

Interplay of diruthenium catalyst in controlling enantioselective propargylic substitution reactions with visible light-generated alkyl radicals

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Table of Contents

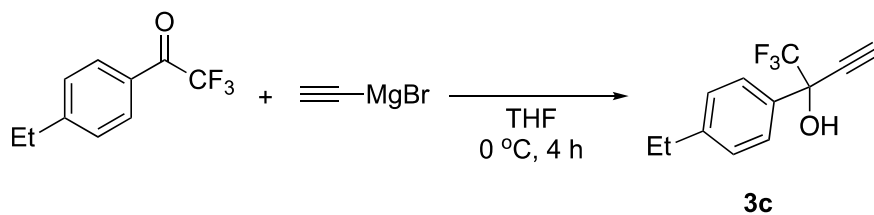
1. Supplementary Methods	S2
1.1. General methods	S2
1.2. General procedure for the preparation of 3 and 8	S2
1.3. General procedure for the preparation of 4	S4
1.4. General procedure for the preparation of 5, 7, and 9	S6
1.5. Large-Scale Preparation of 7aa	S20
1.6. Preparation of 10	S21
1.7. Preparation of 11	S21
1.8. Preparation of 12	S22
1.9. Preparation of 13	S22
1.10 Preparation of 14	S23
1.11. Stoichiometric reaction of 14 with 4a	S23
1.12. Catalytic reaction of 3a with 4a by using 14 as a catalyst	S24
1.13. Reactions in the presence of TEMPO	S24
1.14. Deuterium labeling reaction	S24
1.15. Stern–Volmer analysis	S25
1.16. Light on/off experiment	S25
1.17. Cyclic voltammetric studies	S25
1.18. Time profile experiment	S27
1.19. Determination of quantum yields	S27
1.20. X-ray crystallographic study	S28
1.21. DFT calculations	S31
1.22. NMR Charts	S35
1.23: HPLC Charts	S87
2. Supplementary References	S129

1. Supplementary Methods

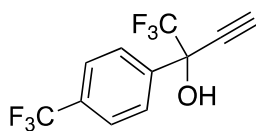
1.1. General methods

All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. **1**,¹ **2**,² **3a**,³ **3b**,⁴ **3d**,⁵ **3e**,⁶ **3f**,⁶ **3g**,⁷ **3i**,⁸ **3j**,⁶ **3n**,⁶ **4a**,⁹ **4b**,⁹ **4c**,⁹ **4d**,^{S9} **4e**,¹⁰ **4f**,⁹ **4g**,¹¹ **4j**,¹² **4k**,¹³ **4l**,¹² **4m**,¹⁰ **4n**,¹⁴ **4p**,¹² **4q**,⁹ **4r**,¹⁵ **4t**,¹⁶ **4u**,¹⁷ **4v**,¹¹ **14**,⁵ **16**,¹⁸ **[Ru]-1**,¹⁹ and **[Ru]-2**¹⁹ were prepared according to the literature procedures. Other reagents include starting materials for the preparation of **1**, **2**, **3a–3n**, **4a–4v**, **5**, **8**, **14**, **16**, **[Ru]-1**, and **[Ru]-2**, *fac*-[Ir(ppy)₃] (ppy = 2-(pyridyl)phenyl), *fac*-[Ir(Fppy)₃] (Fppy = 3,5-difluoro-2-(pyridyl)phenyl), [Ir(ppy)₂(dtbbpy)]PF₆ (dtbbpy = 4,4'-di-tert-butyl-2,2'-bipyridine), NH₄BF₄, Lewis acids (BF₃·Et₂O, B(OH)₃, BCl₃, Sc(OTf)₃ (OTf = trifluoromethanesulfonate)), TEMPO, and solvents were obtained from commercial sources. Solvents were dried by general methods and degassed before use. Flash column chromatography was carried out on a Yamazen YFLC-AI-580 system. Gas chromatography–mass spectroscopy (GC–MS) was performed on a Shimadzu GCMS-QP2010 PLUS instrument. HPLC analyses were performed on Hitachi L-7100 and GL-7410 apparatuses equipped with a UV detector using 25 cm x 4.6 mm DAICEL Chiralpak columns. Specific rotations were measured on a JASCO DIP-1000 polarimeter. X-ray analysis was performed by a Rigaku XtaLAB Synergy-S diffractometer. Photoluminescence spectra were measured on a Shimadzu RF-5300PC spectrophotometer. Melting points were measured by using a Stanford Research Systems OptiMelt MPA100. High-resolution FAB mass spectra were measured on a JEOL JMS-700 mass spectrometer. Specific rotations were measured on a JASCO DIP-1000 polarimeter. ¹H NMR (400 MHz), ¹³C{¹H} NMR (100 MHz), and ¹⁹F NMR (376 MHz, referenced to CF₃C₆H₅ in CDCl₃ at δ –64.0) spectra were measured in CDCl₃, (CD₃)₂CO or CD₃CN on a JEOL ECS-400 spectrometer with δ values in ¹H and ¹³C{¹H} NMR calibrated by using residual peaks of CHCl₃ (¹H: 7.26; ¹³C: 77.0), (CD₂H)₂CO (¹H, 2.09; ¹³C: 206.0), CD₂HCN (¹H, 1.93; ¹³C: 117.7) respectively.

1.2. General procedure for the preparation of propargylic alcohol substrates (**3** and **8**) (taking 1,1,1-trifluoro-2-(4-ethylphenyl)but-3-yn-2-ol (**3c**) as a typical example)

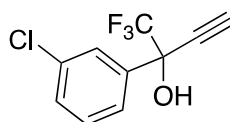


To a solution of 2,2,2-trifluoro-1-(4-ethylphenyl)ethan-1-one (3.00 mmol, 607 mg) in anhydrous THF (15 mL) was added ethynylmagnesium bromide (0.5 M in THF, 9.0 mL, 4.5 mmol) at 0 °C. After stirring for 4 h, the mixture was quenched by saturated NH₄Cl aq. (4 mL), and the solution was extracted with Et₂O (10 ml × 2). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography with hexane/EtOAc (95:5–90:10) to give 1,1,1-trifluoro-2-(4-ethylphenyl)but-3-yn-2-ol as a pale yellow oil (588.8 mg, 2.58 mmol, 86% isolated yield based on the amount of 2,2,2-trifluoro-1-(4-ethylphenyl)ethan-1-one). ¹H NMR (400 MHz, (CD₃)₂CO): δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.67 (s, 1H), 3.49 (s, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); ¹³C{¹H} NMR (100 MHz, (CD₃)₂CO): δ 145.7, 133.8, 127.7, 127.4, 124.1 (q, ¹*J*_{CF} = 283.7 Hz), 80.3, 77.1, 72.4 (q, ²*J*_{CF} = 31.6 Hz), 28.4, 15.2; ¹⁹F NMR (376 MHz, (CD₃)₂CO): δ –82.4 (s); HRMS (FAB+) (*m/z*): [*M*]⁺ calcd. for C₁₂H₁₁F₃O: 228.0762; found: 228.0763.



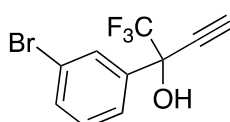
3h

1,1,1-Trifluoro-2-(4-(trifluoromethyl)phenyl)but-3-yn-2-ol (3h). A pale yellow oil (683.8 mg, 2.55 mmol, 85% isolated yield based on the amount of 2,2,2-trifluoro-1-(4-(trifluoromethyl)phenyl)ethan-1-one). ^1H NMR (400 MHz, CDCl_3): δ 7.88 (d, J = 8.4 Hz, 2H), 7.69 (t, J = 8.4 Hz, 2H), 3.37 (s, 1H), 2.87 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ 141.3, 131.7 (q, $^1J_{\text{CF}}$ = 32.2 Hz), 128.8, 125.9 (q, $^3J_{\text{CF}}$ = 3.5 Hz), 124.9 (q, $^2J_{\text{CF}}$ = 270.2 Hz), 124.2 (q, $^3J_{\text{CF}}$ = 284.0 Hz), 79.7, 78.7, 72.6 (q, $^2J_{\text{CF}}$ = 31.9 Hz) (^{13}C NMR spectrum of this compound was measured in acetone- d_6 because some peaks of this compound overlapped with those of CDCl_3); ^{19}F NMR (376 MHz, CDCl_3): δ -62.9 (s), -80.4 (s); HRMS (FAB+) (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{11}\text{H}_7\text{F}_6\text{O}$, 269.0401; found, 269.0401.



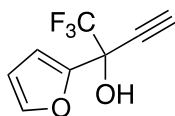
3k

1,1,1-Trifluoro-2-(3-chlorophenyl)but-3-yn-2-ol (3k). A pale yellow oil (667.1 mg, 2.49 mmol, 83% isolated yield based on the amount of 1-(3-chlorophenyl)-2,2,2-trifluoroethan-1-one). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 7.75 (br, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.41 (dq, J = 8.1, 1.1 Hz, 1H), 7.36 (pseudo t, J = 7.8 Hz, 1H), 3.26 (s, 1H), 2.85 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ 136.4, 134.3, 129.9, 129.5, 127.4, 125.3, 122.8 (q, $^1J_{\text{CF}}$ = 284.3 Hz), 78.8, 77.2, 72.3 (q, $^2J_{\text{CF}}$ = 32.6 Hz); ^{19}F NMR (376 MHz, $(\text{CD}_3)_2\text{CO}$): δ -82.0 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{10}\text{H}_6\text{ClF}_3\text{O}$, 234.0059; found: 234.0068.



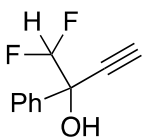
3l

1,1,1-Trifluoro-2-(3-bromophenyl)but-3-yn-2-ol (3l). A pale yellow oil (667.1 mg, 2.40 mmol, 80% isolated yield based on the amount of 1-(3-bromophenyl)-2,2,2-trifluoroethan-1-one). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ 8.09 (br, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.76 (dq, J = 8.0, 1.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.09 (s, 1H), 3.68 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ 138.6, 132.3, 130.0, 129.9, 126.1, 123.4 (q, $^1J_{\text{CF}}$ = 284.0 Hz), 121.6, 79.0, 77.6, 71.6 (q, $^2J_{\text{CF}}$ = 31.9 Hz); ^{19}F NMR (376 MHz, $(\text{CD}_3)_2\text{CO}$, 376 MHz): δ -80.7 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{10}\text{H}_6\text{BrF}_3\text{O}$, 277.9554; found: 277.9565.



3m

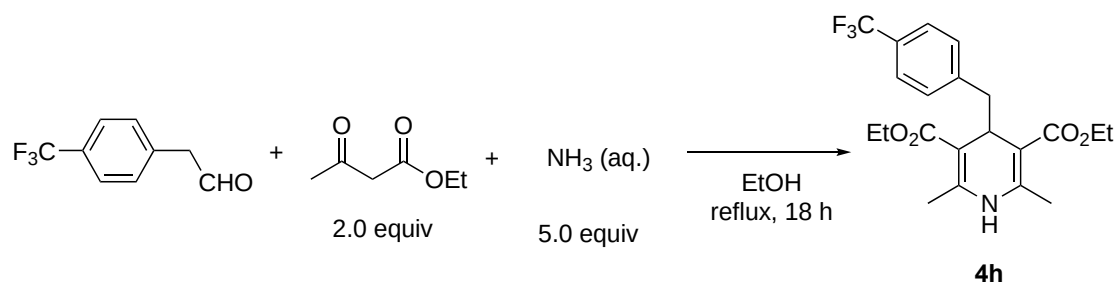
1,1,1-Trifluoro-2-(furan-2-yl)but-3-yn-2-ol (3m). A pale yellow oil (427.7 mg, 2.25 mmol, 75% isolated yield based on the amount of 2,2,2-trifluoro-1-(furan-2-yl)ethan-1-one). ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, $J = 2.0$, 1H), 6.69 (dd, $J = 3.3$, 0.9 Hz, 1H), 6.42 (dd, $J = 3.3$, 2.0 Hz, 1H), 3.52 (br, 1H), 2.77 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 146.8, 144.2, 122.4 (q, $^1J_{\text{CF}} = 284.6$ Hz), 111.1, 110.8, 76.7, 76.3, 69.0 (q, $^2J_{\text{CF}} = 34.5$ Hz); ^{19}F NMR (376 MHz, CDCl_3): δ -81.5 (s); HRMS (FAB+) (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_8\text{H}_6\text{F}_3\text{O}_2$, 191.0320; found: 191.0318.



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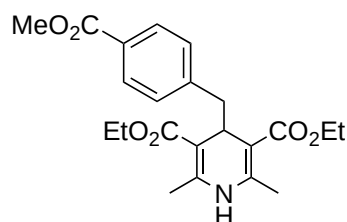
1,1-Difluoro-2-phenylbut-3-yn-2-ol (8). A pale yellow oil (477.3 mg, 2.61 mmol, 87% isolated yield based on the amount of 2,2-difluoro-1-phenylethan-1-one). ^1H NMR (400 MHz, CDCl_3): δ 7.69 (dd, $J = 7.6$, 1.6 Hz, 2H), 7.47–7.38 (m, 3H), 5.72 (t, $J = 56.0$ Hz, 1H), 3.02 (s, 1H), 2.80 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ 137.8, 128.8, 128.1, 127.0, 115.4 (t, $^1J_{\text{CF}} = 249.6$ Hz), 81.2, 76.9, 72.3 (t, $^2J_{\text{CF}} = 23.5$ Hz) (^{13}C NMR spectrum of this compound was measured in acetone- d_6 because some peaks of this compound overlapped with those of CDCl_3); ^{19}F NMR (376 MHz, CDCl_3): δ -129.3 (dd, $^2J_{\text{FF}} = 276$ Hz, $^2J_{\text{HF}} = 60$ Hz), -129.2 (dd, $^2J_{\text{FF}} = 276$ Hz, $^2J_{\text{HF}} = 60$ Hz); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{10}\text{H}_8\text{F}_2\text{O}$, 182.0543; found, 182.0548.

1.3. General procedure for the preparation of 4-alkyl-1,4-dihydropyridine derivatives (4) (taking diethyl 2,6-dimethyl-4-(4-(trifluoromethyl)benzyl)-1,4-dihydropyridine-3,5-dicarboxylate (4h) as a typical example)



In a 50 mL Schlenk flask were placed 2-(4-(trifluoromethyl)phenyl)acetaldehyde (940.8 mg, 5.00 mmol), ethyl acetoacetate (1301.4 mg, 10.00 mmol), and ethanol (20 mL) at room temperature under N_2 , where an aqueous solution of 28 wt % NH_3 (1.5 mL, *ca.* 25 mmol) was added. The reaction mixture was stirred and refluxed for 18 h by using an oil bath, then was dried in vacuo. The residue was further purified by column chromatography (SiO_2) with a mixture of *n*-hexane/ethyl acetate (7:3) as an eluent to afford diethyl 2,6-dimethyl-4-(4-(trifluoromethyl)benzyl)-1,4-dihydropyridine-3,5-dicarboxylate (**4h**) as a white solid (1070.1 mg, 2.60 mmol, 52% yield based on the amount of 2-(4-(trifluoromethyl)phenyl)acetaldehyde). mp: 129.0–130.2 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.40 (d, $J = 7.8$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 6.02 (s, 1H), 4.18 (t, $J = 5.7$ Hz, 1H), 4.08–3.92 (m, 4H), 2.60 (d, $J = 5.7$ Hz, 2H), 2.16 (s, 6H), 1.17 (t, $J = 7.2$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ

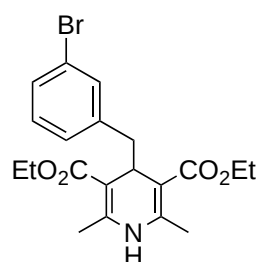
167.6, 145.9, 143.6, 130.1, 127.8 (q, $^2J_{\text{CF}} = 31.9$ Hz), 124.4 (q, $^1J_{\text{CF}} = 270.2$ Hz), 124.0 (q, $^3J_{\text{CF}} = 2.9$ Hz), 101.2, 59.6, 42.1, 35.3, 18.9, 14.1; ^{19}F NMR (376 MHz, CDCl_3): δ -63.7 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{21}\text{H}_{24}\text{F}_3\text{NO}_4$, 411.1657; found, 411.1653.



4i

Diethyl 4-(4-(methoxycarbonyl)benzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4i).

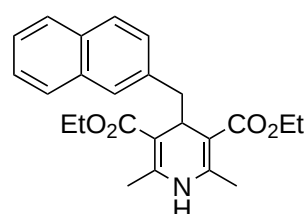
A white solid (762.2 mg, 1.90 mmol, 38% isolated yield, based on the amount of methyl 4-(2-oxoethyl)benzoate). mp: 86.5–88.0 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 5.20 (s, 1H), 4.24 (t, $J = 5.5$ Hz, 1H), 4.15–4.02 (m, 4H), 3.89 (s, 1H), 2.65 (d, $J = 5.5$ Hz, 2H), 2.15 (s, 6H), 1.24 (t, $J = 7.4$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.6, 167.4, 145.5, 145.2, 130.1, 128.5, 127.6, 101.4, 59.7, 51.9, 42.2, 35.4, 19.2, 14.3; HRMS (FAB+) (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{22}\text{H}_{28}\text{NO}_6$, 402.1917; found, 402.1936.



4o

Diethyl 4-(3-bromobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4o).

A white solid (971.3 mg, 2.30 mmol, 46% isolated yield, based on the amount of 2-(3-bromobenzyl)acetaldehyde). mp: 88.3–89.5 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.27 (ddd, $J = 7.8, 2.0, 0.9$ Hz, 1H), 7.20 (t, $J = 2.0$ Hz, 1H), 7.03 (t, $J = 7.8$ Hz, 1H), 6.91 (d of pseudo t, $J = 7.8, 1.6$ Hz, 1H), 5.36 (s, 1H), 4.19 (t, $J = 5.6$ Hz, 1H), 4.15–4.04 (m, 4H), 2.54 (d, $J = 5.6$ Hz, 2H), 2.18 (s, 6H), 1.26 (t, $J = 7.2$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.6, 145.7, 141.7, 133.0, 128.8, 128.7, 128.6, 121.3, 101.4, 59.7, 41.9, 35.4, 19.2, 14.3; HRMS (FAB+) (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{25}\text{BrNO}_4$, 422.0967; found, 422.0946.

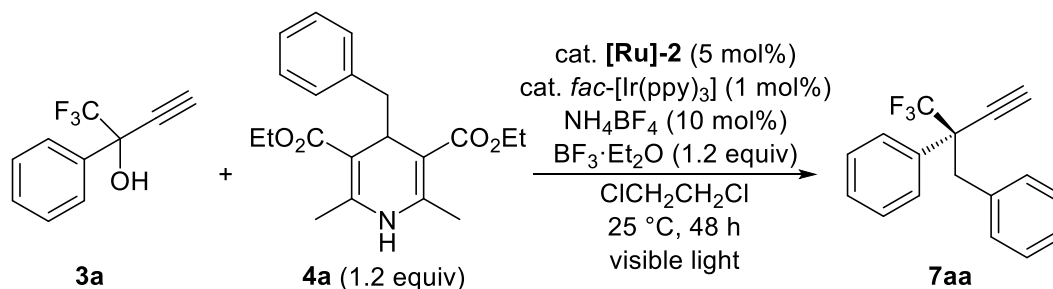


4s

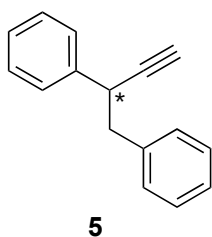
Diethyl 2,6-dimethyl-4-(naphthalen-2-ylmethyl)-1,4-dihydropyridine-3,5-dicarboxylate (4s). A white solid (846.0 mg, 2.15 mmol, 43% isolated yield, based on the amount of 2-(4-(naphthalen-2-ylmethyl))acetaldehyde). mp: 119.0–120.6 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.78–7.71 (m, 2H),

7.65 (d, $J = 8.8$ Hz, 1H), 7.43 (s, 1H), 7.41–7.36 (m, 2H), 7.20 (dd, $J = 8.0$ Hz, 1.2 Hz, 1H), 5.09 (s, 1H), 4.28 (t, $J = 5.4$ Hz, 1H), 4.10–3.95 (m, 4H), 2.75 (d, $J = 5.2$ Hz, 2H), 2.12 (s, 6H), 1.19 (t, $J = 7.2$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.8, 145.4, 137.0, 133.2, 131.9, 129.1, 128.2, 127.4 (overlapping), 126.3, 125.5, 124.9, 101.8, 59.6, 42.4, 35.6, 19.2, 14.3; HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{24}\text{H}_{27}\text{NO}_4$, 393.1940; found, 393.1951.

1.4. General procedure for the preparation of chiral propargylic alkylation products (5, 7, and 9) (taking (*R*)-(2-(trifluoromethyl)but-3-yn-1,2-diyl)dibenzene (7aa) as a typical example)

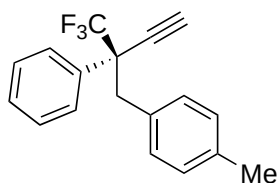


In an oven dried 20 mL Schlenk flask were placed **[Ru]-2** (6.3 mg, 0.0050 mmol) and NH_4BF_4 (1.1 mg, 0.010 mmol) under N_2 . Anhydrous $\text{ClCH}_2\text{CCH}_2\text{Cl}$ (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg, 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*- $[\text{Ir}(\text{ppy})_3]$ (0.7 mg, 0.0011 mmol), and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (15 μL , 17 mg, 0.12 mmol) were added under N_2 at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 $^\circ\text{C}$, and was illuminated from the bottom of the bath with an Aitech System TMN100 $\times$ 120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography (SiO_2) with *n*-hexane as an eluent to afford (*R*)-(2-(trifluoromethyl)but-3-yn-1,2-diyl)dibenzene (**7aa**) as a colorless oil (22.2 mg, 0.081 mmol, 81% yield based on the amount of **3a**). $[\alpha]_{\text{D}}^{20} = -12.2$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.68–7.64 (m, 2H), 7.39–7.33 (m, 3H), 7.22–7.09 (m, 3H), 7.00–6.97 (m, 2H), 3.52 (d, $J = 13.2$ Hz, 1H), 3.42 (d, $J = 13.2$ Hz, 1H), 2.66 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 134.4, 133.3, 130.8, 128.5, 128.5, 128.3, 127.6, 127.0, 125.7 (q, $^1J_{\text{CF}} = 282.7$ Hz), 79.0 (q, $^3J_{\text{CF}} = 1.9$ Hz), 78.1, 53.0 (q, $^2J_{\text{CF}} = 26.5$ Hz), 40.7; ^{19}F NMR (376 MHz, CDCl_3): δ –73.5 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_3$, 274.0969; found: 274.0964. The enantiomeric excess of **7aa** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*-PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 14.6 min (major) and 19.9 min (minor), 94% ee.



