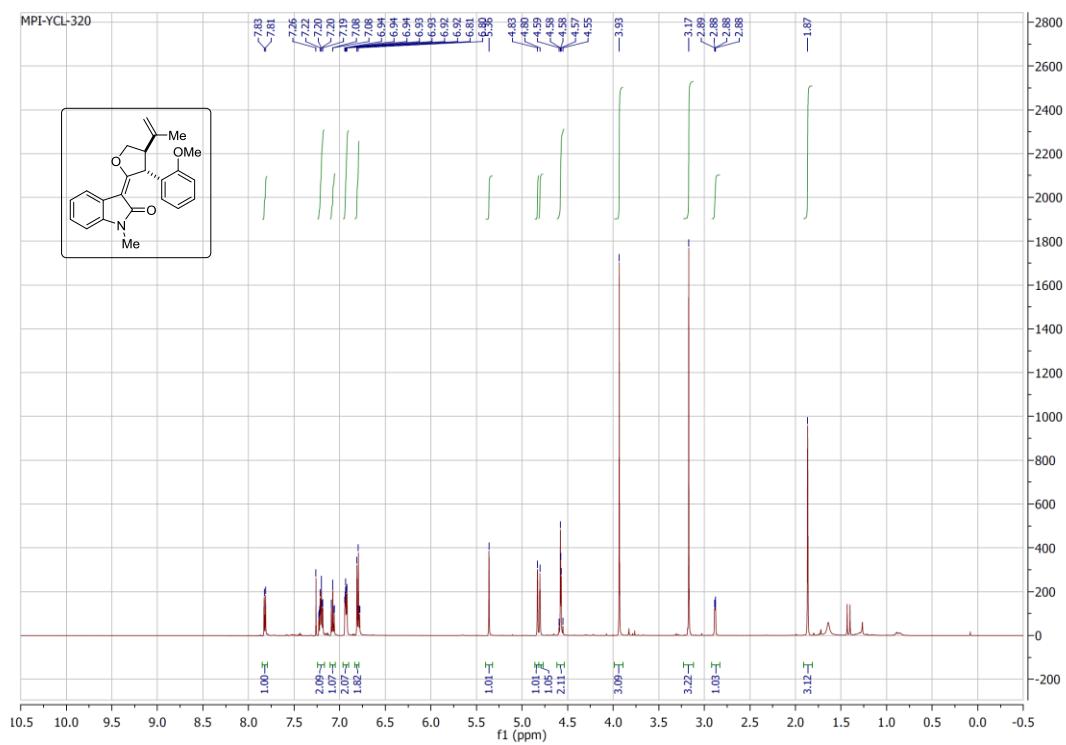
Supplementary Figure 110. ^1H and ^{13}C NMR spectra for 14b.



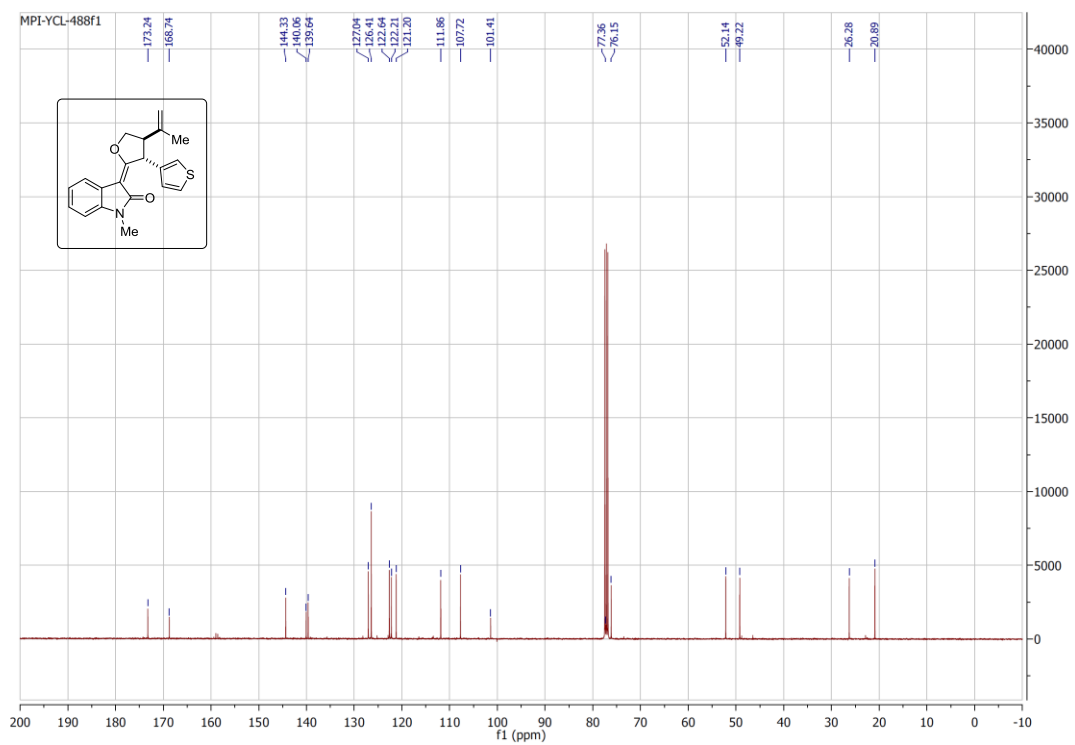
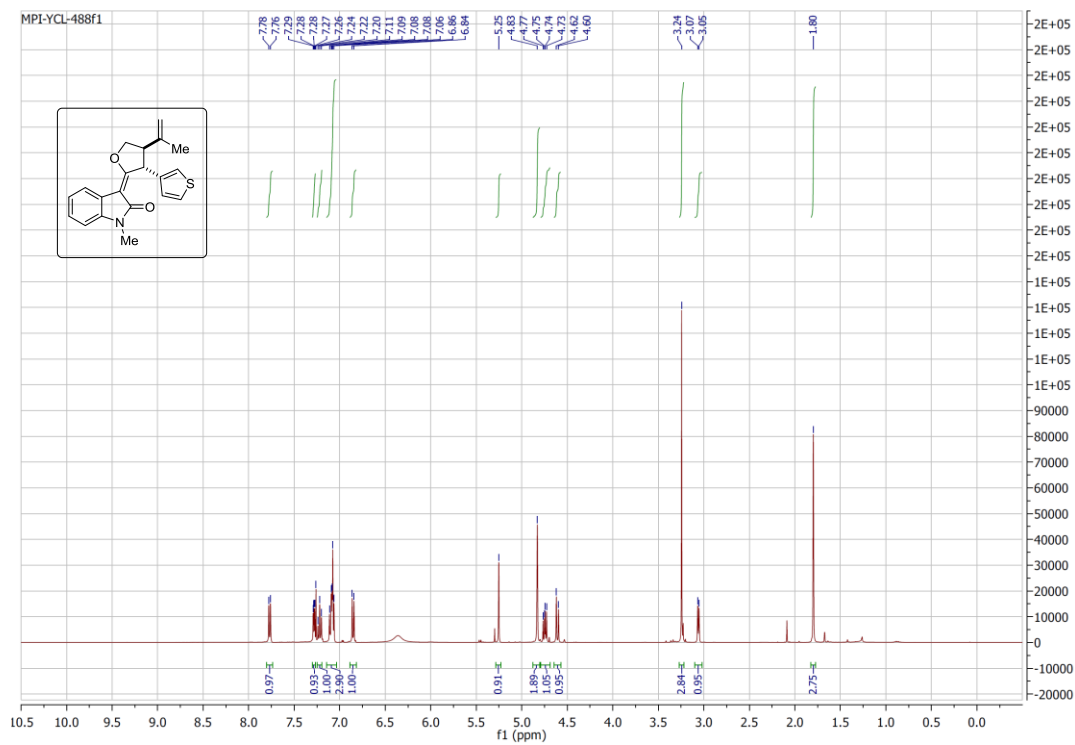
Supplementary Figure 111. ^1H and ^{13}C NMR spectra for 14c.



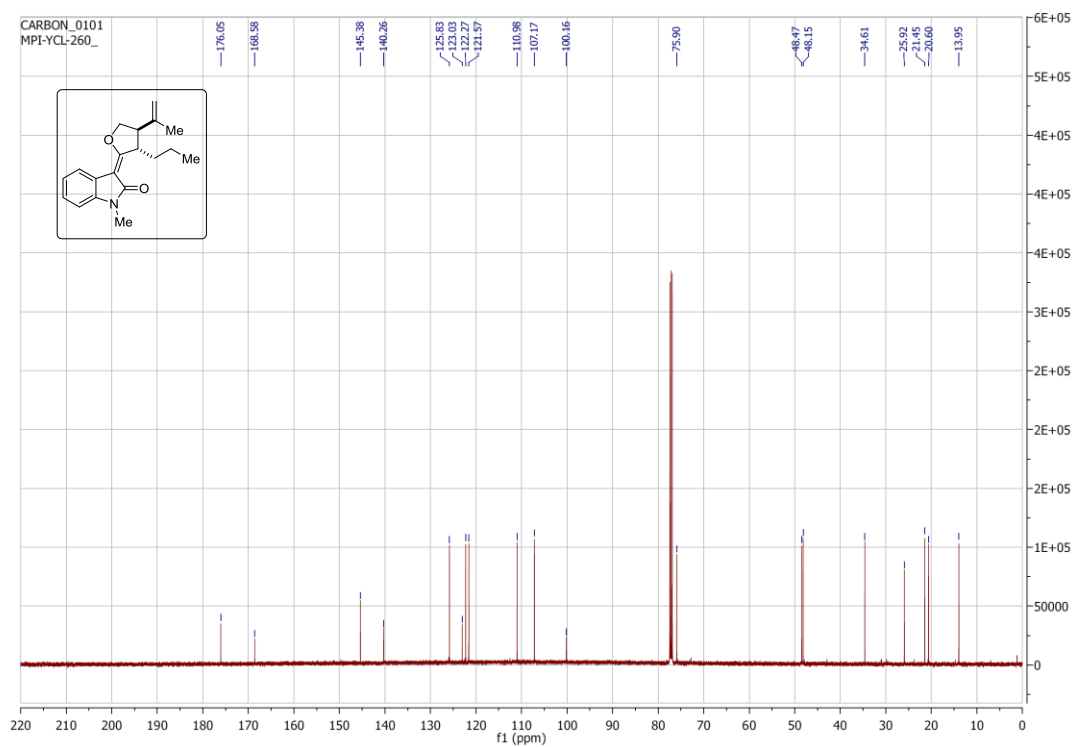
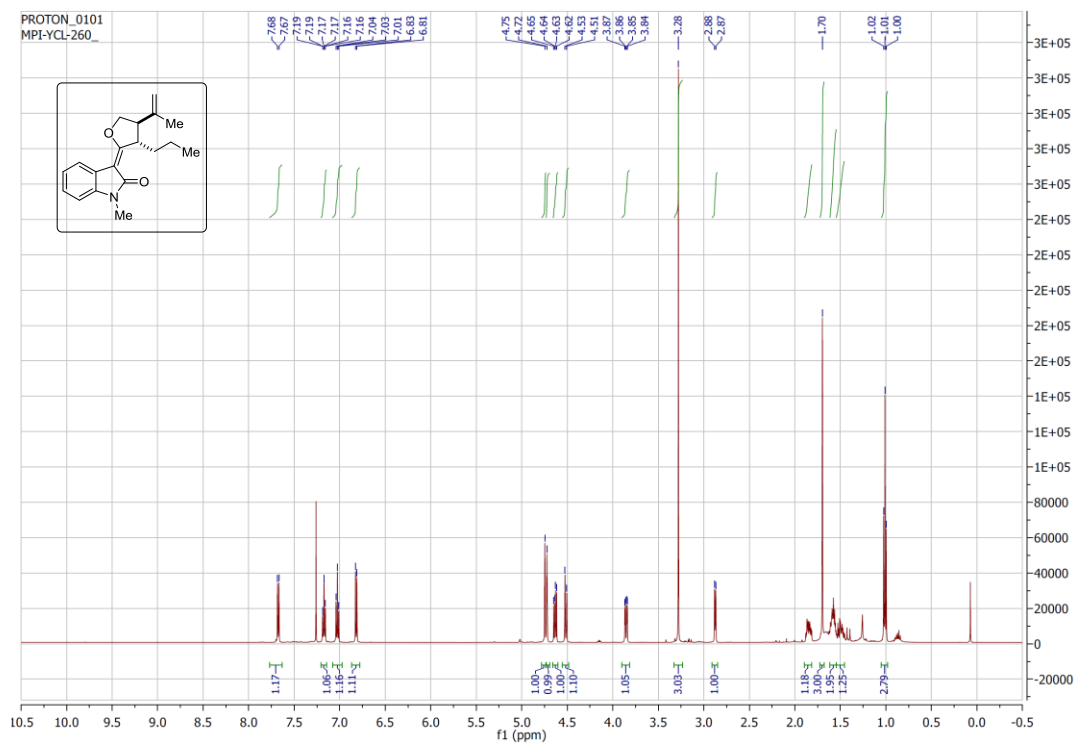
Supplementary Figure 112. ^1H and ^{13}C NMR spectra for 14d.



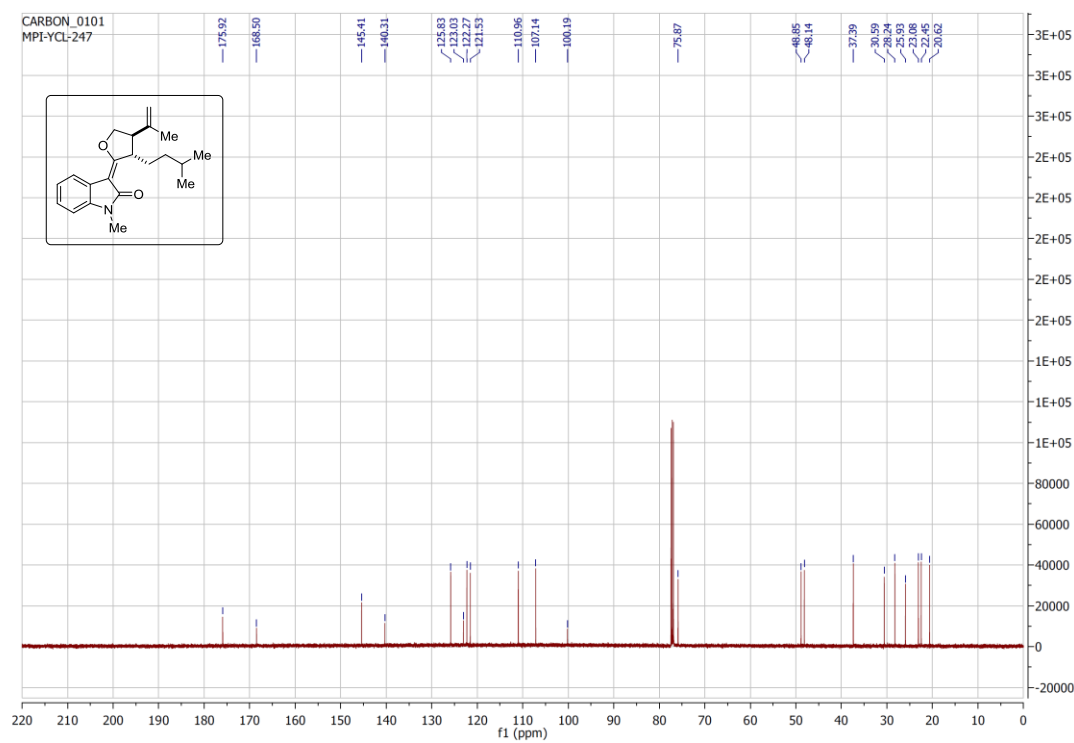
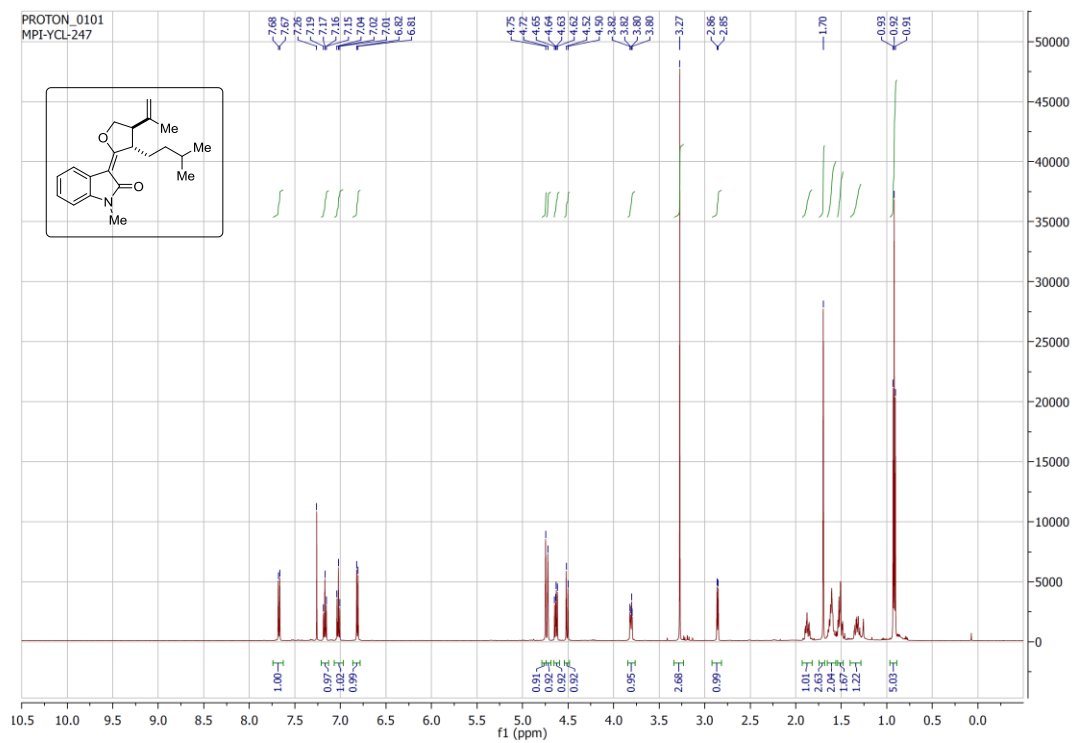
Supplementary Figure 113. ¹H and ¹³C NMR spectra for 14e.



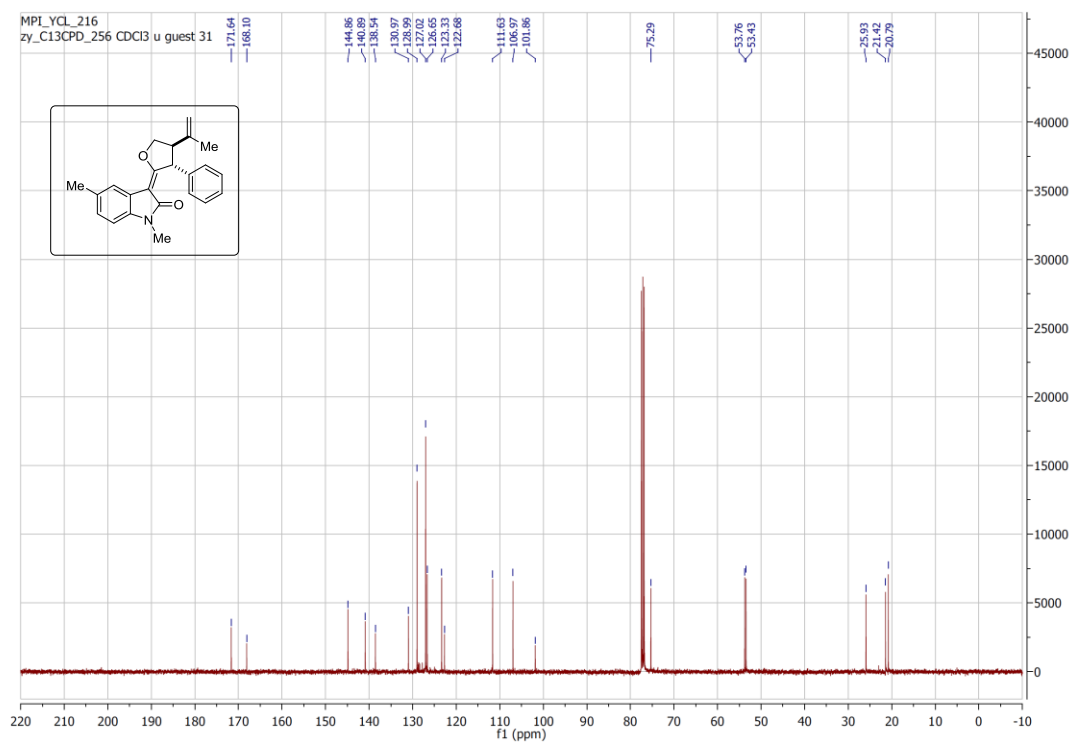
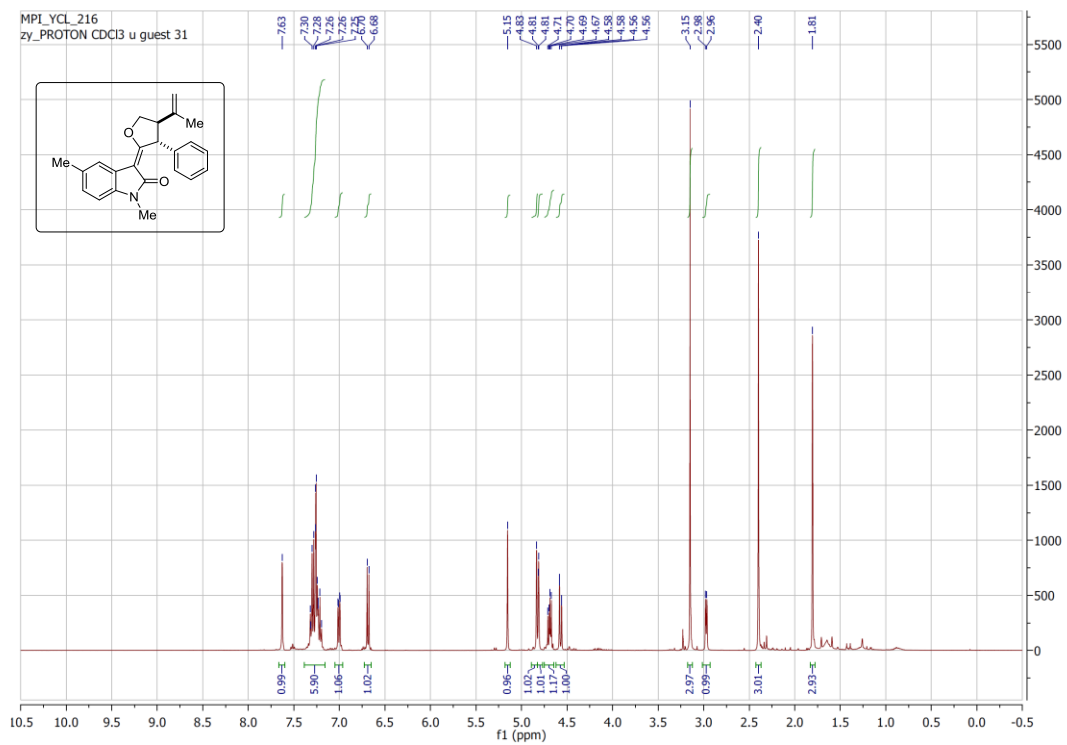
Supplementary Figure 115. ¹H and ¹³C NMR spectra for 14g.



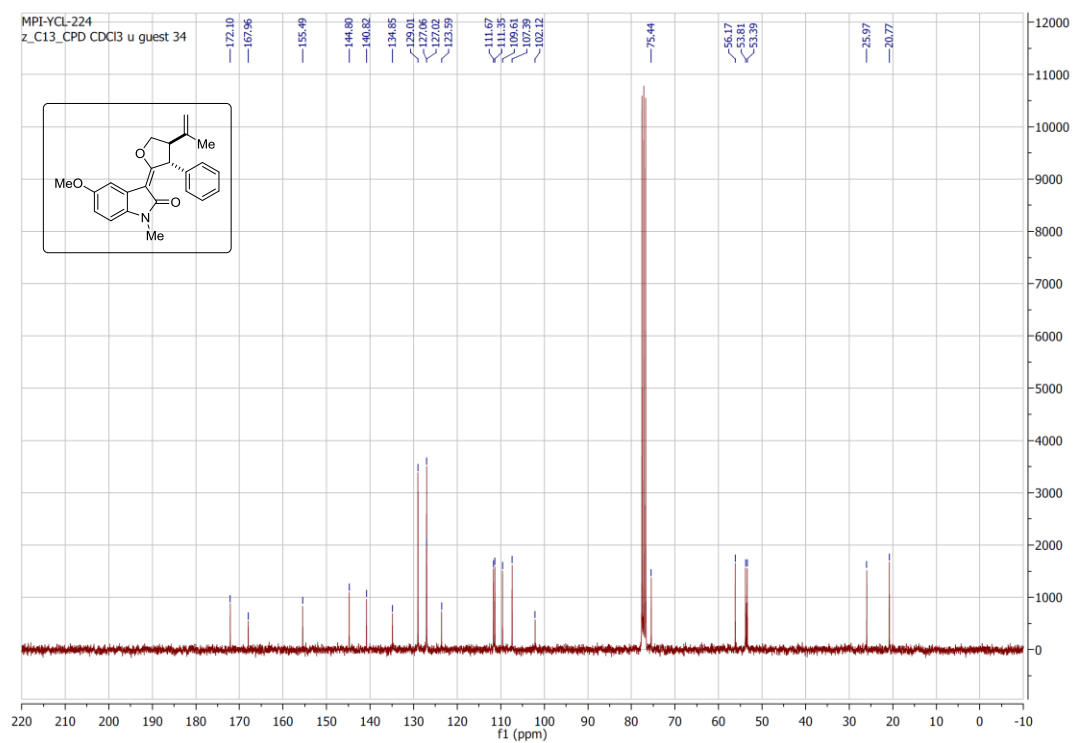
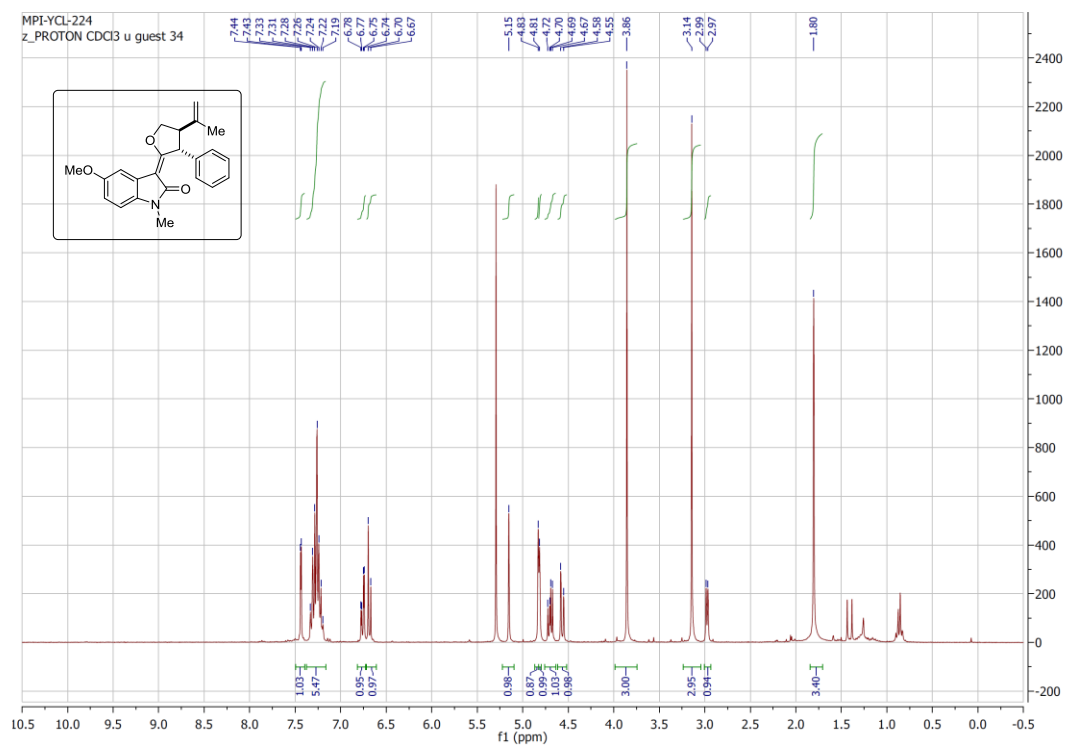
Supplementary Figure 116. ^1H and ^{13}C NMR spectra for 14h.



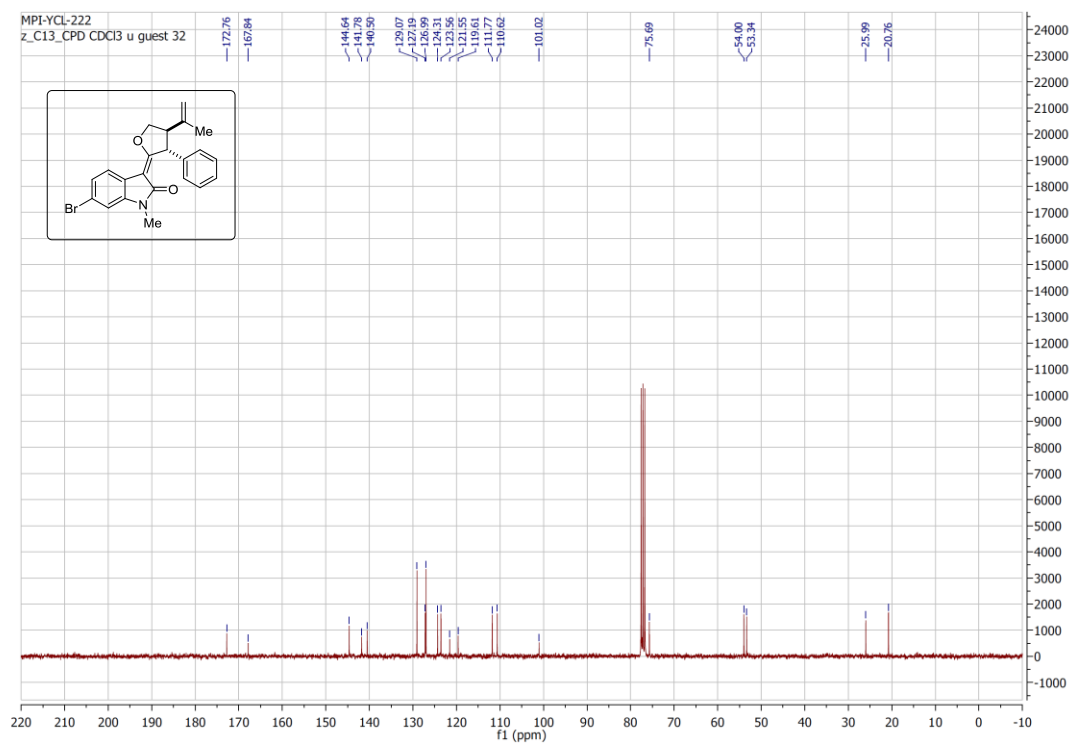
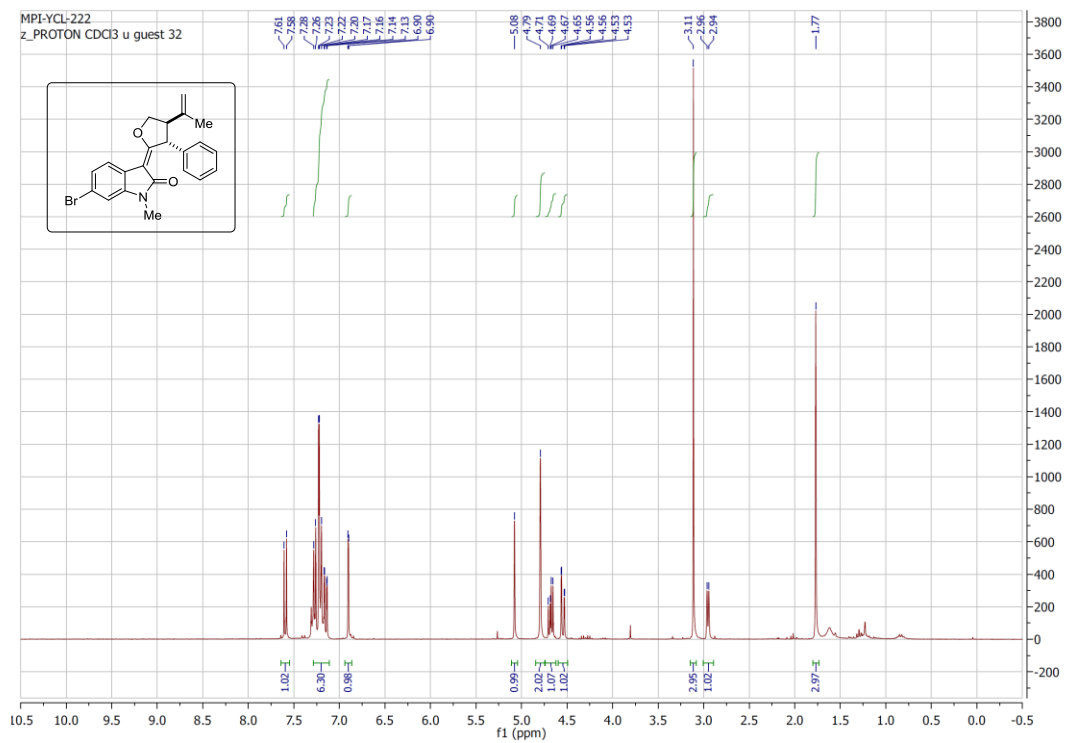
Supplementary Figure 117. ^1H and ^{13}C NMR spectra for 14i.



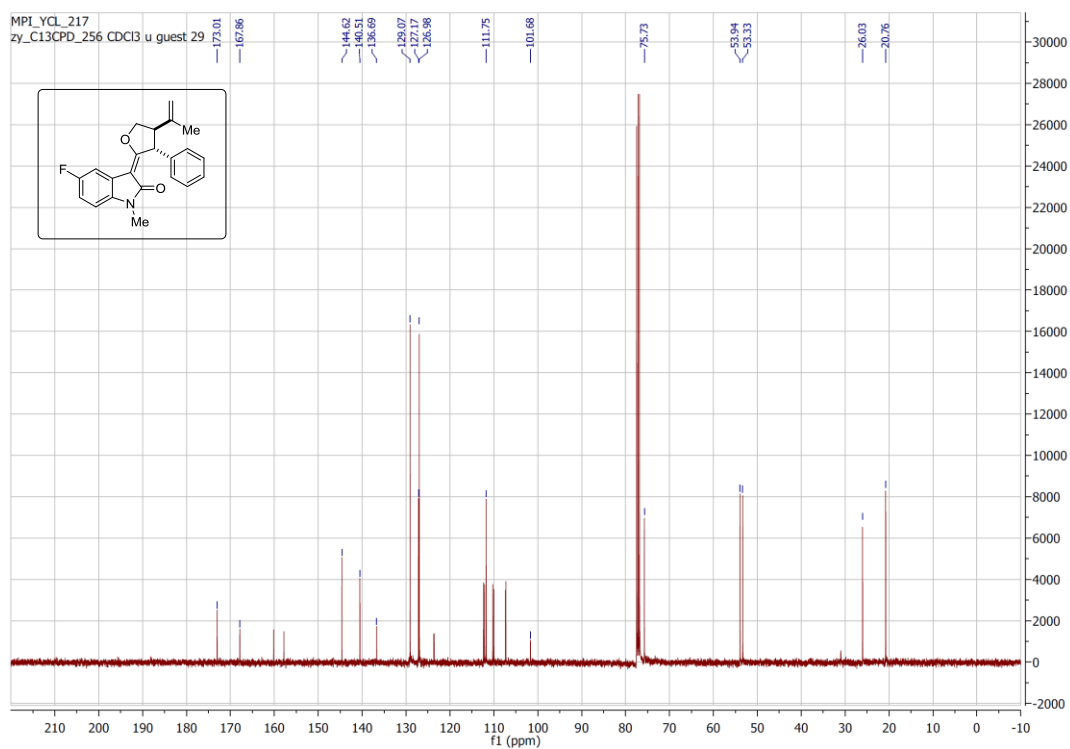
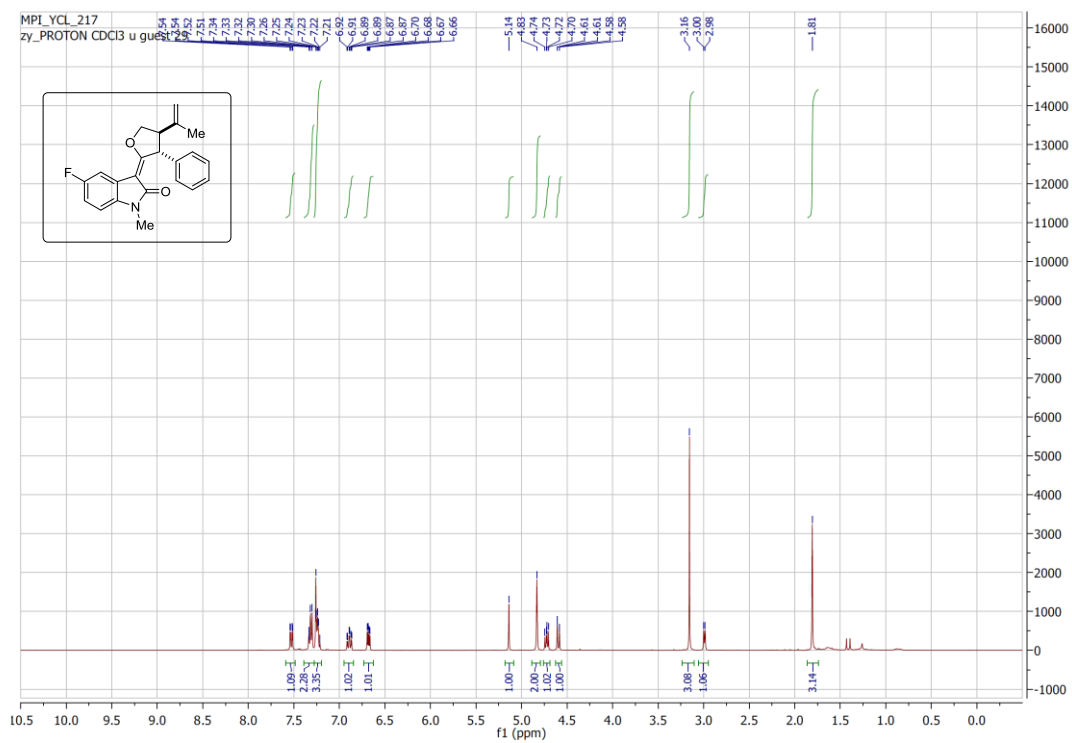
Supplementary Figure 118. ¹H and ¹³C NMR spectra for 14j.