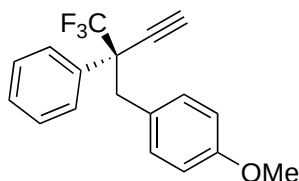
But-3-yn-1,2-diyl dibenzene (5). A colorless oil (15.1 mg, 0.073 mmol, 73% yield based on the amount of **1**). $[\alpha]_{\text{D}}^{20} = -14.8$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.19 (m, 8H), 7.13 (d, $J = 7.2$ Hz, 2H), 3.88 (ddd, $J = 7.8, 6.8, 2.5$ Hz, 1H), 3.06 (dd, $J = 13.2, 7.8$ Hz, 1H), 3.04 (dd, $J = 13.2, 6.8$ Hz, 1H), 2.28 (d, $J = 2.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 140.7, 138.6,

129.4, 128.4, 128.1, 127.6, 126.9, 126.5, 85.3, 71.9, 44.7, 39.8; HRMS (FAB+) (m/z): $[M+H]^+$ calcd. for $C_{16}H_{15}$, 207.1174; found: 207.1173. The enantiomeric excess of **5** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 21.8 min (minor) and 44.7 min (major), 48% ee.



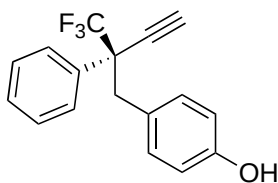
7ab

(R)-1-Methyl-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ab). A colorless oil (22.5 mg, 0.078 mmol, 78% yield based on the amount of **3a**). $[\alpha]_D^{20} = +21.9$ (0.5 M in $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 7.68–7.64 (m, 2H), 7.39–7.33 (m, 3H), 6.92 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 3.48 (d, J = 13.6 Hz, 1H), 3.38 (d, J = 13.6 Hz, 1H), 2.65 (s, 1H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.5, 133.4, 131.2, 130.6, 128.5 (overlapping), 128.3, 128.2, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 79.1, 78.0, 53.0 (q, $^2J_{CF}$ = 26.2 Hz), 40.3, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.5 (s); HRMS (FAB+) (m/z): $[M]^+$ calcd. for $C_{18}H_{15}F_3$, 288.1126; found: 288.1128. The enantiomeric excess of **7ab** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 13.7 min (major) and 18.9 min (minor), 94% ee.



7ac

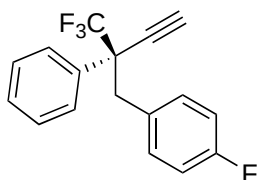
(R)-1-Methyl-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ac). A colorless oil (24.0 mg, 0.079 mmol, 79% yield based on the amount of **3a**). $[\alpha]_D^{20} = +66.9$ (0.5 M in $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 7.68–7.64 (m, 2H), 7.40–7.33 (m, 3H), 6.89 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 3.72 (s, 3H), 3.46 (d, J = 13.6 Hz, 1H), 3.37 (d, J = 13.6 Hz, 1H), 2.65 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.5, 133.4, 131.7, 128.5 (overlapping), 128.3, 126.3, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 113.0, 79.1 (q, $^3J_{CF}$ = 1.9 Hz), 78.0, 55.0, 53.1 (q, $^2J_{CF}$ = 26.2 Hz), 39.9; ^{19}F NMR (376 MHz, $CDCl_3$, 376 MHz): δ -71.7 (s); HRMS (FAB+) (m/z): $[M]^+$ calcd. for $C_{18}H_{15}F_3O$, 304.1075; found, 304.1088. The enantiomeric excess of **7ac** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*PrOH = 90/10, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 20.1 min (major) and 23.7 min (minor), 92% ee.



7ad

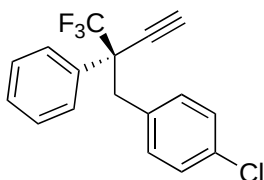
(R)-4-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)phenol (7ad). A colorless oil (20.3 mg, 0.070 mmol, 70% yield based on the amount of **3a**). $[\alpha]_D^{20} = -40.9$ (0.5 M in $CHCl_3$); 1H NMR (400 MHz,

CDCl₃): δ 7.66–7.62 (m, 2H), 7.39–7.33 (m, 3H), 6.84 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 8.8 Hz, 2H), 3.44 (d, J = 13.8 Hz, 1H), 3.35 (d, J = 13.8 Hz, 1H), 2.65 (s, 1H), 2.1–1.3 (br, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 154.5, 133.4, 131.9, 128.5, 128.5, 128.3, 126.6, 125.7 (q, ¹ J_{CF} = 282.7 Hz), 114.5, 79.1 (q, ³ J_{CF} = 1.9 Hz), 78.0, 53.2 (q, ² J_{CF} = 26.2 Hz), 40.0; ¹⁹F NMR (376 MHz, CDCl₃): δ –73.3 (s); HRMS (FAB+) (m/z): [M]⁺ calcd. for C₁₇H₁₃F₃O, 290.0918; found, 290.0912. The enantiomeric excess of **7ad** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ⁱPrOH = 80/20, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 19.8 min (major) and 31.3 min (minor), 92% ee.



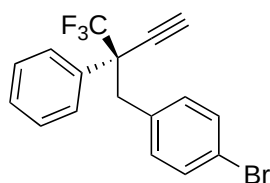
7ae

(R)-1-Fluoro-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ae). A colorless oil (23.4 mg, 0.080 mmol, 80% yield based on the amount of **3a**). [α]_D²⁰ = –17.1 (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.65–7.61 (m, 2H), 7.39–7.34 (m, 3H), 6.93 (dd, J = 8.8, 5.6 Hz, 2H), 6.80 (pseudo t, J = 8.8 Hz, 2H), 3.47 (d, J = 13.2 Hz, 1H), 3.39 (d, J = 13.2 Hz, 1H), 2.66 (s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 162.0 (d, ¹ J_{CF} = 244.4 Hz), 133.2, 132.2 (d, ³ J_{CF} = 7.6 Hz), 130.0 (d, ⁴ J_{CF} = 2.8 Hz), 128.7, 128.4, 128.4, 125.6 (q, ¹ J_{CF} = 279.5 Hz), 114.5 (d, ² J_{CF} = 21.0 Hz), 78.8 (q, ³ J_{CF} = 1.9 Hz), 78.2, 53.0 (q, ² J_{CF} = 26.8 Hz), 40.0; ¹⁹F NMR (376 MHz, CDCl₃): δ –73.4 (s), –117.3 (s); HRMS (FAB+) (m/z): [M+H]⁺ calcd. for C₁₇H₁₃F₄, 293.0953; found, 293.0962. The enantiomeric excess of **7ae** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ⁱPrOH = 99/1, flow rate = 0.3 mL/min, λ = 220 nm, retention time: 32.2 min (major) and 35.0 min (minor), 92% ee.



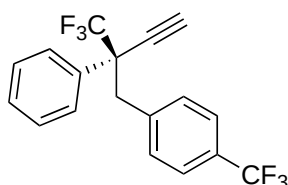
7af

(R)-1-Chloro-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7af). A white solid (22.8 mg, 0.074 mmol, 74% yield based on the amount of **3a**). mp: 56.4–57.8 °C; [α]_D²⁰ = –19.5 (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.65–7.61 (m, 2H), 7.40–7.34 (m, 3H), 7.08 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 8.2 Hz, 2H), 3.47 (d, J = 13.6 Hz, 1H), 3.38 (d, J = 13.6 Hz, 1H), 2.67 (s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 133.0, 132.8, 132.0, 128.7, 128.4 (overlapping), 127.8, 125.6 (q, ¹ J_{CF} = 282.7 Hz), 78.7 (q, ³ J_{CF} = 1.9 Hz), 78.3, 52.9 (q, ² J_{CF} = 26.2 Hz), 40.1; ¹⁹F NMR (376 MHz, CDCl₃): δ –73.5 (s); HRMS (FAB+) [M]⁺ (m/z): calcd. for C₁₇H₁₂ClF₃, 308.0580; found: 308.0570. The enantiomeric excess of **7af** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ⁱPrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 17.3 min (major) and 25.4 min (minor), 90% ee.



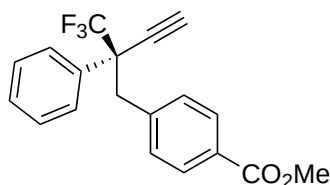
7ag

(R)-1-Bromo-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ag). A colorless oil (24.0 mg, 0.068 mmol, 68% yield based on the amount of **3a**). $[\alpha]_D^{20} = -49.5$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.65–7.61 (m, 2H), 7.38–7.34 (m, 3H), 7.23 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 3.45 (d, $J = 13.6$ Hz, 1H), 3.36 (d, $J = 13.6$ Hz, 1H), 2.67 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 133.3, 133.0, 132.4, 130.7, 128.7, 128.4 (overlapping), 125.6 (q, $^1J_{\text{CF}} = 282.7$ Hz), 121.2, 78.7 (q, $^3J_{\text{CF}} = 2.4$ Hz), 78.4, 52.8 (q, $^2J_{\text{CF}} = 26.8$ Hz), 40.2; ^{19}F NMR (376 MHz, CDCl_3): δ -73.5; HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{17}\text{H}_{12}\text{BrF}_3$, 352.0074; found, 352.0083. The enantiomeric excess of **7ag** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 15.4 min (major) and 23.7 min (minor), 94% ee.



7ah

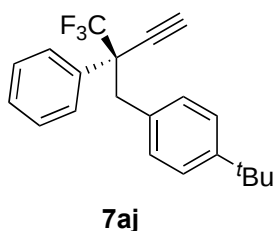
(R)-1-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)-4-(trifluoromethyl)benzene (7ah). A white solid (25.3 mg, 0.074 mmol, 74% yield based on the amount of **3a**). mp: 54.5–55.5 °C; $[\alpha]_D^{20} = -49.1$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.66–7.62 (m, 2H), 7.39–7.35 (m, 5H), 7.08 (d, 2H, $J = 8.4$ Hz), 3.56 (d, $J = 13.4$ Hz, 1H), 3.46 (d, $J = 13.4$ Hz, 1H), 2.68 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ 140.1, 133.6, 132.3, 129.6, 129.5 (q, $^2J_{\text{CF}} = 31.6$ Hz), 129.4, 129.2, 126.6 (q, $^1J_{\text{CF}} = 282.4$ Hz), 125.2 (q, $^1J_{\text{CF}} = 269.8$ Hz), 125.0 (q, $^3J_{\text{CF}} = 2.8$ Hz), 80.8, 79.1, 53.4 (q, $^2J_{\text{CF}} = 27.2$ Hz), 40.2 (^{13}C NMR spectrum of this compound was measured in acetone- d_6 because some peaks of this compound overlapped with those of CDCl_3); ^{19}F NMR (376 MHz, CDCl_3): δ -64.1 (s), -73.6 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{12}\text{F}_6$, 342.0843; found, 342.0856. The enantiomeric excess of **7ah** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 11.4 min (major) and 15.6 min (minor), 91% ee.



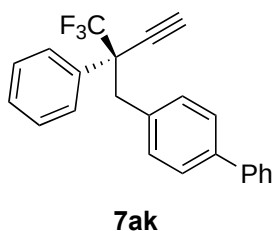
7ai

Methyl (R)-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzoate (7ai). A pale yellow solid (24.9 mg, 0.075 mmol, 75% yield based on the amount of **3a**). mp: 74.0–75.5 °C; $[\alpha]_D^{20} = -45.6$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.79 (d, $J = 8.4$ Hz, 2H), 7.65–7.62 (m, 2H), 7.38–7.33 (m, 3H), 7.05 (d, $J = 8.4$ Hz, 2H), 3.86 (s, 3H), 3.56 (d, $J = 14.0$ Hz, 1H), 3.47 (d, $J = 14.0$ Hz, 1H), 2.67 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 166.9, 139.7, 133.0, 130.8, 128.9, 128.8, 128.7, 128.4, 125.6 (q, $^1J_{\text{CF}} = 282.7$ Hz), 78.6 (q, $^3J_{\text{CF}} = 1.9$ Hz), 78.4, 52.8 (q, $^2J_{\text{CF}} = 26.8$ Hz), 52.0, 40.7; ^{19}F

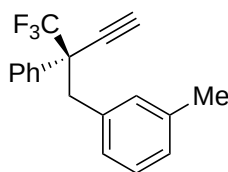
NMR (376 MHz, CDCl₃): δ –73.5 (s); HRMS (FAB+) (m/z): [M+H]⁺ calcd. for C₁₉H₁₆F₃O₂, 333.1102; found, 333.1107. The enantiomeric excess of **7ai** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*PrOH = 90/10, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 18.9 min (major) and 31.1 min (minor), 96% ee.



(R)-1-(tert-Butyl)-4-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7aj). A white solid (23.1 mg, 0.070 mmol, 70% yield based on the amount of **3a**). mp: 88.7–89.9 °C; [α]_D²⁰ = –13.2 (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.69–7.66 (m, 2H), 7.39–7.33 (m, 3H), 7.13 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 3.50 (d, J = 13.6 Hz, 1H), 3.39 (d, J = 13.6 Hz, 1H), 2.65 (s, 1H), 1.24 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.6, 133.5, 131.3, 130.3, 128.5, 128.5, 128.2, 125.7 (q, ¹ J_{CF} = 282.7 Hz), 124.5, 79.2 (q, ³ J_{CF} = 1.9 Hz), 77.8, 52.9 (q, ² J_{CF} = 26.2 Hz), 40.0, 34.3, 31.3; ¹⁹F NMR (376 MHz, CDCl₃): δ –72.0 (s); HRMS (FAB+) (m/z): [M]⁺ calcd. for C₂₁H₂₁F₃, 330.1595; found, 330.1594. The enantiomeric excess of **7aj** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 9.9 min (major) and 17.9 min (minor), 84% ee.

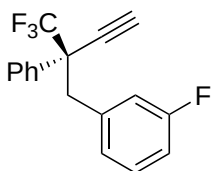


(R)-4-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)-1,1'-biphenyl (7ak). A white solid (24.9 mg, 0.071 mmol, 71% yield based on the amount of **3a**). mp: 102.6–103.7 °C; [α]_D²⁰ = –46.4 (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.71–7.67 (m, 2H), 7.52 (dd, J = 7.2, 1.2 Hz, 2H), 7.42–7.34 (m, 7H), 7.30 (tt, J = 7.4, 1.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2H), 3.56 (d, J = 13.2 Hz, 1H), 3.47 (d, J = 13.2 Hz, 1H), 2.69 (s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 140.6, 139.7, 133.4, 133.3, 131.1, 128.7, 128.6, 128.5, 128.3, 127.2, 126.9, 126.2, 125.7 (q, ¹ J_{CF} = 283.7 Hz), 79.0, 78.1, 53.0 (q, ² J_{CF} = 26.5 Hz), 40.3; ¹⁹F NMR (376 MHz, CDCl₃): δ –71.8 (s); HRMS (FAB+) (m/z): [M]⁺ calcd. for C₂₃H₁₇F₃, 350.1282; found: 350.1270. The enantiomeric excess of **7ak** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.4 min (minor) and 12.4 min (major), 83% ee.



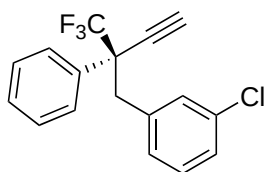
7al

(R)-1-Methyl-3-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7al). A colorless oil (21.0 mg, 0.073 mmol, 73% yield based on the amount of **3a**). $[\alpha]_D^{20} = -14.9$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.67–7.64 (m, 2H), 7.38–7.33 (m, 3H), 7.00 (pseudo t, $J = 7.4$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 6.79 (br, 1H), 6.76 (d, $J = 6.8$ Hz, 1H), 3.47 (d, $J = 13.4$ Hz, 1H), 3.38 (d, $J = 13.4$ Hz, 1H), 2.65 (s, 1H), 2.19 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 137.0, 134.2, 133.4, 131.7, 128.5, 128.2, 127.7, 127.7, 127.4, 127.2, 125.7 (q, $^1J_{\text{CF}} = 282.7$ Hz), 79.0 (q, $^3J_{\text{CF}} = 1.9$ Hz), 78.0, 53.0 (q, $^2J_{\text{CF}} = 26.2$ Hz), 40.7, 21.3; ^{19}F NMR (376 MHz, CDCl_3): δ -72.0 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{15}\text{F}_3$, 288.1126; found, 288.1137. The enantiomeric excess of **7al** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 13.6 min (major) and 17.7 min (minor), 90% ee.



7am

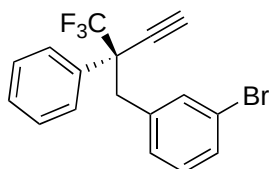
(R)-1-Fluoro-3-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7am). A colorless oil (23.4 mg, 0.080 mmol, 80% yield based on the amount of **3a**). $[\alpha]_D^{20} = -48.0$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.67–7.62 (m, 2H), 7.42–7.34 (m, 3H), 7.07 (dd, $J = 14.0, 8.6$ Hz, 1H), 6.85 (ddd, $J = 8.6, 7.6, 2.8$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 6.72 (dd, $J = 7.6, 2.4$ Hz, 1H), 3.50 (d, $J = 13.2$ Hz, 1H), 3.41 (d, $J = 13.2$ Hz, 1H), 2.69 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 162.1 (d, $^1J_{\text{CF}} = 243.4$ Hz), 136.8 (d, $^3J_{\text{CF}} = 7.7$ Hz), 133.0, 128.9 (d, $^3J = 8.6$ Hz), 128.7, 128.4 (overlapping), 126.5 (d, $^4J_{\text{CF}} = 1.9$ Hz), 125.5 (q, $^1J_{\text{CF}} = 283.0$ Hz), 117.6 (d, $^2J_{\text{CF}} = 22.0$ Hz), 114.0 (d, $^2J_{\text{CF}} = 20.1$ Hz), 78.7 (q, $^3J_{\text{CF}} = 1.9$ Hz), 78.3, 52.8 (q, $^2J_{\text{CF}} = 26.8$ Hz), 40.4; ^{19}F NMR (376 MHz, CDCl_3): δ -73.6 (s), -115.7 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{17}\text{H}_{12}\text{F}_4$, 292.0875; found, 292.0872. The enantiomeric excess of **7am** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 11.9 min (major) and 16.0 min (minor), 90% ee.



7an

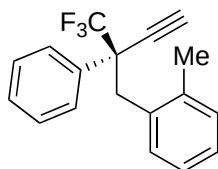
(R)-1-Chloro-3-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7an). A colorless oil (23.8 mg, 0.077 mmol, 77% yield based on the amount of **3a**). $[\alpha]_D^{20} = -13.5$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.66–7.61 (m, 2H), 7.40–7.34 (m, 3H), 7.13 (ddd, $J = 8.0, 2.1, 0.9$ Hz, 1H), 7.03 (t, $J = 8.0$ Hz, 1H), 7.00 (pseudo t, $J = 2.0$ Hz, 1H), 6.82 (d of pseudo t, $J = 8.0, 1.4$ Hz, 1H), 3.47 (d,

$J = 13.8$ Hz, 1H), 3.38 (d, $J = 13.8$ Hz, 1H), 2.70 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 136.3, 133.3, 133.0, 130.9, 128.8, 128.8, 128.4 (overlapping), 127.2, 125.5 (q, $^1J_{\text{CF}} = 282.7$ Hz), 78.6 (q, $^3J_{\text{CF}} = 1.9$ Hz), 78.4, 52.8 (q, $^2J_{\text{CF}} = 26.8$ Hz), 40.4; ^{19}F NMR (376 MHz, CDCl_3): δ -73.5 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{17}\text{H}_{12}\text{ClF}_3$, 308.0580; found, 308.0578. The enantiomeric excess of **7an** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 22.4 min (major) and 33.0 min (minor), 91% ee.



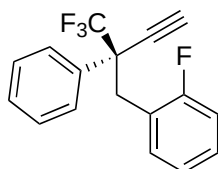
7ao

(R)-1-Bromo-3-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ao). A colorless oil (25.4 mg, 0.072 mmol, 72% yield based on the amount of **3a**). $[\alpha]_{\text{D}}^{20} = -44.5$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.65–7.61 (m, 2H), 7.39–7.35 (m, 3H), 7.29 (ddd, $J = 8.0, 2.0, 0.9$ Hz, 1H), 7.16 (t, $J = 2.0$ Hz, 1H), 6.97 (t, $J = 8.0$ Hz, 1H), 6.86 (d of pseudo t, $J = 8.0, 1.4$ Hz, 1H), 3.46 (d, $J = 13.6$ Hz, 1H), 3.37 (d, $J = 13.6$ Hz, 1H), 2.70 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 136.6, 133.8, 133.0, 130.1, 129.3, 129.1, 128.8, 128.4, 128.4, 125.5 (q, $^1J_{\text{C-F}} = 282.7$ Hz), 121.5, 78.6 (q, $^3J_{\text{CF}} = 1.9$ Hz), 78.5, 52.9 (q, $^2J_{\text{CF}} = 26.8$ Hz), 40.4; ^{19}F NMR (376 MHz, CDCl_3): δ -73.4 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{17}\text{H}_{12}\text{BrF}_3$, 352.0074; found, 352.0073. The enantiomeric excess of **7ao** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 19.5 min (major) and 27.8 min (minor), 93% ee.



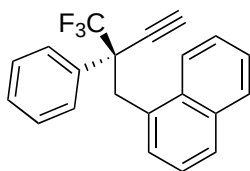
7ap

(R)-1-Methyl-2-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7ap). A colorless oil (21.3 mg, 0.074 mmol, 74% yield based on the amount of **3a**). $[\alpha]_{\text{D}}^{20} = -50.8$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.68–7.64 (m, 2H), 7.39–7.35 (m, 3H), 7.10 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.07 (pseudo t of d $J = 7.8, 1.5$ Hz, 1H), 6.88 (pseudo t of d, $J = 7.2, 2.0$ Hz, 1H), 6.68 (d, $J = 7.6$ Hz, 1H), 3.61 (d, $J = 14.4$ Hz, 1H), 3.44 (d, $J = 14.4$ Hz, 1H), 2.55 (s, 1H), 2.25 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): δ 138.3, 134.6, 133.6, 130.7, 130.6, 129.2, 129.1, 128.9, 127.3, 126.7 (q, $^1J_{\text{CF}} = 282.1$ Hz), 125.4, 79.4, 79.2 (q, $^3J_{\text{CF}} = 1.9$ Hz), 52.9 (q, $^2J_{\text{CF}} = 26.9$ Hz), 36.7, 19.9 (^{13}C NMR spectrum of this compound was measured in acetone- d_6 because some peaks of this compound overlapped with those of CDCl_3); ^{19}F NMR (376 MHz, CDCl_3): δ -73.5 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{15}\text{F}_3$, 288.1126; found, 288.1112. The enantiomeric excess of **7ap** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 14.4 min (major) and 20.0 min (minor), 90% ee.



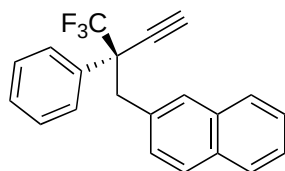
7aq

(R)-1-Fluoro-2-(2-phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzene (7aq). A colorless oil (22.8 mg, 0.078 mmol, 78% yield based on the amount of **3a**). $[\alpha]_D^{20} = -47.0$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.71–7.67 (m, 2H), 7.38–7.33 (m, 3H), 7.18–7.11 (m, 1H), 7.02–6.85 (m, 3H), 3.62 (d, $J = 13.6$ Hz, 1H), 3.51 (d, $J = 13.6$ Hz, 1H), 2.64 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 161.4 (d, $^1J_{\text{CF}} = 245.3$ Hz), 133.4, 132.0 (d, $^3J_{\text{CF}} = 3.8$ Hz), 128.8 (d, $^3J_{\text{CF}} = 8.6$ Hz), 128.6, 128.4, 128.2, 125.6 (q, $^1J_{\text{CF}} = 282.7$ Hz), 123.2 (d, $^4J_{\text{CF}} = 3.8$ Hz), 121.8 (d, $^2J_{\text{CF}} = 14.4$ Hz), 115.0 (d, $^2J_{\text{CF}} = 23.0$ Hz), 78.8 (q, $^3J_{\text{CF}} = 1.9$ Hz), 77.6, 52.3 (q, $^2J_{\text{CF}} = 26.8$ Hz), 33.1; ^{19}F NMR (376 MHz, CDCl_3): δ -73.4 (s), -116.8 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{17}\text{H}_{12}\text{F}_4$, 292.0875; found, 292.0865. The enantiomeric excess of **7aq** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 15.6 min (major) and 18.7 min (minor), 93% ee.



7ar

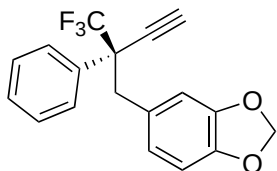
(R)-1-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)naphthalene (7ar). A white solid (22.4 mg, 0.069 mmol, 69% yield based on the amount of **3a**). mp: 83.6–84.2 °C; $[\alpha]_D^{20} = +26.9$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 8.11–8.06 (m, 1H), 7.82–7.77 (m, 1H), 7.70–7.66 (m, 3H), 7.47–7.41 (m, 2H), 7.37–7.33 (m, 2H), 7.17 (pseudo t, $J = 7.8$ Hz, 1H), 6.94 (d, $J = 6.8$ Hz, 1H), 4.16 (d, $J = 14.4$ Hz, 1H), 3.89 (d, $J = 14.4$ Hz, 1H), 2.41 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 134.0, 133.5, 133.0, 130.5, 128.6, 128.5, 128.4 (overlapping), 128.3, 127.6, 125.9 (q, $^1J_{\text{CF}} = 283.0$ Hz), 125.5, 125.3, 124.7, 124.2, 79.2 (q, $^3J_{\text{CF}} = 2.0$ Hz), 78.0, 52.4 (q, $^2J_{\text{CF}} = 26.5$ Hz), 36.1; ^{19}F NMR (376 MHz, CDCl_3): δ -71.9 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{21}\text{H}_{15}\text{F}_3$, 324.1126; found, 324.1132. The enantiomeric excess of **7ar** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 10.4 min (minor) and 12.9 min (major), 91% ee.



7as

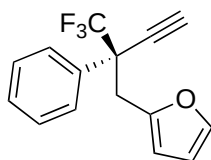
(R)-2-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)naphthalene (7as). A colorless oil (23.0 mg, 0.071 mmol, 71% yield based on the amount of **3a**). $[\alpha]_D^{20} = +37.9$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.74 (dd, $J = 5.6, 3.3$ Hz, 1H), 7.71–7.67 (m, 2H), 7.65 (dd, $J = 6.3, 3.3$ Hz, 1H), 7.75–7.62 (m, 4H), 7.58 (d, $J = 8.3$ Hz, 1H), 7.47 (br, 1H), 7.41 (d, $J = 5.6$ Hz, 1H), 7.40 (d, $J = 6.3$ Hz,

1H), 7.38–7.33 (m, 3H), 7.07 (dd, $J = 8.3, 1.8$ Hz, 1H), 3.69 (d, $J = 13.4$ Hz, 1H), 3.60 (d, $J = 13.4$ Hz, 1H), 2.66 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 133.4, 132.9, 132.4, 131.9, 129.9, 128.7, 128.6, 128.5, 128.3, 127.7, 127.4, 126.9, 125.7, 125.7 (q, $^1J_{\text{CF}} = 282.7$ Hz), 125.7, 79.0 (q, $^3J_{\text{CF}} = 1.9$ Hz), 78.2, 53.1 (q, $^2J_{\text{CF}} = 26.5$ Hz), 40.9; ^{19}F NMR (376 MHz, CDCl_3): δ –73.4 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{21}\text{H}_{15}\text{F}_3$, 324.1126; found: 324.1115. The enantiomeric excess of **7as** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 22.3 min (minor) and 26.3 min (major), 95% ee.



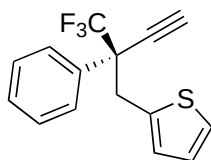
7at

(R)-5-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)benzo[d][1,3]dioxole (7at). A colorless oil (21.0 mg, 0.066 mmol, 66% yield based on the amount of **3a**). $[\alpha]_{\text{D}}^{20} = +52.5$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.67–7.64 (m, 2H), 7.40–7.34 (m, 3H), 6.57 (d, $J = 8.1$ Hz, 1H), 6.49 (d, $J = 1.3$ Hz, 1H), 6.44 (dd, $J = 8.1, 2.2$ Hz, 1H), 5.86 (dd, $J = 2.2, 1.3$ Hz, 1H), 3.43 (d, $J = 13.6$ Hz, 1H), 3.34 (d, $J = 13.6$ Hz, 1H), 2.68 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 146.8, 146.5, 133.3, 128.6, 128.4, 128.3, 127.9, 125.6 (q, $^1J_{\text{CF}} = 283.0$ Hz), 124.2, 111.0, 107.5, 100.8, 79.0, 78.1, 53.1 (q, $^2J_{\text{CF}} = 26.2$ Hz), 40.5; ^{19}F NMR (376 MHz, CDCl_3): δ –73.4 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{13}\text{F}_3\text{O}_2$, 318.0868; found, 318.0865. The enantiomeric excess of **7at** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 90/10, flow rate = 1.0 mL/min, $\lambda = 220$ nm, retention time: 22.7 min (minor) and 48.1 min (major), 91% ee.



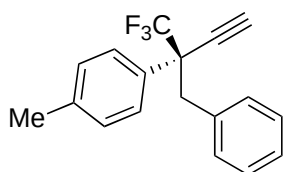
7au

(R)-2-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)furan (7au). A colorless oil (19.7 mg, 0.080 mmol, 80% yield based on the amount of **3a**). $[\alpha]_{\text{D}}^{20} = -16.2$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.64–7.60 (m, 2H), 7.44–7.35 (m, 4H), 6.42 (d, $J = 3.2$ Hz, 1H), 6.00–5.99 (m, 1H), 6.73–6.72 (m, 1H), 6.42 (d, $J = 3.2$ Hz, 1H), 6.00 (ddd, $J = 3.2, 2.4, 0.8$ Hz, 1H), 2.74 (s, 1H), 2.29 (d, $J = 0.8$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 153.3, 146.0, 134.2, 128.8, 128.5, 128.3, 124.1 (q, $^1J_{\text{CF}} = 284.6$ Hz), 111.0, 106.4, 78.2 (q, $^3J_{\text{CF}} = 1.9$ Hz), 75.7, 52.3 (q, $^2J_{\text{CF}} = 29.7$ Hz), 13.6; ^{19}F NMR (376 MHz, CDCl_3): δ –72.2 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{O}$, 264.0762; found, 264.0752. The enantiomeric excess of **7au** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 21.0 min (major) and 27.2 min (minor), 90% ee.



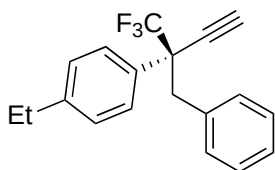
7av

(R)-2-(2-Phenyl-2-(trifluoromethyl)but-3-yn-1-yl)thiophene (7av). A colorless oil (21.0 mg, 0.075 mmol, 75% yield based on the amount of **3a**). $[\alpha]_D^{20} = -12.5$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.71–7.67 (m, 2H), 7.42–7.36 (m, 3H), 7.03 (dd, $J = 5.1, 1.2$ Hz, 1H), 6.80 (dd, $J = 5.1, 3.7$ Hz, 1H), 6.72 (d, $J = 3.7$ Hz, 1H), 3.80 (d, $J = 14.8$ Hz, 1H), 3.68 (d, $J = 14.8$ Hz, 1H), 2.66 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 135.8, 132.8, 128.8, 128.6, 128.4, 128.2, 126.0, 125.3 (q, $^1J_{\text{CF}} = 282.7$ Hz), 124.9, 78.9 (q, $^3J_{\text{CF}} = 1.9$ Hz), 77.7, 52.9 (q, $^2J_{\text{CF}} = 27.2$ Hz), 35.4; ^{19}F NMR (376 MHz, CDCl_3): δ -74.1 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{S}$, 280.0534; found, 280.0522. The enantiomeric excess of **7av** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 15.4 min (major) and 22.9 min (minor), 94% ee.



7ba

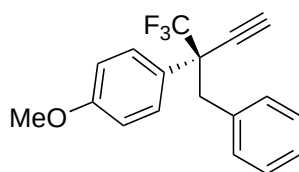
(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-methylbenzene (7ba). A colorless oil (23.4 mg, 0.081 mmol, 81% yield based on the amount of **3b**). $[\alpha]_D^{20} = -44.6$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.53 (d, $J = 8.0$ Hz, 2H), 7.18–7.10 (m, 5H), 7.00 (d, $J = 8.0, 1.6$ Hz, 2H), 3.50 (d, $J = 13.4$ Hz, 1H), 3.40 (d, $J = 13.4$ Hz, 1H), 2.63 (s, 1H), 2.35 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 138.4, 134.5, 130.8, 130.3, 129.0, 128.3, 127.5, 126.9, 125.7 (q, $^1J_{\text{CF}} = 282.7$ Hz), 79.1 (q, $^3J_{\text{CF}} = 2.0$ Hz), 77.8, 52.6 (q, $^2J_{\text{CF}} = 26.5$ Hz), 40.6, 21.0; ^{19}F NMR (376 MHz, CDCl_3): δ -72.1 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{15}\text{F}_3$, 288.1126; found, 288.1123. The enantiomeric excess of **7ba** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 15.1 min (major) and 22.2 min (minor), 90% ee.



7ca

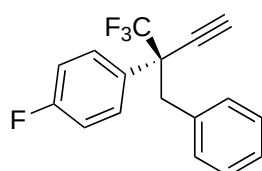
(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-ethylbenzene (7ca). A colorless oil (23.0 mg, 0.076 mmol, 76% yield based on the amount of **3c**). $[\alpha]_D^{20} = -47.4$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.56 (d, $J = 7.6$ Hz, 2H), 7.21–7.10 (m, 5H), 7.01 (dd, $J = 8.0, 1.6$ Hz, 2H), 3.51 (d, $J = 13.2$ Hz, 1H), 3.41 (d, $J = 13.2$ Hz, 1H), 2.66 (q, $J = 7.7$ Hz, 2H), 2.63 (s, 1H), 1.25 (t, $J = 7.7$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 144.6, 134.6, 130.8, 130.6, 128.4, 127.7, 127.5, 126.9, 125.7 (q, $^1J_{\text{CF}} = 282.7$ Hz), 79.2 (q, $^3J_{\text{CF}} = 2.9$ Hz), 77.8, 52.6 (q, $^2J_{\text{CF}} = 26.5$ Hz), 40.7, 28.3, 15.2; ^{19}F NMR (376 MHz, CDCl_3): δ -73.6 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{19}\text{H}_{17}\text{F}_3$, 302.1282; found, 302.1280. The enantiomeric excess of **7ca** was determined by HPLC analysis; DAICEL Chiralpak

OJ-H, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.7 min (major) and 14.6 min (minor), 90% ee.



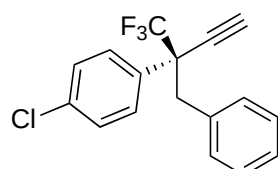
7da

(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-methylbenzene (7da). A colorless oil (21.6 mg, 0.071 mmol, 71% yield based on the amount of **3d**). $[\alpha]_D^{20} = -43.6$ (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, J = 9.0 Hz, 2H), 7.20–7.11 (m, 3H), 7.01 (dd, J = 7.6, 1.6 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H), 3.50 (d, J = 13.4 Hz, 1H), 3.40 (d, J = 13.4 Hz, 1H), 2.63 (s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.6, 134.5, 130.8, 129.7, 127.6, 126.9, 125.7 (q, $^1J_{CF}$ = 282.7 Hz), 125.2, 113.5, 79.2 (q, $^3J_{CF}$ = 2.0 Hz), 77.8, 55.2, 52.3 (q, $^2J_{CF}$ = 26.5 Hz), 40.6; ¹⁹F NMR (376 MHz, CDCl₃): δ -74.0 (s); HRMS (FAB+) (m/z): [M+H]⁺ calcd. for C₁₈H₁₆F₃O, 304.1153; found: 305.1140. The enantiomeric excess of **7da** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*PrOH = 90/10, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 23.2 min (major) and 34.6 min (minor), 91% ee.



7ea

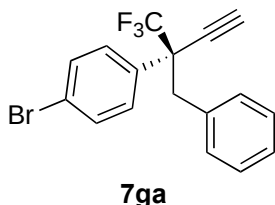
(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-fluorobenzene (7ea). A colorless oil (22.5 mg, 0.077 mmol, 77% yield based on the amount of **3e**). $[\alpha]_D^{20} = -58.8$ (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.62 (dd, J = 8.6, 5.0 Hz, 2H), 7.20–7.10 (m, 3H), 7.04 (pseudo t, J = 8.4 Hz, 2H), 6.98 (dd, J = 8.0, 1.6 Hz, 2H), 3.46 (d, J = 13.2 Hz, 1H), 3.41 (d, J = 13.2 Hz, 1H), 2.67 (s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 162.7 (d, $^1J_{CF}$ = 247.3 Hz), 134.1, 130.7, 130.4 (d, $^3J_{CF}$ = 7.7 Hz), 129.1 (d, $^4J_{CF}$ = 2.9 Hz), 127.7, 127.1, 125.6 (q, $^1J_{CF}$ = 282.7 Hz), 115.2 (d, $^2J_{CF}$ = 21.1 Hz), 78.8 (q, $^3J_{CF}$ = 2.9 Hz), 78.2, 52.5 (q, $^2J_{CF}$ = 26.7 Hz), 40.8; ¹⁹F NMR (376 MHz, CDCl₃): δ -73.8 (s), -115.1 (s); HRMS (FAB+) (m/z): [M+H]⁺ calcd. for C₁₇H₁₃F₄, 293.0953; found, 293.0945. The enantiomeric excess of **7ea** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 9.0 min (major) and 10.0 min (minor), 94% ee.



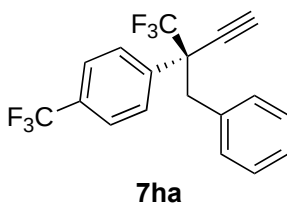
7fa

(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-chlorobenzene (7fa). A colorless oil (22.8 mg, 0.074 mmol, 74% yield based on the amount of **3f**). $[\alpha]_D^{20} = -54.2$ (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.21–7.11 (m, 3H), 6.99 (dd, J = 8.0, 1.6 Hz, 2H), 3.47 (d, J = 13.6 Hz, 1H), 3.42 (d, J = 13.6 Hz, 1H), 2.68 (s, 1H); ¹³C{¹H} NMR

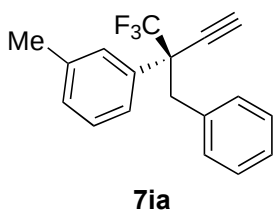
(100 MHz, CDCl₃): δ 134.7, 134.0, 131.9, 130.7, 129.9, 128.5, 127.7, 127.1, 125.5 (q, $^1J_{\text{CF}} = 282.7$ Hz), 78.6 (q, $^3J_{\text{CF}} = 1.9$ Hz), 78.4, 52.6 (q, $^2J_{\text{CF}} = 26.8$ Hz), 40.6; ^{19}F NMR (376 MHz, CDCl₃): δ -72.0 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for C₁₇H₁₂ClF₃, 308.0580; found: 308.0590. The enantiomeric excess of **7fa** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 15.2 min (major) and 16.6 min (minor), 90% ee.



(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-bromobenzene (7ga). A white solid (24.7 mg, 0.070 mmol, 70% yield based on the amount of **3g**). mp: 49.2–59.3 °C; $[\alpha]_{\text{D}}^{20} = -20.3$ (0.5 M in CHCl₃); ^1H NMR (400 MHz, CDCl₃): δ 7.53–7.46 (m, 4H), 7.20–7.11 (m, 3H), 6.98 (dd, $J = 8.0, 1.6$ Hz, 2H), 3.46 (d, $J = 13.2$ Hz, 1H), 3.41 (d, $J = 13.2$ Hz, 1H), 2.67 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃): δ 133.9, 132.5, 131.4, 130.7, 130.3, 127.7, 127.2, 125.4 (q, $^1J_{\text{CF}} = 283.0$ Hz), 123.0, 78.5 (q, $^3J_{\text{CF}} = 1.9$ Hz), 78.4, 52.7 (q, $^2J_{\text{CF}} = 26.8$ Hz), 40.6; ^{19}F NMR (376 MHz, CDCl₃): δ -73.7 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for C₁₇H₁₂BrF₃, 352.0074; found: 352.0083. The enantiomeric excess of **7ga** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 8.8 min (major) and 9.8 min (minor), 92% ee.

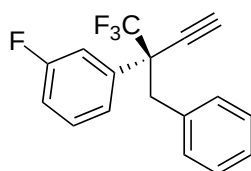


(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-4-(trifluoromethyl)benzene (7ha). A colorless oil (28.4 mg, 0.083 mmol, 83% yield based on the amount of **3h**). $[\alpha]_{\text{D}}^{20} = -50.2$ (0.5 M in CHCl₃); ^1H NMR (400 MHz, CDCl₃): δ 7.78 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.21–7.10 (m, 3H), 6.97 (dd, $J = 7.6, 1.4$ Hz, 2H), 3.50 (d, $J = 13.6$ Hz, 1H), 3.46 (d, $J = 13.6$ Hz, 1H), 2.72 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃): δ 137.5, 133.7, 130.7, 129.0, 128.4 (q, $^2J_{\text{CF}} = 12.8$ Hz), 127.8, 127.3, 125.4 (q, $^1J_{\text{CF}} = 283.0$ Hz), 125.2 (q, $^3J_{\text{CF}} = 3.5$ Hz), 123.8 (q, $^1J_{\text{CF}} = 270.9$ Hz), 78.8, 78.3 (q, $^3J_{\text{CF}} = 1.9$ Hz), 53.0 (q, $^2J_{\text{CF}} = 26.8$ Hz), 40.7; ^{19}F NMR (376 MHz, CDCl₃): δ -64.3 (s), -73.3 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for C₁₈H₁₂F₆, 342.0843; found: 342.0847. The enantiomeric excess of **7ha** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 9.7 min (major) and 10.7 min (minor), 93% ee.



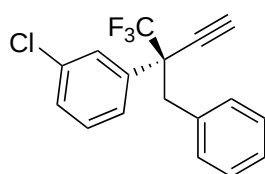
(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-3-methylbenzene (7ia). A colorless oil (19.3 mg, 0.067 mmol, 67% yield based on the amount of **3i**). $[\alpha]_{\text{D}}^{20} = -49.4$ (0.5 M in CHCl₃); ^1H NMR (400

MHz, CDCl₃): δ 7.47–7.44 (br, 2H), 7.25 (pseudo t, J = 8.0 Hz, 1H), 7.21–7.10 (m, 4H), 6.99 (dd, J = 8.0, 1.6 Hz, 2H), 3.51 (d, J = 13.6 Hz, 1H), 3.40 (d, J = 13.6 Hz, 1H), 2.64 (s, 1H), 2.36 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 137.9, 134.5, 133.2, 130.8, 129.3, 129.2, 128.1, 127.5, 126.9, 125.7 (q, ¹ J_{CF} = 282.7 Hz), 125.4, 79.1 (q, ³ J_{CF} = 2.0 Hz), 78.0, 52.9 (q, ² J_{CF} = 26.2 Hz), 40.7, 21.6; ¹⁹F NMR (376 MHz, CDCl₃): δ –73.4 (s); HRMS (FAB+) (m/z): [M+H]⁺ calcd. for C₁₈H₁₆F₃, 289.1204; found, 289.1203. The enantiomeric excess of **7ia** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ⁱPrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 13.9 min (major) and 15.4 min (minor), 90% ee.



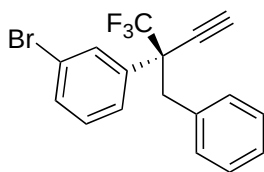
7ja

(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-3-fluorobenzene (7ja). A colorless oil (21.0 mg, 0.072 mmol, 72% yield based on the amount of **3j**). $[\alpha]_D^{20}$ = –18.5 (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.44 (br d, J = 8.0 Hz, 1H), 7.40–7.30 (m, 2H), 7.20–7.10 (m, 3H), 7.05 (pseudo t of dd, J = 8.3, 2.8, 0.9 Hz, 1H), 6.98 (d, J = 8.0, 1.6 Hz, 2H), 3.47 (d, J = 13.4 Hz, 1H), 3.42 (d, J = 13.4 Hz, 1H), 2.68 (s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 162.5 (d, ¹ J_{CF} = 245.3 Hz), 136.0 (d, ³ J_{CF} = 7.7 Hz), 133.9, 130.7, 129.7 (d, ³ J_{CF} = 7.7 Hz), 127.7, 127.2, 125.0 (q, ¹ J_{CF} = 282.7 Hz), 124.1, 116.1 (d, ² J_{CF} = 24.0 Hz), 115.6 (d, ² J_{CF} = 21.1 Hz), 78.4, 77.2, 52.9 (q, ² J_{CF} = 27.1 Hz), 40.8; ¹⁹F NMR (376 MHz, CDCl₃): δ –73.4 (s), –113.8 (s); HRMS (FAB+) (m/z): [M]⁺ calcd. for C₁₇H₁₂F₄, 292.0875; found, 292.0878. The enantiomeric excess of **7ja** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ⁱPrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 11.9 min (major) and 16.0 min (minor), 90% ee.



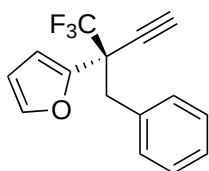
7ka

(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-3-chlorobenzene (7ka). A colorless oil (20.1 mg, 0.065 mmol, 65% yield based on the amount of **3k**). $[\alpha]_D^{20}$ = –50.0 (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.64 (br, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.33 (dt, J = 8.0, 1.8 Hz, 1H), 7.29 (pseudo t, J = 7.4 Hz, 1H), 7.21–7.11 (m, 3H), 6.99 (dd, J = 7.6, 1.2 Hz, 1H), 3.47 (d, J = 13.6 Hz, 1H), 3.42 (d, J = 13.6 Hz, 1H), 2.69 (s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 135.5, 134.3, 133.9, 130.7, 129.4, 128.9, 128.8, 127.7, 127.2, 126.6, 125.4 (q, ¹ J_{CF} = 283.0 Hz), 78.6, 78.4 (q, ³ J_{CF} = 2.0 Hz), 52.9 (q, ² J_{CF} = 24.8 Hz), 40.7; ¹⁹F NMR (376 MHz, CDCl₃): δ –73.4 (s); HRMS (FAB+) (m/z): [M]⁺ calcd. for C₁₇H₁₂ClF₃, 308.0580; found: 308.0576. The enantiomeric excess of **7ka** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ⁱPrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 27.9 min (major) and 35.2 min (minor), 95% ee.