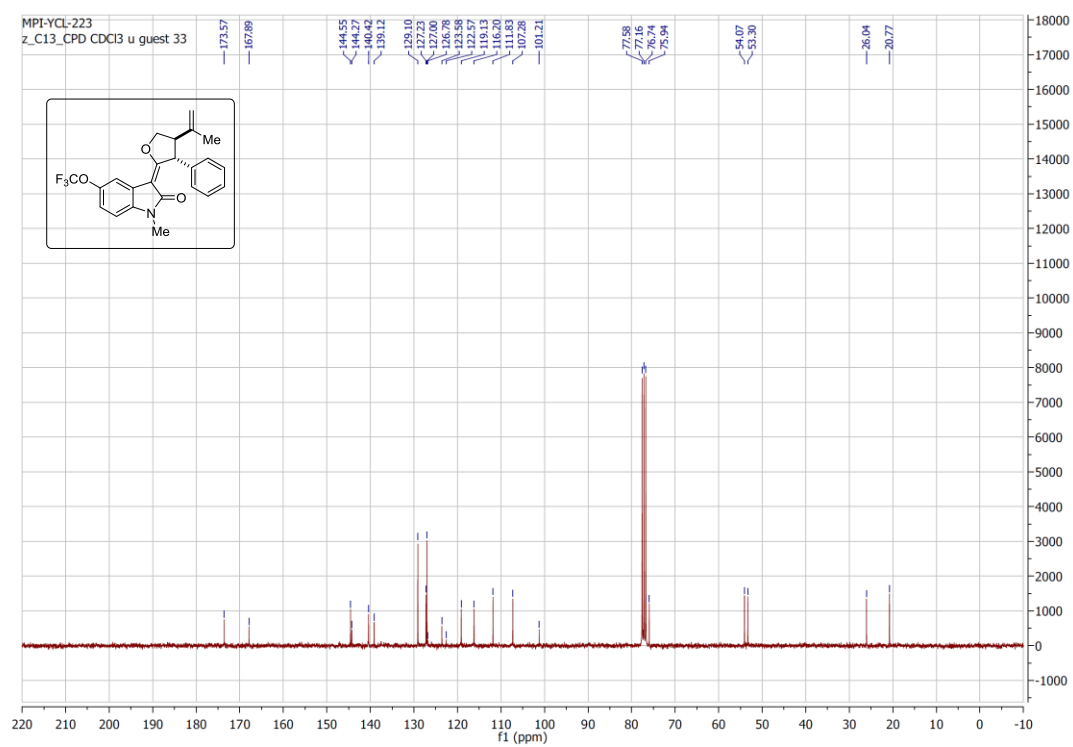
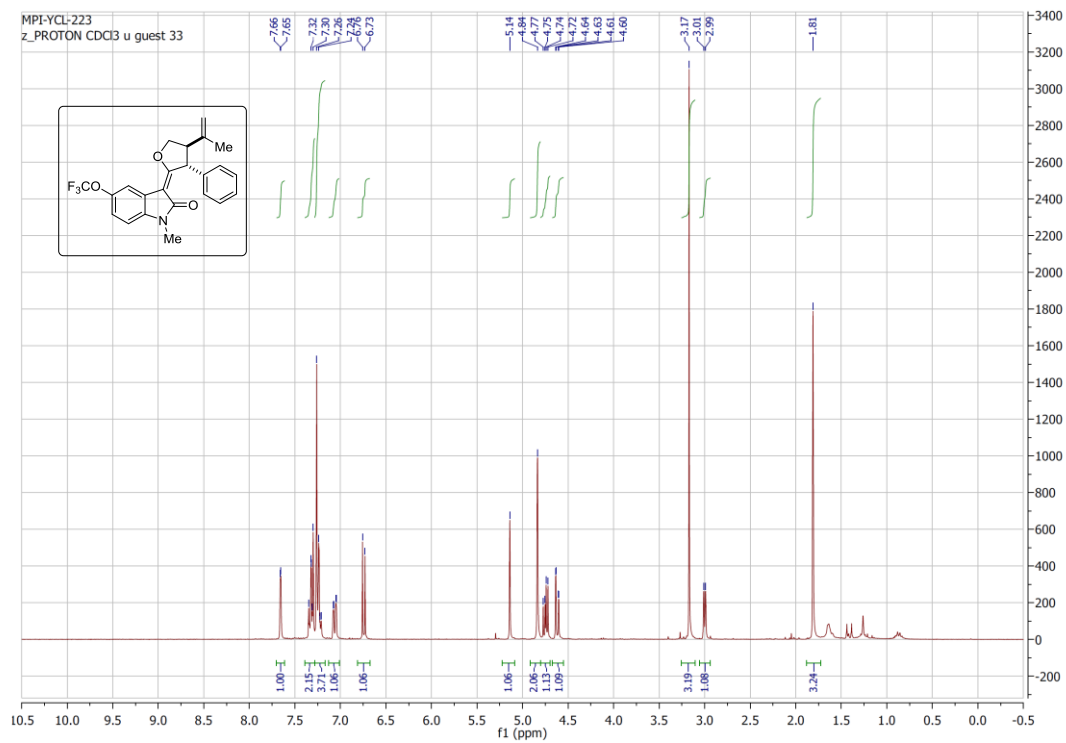
Supplementary Figure 119. ^1H and ^{13}C NMR spectra for 14k.



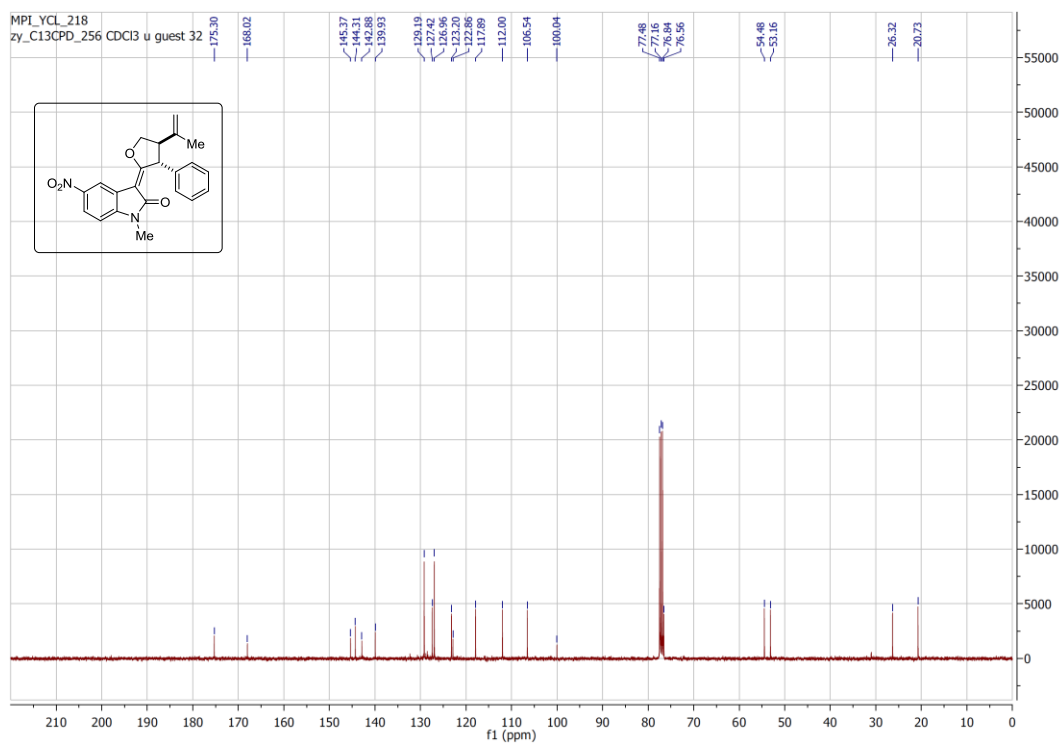
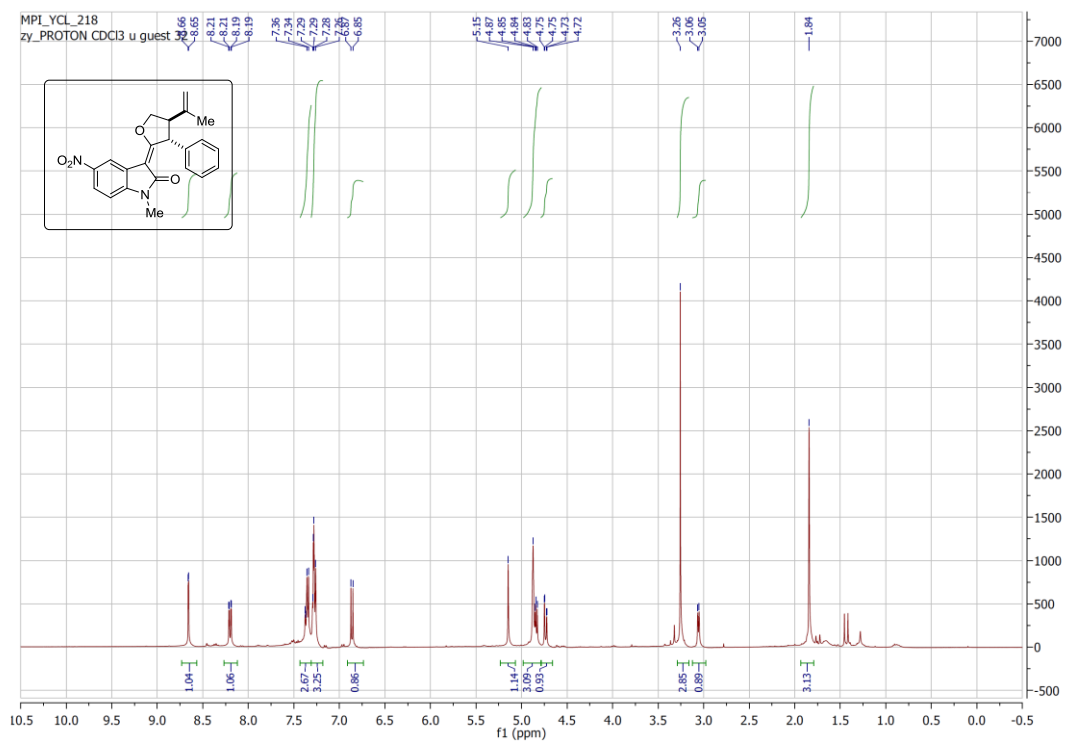
Supplementary Figure 120. ^1H and ^{13}C NMR spectra for **14l**.



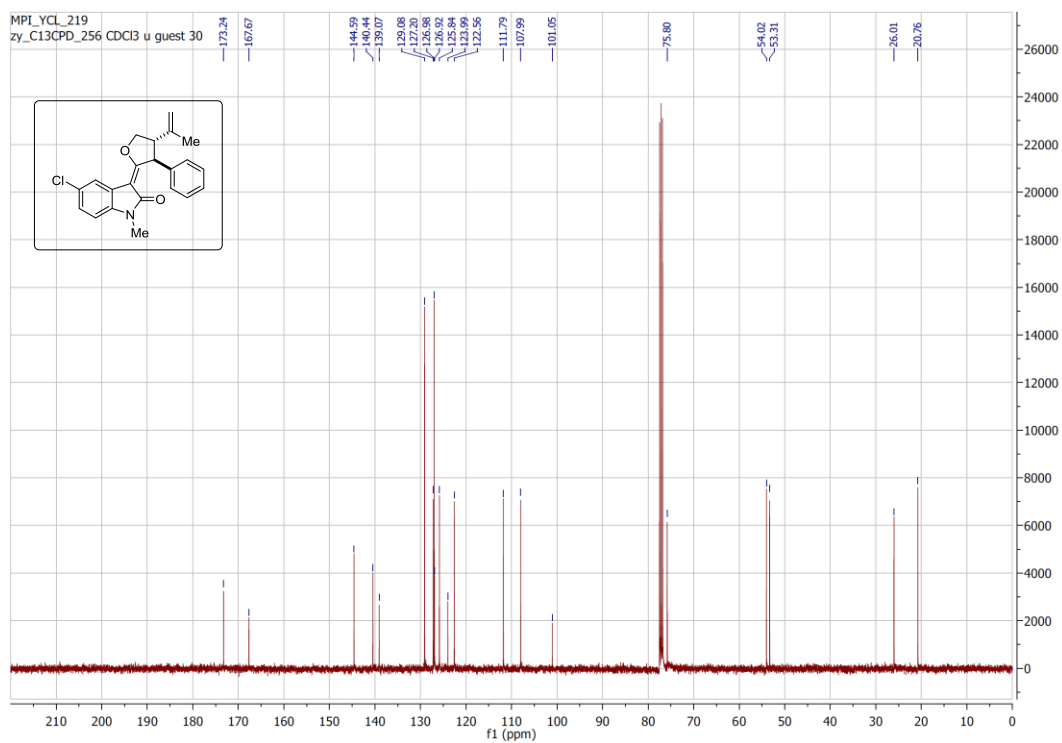
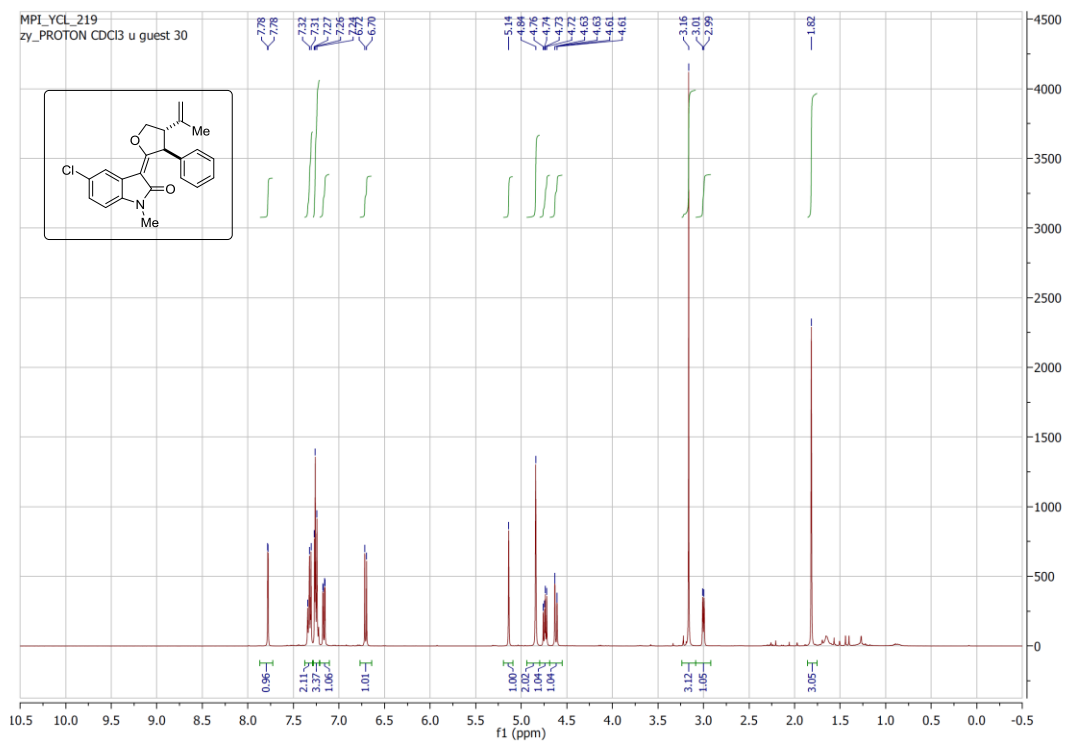
Supplementary Figure 121. ^1H and ^{13}C NMR spectra for 14m.



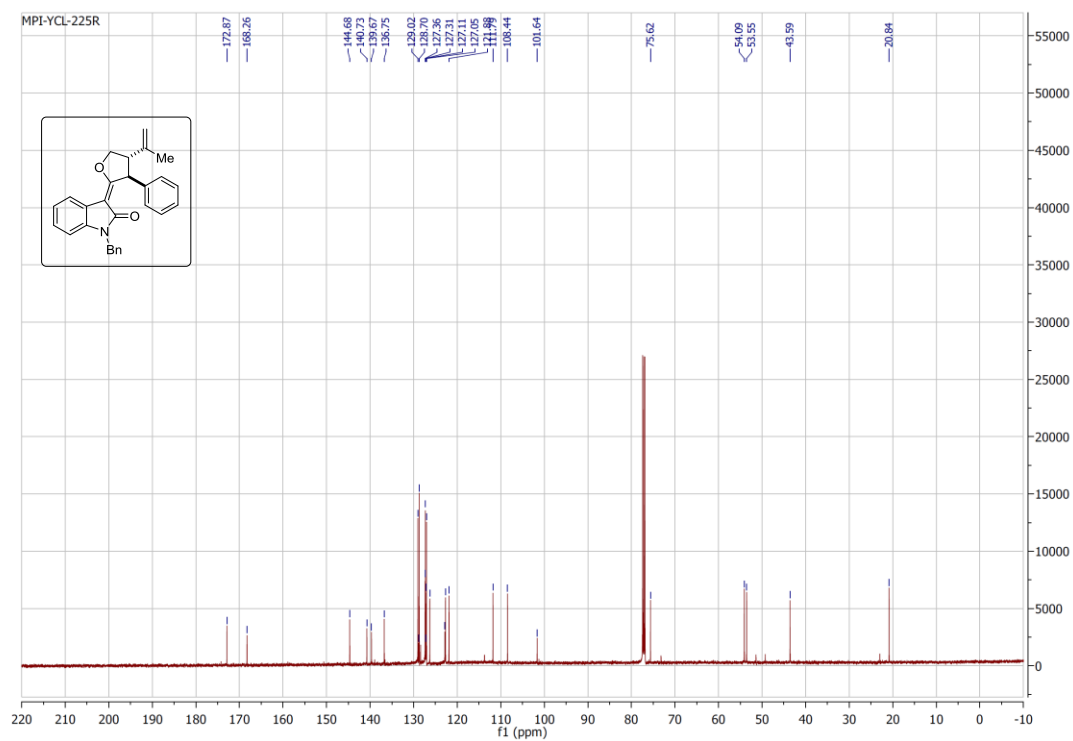
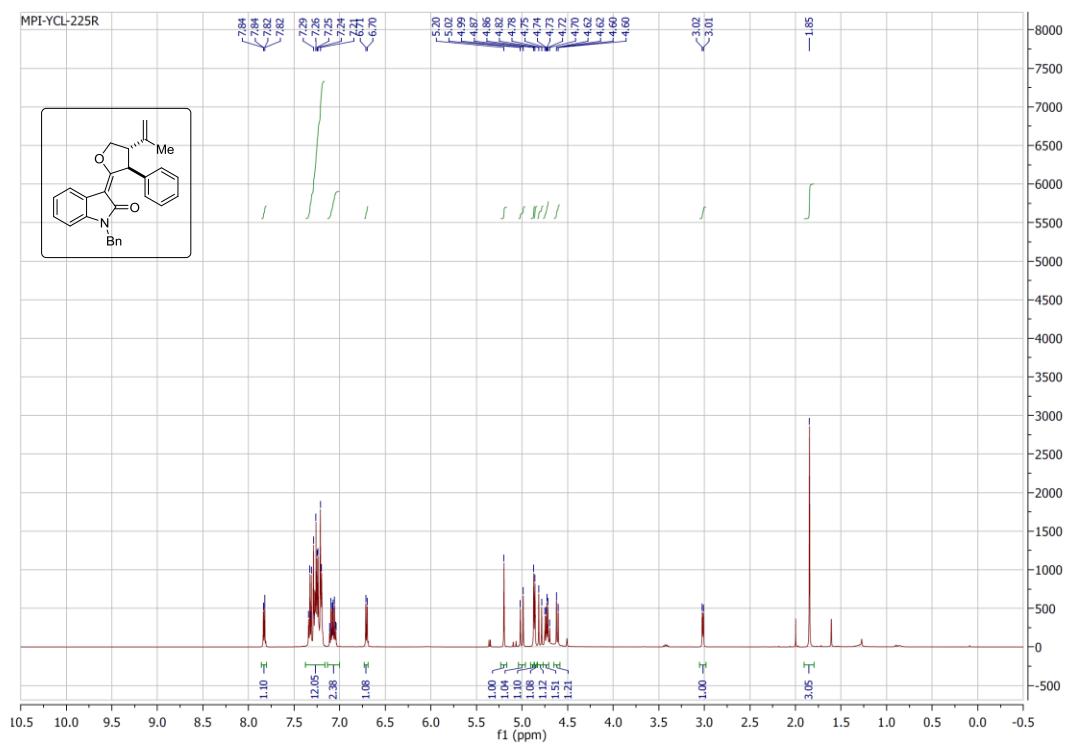
Supplementary Figure 122. ^1H and ^{13}C NMR spectra for 14n.



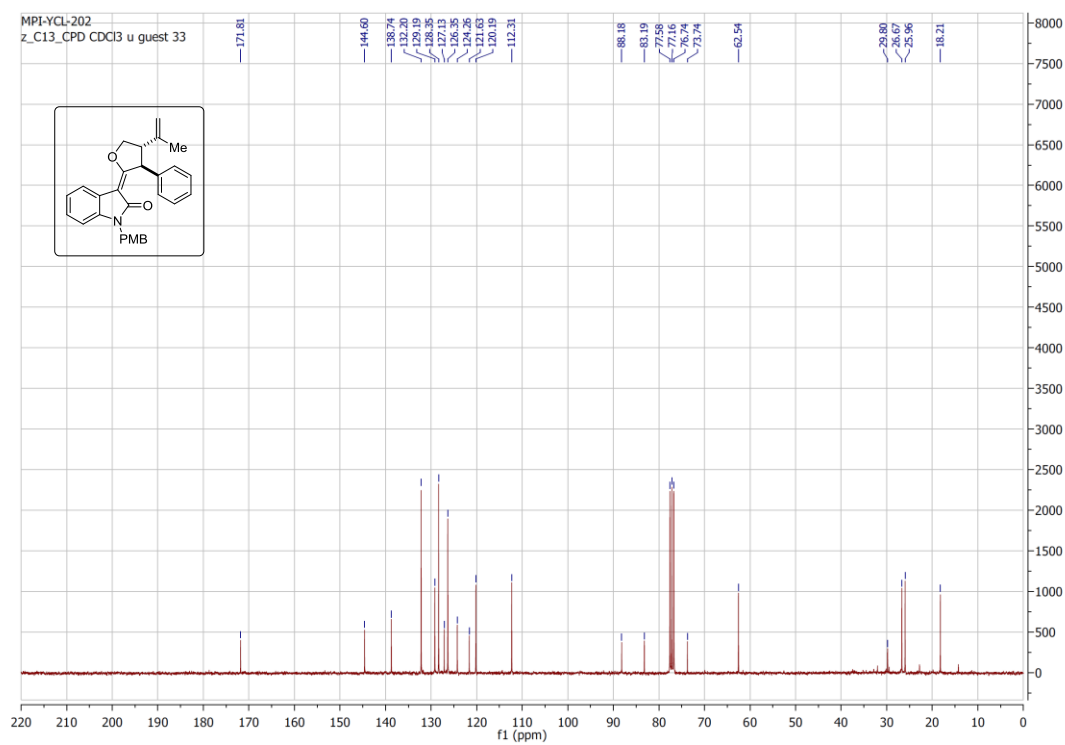
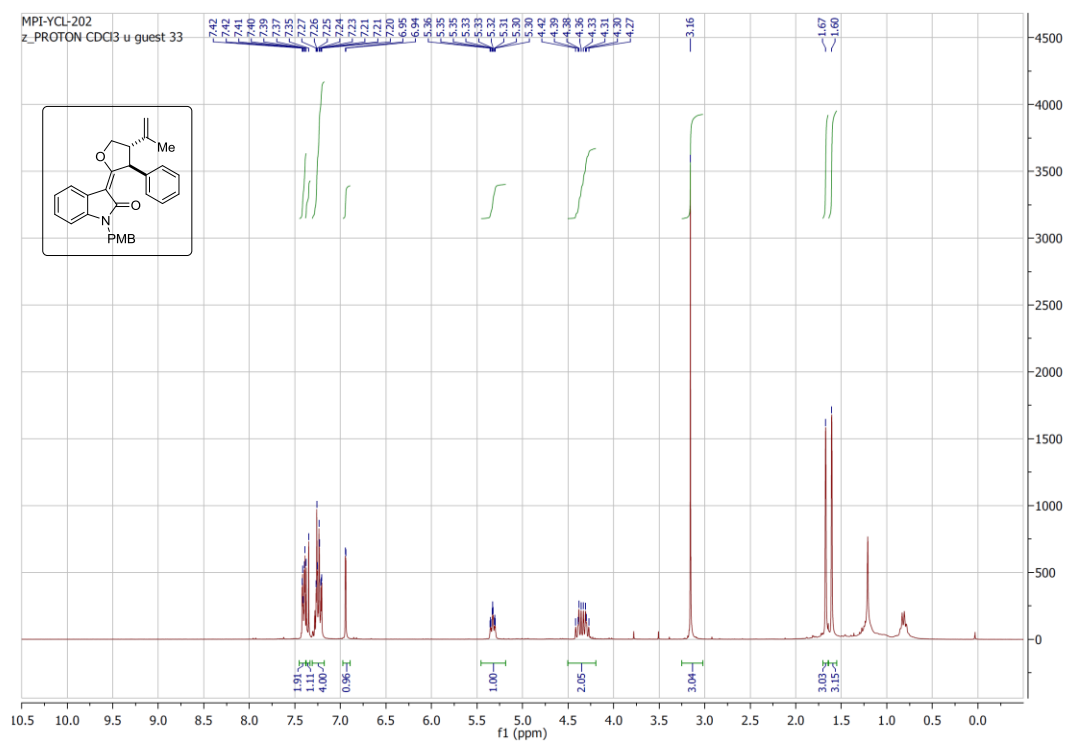
Supplementary Figure 123. ^1H and ^{13}C NMR spectra for 14o.



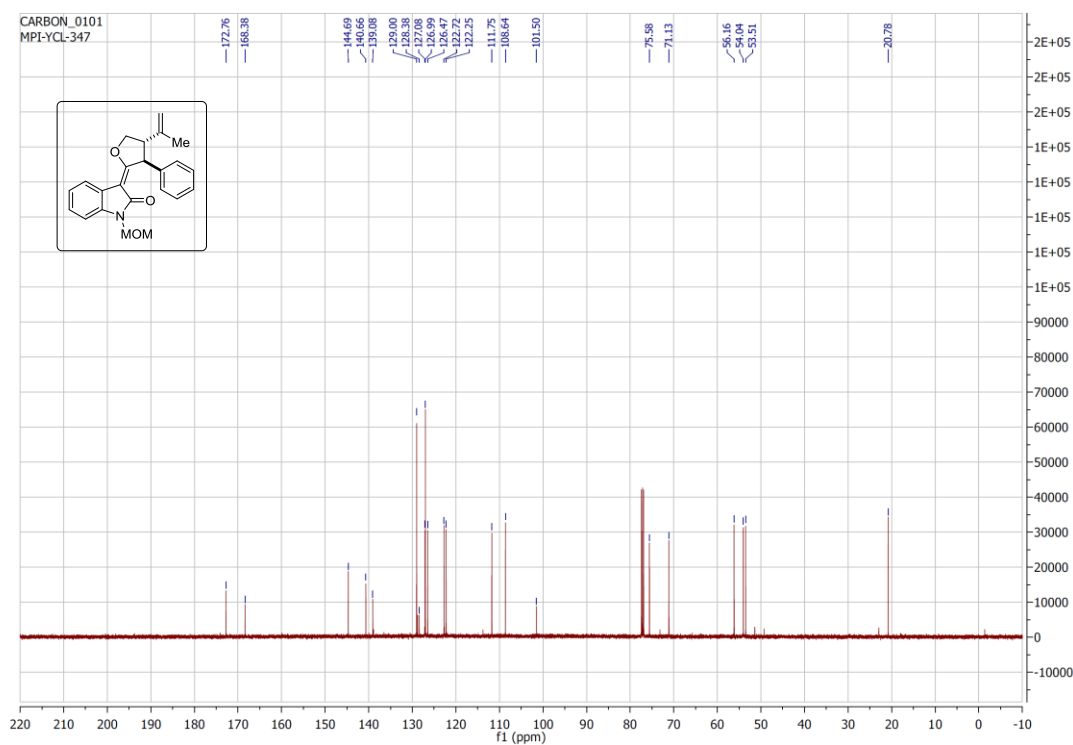
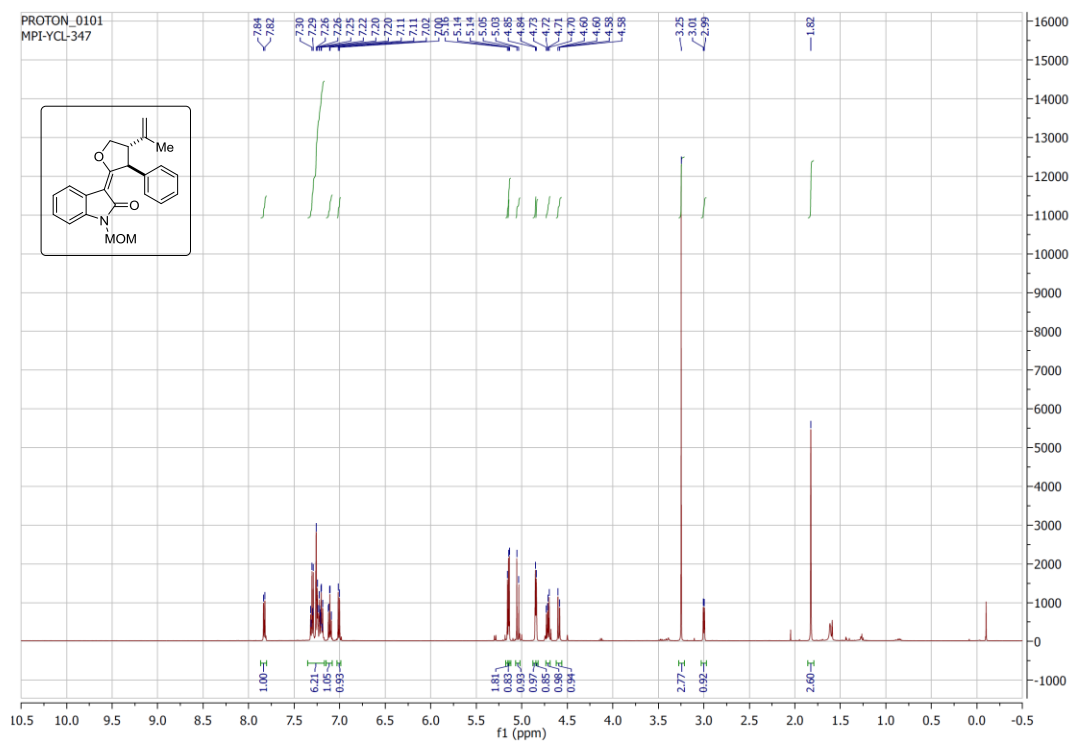
Supplementary Figure 124. ¹H and ¹³C NMR spectra for 14p.



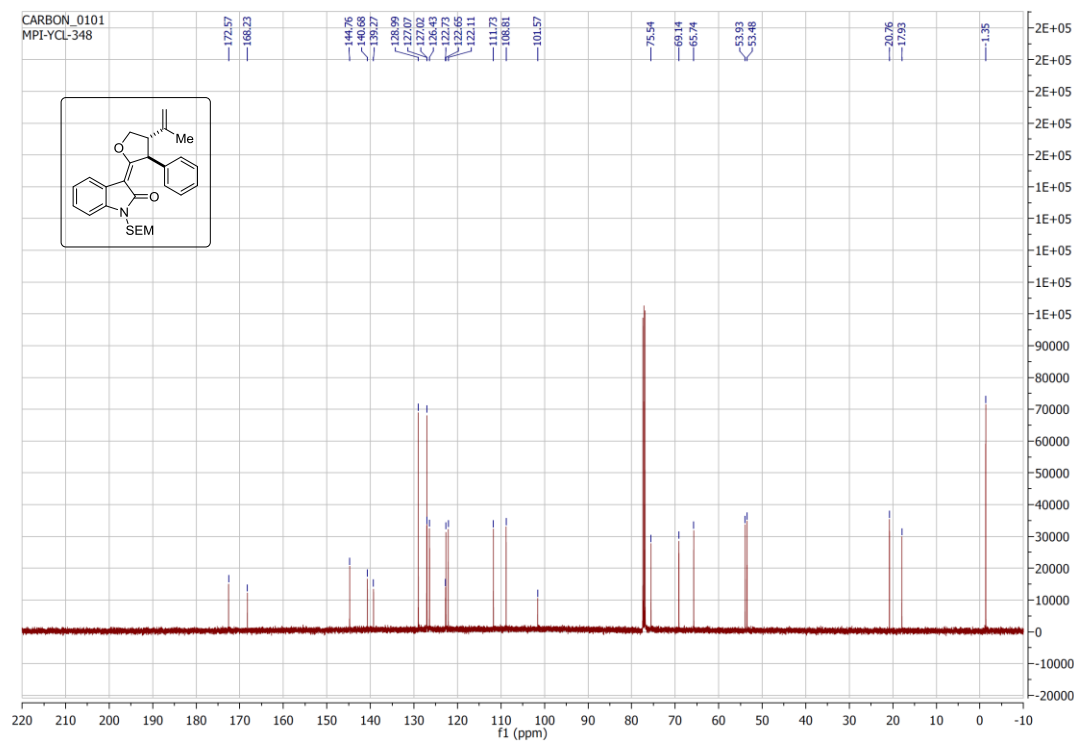
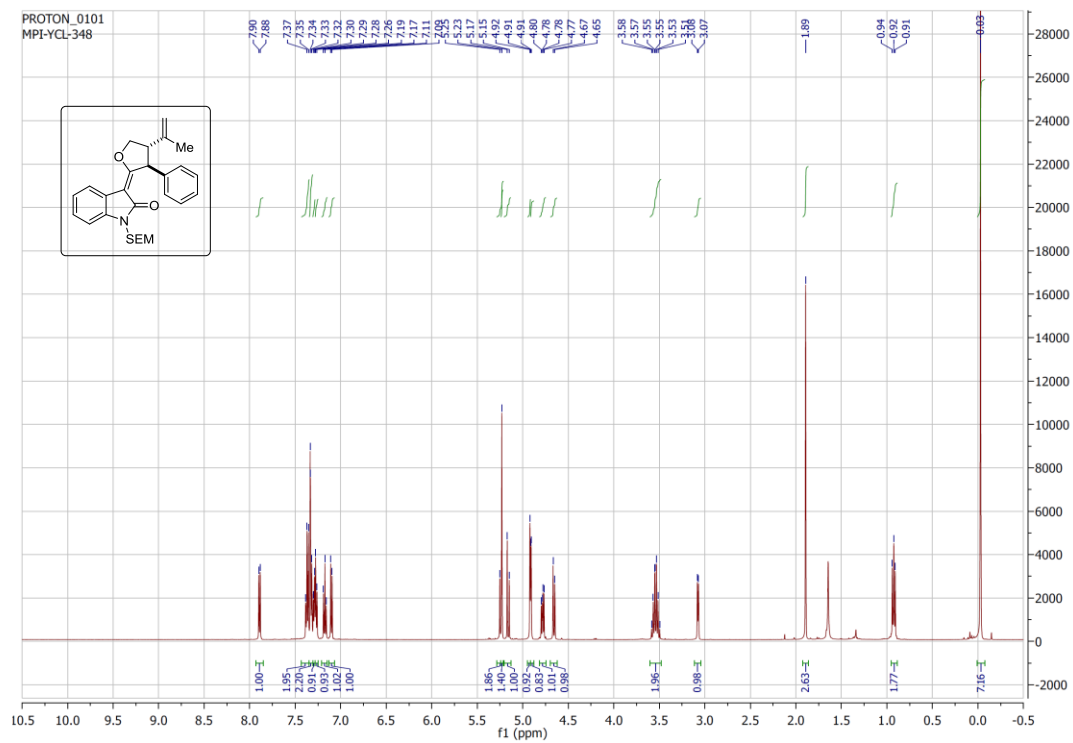
Supplementary Figure 125. ^1H and ^{13}C NMR spectra for 14q.