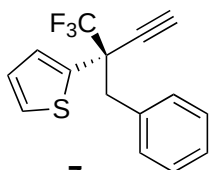
7la

(R)-1-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)-3-bromobenzene (7la). A colorless oil (24.7 mg, 0.070 mmol, 70% yield based on the amount of **3l**). $[\alpha]_D^{20} = -45.9$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.79 (br, 1H), 7.58(d of pseudo quint, $J = 8.0, 0.9$ Hz, 1H), 7.49 (ddd, $J = 8.0, 1.8, 0.9$ Hz, 1H), 7.23 (t, $J = 8.0$ Hz, 1H), 7.19–7.11 (m, 3H), 6.99 (dd, $J = 8.0, 1.6$ Hz, 1H), 3.46 (d, $J = 13.4$ Hz, 1H), 3.41 (d, $J = 13.4$ Hz, 1H), 2.69 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 135.7, 133.8, 131.8, 131.7, 130.7, 129.7, 127.7, 127.2, 127.1, 125.4 (q, $^1J_{\text{CF}} = 283.0$ Hz), 122.5, 78.7, 78.3 (q, $^3J_{\text{CF}} = 1.9$ Hz), 52.8 (q, $^2J_{\text{CF}} = 26.5$ Hz), 40.7; ^{19}F NMR (376 MHz, CDCl_3): δ -73.4 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{17}\text{H}_{12}\text{BrF}_3$, 352.0074; found, 352.0070. The enantiomeric excess of **7la** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 14.1 min (minor) and 18.4 min (major), 90% ee.



7ma

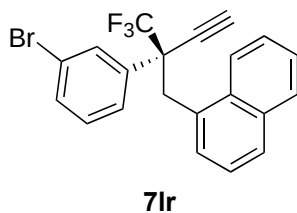
(R)-2-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)furan (7ma). A colorless oil (20.1 mg, 0.076 mmol, 76% yield based on the amount of **3m**). $[\alpha]_D^{20} = -11.0$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.50 (dd, $J = 2.0, 0.8$ Hz, 1H), 7.21–7.15 (m, 3H), 6.97 (dd, $J = 7.6, 1.8$ Hz, 2H), 6.40 (dd, $J = 3.6, 0.8$ Hz, 1H), 6.32 (dd, $J = 3.6$ Hz, 2.0 Hz, 1H), 3.61 (d, $J = 12.8$ Hz, 1H), 3.22 (d, $J = 12.8$ Hz, 1H), 2.47 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3CN): δ 147.2, 144.4, 134.6, 130.9, 128.2, 127.7, 125.2 (q, $^1J_{\text{CF}} = 282.7$ Hz), 112.8, 111.2, 77.5, 76.9 (q, $^3J_{\text{CF}} = 1.9$ Hz), 49.7 (q, $^2J_{\text{CF}} = 28.1$ Hz), 38.7; ^{19}F NMR (376 MHz, CDCl_3): δ -74.7 (s). HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{O}$, 264.0762; found, 264.0758. The enantiomeric excess of **7ma** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/ i PrOH = 99/1, flow rate = 0.5 mL/min, $\lambda = 220$ nm, retention time: 13.2 min (minor) and 16.0 min (major), 96% ee.



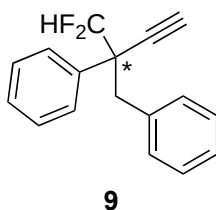
7na

(S)-2-(2-Benzyl-1,1,1-trifluorobut-3-yn-2-yl)thiophene (7na). A colorless oil (18.2 mg, 0.065 mmol, 65% yield based on the amount of **3n**). $[\alpha]_D^{20} = -51.6$ (0.5 M in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.30 (dd, $J = 4.9, 1.4$ Hz, 1H), 7.22–7.14 (m, 4H), 7.04 (dd, $J = 8.0, 1.6$ Hz, 1H), 6.98 (dd, $J = 4.9, 3.6$ Hz, 1H), 3.41 (d, $J = 12.8$ Hz, 1H), 3.36 (d, $J = 12.8$ Hz, 1H), 2.60 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3CN): δ 137.3, 134.0, 130.6, 128.3, 127.6, 127.2, 126.8, 126.3, 125.1 (q, $^1J_{\text{CF}} = 282.7$ Hz), 78.5, 76.8, 50.5 (q, $^2J_{\text{CF}} = 28.1$ Hz), 42.6 (^{13}C NMR spectrum of this compound was measured in acetonitrile- d_6 because some peaks of this compound overlapped with those of CDCl_3); ^{19}F NMR (376 MHz, CDCl_3): δ -75.1 (s); HRMS (FAB+) (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{S}$, 280.0534; found, 280.0527. The enantiomeric excess of **7na** was determined by HPLC analysis; DAICEL Chiralpak

OJ-H, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 18.4 min (minor) and 23.6 min (major), 90% ee.



(*R*)-1-(2-(3-Bromophenyl)-2-(trifluoromethyl)but-3-yn-1-yl)naphthalene (7lr). A white solid (24.6 mg, 0.061 mmol, 61% yield based on the amount of **3l**). mp: 95.2–96.4 °C; $[\alpha]_D^{20}$ = +36.9 (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.08–8.02 (m, 1H), 7.85–7.79 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.51–7.41 (m, 3H), 7.22 (pseudo t, *J* = 7.0 Hz, 1H), 7.20 (pseudo t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 4.14 (d, *J* = 14.4 Hz, 1H), 3.85 (d, *J* = 14.4 Hz, 1H), 2.45 (s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 136.3, 133.6, 132.9, 131.8, 131.6, 130.0, 129.8, 128.6, 128.4, 127.9, 126.9, 125.6 (q, ¹*J*_{CF} = 283.0 Hz), 125.5, 125.4, 124.7, 124.1, 122.6, 78.7, 78.5 (q, ³*J*_{CF} = 1.9 Hz), 52.3 (q, ²*J*_{CF} = 26.8 Hz), 36.2; ¹⁹F NMR (376 MHz, CDCl₃): δ –71.6 (s); HRMS (FAB+) (*m/z*): [*M*]⁺ calcd. for C₂₁H₁₄BrF₃, 402.0231; found, 402.0240. The enantiomeric excess of **7lr** was determined by HPLC analysis; DAICEL Chiralpak OD, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 13.6 min (minor) and 18.9 min (major), 91% ee. Colorless needle crystals suitable for X-ray analysis were obtained by recrystallization from Et₂O, after additional purification of (*R*)-isomer by HPLC.



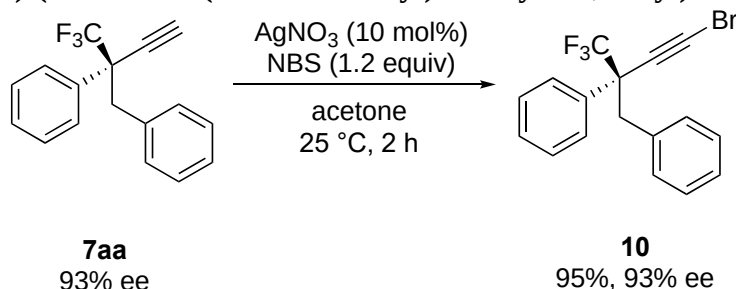
(*R*)-2-(2-(Difluoromethyl)but-3-yn-1,2-diyl)dibenzene (9). A colorless oil (19.2 mg, 0.075 mmol, 75% yield based on the amount of **8**). $[\alpha]_D^{20}$ = –32.7 (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.61 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.40–7.31 (m, 3H), 7.22–7.15 (m, 3H), 7.07 (dd, *J* = 7.2, 2.4 Hz, 2H), 5.95 (t, *J* = 56.2 Hz, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 3.31 (dd, *J* = 13.2, 0.8 Hz, 1H), 2.62 (s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 135.2, 134.9, 130.7, 128.3, 128.2, 128.1, 127.7, 126.9, 116.5 (t, ¹*J*_{CF} = 250.1 Hz), 80.8 (dd, ³*J*_{CF} = 5.7, 3.8 Hz), 77.5, 51.1 (t, ²*J*_{CF} = 20.1 Hz), 41.2 (t, ³*J*_{CF} = 2.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃): δ –123.3 (dd, ²*J*_{FF} = 268 Hz, ²*J*_{HF} = 54 Hz), –126.5 (dd, dd, ²*J*_{FF} = 268 Hz, ²*J*_{HF} = 54 Hz); HRMS (FAB+) (*m/z*): [*M*+H]⁺ calcd. for C₁₇H₁₅F₂, 257.1142; found, 257.1137. The enantiomeric excess of **9** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*PrOH = 99/1, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 19.4 min (major) and 30.4 min (minor), 63% ee.

1.5. Large-Scale Preparation of **7aa**

In an oven dried 100 mL Schlenk flask were placed [**Ru**]-**2** (63.0 mg, 0.050 mmol) and NH₄BF₄ (11.0 mg, 0.10 mmol) under N₂. Anhydrous ClCH₂CCH₂Cl (20 mL) was added, and then the mixture was magnetically stirred at room temperature for 60 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-

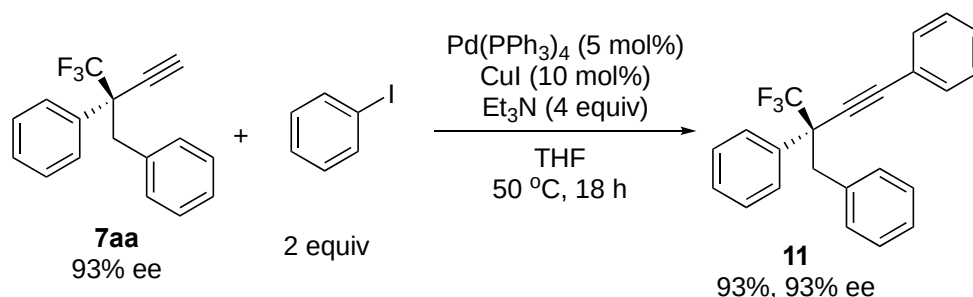
ol (**3a**) (200 mg, 1.0 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (412.1 mg, 1.2 mmol), *fac*-[Ir(ppy)₃] (6.4 mg, 0.01 mmol), and BF₃·Et₂O (148 μL, 170 mg, 1.20 mmol) were added under N₂ at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography (SiO₂) with *n*-hexane as an eluent to afford (*R*)-(2-(trifluoromethyl)but-3-yn-1,2-diyl)dibenzene (**7aa**) as a colorless oil (205.5 mg, 0.75 mmol, 75% yield based on the amount of **3a**) with 93% ee.

1.6. Preparation of (*S*)-(4-bromo-2-(trifluoromethyl)but-3-yn-1,2-diyl)dibenzene (**10**)



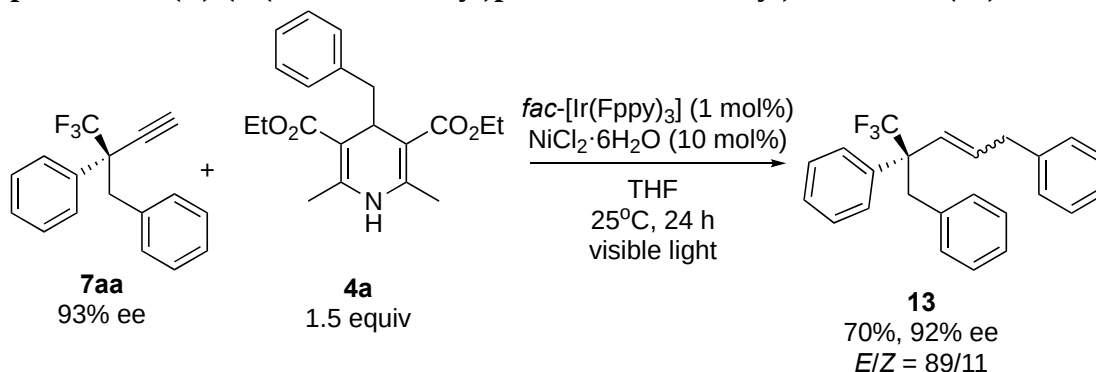
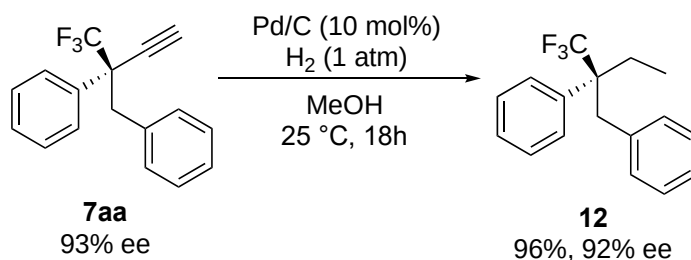
In a 20 mL Schlenk flask were placed (*R*)-**7aa** (27.4 mg, 0.10 mmol, 93% ee), *N*-bromosuccinimide (NBS) (21.4 mg, 0.12 mmol) and AgNO₃ (1.7 mg, 0.010 mmol) under N₂, where acetone (5.0 mL) was added at room temperature. And the mixture was stirred at room temperature for 2 h. The volatiles were then removed *in vacuo*, and the residue was purified by column chromatography (SiO₂) with *n*-hexane as an eluent to afford (*S*)-(4-bromo-2-(trifluoromethyl)but-3-yn-1,2-diyl)dibenzene (**10**) as a colorless oil (33.6 mg, 0.95 mmol, 95% yield based on the amount of **7aa**). [α]_D²⁰ = −41.3 (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.60–7.56 (m, 2H), 7.38–7.33 (m, 3H), 7.19–7.11 (m, 3H), 6.95 (dd, *J* = 7.8, 1.4 Hz, 2H), 3.49 (d, *J* = 13.4 Hz, 1H), 3.42 (d, *J* = 13.4 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 134.3, 133.5, 130.7, 128.6, 128.4, 128.3, 127.6, 127.0, 125.5 (q, ¹*J*_{CF} = 283.0 Hz), 75.5, 54.2 (q, ²*J*_{CF} = 26.5 Hz), 49.6, 41.0; ¹⁹F NMR (376 MHz, CDCl₃): δ −73.2 (s); HRMS (FAB+) (*m/z*): [*M*]⁺ calcd. for C₁₇H₁₂BrF₃, 352.0074; found: 352.0080. The enantiomeric excess of **10** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*PrOH = 100/0, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 16.0 min (major) and 19.4 min (minor), 93% ee.

1.7. Preparation of (*S*)-(2-(trifluoromethyl)but-3-yn-1,2,4-triyl)tribenzene (**11**)



In a 20 mL Schlenk flask were placed (*R*)-**7aa** (27.4 mg, 0.10 mmol, 93% ee), iodobenzene (40.8 mg, 0.20 mmol), Pd(PPh₃)₄ (5.8 mg, 0.0050 mmol), CuI (1.9 mg, 0.010 mmol), and Et₃N (56 μL, 0.40 mmol) under N₂, where THF (2.0 mL) was added at room temperature. And the mixture was stirred at 50 °C for 18 h. The volatiles were then removed *in vacuo*, and the residue was purified by column

chromatography (SiO₂) with *n*-hexane as an eluent to afford (*S*)-(2-(trifluoromethyl)but-3-yn-1,2,4-triyl)tribenzene (**11**) as a white solid. (32.6 mg, 0.93 mmol, 93% yield based on the amount of **7aa**). mp: 57.0–58.5 °C; [α]_D²⁰: –53.5 (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.70 (br d, *J* = 8.0 Hz, 2H), 7.45 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.40–7.33 (m, 6H), 7.19–7.10 (m, 3H), 7.04 (dd, *J* = 7.6, 1.6 Hz, 2H), 3.58 (d, *J* = 13.2 Hz, 1H), 3.50 (d, *J* = 13.2 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 134.8, 134.3, 131.7, 130.8, 128.7, 128.6, 128.4, 128.3, 128.3, 127.5, 126.9, 125.9 (q, ¹*J*_{CF} = 283.3 Hz), 122.2, 89.6, 84.5, 53.6 (q, ²*J*_{CF} = 26.5 Hz), 41.2; ¹⁹F NMR (376 MHz, CDCl₃): δ –73.2; HRMS (FAB+) (*m/z*): [M]⁺ calcd. for C₂₃H₁₇F₃, 350.1282; found: 350.1289. The enantiomeric excess of **11** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/^{*i*}PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: 8.0 min (major) and 9.5 min (minor), 93% ee.



where THF (2.0 mL) was added at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 24 h. *E/Z* ratio of (*R*)-(2-(trifluoromethyl)pent-3-ene-1,2,5-triyl)tribenzene in the crude mixture was determined to be 55/45 by quantitative measurement of GC-MS. The volatiles were then removed *in vacuo*, and the residue was purified by column chromatography (SiO₂) with *n*-hexane as an eluent to afford a mixture of (*R,E*)-(2-(trifluoromethyl)pent-3-ene-1,2,5-triyl)tribenzene (*(E)*-**13**) and (*R,Z*)-(2-(trifluoromethyl)pent-3-ene-1,2,5-triyl)tribenzene (*(Z)*-**13**) as a colorless oil (*E/Z* = 89/11, 25.6 mg, 0.70 mmol, 70% yield based on the amount of **7aa**). $[\alpha]_D^{20} = -26.5$ (0.5 M in CHCl₃); ¹H NMR (400 MHz, CDCl₃): (*E*)-**13**: δ 7.48–7.44 (m, 2H), 7.36–7.27 (m, 5H), 7.22 (t of pseudo t, *J* = 7.2, 1.7 Hz, 1H), 7.18–7.07 (m, 5H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 2H), 5.93 (dtq, *J* = 16.0, 6.9, 1.6 Hz, 1H), 5.65 (dq, *J* = 16.0, 1.3 Hz, 1H), 3.50 (d, *J* = 14.2 Hz, 1H), 3.47 (d, *J* = 6.9 Hz, 2H), 3.37 (d, *J* = 14.2 Hz, 1H); (*Z*)-**13** (¹H NMR resonances due to 11H of aromatic CH, 1H of CH=CHCH₂, and 3H of CH₂ overlapping with those of (*E*)-**13** (δ 7.48–7.06, 5.97–5.88, and 3.53–3.49, respectively): 6.95 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.90 (dd, *J* = 8.2, 1.4 Hz, 2H), 5.83 (dq, *J* = 12.0, 1.8 Hz, 1H), (m, 3H, 3H of two CH₂ resonances overlapping with those of (*E*)-**13**), 3.33 (d, *J* = 13.6 Hz, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃, 100 MHz): (*E*)-**13**: δ 139.6, 137.4, 135.6, 133.3, 131.0, 129.2, 129.1, 128.6, 128.5, 128.0, 127.7, 127.6, 127.3 (q, ¹*J*_{CF} = 283.3 Hz), 126.5, 126.2, 55.2 (q, ²*J*_{CF} = 23.0 Hz), 40.7, 39.5; (*Z*)-**13**: δ 139.7, 137.9, 136.2, 136.0, 131.3, 129.3, 128.8, 128.3, 128.1, 126.8, 126.6, 126.6 (q, ¹*J*_{CF} = 277.9 Hz), 126.0, 55.1 (q, ²*J*_{CF} = 23.0 Hz), 42.9, 35.6; ¹⁹F NMR (376 MHz, CDCl₃): δ –69.9; HRMS (FAB+) (*m/z*): [*M*]⁺ calcd. for C₂₄H₂₁F₃, 366.1595; found, 366.1605. The enantiomeric excess of **13** was determined by HPLC analysis; DAICEL Chiralpak OJ-H, hexane/*i*PrOH = 99/1, flow rate = 0.5 mL/min, λ = 220 nm, retention time: (*E*)-**13**: 13.8 min (minor) and 15.8 min (major), 92% ee; (*Z*)-**13**: 11.9 min (minor) and 18.3 min (major), 92% ee.

1.10. Preparation of **14**

In an oven dried 20 mL Schlenk flask were placed [**Ru**]-**1** (30.0 mg, 0.026 mmol), NH₄BF₄ (5.5 mg, 0.052 mmol) under N₂. Anhydrous ClCH₂CCH₂Cl (3.0 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **3a** (52.0 mg, 0.26 mmol) and BF₃·Et₂O (8 μL, 9 mg, 0.065 mmol), the mixture was stirred at 25 °C for 24 h. Then, the solvent was filtered to remove residual inorganic salts. The filtrate was concentrated under reduced pressure, where conversion of [**Ru**]-**1** into **14** (98% NMR yield) was confirmed by ¹H NMR by using 1,1,2,2-tetrachloroethane as an internal standard. The residue was washed with hexane (5 mL × 3) and Et₂O (5 mL × 3) to give reddish brown solid (**14**) in 71% yield (25.8 mg, 0.018 mmol) (Fig. 6a).⁵

1.11. Stoichiometric reaction of **14** with **4a**

In an oven dried 20 mL Schlenk flask were placed **14** (138 mg, 0.10 mmol) and under N₂. Anhydrous ClCH₂CCH₂Cl (2.0 mL) was added and then, 1,1,1-trifluoro-2-(*p*-tolyl)but-3-yn-2-ol (**3b**) (21.4 mg, 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)₃] (0.7 mg, 0.0011 mmol) were added under N₂ at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography

(SiO₂) with *n*-hexane as an eluent to afford (*R*)-(2-(trifluoromethyl)but-3-yn-1,2-diyl)dibenzene (**7aa**) as a colorless oil (18.1 mg, 0.066 mmol, 66% yield based on the amount of **3a**) with 88% ee (Fig. 6b).

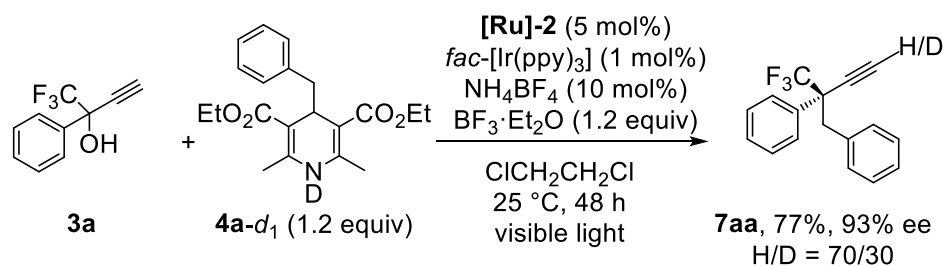
1.12. Catalytic reaction of **3a** with **4a** by using **14** as a catalyst

In an oven dried 20 mL Schlenk flask were placed **14** (6.9 mg, 0.0050 mmol) and under N₂. Anhydrous ClCH₂CCH₂Cl (2.0 mL) was added, and then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg, 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)₃] (0.7 mg, 0.0011 mmol), and BF₃·Et₂O (15 μL, 17 mg, 0.12 mmol) were added under N₂ at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography (SiO₂) with *n*-hexane as an eluent to afford (*R*)-(2-(trifluoromethyl)but-3-yn-1,2-diyl)dibenzene (**7aa**) as a colorless oil (23.3 mg, 0.085 mmol, 85% yield based on the amount of **3a**) with 85% ee (Fig. 6c).

1.13. Reactions in the presence of TEMPO

In an oven dried 20 mL Schlenk flask were placed [Ru]-**2** (6.3 mg, 0.0050 mmol) and NH₄BF₄ (1.1 mg, 0.010 mmol) under N₂. Anhydrous ClCH₂CCH₂Cl (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg, 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)₃] (0.7 mg, 0.0011 mmol), and BF₃·Et₂O (15 μL, 17 mg, 0.12 mmol) were added under N₂ at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the crude yield of 1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (**15**)²⁰ (34% NMR yield) was determined by ¹H NMR in CDCl₃, where 1,1,2,2-tetrachloroethane (16.8 mg, 0.100 mmol) was added as an internal standard (Fig. 6d).