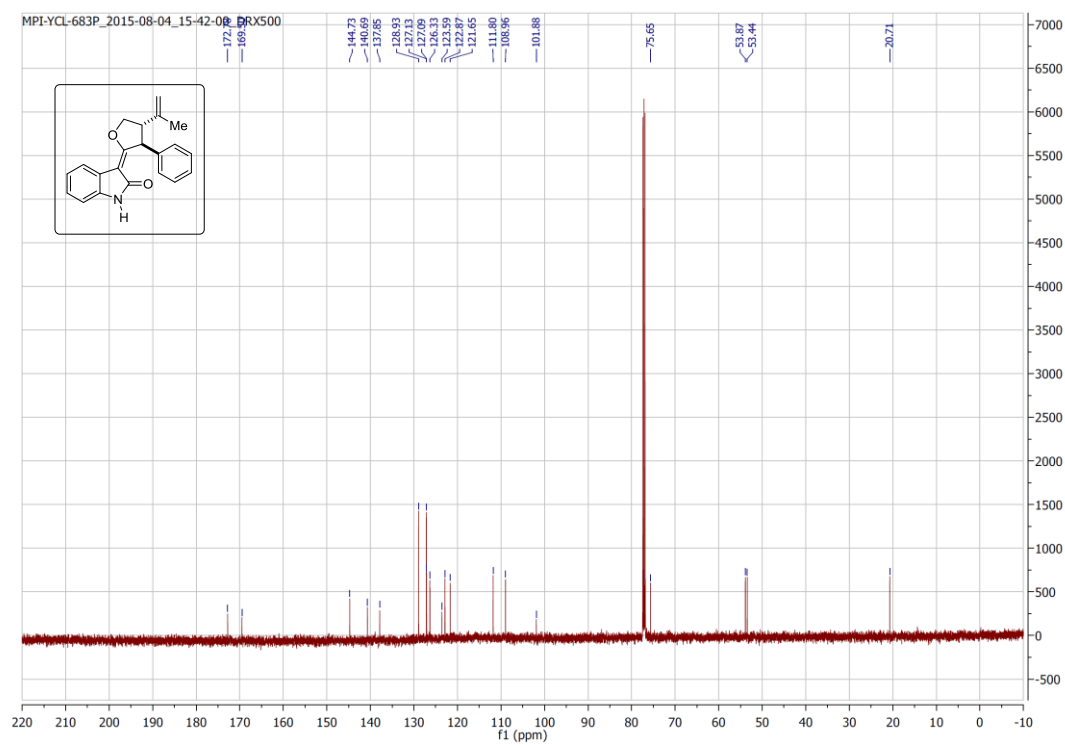
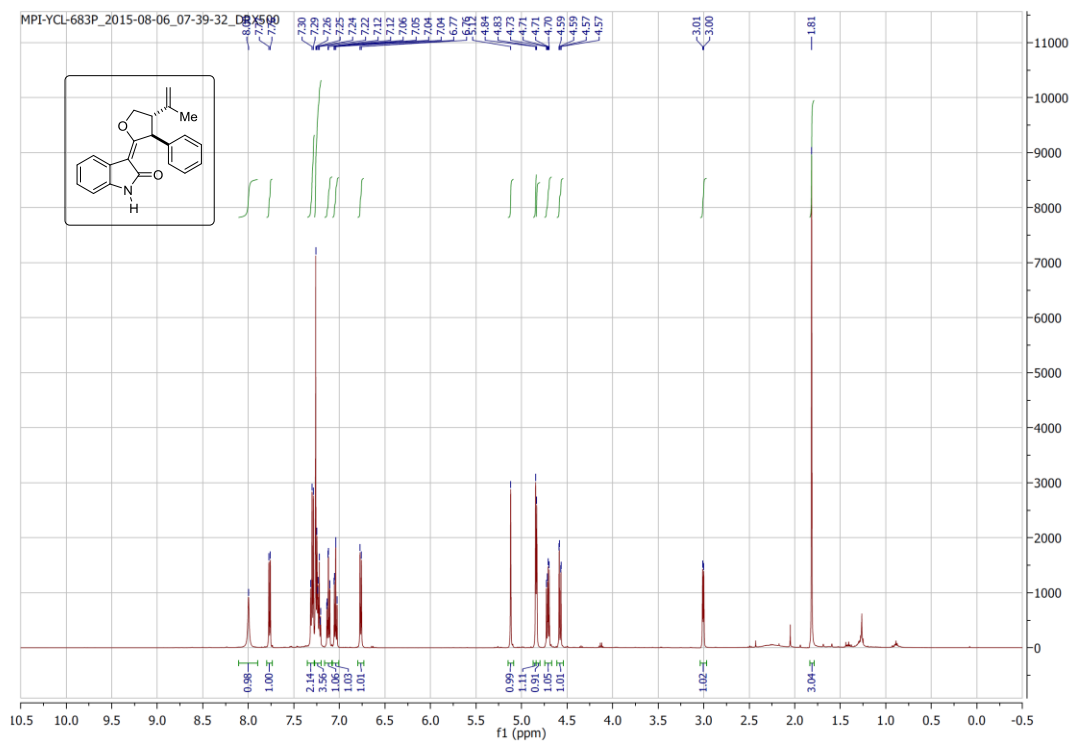
Supplementary Figure 126. ^1H and ^{13}C NMR spectra for 14r.



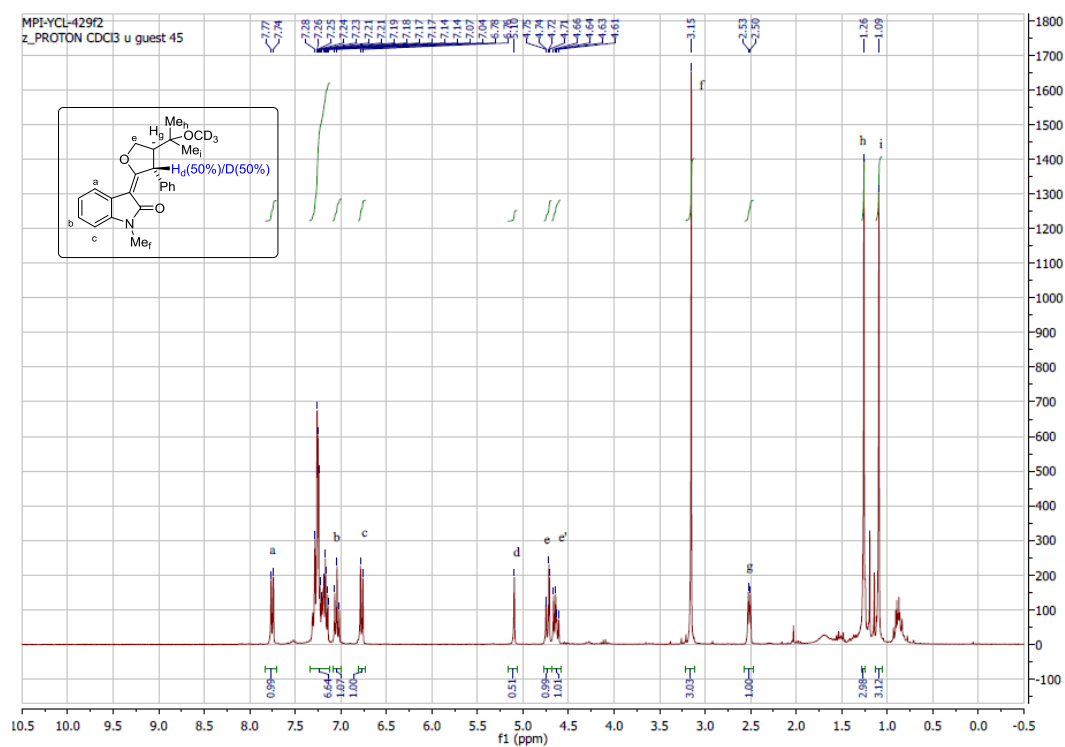
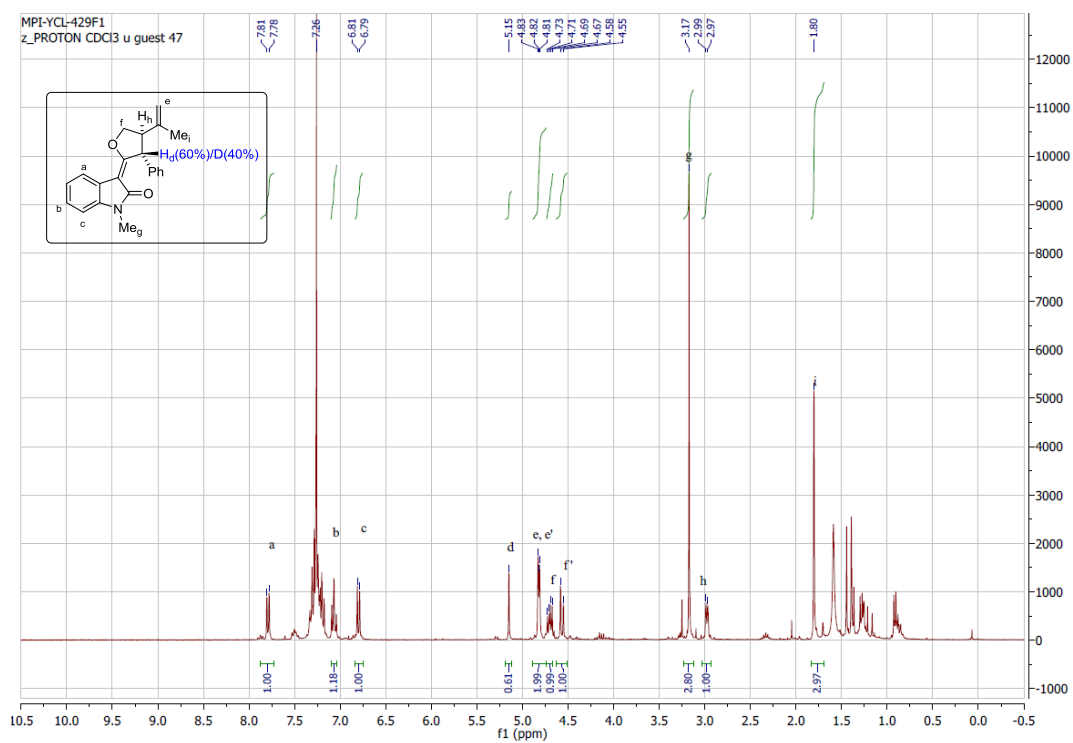
Supplementary Figure 127. ^1H and ^{13}C NMR spectra for 14s.



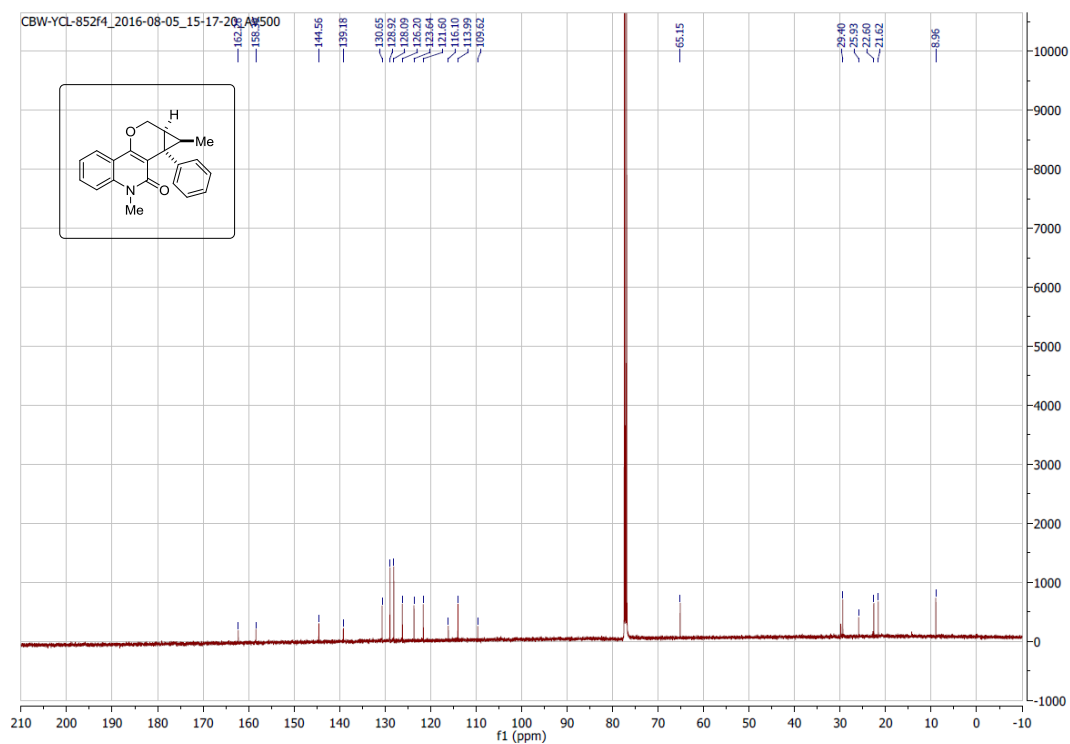
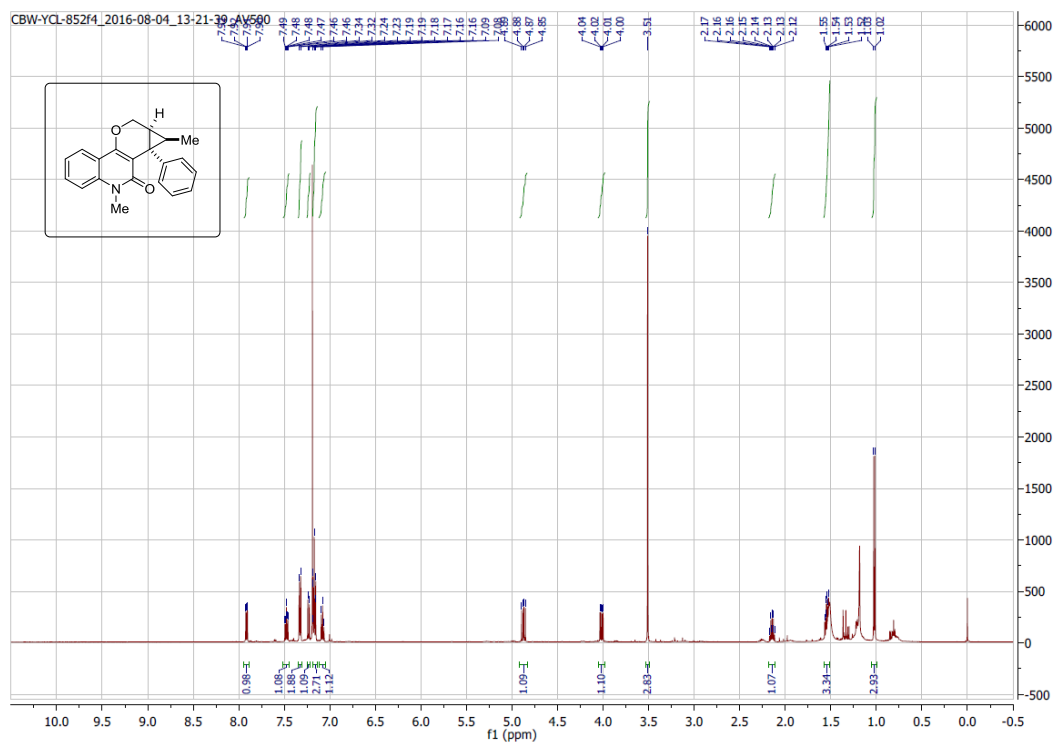
Supplementary Figure 128. ^1H and ^{13}C NMR spectra for 14t.



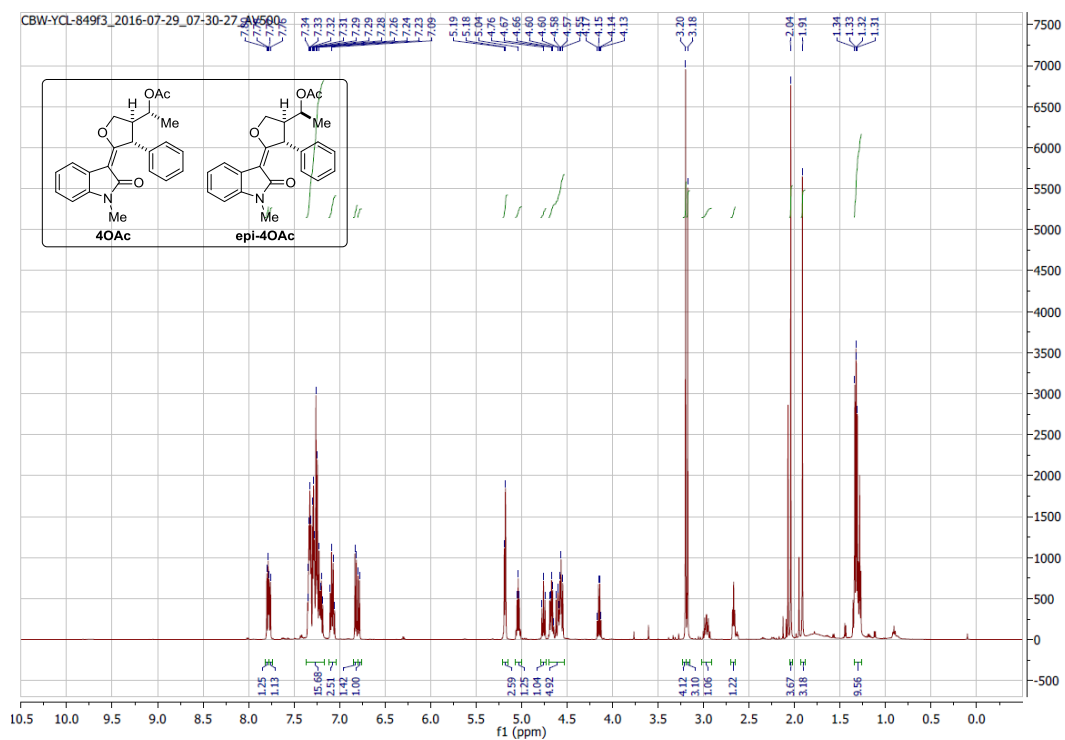
Supplementary Figure 129. ¹H and ¹³C NMR spectra for 14u.



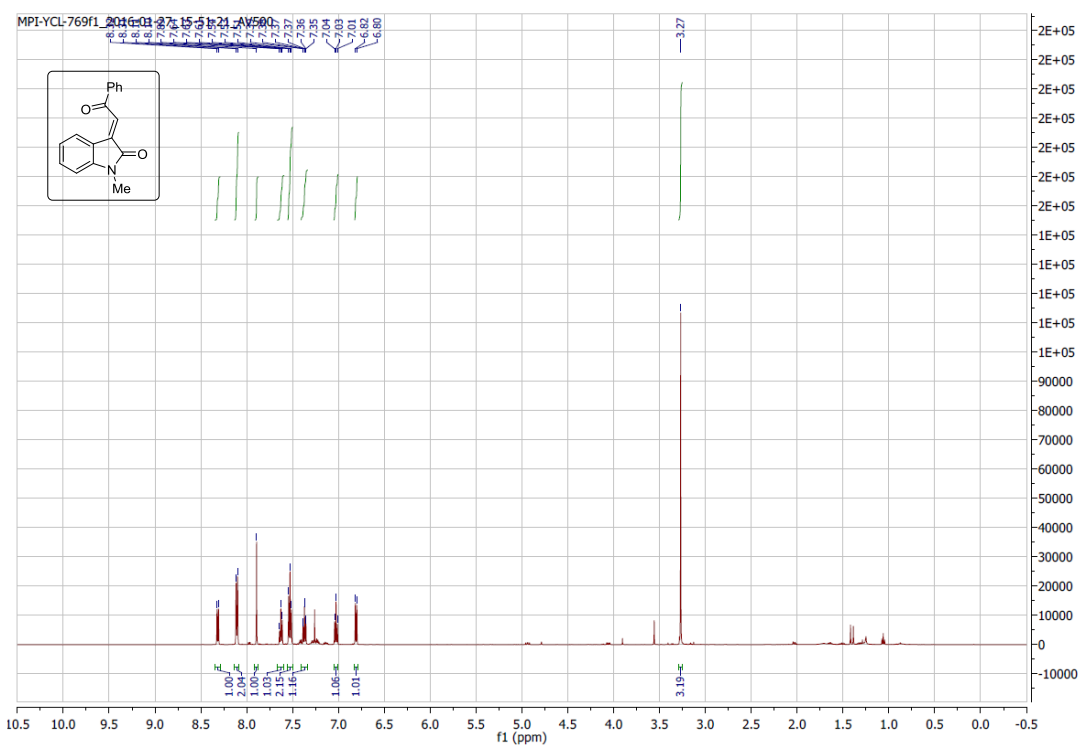
Supplementary Figure 130. ^1H NMR spectra for **14** and **20** with deuterated CD_3OD as nucleophile.



Supplementary Figure 131. ^1H and ^{13}C NMR spectra for **epi-3a**.

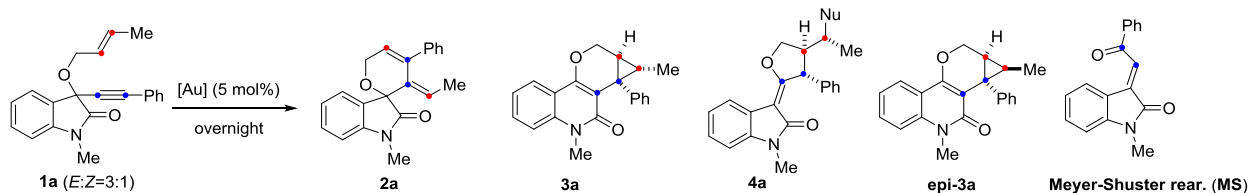


Supplementary Figure 133. ^1H NMR spectrum for 4OAc.



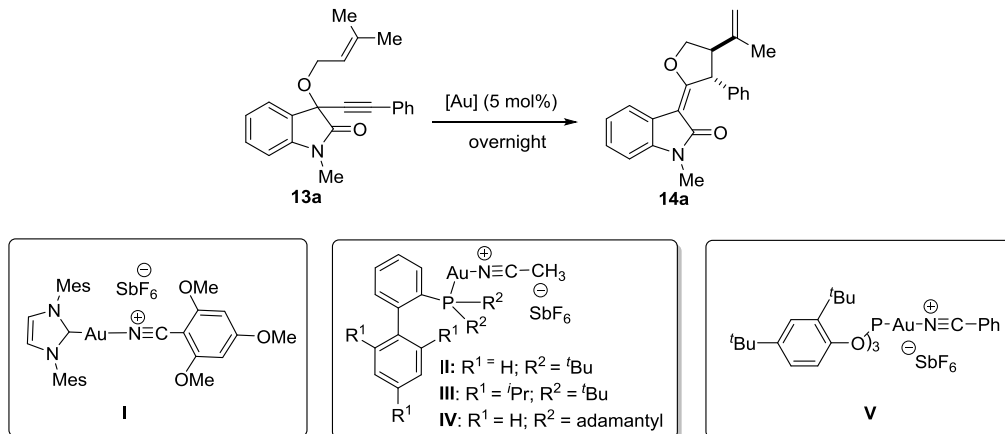
Supplementary Figure 134. ^1H NMR spectrum for MS.

Supplementary Table 1. Complete screening of 1,6-enyne cycloisomerization (**1a**)



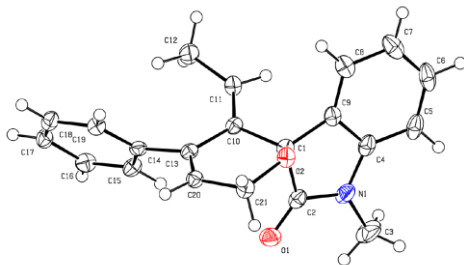
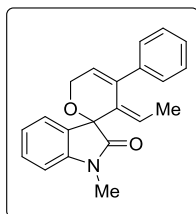
Entry	[Au]	mol%	Solvent	Nu (eq)	Temp.	Yield (%)					
						2a	3a	4a	epi-3a	MS	1a (Z)
1	Au(BF ₄)PPh ₃	5	DCM	-	rt	33	-	-	-	-	-
2	AuCl ₃	5	DCM	-	rt	-	23	-	-	-	-
3	AuCl ₃	20	DCM	-	rt	Messy					
4	I	5	DCM	-	rt	43	7	-	-	-	-
5	II	5	DCM	-	rt	-	57	-	-	-	-
6	III	5	DCM	-	rt	-	67	-	20	-	-
7	III	3	DCM	-	rt	-	27	-	-	-	-
8	IV	5	DCM	-	rt	-	43	-	-	-	-
9	V	5	DCM	-	rt	60	-	-	-	-	10
10	V	3	DCM	-	rt	58	-	-	-	-	-
11	III	5	Toluene	-	rt	messy					
12	III	5	ACN	-	rt	no reaction					
13	III	5	DMF	-	rt	no reaction					
14	III	5	THF	-	rt	THF polymerized					
15	V	5	Toluene	-	rt	40	-	-	-	-	-
16	V	5	ACN	-	rt	no reaction					
17	V	5	DMF	-	rt	no reaction					
18	V	5	THF	-	rt	THF polymerized					
19	II	5	DCM	MeOH(20.0)	rt	no reaction					
20	II	5	DCE	MeOH(20.0)	60 °C	-	-	62	-	19	-
21	III	5	DCE	MeOH(20.0)	60 °C	-	-	56	-	-	-
22	IV	5	DCE	MeOH(20.0)	60 °C	-	-	50	-	-	-
23	V	5	DCE	MeOH(20.0)	60 °C	-	-	20	-	-	-
24	II	5	DCE	H ₂ O (20.0)	60 °C	-	30	23 (4OH)	15	-	-
25	II	5	DCE	AcOH (20.0)	60 °C	-	20	56 (4OAc)	13	-	-
26	II	5	DCE	Indole(2.0)	60 °C	-	37	-	-	23	-
27	II	5	DCE	MeOH(10.0)	60 °C	-	-	73	-	18	-
28	II	3	DCE	MeOH(10.0)	60 °C	-	-	64	-	-	-
29	II	5	DCE	MeOH(3.0)	60 °C	-	11	56	-	7	-
30	II	5	DCE	MeOH(1.0)	60 °C	-	32	43	-	-	-
31	II	5	DCE	MeOH(0.5)	60 °C	-	24	30	-	-	-

Supplementary Table 2. Complete screening of 1,6-enyne cycloisomerization (**13a**)



Entry	[Au] (5 mol%)	Conc. [M]	Solvent	Yield 14 (%)
1	Au(OTf)PPh ₃	0.10	DCM	19
2	Au(BF ₄)PPh ₃	0.01	DCM	no reaction
3	AuCl ₃	0.10	DCM	no reaction
4	I	0.10	DCM	no reaction
5	I	0.20	DCM	messy
6	II	0.10	DCM	50
7	III	0.10	DCM	49
8	IV	0.10	DCM	40
9	V	0.10	DCM	17
10	II	0.10	Toluene	40
11	II	0.10	Ether	38
12	II	0.10	THF	95
13	II (3 mol%)	0.10	THF	91
14	II	0.10	1,4-dioxane	59
15	II	0.10	MeNO ₂	38
16	II	0.10	DMF	no reaction
17	II	0.10	ACN	no reaction

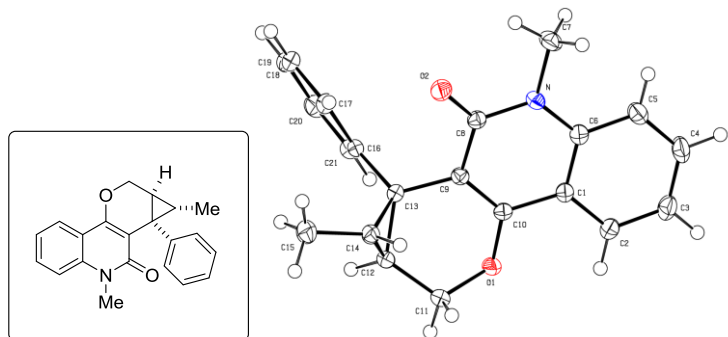
Supplementary Table 3. Crystal data and structure refinement for **2a**.



Identification code	CCDC# 1448677
Chemical formula	C ₂₁ H ₁₉ NO ₂
Formula weight	317.37 g/mol
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal size	0.042 x 0.227 x 0.279 mm
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 12.8527(5) Å α = 90° b = 9.9453(4) Å β = 114.4410(10)° c = 13.9172(5) Å γ = 90°
Volume	1619.54(11) Å ³
Z	4
Density (calculated)	1.302 g/cm ³
Absorption coefficient	0.662 mm ⁻¹
F(000)	672
Diffractometer	Bruker APEX-II CCD
Theta range for data collection	3.78 to 65.31°
Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16
Reflections collected	13387
Independent reflections	2757 [R(int) = 0.0417]
Coverage of independent reflections	99.5%
Absorption correction	none
Max. and min. transmission	0.9730 and 0.8370
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F ²

Refinement program	SHELXL-2014 (Sheldrick 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2757 / 0 / 219
Goodness-of-fit on F^2	1.025
Final R indices	2323 data; $I > 2\sigma(I)$ $R1 = 0.0481$, $wR2 = 0.1171$
	all data $R1 = 0.0585$, $wR2 = 0.1243$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2 + 0.8411P]$
	where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.258 and -0.290 eÅ ⁻³
R.M.S. deviation from mean	0.055 eÅ ⁻³

Supplementary Table 4. Crystal data and structure refinement for **3a**.



Identification code	CCDC# 1448646
Empirical formula	C ₂₁ H ₁₉ NO ₂
Formula weight	317.37
Temperature/K	173(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	13.3456(6)
b/Å	7.5048(3)
c/Å	16.0725(7)
α/°	90
β/°	99.871(4)
γ/°	90
Volume/Å³	1585.93(11)
Z	4
ρ_{calc}/cm³	1.329
μ/mm⁻¹	0.085
F(000)	672.0
Crystal size/mm³	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.146 to 58.228
Index ranges	-16 ≤ h ≤ 18, -10 ≤ k ≤ 10, -21 ≤ l ≤ 21
Reflections collected	21487
Independent reflections	3879 [R _{int} = 0.0357, R _{sigma} = 0.0290]
Data/restraints/parameters	3879/0/219
Goodness-of-fit on F²	1.026

Final R indexes [$I \geq 2\sigma(I)$]

$R_1 = 0.0444$, $wR_2 = 0.1023$

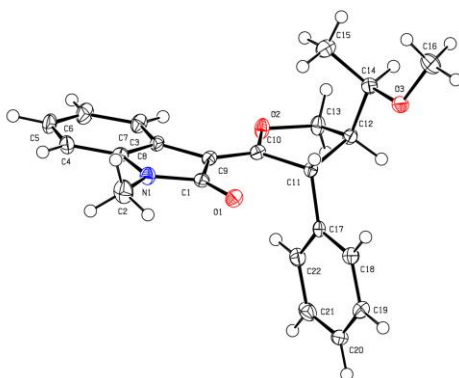
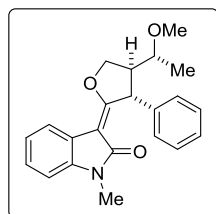
Final R indexes [all data]

$R_1 = 0.0576$, $wR_2 = 0.1093$

Largest diff. peak/hole / $e \text{ \AA}^{-3}$

0.28/-0.25

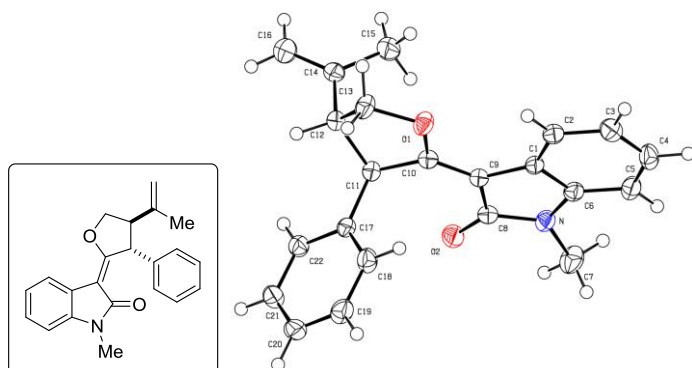
Supplementary Table 5. Crystal data and structure refinement for 4a.



Identification code	CCDC# 1448652
Empirical formula	C ₂₂ H ₂₃ NO ₃
Formula weight	349.41
Temperature/K	100.03
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	14.9063(10)
b/Å	7.2965(4)
c/Å	17.0837(11)
α/°	90
β/°	102.332(2)
γ/°	90
Volume/Å³	1815.2(2)
Z	4
ρ_{calc}/cm³	1.279
μ/mm⁻¹	0.085
F(000)	744.0
Crystal size/mm³	0.603 × 0.388 × 0.378
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.882 to 55.796
Index ranges	-19 ≤ h ≤ 19, -9 ≤ k ≤ 9, -22 ≤ l ≤ 22
Reflections collected	35891
Independent reflections	4339 [R _{int} = 0.0490, R _{sigma} = 0.0314]
Data/restraints/parameters	4339/0/238

Goodness-of-fit on F^2	1.076
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0466$, $wR_2 = 0.1015$
Final R indexes [all data]	$R_1 = 0.0646$, $wR_2 = 0.1102$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.35/-0.27

Supplementary Table 6. Crystal data and structure refinement for **14a**.



Identification code	CCDC# 1448645
Empirical formula	C ₂₂ H ₂₁ NO ₂
Formula weight	331.40
Temperature/K	173(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	10.5511(7)
b/Å	9.3096(5)
c/Å	17.9883(10)
α/°	90
β/°	90.151(6)
γ/°	90
Volume/Å³	1766.93(19)
Z	4
ρ_{calc}/cm³	1.246
μ/mm⁻¹	0.079
F(000)	704.0
Crystal size/mm³	0.3 × 0.25 × 0.15
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.528 to 53.996
Index ranges	-13 ≤ h ≤ 12, -11 ≤ k ≤ 11, -22 ≤ l ≤ 22
Reflections collected	16629
Independent reflections	3819 [R _{int} = 0.0392, R _{sigma} = 0.0338]
Data/restraints/parameters	3819/0/228

Goodness-of-fit on F^2	1.036
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0436$, $wR_2 = 0.0994$
Final R indexes [all data]	$R_1 = 0.0599$, $wR_2 = 0.1088$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.21/-0.24

Supplementary Table 7. Summary of primary screening data for Hh, Wnt and Autophagy inhibition. Data are mean values of three independent experiments ($n = 3$) $\pm$ s.d.. n.a.: No activity.

Compound	Inhibition of Hh signaling IC50 [μ M]	Inhibition of Wnt signaling IC50 [μ M]	Inhibition of Autophagy IC50 [μ M]
2a	n.a	n.a	n.a
2b	n.a	n.a	n.a
2c	n.a	n.a	n.a
2d	n.a	n.a	n.a
2e	n.a	n.a	n.a
2f	n.a	n.a	n.a
2g	n.a	n.a	n.a
2h	n.a	n.a	n.a
2i	n.a	n.a	n.a
2j	n.a	n.a	n.a
2k	n.a	n.a	n.a
2l	n.a	n.a	n.a
3a	n.a	12 (1.32)	n.a
3b	n.a	n.a	5.61 (0.25)
3c	n.a	n.a	n.a
3d	n.a	17 (4.03)	n.a
3e	n.a	n.a	n.a
3f	n.a	n.a	4.81 (0.25)
3g	n.a	n.a	n.a
3h	n.a	8.6 (2.32)	n.a
3i	9.6 (2.98)	n.a	n.a
3j	n.a	4.2 (1.35)	n.a
4a	n.a	n.a	n.a
4b	n.a	n.a	n.a
4c	n.a	n.a	n.a
4d	6.8 (1.89)	n.a	n.a
4e	n.a	n.a	n.a
4f	n.a	n.a	8.33 (0.11)
4g	6.26 (2.56)	n.a	n.a
4h	n.a	n.a	n.a
4i	n.a	n.a	6.88 (0.36)
4j	n.a	n.a	n.a

4k	n.a	n.a	n.a
4l	n.a	n.a	n.a
4m	n.a	n.a	n.a
14a	5.26 (1.25)	n.a	8.92 (0.74)
14b	n.a	n.a	n.a
14c	n.a	n.a	n.a
14d	n.a	n.a	n.a
14e	6.96 (2.66)	17.03 (6.22)	n.a
14f	n.a	n.a	n.a
14g	n.a	n.a	n.a
14h	n.a	n.a	n.a
14i	n.a	n.a	n.a
14j	n.a	n.a	n.a
14k	n.a	n.a	n.a
14l	n.a	n.a	n.a
14m	6.53 (0.56)	13.65 (3.89)	6.71 (0.79)
14n	n.a	n.a	n.a
14o	n.a	n.a	n.a
14p	n.a	n.a	6.47 (0.60)
14q	2.75 (0.62)	n.a	n.a
14r	3.13 (1.02)	n.a	n.a
14s	9.56 (3.32)	n.a	n.a
14t	6.33 (0.65)	n.a	n.a
14u	n.a	n.a	n.a

Supplementary Table 8. Reactivity of the compounds towards GSH.

Compounds (30 μ M) were incubated with 5 μ M GSH or PBS. Reactivity of the compounds towards GSH was measured by HPLC. Numbers are percent abundance of the compounds in GSH as compared to their abundance in PBS. Data are mean values of three independent experiments ($n = 3$) $\pm$ s.d

Compound	1 h	24 h	48 h
2d	102.0 (4.6)	95.8 (6.9)	89.1 (8.3)
3f	90.9 (3.9)	80.5 (5.1)	76.7 (2.8)
3j	100.6 (1.5)	96.5 (5.2)	94.0 (2.3)
4i	104.4 (8.2)	89.7 (6.2)	87.9 (5.9)
14q	99.9 (2.9)	96.8 (3.7)	90.3 (1.5)
14r	98.3 (4.6)	95.1 (3.6)	92.2 (3.6)

Supplementary Methods

General information

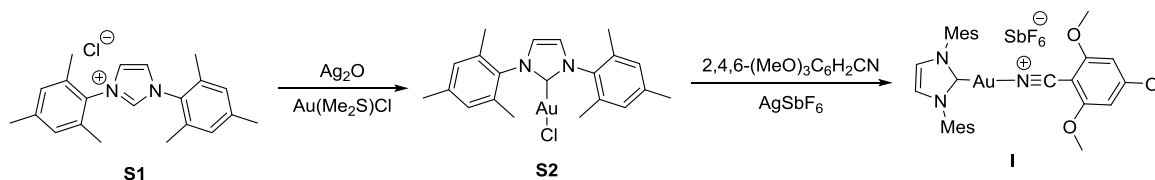
All commercially obtained chemicals and reagents were used without further purification. Dry dichloromethane, THF, DMF were used the Solvent Purification System M-BRAUN Glovebox Technology SPS-800. All reactions were performed in flame dried glassware with dry solvent under argon atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator. Compounds were visualized by irradiation with UV light. Column chromatography was performed by using silica gel Merck 60 (particle size 0.040-0.063 mm).

^1H -NMR and ^{13}C -NMR were recorded on a *Bruker DPX300* (300 MHz), *Bruker DRX400* (400 MHz), *Bruker DRX500* (500MHz), *Bruker DRX600* (600 MHz) and *Varian INOVA500* (500 MHz) at 300 K using CDCl_3 or *d*-DMSO as solvent. Chemical shifts of spectra were expressed in parts per million (ppm, δ) and calibrated relative to residual proton and carbon signals in deuterated NMR solvent (CDCl_3 : $\delta = 7.26$ ppm for ^1H -NMR and $\delta = 77.16$ ppm for ^{13}C -NMR. *d*-DMSO: $\delta = 2.50$ ppm for ^1H -NMR and $\delta = 39.52$ ppm for ^{13}C -NMR). Multiplicities are indicated as following: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (J) are represented in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a LTQ Orbitrap mass spectrometer coupled to an Acceka HPLC-System (HPLC column: Hypersyl GOLD, 50 mm x 1 mm, particle size 1.9 μm , ionization method: electron spray ionization).

The substrates of 1-methylisatin [2058-74-4] and 1-benzyl-1*H*-indole-2,3-dione [1217-89-6] were directly purchased from Sigma-Aldrich for later studies. The substrate of 1,6-enynes with the substituent of (*E*)-crotyl group were prepared from crotyl bromide [29576-14-5] with a small amount of inseparable (*Z*)-isomer. Inseparable (*Z*)-isomers were proceed through the 1,6-enyne synthesizes and following gold catalyzed cycloisomerization reactions. The ratio of (*E,Z*)-isomers in 1,6-enynes were determined by ^1H -NMR, and the yield of gold catalyzed cycloisomerizations was calculated on the basis of (*E,Z*)-mixture. For NMR spectra of the compounds in this article, see Supplementary Figures 4-129.