1.14. Deuterium labeling reaction



In an oven dried 20 mL Schlenk flask were placed [Ru]-**2** (6.3 mg, 0.0050 mmol) and NH₄BF₄ (1.1 mg, 0.010 mmol) under N₂. Anhydrous ClCH₂CCH₂Cl (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg, 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1-deuterium-4-hydropyridine-3,5-dicarboxylate (**4a-d₁**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)₃] (0.7 mg, 0.0011 mmol), and BF₃·Et₂O (15 μL, 17 mg, 0.12 mmol) were added under N₂ at room temperature. The reaction flask was

placed in an As One LTB-125 constant low temperature water bath set at 25 °C, and was illuminated from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source for 48 h. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography (SiO₂) with *n*-hexane as an eluent to afford (*R*)-(2-(trifluoromethyl)but-3-yn-1,2-diyl)dibenzene (**7aa**) as a colorless oil (21.1 mg, 0.077 mmol, 77% yield based on the amount of **3a**) with 93% ee. The ratio of H/D is determined by ¹H NMR to be 70/30 at δ 2.66.

1.15. Stern–Volmer analysis

Luminescence quenching experiments for the THF solution of *fac*-[Ir(ppy)₃] (2.0 μmol/L, prepared by stepwise dilutions of *fac*-[Ir(ppy)₃] (1.3 mg, 2.0 μmol) with ClCH₂CH₂Cl) with **3a**, **4a** or **16** in selected concentrations were performed on a Shimadzu RF-5300PC spectrophotometer, where the solutions containing *fac*-[Ir(ppy)₃] and **3a**, **4a** or **16** were excited at λ_{max} = 440 nm, and emissions were measured at λ = 494 nm.

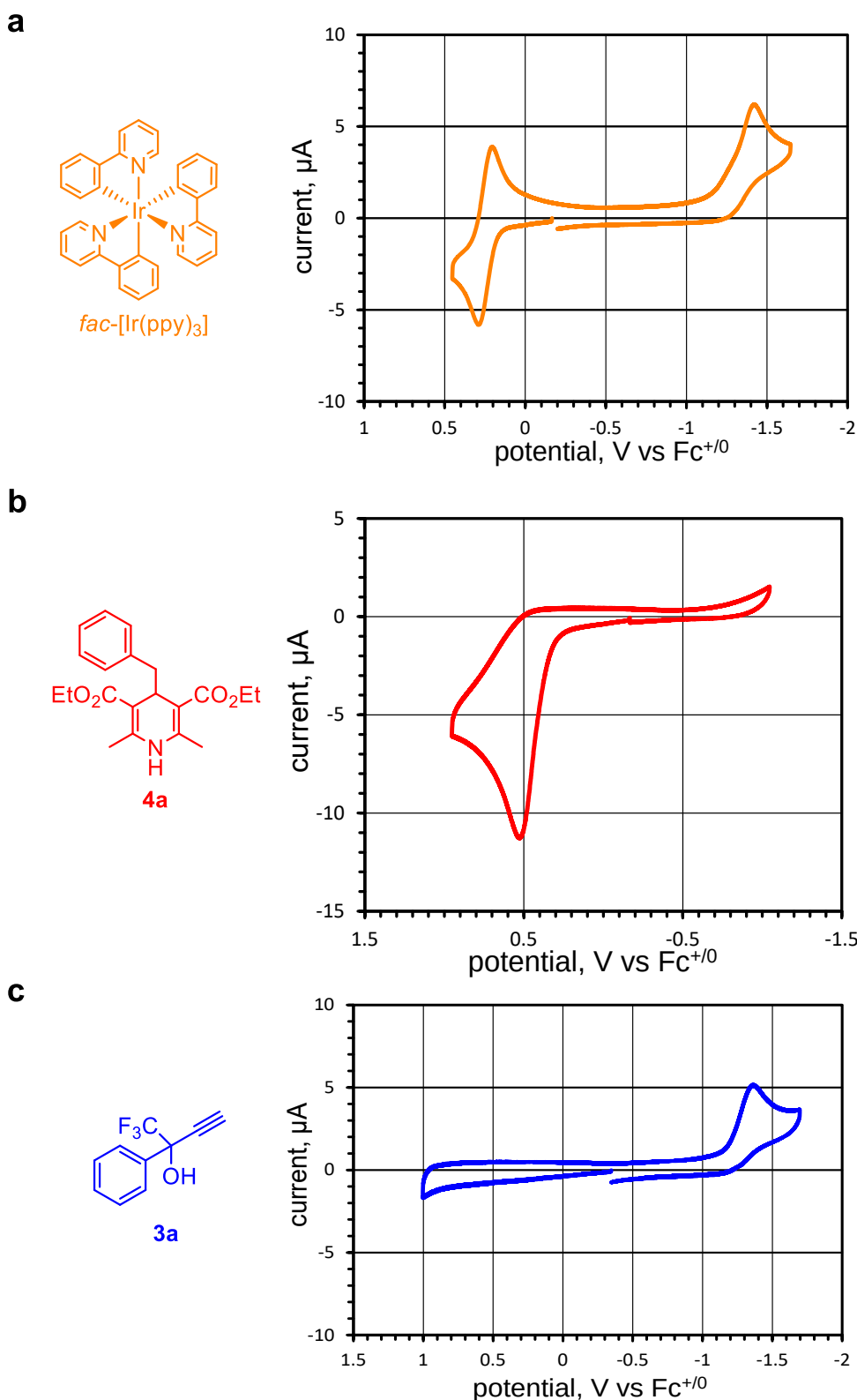
From the slopes (100.5 for **3a**, 208.3 for **4a** and 32.6 for **16**), obtained by the plot and the excited-state lifetime of *fac*-[Ir(ppy)₃] (τ = 1.9 μs),²¹ the rate constants were calculated to be at, *k*_{3a} = (5.3 ± 0.2) × 10⁷ M⁻¹ s⁻¹ (**3a**), *k*_{4a} = (1.10 ± 0.05) × 10⁸ M⁻¹ s⁻¹ (**4a**) and *k*₁₆ = (1.72 ± 0.07) × 10⁷ M⁻¹ s⁻¹ (**16**), respectively, by using the Stern–Volmer linear correlation relationship (Fig. 7a).²²

1.16. Light on/off experiments

In an oven dried 20 mL Schlenk flask were placed [**Ru**]-**2** (6.3 mg, 0.0050 mmol) and NH₄BF₄ (1.1 mg, 0.010 mmol) under N₂. Anhydrous ClCH₂CCH₂Cl (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg, 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)₃] (0.7 mg, 0.0011 mmol), and BF₃·Et₂O (15 μL, 17 mg, 0.12 mmol) were added under N₂ at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 °C. The reaction was conducted for 32 h under alternating periods of (1) irradiation from the bottom of the bath with an Aitech System TMN100×120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source, and (2) darkness with the reaction vessel wrapped with aluminum foil, where yields of **7aa** were determined every 4 hours by quantitative measurements of gas chromatography–mass spectroscopy (GC-MS) recorded on a Shimadzu GCMS-QP2010 PLUS instrument, where *n*-octane was added as an internal standard (Fig. 7b).

1.17. Cyclic voltammetric studies

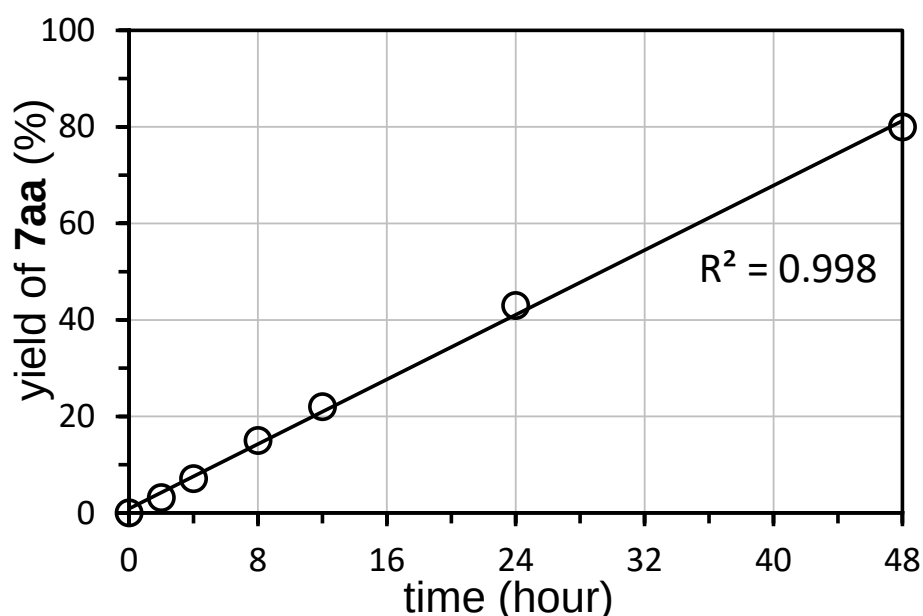
Cyclic voltammograms were recorded on an ALS/Chi model 610C electrochemical analyzer in ClCH₂CH₂Cl containing 1 mM of sample and 0.1 M of ⁿBu₄NPF₆ as a supporting electrolyte using glassy carbon working electrode and platinum wire counter electrode at a scan rate of 0.1 V/s at room temperature. All potentials were measured against Ag/AgNO₃ reference electrode (0.01 M AgNO₃, 0.1 M ⁿBu₄ClO₄, MeCN) and converted to the values vs FeCp₂⁺⁰ (Cp = η⁵-C₅H₅). The cyclic voltammograms of *fac*-[Ir(ppy)₃], **4a**, and **3a** in ClCH₂CH₂Cl are shown in Supplementary Fig. 1.



Supplementary Fig. 1: Cyclic voltammetric studies. **a** Cyclic voltammogram of *fac*-[Ir(ppy)₃] in $\text{ClCH}_2\text{CH}_2\text{Cl}$. $E_{1/2}(\text{Ir}/\text{Ir}^-) = -1.60$ V vs $\text{FcCp}_2^{+/0}$, $E_{\text{pa}}(\text{Ir}/\text{Ir}^+) = +0.25$ V vs $\text{FcCp}_2^{+/0}$. Therefore, $E_{\text{pc}}(\text{Ir}^*/\text{Ir}^-) = +0.90$ V vs $\text{FcCp}_2^{+/0}$, $E_{1/2}(\text{Ir}^{*+}) = -2.25$ V vs $\text{FcCp}_2^{+/0}$, based on the emission energy of *fac*-[Ir(ppy)₃] at 2.50 eV.²³ **b** Cyclic voltammogram of **4a** in THF. $E_{\text{pa}}(\mathbf{4a}/\mathbf{4a}^+) = +0.53$ V vs $\text{FcCp}_2^{+/0}$. **c** Cyclic voltammogram of **3a** in $\text{ClCH}_2\text{CH}_2\text{Cl}$. $E_{\text{pc}}(\mathbf{3a}/\mathbf{3a}^-) = -1.36$ V vs $\text{FcCp}_2^{+/0}$.

1.18. Time profile experiment

In an oven dried 20 mL Schlenk flask were placed **[Ru]-2** (6.3 mg, 0.0050 mmol) and NH_4BF_4 (1.1 mg, 0.010 mmol) under N_2 . Anhydrous $\text{ClCH}_2\text{CCH}_2\text{Cl}$ (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg, 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)₃] (0.7 mg, 0.0011 mmol), and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (15 μL , 17 mg, 0.12 mmol) were added under N_2 at room temperature. The reaction flask was placed in an As One LTB-125 constant low temperature water bath set at 25 $^\circ\text{C}$, and was illuminated from the bottom of the bath with an Aitech System TMN100 $\times$ 120–22WD 12 W white LED lamp (400 nm to 750 nm) at a distance of approximately 2 cm from the light source. Yields of **7aa** at selected times (2, 4, 8, 12, 24 and 48 h) were determined by quantitative measurements of gas chromatography–mass spectroscopy (GC-MS) recorded on a Shimadzu GCMS-QP2010 PLUS instrument, where *n*-octane was added as an internal standard (Supplementary Fig. 2). The reaction rate was calculated as $k_{7\text{aa}} = (2.33 \pm 0.04) \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$.

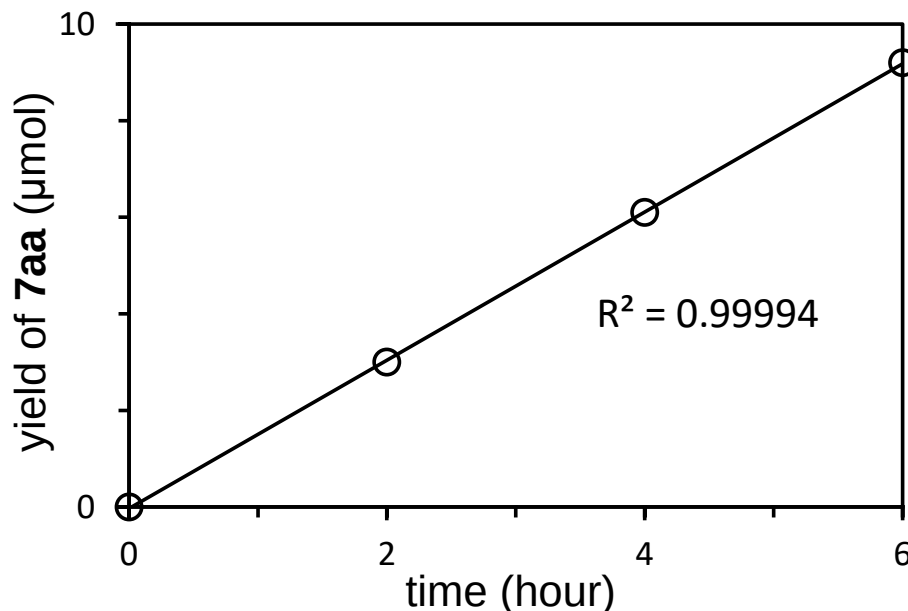


Supplementary Fig. 2: Time profile experiment.

1.19. Determination of quantum yields

In an oven dried 20 mL Schlenk flask were placed **[Ru]-2** (6.3 mg, 0.0050 mmol) and NH_4BF_4 (1.1 mg, 0.010 mmol) under N_2 . Anhydrous $\text{ClCH}_2\text{CCH}_2\text{Cl}$ (2.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 30 min. Then, 1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (**3a**) (20.0 mg, 0.10 mmol), diethyl 4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**4a**) (41.2 mg, 0.12 mmol), *fac*-[Ir(ppy)₃] (0.7 mg, 0.0011 mmol), and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (15 μL , 17 mg, 0.12 mmol) were added under N_2 at room temperature. The reaction flask was illuminated from the side with an Ushio SX-U1251HQ ultrahigh pressure 250 W Hg lamp equipped with a 440-nm band pass filter (Kenko B440) at a distance of approximately 2 cm from the light source for 6 h. The volatiles were removed in vacuo, and the crude yield of **7aa** (0.00920 mmol, 9.2% NMR yield based on the amount of **3a**) was determined by ^1H NMR in CDCl_3 , where 1,1,2,2-tetrachloroethane (16.8 mg, 0.100 mmol) was added as an internal standard. Independently, the yields of **7aa** were

determined by terminating the reactions at 2 and 4 h, which clarified a zero-order reaction rate at $4.26 \times 10^{-8} \text{ mol s}^{-1}$. The irradiated light intensity to a 2.5 mL solution in 50-mL Schlenk was estimated to be $8.50 \times 10^{-7} \text{ E s}^{-1}$ at 440 nm by using $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ as a chemical actinometer.²⁴ Thus, the quantum yield of the photoredox- and ruthenium-catalyzed reaction of **3a** with **4a** to afford propargylic alkylated product **7aa** is given as $\Phi = 0.0502 \pm 0.0003$ (Supplementary Fig. 3).



Supplementary Fig. 3: Quantum yield determination.

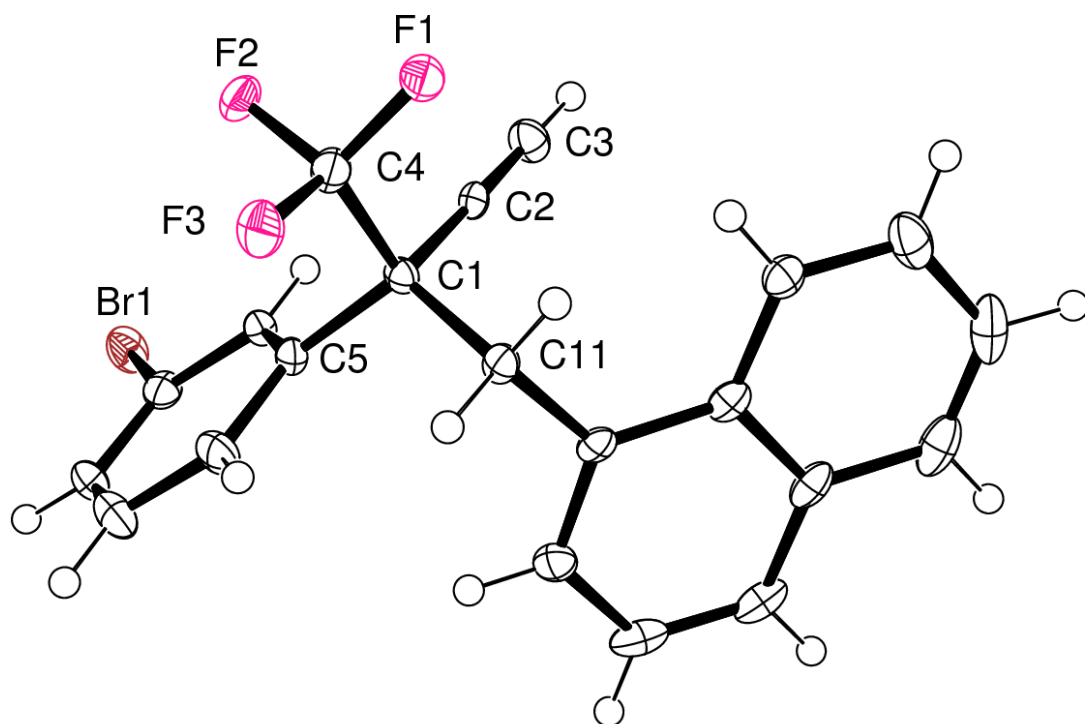
1.20. X-ray crystallographic study of (*R*)-1-(2-(3-bromophenyl)-1,1,1-trifluorobut-3-yn-2-yl)naphthalene (**7lr**)

Diffraction data for a crystal of **7lr** were collected for the 2θ range of 4.5° to 62.2° at -180°C on a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and VariMax optics using multi-layer mirror monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation, and VariMax optics. Intensity data were corrected for Lorentz and polarization effect and for empirical absorptions (CrysAlisPro),²⁵ while structure solutions and refinements were carried out by using CrystalStructure package.²⁶ Positions of non-hydrogen atoms were determined by direct methods (SHELXT Version 2014/5),²⁷ and subsequent Fourier syntheses (SHELXL Version 2016/6),²⁸ and were refined on F_o^2 with all the unique reflections by full-matrix least squares with anisotropic thermal parameters. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Anomalous dispersion effects were included in F_c ,²⁹ and mass attenuation coefficients, values for $\Delta f'$ and $\Delta f''$, and neutral atom scattering factors were taken from references.³⁰⁻³² The absolute configuration of **7lr** with a chiral center at the C(1) atom was determined to be (*R*), with the Flack parameter refined to be $-0.005(5)$. Details of the crystal and data collection parameters of (*R*)-**7lr** are summarized in Supplementary Table 1. An ORTEP drawing of (*R*)-**7lr** is shown in Supplementary Fig. 4.

Supplementary Table 1 Crystallographic data for (*R*)-**7Ir**

compound	(<i>R</i>)- 7Ir
chemical formula	C ₂₁ H ₁₄ BrF ₃
CCDC number	2172478
formula weight	403.24
crystal size, mm ³	0.131 × 0.066 × 0.037
crystal color, habit	colorless, needle
temperature, °C	−180
crystal system	monoclinic
space group	<i>P</i> 2 ₁ (no. 4)
<i>a</i> , Å	9.1554(4)
<i>b</i> , Å	7.1034(3)
<i>c</i> , Å	13.5438(6)
α, deg	90
β, deg	103.113(4)
γ, deg	90
<i>V</i> , Å ³	857.85(7)
<i>Z</i>	2
<i>d</i> _{calcd} , g, cm ^{−3}	1.561
<i>F</i> (000)	404
μ, cm ^{−1}	24.327
transmission factors range	0.847 – 0.914
number of measured reflections	13715
number of unique reflections	4344
number of refined parameters	226
<i>R</i> _{int}	0.0457
<i>R</i> 1 (<i>I</i> > 2 σ(<i>I</i>)) ^a	0.0297
<i>wR</i> 2 (all data) ^b	0.0564
GOF ^c	1.000
maximum residual peak / hole, e Å ^{−3}	+0.30 / −0.33
Flack parameter	−0.005(5)

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + rP]$, $P = (\text{Max}(F_o^2, 0) + 2 F_c^2)/3$ [$r = 3.65$]. ^c $\text{GOF} = [\sum w(F_o^2 - F_c^2)^2 / (N_o - N_{\text{params}})]^{1/2}$.



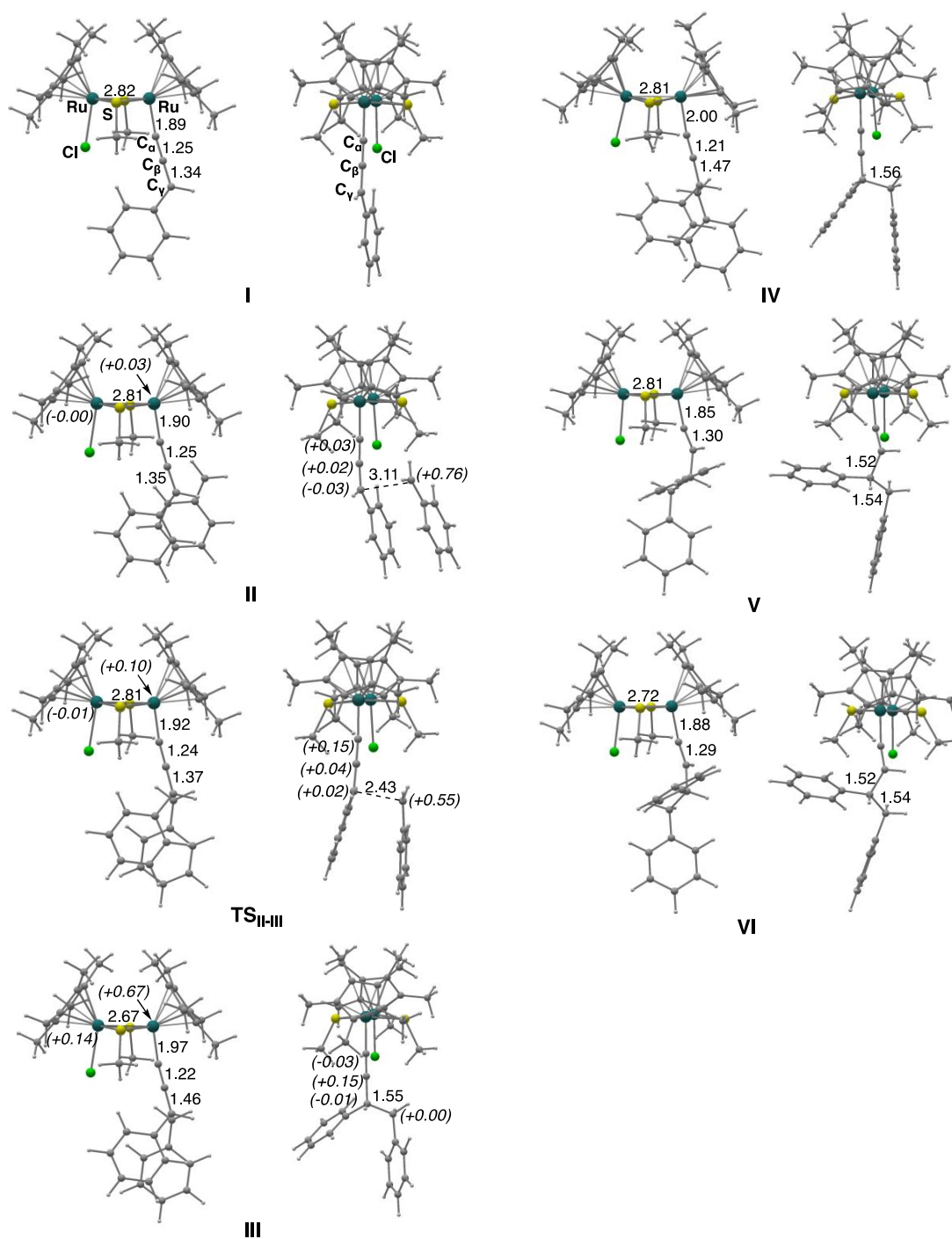
Supplementary Fig. 4: ORTEP drawing of (*R*)-**7Ir**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): C(1)–C(2): 1.468(4), C(1)–C(4): 1.535(4), C(1)–C(5): 1.548(4), C(1)–C(11): 1.556(4), C(2)–C(3): 1.188(5); C(2)–C(1)–C(4): 106.6(2), C(2)–C(1)–C(5): 111.3(2), C(4)–C(1)–C(5): 106.9(2), C(2)–C(1)–C(11): 110.4(3), C(4)–C(1)–C(11): 108.1(2), C(5)–C(1)–C(11): 113.2(2), C(3)–C(2)–C(1): 178.4(3).

1.21. DFT calculations

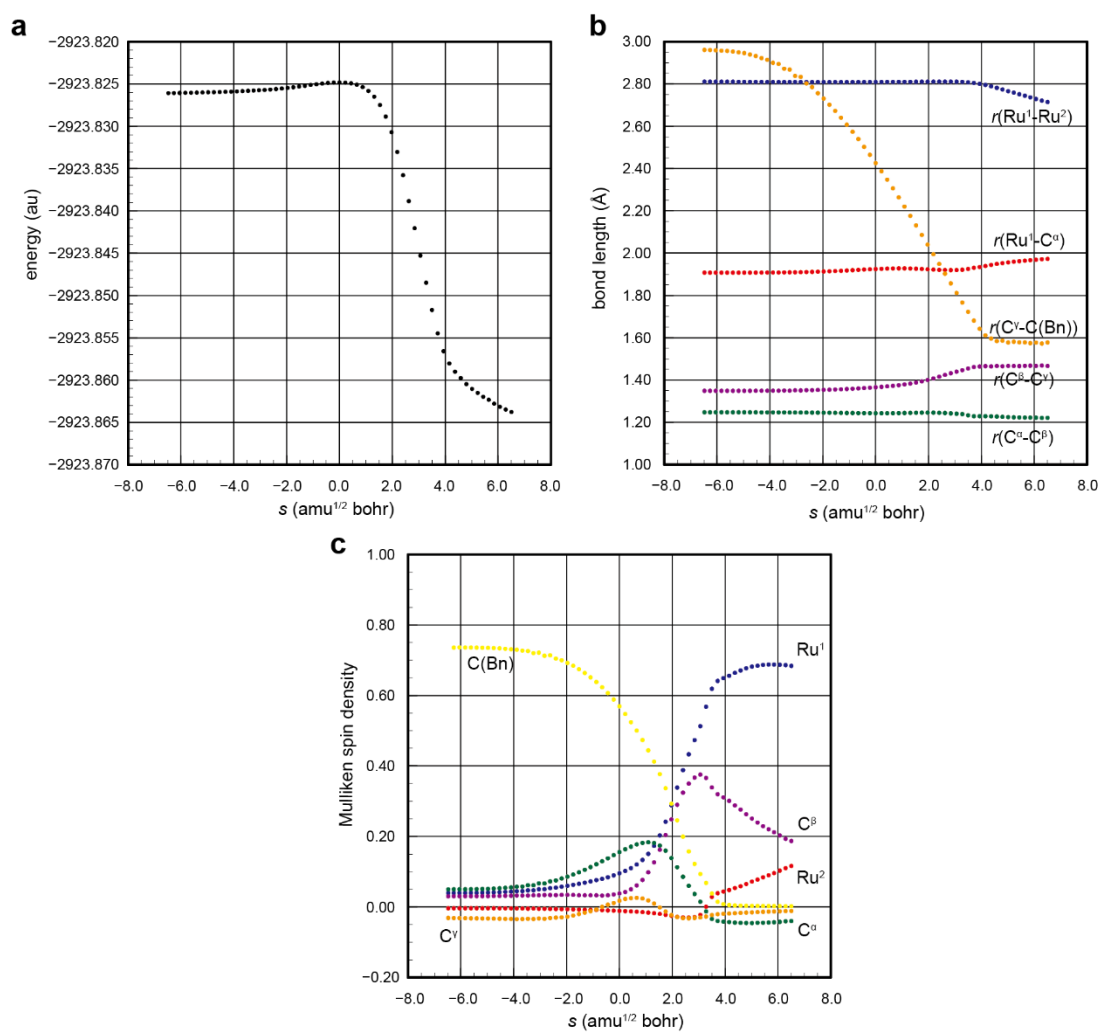
DFT calculations were carried out with the Gaussian16 (Revision A.03) program package.³³ Geometry optimization and analytical vibrational frequency analysis were performed by ω B97XD Kohn-Sham DFT^{34,35} (restricted KS method for singlet state and unrestricted KS method for doublet and triplet states).³⁵ In the numerical integration, a larger grid (*superfinegrid*) was used.³³ Pople's 6-311G** basis set³⁶ for C, H, S, and Cl atoms and the SDD basis set³⁷ with the effective core potential for Ru atom were used for the Gaussian basis functions (5d-type). The solvent effects of dichloroethane were estimated by the IEF-PCM method^{38,39} for the gas phase optimized structures. For the IEF-PCM calculations, the ω B97XD functional was used with the larger basis set (Pople's 6-311++G** basis set³⁶ for C, H, N, O, S, and Cl atoms (5d-type) and the SDD basis set for Ru atom; ω B97XD(IEFPCM)/(SDD, 6-311++G**)// ω B97XD(IEFPCM)/(SDD, 6-311G**)). The Gibbs free energy at 298K was estimated by the IEF-PCM energy and the gas-phase thermal correction term (T). All the results are summarized in [Supplementary Table 2](#) and [Supplementary Figs. 5–8](#).

Supplementary Table 2 Total electronic energy E and Gibbs free energy $G^{298.15K}$ (a. u.)

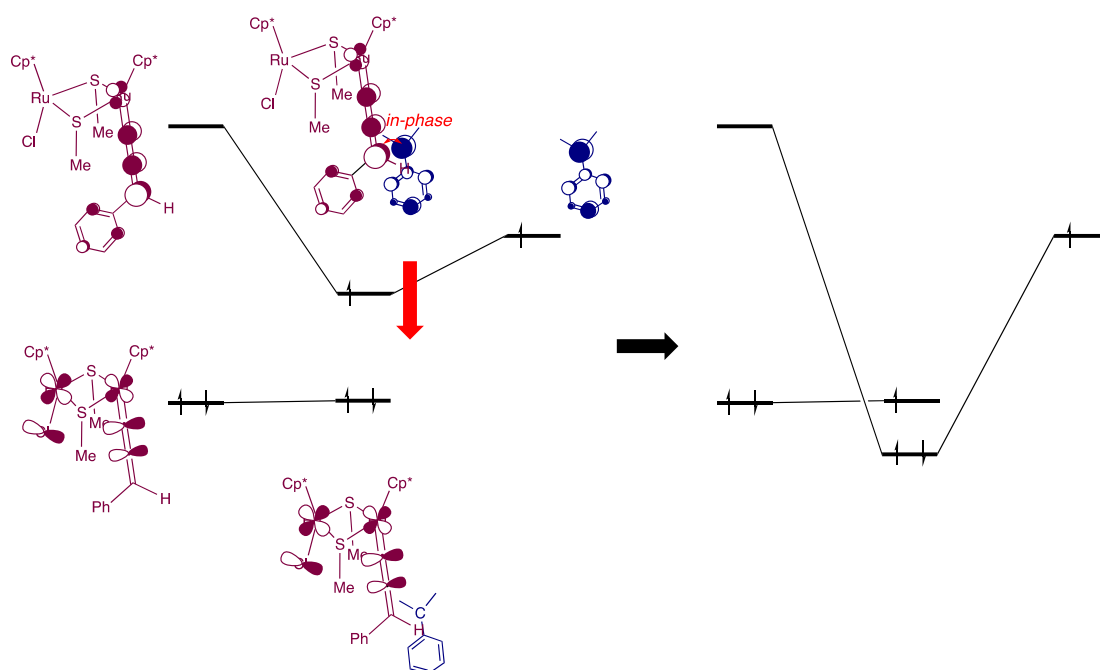
	ω B97XD/(SDD, 6-311G**)		ω B97XD(IEFPCM)/(SDD, 6-311++G**)	
	E	T	E	$G^{298.15K}$
I	-2652.931215	0.577572	-2652.987526	-2652.409954
Bn $\cdot$	-270.878749	0.085445	-270.884482	-270.799037
II	-2923.827178	0.683276	-2923.885964	-2923.202688
TS_{II-III}	-2923.824805	0.685582	-2923.882584	-2923.197002
III	-2923.871077	0.688734	-2923.937231	-2923.248497
IV	-2924.089301	0.688499	-2924.116165	-2923.427666
V	-2924.502562	0.703703	-2924.566060	-2923.862357
VI	-2924.163164	0.701287	-2924.351071	-2923.649784
$^2[\text{Ir}(\text{ppy})_3]^-$	-1540.585524	0.417328	-1540.672281	-1540.254953
$^1[\text{Ir}(\text{ppy})_3]$	-1540.580980	0.424514	-1540.608779	-1540.184265
PyH $^+$	-861.641565	0.252167	-861.717414	-861.465247
Py	-861.257404	0.238104	-861.277723	-861.039619



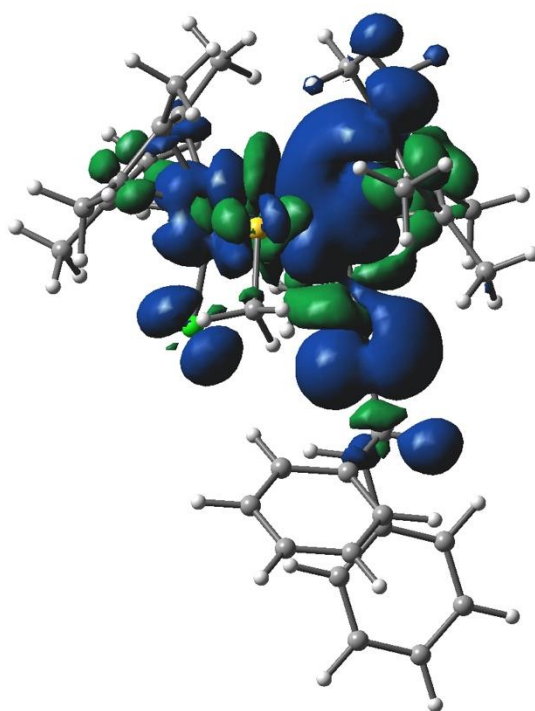
Supplementary Fig. 5: Structures optimized at ω B97X-D/(SDD, 6-311G**) level of theory. Bond lengths are given in Å.



Supplementary Fig. 6: Profiles for **TSII-III**. **a** Potential energy profile along IRC for **TSII-III**. **b** Changes in bond lengths along the IRC for **TSII-III**. **c** Changes in Mulliken spin density along the IRC for **TSII-III**.



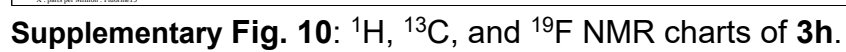
Supplementary Fig. 7: Change in SOMO along the reaction.

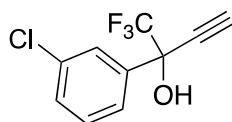


Supplementary Fig. 8: Spin density in **III**.

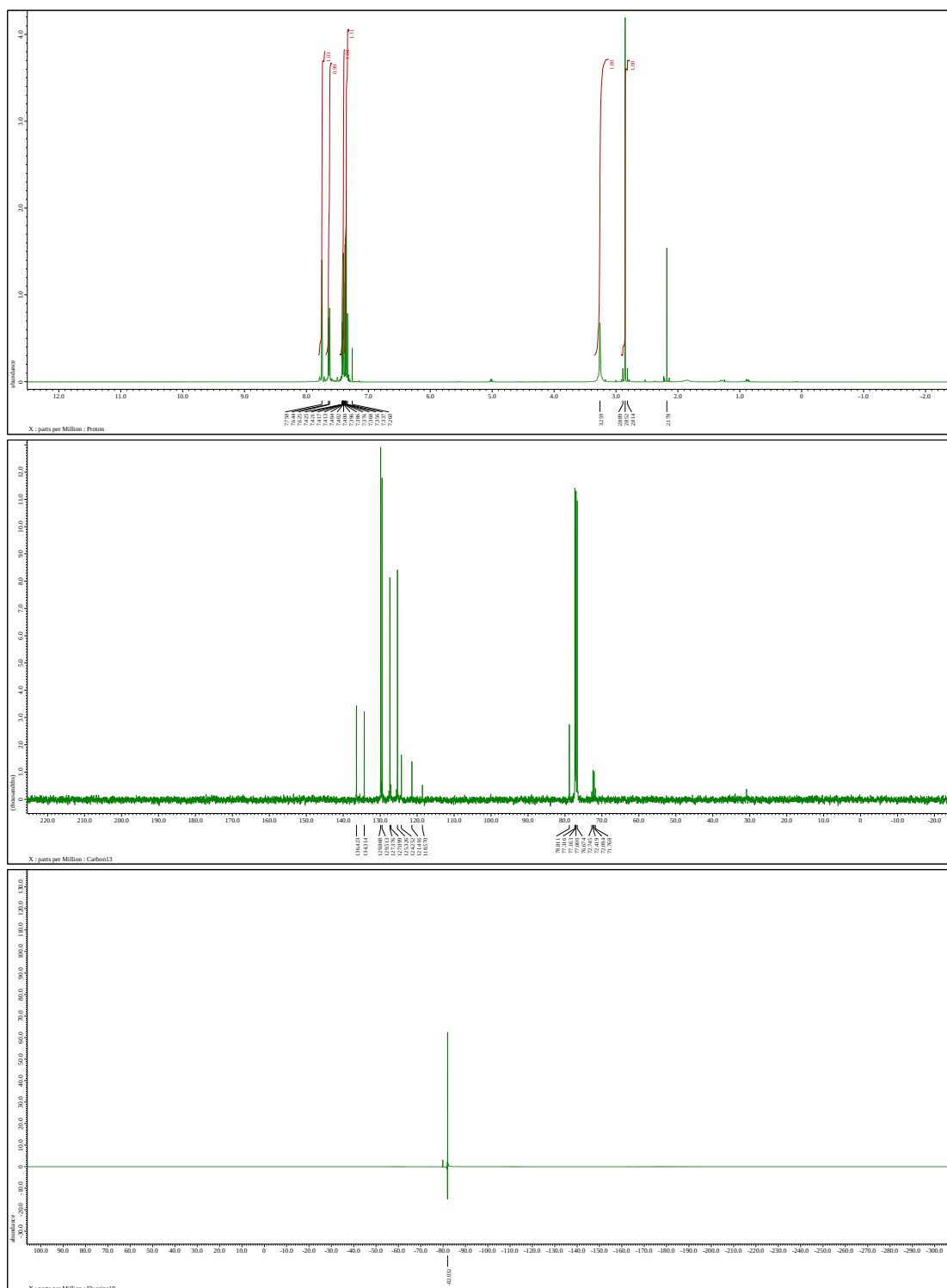
CC1=CC=C(C(C1)(O)C(F)(F)F)C#C

Supplementary Fig. 9: ^1H , ^{13}C , and ^{19}F NMR charts of **3c**.

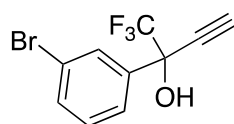




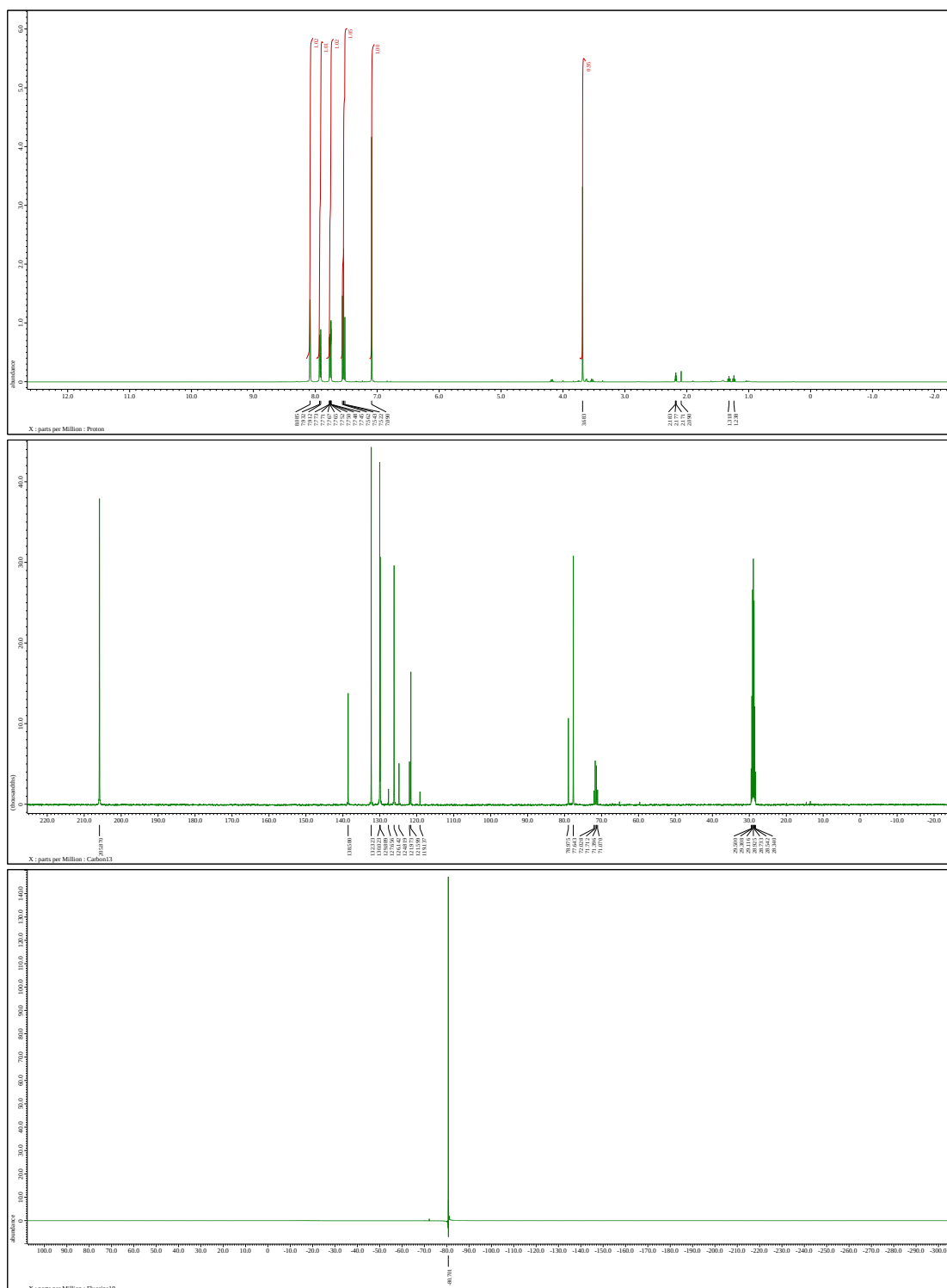
3k



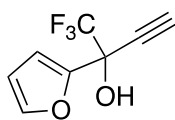
Supplementary Fig. 11: ¹H, ¹³C, and ¹⁹F NMR charts of **3k.**



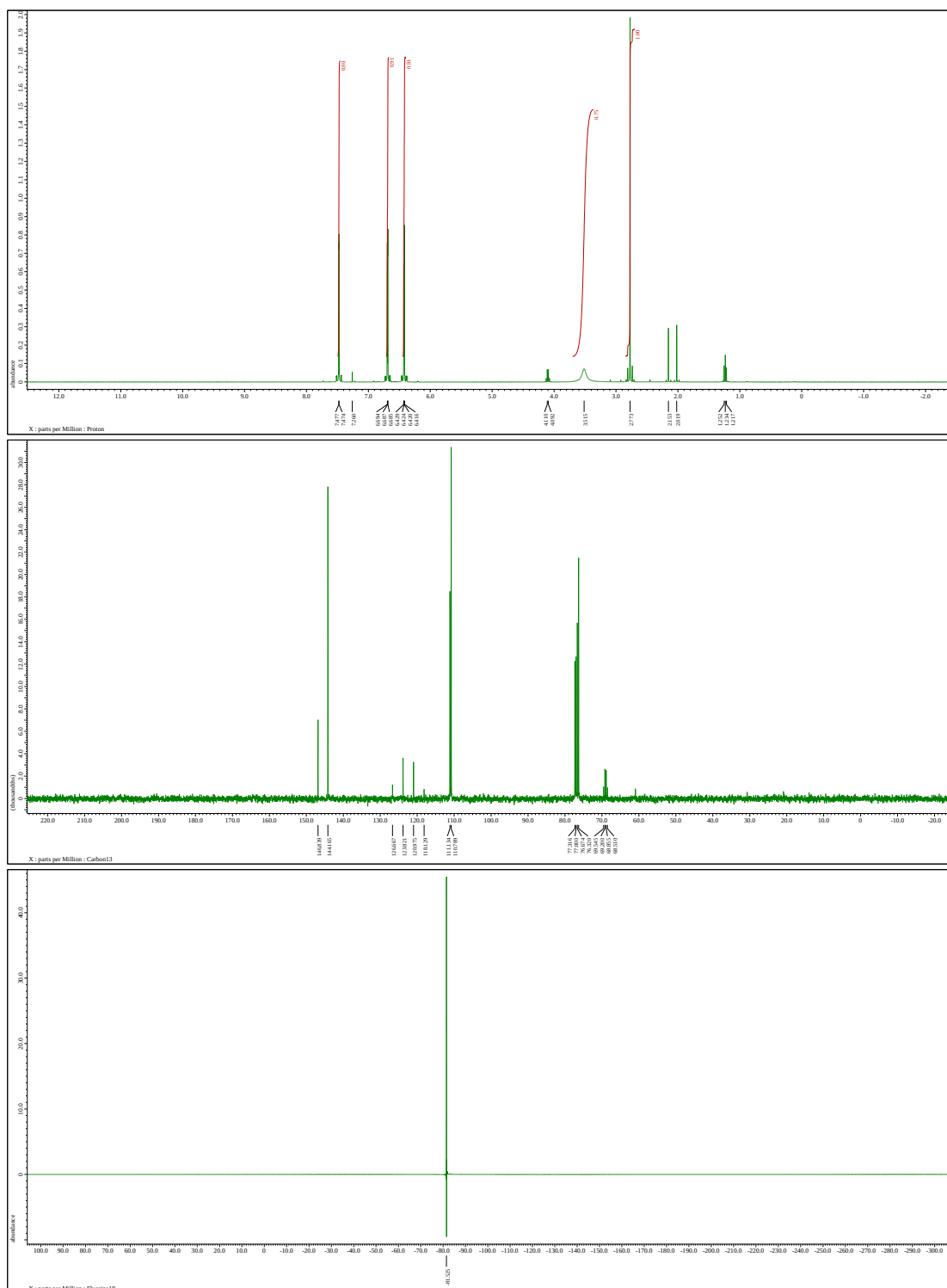
31

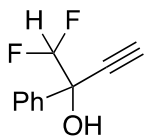


Supplementary Fig. 12: ^1H , ^{13}C , and ^{19}F NMR charts of **31**.