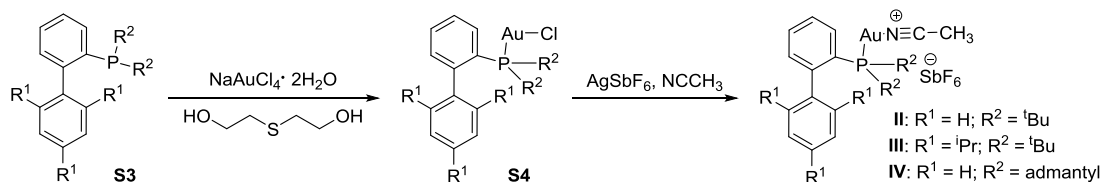
The known gold complexes (**I**¹, **II** [866641-66-9], **III** [1140531-94-7], **IV**² and **V**^{2,3}) were either purchased from Sigma-Aldrich or synthesized as following :

Synthesis of gold(I) catalysts (**I**)



To a solution of the 1,3-dimesitylimidazolium chloride **S1** (1 mmol) in DCM was added Ag_2O (0.5 mmol). The suspension became clear after stirring for 3 h at 23 °C. A solution of $[\text{Au}(\text{Me}_2\text{S})\text{Cl}]$ (1 mmol) in DCM was added dropwise, the reaction mixture was stirred for another 4 h, the solution was filtered through Celite, and the solvent was partially evaporated. Addition of hexane resulted in the precipitation of the gold(I) complex (**S2**). A solution of **S2** (0.10 mmol) and 2,4,6-trimethoxybenzonitrile (0.10 mmol) in DCM was added over solid AgSbF_6 (0.10 mmol) and stirred for 5 min. The mixture was filtered (HPLC Teflon filter) and the solid residue washed with DCM twice. The gold complex precipitated from the filtrate upon addition of Et_2O . Filtration and air-drying furnished a bright white solid (**I**).

Synthesis of gold(I) catalysts (**II**, **III**, **IV**)

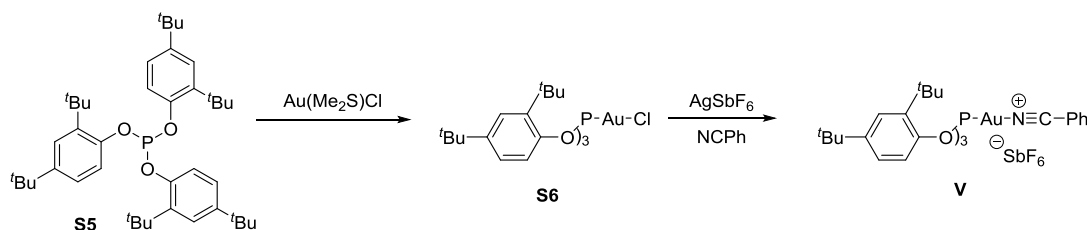


At 0 °C, to the orange solution of sodium tetrachloroaurate dihydrate (1 mmol) in water was slowly added 2,2'-thiodiethanol (3 mmol) with 45 min stirring. The corresponded phosphine ligand (1 mmol) was added to the mixture and a white precipitate was formed during the process. After stirring for 20 min, the solid was filtered off, washed with MeOH, and dried in vacuo to provide the $\text{Au}(\text{L})\text{Cl}$ (**S4**) .

At 0 °C, to a solution of **S4** (0.5 mmol) in DCM was added MeCN (1 mmol), followed by the addition of AgSbF_6 (0.5 mmol). The reaction mixture was stirred at room temperature overnight,

the crude product was filtered through a pad of Celite®, and the solvent was again filtered through a syringe filter to give a clear solution. After the evaporation of solvent, white solids were obtained as the desired cationic gold(I) complexes (**II**, **III**, or **IV**).

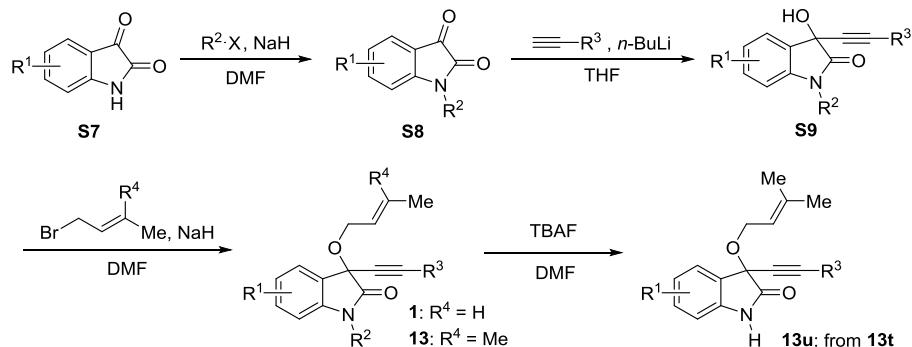
Synthesis of gold(I) catalysts (**V**)



At 0 °C, to a solution of $\text{Au}(\text{Me}_2\text{S})\text{Cl}$ (1 mmol) in DCM was slowly added a solution of tris(2,4-di-tert-butylphenyl) phosphite (1.05 mmol) in DCM and the resulting reaction mixture was allowed to warm to room temperature. The reaction was monitored by the consumption of the ligand through TLC. After the reaction was complete, the mixture was filtered through a syringe filter and concentrated to provide the desired $\text{Au}(\text{I})\text{Cl}$ complex (**S6**).

At 0 °C, to a solution of **S6** (1.00 mmol) and PhCN (1.1 mmol) in DCM was added AgSbF_6 (1.00 mmol). A white precipitate appeared immediately and the reaction mixture was further stirred at room temperature overnight. The resulting reaction mixture was filtered through a pad of Celite®, and the solvent was again filtered through a syringe filter to give a clear solution. After the evaporation of solvent and drying *in vacuo*, white solids were obtained as the desired cationic gold(I) complexes (**V**).

Preparation of starting materials



General procedure A

To a solution of a isatin analog (10 mmol) in DMF (30 ml) at 0 °C was added NaH 60% wt (12 mmol) in one portion and the mixture was stirred at the same temperature for 1 h. To the resulting mixture was added dropwise the respective alkyl halide (13 mmol). The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with $\text{NH}_4\text{Cl}_{(\text{sat})}$ and diluted with EtOAc (100 ml). After extraction, the organic layer was washed with H_2O (300 ml) three times and once with brine, dried over $\text{MgSO}_{4(\text{s})}$, filtered, and concentrated under reduced pressure to provide the crude product. The product was purified by flash column chromatography (petroleum ether (PE) / EtOAc (EA) mixture as eluent) to afford the desired product.

General procedure B

At -78 °C, to a solution of acetylene (2.4 mmol) in THF (30 ml) was slowly added 2.5 M $n\text{-BuLi}$ in hexanes (2.3 mmol) and the mixture was stirred for 1 h at the same temperature. The N -protected isatin analog (2 mmol) was then added to the reaction mixture in one portion. Afterwards, the resulting mixture was slowly warmed to room temperature and stirred overnight. The reaction was quenched with $\text{NH}_4\text{Cl}_{(\text{sat})}$ and extracted with EtOAc (30 ml) three times. The combined organic layers were washed with brine and dried over $\text{MgSO}_{4(\text{s})}$. After concentration under reduced pressure, the crude product was purified by flash column chromatography (EtOAc / petroleum ether or DCM / EtOAc mixture as eluent) to afford the desired product.

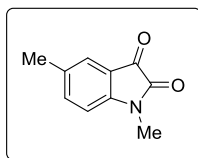
General procedure C

To a solution of the propargyl alcohol (0.5 mmol) in DMF (5 ml) at 0 °C was added NaH 60% wt (0.55 mmol) in one portion and the mixture was stirred at same temperature for 1 h. To the resulting mixture was added dropwise the respective allylic halide (0.6 mmol). The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with $\text{NH}_4\text{Cl}_{(\text{sat})}$ and the mixture was diluted with EtOAc (50 ml). After extraction, the organic layer was washed with H_2O (50 ml) three times and once with brine, dried over $\text{MgSO}_{4(\text{s})}$, filtered, and concentrated under reduced pressure to provide the crude product. The product was purified by flash column chromatography (petroleum ether / EtOAc mixture as eluent) to afford the desired product.

General procedure D

Tetrabutylammonium fluoride (1.0 M in THF, 15 μl , 0.015 mmol) was added to a solution of **1as** (22 mg, 0.05 mmol) in DMF (2 ml). After 1 h stirring at 100 °C, the reaction mixture was cooled, and then diluted with water and ethyl acetate. The aqueous phase was extracted twice with ethyl acetate. The combined organic phases were washed with 1N HCl and saturated aqueous NaHCO_3 (2 mL), dried over $\text{MgSO}_{4(\text{s})}$ and concentrated to give the crude product, which was further purified by silica gel column chromatography to afford the desired product.

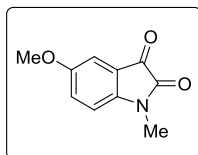
1,5-dimethylindoline-2,3-dione (S8a) was prepared according to the general procedure A, by



using 5-methylindoline-2,3-dione (150 mg, 0.93 mmol) and iodomethane.

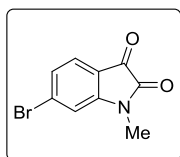
After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.30) as eluents, the desired product was obtained in 89% yield (145 mg, 0.83 mmol) as a red solid. The analytical data were identical to literature data.⁴ **^1H NMR** (500 MHz, CDCl_3) δ 7.41 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 3.23 (s, 3H), 2.34 (s, 3H).

5-methoxy-1-methylindoline-2,3-dione (S8b) was prepared according to the general procedure



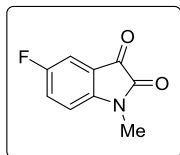
A, by using 5-methoxyindoline-2,3-dione (1074 mg, 6.06 mmol) and iodomethane. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.23) as eluents the desired product was obtained in 89% yield (1026 mg, 5.37 mmol) as a black solid. The analytical data were identical to literature data.⁵ **¹H NMR** (400 MHz, CDCl₃) δ 7.13 (dd, J = 8.5, 2.7 Hz, 1H), 7.09 (d, J = 2.7 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 3.78 (s, 3H), 3.19 (s, 3H).

6-bromo-1-methylindoline-2,3-dione (S8c) was prepared according to the general procedure A,



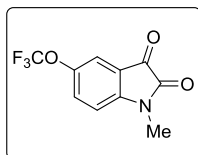
by using 6-bromoindoline-2,3-dione (1370 mg, 6.06 mmol) and iodomethane. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.65) as eluents the desired product was obtained in 80% yield (1162 mg, 4.84 mmol) as an orange solid. The analytical data were identical to literature data.⁵ **¹H NMR** (400 MHz, CDCl₃) δ 7.47 (d, J = 8.0 Hz, 1H), 7.30 (dd, J = 8.0, 1.5 Hz, 1H), 7.10 (d, J = 1.5 Hz, 1H), 3.26 (s, 3H).

5-fluoro-1-methylindoline-2,3-dione (S8d) was prepared according to the general procedure A,



by using 5-fluoroindoline-2,3-dione (1001 mg, 6.06 mmol) and iodomethane. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.3) as eluents the desired product was obtained in 87% yield (945 mg, 5.27 mmol) as a dark red solid. The analytical data were identical to literature data.⁴ **¹H NMR** (400 MHz, CDCl₃) δ 7.39 – 7.25 (m, 2H), 6.89 (dd, J = 8.5, 3.6 Hz, 1H), 3.26 (s, 3H).

1-methyl-5-(trifluoromethoxy)indoline-2,3-dione (S8e) was prepared according to the general

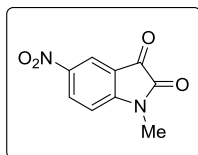


procedure A, by using 5-(trifluoromethoxy)indoline-2,3-dione (420 mg, 1.82 mmol) and iodomethane. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.35) as eluents the desired product was obtained in

94% yield (418 mg, 1.71 mmol) as a red solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.56 – 7.38 (m, 2H), 6.95 (d, J = 8.3 Hz, 1H), 3.26 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 182.5, 158.0, 149.9,

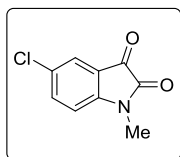
145.4, 145.4, 131.3, 120.5 (q, $J = 258.2$ Hz), 118.5, 118.0, 111.2, 26.5. **HRMS** (ESI): Calcd for $(M + H)^+ [C_{10}H_7O_3NF_3]^+$: 246.0373, found: 246.0379.

1-methyl-5-nitroindoline-2,3-dione (S8f) was prepared according to the general procedure A,



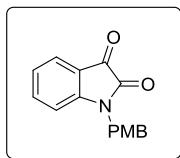
by using 5-nitroindoline-2,3-dione (800 mg, 4.16 mmol) and iodomethane. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 ($R_f = 0.13$) as eluents the desired product was obtained in 99% yield (849 mg, 4.12 mmol) as a brown solid. The analytical data were identical to literature data.⁶ **1H NMR** (500 MHz, $CDCl_3$) δ 8.56 (dd, $J = 8.7, 2.3$ Hz, 1H), 8.48 (d, $J = 2.3$ Hz, 1H), 7.05 (d, $J = 8.7$ Hz, 1H), 3.36 (s, 3H).

5-chloro-1-methylindoline-2,3-dione (S8g) was prepared according to the general procedure A,



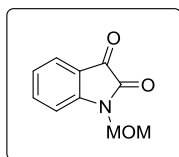
by using 5-chloroindoline-2,3-dione (1100 mg, 6.06 mmol) and iodomethane. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 ($R_f = 0.33$) as eluents the desired product was obtained in 96% yield (1142 mg, 5.84 mmol) as a red solid. The analytical data were identical to literature data.⁴ **1H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, $J = 8.3, 2.2$ Hz, 1H), 7.52 (d, $J = 2.2$ Hz, 1H), 6.86 (d, $J = 8.3$ Hz, 1H), 3.23 (s, 3H).

1-(4-methoxybenzyl)indoline-2,3-dione (S8h) was prepared according to the general procedure



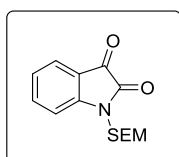
A, by using indoline-2,3-dione (2.000 g, 13.59 mmol) and 4-methoxybenzyl chloride. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 ($R_f = 0.53$) as eluents the desired product was obtained in 95% yield (3.452 g, 12.91 mmol) as an orange solid. The analytical data were identical to literature data.⁷ **1H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, $J = 7.6, 0.8$ Hz, 1H), 7.48 (td, $J = 7.6, 1.3$ Hz, 1H), 7.31-7.22 (m, 2H), 7.08 (t, $J = 7.6$ Hz, 1H), 6.89 – 6.85 (m, 2H), 6.80 (d, $J = 8.0$ Hz, 1H), 4.87 (s, 2H), 3.79 (s, 3H).

1-(methoxymethyl)indoline-2,3-dione (S8i) was prepared according to the general procedure A,



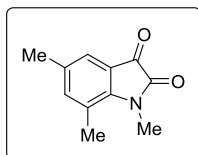
by using indoline-2,3-dione (2.000 g, 13.95 mmol) and chloromethyl methyl ether. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.51) as eluents the desired product was obtained in 64% yield (1.662 g, 8.69 mmol) as an orange solid. The analytical data were identical to the literature data.⁸ **¹H NMR** (500 MHz, CDCl₃) δ 7.65 (d, J = 7.7 Hz, 1H), 7.62 (td, J = 7.7, 1.2 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 5.16 (s, 2H), 3.38 (s, 3H).

1-((2-(trimethylsilyl)ethoxy)methyl)indoline-2,3-dione (S8j) was prepared according to the



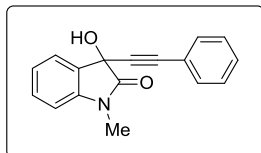
general procedure A, by using indoline-2,3-dione (2.000 g, 13.59 mmol) and 2-(trimethylsilyl)ethoxymethyl chloride. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.79) as eluents the desired product was obtained in 97% yield (3.640 g, 13.12 mmol) as an orange solid. The analytical data were identical to the literature data.⁹ **¹H NMR** (500 MHz, CDCl₃) δ 7.69 – 7.60 (m, 2H), 7.18 (td, J = 7.6, 0.7 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 5.18 (s, 2H), 3.60 (dd, J = 8.3, 7.8 Hz, 2H), 0.93 (dd, J = 8.3, 7.8 Hz, 2H), -0.02 (s, 9H).

1,5,7-trimethylindoline-2,3-dione (S8k) was prepared according to the general procedure A, by



using 5,7-dimethylindoline-2,3-dione (1000 mg, 5.71 mmol) and iodomethane. After silica gel column chromatography with EtOAc / DCM = 1/2 (R_f = 0.3) as eluents the desired product was obtained in 72% yield (781 mg, 4.13 mmol) as a dark red solid. **¹H NMR** (500 MHz, CDCl₃) δ 7.25 (s, 1H), 7.13 (s, 1H), 3.48 (s, 3H), 2.51 (s, 3H), 2.27 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 184.15, 159.49, 146.92, 142.83, 133.72, 123.83, 121.71, 118.76, 29.78, 20.47, 18.79. **HRMS** (ESI): Calcd for (M + H)⁺ [C₁₁H₁₂O₂N]⁺: 190.0863, found: 190.0869.

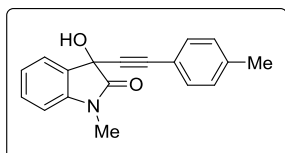
3-hydroxy-1-methyl-3-(phenylethynyl)indolin-2-one (S9a) was prepared according to the



general procedure B, by using 1-methylisatin (1.000 g, 6.21 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.32) as eluents the desired product was

obtained in 81% yield (1.326 g, 5.04 mmol) as a pale yellow solid. The analytical data were identical to the literature data.¹⁰ **¹H NMR** (500 MHz, CDCl₃) δ 7.61 (dd, J = 7.6, 0.7 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.38 (td, J = 7.6, 1.2 Hz, 1H), 7.34 – 7.21 (m, 3H), 7.16 (td, J = 7.6, 0.7 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 3.86 (s, 1H), 3.23 (s, 3H).

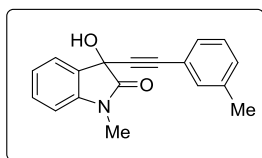
3-hydroxy-1-methyl-3-(p-tolyethynyl)indolin-2-one (S9b) was prepared according to the



general procedure B, by using 1-methylisatin (500 mg, 3.10 mmol) and 4-ethynyltoluene. After silica gel column chromatography with EtOAc / DCM = 1/15 (R_f = 0.34) as eluents the desired product was obtained in

88% yield (755 mg, 2.72 mmol) as a yellow solid. The analytical data were identical to the literature data.¹⁰ **¹H NMR** (500 MHz, CDCl₃) δ 7.61 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 7.6 Hz, 1H), 3.82 (s, 1H), 3.23 (s, 3H), 2.32 (s, 3H).

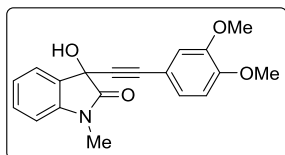
3-hydroxy-1-methyl-3-(m-tolyethynyl)indolin-2-one (S9c) was prepared according to the



general procedure B, by using 1-methylisatin (300 mg, 1.86 mmol) and 3-ethynyltoluene. After silica gel column chromatography with EtOAc / DCM = 1/15 (R_f = 0.32) as eluents the desired product was obtained in

90% yield (466 mg, 1.68 mmol) as a pale yellow solid. **mp**: 159 - 161 °C **¹H NMR** (500 MHz, CDCl₃) δ 7.61 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.20 – 7.08 (m, 3H), 6.85 (d, J = 7.6 Hz, 1H), 3.84 (s, 1H), 3.23 (d, J = 0.9 Hz, 3H), 2.27 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 174.10, 143.21, 138.04, 132.78, 130.59, 130.00, 129.25, 129.12, 128.23, 124.85, 123.86, 121.55, 108.96, 86.69, 85.29, 69.69, 26.77, 21.24. **HRMS** (ESI): Calcd for (M + Na)⁺ [C₁₈H₁₅O₂NNa]⁺: 300.0995, found: 300.1004.

3-((3,4-dimethoxyphenyl)ethynyl)-3-hydroxy-1-methylindolin-2-one (S9d) was prepared

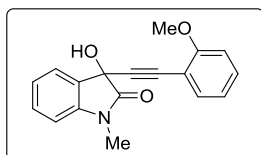


according to the general procedure B, by using 1-methylisatin (100 mg, 0.62 mmol) and 3,4-dimethoxyphenyl acetylene. After silica gel column chromatography with EtOAc / DCM = 1/6 (R_f = 0.35) as eluents the

desired product was obtained in 90% yield (180 mg, 0.56 mmol) as a pale yellow solid. **mp**: 160

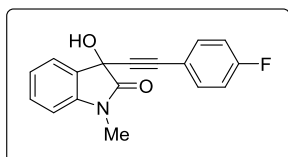
- 161 °C $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.58 (dd, $J = 7.$, 0.6 Hz, 1H), 7.28 (td, $J = 7.6$, 1.1 Hz, 1H), 7.09 (td, $J = 7.6$, 0.6 Hz, 1H), 6.96 (dd, $J = 8.3$, 1.8 Hz, 1H), 6.87 (d, $J = 1.8$ Hz, 1H), 6.74 (d, $J = 7.6$ Hz, 1H), 6.63 (d, $J = 8.3$ Hz, 1H), 5.12 (s, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 3.12 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 174.32, 149.79, 148.32, 142.76, 130.17, 129.39, 125.44, 124.52, 123.61, 114.62, 113.74, 110.71, 108.75, 86.27, 84.24, 69.53, 55.71, 26.49. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{19}\text{H}_{17}\text{O}_4\text{NNa}]^+$: 346.1050, found: 346.1055.

3-hydroxy-3-((2-methoxyphenyl)ethynyl)-1-methylindolin-2-one (S9e) was prepared



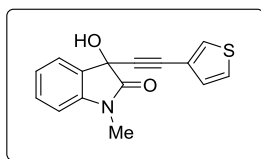
according to the general procedure B, by using 1-methylisatin (300 mg, 1.86 mmol) and 2-ethynylanisole. After silica gel column chromatography with EtOAc / DCM = 1/10 ($R_f = 0.24$) as eluents the desired product was obtained in 92% yield (503 mg, 1.71 mmol) as a white solid. The analytical data were identical to the literature data.¹⁰ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.62 (dd, $J = 7.6$, 0.8 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.29 (ddd, $J = 8.0$, 7.6, 1.7 Hz, 1H), 7.15 (td, $J = 8.0$, 0.8 Hz, 1H), 6.90 – 6.81 (m, 3H), 3.85 (s, 3H), 3.24 (s, 3H).

3-((4-fluorophenyl)ethynyl)-3-hydroxy-1-methylindolin-2-one (S9f) was prepared according



to the general procedure B, by using 1-methylisatin (288 mg, 1.79 mmol) and 1-ethynyl-4-fluorobenzene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 ($R_f = 0.32$) as eluents the desired product was obtained in 84% yield (422 mg, 1.50 mmol) as a white solid. **mp**: 159 - 160 °C $^1\text{H NMR}$ (500 MHz, cdcl_3) δ 7.60 (d, $J = 7.6$ Hz, 1H), 7.45 – 7.34 (m, 3H), 7.16 (t, $J = 7.6$ Hz, 1H), 6.96 (t, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 7.6$ Hz, 1H), 3.80 (s, 1H), 3.24 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, cdcl_3) δ 174.07, 163.01 (d, $J = 250.6$ Hz), 143.17, 134.21 (d, $J = 8.6$ Hz), 130.66, 129.00, 124.83, 123.93, 117.86 (d, $J = 3.5$ Hz), 115.68 (d, $J = 22.2$ Hz), 109.02, 85.46 (d, $J = 1.5$ Hz), 85.39, 69.64, 26.79. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{17}\text{H}_{13}\text{O}_2\text{NF}]^+$: 282.0925, found: 282.0924.

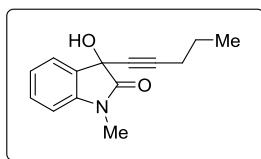
3-hydroxy-1-methyl-3-(thiophen-3-ylethynyl)indolin-2-one (S9g) was prepared according to



the general procedure B, by using 1-methylisatin (292 mg, 1.81 mmol) and 3-ethynylthiophene. After silica gel column chromatography with EtOAc / petroleum ether = 1/10 (R_f = 0.38) as eluents the desired product

was obtained in 87% yield (426 mg, 1.58 mmol) as a brown solid. **mp**: 199 - 201 °C **^1H NMR** (500 MHz, CDCl_3) δ 7.60 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 2.9 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.22 (dd, J = 5.0, 2.9 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 5.0 Hz, 1H), 6.86 (d, J = 7.6 Hz, 1H), 3.58 (s, 1H), 3.24 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 173.95, 143.24, 130.68, 130.51, 130.10, 128.92, 125.48, 124.87, 123.89, 120.82, 109.00, 85.28, 81.77, 69.71, 26.80. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{15}\text{H}_{12}\text{O}_2\text{NS}$] $^+$: 270.0583, found: 270.0591.

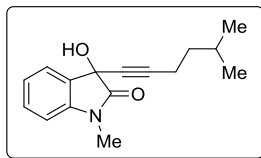
3-hydroxy-1-methyl-3-(pent-1-yn-1-yl)indolin-2-one (S9h) was prepared according to the



general procedure B, by using 1-methylisatin (1.000 g, 6.21 mmol) and 1-pentyne. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.26) as eluents the desired product was obtained in 72%

yield (1.021 g, 4.45 mmol) as a brown solid. **mp**: 122 - 124 °C **^1H NMR** (300 MHz, CDCl_3) δ 7.52 (dd, J = 7.6, 0.8 Hz, 1H), 7.35 (td, J = 7.6, 1.3 Hz, 1H), 7.13 (td, J = 7.6, 0.8 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 3.21 (s, 3H), 2.18 (t, J = 7.1 Hz, 2H), 1.51 (qt, J = 7.4, 7.1 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, CDCl_3) δ 174.42, 143.12, 130.41, 129.42, 124.58, 123.78, 108.87, 88.03, 77.36, 69.30, 26.69, 21.80, 20.93, 13.57. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}$] $^+$: 230.1176, found: 230.1184.

3-hydroxy-1-methyl-3-(5-methylhex-1-yn-1-yl)indolin-2-one (S9i) was prepared according to

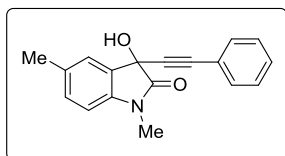


the general procedure B, by using 1-methylisatin (200 mg, 1.24 mmol) and 5-methyl-1-hexyne. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.44) as eluents the desired product

was obtained in 51% yield (162 mg, 0.63 mmol) as a brown solid. **mp**: 99 - 100 °C **^1H NMR** (300 MHz, CDCl_3) δ 7.51 (dd, J = 7.6, 0.8 Hz, 1H), 7.32 (td, J = 7.6, 1.3 Hz, 1H), 7.11 (td, J = 7.6, 0.8 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 4.12 (s, 1H), 3.18 (s, 3H), 2.18 (t, J = 7.4 Hz, 2H), 1.66 - 1.50 (m, 1H), 1.36 (td, J = 7.4, 7.4 Hz, 2H), 0.82 (dd, J = 6.6, 0.9 Hz, 6H). **^{13}C NMR** (75

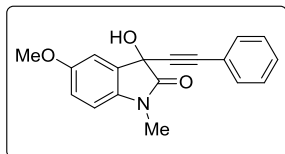
MHz, CDCl₃) δ 174.58, 142.96, 130.24, 129.59, 124.51, 123.71, 108.78, 88.07, 77.36, 69.25, 37.16, 27.32, 26.61, 22.16, 16.95. **HRMS** (ESI): Calcd for (M + Na)⁺ [C₁₆H₁₉O₂NNa]⁺: 280.1308, found: 280.1314.

3-hydroxy-1,5-dimethyl-3-(phenylethynyl)indolin-2-one (S9j) was prepared according to the



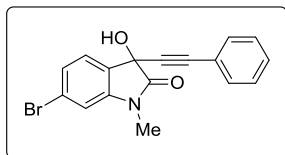
general procedure B, by using **S8a** (88 mg, 0.50 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (*R_f* = 0.29) as eluents the desired product was obtained in 88% yield (122 mg, 0.44 mmol) as a brown solid. **mp**: 189 - 191 °C **¹H NMR** (500 MHz, CDCl₃) δ 7.49 – 7.40 (m, 3H), 7.37 – 7.22 (m, 3H), 7.17 (dd, *J* = 7.9, 0.8 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 3.73 (s, 1H), 3.22 (s, 3H), 2.37 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 173.96, 140.84, 133.63, 132.21, 130.88, 129.09, 128.92, 128.34, 125.59, 121.82, 108.75, 86.41, 85.80, 69.79, 26.81, 21.20. **HRMS** (ESI): Calcd for (M + H)⁺ [C₁₈H₁₆O₂N]⁺: 278.1176, found: 278.1177.

3-hydroxy-5-methoxy-1-methyl-3-(phenylethynyl)indolin-2-one (S9k) was prepared



according to the general procedure B, by using **S8b** (585 mg, 3.06 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (*R_f* = 0.25) as eluents the desired product was obtained in 82% yield (734 mg, 2.50 mmol) as a brown solid. **mp**: 157 - 158 °C **¹H NMR** (500 MHz, CDCl₃) δ 7.41 (d, *J* = 7.1 Hz, 2H), 7.37 – 7.18 (m, 4H), 6.89 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 4.41 (s, 1H), 3.82 (s, 3H), 3.19 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 173.96, 156.92, 136.44, 132.18, 130.21, 129.03, 128.28, 121.78, 115.49, 111.56, 109.52, 86.46, 85.76, 70.00, 56.04, 26.82. **HRMS** (ESI): Calcd for (M + H)⁺ [C₁₈H₁₆O₃N]⁺: 294.1125, found: 294.1126.

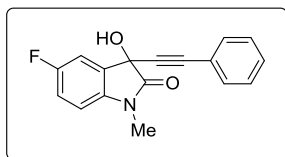
6-bromo-3-hydroxy-1-methyl-3-(phenylethynyl)indolin-2-one (S9l) was prepared according



to the general procedure B, by using **S8c** (400 mg, 1.67 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (*R_f* = 0.46) as eluents the desired product was

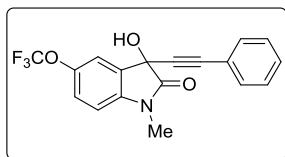
obtained in % yield (492 mg, 1.44 mmol) as a pale yellow solid. **mp**: 177 - 179 °C ^1H NMR (500 MHz, CDCl_3) δ 7.46 (d, J = 7.9 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.34 – 7.23 (m, 9H), 7.00 (d, J = 1.6 Hz, 2H), 3.89 (s, 2H), 3.21 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 174.03, 144.39, 132.16, 129.22, 128.35, 128.05, 126.71, 126.13, 124.28, 121.51, 112.56, 86.78, 85.04, 69.29, 26.88. HRMS (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{17}\text{H}_{12}\text{O}_2\text{NBrNa}]^+$: 363.9944, found: 363.9951.

5-fluoro-3-hydroxy-1-methyl-3-(phenylethynyl)indolin-2-one (S9m) was prepared according



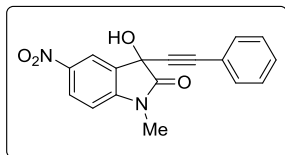
to the general procedure B, by using **S8d** (400 mg, 2.23 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 2/3 (R_f = 0.34) as eluents the desired product was obtained in 55% yield (345 mg, 1.23mmol) as a brown solid. The analytical data were identical to the literature data.¹⁰ ^1H NMR (500 MHz, CDCl_3) δ 7.44 (d, J = 7.4 Hz, 2H), 7.39 (dd, J = 7.2, 1.9 Hz, 1H), 7.37 – 7.26 (m, 3H), 7.09 (td, J = 8.7, 2.0 Hz, 1H), 6.79 (dd, J = 8.4, 3.7 Hz, 1H), 4.43 (s, 1H), 3.24 (s, 3H).

3-hydroxy-1-methyl-3-(phenylethynyl)-5-(trifluoromethoxy)indolin-2-one (S9n) was



prepared according to the general procedure B, by using **S8e** (500 mg, 2.04 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.33) as eluents the desired product was obtained in 68% yield (485 mg, 1.40 mmol) as a yellow solid. **mp**: 130 - 133 °C ^1H NMR (500 MHz, CDCl_3) δ 7.50 (s, 1H), 7.43 (d, J = 7.0 Hz, 2H), 7.33 - 7.24 (m, 4H), 6.84 (d, J = 8.5 Hz, 1H), 3.90 (s, 1H), 3.24 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 173.93, 145.65, 141.80, 132.24, 130.39, 129.38, 128.42, 123.66, 121.39, 120.66 (d, J = 257.0 Hz), 118.91, 109.59, 87.18, 84.79, 69.54, 26.96. HRMS (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{18}\text{H}_{13}\text{O}_3\text{NF}_3]^+$: 348.0842, found: 348.0848.

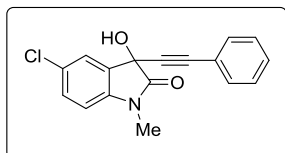
3-hydroxy-1-methyl-5-nitro-3-(phenylethynyl)indolin-2-one (S9o) was prepared according to



the general procedure B, by using **S8f** (400 mg, 1.94 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.22) as eluents the desired product was

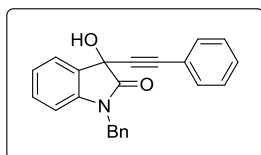
obtained in 58% yield (346 mg, 1.12 mmol) as a brown solid. **mp**: 176 - 178 °C **¹H NMR** (400 MHz, CDCl₃) δ 8.48 (d, *J* = 2.3 Hz, 1H), 8.33 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.36 – 7.21 (m, 3H), 6.94 (d, *J* = 8.7 Hz, 1H), 4.50 (s, 1H), 3.29 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 174.24, 148.57, 144.41, 132.25, 129.89, 129.59, 128.46, 127.46, 121.02, 120.96, 108.79, 87.77, 84.00, 68.98, 27.23. **HRMS** (ESI): Calcd for (M + H)⁺ [C₁₇H₁₃O₄N₂]⁺: 309.0870, found: 309.0868.

5-chloro-3-hydroxy-1-methyl-3-(phenylethynyl)indolin-2-one (S9p) was prepared according



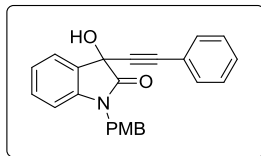
to the general procedure B, by using **S8g** (400 mg, 2.04 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (*R_f* = 0.53) as eluents the desired product was obtained in 94% yield (574 mg, 1.93 mmol) as a brown solid. The analytical data were identical to the literature data.¹⁰ **¹H NMR** (500 MHz, CDCl₃) δ 7.59 (d, *J* = 2.0 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.36 – 7.29 (m, 2H), 7.29 – 7.22 (m, 2H), 6.76 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.15 (s, 1H), 3.21 (d, *J* = 1.9 Hz, 3H).

1-benzyl-3-hydroxy-3-(phenylethynyl)indolin-2-one (S9q) was prepared according to the



general procedure B, by using 1-benzyl-1H-indole-2,3-dione (500 mg, 2.11 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (*R_f* = 0.29) as eluents the desired product was obtained in 71% yield (511 mg, 1.51 mmol) as a white solid. The analytical data were identical to the literature data.¹⁰ **¹H NMR** (500 MHz, CDCl₃) δ 7.62 (d, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 2H), 7.37 – 7.20 (m, 11H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.4 Hz, 1H), 4.94 (s, 2H), 3.58 (s, 1H).

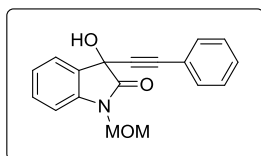
3-hydroxy-1-(4-methoxybenzyl)-3-(phenylethynyl)indolin-2-one (S9r) was prepared



according to the general procedure B, by using **S8h** (134 mg, 0.50 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (*R_f* = 0.39) as eluents the desired product was obtained in 38% yield (70 mg, 0.19 mmol) as a pale yellow solid. **mp**: 228 - 229 °C **¹H NMR**

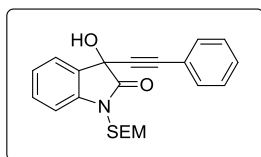
(500 MHz, DMSO) δ 7.52 (dd, J = 7.6, 0.7 Hz, 1H), 7.47 – 7.34 (m, 4H), 7.34 – 7.24 (m, 4H), 7.10 (td, J = 7.6, 0.7 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 4.87 (d, J = 15.5 Hz, 1H), 4.82 (d, J = 15.5 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 173.14, 158.65, 141.50, 131.49, 130.27, 129.88, 129.17, 128.73, 128.65, 127.80, 124.22, 123.11, 121.17, 114.07, 109.81, 87.58, 84.41, 68.81, 55.04, 42.25. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{24}\text{H}_{20}\text{O}_3\text{N}]^+$: 370.1438, found: 370.1452.

3-hydroxy-1-(methoxymethyl)-3-(phenylethynyl)indolin-2-one (S9s) was prepared according



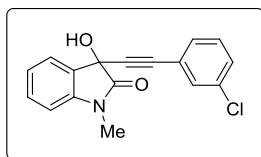
to the general procedure B, by using **S8i** (200 mg, 1.05 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/3 (R_f = 0.37) as eluents the desired product was obtained in 73% yield (224 mg, 0.76 mmol) as a brown solid. **mp**: 158 - 159 °C ^1H NMR (300 MHz, CDCl_3) δ 7.62 (dd, J = 7.6, 0.8 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.34 (dd, J = 7.6, 1.3 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.17 (td, J = 7.6, 0.8 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 5.15 (d, J = 11.0 Hz, 1H), 5.11 (d, J = 11.0 Hz, 1H), 4.22 (s, 1H), 3.33 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 174.85, 141.36, 132.16, 130.72, 129.18, 128.68, 128.35, 124.99, 124.37, 121.62, 110.51, 86.84, 85.44, 71.97, 69.93, 56.52. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{18}\text{H}_{15}\text{O}_3\text{NNa}]^+$: 316.0944, found: 316.0950.

3-hydroxy-3-(phenylethynyl)-1-((2-(trimethylsilyl)ethoxy)methyl)indolin-2-one (S9t) was



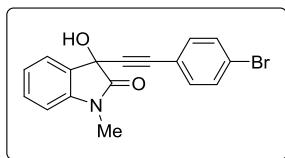
prepared according to the general procedure B, by using **S8j** (100 mg, 0.36 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f = 0.44) as eluents the desired product was obtained in 52% yield (71 mg, 0.19 mmol) as a brown solid. **mp**: 97 - 99 °C ^1H NMR (300 MHz, CDCl_3) δ 7.62 (dd, J = 7.6, 0.9 Hz, 1H), 7.47 – 7.23 (m, 6H), 7.19 (td, J = 7.6, 0.9 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 5.21 (d, J = 11.1 Hz, 1H), 5.15 (d, J = 11.1 Hz, 1H), 3.69 – 3.56 (m, 2H), 1.69 (s, 1H), 0.99 – 0.87 (m, 2H), -0.05 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 174.44, 141.65, 132.19, 130.74, 129.22, 128.56, 128.38, 124.93, 124.25, 121.64, 110.64, 86.83, 85.46, 70.04, 69.95, 66.42, 17.85, -1.34. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{22}\text{H}_{25}\text{O}_3\text{NSiNa}]^+$: 402.1496, found: 402.1508.

3-((3-chlorophenyl)ethynyl)-3-hydroxy-1-methylindolin-2-one (S9u) was prepared according



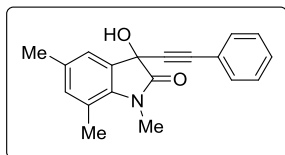
to the general procedure B, by using 1-methylisatin (337 mg, 2.09 mmol) and 3-chloro-1-ethynylbenzene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.38) as eluents the desired product was obtained in 79% yield (489 mg, 1.64 mmol) as a pale yellow solid. **mp**: 147 - 149 °C **^1H NMR** (500 MHz, CDCl_3) δ 7.60 (dd, J = 7.6, 0.8 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.39 (td, J = 7.6, 1.2 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.17 (td, J = 7.6, 0.8 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 3.86 (s, 1H), 3.24 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 173.88, 143.23, 134.25, 132.06, 130.80, 130.29, 129.61, 129.44, 128.77, 124.89, 123.99, 123.48, 109.08, 86.88, 84.95, 69.62, 26.82. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{17}\text{H}_{13}\text{O}_2\text{NCl}]^+$: 298.0629, found: 298.0634.

3-((4-bromophenyl)ethynyl)-3-hydroxy-1-methylindolin-2-one (S9v) was prepared according



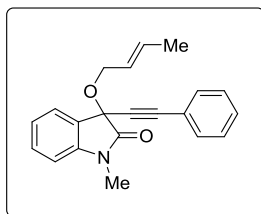
to the general procedure B, by using 1-methylisatin (300 mg, 1.86 mmol) and 1-bromo-4-ethynylbenzene. After silica gel column chromatography with EtOAc / DCM = 1/15 (R_f = 0.31) as eluents the desired product was obtained in 85% yield (543 mg, 1.59 mmol) as a pale yellow solid. The analytical data were identical to the literature data.¹⁰ **^1H NMR** (300 MHz, CDCl_3) δ 7.63 (d, J = 7.4 Hz, 1H), 7.48 – 7.35 (m, 3H), 7.32 – 7.24 (m, 2H), 7.18 (t, J = 7.7 Hz, 1H), 6.86 (d, J = 7.7 Hz, 1H), 4.42 (s, 1H), 3.24 (s, 3H).

3-hydroxy-1,5,7-trimethyl-3-(phenylethynyl)indolin-2-one (S9w) was prepared according to



the general procedure B, by using **S8k** (400 mg, 2.11 mmol) and phenylacetylene. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.32) as eluents the desired product was obtained in 64% yield (393 mg, 1.35 mmol) as a brown solid. **mp**: 172 - 174 °C **^1H NMR** (500 MHz, CDCl_3) δ 7.43 (d, J = 8.0 Hz, 2H), 7.35 – 7.20 (m, 4H), 6.90 (s, 1H), 3.59 (s, 1H), 3.48 (s, 3H), 2.51 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 174.64, 138.38, 134.78, 133.49, 132.19, 129.61, 129.03, 128.31, 123.51, 121.90, 120.36, 86.29, 86.09, 69.30, 30.18, 20.86, 18.89. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}]^+$: 292.1332, found: 292.1336.

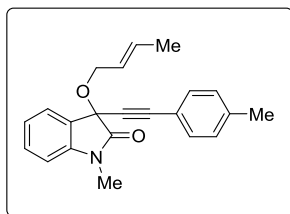
(E)-3-(but-2-en-1-yloxy)-1-methyl-3-(phenylethynyl)indolin-2-one (1a) was prepared



according to the general procedure C, by using **S9a** (582 mg, 2.21 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.34) as eluents the desired product was obtained in 91% yield (640 mg, 2.02 mmol, 82% (E)-isomer) as a pale

yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.55 (d, J = 7.4 Hz, 1H, E and Z), 7.46 (dd, J = 8.0, 1.6 Hz, 2H, E and Z), 7.35 (td, J = 7.6, 0.8 Hz, 1H, E and Z), 7.32 – 7.22 (m, 3H, E and Z), 7.13 (td, J = 7.6, 0.8 Hz, 1H, E and Z), 6.82 (d, J = 7.6 Hz, 1H, E and Z), 5.80 – 5.69 (m, 1H, E and Z), 5.68 – 5.58 (m, 1H, E and Z), 4.53 (dd, J = 10.7, 6.0 Hz, 1H, Z), 4.47 (dd, J = 10.7, 6.0 Hz, 1H, Z), 4.39 (dd, J = 10.7, 6.3 Hz, 4H, E), 4.31 (dd, J = 10.7, 6.3 Hz, 1H, E), 3.21 (s, 3H, Z), 3.21 (s, 3H, E), 1.68 (dd, J = 6.3, 1.0 Hz, 3H, E), 1.64 (d, J = 5.3 Hz, 3H, Z). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{21}\text{H}_{19}\text{O}_2\text{NNa}$] $^+$: 340.1308, found: 340.1319.

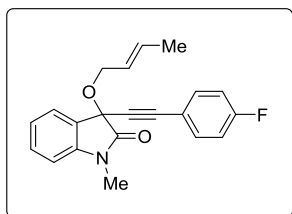
(E)-3-(but-2-en-1-yloxy)-1-methyl-3-(p-tolyethynyl)indolin-2-one (1b) was prepared



according to the general procedure C, by using **S9b** (180 mg, 0.65 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.30) as eluents the desired product was obtained in 57% yield (122 mg, 0.37 mmol, 77% (E)-isomer) as a

brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.55 (d, J = 7.6 Hz, 1H, E and Z), 7.35 (d, J = 8.0 Hz, 3H, E and Z), 7.12 (t, J = 7.6 Hz, 1H, E and Z), 7.08 (d, J = 8.0 Hz, 2H, E and Z), 6.82 (d, J = 7.6 Hz, 1H, E and Z), 5.77 – 5.68 (m, 1H, E and Z), 5.68 – 5.58 (m, 1H, E and Z), 4.52 (dd, J = 10.6, 5.8 Hz, 1H, Z), 4.47 (dd, J = 10.6, 5.8 Hz, 1H, Z), 4.38 (dd, J = 10.3, 6.6 Hz, 1H, E), 4.31 (dd, J = 10.3, 6.6 Hz, 1H, E), 3.21 (s, 3H, Z), 3.20 (s, 3H, E), 2.32 (s, 3H, E and Z), 1.67 (d, J = 6.2 Hz, 3H, E), 1.64 (d, J = 5.7 Hz, 3H, Z). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{22}\text{H}_{21}\text{O}_2\text{NNa}$] $^+$: 354.1465, found: 354.1479.

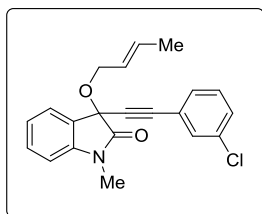
(E)-3-(but-2-en-1-yloxy)-3-((4-fluorophenyl)ethynyl)-1-methylindolin-2-one (1c) was



prepared according to the general procedure C, by using **S9f** (234 mg, 0.70 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f = 0.32) as eluents the desired product was obtained in 98% yield (234 mg, 0.70 mmol, 78% (E)-

isomer) as a brown oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.54 (d, J = 7.5 Hz, 1H, E and Z), 7.51 – 7.39 (m, 2H, E and Z), 7.37 (td, J = 7.5, 0.8 Hz, 1H, E and Z), 7.14 (t, J = 7.5 Hz, 1H, E and Z), 6.98 (t, J = 8.7 Hz, 2H, E and Z), 6.84 (d, J = 7.5 Hz, 1H, E and Z), 5.78 – 5.68 (m, 1H, E and Z), 5.67 – 5.57 (m, 1H, E and Z), 4.47 (dd, J = 11.0, 6.5 Hz, 1H, Z), 4.42 (dd, J = 10.9, 6.6 Hz, 1H, Z), 4.34 (dd, J = 10.5, 6.5 Hz, 1H, E), 4.26 (dd, J = 10.5, 6.4 Hz, 1H, E), 3.23 (s, 3H, Z), 3.23 (s, 3H, E), 1.67 (d, J = 6.3 Hz, 3H, E), 1.63 (d, J = 6.1 Hz, 3H, Z). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{21}\text{H}_{18}\text{O}_2\text{NFNa}]^+$: 358.1214, found: 358.1229.

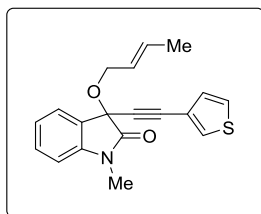
(E)-3-(but-2-en-1-yloxy)-3-((3-chlorophenyl)ethynyl)-1-methylindolin-2-one (1d) was



prepared according to the general procedure C, by using **S9u** (200 mg, 0.67 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f = 0.30) as eluents the desired product was obtained in 94% yield (223 mg, 0.63 mmol, 80% (E)-isomer)

as a brown oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.53 (d, J = 6.6 Hz, 1H, E and Z), 7.45 (s, 1H, E and Z), 7.37 (td, J = 7.8, 1.2 Hz, 1H, E and Z), 7.34 (d, J = 7.7 Hz, 1H, E and Z), 7.30 (d, J = 8.1 Hz, 1H, E and Z), 7.22 (t, J = 7.9 Hz, 1H, E and Z), 7.14 (td, J = 7.6, 0.8 Hz, 1H, E and Z), 6.84 (d, J = 7.8 Hz, 1H, E and Z), 5.77 – 5.70 (m, 1H, E and Z), 5.70 – 5.59 (m, 1H, E and Z), 4.49 (dd, J = 11.1, 6.7 Hz, 1H, Z), 4.42 (dd, J = 11.1, 6.6 Hz, 1H, Z), 4.35 (dd, J = 10.6, 6.4 Hz, 1H, E), 4.27 (dd, J = 10.6, 6.4 Hz, 1H, E), 3.24 (s, 3H, Z), 3.23 (s, 3H, E), 1.68 (dd, J = 6.3, 1.0 Hz, 3H, E), 1.63 (d, J = 6.2 Hz, 1H, Z). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{21}\text{H}_{18}\text{O}_2\text{NClNa}]^+$: 374.0918, found: 370.0934.

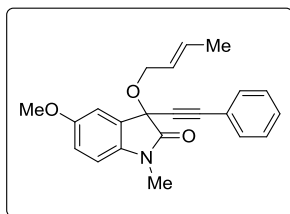
(E)-3-(but-2-en-1-yloxy)-1-methyl-3-(thiophen-3-ylethynyl)indolin-2-one (1e) was prepared



according to the general procedure C, by using **S9g** (200 mg, 0.74 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/6 (R_f = 0.31) as eluents the desired product was obtained in 88% yield (211 mg, 0.65 mmol, 83% (E)-isomer) as a yellow

oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.53 (d, J = 7.6 Hz, 1H, E and Z), 7.50 (dd, J = 3.0, 0.9 Hz, 1H, E and Z), 7.36 (td, J = 7.6, 1.2 Hz, 1H, E and Z), 7.22 (dd, J = 5.0, 3.0 Hz, 1H, E and Z), 7.16 – 7.09 (m, 2H, E and Z), 6.83 (d, J = 7.6 Hz, 1H, E and Z), 5.77 – 5.67 (m, 1H, E and Z), 5.67 – 5.57 (m, 1H, E and Z), 4.48 (dd, J = 11.2, 6.3 Hz, 1H, Z), 4.42 (dd, J = 11.2, 6.3 Hz, 1H, Z), 4.35 (dd, J = 10.7, 6.3 Hz, 1H, E), 4.27 (dd, J = 10.7, 6.3 Hz, 1H, E), 3.22 (s, 3H, Z), 3.21 (s, 3H, E), 1.67 (dd, J = 6.3, 1.1 Hz, 3H, E), 1.63 (dd, J = 5.9, 0.5 Hz, 1H, Z). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{19}\text{H}_{17}\text{O}_2\text{NSNa}]^+$: 346.0872, found: 346.0882.

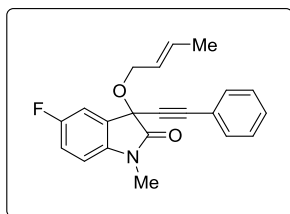
(E)-3-(but-2-en-1-yloxy)-5-methoxy-1-methyl-3-(phenylethynyl)indolin-2-one (1f) was



prepared according to the general procedure C, by using **S9k** (200 mg, 0.68 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f = 0.33) as eluents the desired product was obtained in 92% yield (218 mg, 0.63 mmol, 83% (E)-

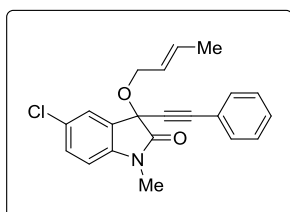
isomer) as a brown oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.46 (d, J = 6.6 Hz, 2H, E and Z), 7.38 – 7.23 (m, 3H, E and Z), 7.17 (d, J = 2.5 Hz, 1H, E and Z), 6.88 (dd, J = 8.5, 2.5 Hz, 1H, E and Z), 6.74 (d, J = 8.5 Hz, 1H, E and Z), 5.78 – 5.68 (m, 1H), 5.69 – 5.59 (m, 1H), 4.50 (dd, J = 11.3, 6.0 Hz, 1H, Z), 4.45 (dd, J = 11.3, 6.0 Hz, 1H, Z), 4.36 (dd, J = 10.7, 6.4 Hz, 1H, E), 4.29 (dd, J = 10.7, 6.4 Hz, 1H, E), 3.81 (s, 3H, E and Z), 3.20 (s, 3H, Z), 3.19 (s, 3H, E), 1.68 (dd, J = 6.3, 1.0 Hz, 3H, E), 1.64 (d, J = 5.4 Hz, 3H, Z). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{22}\text{H}_{21}\text{O}_3\text{NNa}]^+$: 370.1414, found: 370.1427.

(E)-3-(but-2-en-1-yloxy)-5-fluoro-1-methyl-3-(phenylethynyl)indolin-2-one (1g) was



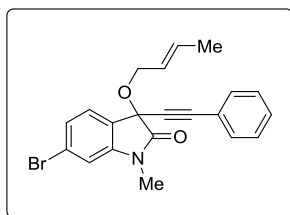
prepared according to the general procedure C, by using **S9m** (200 mg, 0.71 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/6 (R_f = 0.34) as eluents the desired product was obtained in 81% yield (194 mg, 0.58 mmol, 77% (E)-isomer) as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.46 (d, J = 6.6 Hz, 2H, E and Z), 7.41 – 7.23 (m, 4H, E and Z), 7.06 (td, J = 8.7, 2.6 Hz, 1H, E and Z), 6.76 (dd, J = 8.7, 3.9 Hz, 1H, E and Z), 5.81 – 5.70 (m, 1H, E and Z), 5.70 – 5.56 (m, 1H, E and Z), 4.55 (dd, J = 11.0, 6.7 Hz, 1H, Z), 4.49 (dd, J = 11.0, 6.7 Hz, 1H, Z), 4.41 (dd, J = 10.7, 6.4 Hz, 1H, E), 4.34 (dd, J = 10.7, 6.4 Hz, 1H, E), 3.21 (s, 3H, Z), 3.21 (s, 3H, E), 1.69 (dd, J = 6.4, 1.1 Hz, 3H, E), 1.66 (d, J = 6.7 Hz, 1H, Z). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{21}\text{H}_{18}\text{O}_2\text{NFNa}$] $^+$: 358.1214, found: 358.1228.

(E)-3-(but-2-en-1-yloxy)-5-chloro-1-methyl-3-(phenylethynyl)indolin-2-one (1h) was



prepared according to the general procedure C, by using **S9p** (200 mg, 0.67 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/6 (R_f = 0.34) as eluents the desired product was obtained in 80% yield (190 mg, 0.54 mmol, 77% (E)-isomer) as a brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.52 (d, J = 2.1 Hz, 1H, E and Z), 7.47 (d, J = 6.7 Hz, 2H, E and Z), 7.36 – 7.25 (m, 4H, E and Z), 6.76 (d, J = 8.3 Hz, 1H, E and Z), 5.80 – 5.67 (m, 1H, E and Z), 5.67 – 5.55 (m, 1H, E and Z), 4.57 (dd, J = 11.0, 6.8 Hz, 1H, Z), 4.51 (dd, J = 11.0, 6.8 Hz, 1H, Z), 4.43 (dd, J = 10.6, 6.5 Hz, 1H, E), 4.35 (dd, J = 10.6, 6.5 Hz, 1H, E), 3.21 (d, J = 3.6 Hz, 3H, Z), 3.20 (s, 3H, E), 1.69 (dd, J = 6.4, 0.9 Hz, 3H, E), 1.67 (d, J = 6.7 Hz, 3H, Z). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{21}\text{H}_{18}\text{O}_2\text{NClNa}$] $^+$: 374.0918, found: 374.0932.

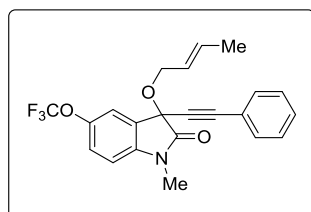
(E)-6-bromo-3-(but-2-en-1-yloxy)-1-methyl-3-(phenylethynyl)indolin-2-one (1i) was



prepared according to the general procedure C, by using **S9l** (200 mg, 0.58 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/8 (R_f = 0.37) as eluents the desired product was obtained in 93% yield (220 mg, 0.56 mmol, 76% (E)-isomer) as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.45 (d, J = 6.7 Hz, 2H, E and Z), 7.43 –

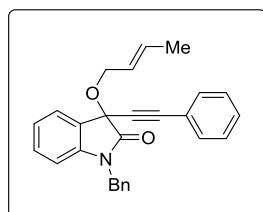
7.38 (m, 1H, E and Z), 7.36 – 7.25 (m, 4H, E and Z), 6.99 (d, $J = 1.6$ Hz, 1H, E and Z), 5.79 – 5.67 (m, 1H, E and Z), 5.66 – 5.56 (m, 1H, E and Z), 4.53 (dd, $J = 11.0, 6.7$ Hz, 1H, Z), 4.47 (dd, $J = 11.0, 6.7$ Hz, 1H, Z), 4.39 (dd, $J = 10.7, 6.5$ Hz, 1H, E), 4.31 (dd, $J = 10.7, 6.5$ Hz, 1H, E), 3.21 (s, 3H, Z), 3.20 (s, 3H, E), 1.68 (dd, $J = 6.4, 1.2$ Hz, 3H, E), 1.65 (d, $J = 6.7$ Hz, 3H, Z). **HRMS** (ESI): Calcd for $(M + Na)^+$ $[C_{21}H_{18}O_2NBrNa]^+$: 418.0413, found: 418.0430.

(E)-3-(but-2-en-1-yloxy)-1-methyl-3-(phenylethynyl)-5-(trifluoromethoxy)indolin-2-one (1j)



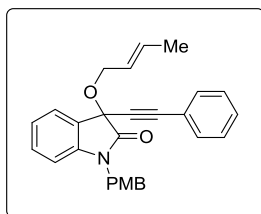
was prepared according to the general procedure C, by using **S9n** (200 mg, 0.58 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/5 ($R_f = 0.29$) as eluents the desired product was obtained in 80% yield (202 mg, 0.50 mmol, 80% (E)-isomer) as a pale yellow oil. **1H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, $J = 6.7$ Hz, 2H, E and Z), 7.44 (d, $J = 1.5$ Hz, 1H, E and Z), 7.37 – 7.28 (m, 3H, E and Z), 7.24 (d, $J = 8.5$ Hz, 1H, E and Z), 6.82 (d, $J = 8.5$ Hz, 1H, E and Z), 5.80 – 5.68 (m, 1H, E and Z), 5.67 – 5.59 (m, 1H, E and Z), 4.57 (dd, $J = 11.0, 6.7$ Hz, 1H, Z), 4.50 (dd, $J = 11.0, 6.7$ Hz, 1H, Z), 4.43 (dd, $J = 10.7, 6.5$ Hz, 1H, E), 4.36 (dd, $J = 10.7, 6.5$ Hz, 1H, E), 3.24 (s, 3H, Z), 3.23 (s, 3H, E), 1.69 (dd, $J = 6.4, 1.1$ Hz, 3H, E), 1.65 (d, $J = 6.7$ Hz, 3H, Z). **HRMS** (ESI): Calcd for $(M + Na)^+$ $[C_{22}H_{18}O_3NF_3Na]^+$: 424.1131, found: 424.1142.

(E)-1-benzyl-3-(but-2-en-1-yloxy)-3-(phenylethynyl)indolin-2-one (1k)



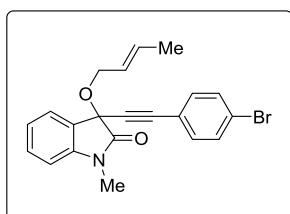
according to the general procedure C, by using **S9q** (200 mg, 0.59 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/8 ($R_f = 0.33$) as eluents the desired product was obtained in 90% yield (195 mg, 0.60 mmol, 76% (E)-isomer) as a brown oil. **1H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, $J = 7.1$ Hz, 1H, E and Z), 7.49 (d, $J = 6.5$ Hz, 2H, E and Z), 7.46 – 7.17 (m, 9H, E and Z), 7.10 (t, $J = 7.5$ Hz, 1H, E and Z), 6.71 (d, $J = 7.5$ Hz, 1H, E and Z), 5.84 – 5.71 (m, 1H, E and Z), 5.71 – 5.62 (m, 1H, E and Z), 4.93 (s, 2H, E and Z), 4.56 (dd, $J = 10.5, 5.0$ Hz, 1H, Z), 4.51 (dd, $J = 10.5, 5.0$ Hz, 1H, Z), 4.43 (dd, $J = 10.6, 6.4$ Hz, 1H, E), 4.37 (dd, $J = 10.6, 6.4$ Hz, 1H, E), 1.70 (d, $J = 6.2$ Hz, 3H, E), 1.66 (d, $J = 5.1$ Hz, 3H, Z). **HRMS** (ESI): Calcd for $(M + Na)^+$ $[C_{27}H_{23}O_2NNa]^+$: 416.1621, found: 416.1637.

(E)-3-(but-2-en-1-yloxy)-1-(4-methoxybenzyl)-3-(phenylethynyl)indolin-2-one (1l) was



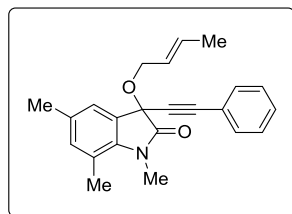
prepared according to the general procedure C, by using **S9r** (96 mg, 0.26 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/6 (R_f = 0.38) as eluents the desired product was obtained in 87% yield (96 mg, 0.23 mmol, 73% (E)-isomer) as a yellow oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.55 (d, J = 7.5 Hz, 1H, E and Z), 7.48 (d, J = 6.5 Hz, 2H, E and Z), 7.36 – 7.19 (m, 6H, E and Z), 7.09 (t, J = 7.5 Hz, 1H, E and Z), 6.85 (d, J = 8.6 Hz, 2H, E and Z), 6.73 (d, J = 7.5 Hz, 1H, E and Z), 5.80 – 5.70 (m, 1H, E and Z), 5.70 – 5.60 (m, 1H, E and Z), 4.87 (s, 2H, E and Z), 4.52 (dd, J = 10.4, 5.5 Hz, 1H, Z), 4.48 (dd, J = 10.3, 5.5 Hz, 1H, Z), 4.39 (dd, J = 10.7, 6.4 Hz, 1H, E), 4.34 (dd, J = 10.7, 6.4 Hz, 1H, E), 3.77 (s, 3H, E and Z), 1.69 (d, J = 6.3 Hz, 3H, E), 1.65 (d, J = 5.4 Hz, 3H, Z). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{28}\text{H}_{25}\text{O}_3\text{NNa}$] $^+$: 446.1727, found: 446.1737.

(E)-3-((4-bromophenyl)ethynyl)-3-(but-2-en-1-yloxy)-1-methylindolin-2-one (1m) was



prepared according to the general procedure C, by using **S9v** (130 mg, 0.38 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.35) as eluents the desired product was obtained in 66% yield (100 mg, 0.25 mmol, 76% (E)-isomer) as a brown oil. **^1H NMR** (600 MHz, CDCl_3) δ 7.53 (d, J = 7.8 Hz, 1H, E and Z), 7.42 (d, J = 8.6 Hz, 2H, E and Z), 7.37 (td, J = 7.8, 1.2 Hz, 1H, E and Z), 7.31 (d, J = 8.6 Hz, 2H, E and Z), 7.14 (td, J = 7.8, 0.9 Hz, 1H, E and Z), 6.84 (d, J = 7.8 Hz, 1H, E and Z), 5.76 – 5.67 (m, 1H, E and Z), 5.67 – 5.57 (m, 1H, E and Z), 4.45 (dd, J = 11.0, 6.7 Hz, 1H, Z), 4.40 (dd, J = 11.0, 6.7 Hz, 1H, Z), 4.32 (dd, J = 10.6, 6.5 Hz, 1H, E), 4.24 (dd, J = 10.6, 6.5 Hz, 1H, E), 3.23 (s, 3H, Z), 3.22 (s, 3H, E), 1.67 (dd, J = 6.4, 1.2 Hz, 3H, E), 1.62 (dd, J = 6.7, 1.3 Hz, 3H, Z). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{21}\text{H}_{18}\text{O}_2\text{NBrNa}$] $^+$: 418.0413, found: 418.0421.

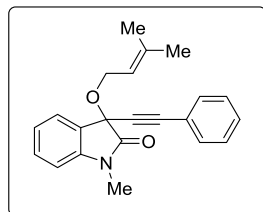
(E)-3-(but-2-en-1-yloxy)-1,5,7-trimethyl-3-(phenylethynyl)indolin-2-one (1n) was prepared



according to the general procedure C, by using **S9w** (200 mg, 0.69 mmol) and crotyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f = 0.38) as eluents, the desired product was obtained in 95% yield (225 mg, 0.65 mmol, 80% (E)-isomer) as a

brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.49 (d, J = 6.5 Hz, 2H, E and Z), 7.35 – 7.30 (m, 3H, E and Z), 7.23 (s, 1H, E and Z), 6.91 (s, 1H, E and Z), 5.81 – 5.70 (m, 1H, E and Z), 5.70 – 5.60 (m, 1H, E and Z), 4.53 (dd, J = 11.3, 6.1 Hz, 1H, Z), 4.49 (dd, J = 11.3, 6.1 Hz, 1H, Z), 4.33 (dd, J = 10.7, 6.4 Hz, 1H, E), 3.51 (s, 3H), 3.50 (s, 3H), 2.54 (s, 3H), 2.33 (s, 3H), 1.71 (d, J = 6.3 Hz, 3H), 1.68 (d, J = 6.1 Hz, 3H). **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{23}\text{H}_{23}\text{O}_2\text{NNa}$] $^+$: 368.1621, found: 368.1632.

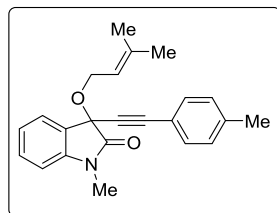
1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)indolin-2-one (13a) was prepared



according to the general procedure C, by using **S9a** (79 mg, 0.30 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.32) as eluents the desired product was obtained in 93% yield (92 mg, 0.28 mmol) as a brown oil. ^1H

NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 6.3 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.30 - 7.26 (m, 3H), 7.13 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 5.39 (t, J = 7.1 Hz, 1H), 4.42 (dd, J = 10.4, 7.1 Hz, 1H), 4.35 (dd, J = 10.4, 7.1 Hz, 1H), 3.23 (s, 3H), 1.72 (s, 3H), 1.64 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.08, 143.41, 138.39, 132.26, 130.54, 129.04, 128.32, 128.27, 125.13, 123.56, 121.98, 120.51, 108.76, 87.80, 83.98, 74.26, 62.51, 26.60, 25.97, 18.22. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}$] $^+$: 332.1645, found: 332.1645.

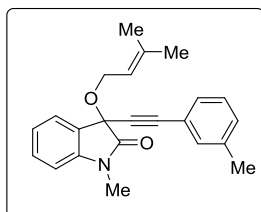
1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(p-tolylethynyl)indolin-2-one (13b) was prepared



according to the general procedure C, by using **S9b** (100 mg, 0.36 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.33) as eluents the desired product was obtained in 90% yield (112 mg, 0.32 mmol) as a brown oil.

¹H NMR (500 MHz, CDCl₃) δ 7.55 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 1H), 5.39 (t, *J* = 6.5 Hz, 1H), 4.42 (dd, *J* = 8.0, 6.5 Hz, 1H), 4.36 (dd, *J* = 8.0, 6.5 Hz, 1H), 3.21 (s, 3H), 2.31 (s, 3H), 1.71 (s, 3H), 1.64 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 172.05, 143.30, 139.16, 138.13, 132.06, 130.40, 129.00, 128.28, 124.99, 123.42, 120.52, 118.82, 108.66, 87.95, 83.25, 74.22, 62.37, 26.45, 25.86, 21.53, 18.12. **HRMS** (ESI): Calcd for (M + H)⁺ [C₂₃H₂₄O₂N]⁺: 346.1802, found: 346.1804.

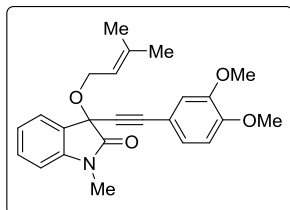
1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(m-tolylethynyl)indolin-2-one (13c) was prepared



according to the general procedure C, by using **S9c** (131 mg, 0.47 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/7 (*R_f* = 0.29) as eluents the desired product was obtained in 78% yield (127 mg, 0.37 mmol) as a brown oil.

¹H NMR (500 MHz, cdcl₃) δ 7.68 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.48 (td, *J* = 7.6, 0.5 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.23 (m, 2H), 6.96 (d, *J* = 7.6 Hz, 1H), 5.52 (t, *J* = 7.4 Hz, 1H), 4.57 (dd, *J* = 10.5, 7.4 Hz, 1H), 4.50 (dd, *J* = 10.5, 7.4 Hz, 1H), 3.35 (s, 3H), 2.42 (s, 3H), 1.85 (s, 3H), 1.78 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 172.12, 143.39, 138.33, 138.02, 132.85, 130.50, 129.93, 129.30, 128.36, 128.22, 125.11, 123.54, 121.76, 120.56, 108.73, 88.06, 83.58, 74.25, 62.50, 26.57, 25.97, 21.25, 18.22. **HRMS** (ESI): Calcd for (M + Na)⁺ [C₂₃H₂₃O₂NNa]⁺: 368.1621, found: 368.1623.

3-((3,4-dimethoxyphenyl)ethynyl)-1-methyl-3-((3-methylbut-2-en-1-yl)oxy)indolin-2-one (13d) was prepared according to the general procedure C, by using **S9d**

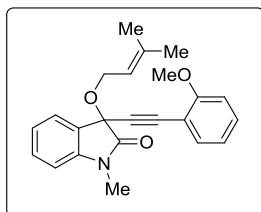


(**13d**) was prepared according to the general procedure C, by using **S9d** (223 mg, 0.69 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/1 (*R_f* = 0.59) as eluents the desired product was obtained in 94% yield (256 mg, 0.64 mmol) as a brown oil.

¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, *J* = 7.4, 0.6 Hz, 1H), 7.33 (td, *J* = 7.8, 1.1 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.05 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.94 (d, *J* = 1.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.37 (t, *J* = 7.2 Hz, 1H), 4.42 – 4.32 (m, 1H), 4.32 – 4.23 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.20 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 172.05, 149.92, 148.42, 143.23, 138.28, 130.41, 128.04, 125.66, 124.95,

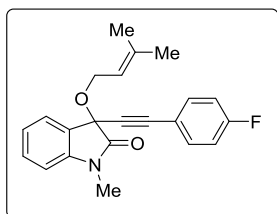
123.44, 120.33, 114.66, 113.87, 110.75, 108.68, 87.72, 82.36, 74.22, 62.25, 55.92, 55.85, 26.47, 25.87, 18.10. **HRMS** (ESI): Calcd for $(M + Na)^+$ $[C_{24}H_{25}O_4NNa]^+$: 414.1676, found: 414.1688.

3-((2-methoxyphenyl)ethynyl)-1-methyl-3-((3-methylbut-2-en-1-yl)oxy)indolin-2-one (13e)



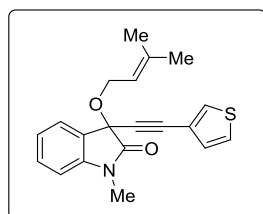
was prepared according to the general procedure C, by using **S9e** (100 mg, 0.34 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.16) as eluents the desired product was obtained in 61% yield (75 mg, 0.21 mmol) as a brown oil. **1H NMR** (500 MHz, $cdCl_3$) δ 7.57 (d, J = 7.6 Hz, 1H), 7.40 (dd, J = 7.6, 1.5 Hz, 1H), 7.33 (td, J = 7.6, 0.5 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.90 – 6.78 (m, 3H), 5.41 (t, J = 7.3 Hz, 1H), 4.55 (dd, J = 10.4, 7.3 Hz, 1H), 4.48 (dd, J = 10.4, 7.3 Hz, 1H), 3.83 (s, 3H), 3.21 (s, 3H), 1.72 (s, 3H), 1.67 (s, 3H). **^{13}C NMR** (126 MHz, $cdCl_3$) δ 172.10, 160.79, 143.41, 138.14, 133.99, 130.47, 130.39, 128.61, 125.23, 123.43, 120.74, 120.36, 111.35, 110.86, 108.64, 87.64, 84.76, 74.33, 62.49, 55.87, 26.53, 25.97, 18.20. **HRMS** (ESI): Calcd for $(M + Na)^+$ $[C_{23}H_{24}O_3NNa]^+$: 384.1570, found: 384.1574.

3-((4-fluorophenyl)ethynyl)-1-methyl-3-((3-methylbut-2-en-1-yl)oxy)indolin-2-one (13f)



was prepared according to the general procedure C, by using **S9f** (100 mg, 0.36 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.37) as eluents, the desired product was obtained in 74% yield (92 mg, 0.26 mmol) as a brown oil. **1H NMR** (500 MHz, $cdCl_3$) δ 7.54 (dd, J = 7.6, 0.8 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.36 (td, J = 7.6, 0.8 Hz, 1H), 7.13 (td, J = 7.6, 0.8 Hz, 1H), 6.97 (t, J = 8.8 Hz, 2H), 6.84 (d, J = 7.6 Hz, 1H), 5.41 – 5.35 (m, 1H), 4.37 (dd, J = 10.5, 7.3 Hz, 1H), 4.31 (dd, J = 10.5, 7.1 Hz, 1H), 3.22 (s, 3H), 1.71 (s, 3H), 1.63 (s, 3H). **^{13}C NMR** (126 MHz, $cdCl_3$) δ 171.99, 162.97 (d, J = 250.5 Hz), 143.39, 138.45, 134.24 (d, J = 8.5 Hz), 130.60, 128.05, 125.07, 123.58, 120.40, 118.03 (d, J = 3.5 Hz), 115.66 (d, J = 22.1 Hz), 108.80, 86.61, 83.81, 74.23, 62.47, 26.59, 25.95, 18.19. **HRMS** (ESI): Calcd for $(M + Na)^+$ $[C_{22}H_{20}O_2NFNa]^+$: 372.1370, found: 372.1376.

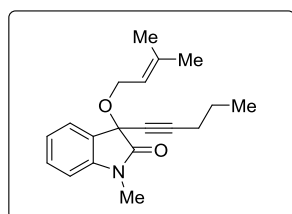
1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(thiophen-3-ylethynyl)indolin-2-one (13g) was



prepared according to the general procedure C, by using **S9g** (50 mg, 0.19 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/6 (R_f = 0.43) as eluents the desired product was obtained in 83% yield (52 mg, 0.15 mmol) as a

brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.54 (d, J = 7.6 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.36 (td, J = 7.6, 1.1 Hz, 1H), 7.22 (dd, J = 5.0, 3.0 Hz, 1H), 7.17 – 7.07 (m, 2H), 6.83 (d, J = 7.6 Hz, 1H), 5.38 (t, J = 7.3 Hz, 1H), 4.39 (dd, J = 10.4, 7.3 Hz, 1H), 4.32 (dd, J = 10.4, 7.3 Hz, 1H), 3.22 (s, 3H), 1.71 (s, 3H), 1.63 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.05, 143.40, 138.39, 130.55, 130.42, 130.20, 128.16, 125.37, 125.13, 123.56, 121.05, 120.49, 108.77, 83.66, 82.95, 74.31, 62.50, 26.60, 25.97, 18.22. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{20}\text{H}_{19}\text{O}_2\text{NSNa}$] $^+$: 360.1029, found: 360.1045.

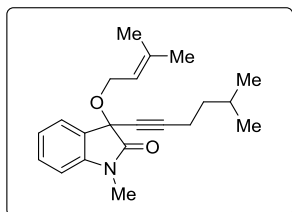
1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(pent-1-yn-1-yl)indolin-2-one (13h) was prepared



according to the general procedure C, by using **S9h** (48 mg, 0.21 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.80) as eluents the desired product was obtained in 99% yield (61 mg, 0.21 mmol) as a yellow oil.

$^1\text{H NMR}$ (500 MHz, cdcl_3) δ 7.46 (dd, J = 7.6, 0.8 Hz, 1H), 7.31 (td, J = 7.6, 1.2 Hz, 1H), 7.09 (td, J = 7.6, 0.8 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 5.34 (t, J = 7.2 Hz, 1H), 4.31 (dd, J = 10.5, 7.2 Hz, 1H), 4.25 (dd, J = 10.5, 7.2 Hz, 1H), 3.18 (s, 3H), 2.22 (td, J = 7.2, 1.9 Hz, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.53 (qt, J = 7.2, 7.2 Hz, 2H), 0.95 (t, J = 7.2 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, cdcl_3) δ 172.43, 143.30, 138.01, 130.24, 128.69, 124.84, 123.39, 120.61, 108.59, 89.21, 75.19, 73.90, 62.16, 26.45, 25.92, 21.87, 21.05, 18.13, 13.60. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}$] $^+$: 298.1802, found: 298.1807.