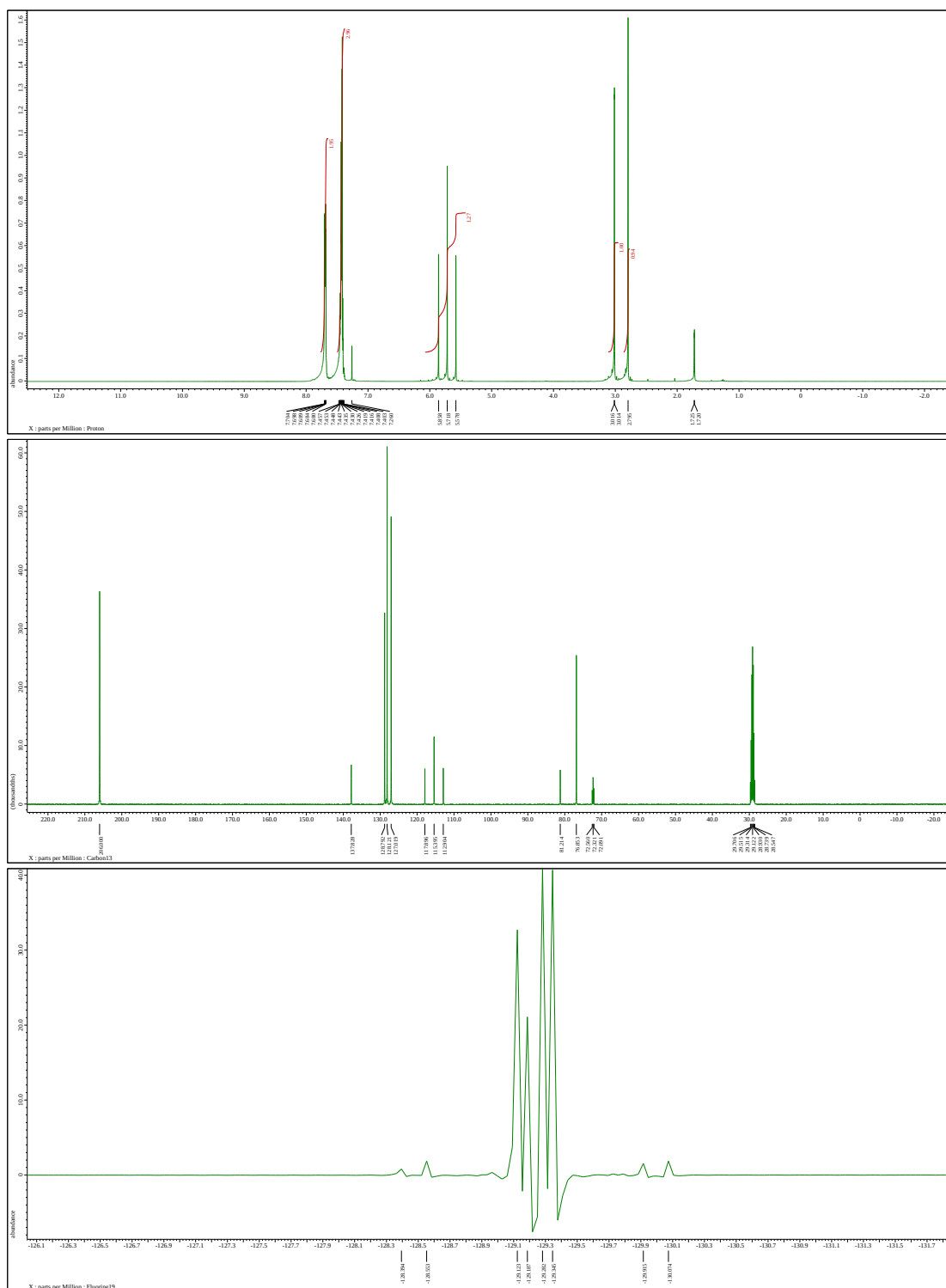


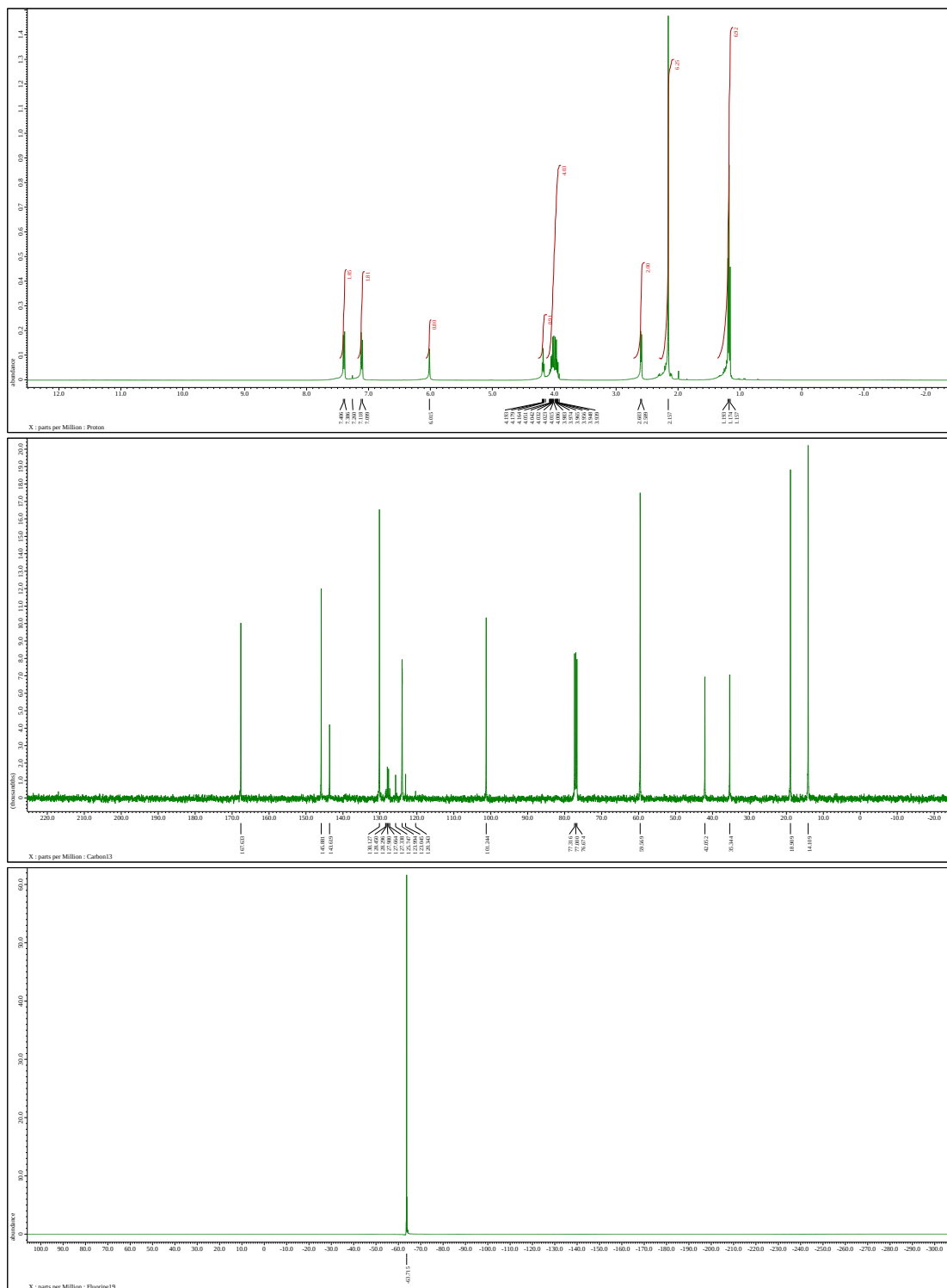
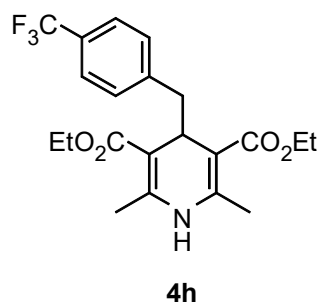
3m



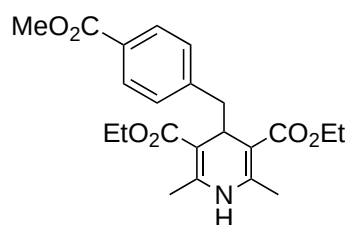


8

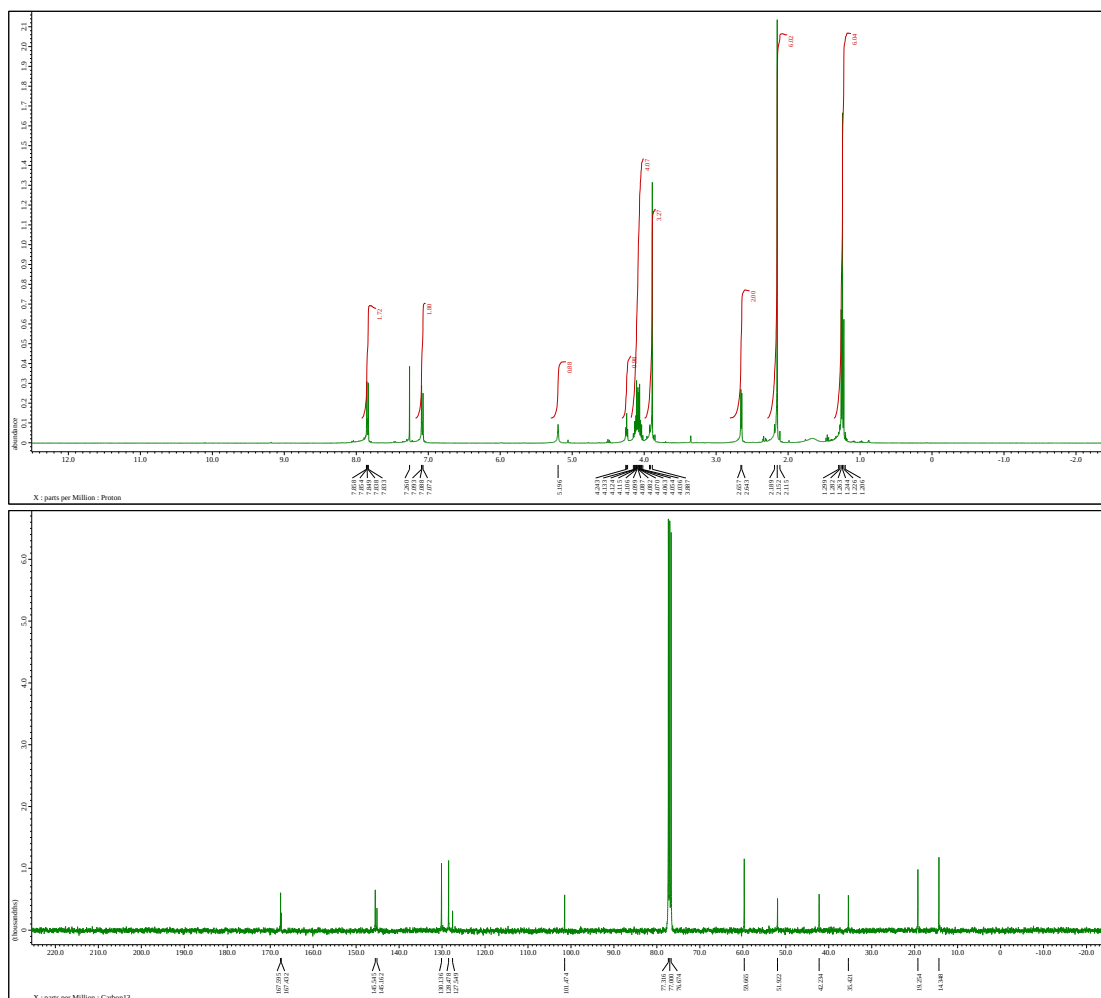




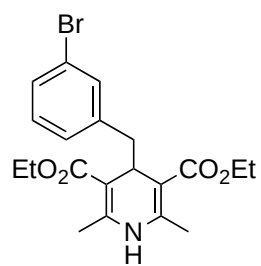
Supplementary Fig. 15: ¹H, ¹³C, and ¹⁹F NMR charts of **4h**.



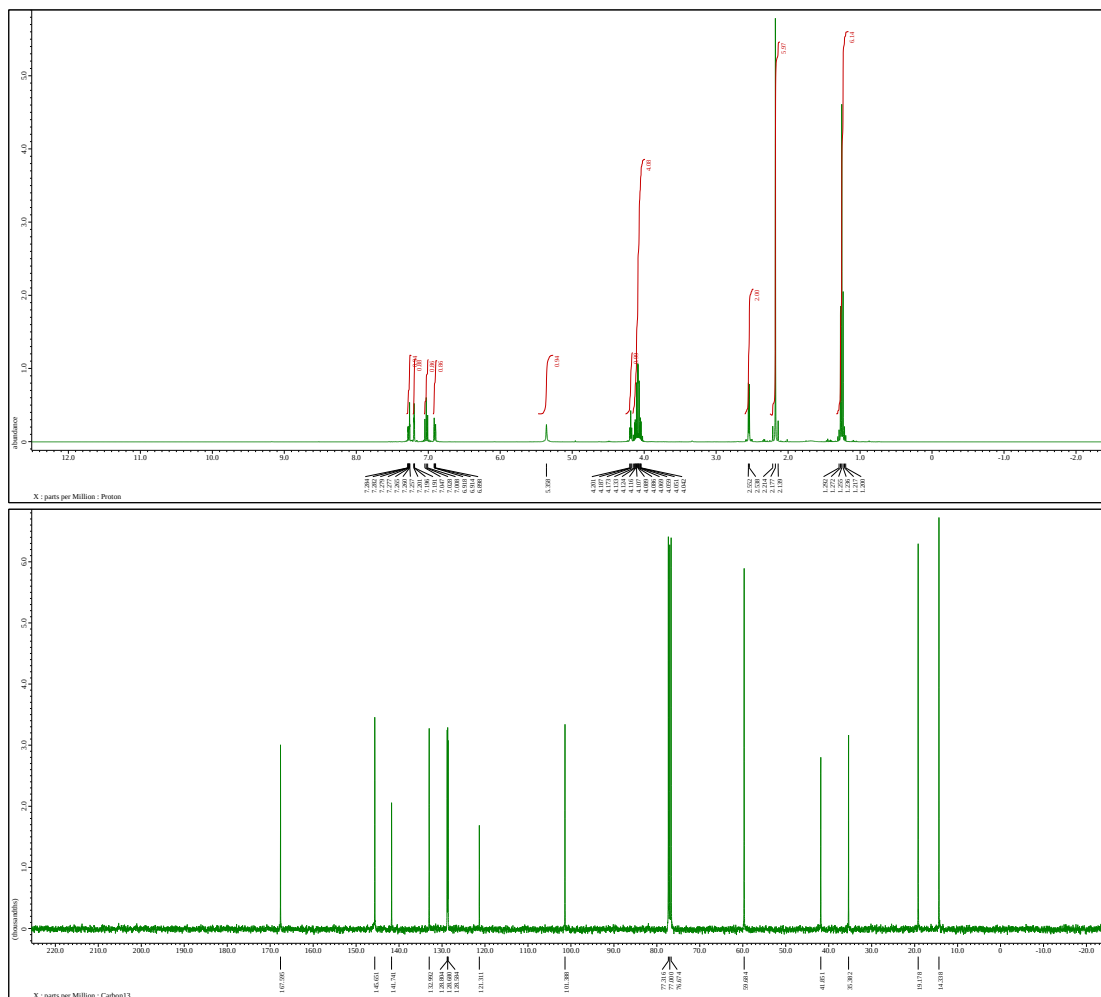
4i



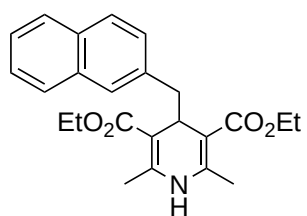
Supplementary Fig. 16: ¹H and ¹³C NMR charts of **4i**.



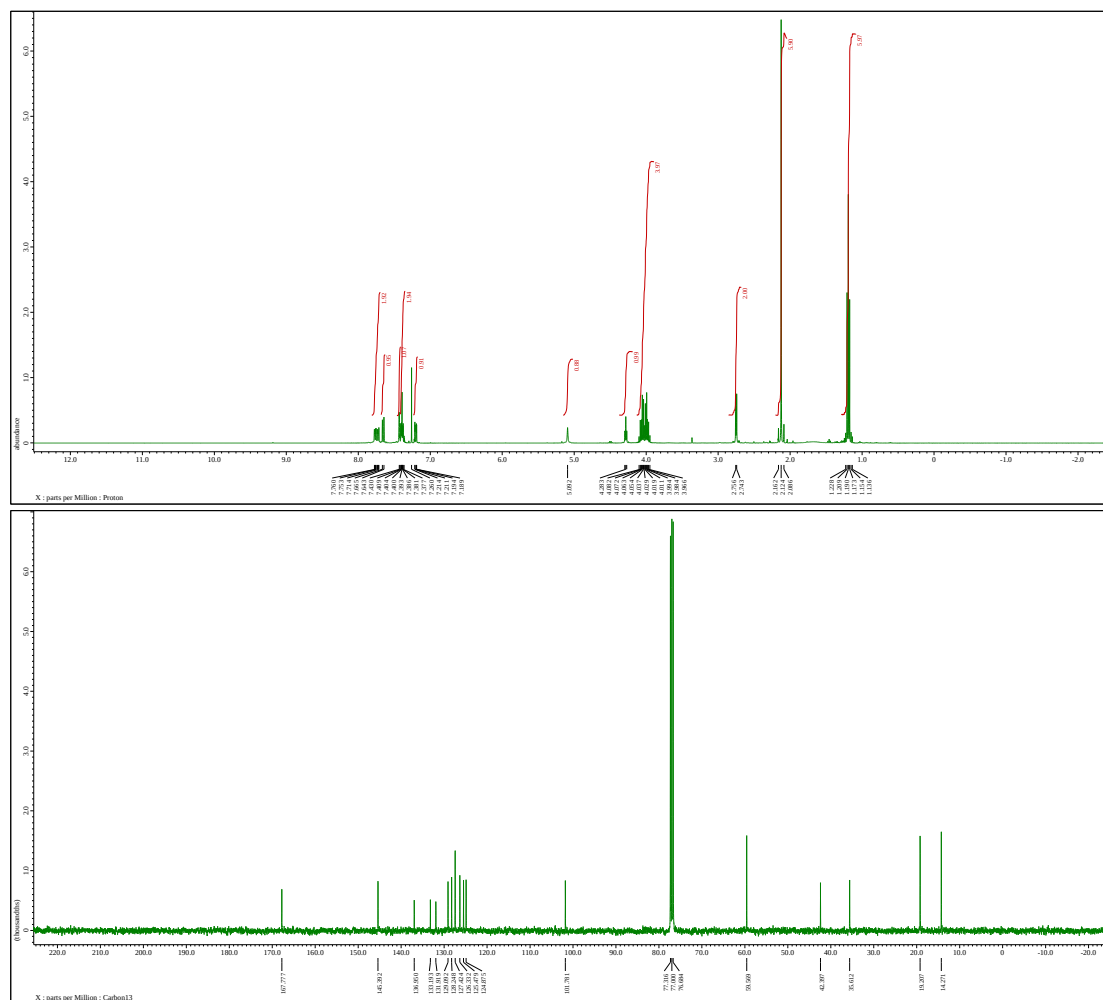
4o

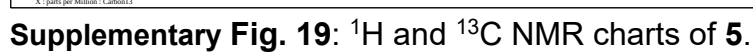


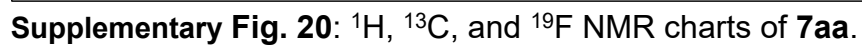
Supplementary Fig. 17: ¹H and ¹³C NMR charts of **4o.**