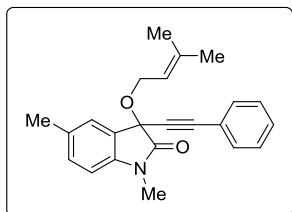
1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(5-methylhex-1-yn-1-yl)indolin-2-one (13i) was



prepared according to the general procedure C, by using **S9i** (64 mg, 0.25 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.8) as eluents the desired product was obtained in 86% yield (70 mg, 0.22

mmol) as a yellow oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.45 (dd, J = 7.4, 0.7 Hz, 1H), 7.31 (td, J = 7.8, 1.2 Hz, 1H), 7.09 (td, J = 7.6, 0.8 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 5.40 – 5.30 (m, 1H), 4.31 (dd, J = 10.5, 7.3 Hz, 1H), 4.24 (dd, J = 10.5, 7.1 Hz, 1H), 3.18 (s, 3H), 2.24 (td, J = 7.4, 1.6 Hz, 2H), 1.69 (s, 3H), 1.67 – 1.61 (m, 1H), 1.61 (s, 3H), 1.41 (td, J = 7.4, 7.4 Hz, 2H), 0.86 (d, J = 2.3 Hz, 3H), 0.85 (d, J = 2.3 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 172.42, 143.29, 137.98, 130.23, 128.68, 124.84, 123.38, 120.62, 108.58, 89.47, 74.84, 73.90, 62.15, 37.33, 27.44, 26.45, 25.91, 22.22, 18.13, 17.12. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{21}\text{H}_{27}\text{O}_2\text{NNa}$] $^+$: 348.1934, found: 348.1949.

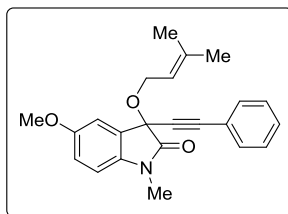
1,5-dimethyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)indolin-2-one (13j) was



prepared according to the general procedure C, by using **S9j** (44 mg, 0.16 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.59) as eluents the desired product was obtained in 82% yield (45 mg, 0.13

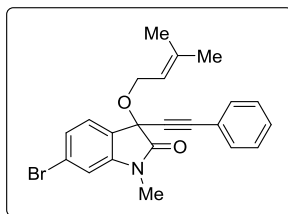
mmol) as a brown oil. **^1H NMR** (300 MHz, CDCl_3) δ 7.50 – 7.39 (m, 2H), 7.33 (s, 1H), 7.29 – 7.18 (m, 3H), 7.11 (d, J = 7.9 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 5.36 (t, J = 7.2 Hz, 1H), 4.41 (d, J = 10.5, 7.2 Hz, 1H), 4.31 (d, J = 10.5, 7.2 Hz, 1H), 3.16 (s, 3H), 2.32 (s, 3H), 1.68 (s, 3H), 1.62 (s, 3H). **^{13}C NMR** (75 MHz, CDCl_3) δ 171.99, 140.92, 138.34, 133.22, 132.20, 130.74, 128.97, 128.28, 128.13, 125.78, 121.96, 120.51, 108.49, 87.70, 84.06, 74.30, 62.41, 26.56, 25.96, 21.17, 18.19. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{23}\text{H}_{23}\text{O}_2\text{NNa}$] $^+$: 368.1621, found: 368.1637.

5-methoxy-1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)indolin-2-one (13k)



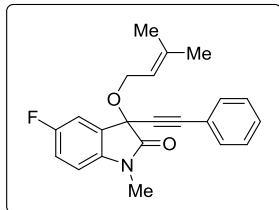
was prepared according to the general procedure C, by using **S9k** (97 mg, 0.33 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.35) as eluents the desired product was obtained in 74% yield (89 mg, 0.25 mmol) as a brown oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.51 – 7.37 (m, 2H), 7.31 – 7.19 (m, 3H), 7.14 (d, J = 2.5 Hz, 1H), 6.85 (dd, J = 8.5, 2.5 Hz, 1H), 6.71 (d, J = 8.5 Hz, 1H), 5.37 (t, J = 7.5 Hz, 1H), 4.37 (dd, J = 10.5, 7.5 Hz, 1H), 4.30 (dd, J = 10.5, 7.5 Hz, 1H), 3.77 (s, 3H), 3.16 (s, 3H), 1.68 (s, 3H), 1.62 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 171.65, 156.56, 138.31, 136.55, 132.07, 129.01, 128.92, 128.18, 121.72, 120.27, 115.10, 111.78, 109.16, 87.63, 83.85, 74.42, 62.32, 55.85, 26.49, 25.82, 18.08. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{23}\text{H}_{24}\text{O}_3\text{N}$] $^+$: 362.1750, found: 362.1760.

6-bromo-1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)indolin-2-one (13l) was



prepared according to the general procedure C, by using **S9l** (117 mg, 0.34 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.91) as eluents the desired product was obtained in 46% yield (65 mg, 0.16 mmol) as a brown oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.45 – 7.38 (m, 2H), 7.36 (d, J = 7.9 Hz, 1H), 7.31 – 7.18 (m, 4H), 6.94 (d, J = 1.6 Hz, 1H), 5.33 (t, J = 7.2 Hz, 1H), 4.39 (dd, J = 10.2, 7.2 Hz, 1H), 4.30 (dd, J = 10.2, 7.2 Hz, 1H), 3.16 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 171.81, 144.60, 138.74, 132.20, 129.19, 128.35, 127.13, 126.35, 124.26, 121.63, 120.19, 112.31, 88.18, 83.19, 73.74, 62.54, 29.80, 26.67, 25.96, 18.21. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{22}\text{H}_{20}\text{O}_2\text{NBrNa}$] $^+$: 432.0570, found: 432.0571.

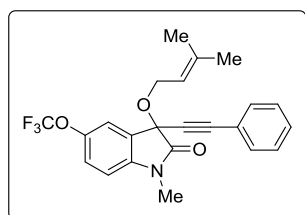
5-fluoro-1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)indolin-2-one (13m) was



prepared according to the general procedure C, by using **S9m** (40 mg, 0.14 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.45) as eluents the desired product was obtained in 99% yield (49 mg, 0.14

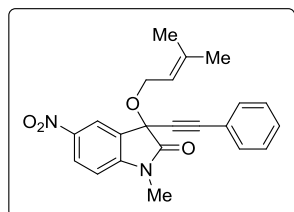
mmol) as a yellow oil. **¹H NMR** (300 MHz, CDCl₃) δ 7.56 – 7.36 (m, 2H), 7.33 – 7.17 (m, 4H), 7.02 (td, *J* = 8.6, 2.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 4.0 Hz, 1H), 5.34 (t, *J* = 7.4 Hz, 1H), 4.42 (dd, *J* = 10.3, 7.4 Hz, 1H), 4.34 (dd, *J* = 10.3, 7.4 Hz, 1H), 3.17 (s, 3H), 1.68 (s, 3H), 1.62 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 171.78, 159.68 (d, *J* = 242.5 Hz), 139.24 (d, *J* = 2.0 Hz), 138.77, 132.22, 129.67 (d, *J* = 7.9 Hz), 129.21, 128.35, 121.60, 120.19, 116.78 (d, *J* = 23.6 Hz), 113.18 (d, *J* = 25.1), 88.29, 83.22, 77.36, 74.12, 62.59, 26.67, 25.94, 18.19. **HRMS** (ESI): Calcd for (M + Na)⁺ [C₂₂H₂₀O₂NFNa]⁺: 372.1370, found: 372.1375.

1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)-5-(trifluoromethoxy)indolin-2-one (13n)



one (13n) was prepared according to the general procedure C, by using **S9n** (102 mg, 0.29 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/4 (*R_f* = 0.57) as eluents the desired product was obtained in 59% yield (72 mg, 0.17 mmol) as a brown oil. **¹H NMR** (300 MHz, CDCl₃) δ 7.54 – 7.36 (m, 3H), 7.34 – 7.14 (m, 4H), 6.80 (d, *J* = 8.5 Hz, 1H), 5.36 (t, *J* = 7.3 Hz, 1H), 4.44 (dd, *J* = 10.1, 7.3 Hz, 1H), 4.36 (dd, *J* = 10.1, 7.3 Hz, 1H), 3.19 (s, 3H), 1.69 (s, 3H), 1.62 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 171.83, 145.33 (d, *J* = 1.9 Hz), 141.94, 138.96, 132.24, 129.66, 129.30, 128.39, 123.60, 121.51, 120.62 (q, *J* = 257.1 Hz), 120.09, 119.07, 88.55, 82.93, 73.95, 62.67, 29.80, 26.70, 25.94, 18.13. **HRMS** (ESI): Calcd for (M + Na)⁺ [C₂₃H₂₀O₃NF₃Na]⁺: 438.1288, found: 438.11289.

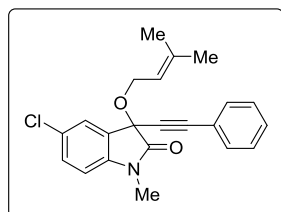
1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-5-nitro-3-(phenylethynyl)indolin-2-one (13o)



was prepared according to the general procedure C, by using **S9o** (40 mg, 0.13 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/4 (*R_f* = 0.26) as eluents the desired product was obtained in 90% yield (44 mg, 0.12 mmol) as a yellow oil. **¹H NMR** (300 MHz, CDCl₃) δ 8.43 (d, *J* = 2.3 Hz, 1H), 8.33 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.59 – 7.44 (m, 2H), 7.42 – 7.28 (m, 3H), 6.93 (d, *J* = 8.7 Hz, 1H), 5.39 (t, *J* = 7.2 Hz, 1H), 4.59 (dd, *J* = 10.4, 7.5 Hz, 1H), 4.51 (dd, *J* = 10.4, 7.2 Hz, 1H), 3.29 (s, 3H), 1.74 (s, 3H), 1.70 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 172.07, 148.73, 144.10, 139.36, 132.28, 129.55,

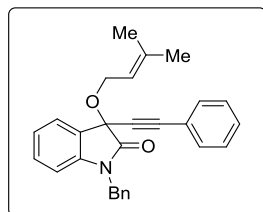
129.35, 128.48, 127.44, 121.08, 119.88, 108.52, 89.44, 81.97, 73.21, 62.93, 29.80, 26.98, 25.98, 18.26. **HRMS** (ESI): Calcd for $(M + H)^+$ $[C_{22}H_{21}O_4N_2]^+$: 377.1496, found: 377.1501.

5-chloro-1-methyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)indolin-2-one (13p) was



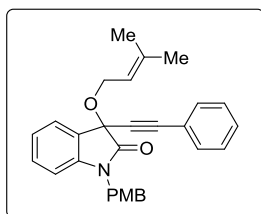
prepared according to the general procedure C, by using **S9p** (37 mg, 0.12 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.49) as eluents the desired product was obtained in 99% yield (45 mg, 0.12 mmol) as a yellow oil. **1H NMR** (300 MHz, $CDCl_3$) δ 7.53 (d, J = 2.1 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.38 – 7.20 (m, 4H), 6.76 (d, J = 8.3 Hz, 1H), 5.39 (t, J = 7.2 Hz, 1H), 4.48 (dd, J = 10.3, 7.3 Hz, 1H), 4.41 (dd, J = 10.3, 7.3 Hz, 1H), 3.21 (s, 3H), 1.73 (s, 3H), 1.67 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.60, 141.82, 138.85, 132.23, 130.39, 129.80, 129.25, 128.91, 128.37, 125.55, 121.57, 120.17, 109.75, 88.47, 83.06, 73.92, 62.63, 26.66, 25.96, 18.22. **HRMS** (ESI): Calcd for $(M + Na)^+$ $[C_{22}H_{20}O_2NClNa]^+$: 388.1075, found: 388.1087.

1-benzyl-3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)indolin-2-one (13q) was prepared



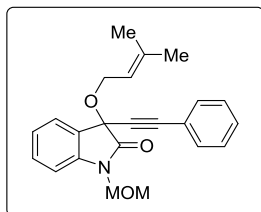
according to the general procedure C, by using **S9q** (47 mg, 0.14 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.69) as eluents the desired product was obtained in 90% yield (51 mg, 0.13 mmol) as a brown oil. **1H NMR** (300 MHz, $CDCl_3$) δ 7.57 (d, J = 6.6 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.38 – 7.17 (m, 9H), 7.10 (t, J = 7.6 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 5.44 (t, J = 7.5 Hz, 1H), 4.96 (d, J = 15.8 Hz, 1H), 4.90 (d, J = 15.8 Hz, 1H), 4.46 (dd, J = 10.4, 7.5 Hz, 1H), 4.40 (dd, J = 10.4, 7.5 Hz, 1H), 1.74 (s, 3H), 1.68 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.18, 142.41, 138.58, 135.38, 132.23, 130.40, 129.05, 128.94, 128.32, 128.21, 127.82, 127.30, 125.14, 123.59, 121.91, 120.40, 109.79, 87.89, 83.94, 74.30, 62.44, 44.02, 25.96, 18.20. **HRMS** (ESI): Calcd for $(M + Na)^+$ $[C_{28}H_{25}O_2NNa]^+$: 430.1778, found: 430.1792.

1-(4-methoxybenzyl)-3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)indolin-2-one (13r)



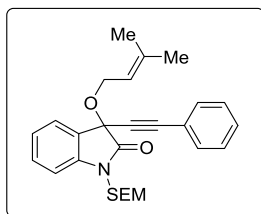
was prepared according to the general procedure C, by using **S9r** (50 mg, 0.14 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.60) as eluents the desired product was obtained in 90% yield (53 mg, 0.12 mmol) as a transparent oil. **^1H NMR** (300 MHz, CDCl_3) δ 7.57 (dd, J = 7.4, 0.8 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.41 – 7.19 (m, 6H), 7.10 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 7.8 Hz, 1H), 5.44 (t, J = 7.6 Hz, 1H), 4.90 (d, J = 15.5 Hz, 1H), 4.84 (d, J = 15.5 Hz, 1H), 4.44 (dd, J = 10.4, 7.6 Hz, 1H), 4.39 (dd, J = 10.4, 7.6 Hz, 1H), 3.77 (s, 3H), 1.75 (s, 3H), 1.68 (s, 3H). **^{13}C NMR** (75 MHz, CDCl_3) δ 172.12, 159.23, 142.45, 138.52, 132.23, 130.37, 129.03, 128.74, 128.31, 128.22, 127.44, 125.11, 123.52, 121.93, 120.42, 114.31, 109.81, 87.81, 84.00, 74.31, 62.40, 55.33, 43.53, 25.95, 18.20. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{29}\text{H}_{27}\text{O}_3\text{NNa}$] $^+$: 460.1883, found: 460.1878.

1-(methoxymethyl)-3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)indolin-2-one (13s)



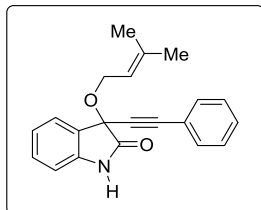
was prepared according to the general procedure C, by using **S9s** (191 mg, 0.65 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f = 0.75) as eluents the desired product was obtained in 89% yield (210 mg, 0.58 mmol) as a yellow oil. **^1H NMR** (300 MHz, CDCl_3) δ 7.58 (dd, J = 7.5, 0.8 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.36 (td, J = 7.8, 1.3 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.17 (td, J = 7.6, 0.9 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 5.41 (t, J = 7.7 Hz, 1H), 5.14 (s, 2H), 4.43 (dd, J = 10.4, 7.7 Hz, 1H), 4.35 (dd, J = 10.5, 7.7 Hz, 1H), 3.37 (s, 3H), 1.72 (s, 3H), 1.65 (s, 3H). **^{13}C NMR** (75 MHz, CDCl_3) δ 172.53, 141.53, 138.55, 132.13, 130.59, 129.06, 128.28, 127.72, 125.17, 124.00, 121.74, 120.26, 110.20, 88.07, 83.71, 74.45, 71.73, 62.41, 56.41, 25.88, 18.11. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{23}\text{H}_{23}\text{O}_3\text{NNa}$] $^+$: 384.1570, found: 384.1585.

3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)-1-((2-(trimethylsilyl)ethoxy)methyl)indolin-2-one (13t)



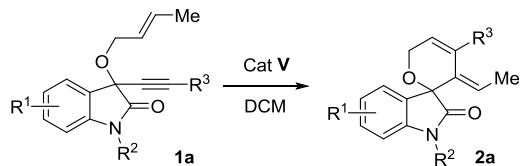
indolin-2-one (13t) was prepared according to the general procedure C, by using **S9t** (57 mg, 0.15 mmol) and 3,3-dimethylallyl bromide. After silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.63) as eluents the desired product was obtained in 76% yield (51 mg, 0.11 mmol) as a brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.57 (d, J = 7.5 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.36 (td, J = 7.8, 1.2 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.16 (td, J = 7.6, 0.9 Hz, 1H), 7.07 (d, J = 7.8 Hz, 1H), 5.45 – 5.32 (m, 1H), 5.19 (d, J = 11.1 Hz, 1H), 5.16 (d, J = 11.1 Hz, 1H), 4.42 – 4.35 (m, 1H), 4.35 – 4.29 (m, 1H), 3.62 (d, J = 7.9 Hz, 1H), 3.60 (d, J = 7.8 Hz, 1H), 1.72 (s, 3H), 1.64 (s, 3H), 0.96 – 0.89 (m, 2H), -0.05 (s, 9H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 172.45, 141.78, 138.57, 132.23, 130.59, 129.07, 128.31, 127.81, 125.17, 123.97, 121.87, 120.33, 110.38, 88.02, 83.83, 74.54, 69.81, 66.30, 62.44, 25.95, 18.19, 17.85, -1.37. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{27}\text{H}_{33}\text{O}_3\text{NSiNa}]^+$: 470.2122, found: 470.2137.

3-((3-methylbut-2-en-1-yl)oxy)-3-(phenylethynyl)indolin-2-one (13u)



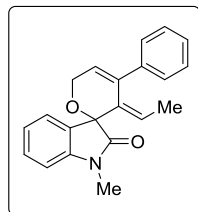
to the general procedure D, by using **13t** (120 mg, 0.27 mmol) as starting material. After silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.21) as eluents, the desired product was obtained in 40% yield (34 mg, 0.11 mmol) as a brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.94 (s, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.46 (dd, J = 8.1, 1.5 Hz, 2H), 7.35 – 7.24 (m, 4H), 7.11 (td, J = 7.6, 0.8 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 5.41 (t, J = 7.2 Hz, 1H), 4.37 (dd, J = 10.2, 7.2 Hz, 1H), 4.31 (dd, J = 10.5, 7.2 Hz, 1H), 1.72 (s, 3H), 1.64 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 174.49, 140.66, 138.59, 132.25, 130.59, 129.07, 128.57, 128.32, 125.46, 123.55, 121.90, 120.38, 110.88, 87.88, 83.81, 74.78, 62.48, 25.93, 18.19. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{21}\text{H}_{19}\text{O}_2\text{NNa}]^+$: 340.1308, found: 340.1322.

Gold catalyzed single cleavage rearrangement



At 0 °C, to a DCM (0.6 ml) solution of 1,6-enyne (0.1 mmol) was added a solution of cat. **V** (5.9 mg, 5 μ mol) in DCM (0.4 ml). After warming to room temperature, the reaction mixture was stirred overnight and then passed through a short pad of silica gel (Et₂O as the eluent). The resulting solution was concentrated under reduced pressure, followed by silica gel column chromatography (EA / PE as the eluent) to obtain the desired product.

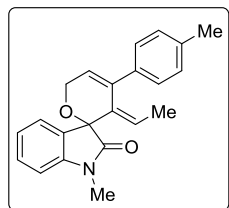
(E)-3'-ethylidene-1-methyl-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one (2a) was



prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1a** (30 mg, 0.09 mmol, 82% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.20) as eluents, the desired product was obtained

in 60% yield (18 mg, 0.06 mmol) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, J = 7.6 Hz, 1H), 7.40 (td, J = 7.6, 1.1 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 7.25 (dd, J = 8.1, 1.3 Hz, 2H), 7.09 (td, J = 7.6, 1.1 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.11 (s, 1H), 5.49 (q, J = 7.3 Hz, 1H), 4.87 (dd, J = 17.8, 2.9 Hz, 1H), 4.65 (dd, J = 17.8, 3.1 Hz, 1H), 3.30 (s, 3H), 1.19 (d, J = 7.3 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 174.34, 143.80, 141.86, 136.54, 130.84, 129.76, 129.40, 128.48, 128.39, 127.23, 127.17, 125.95, 124.84, 122.96, 108.73, 79.61, 63.77, 26.35, 16.34. HRMS (ESI): Calcd for (M + Na)⁺ [C₂₁H₁₉O₂NNa]⁺: 340.1308, found: 340.1321.

(E)-3'-ethylidene-1-methyl-4'-(p-tolyl)-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one (2b)

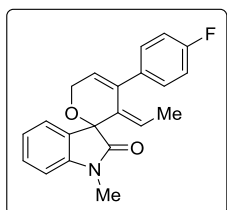


was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1b** (40 mg, 0.12 mmol, 77% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f = 0.35) as eluents,

the desired product was obtained in 60% yield (24 mg, 0.07 mmol) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 7.5 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.12 (d, J = 8.1 Hz, 2H),

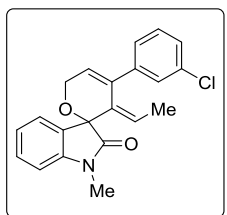
7.09 (d, $J = 8.1$ Hz, 2H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.89 (d, $J = 7.5$ Hz, 1H), 6.04 (s, 1H), 5.44 (q, $J = 7.3$ Hz, 1H), 4.80 (dd, $J = 17.7, 3.0$ Hz, 1H), 4.59 (dd, $J = 17.7, 3.0$ Hz, 1H), 3.26 (s, 3H), 2.35 (s, 3H), 1.16 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 174.45, 143.84, 139.01, 136.96, 136.57, 131.02, 129.75, 129.56, 129.21, 127.91, 127.15, 125.91, 124.87, 122.99, 108.76, 79.74, 63.86, 26.42, 21.29, 16.45. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+ [\text{C}_{22}\text{H}_{21}\text{O}_2\text{NNa}]^+$: 354.1465, found: 354.1480.

(E)-3'-ethylidene-4'-(4-fluorophenyl)-1-methyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one (2c)



one (2c) was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1c** (49 mg, 0.15 mmol, 78% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 ($R_f = 0.18$) as eluents, the desired product was obtained in 51% yield (25 mg, 0.07 mmol) as a yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.41 – 7.31 (m, 1H), 7.17 (dd, $J = 8.7, 5.5$ Hz, 1H), 7.05 (t, $J = 7.5$ Hz, 1H), 7.00 (t, $J = 8.7$ Hz, 1H), 6.89 (d, $J = 7.5$ Hz, 1H), 6.03 (s, 1H), 5.42 (q, $J = 7.5$ Hz, 1H), 4.81 (dd, $J = 17.8, 3.0$ Hz, 1H), 4.59 (dd, $J = 17.8, 3.0$ Hz, 1H), 3.25 (s, 3H), 1.14 (d, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 174.34, 162.26 (d, $J = 246.1$ Hz), 143.91, 137.96, 135.56, 130.94, 129.90, 129.35, 128.85 (d, $J = 7.8$ Hz), 128.60, 126.16, 124.91, 123.05, 115.44 (d, $J = 21.4$ Hz), 108.81, 79.61, 63.79, 26.41, 16.40. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+ [\text{C}_{21}\text{H}_{18}\text{O}_2\text{NFN}]^+$: 358.1214, found: 358.1223.

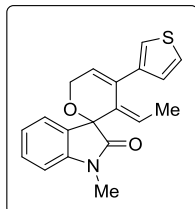
(E)-4'-(3-chlorophenyl)-3'-ethylidene-1-methyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one (2d)



one (2d) was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1d** (48 mg, 0.14 mmol, 80% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 ($R_f = 0.19$) as eluents, the desired product was obtained in 31% yield (15 mg, 0.04 mmol) as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.33 (m, 2H), 7.25 – 7.23 (m, 2H), 7.20 (s, 1H), 7.11 – 7.08 (m, 1H), 7.07 (td, $J = 7.6, 0.9$ Hz, 1H), 6.90 (d, $J = 7.6$ Hz, 1H), 6.08 (s, 1H), 5.44 (q, $J = 7.3$ Hz, 1H), 4.83 (dd, $J = 18.0, 2.9$ Hz, 1H), 4.60 (dd, $J = 18.0, 3.0$ Hz, 1H), 3.25 (s, 3H), 1.16 (d, $J = 7.3$ Hz,

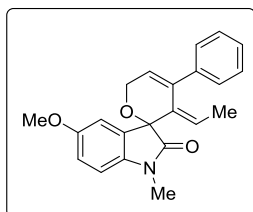
3H). ^{13}C NMR (126 MHz, CDCl_3) δ 174.23, 143.94, 143.73, 135.26, 134.46, 130.48, 129.98, 129.84, 129.46, 129.17, 127.36, 126.42, 125.55, 124.97, 123.11, 108.84, 79.47, 63.79, 26.43, 16.59. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{21}\text{H}_{18}\text{O}_2\text{NCINa}]^+$: 374.0918, found: 374.0929.

(E)-3'-ethylidene-1-methyl-4'-(thiophen-2-yl)-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one



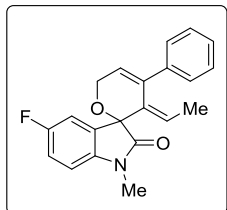
(2e) was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1e** (44 mg, 0.14 mmol, 83% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f = 0.33) as eluents, the desired product was obtained in 45% yield (20 mg, 0.06 mmol) as a dark brown oil. ^1H NMR (300 MHz, CDCl_3) δ 7.46 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 7.10 – 6.98 (m, 2H), 6.93 (d, J = 5.0 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 6.12 (s, 1H), 5.43 (q, J = 7.2 Hz, 1H), 4.79 (dd, J = 17.7, 3.0 Hz, 1H), 4.56 (dd, J = 17.7, 3.0 Hz, 1H), 3.25 (s, 3H), 1.24 (d, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 174.38, 143.78, 142.66, 131.55, 131.10, 129.82, 129.42, 127.80, 127.50, 126.09, 125.52, 124.86, 123.04, 121.07, 108.78, 79.63, 63.71, 26.42, 15.89. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{19}\text{H}_{17}\text{O}_2\text{NSNa}]^+$: 346.0872, found: 346.0884.

(E)-3'-ethylidene-5-methoxy-1-methyl-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one



(2f) was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1f** (45 mg, 0.13 mmol, 83% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.35) as eluents, the desired product was obtained in 51% yield (23 mg, 0.07 mmol) as a dark red oil. ^1H NMR (300 MHz, CDCl_3) δ 7.42 – 7.27 (m, 3H), 7.25 – 7.16 (m, 2H), 7.03 (d, J = 2.5 Hz, 1H), 6.88 (dd, J = 8.5, 2.5 Hz, 1H), 6.80 (d, J = 8.5 Hz, 1H), 6.06 (s, 1H), 5.44 (q, J = 7.4 Hz, 1H), 4.82 (dd, J = 17.8, 3.1 Hz, 1H), 4.60 (dd, J = 17.8, 3.1 Hz, 1H), 3.74 (s, 3H), 3.23 (s, 3H), 1.13 (d, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 174.17, 156.23, 141.87, 137.26, 136.55, 130.77, 130.60, 128.52, 128.38, 127.30, 127.21, 126.23, 113.87, 112.41, 109.08, 79.93, 63.78, 55.99, 26.50, 16.42. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{22}\text{H}_{21}\text{O}_3\text{NNa}]^+$: 370.1414, found: 370.1426.

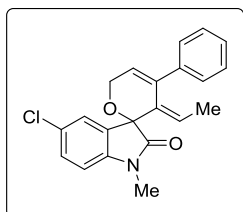
(E)-3'-ethylidene-5-fluoro-1-methyl-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one



(2g) was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1g** (41 mg, 0.12 mmol, 77% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f = 0.35) as eluents,

the desired product was obtained in 51% yield (21 mg, 0.06 mmol) as an orange oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.37 – 7.20 (m, 3H), 7.18 – 7.09 (m, 3H), 7.02 (td, J = 8.7, 2.6 Hz, 1H), 6.78 (dd, J = 8.7, 4.1 Hz, 1H), 6.03 (s, 1H), 5.41 (q, J = 7.3 Hz, 1H), 4.78 (dd, J = 17.9, 3.0 Hz, 1H), 4.55 (dd, J = 17.9, 3.0 Hz, 1H), 3.21 (s, 3H), 1.10 (d, J = 7.3 Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 174.14, 159.38 (d, J = 241.3 Hz), 141.61, 139.75, 136.49, 130.86 (d, J = 7.7 Hz), 130.43, 128.60, 128.28, 127.36, 127.23, 126.53, 115.94 (d, J = 23.5 Hz), 113.04 (d, J = 25.3 Hz), 109.27 (d, J = 8.0 Hz), 79.69, 63.84, 26.58, 16.45. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{21}\text{H}_{18}\text{O}_2\text{NFNa}]^+$: 358.1214, found: 358.1225.

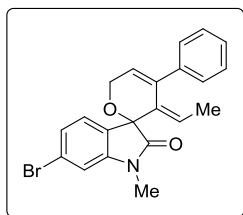
(E)-5-chloro-3'-ethylidene-1-methyl-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one



one (2h) was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1h** (40 mg, 0.11 mmol, 77% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f = 0.34) as eluents,

the desired product was obtained in 50% yield (20 mg, 0.06 mmol) as an orange oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.41 – 7.27 (m, 5H), 7.21 (d, J = 1.8 Hz, 1H), 7.19 (s, 1H), 6.82 (d, J = 8.2 Hz, 1H), 6.07 (d, J = 1.1 Hz, 1H), 5.42 (q, J = 7.3 Hz, 1H), 4.82 (dd, J = 17.8, 3.1 Hz, 1H), 4.59 (dd, J = 17.8, 3.1 Hz, 1H), 3.24 (s, 3H), 1.14 (d, J = 7.3 Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 174.00, 142.40, 141.65, 136.42, 131.03, 130.38, 129.69, 128.60, 128.41, 128.33, 127.35, 127.29, 126.58, 125.27, 109.73, 79.58, 63.83, 26.54, 16.44. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{21}\text{H}_{19}\text{O}_2\text{NCl}]^+$: 352.1099, found: 352.1107.

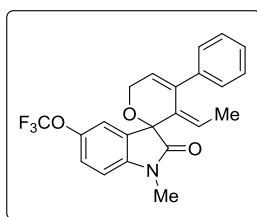
(E)-6-bromo-3'-ethylidene-1-methyl-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one (2i)



one (2i) was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1i** (43 mg, 0.11 mmol, 76% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/8 (R_f = 0.28) as eluents,

the desired product was obtained in 58% yield (25 mg, 0.06 mmol) as an orange oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.35 – 7.22 (m, 4H), 7.21 – 7.16 (m, 3H), 7.05 (d, J = 1.7 Hz, 1H), 6.08 – 6.03 (m, 1H), 5.42 (q, J = 7.1 Hz, 1H), 4.80 (dd, J = 17.8, 3.1 Hz, 1H), 4.57 (dd, J = 17.8, 3.1 Hz, 1H), 3.24 (s, 3H), 1.14 (d, J = 7.1 Hz, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 174.18, 145.20, 141.64, 136.52, 130.51, 128.60, 128.39, 128.36, 127.36, 127.21, 126.34, 126.15, 125.78, 123.57, 112.35, 79.33, 63.86, 26.54, 16.43. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{21}\text{H}_{19}\text{O}_2\text{NBr}]^+$: 396.0594, found: 396.0600.

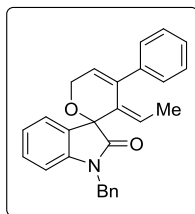
(E)-3'-ethylidene-1-methyl-4'-phenyl-5-(trifluoromethoxy)-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one (2j)



pyran]-2-one (2j) was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1j** (49 mg, 0.12 mmol, 80% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.20) as

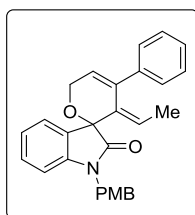
eluents, the desired product was obtained in 65% yield (32 mg, 0.08 mmol) as a brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.39 – 7.27 (m, 4H), 7.24 (d, J = 8.5 Hz, 1H), 7.18 (d, J = 6.8 Hz, 2H), 6.88 (d, J = 8.5 Hz, 1H), 6.09 (s, 1H), 5.43 (q, J = 7.2 Hz, 1H), 4.82 (dd, J = 17.7, 2.8 Hz, 1H), 4.58 (dd, J = 17.7, 3.0 Hz, 1H), 3.27 (s, 3H), 1.15 (d, J = 7.3 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 174.26, 144.95, 142.52, 141.54, 136.64, 130.95, 130.50, 128.63, 128.39, 127.42, 127.21, 126.59, 122.92, 120.67 (d, J = 256.9 Hz), 119.08, 109.17, 79.59, 63.86, 26.60, 16.38. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{22}\text{H}_{19}\text{O}_3\text{NF}_3]^+$: 402.1312, found: 402.1323.

(E)-1-benzyl-3'-ethylidene-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one (2k)



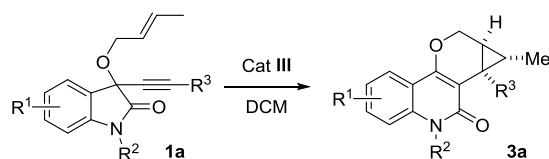
was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1k** (42 mg, 0.11 mmol, 76% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/8 (R_f = 0.31) as eluents, the desired product was obtained in 45% yield (19 mg, 0.05 mmol) as a yellow oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.41 (d, J = 6.8 Hz, 1H), 7.38 – 7.30 (m, 6H), 7.30 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 7.01 (td, J = 7.6, 0.8 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.10 (s, 1H), 5.48 (q, J = 7.1 Hz, 1H), 5.05 (d, J = 15.8 Hz, 1H), 4.89 (d, J = 15.8 Hz, 1H), 4.86 (dd, J = 17.7, 3.0 Hz, 1H), 4.63 (dd, J = 17.7, 3.1 Hz, 1H), 1.16 (d, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 174.59, 142.95, 141.90, 136.64, 135.82, 131.13, 129.68, 129.60, 128.96, 128.58, 128.55, 127.75, 127.35, 127.31, 127.25, 126.06, 124.97, 123.04, 109.83, 79.75, 63.85, 43.87, 16.48. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{27}\text{H}_{24}\text{O}_2\text{N}]^+$: 394.1802, found: 394.1810.

(E)-3'-ethylidene-1-(4-methoxybenzyl)-4'-phenyl-3',6'-dihydrospiro[indoline-3,2'-pyran]-2-one (2l)



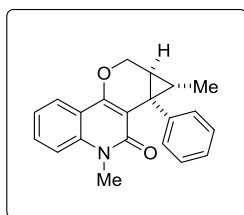
one (2l) was prepared according to the general procedure for the gold catalyzed C-migration reaction, by using **1l** (24 mg, 0.06 mmol, 73% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.35) as eluents, the desired product was obtained in 42% yield (10 mg, 0.02 mmol) as a yellow oil. **^1H NMR** (600 MHz, cdcl_3) δ 7.39 (dd, J = 7.6, 0.9 Hz, 1H), 7.35 – 7.19 (m, 8H), 7.00 (td, J = 7.6, 0.9 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.79 (d, J = 7.8 Hz, 1H), 6.09 (td, J = 3.1, 1.4 Hz, 1H), 5.47 (q, J = 7.0 Hz, 1H), 4.98 (d, J = 15.4 Hz, 1H), 4.85 (dd, J = 17.7, 3.2 Hz, 1H), 4.83 (d, J = 15.4 Hz, 1H), 4.62 (dd, J = 17.7, 3.2 Hz, 1H), 3.78 (s, 3H), 1.15 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, cdcl_3) δ 174.52, 159.22, 142.96, 141.91, 136.65, 131.09, 129.65, 129.59, 128.76, 128.56, 127.87, 127.31, 127.25, 126.02, 124.92, 122.98, 114.36, 109.86, 79.72, 63.86, 55.42, 43.36, 16.51. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{28}\text{H}_{25}\text{O}_3\text{NNa}]^+$: 446.1727, found: 446.1734.

Gold catalyzed acyl-migration reaction



At 0 °C, to a DCM (0.5 ml) solution of 1,6-enyne (0.1 mmol) was added a solution of cat. **III** (4.5 mg, 5 μ mol) in DCM (0.5 ml). After warming to room temperature, the reaction mixture was stirred overnight. After TLC showed full conversion of the starting material, the mixture was passed through a short pad of silica gel (Et₂O as the eluent). The resulting solution was concentrated under reduced pressure, followed by silica gel column chromatography (EA / PE as the eluent) to obtain the desired product.

(1*S*,1*aR*,9*aS*)-1,3-dimethyl-1*a*-phenyl-1*a*,3,9,9*a*-tetrahydrocyclopropa[4,5]pyrano[3,2-



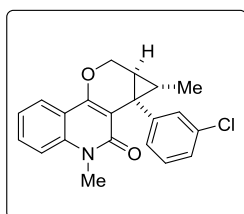
c]quinolin-2(1*H*)-one (**3a**) was prepared according to the general procedure for the gold catalyzed carbonyl-migration reaction, by using **1a** (30 mg, 0.09 mmol, 82% (*E*)-isomer) as starting material. After the purification done by silica gel column chromatography EtOAc / petroleum

ether = 1/5 (*R_f* = 0.24) as eluents, the desired product was obtained in 67% yield (20 mg, 0.06 mmol) as a brown oil. The recrystallization was performed from DCM and petroleum ether.

¹H NMR (500 MHz, cdcl₃) δ 7.94 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.21 – 7.15 (m, 2H), 5.05 (dd, *J* = 11.9, 7.9 Hz, 1H), 3.93 (dd, *J* = 11.9, 7.9 Hz, 1H), 3.57 (s, 3H), 1.61 – 1.54 (m, 1H), 1.30 – 1.23 (m, 4H). **¹³C NMR** (126 MHz, cdcl₃) δ 162.29, 158.12, 140.01, 138.71, 132.63, 130.44, 127.53, 126.50, 123.53, 121.50, 116.44, 115.72, 113.80, 71.77, 31.49, 29.26, 26.70, 26.50, 16.50.

HRMS (ESI): Calcd for (M + Na)⁺ [C₂₁H₁₉O₂NNa]⁺: 340.1308, found: 340.1320.

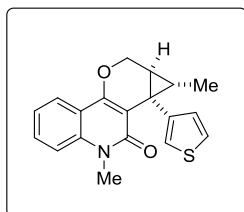
(1*S*,1*aR*,9*aS*)-1*a*-(3-chlorophenyl)-1,3-dimethyl-1*a*,3,9,9*a*-tetrahydrocyclo



propa[4,5]pyrano[3,2-c]quinolin-2(1*H*)-one (**3b**) was prepared according to the general procedure for the gold catalyzed carbonyl-migration reaction, by using **1d** (27 mg, 0.08 mmol, 80% (*E*)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

petroleum ether = 1/7 (R_f = 0.25) as eluents, the desired product was obtained in 52% yield (16 mg, 0.05 mmol) as an orange oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.94 (dd, J = 8.0, 1.5 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.56 (t, J = 1.5 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 7.7 Hz, 2H), 7.18 – 7.13 (m, 1H), 5.03 (dd, J = 11.9, 7.8 Hz, 1H), 3.94 (dd, J = 11.9, 5.9 Hz, 1H), 3.58 (s, 3H), 1.62 – 1.50 (m, 1H), 1.25 (s, 4H). **^{13}C NMR** (126 MHz, CDCl_3) δ 162.25, 158.26, 142.13, 138.85, 133.26, 132.41, 131.20, 130.69, 128.64, 126.84, 123.66, 121.67, 116.40, 115.03, 113.92, 71.42, 31.57, 29.35, 26.61, 26.50, 16.52. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{21}\text{H}_{19}\text{O}_2\text{NCl}]^+$: 352.1099, found: 352.1113.

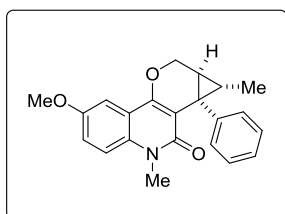
(1S,1aS,9aS)-1,3-dimethyl-1a-(thiophen-3-yl)-1a,3,9,9a-tetrahydrocyclopropa[4,5]pyrano



[3,2-c]quinolin-2(1H)-one (3c) was prepared according to the general procedure for the gold catalyzed carbonyl-migration reaction, by using **1e** (51 mg, 0.16 mmol, 83% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

petroleum ether = 1/7 (R_f = 0.16) as eluents, the desired product was obtained in 59% yield (30 mg, 0.09 mmol) as a yellow oil. **^1H NMR** (300 MHz, CDCl_3) δ 7.92 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.42 (d, J = 2.9 Hz, 1H), 7.35 (d, J = 4.9 Hz, 1H), 7.29 – 7.10 (m, 4H), 5.04 (dd, J = 11.9, 8.0 Hz, 1H), 3.88 (dd, J = 11.9, 6.1 Hz, 1H), 3.61 (s, 3H), 1.63 (t, J = 6.7 Hz, 1H), 1.20 (s, 4H). **^{13}C NMR** (75 MHz, CDCl_3) δ 162.40, 158.21, 140.10, 138.69, 131.47, 130.52, 125.63, 123.51, 123.42, 121.61, 116.47, 115.22, 113.89, 71.97, 31.90, 29.34, 26.14, 21.87, 15.85. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{19}\text{H}_{18}\text{O}_2\text{NS}]^+$: 324.1053, found: 324.1062.

(1S,1aR,9aS)-6-methoxy-1,3-dimethyl-1a-phenyl-1a,3,9,9a-tetrahydrocyclopropa[4,5]

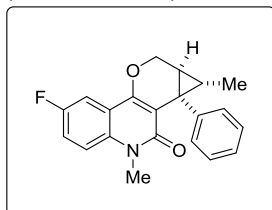


pyrano[3,2-c]quinolin-2(1H)-one (3d) was prepared according to the general procedure for the gold catalyzed carbonyl-migration reaction, by using **1f** (52 mg, 0.15 mmol, 83% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

petroleum ether = 1/5 (R_f = 0.29) as eluents, the desired product was obtained in 40% yield (21 mg, 0.06 mmol) as a brown oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.67 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 2.9 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.22 – 7.12 (m, 2H), 7.11 (dd, J = 9.1, 2.9 Hz, 1H), 5.06

(dd, $J = 11.9, 7.9$ Hz, 1H), 3.92 (dd, $J = 11.9, 6.1$ Hz, 1H), 3.87 (s, 3H), 3.56 (s, 3H), 1.63 – 1.51 (m, 1H), 1.26 (s, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 162.14, 157.94, 154.84, 140.30, 133.70, 132.93, 127.83, 126.80, 119.74, 117.32, 116.55, 115.57, 105.38, 72.21, 56.10, 31.81, 29.68, 27.15, 26.85, 16.78. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{22}\text{H}_{22}\text{O}_3\text{N}]^+$: 348.1594, found: 348.1605.

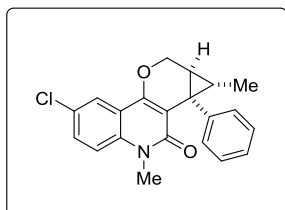
(1S,1aR,9aS)-6-fluoro-1,3-dimethyl-1a-phenyl-1a,3,9,9a-tetrahydrocyclopropa[4,5]pyrano



[3,2-c]quinolin-2(1H)-one (3e) was prepared according to the general procedure for the gold catalyzed carbonyl-migration reaction, by using **1g** (44 mg, 0.13 mmol, 77% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

petroleum ether = 1/7 ($R_f = 0.14$) as eluents, the desired product was obtained in 48% yield (21 mg, 0.06 mmol) as a yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.63 (d, $J = 7.2$ Hz, 2H), 7.57 (dd, $J = 8.9, 1.8$ Hz, 1H), 7.31 – 7.07 (m, 5H), 5.01 (dd, $J = 11.9, 7.8$ Hz, 1H), 3.91 (dd, $J = 11.9, 5.9$ Hz, 1H), 3.52 (s, 3H), 1.59 – 1.49 (m, 1H), 1.22 (s, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 161.96, 159.43, 156.72 (d, $J = 73.4$ Hz), 139.73, 135.26, 132.66, 127.61, 126.65, 118.13 (d, $J = 23.9$ Hz), 117.42 (d, $J = 8.4$ Hz), 116.71, 115.43 (d, $J = 8.0$ Hz), 109.08 (d, $J = 24.1$ Hz), 71.81, 31.61, 29.56, 26.75, 26.52, 16.50. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{21}\text{H}_{19}\text{O}_2\text{NF}]^+$: 336.1394, found: 336.1404.

(1S,1aR,9aS)-6-chloro-1,3-dimethyl-1a-phenyl-1a,3,9,9a-tetrahydrocyclopropa[4,5]pyrano

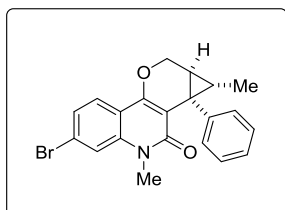


[3,2-c]quinolin-2(1H)-one (3f) was prepared according to the general procedure for the gold catalyzed carbonyl-migration reaction, by using **1h** (44 mg, 0.13 mmol, 77% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

petroleum ether = 1/7 ($R_f = 0.17$) as eluents, the desired product was obtained in 50% yield (22 mg, 0.06 mmol) as a brown oil. ^1H NMR (500 MHz, CDCl_3) δ 7.92 (d, $J = 2.4$ Hz, 1H), 7.66 (d, $J = 7.2$ Hz, 2H), 7.43 (dd, $J = 8.9, 2.4$ Hz, 1H), 7.33 – 7.23 (m, 2H), 7.23 – 7.12 (m, 2H), 5.05 (dd, $J = 11.9, 7.8$ Hz, 1H), 3.96 (dd, $J = 11.9, 5.8$ Hz, 1H), 3.55 (s, 3H), 1.65 – 1.51 (m, 1H),

1.27 (s, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 161.99, 157.03, 139.67, 137.21, 132.65, 130.41, 127.62, 127.31, 126.68, 123.09, 117.56, 116.66, 115.32, 71.79, 31.62, 29.47, 26.71, 26.50, 16.49. HRMS (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{21}\text{H}_{19}\text{O}_2\text{NCl}]^+$: 352.1099, found: 352.1112.

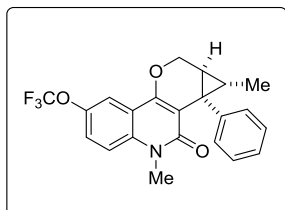
(1S,1aR,9aS)-5-bromo-1,3-dimethyl-1a-phenyl-1a,3,9,9a-tetrahydrocyclopropa[4,5]pyrano



[3,2-c]quinolin-2(1H)-one (3g) was prepared according to the general procedure for the gold catalyzed carbonyl-migration reaction, by using **1i** (51 mg, 0.13 mmol, 76% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

petroleum ether = 1/7 (R_f = 0.30) as eluents, the desired product was obtained in 47% yield (24 mg, 0.06 mmol) as a red oil. ^1H NMR (300 MHz, CDCl_3) δ 7.75 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 7.2 Hz, 2H), 7.36 (s, 1H), 7.34 – 7.19 (m, 4H), 7.17 (d, J = 7.2 Hz, 1H), 5.01 (dd, J = 11.9, 7.8 Hz, 1H), 3.91 (dd, J = 11.9, 5.9 Hz, 1H), 3.50 (s, 3H), 1.53 (t, J = 6.4 Hz, 1H), 1.22 (s, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 162.11, 157.70, 139.70, 139.59, 132.63, 127.61, 126.66, 124.99, 124.84, 124.75, 116.79, 115.95, 115.31, 71.74, 31.54, 29.41, 26.64, 26.46, 16.49. HRMS (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{21}\text{H}_{19}\text{O}_2\text{NBr}]^+$: 396.0594, found: 396.0602.

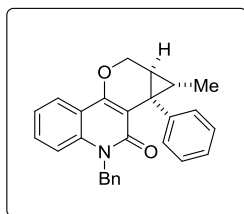
(1S,1aR,9aS)-1,3-dimethyl-1a-phenyl-6-(trifluoromethoxy)-1a,3,9,9a-tetrahydrocyclopropa



[4,5]pyrano[3,2-c]quinolin-2(1H)-one (3h) was prepared according to the general procedure for the gold catalyzed carbonyl-migration reaction, by using **1j** (34 mg, 0.08 mmol, 80% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with

EtOAc / petroleum ether = 1/7 (R_f = 0.24) as eluents, the desired product was obtained in 44% yield (15 mg, 0.04 mmol) as an orange oil. ^1H NMR (500 MHz, CDCl_3) δ 7.79 (s, 1H), 7.65 (d, J = 7.2 Hz, 2H), 7.34 (dd, J = 9.1, 2.0 Hz, 1H), 7.32 – 7.16 (m, 5H), 5.05 (dd, J = 11.9, 7.8 Hz, 1H), 3.97 (dd, J = 11.9, 5.8 Hz, 1H), 3.57 (s, 3H), 1.26 (s, 5H). ^{13}C NMR (126 MHz, CDCl_3) δ 162.04, 157.10, 143.65, 139.63, 137.25, 132.67, 127.64, 126.73, 123.58, 120.73 (d, J = 257.0 Hz), 117.24, 116.85, 115.89, 115.25, 71.75, 31.71, 29.58, 26.79, 26.60, 16.49. HRMS (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{22}\text{H}_{19}\text{O}_3\text{NF}_3]^+$: 402.1312, found: 402.1323.

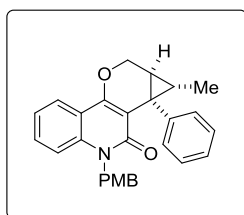
(1S,1aR,9aS)-3-benzyl-1-methyl-1a-phenyl-1a,3,9,9a-tetrahydrocyclopropa[4,5]pyrano[3,2-c]quinolin-2(1H)-one (3i) was prepared according to the general procedure



for the gold catalyzed carbonyl-migration reaction, by using **1k** (46 mg, 0.12 mmol, 76% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether =

1/7 (R_f = 0.40) as eluents, the desired product was obtained in 52% yield (24 mg, 0.06 mmol) as a brown oil. **^1H NMR** (500 MHz, DMSO) δ 7.88 (dd, J = 8.0, 1.5 Hz, 1H), 7.59 (d, J = 7.0 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.32 – 7.12 (m, 9H), 7.05 (d, J = 7.3 Hz, 2H), 5.47 (bs, 1H), 5.27 (bs, 1H), 5.14 (dd, J = 11.9, 8.0 Hz, 1H), 3.99 (dd, J = 12.0, 6.1 Hz, 1H), 1.66 – 1.59 (m, 1H), 1.33 – 1.26 (m, 1H), 1.14 (d, J = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 162.65, 158.66, 140.22, 138.47, 137.22, 132.90, 130.72, 129.00, 127.82, 127.30, 126.80, 123.92, 121.88, 116.94, 115.84, 114.99, 72.17, 45.97, 31.83, 27.11, 26.61, 16.79. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{27}\text{H}_{24}\text{O}_2\text{N}]^+$: 394.1802, found: 394.1809.

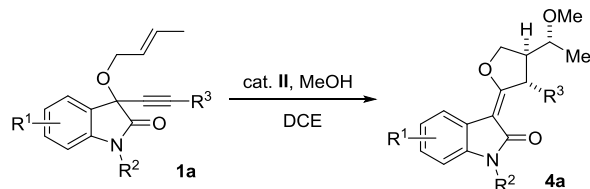
(1S,1aR,9aS)-3-(4-methoxybenzyl)-1-methyl-1a-phenyl-1a,3,9,9a-tetrahydrocyclopropa[4,5]pyrano[3,2-c]quinolin-2(1H)-one (3j) was prepared according to the



general procedure for the gold catalyzed carbonyl-migration reaction, by using **1l** (23 mg, 0.05 mmol, 73% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

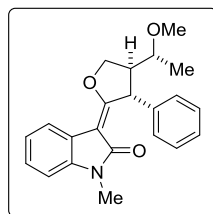
petroleum ether = 1/7 (R_f = 0.28) as eluents, the desired product was obtained in 43% yield (10 mg, 0.02 mmol) as a red oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.94 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 7.6 Hz, 2H), 7.34 (m, 1H), 7.28 – 7.25 (m, 2H), 7.20 – 7.12 (m, 3H), 6.99 (d, J = 8.2 Hz, 2H), 6.74 (d, J = 8.2 Hz, 2H), 5.49 (bs, 1H), 5.19 (bs, 1H), 5.09 (dd, J = 11.9, 8.0 Hz, 1H), 3.96 (dd, J = 11.9, 6.1 Hz, 1H), 3.72 (s, 3H), 1.62 – 1.58 (m, 1H), 1.34 – 1.27 (m, 4H). **^{13}C NMR** (126 MHz, CDCl_3) δ 162.63, 158.94, 158.62, 140.23, 138.46, 132.90, 130.66, 129.32, 128.15, 127.81, 126.77, 123.89, 121.82, 116.94, 115.88, 114.97, 114.43, 72.20, 55.60, 45.40, 31.81, 27.12, 26.60, 16.79. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ $[\text{C}_{28}\text{H}_{25}\text{O}_3\text{NNa}]^+$: 446.1727, found: 446.1734.

Gold catalyzed O-migration reaction with MeOH as nucleophile



To a DCE (1,2-dichloroethane) (0.5 ml) solution of 1,6-enyne (0.5 mmol) and MeOH (41 μ L, 1 mmol) in a pressure tube equipped with a stirring bar was added a solution of cat. II (3.9 mg, 5 μ mol) in DCE (0.5 mL) and the mixture was stirred at 60 °C overnight until TLC showed full conversion of the starting material. After cooling to room temperature, the reaction mixture was passed through a short pad of silica gel (Et₂O as the eluent). The resulting solution was concentrated under reduced pressure, followed by silica gel column chromatography (EA / PE as the eluent) to obtain the desired product.

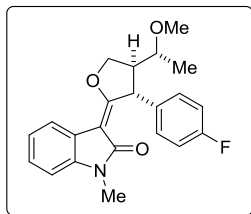
(E)-3-((3R,4S)-4-((R)-1-methoxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)-1-methylindolin-2-one (4a)



methyldindolin-2-one (4a) was prepared from according to the general procedure for the gold catalyzed O-migration reaction with MeOH as nucleophile, by using **1a** (30 mg, 0.09 mmol, 82% (E)-isomer) as starting material. After the purification done by silica gel column chromatography

with EtOAc / petroleum ether = 1/3 (R_f = 0.20) as eluents, the desired product was obtained in 73% yield (24 mg, 0.07 mmol) as a yellow oil. The recrystallization was performed from CHCl₃ and petroleum ether. ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, J = 7.6 Hz, 1H), 7.35 – 7.23 (m, 5H), 7.22 (d, J = 7.6 Hz, 1H), 7.18 (dd, J = 7.6, 1.2 Hz, 1H), 7.06 (td, J = 7.6, 0.9 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 5.06 (s, 1H), 4.73 (dd, J = 9.5, 1.5 Hz, 1H), 4.60 (dd, J = 9.5, 6.5 Hz, 1H), 3.36 – 3.26 (m, 4H), 3.17 (s, 3H), 2.44 (t, J = 6.5 Hz, 1H), 1.28 (d, J = 6.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 172.58, 168.06, 141.13, 140.61, 128.96, 127.08, 126.92, 126.16, 122.81, 122.53, 121.55, 107.17, 101.20, 76.98, 73.23, 56.74, 52.93, 51.21, 25.88, 16.63. HRMS (ESI): Calcd for (M + H)⁺ [C₂₂H₂₄O₃N]⁺: 350.1751, found: 350.1763.

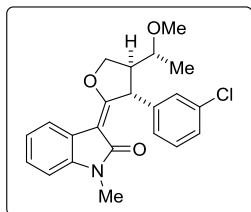
(E)-3-((3R,4S)-3-(4-fluorophenyl)-4-((R)-1-methoxyethyl)dihydrofuran-2(3H)-ylidene)-1-methylindolin-2-one (4b)



methylinolin-2-one (4b) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1c** (36 mg, 0.11 mmol, 78% (*E*)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

petroleum ether = 1/4 ($R_f = 0.14$) as eluents, the desired product was obtained in 58% yield (23 mg, 0.06 mmol) as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.78 (d, $J = 7.6$ Hz, 1H), 7.25 – 7.14 (m, 3H), 7.06 (td, $J = 7.6, 0.8$ Hz, 1H), 6.98 (t, $J = 8.7$ Hz, 2H), 6.80 (d, $J = 7.6$ Hz, 1H), 5.03 (s, 1H), 4.72 (dd, $J = 9.5, 1.5$ Hz, 1H), 4.59 (dd, $J = 9.5, 6.4$ Hz, 1H), 3.37 – 3.30 (m, 4H), 3.18 (s, 3H), 2.42 (t, $J = 6.4$ Hz, 1H), 1.27 (d, $J = 6.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.25, 168.03, 161.77 (d, $J = 245.1$ Hz), 140.63, 136.96, 128.63 (d, $J = 8.0$ Hz), 126.30, 122.67, 122.57, 121.63, 115.81 (d, $J = 21.4$ Hz), 107.25, 101.25, 76.91, 73.21, 56.73, 52.91, 50.42, 25.90, 16.53. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{22}\text{H}_{23}\text{O}_3\text{NF}$] $^+$: 368.1657, found: 368.1669.

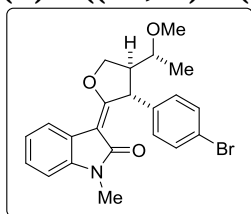
(E)-3-((3R,4S)-3-(3-chlorophenyl)-4-((R)-1-methoxyethyl)dihydrofuran-2(3H)-ylidene)-1-methylindolin-2-one (4c)



methylinolin-2-one (4c) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1d** (34 mg, 0.10 mmol, 80% (*E*)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

petroleum ether = 1/4 ($R_f = 0.15$) as eluents, the desired product was obtained in 67% yield (25 mg, 0.07 mmol) as a brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.78 (d, $J = 7.6$ Hz, 1H), 7.25 – 7.12 (m, 5H), 7.07 (td, $J = 7.6, 0.9$ Hz, 1H), 6.80 (d, $J = 7.6$ Hz, 1H), 5.03 (s, 1H), 4.71 (dd, $J = 9.6, 1.6$ Hz, 1H), 4.58 (dd, $J = 9.6, 6.5$ Hz, 1H), 3.33 (s, 4H), 3.18 (s, 3H), 2.43 (t, $J = 6.5$ Hz, 1H), 1.26 (d, $J = 6.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 171.40, 168.01, 143.18, 140.70, 134.75, 130.18, 127.24, 127.05, 126.39, 125.49, 122.66, 122.59, 121.66, 107.29, 101.48, 76.86, 73.09, 56.75, 52.79, 50.81, 25.91, 16.49. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{22}\text{H}_{23}\text{O}_3\text{NCl}$] $^+$: 384.1361, found: 384.1378.

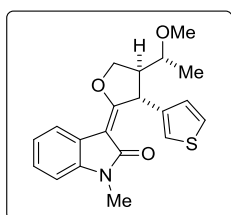
(E)-3-((3R,4S)-3-(4-bromophenyl)-4-((R)-1-methoxyethyl)dihydrofuran-2(3H)-ylidene)-1-



methylinolin-2-one (4d) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1m** (41 mg, 0.10 mmol, 76% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

petroleum ether = 1/4 (R_f = 0.17) as eluents, the desired product was obtained in 75% yield (33 mg, 0.08 mmol) as an orange oil. ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, J = 7.5 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.20 (td, J = 7.5, 0.9 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 7.5 Hz, 1H), 4.99 (s, 1H), 4.71 (dd, J = 9.6, 1.5 Hz, 1H), 4.57 (dd, J = 9.5, 6.5 Hz, 1H), 3.36 – 3.30 (m, 4H), 3.17 (s, 3H), 2.41 (t, J = 6.5 Hz, 1H), 1.26 (d, J = 6.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.77, 167.99, 140.66, 140.30, 132.06, 128.85, 126.37, 122.60, 121.65, 120.85, 107.28, 101.35, 76.88, 73.20, 56.74, 52.76, 50.63, 25.91, 16.49. HRMS (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{22}\text{H}_{23}\text{O}_3\text{NBr}$] $^+$: 428.0856, found: 428.0865.

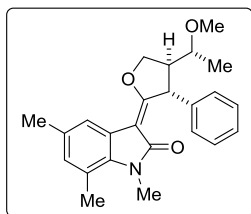
(E)-3-((3R,4S)-4-((R)-1-methoxyethyl)-3-(thiophen-3-yl)dihydrofuran-2(3H)-ylidene)-1-



methylinolin-2-one (4e) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1e** (44 mg, 0.14 mmol, 83% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc /

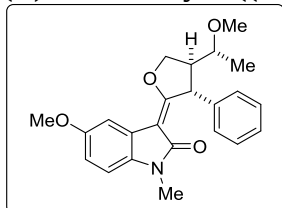
petroleum ether = 1/4 (R_f = 0.10) as eluents, the desired product was obtained in 77% yield (37 mg, 0.10 mmol) as a red oil. ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, J = 7.5 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.18 (td, J = 7.5, 1.2 Hz, 1H), 7.13 – 6.99 (m, 3H), 6.79 (d, J = 7.5 Hz, 1H), 5.16 (s, 1H), 4.73 (dd, J = 9.4, 1.1 Hz, 1H), 4.60 (dd, J = 9.4, 6.3 Hz, 1H), 3.31 (s, 3H), 3.29 – 3.23 (m, 1H), 3.21 (s, 3H), 2.50 (t, J = 6.3 Hz, 1H), 1.25 (d, J = 6.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.29, 168.14, 140.51, 140.13, 127.08, 126.19, 126.16, 122.79, 122.52, 121.57, 120.95, 107.17, 100.93, 76.72, 73.50, 56.73, 51.74, 46.38, 25.91, 16.65. HRMS (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{20}\text{H}_{22}\text{O}_3\text{NS}$] $^+$: 356.1315, found: 356.1326.

(E)-3-((3R,4S)-4-((R)-1-methoxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)-1,5,7-



trimethylindolin-2-one (4f) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1n** (40 mg, 0.12 mmol, 80% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.18) as eluents, the desired product was obtained in 78% yield (34 mg, 0.09 mmol) as a brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.54 (s, 1H), 7.34 – 7.15 (m, 5H), 6.74 (s, 1H), 5.09 (s, 1H), 4.73 (dd, J = 9.5, 1.3 Hz, 1H), 4.58 (dd, J = 9.5, 6.4 Hz, 1H), 3.43 (s, 3H), 3.34 (s, 3H), 3.30 (dd, J = 7.3, 6.3 Hz, 1H), 2.52 (s, 3H), 2.42 (dd, J = 7.3, 6.4 Hz, 1H), 2.34 (s, 3H), 1.29 (d, J = 6.3 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 171.96, 168.64, 141.24, 136.27, 130.78, 130.51, 128.91, 127.04, 126.83, 123.38, 121.33, 118.47, 101.30, 77.00, 73.04, 56.72, 52.89, 51.23, 29.12, 21.06, 19.08, 16.63. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{24}\text{H}_{28}\text{O}_3\text{N}$] $^+$: 378.2064, found: 378.2075.

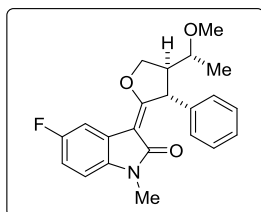
(E)-5-methoxy-3-((3R,4S)-4-((R)-1-methoxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)-1-



methylindolin-2-one (4g) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1f** (47 mg, 0.14 mmol, 83% (E)-isomer) as starting material. After the purification done by silica gel column

chromatography with EtOAc / petroleum ether = 1/3 (R_f = 0.22) as eluents, the desired product was obtained in 64% yield (33 mg, 0.09 mmol) as a brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.44 (d, J = 2.5 Hz, 1H), 7.43 – 7.41 (m, 1H), 7.33 – 7.23 (m, 4H), 7.23 – 7.18 (m, 1H), 6.75 (dd, J = 8.4, 2.5 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 5.06 (s, 1H), 4.73 (dd, J = 9.5, 1.5 Hz, 1H), 4.60 (dd, J = 9.5, 6.3 Hz, 1H), 3.86 (s, 3H), 3.34 (s, 3H), 3.31 (dd, J = 7.4, 6.1 Hz, 1H), 3.14 (s, 3H), 2.44 (dd, J = 7.4, 6.3 Hz, 1H), 1.28 (d, J = 6.1 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.65, 167.94, 155.49, 141.12, 134.78, 128.95, 127.06, 126.91, 123.69, 111.37, 109.52, 107.31, 101.58, 76.95, 73.27, 56.73, 56.18, 52.89, 51.18, 25.96, 16.62. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}$] $^+$: 380.1856, found: 380.1867.

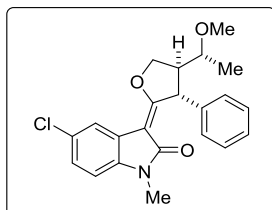
(E)-5-fluoro-3-((3R,4S)-4-((R)-1-methoxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)-1-



methylinolin-2-one (4h) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1g** (39 mg, 0.12 mmol, 77% (E)-isomer) as starting material. After the purification done by silica gel column chromatography

with EtOAc / petroleum ether = 1/3 (R_f = 0.30) as eluents, the desired product was obtained in 63% yield (27 mg, 0.07 mmol) as a brown oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.52 (dd, J = 8.6, 2.6 Hz, 1H), 7.35 – 7.16 (m, 5H), 6.92 – 6.82 (m, 1H), 6.67 (dd, J = 8.6, 4.2 Hz, 1H), 5.04 (s, 1H), 4.75 (dd, J = 9.6, 1.6 Hz, 1H), 4.63 (dd, J = 9.6, 6.4 Hz, 1H), 3.34 (s, 4H), 3.15 (s, 3H), 2.50 – 2.41 (m, 1H), 1.27 (d, J = 6.1 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 173.69, 167.87, 159.01 (d, J = 236.5 Hz), 140.91, 136.63, 129.02, 127.05, 127.03, 123.83 (d, J = 9.9 Hz), 112.04 (d, J = 24.0 Hz), 110.10 (d, J = 26.1 Hz), 107.20 (d, J = 8.6 Hz), 101.08, 76.99, 73.56, 56.76, 52.83, 51.44, 26.01, 16.58. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{22}\text{H}_{24}\text{O}_3\text{N}$] $^+$: 350.1751, found: 350.1757.

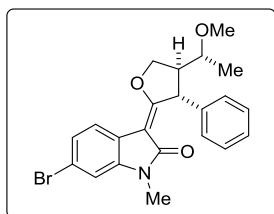
(E)-5-chloro-3-((3R,4S)-4-((R)-1-methoxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)-1-



methylinolin-2-one (4i) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1h** (37 mg, 0.11 mmol, 77% (E)-isomer) as starting material. After the purification done by silica gel column

chromatography with EtOAc / petroleum ether = 1/3 (R_f = 0.28) as eluents, the desired product was obtained in 62% yield (25 mg, 0.07 mmol) as a yellow oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.77 (d, J = 2.0 Hz, 1H), 7.34 – 7.16 (m, 5H), 7.14 (dd, J = 8.2, 2.0 Hz, 1H), 6.68 (d, J = 8.2 Hz, 1H), 5.03 (s, 1H), 4.76 (dd, J = 9.6, 1.5 Hz, 1H), 4.64 (dd, J = 9.6, 6.4 Hz, 1H), 3.36 – 3.29 (m, 4H), 3.15 (s, 3H), 2.46 (t, J = 6.4 Hz, 1H), 1.27 (d, J = 6.1 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 174.19, 167.94, 141.10, 139.26, 129.29, 127.30, 127.15, 125.93, 124.43, 122.80, 108.15, 100.69, 77.26, 77.17, 73.89, 57.04, 53.05, 51.79, 26.25, 16.82. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{22}\text{H}_{23}\text{O}_3\text{NCl}$] $^+$: 384.1361, found: 384.1379.

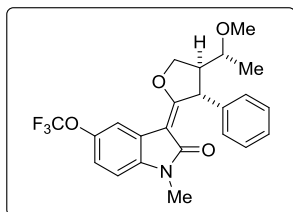
(E)-6-bromo-3-((3R,4S)-4-((R)-1-methoxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)-1-methylindolin-2-one (4j)



methylinolin-2-one (4j) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1i** (42 mg, 0.11 mmol, 76% (E)-isomer) as starting material. After the purification done by silica gel column

chromatography with EtOAc / petroleum ether = 1/3 (R_f = 0.33) as eluents, the desired product was obtained in 70% yield (32 mg, 0.07 mmol) as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.62 (d, J = 7.9 Hz, 1H), 7.40 – 7.19 (m, 6H), 7.17 (d, J = 7.9 Hz, 1H), 6.92 (s, 1H), 5.01 (s, 1H), 4.73 (d, J = 9.5 Hz, 1H), 4.68 – 4.57 (m, 1H), 3.33 (s, 4H), 3.14 (s, 3H), 2.45 (s, 1H), 1.27 (d, J = 5.7 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 173.70, 168.08, 141.97, 141.14, 129.28, 127.35, 127.31, 124.51, 123.79, 121.98, 119.68, 110.79, 100.67, 77.24, 73.78, 57.02, 53.10, 51.76, 26.23, 16.85. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{22}\text{H}_{23}\text{O}_3\text{NBr}$] $^+$: 428.0856, found: 428.0866.

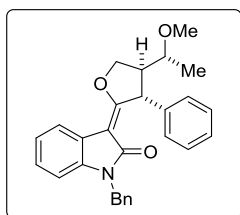
(E)-3-((3R,4S)-4-((R)-1-methoxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)-1-methyl-5-(trifluoromethoxy)indolin-2-one (4k)



(trifluoromethoxy)indolin-2-one (4k) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1j** (35 mg, 0.09 mmol, 80% (E)-isomer) as starting material. After the purification done by silica gel column

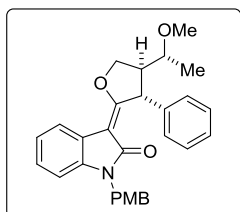
chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.11) as eluents, the desired product was obtained in 71% yield (27 mg, 0.06 mmol) as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.65 (s, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.15 (m, 3H), 7.05 (d, J = 8.4 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 5.04 (s, 1H), 4.77 (dd, J = 9.6, 1.6 Hz, 1H), 4.65 (dd, J = 9.6, 6.5 Hz, 1H), 3.34 (s, 4H), 3.16 (s, 3H), 2.46 (t, J = 6.5 Hz, 1H), 1.27 (d, J = 6.1 Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 174.27, 167.88, 144.29, 140.82, 139.03, 129.05, 127.06, 123.76, 120.91 (d, J = 255.9 Hz), 118.92, 116.15, 107.17, 100.61, 76.97, 73.80, 56.77, 52.80, 51.60, 32.77, 26.04, 16.57. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{23}\text{H}_{23}\text{O}_4\text{NF}_3$] $^+$: 434.1574, found: 434.1573.

(E)-1-benzyl-3-((3R,4S)-4-((R)-1-methoxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)



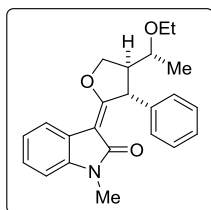
indolin-2-one (4l) was prepared according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1k** (39 mg, 0.10 mmol, 76% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.29) as eluents, the desired product was obtained in 69% yield (29 mg, 0.07 mmol) as a yellow oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.81 (d, J = 6.4 Hz, 1H), 7.37 – 7.13 (m, 11H), 7.12 – 7.05 (m, 1H), 7.05 – 7.00 (m, 1H), 6.68 (d, J = 7.4 Hz, 1H), 5.10 (s, 1H), 5.01 (d, J = 15.8 Hz, 1H), 4.81 – 4.74 (m, 2H), 4.63 (dd, J = 9.5, 6.6 Hz, 1H), 3.36 (s, 4H), 2.47 (t, J = 6.6 Hz, 1H), 1.31 (d, J = 6.1 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 172.95, 167.98, 141.13, 139.75, 137.01, 128.95, 128.65, 127.33, 127.27, 127.10, 126.92, 126.09, 122.96, 122.60, 121.62, 108.20, 101.07, 76.91, 73.35, 56.74, 53.03, 51.30, 43.43, 16.72. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{26}\text{H}_{28}\text{O}_3\text{N}]^+$: 426.2064, found: 426.2076.

(E)-1-(4-methoxybenzyl)-3-((3R,4S)-4-((R)-1-methoxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)indolin-2-one (4m)



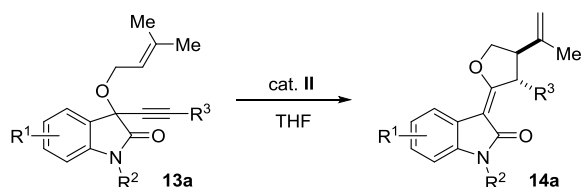
ylidene)indolin-2-one (4m) was prepared from according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1l** (25 mg, 0.06 mmol, 73% (E)-isomer) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/3 (R_f = 0.28) as eluents, the desired product was obtained in 60% yield (16 mg, 0.04 mmol) as a brown oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.79 (d, J = 7.5 Hz, 1H), 7.36 – 7.25 (m, 4H), 7.25 – 7.20 (m, 1H), 7.14 (d, J = 8.6 Hz, 2H), 7.07 (td, J = 7.5, 1.2 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.77 (d, J = 8.6 Hz, 2H), 6.69 (d, J = 7.6 Hz, 1H), 5.09 (s, 1H), 4.94 (d, J = 15.6 Hz, 1H), 4.75 (dd, J = 9.6, 1.5 Hz, 1H), 4.70 (d, J = 15.6 Hz, 1H), 4.61 (dd, J = 9.6, 6.6 Hz, 1H), 3.74 (s, 3H), 3.36 (s, 4H), 2.46 (t, J = 6.6 Hz, 1H), 1.31 (d, J = 6.1 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 173.09, 168.20, 159.15, 141.40, 140.04, 129.42, 129.21, 128.95, 127.37, 127.17, 126.33, 123.23, 122.85, 121.82, 114.34, 108.46, 101.40, 77.16, 73.57, 57.00, 55.62, 53.30, 51.52, 43.14, 16.99. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{29}\text{H}_{30}\text{O}_4\text{N}]^+$: 456.2169, found: 456.2179.

(E)-3-(-4-(-1-ethoxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)-1-methylindolin-2-one (4n)



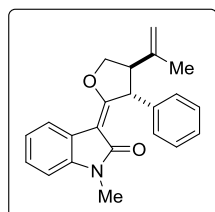
was prepared from according to the general procedure for the gold catalyzed *O*-migration reaction with MeOH as nucleophile, by using **1l** (30 mg, 0.09 mmol, 82% (*E*)-isomer) as starting material. After the purification done by silica gel column chromatography with Et₂O / petroleum ether = 1/2 (*R_f* = 0.25) as eluents, the desired product was obtained in 76% yield (26 mg, 0.07 mmol) as a yellow oil. **¹H NMR** (500 MHz, CDCl₃) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 5.06 (s, 1H), 4.74 (d, *J* = 9.5 Hz, 1H), 4.59 (dd, *J* = 9.4, 6.5 Hz, 1H), 3.66 – 3.57 (m, 1H), 3.43 – 3.32 (m, 2H), 3.17 (s, 3H), 2.43 (t, *J* = 6.5 Hz, 1H), 1.29 (d, *J* = 6.1 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 172.70, 168.07, 141.01, 140.54, 128.95, 127.06, 126.91, 126.12, 122.78, 122.48, 121.55, 107.17, 101.16, 75.23, 73.31, 64.51, 52.98, 51.23, 25.89, 17.47, 15.55. **HRMS** (ESI): Calcd for (M + H)⁺ [C₂₃H₂₆O₃N]⁺: 364.1907, found: 364.1902.

Gold catalyzed O-migration reaction



To a THF (0.6 ml) solution of the 1,6-enyne (0.1 mmol) was added a solution of cat. **II** (3.9 mg, 5 μ mol) in THF (0.4 ml). After warming to room temperature, the reaction mixture was stirred overnight and TLC showed full conversion of the starting material. The reaction mixture was passed through a short pad of silica gel (Et₂O as the eluent). The resulting solution was concentrated under reduced pressure, followed by silica gel column chromatography (EtOAc / petroleum ether as the eluent) to obtain the desired product.

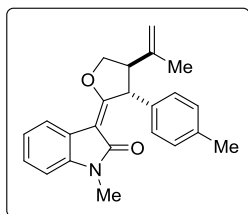
(E)-1-methyl-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)indolin-2-



one (14a) was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13a** (49 mg, 0.15 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.26) as eluents, the desired product

was obtained in 95% yield (47 mg, 0.14 mmol) as a brown oil. The recrystallization was performed from DCM and petroleum ether. **¹H NMR** (500 MHz, cdcl₃) δ 7.79 (d, J = 7.4 Hz, 1H), 7.36 – 7.13 (m, 6H), 7.06 (t, J = 7.6 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 5.15 (s, 1H), 4.83 (s, 1H), 4.81 (s, 1H), 4.69 (dd, J = 9.4, 6.1 Hz, 1H), 4.56 (d, J = 9.4 Hz, 1H), 3.16 (s, 3H), 2.97 (d, J = 6.1 Hz, 1H), 1.80 (s, 3H). **¹³C NMR** (126 MHz, cdcl₃) δ 171.96, 168.05, 144.82, 140.85, 140.70, 129.00, 127.05, 127.03, 126.30, 122.69, 122.56, 121.59, 111.65, 107.23, 101.76, 75.39, 53.84, 53.46, 25.89, 20.77. **HRMS** (ESI): Calcd for (M + H)⁺ [C₂₂H₂₂O₂N]⁺: 332.1645, found: 332.1660.

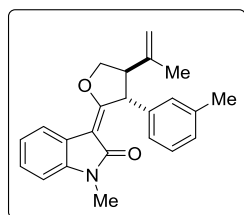
(E)-1-methyl-3-((3S,4S)-4-(prop-1-en-2-yl)-3-(p-tolyl)dihydrofuran-2(3H)-ylidene)indolin-



2-one (14b) was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13b** (37 mg, 0.11 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.25) as eluents,

the desired product was obtained in 83% yield (31 mg, 0.09 mmol) as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.79 (d, J = 7.6 Hz, 1H), 7.19 (td, J = 7.6, 1.2 Hz, 1H), 7.15 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 7.06 (td, J = 7.6, 1.2 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 5.10 (s, 1H), 4.81 (s, 1H), 4.80 (s, 1H), 4.69 (dd, J = 9.4, 6.0 Hz, 1H), 4.55 (dd, J = 9.4, 1.1 Hz, 1H), 3.17 (s, 3H), 2.96 (d, J = 6.0 Hz, 1H), 2.29 (s, 3H), 1.79 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.26, 168.06, 144.90, 140.67, 137.85, 136.62, 129.69, 126.89, 126.22, 122.74, 122.52, 121.55, 111.54, 107.20, 101.62, 75.43, 53.54, 53.52, 25.89, 21.18, 20.77. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{23}\text{H}_{24}\text{O}_2\text{N}$] $^+$: 346.1802, found: 346.1804.

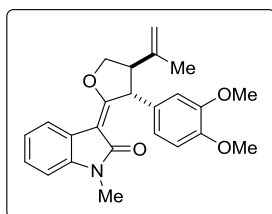
(E)-1-methyl-3-((3S,4S)-4-(prop-1-en-2-yl)-3-(m-tolyl)dihydrofuran-2(3H)-ylidene)indolin-



2-one (14c) was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13c** (18 mg, 0.05 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.25) as eluents,

the desired product was obtained in 77% yield (14 mg, 0.04 mmol) as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.80 (d, J = 7.5 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.11 – 7.00 (m, 4H), 6.80 (d, J = 7.7 Hz, 1H), 5.12 (s, 1H), 4.83 (s, 1H), 4.81 (s, J = 1.2 Hz, 1H), 4.69 (dd, J = 9.4, 6.0 Hz, 1H), 4.55 (dd, J = 9.4, 0.8 Hz, 1H), 3.18 (s, 3H), 2.96 (d, J = 6.0 Hz, 1H), 2.32 (s, 3H), 1.80 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.10, 168.11, 144.91, 140.75, 140.71, 138.62, 128.85, 127.93, 127.67, 126.26, 124.04, 122.77, 122.57, 121.57, 111.58, 107.23, 101.75, 75.35, 53.80, 53.56, 25.92, 21.70, 20.82. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{23}\text{H}_{24}\text{O}_2\text{N}$] $^+$: 346.1802, found: 346.1815.

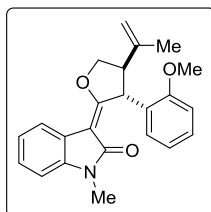
(E)-3-((3S,4S)-3-(3,4-dimethoxyphenyl)-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)-1-



methylinolin-2-one (14d) was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13d** (41 mg, 0.10 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/1 (R_f =

0.55) as eluents, the desired product was obtained in 56% yield (23 mg, 0.06 mmol) as a brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.79 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.83 (s, 1H), 6.81 (d, J = 7.6 Hz, 1H), 6.79 – 6.71 (m, 2H), 5.11 (s, 1H), 4.83 (s, 1H), 4.81 (s, 1H), 4.70 (dd, J = 9.4, 6.0 Hz, 1H), 4.55 (d, J = 9.4 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.19 (s, 3H), 2.97 (d, J = 6.0 Hz, 1H), 1.80 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.07, 168.10, 149.38, 148.20, 144.83, 140.67, 133.41, 126.28, 122.71, 122.56, 121.58, 118.65, 111.63, 111.48, 110.83, 107.24, 101.72, 75.48, 56.09, 55.98, 53.56, 53.37, 25.91, 20.80. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{24}\text{H}_{26}\text{O}_4\text{N}$] $^+$: 392.1856, found: 392.1846.

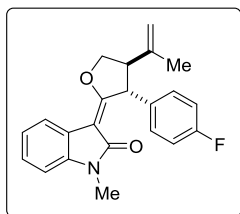
(E)-3-((3S,4S)-3-(2-methoxyphenyl)-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)-1-



methylinolin-2-one (14e) was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13e** (60 mg, 0.17 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.31) as eluents,

the desired product was obtained in 46% yield (28 mg, 0.08 mmol) as a brown oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.82 (d, J = 7.5 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.08 (td, J = 7.5, 0.9 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.80 (d, J = 7.5 Hz, 2H), 5.36 (s, 1H), 4.83 (s, 1H), 4.80 (s, 1H), 4.62 – 4.54 (m, 2H), 3.93 (s, 3H), 3.17 (s, 3H), 2.92 – 2.83 (m, 1H), 1.87 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.63, 168.06, 157.02, 145.33, 140.64, 128.82, 128.36, 126.56, 126.11, 122.82, 122.46, 121.52, 120.50, 110.96, 110.83, 107.15, 101.90, 75.44, 55.57, 51.73, 49.24, 25.86, 21.24. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{23}\text{H}_{24}\text{O}_3\text{N}$] $^+$: 362.1751, found: 362.1757.

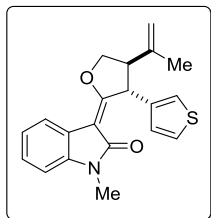
(E)-3-(((3S,4S)-3-(4-fluorophenyl)-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)-1-



methylinolin-2-one (14f) was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13f** (31 mg, 0.09 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.33) as eluents,

the desired product was obtained in 78% yield (24 mg, 0.07 mmol) as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.79 (d, J = 7.6 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.07 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 8.6 Hz, 1H), 6.98 (d, J = 8.6 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 5.12 (s, 1H), 4.86 – 4.80 (m, 2H), 4.68 (dd, J = 9.5, 6.0 Hz, 1H), 4.57 (dd, J = 9.5, 1.0 Hz, 1H), 3.18 (s, 3H), 2.96 (d, J = 6.0 Hz, 1H), 1.80 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 171.61, 168.02, 161.86 (d, J = 245.4 Hz), 144.58, 140.72, 136.63 (d, J = 3.4 Hz), 128.60 (d, J = 8.0 Hz), 126.45, 122.62, 122.55, 121.67, 115.85 (d, J = 21.5 Hz), 111.84, 107.32, 101.83, 75.36, 53.48, 53.07, 25.91, 20.72. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{22}\text{H}_{21}\text{O}_2\text{NF}]^+$: 350.1551, found: 350.1554.

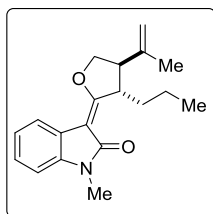
(E)-1-methyl-3-(((3R,4R)-4-(prop-1-en-2-yl)-3-(thiophen-3-yl)dihydrofuran-2(3H)-ylidene)indolin-2-one (14g)



was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13g** (35 mg, 0.10 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/6 (R_f = 0.39) as eluents, the desired product was obtained in 67% yield (23 mg, 0.07 mmol) as a yellow oil.

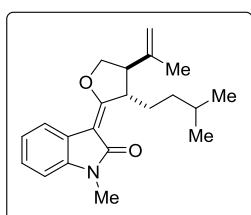
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (d, J = 7.6 Hz, 1H), 7.28 (dd, J = 4.9, 3.0 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.15 – 7.04 (m, 3H), 6.85 (d, J = 7.6 Hz, 1H), 5.25 (s, 1H), 4.83 (s, 2H), 4.75 (dd, J = 9.4, 6.0 Hz, 1H), 4.61 (d, J = 9.4 Hz, 1H), 3.24 (s, 3H), 3.06 (d, J = 6.0 Hz, 1H), 1.80 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.24, 168.74, 144.33, 140.06, 139.64, 127.04, 126.41, 122.64, 122.21, 121.20, 111.86, 107.72, 101.41, 77.36, 76.15, 52.14, 49.22, 26.28, 20.89. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{20}\text{H}_{20}\text{O}_2\text{NS}]^+$: 338.1209, found: 338.1219.

(E)-1-methyl-3-((3R,4S)-4-(prop-1-en-2-yl)-3-propyldihydrofuran-2(3H)-ylidene)indolin-2-



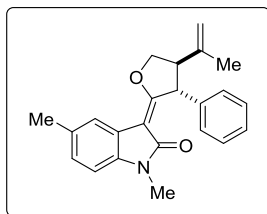
one (14h) was prepared according to the general procedure for the gold catalyzed O-migration reaction with 10 mol% catalyst loading, by using **13h** (18 mg, 0.06 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.29) as eluents, the desired product was obtained in 50% yield (9 mg, 0.03 mmol) as a yellow oil. ^1H NMR (500 MHz, cdcl_3) δ 7.68 (d, J = 7.6 Hz, 1H), 7.17 (td, J = 7.6, 0.9 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 4.75 (s, 1H), 4.72 (s, 1H), 4.63 (dd, J = 9.4, 6.2 Hz, 1H), 4.52 (d, J = 9.4 Hz, 1H), 3.85 (dd, J = 10.3, 3.2 Hz, 1H), 3.28 (s, 3H), 2.88 (d, J = 6.2 Hz, 1H), 1.90 – 1.80 (m, 1H), 1.70 (s, 2H), 1.61 – 1.55 (m, 1H), 1.55 – 1.45 (m, 1H), 1.01 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, cdcl_3) δ 176.05, 168.58, 145.38, 140.26, 125.83, 123.03, 122.27, 121.57, 110.98, 107.17, 100.16, 75.90, 48.47, 48.15, 34.61, 25.92, 21.45, 20.60, 13.95. HRMS (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}$] $^+$: 298.1802, found: 298.1805.

(E)-3-((3R,4S)-3-isopentyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)-1-methylindolin-



2-one (14i) was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13i** (35 mg, 0.11 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.31) as eluents, the desired product was obtained in 36% yield (12 mg, 0.04 mmol) as a yellow oil. ^1H NMR (500 MHz, cdcl_3) δ 7.45 (dd, J = 7.6, 0.7 Hz, 1H), 7.31 (td, J = 7.6, 1.2 Hz, 1H), 7.09 (td, J = 7.6, 0.7 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 5.34 (t, J = 7.2 Hz, 1H), 4.31 (dd, J = 10.5, 7.2 Hz, 1H), 4.24 (dd, J = 10.5, 7.2 Hz, 1H), 3.18 (s, 3H), 2.24 (td, J = 7.4, 1.6 Hz, 2H), 1.69 (s, 3H), 1.67 – 1.61 (m, 2H), 1.41 (td, J = 7.4 Hz, 2H), 0.85 (dd, J = 6.6, 2.3 Hz, 7H). ^{13}C NMR (126 MHz, cdcl_3) δ 172.42, 143.29, 137.98, 130.23, 128.68, 124.84, 123.38, 120.62, 108.58, 89.47, 74.84, 73.90, 62.15, 37.33, 27.44, 26.45, 25.91, 22.22, 18.13, 17.12. HRMS (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{21}\text{H}_{27}\text{O}_2\text{NNa}$] $^+$: 348.1934, found: 348.1945.

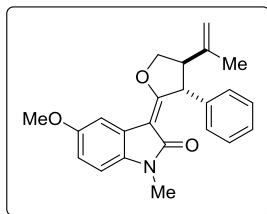
(E)-1,5-dimethyl-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-



ylidene)indolin-2-one (14j) was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13j** (24 mg, 0.07 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f =

0.27) as eluents, the desired product was obtained in 76% yield (18 mg, 0.05 mmol) as a brown oil. **^1H NMR** (400 MHz, CDCl_3) δ 7.66 (s, 1H), 7.35 – 7.23 (m, 5H), 7.03 (dd, J = 7.8, 0.8 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 5.18 (s, 1H), 4.86 (s, 1H), 4.84 (s, 1H), 4.72 (dd, J = 9.6, 6.0 Hz, 1H), 4.60 (dd, J = 9.5, 1.0 Hz, 1H), 3.18 (s, 3H), 3.00 (d, J = 6.0 Hz, 1H), 2.43 (s, 3H), 1.84 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 171.64, 168.10, 144.86, 140.89, 138.54, 130.97, 128.99, 127.02, 126.65, 123.33, 122.68, 111.63, 106.97, 101.86, 75.29, 53.76, 53.43, 25.93, 21.42, 20.79. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{23}\text{H}_{24}\text{O}_2\text{N}$] $^+$: 346.1802, found: 346.1812.

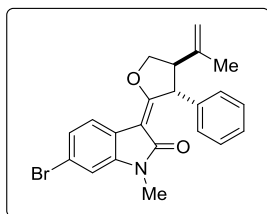
(E)-5-methoxy-1-methyl-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-



ylidene)indolin-2-one (14k) was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13k** (27 mg, 0.07 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f =

0.27) as eluents, the desired product was obtained in 66% yield (18 mg, 0.05 mmol) as a yellow oil. **^1H NMR** (300 MHz, CDCl_3) δ 7.44 (d, J = 2.5 Hz, 1H), 7.37 – 7.16 (m, 5H), 6.76 (dd, J = 8.4, 2.5 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 5.15 (s, 1H), 4.83 (s, 1H), 4.81 (s, 1H), 4.70 (dd, J = 9.5, 6.0 Hz, 1H), 4.57 (d, J = 9.5 Hz, 1H), 3.86 (s, 3H), 3.14 (s, 3H), 2.98 (d, J = 6.0 Hz, 1H), 1.80 (s, 3H). **^{13}C NMR** (75 MHz, CDCl_3) δ 172.10, 167.96, 155.49, 144.80, 140.82, 134.85, 129.01, 127.06, 127.02, 123.59, 111.67, 111.35, 109.61, 107.39, 102.12, 75.44, 56.17, 53.81, 53.39, 25.97, 20.77. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{23}\text{H}_{23}\text{O}_3\text{NNa}$] $^+$: 384.1570, found: 384.1579.

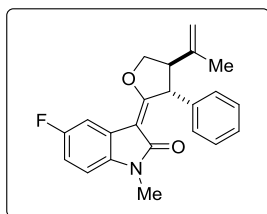
(E)-6-bromo-1-methyl-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)indolin-2-one (14l) was prepared according to the general



procedure for the gold catalyzed O-migration reaction, by using **13l** (27 mg, 0.07 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f =

0.54) as eluents, the desired product was obtained in 69% yield (19 mg, 0.05 mmol) as a brown oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.59 (d, J = 8.0 Hz, 1H), 7.40 – 7.17 (m, 6H), 6.90 (d, J = 1.7 Hz, 1H), 5.08 (s, 1H), 4.79 (s, 2H), 4.68 (dd, J = 9.5, 6.0 Hz, 1H), 4.55 (dd, J = 9.5, 1.1 Hz, 1H), 3.11 (s, 3H), 2.95 (d, J = 6.0 Hz, 1H), 1.77 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 172.76, 167.84, 144.64, 141.78, 140.50, 129.07, 127.19, 126.99, 124.31, 123.56, 121.55, 119.61, 111.77, 110.62, 101.02, 75.69, 54.00, 53.34, 25.99, 20.76. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{22}\text{H}_{21}\text{O}_2\text{NBr}]^+$: 410.0750, found: 410.1757.

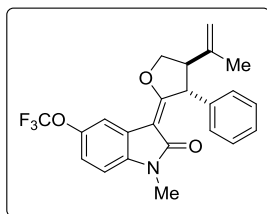
(E)-5-fluoro-1-methyl-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)indolin-2-one (14m) was prepared according to the general



procedure for the gold catalyzed O-migration reaction, by using **13m** (31 mg, 0.09 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f =

0.33) as eluents, the desired product was obtained in 62% yield (19 mg, 0.05 mmol) as a yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (dd, J = 8.9, 2.6 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.28 – 7.19 (m, 3H), 6.89 (td, J = 8.9, 2.6 Hz, 1H), 6.68 (dd, J = 8.9, 4.2 Hz, 1H), 5.14 (s, 1H), 4.83 (s, 2H), 4.72 (dd, J = 9.5, 6.1 Hz, 1H), 4.60 (dd, J = 9.5, 1.0 Hz, 1H), 3.16 (s, 3H), 2.99 (d, J = 6.1 Hz, 1H), 1.81 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.01, 167.86, 158.99 (d, J = 236.7 Hz), 144.62, 140.51, 136.69, 129.07, 127.17, 126.98, 123.64 (d, J = 10.0 Hz), 112.22 (d, J = 24.0 Hz), 111.75, 101.68, 110.13 (d, J = 26.0 Hz), 107.31 (d, J = 8.5 Hz), 75.73, 53.94, 53.33, 26.03, 20.76. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{22}\text{H}_{21}\text{O}_2\text{NF}]^+$: 350.1551, found: 350.1558.

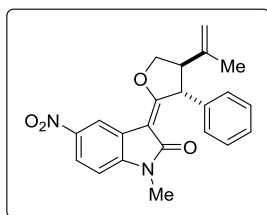
(E)-1-methyl-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)-5-(trifluoromethoxy)indolin-2-one (14n) was prepared according to the



general procedure for the gold catalyzed O-migration reaction, by using **13n** (28 mg, 0.07 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/4

(R_f = 0.38) as eluents, the desired product was obtained in 74% yield (21 mg, 0.05 mmol) as a brown oil. **^1H NMR** (300 MHz, CDCl_3) δ 7.66 (d, J = 1.5 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.28 – 7.17 (m, 3H), 7.06 (dd, J = 8.4, 1.3 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 5.14 (s, 1H), 4.84 (s, 2H), 4.75 (dd, J = 9.6, 6.1 Hz, 1H), 4.62 (dd, J = 9.6, 1.1 Hz, 1H), 3.17 (s, 3H), 3.00 (d, J = 5.9 Hz, 1H), 1.81 (s, 3H). **^{13}C NMR** (75 MHz, CDCl_3) δ 173.57, 167.89, 144.55, 144.27, 140.42, 139.12, 129.10, 127.23, 127.00, 124.68 (d, J = 317.8 Hz), 123.58, 119.13, 116.20, 111.83, 107.28, 101.21, 75.94, 54.07, 53.30, 26.04, 20.77. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{23}\text{H}_{21}\text{O}_3\text{NF}_3$] $^+$: 416.1468, found: 416.1460.

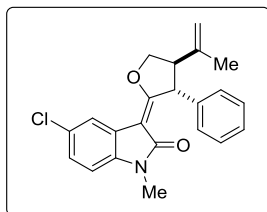
(E)-1-methyl-5-nitro-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)indolin-2-one (14o) was prepared according to the general



procedure for the gold catalyzed O-migration reaction, by using **13o** (28 mg, 0.07 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f =

0.18) as eluents, the desired product was obtained in 64% yield (18 mg, 0.05 mmol) as a yellow oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.66 (d, J = 2.3 Hz, 1H), 8.20 (dd, J = 8.3, 2.3 Hz, 1H), 7.43 – 7.31 (m, 2H), 7.31 - 7.18 (m, 3H), 6.86 (d, J = 8.6 Hz, 1H), 5.15 (s, 1H), 4.98 – 4.78 (m, 3H), 4.74 (dd, J = 9.6, 1.0 Hz, 1H), 3.26 (s, 3H), 3.06 (d, J = 5.8 Hz, 1H), 1.84 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 175.30, 168.02, 145.37, 144.31, 142.88, 139.93, 129.19, 127.42, 126.96, 123.20, 122.86, 117.89, 112.00, 106.54, 100.04, 76.56, 54.48, 53.16, 26.32, 20.73. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{22}\text{H}_{20}\text{O}_4\text{N}_2$] $^+$: 377.1496, found: 377.1503.

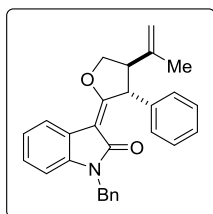
(E)-5-chloro-1-methyl-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)indolin-2-one (14p) was prepared according to the general



procedure for the gold catalyzed O-migration reaction, by using **13p** (31 mg, 0.08 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/5 (R_f =

0.29) as eluents, the desired product was obtained in 65% yield (20 mg, 0.05 mmol) as a yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, J = 2.1 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.28 – 7.21 (m, 3H), 7.17 (dd, J = 8.3, 2.1 Hz, 1H), 6.71 (d, J = 8.3 Hz, 1H), 5.14 (s, 1H), 4.84 (s, 2H), 4.74 (dd, J = 9.5, 6.0 Hz, 1H), 4.62 (dd, J = 9.5, 1.1 Hz, 1H), 3.16 (s, 3H), 3.00 (d, J = 6.0 Hz, 1H), 1.82 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.24, 167.67, 144.59, 140.44, 139.07, 129.08, 127.20, 126.98, 126.92, 125.84, 123.99, 122.56, 111.79, 107.99, 101.05, 75.80, 54.02, 53.31, 26.01, 20.76. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{22}\text{H}_{21}\text{O}_2\text{NCl}$] $^+$: 366.1255, found: 366.1267.

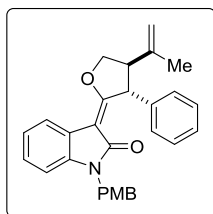
(E)-1-benzyl-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)indolin-2-



one (14q) was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13q** (25 mg, 0.06 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.61) as eluents, the desired product

was obtained in 96% yield (24 mg, 0.06 mmol) as a yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.83 (dd, J = 7.2, 1.1 Hz, 1H), 7.37 – 7.16 (m, 10H), 7.14 – 7.00 (m, 2H), 6.71 (d, J = 7.2 Hz, 1H), 5.20 (s, 1H), 5.00 (d, J = 15.9 Hz, 1H), 4.87 (s, 1H), 4.86 (s, 1H), 4.80 (d, J = 15.9 Hz, 1H), 4.73 (dd, J = 9.5, 6.0 Hz, 1H), 4.61 (dd, J = 9.5, 1.2 Hz, 1H), 3.02 (d, J = 6.0 Hz, 1H), 1.85 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.87, 168.26, 144.68, 140.73, 139.67, 136.75, 129.02, 128.70, 128.41, 127.36, 127.31, 127.11, 127.05, 126.28, 122.84, 122.69, 121.88, 111.79, 108.44, 101.64, 75.62, 54.09, 53.55, 43.59, 20.84. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{28}\text{H}_{26}\text{O}_2\text{N}$] $^+$: 408.1958, found: 408.1958.

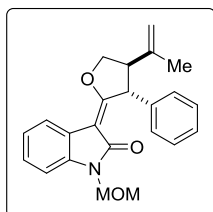
(E)-1-(4-methoxybenzyl)-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)indolin-2-one (14r) was prepared according to the general procedure



for the gold catalyzed O-migration reaction, by using **13r** (33 mg, 0.08 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/4 (R_f = 0.30) as eluents,

the desired product was obtained in 83% yield (27 mg, 0.06 mmol) as a brown oil. **^1H NMR** (400 MHz, CDCl_3) δ 7.82 (dd, J = 7.5, 0.9 Hz, 1H), 7.43 – 7.20 (m, 5H), 7.16 (d, J = 8.6 Hz, 2H), 7.13 – 6.98 (m, 2H), 6.79 (d, J = 8.6 Hz, 2H), 6.71 (d, J = 7.5 Hz, 1H), 5.20 (s, 1H), 4.94 (d, J = 15.6 Hz, 1H), 4.87 (s, 1H), 4.85 (s, 1H), 4.77 – 4.67 (m, 2H), 4.59 (dd, J = 9.5, 1.0 Hz, 1H), 3.75 (s, 3H), 3.01 (d, J = 5.8 Hz, 1H), 1.84 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 172.24, 167.95, 158.84, 144.73, 140.83, 139.82, 129.03, 128.99, 128.68, 127.03, 127.01, 126.20, 122.84, 122.61, 121.59, 114.04, 111.72, 108.25, 101.63, 75.42, 55.33, 53.91, 53.51, 42.89, 20.85. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ [$\text{C}_{29}\text{H}_{28}\text{O}_3\text{N}$] $^+$: 438.2064, found: 438.2065.

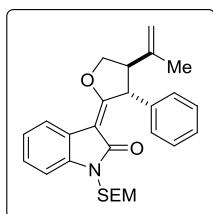
(E)-1-(methoxymethyl)-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)indolin-2-one (14s) was prepared according to the general procedure



for the gold catalyzed O-migration reaction, by using **13s** (39 mg, 0.11 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/7 (R_f = 0.37) as eluents,

the desired product was obtained in 97% yield (38 mg, 0.10 mmol) as a brown oil. **^1H NMR** (500 MHz, cdcl_3) δ 7.83 (d, J = 6.9 Hz, 1H), 7.35 – 7.17 (m, 6H), 7.11 (td, J = 7.7, 0.9 Hz, 1H), 7.01 (d, J = 7.7 Hz, 1H), 5.15 (d, J = 10.9 Hz, 1H), 5.14 (s, 1H), 5.04 (d, J = 10.9 Hz, 1H), 4.85 (s, 1H), 4.84 (s, 1H), 4.71 (dd, J = 9.5, 5.7 Hz, 1H), 4.59 (dd, J = 9.5, 1.2 Hz, 1H), 3.25 (s, 3H), 3.00 (d, J = 5.7 Hz, 1H), 1.82 (s, 3H). **^{13}C NMR** (126 MHz, cdcl_3) δ 172.76, 168.38, 144.69, 140.66, 139.08, 129.00, 128.38, 127.08, 126.99, 126.47, 122.72, 122.25, 111.75, 108.64, 101.50, 75.58, 71.13, 56.16, 54.04, 53.51, 20.78. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{23}\text{H}_{23}\text{O}_3\text{NNa}$] $^+$: 384.1570, found: 384.1584.

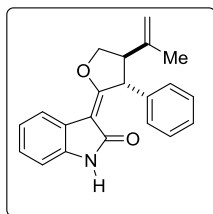
(E)-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)-1-((2-(trimethylsilyl)ethoxy)methyl)indolin-2-one (14t) was prepared according



to the general procedure for the gold catalyzed O-migration reaction, by using **13t** (22 mg, 0.05 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/10 (R_f =

0.42) as eluents, the desired product was obtained in 51% yield (11 mg, 0.03 mmol) as a yellow oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.89 (d, J = 7.6 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.33 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 5.9 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 5.24 (d, J = 11.0 Hz, 1H), 5.23 (s, 1H), 5.16 (d, J = 11.0 Hz, 1H), 4.92 (s, 1H), 4.91 (d, J = 1.1 Hz, 1H), 4.78 (dd, J = 9.4, 6.2 Hz, 1H), 4.66 (d, J = 9.4 Hz, 1H), 3.60 – 3.48 (m, 2H), 3.08 (d, J = 6.2 Hz, 1H), 1.89 (s, 3H), 0.92 (dd, J = 8.2, 8.0 Hz, 2H), -0.03 (s, 9H). **^{13}C NMR** (126 MHz, CDCl_3) δ 172.57, 168.23, 144.76, 140.68, 139.27, 128.99, 127.07, 127.02, 126.43, 122.73, 122.65, 122.11, 111.73, 108.81, 101.57, 75.54, 69.14, 65.74, 53.93, 53.48, 20.76, 17.93, -1.35. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{27}\text{H}_{33}\text{O}_3\text{NSiNa}$] $^+$: 470.2122, found: 470.2137.

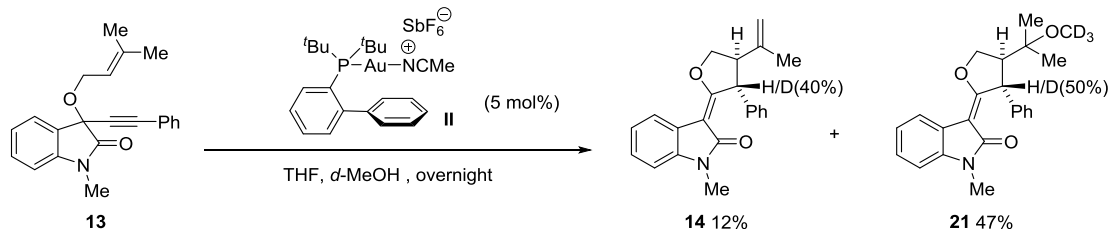
(E)-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)indolin-2-one (14u)



was prepared according to the general procedure for the gold catalyzed O-migration reaction, by using **13u** (33 mg, 0.01 mmol) as starting material. After the purification done by silica gel column chromatography with EtOAc / petroleum ether = 1/2 (R_f = 0.23) as eluents, the desired product was obtained

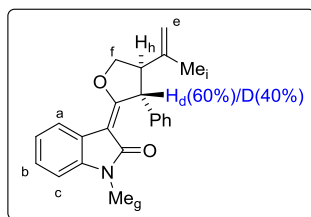
in 95% yield (31 mg, 0.10 mmol) as a yellow oil. **^1H NMR** (500 MHz, CDCl_3) δ 7.89 (s, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.28 – 7.18 (m, 3H), 7.12 (td, J = 7.6, 1.0 Hz, 1H), 7.04 (td, J = 7.6, 0.6 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 5.12 (s, 1H), 4.84 (s, 1H), 4.83 (s, 1H), 4.71 (dd, J = 9.5, 6.0 Hz, 1H), 4.58 (dd, J = 9.5, 1.0 Hz, 1H), 3.00 (d, J = 6.0 Hz, 1H), 1.81 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 172.78, 169.50, 144.73, 140.69, 137.85, 128.93, 127.13, 127.09, 126.33, 123.59, 122.87, 121.65, 111.80, 108.96, 101.88, 75.65, 53.87, 53.44, 20.71. **HRMS** (ESI): Calcd for $(\text{M} + \text{Na})^+$ [$\text{C}_{21}\text{H}_{19}\text{O}_2\text{NNa}$] $^+$: 340.1308, found: 340.1312.

Gold catalyzed O-migration reaction with deuterated CD₃OD as nucleophile



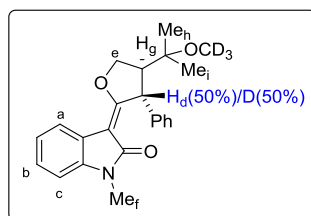
At 0 °C, to a THF (0.4 ml) solution of **13** (0.08 mmol) and *d*-MeOH (53 μ L, 0.75 mmol) was added a solution of cat. **II** (3 mg, 4 μ mol) in THF (0.4 mL). The reaction mixture was stirred at room temperature overnight. Afterwards, the reaction mixture was passed through a short pad of silica gel (Et₂O as the eluent). The resulting solution was concentrated under reduced pressure, followed by silica gel column chromatography (EA/PE=1:4) to obtain compounds **14** in 12% yield (3 mg, 0.01 mmol, *D*-40%) as a yellow oil and **21** in 47% yield (13 mg, 0.04 mmol, *D*-50%) as a yellow oil.

(E)-1-methyl-3-((3S,4S)-3-phenyl-4-(prop-1-en-2-yl)dihydrofuran-2(3H)-ylidene)indolin-2-one (**14**)



one (14) ¹H NMR (300 MHz, cdcl₃) δ 7.79 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.13 (m, 6H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.15 (s, 0.6H), 4.83 (s, 1H), 4.81 (s, 1H), 4.69 (dd, *J* = 9.4, 6.1 Hz, 1H), 4.56 (d, *J* = 9.4 Hz, 1H), 3.17 (s, 3H), 2.98 (d, *J* = 6.1 Hz, 1H), 1.80 (s, 3H).

(E)-3-((3R,4S)-4-(2-(methoxy-d₃)propan-2-yl)-3-phenyldihydrofuran-2(3H)-ylidene)-1-methylindolin-2-one (**20**)

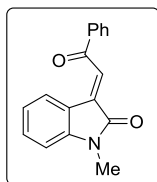


methylindolin-2-one (20) ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.12 (m, 6H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 5.10 (s, 0.5H), 4.73 (dd, *J* = 9.9, 1.7 Hz, 1H), 4.64 (dd, *J* = 9.9, 6.8 Hz, 1H), 3.15 (s, 3H), 2.51 (d, *J* = 6.8 Hz, 1H), 1.26 (s, 3H), 1.09 (s, 3H).

For NMR spectra of compounds in this experiment, see Supplementary Figures 130.

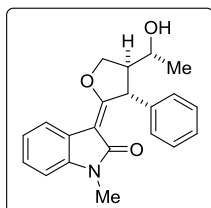
Compounds isolated from the condition screening

(E)-1-methyl-3-(2-oxo-2-phenylethylidene)indolin-2-one (MS) ^1H NMR (500 MHz, CDCl_3) δ



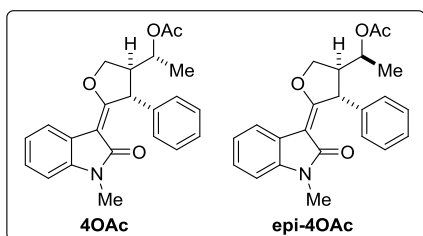
8.32 (d, $J = 7.7$ Hz, 1H), 8.11 (d, $J = 7.5$ Hz, 2H), 7.89 (s, 1H), 7.63 (t, $J = 7.5$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 2H), 7.37 (td, $J = 7.7$, 0.9 Hz, 1H), 7.03 (t, $J = 7.7$ Hz, 1H), 6.81 (d, $J = 7.7$ Hz, 1H), 3.27 (s, 3H).¹¹

(E)-3-(-4-(-1-hydroxyethyl)-3-phenyldihydrofuran-2(3H)-ylidene)-1-methylindolin-2-one



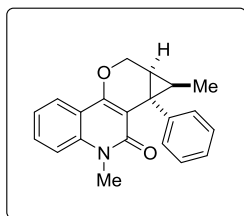
(4OH) ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, $J = 7.5$ Hz, 1H), 7.34 – 7.23 (m, 4H), 7.23 – 7.14 (m, 2H), 7.06 (t, $J = 7.5$ Hz, 1H), 6.76 (d, $J = 7.5$ Hz, 1H), 5.07 (s, 1H), 4.81 (d, $J = 9.6$ Hz, 1H), 4.62 (dd, $J = 9.6$, 6.3 Hz, 1H), 3.89 (qd, $J = 6.3$ Hz, 6.3 Hz, 1H), 3.12 (s, 3H), 2.40 (dd, $J = 6.3$ Hz, 1H), 1.35 (d, $J = 6.3$ Hz, 3H), 1.25 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.52, 168.14, 140.97, 140.49, 129.00, 127.04, 127.00, 126.20, 122.70, 122.53, 121.66, 107.26, 101.20, 72.92, 68.34, 54.15, 51.51, 25.88, 21.70. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}]^+$: 336.1594, found: 336.1589.

1-(-5-((E)-1-methyl-2-oxoindolin-3-ylidene)-4-phenyltetrahydrofuran-3-yl)ethyl acetate



(4OAc) Here we obtained a pair of HPLC inseparable epimeric mixtures at the carbon next to acetate in the ratio 4/3 (4OAc/epi-4OAc). ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, $J = 7.3$ Hz, 1H, 4OAc), 7.77 (d, $J = 7.2$ Hz, 1H, epi-4OAc), 7.35 – 7.18 (m, 6H, 4OAc and epi-4OAc), 7.10 – 7.05 (m, 1H, 4OAc and epi-4OAc), 6.82 (d, $J = 7.7$ Hz, 1H, 4OAc), 6.79 (d, $J = 7.7$ Hz, 1H, epi-4OAc), 5.19 – 5.18 (m, 1H, 4OAc and epi-4OAc), 5.04 (qd, $J = 6.3$, 6.3 Hz, 1H, 4OAc), 4.76 (dd, $J = 8.7$, 8.7 Hz, 1H, epi-4OAc), 4.69 – 4.55 (m, 2H, 4OAc and epi-4OAc), 3.20 (s, 3H, 4OAc), 3.18 (s, 3H, epi-4OAc), 3.00 – 2.93 (m, 1H, epi-4OAc), 2.67 (t, $J = 6.3$ Hz, 1H, 4OAc), 2.04 (s, 3H, 4OAc), 1.91 (s, 3H, epi-4OAc), 1.34 – 1.27 (m, 3H, 4OAc and epi-4OAc). **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{23}\text{H}_{24}\text{O}_4\text{N}]^+$: 378.1700, found: 378.1700.

1,3-dimethyl-1a-phenyl-1a,3,9,9a-tetrahydrocyclopropa[4,5]pyrano[3,2-c]quinolin-



2(1H)-one (epi-3a) ^1H NMR (500 MHz, CDCl_3) δ 7.91 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.51 – 7.45 (m, 1H), 7.33 (d, $J = 7.0$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 1H), 7.19 – 7.14 (m, 3H), 7.08 (t, $J = 7.3$ Hz, 1H), 4.87 (dd, $J = 12.3, 8.5$ Hz, 1H), 4.02 (dd, $J = 12.3, 5.3$ Hz, 1H), 3.51 (s, 3H), 2.14 (dq, $J = 8.1, 6.4$ Hz, 1H), 1.58 – 1.51 (m, 1H), 1.02 (d, $J = 6.4$ Hz, 3H). ^{13}C

NMR (126 MHz, CDCl_3) δ 162.26, 158.39, 144.56, 139.18, 130.65, 128.92, 128.09, 126.20, 123.64, 121.60, 116.10, 113.99, 109.62, 65.15, 29.40, 25.93, 22.60, 21.62, 8.96. **HRMS** (ESI): Calcd for $(\text{M} + \text{H})^+$ $[\text{C}_{21}\text{H}_{20}\text{O}_2\text{N}]^+$: 318.1489, found: 318.1489.

For NMR spectra of compounds in this section, see Supplementary Figures 131-134.

Supplementary References

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