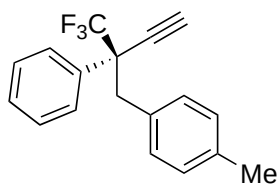


4s

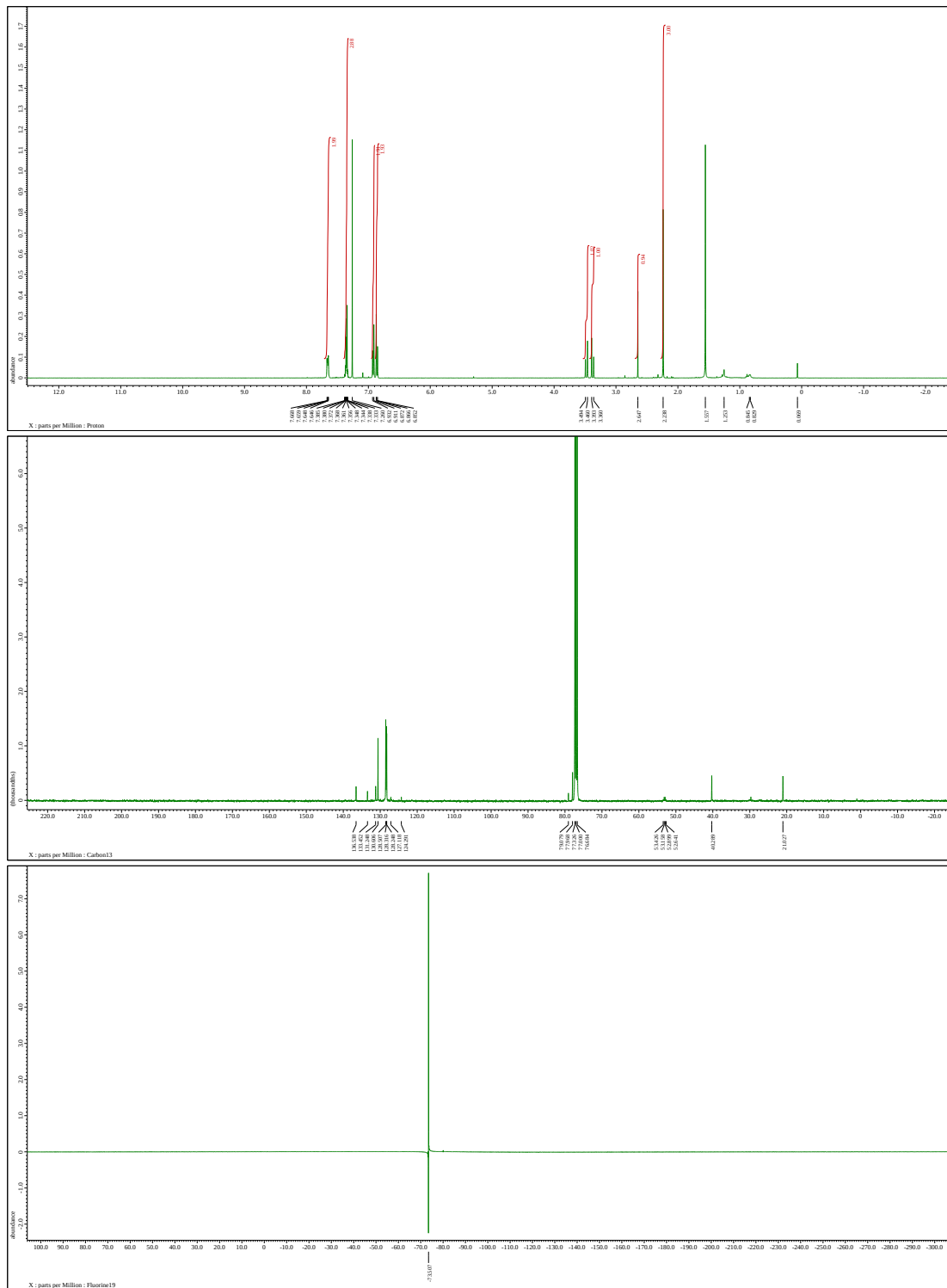




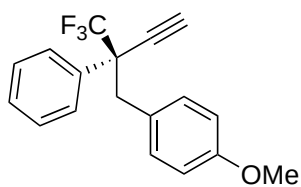




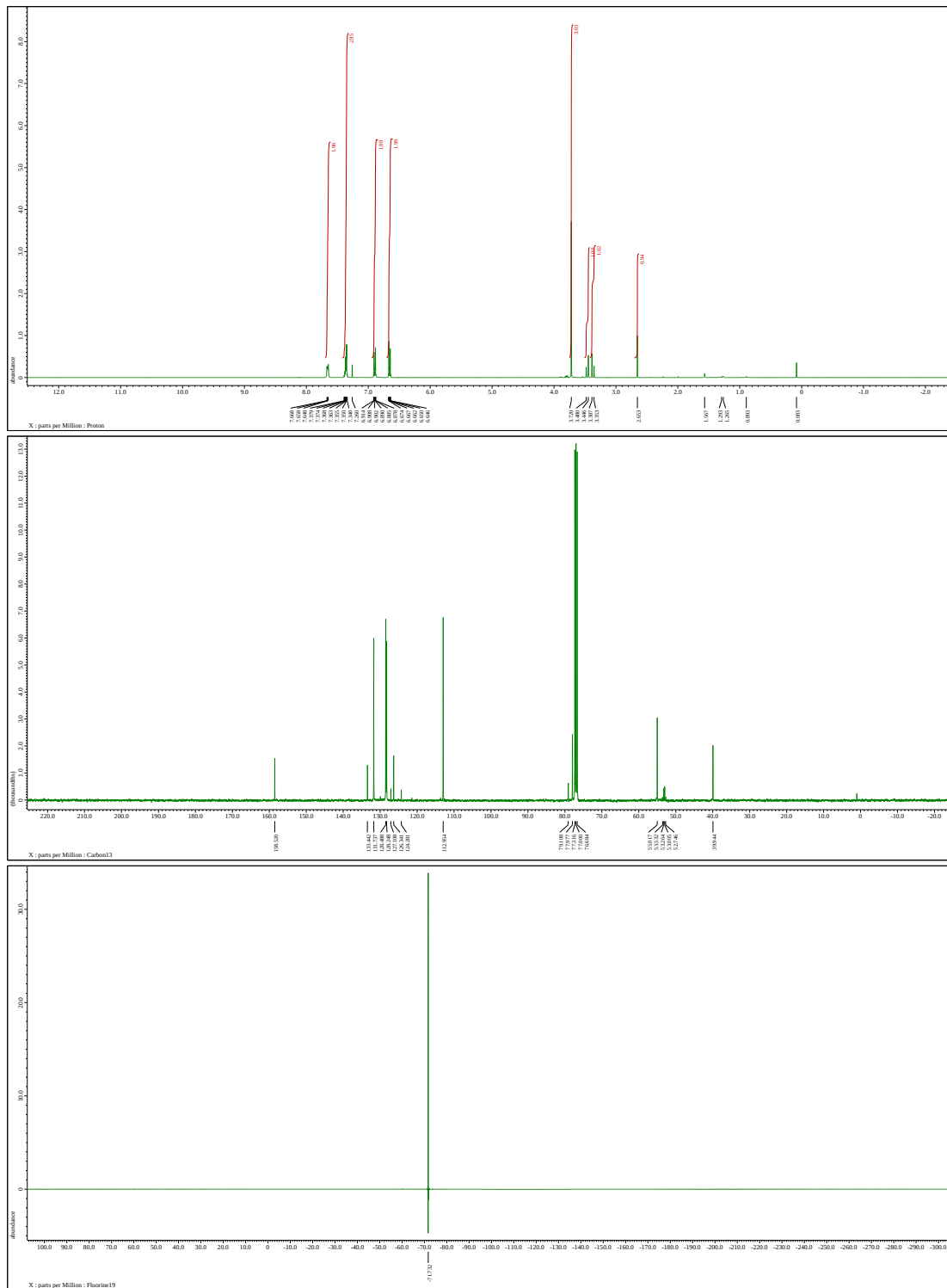
7ab



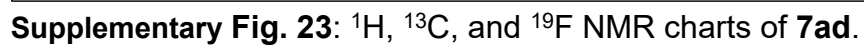
Supplementary Fig. 21: ^1H , ^{13}C , and ^{19}F NMR charts of **7ab.**

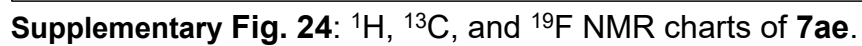


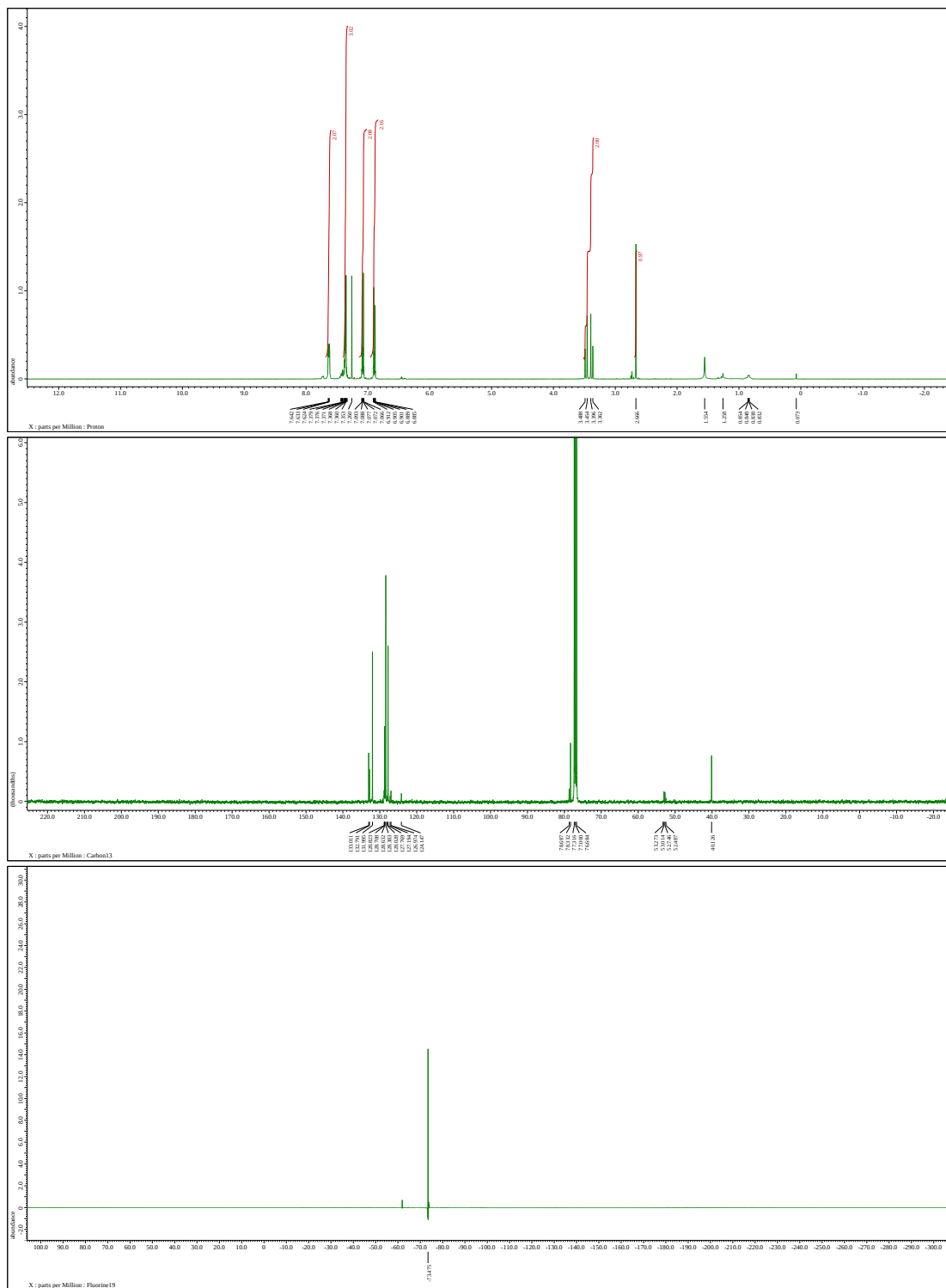
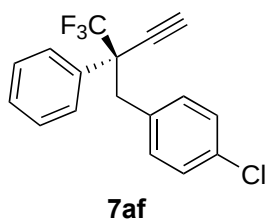
7ac



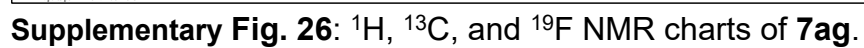
Supplementary Fig. 22: ¹H, ¹³C, and ¹⁹F NMR charts of **7ac.**

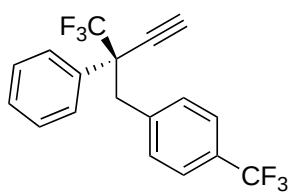




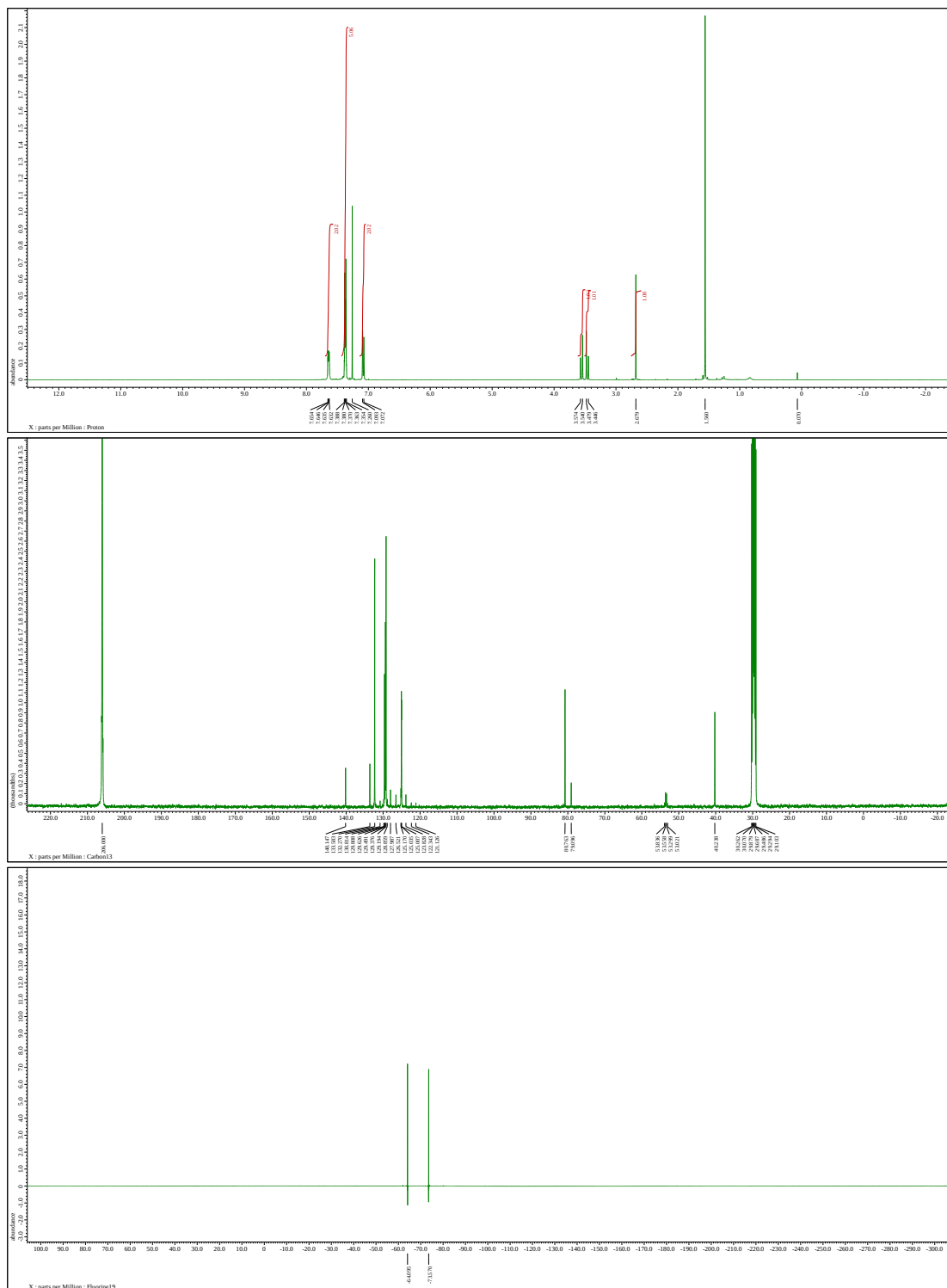


Supplementary Fig. 25: ^1H , ^{13}C , and ^{19}F NMR charts of **7af**.

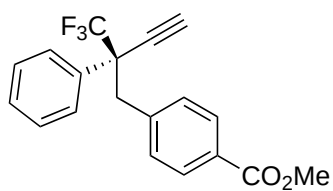




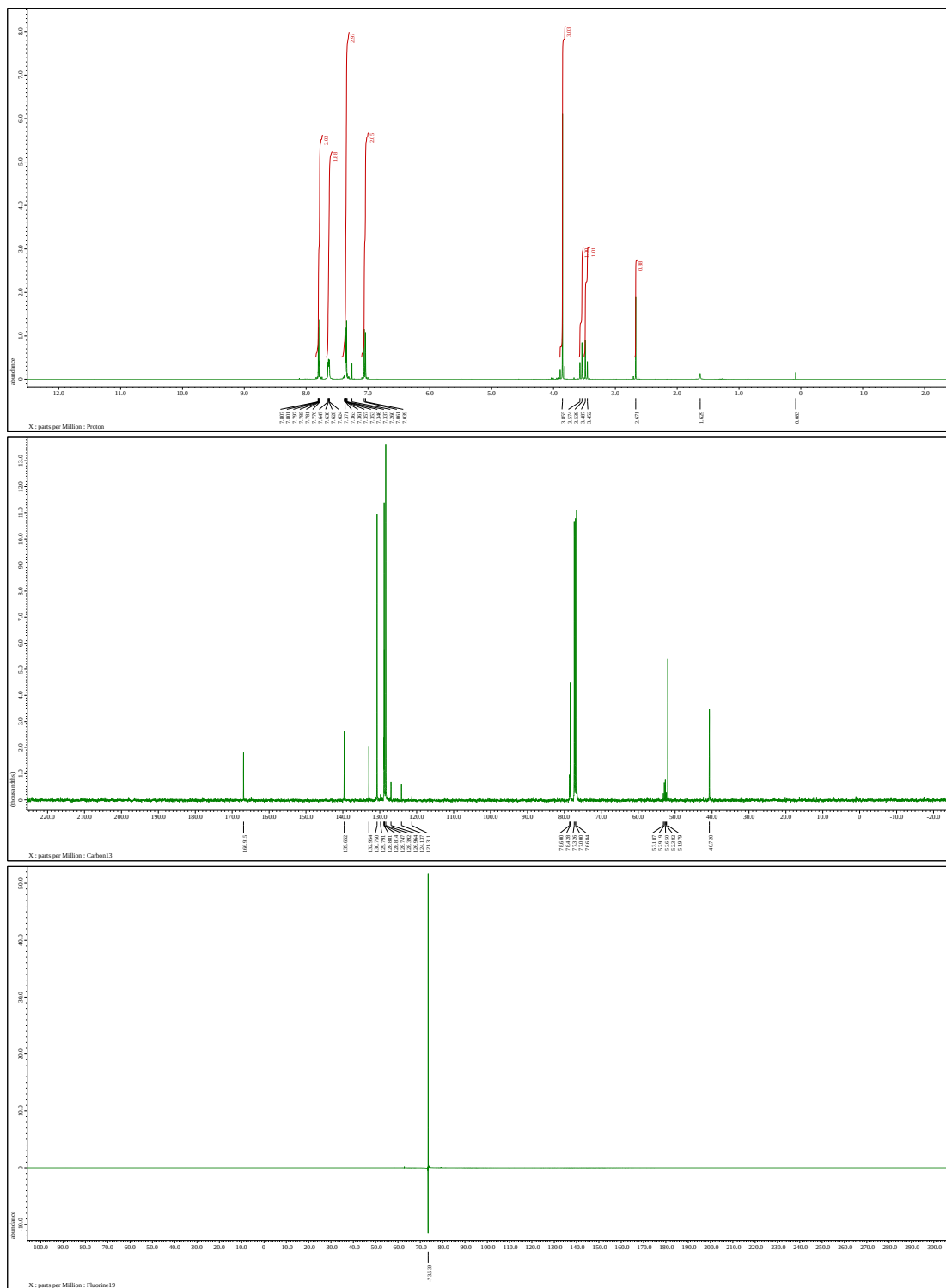
7ah



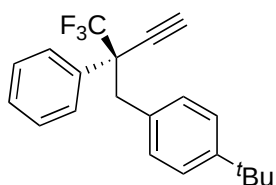
Supplementary Fig. 27: ¹H, ¹³C, and ¹⁹F NMR charts of **7ah.**



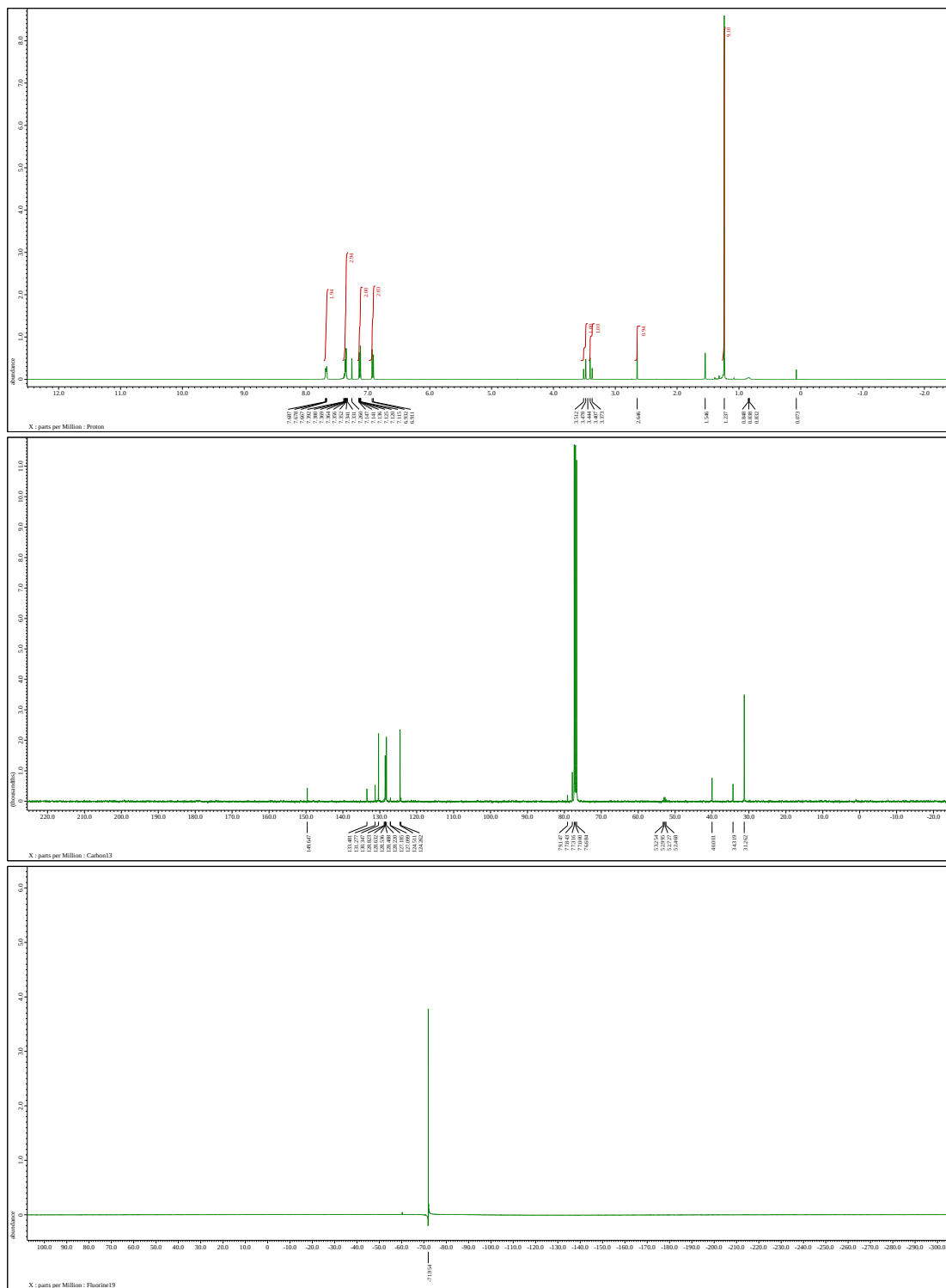
7ai



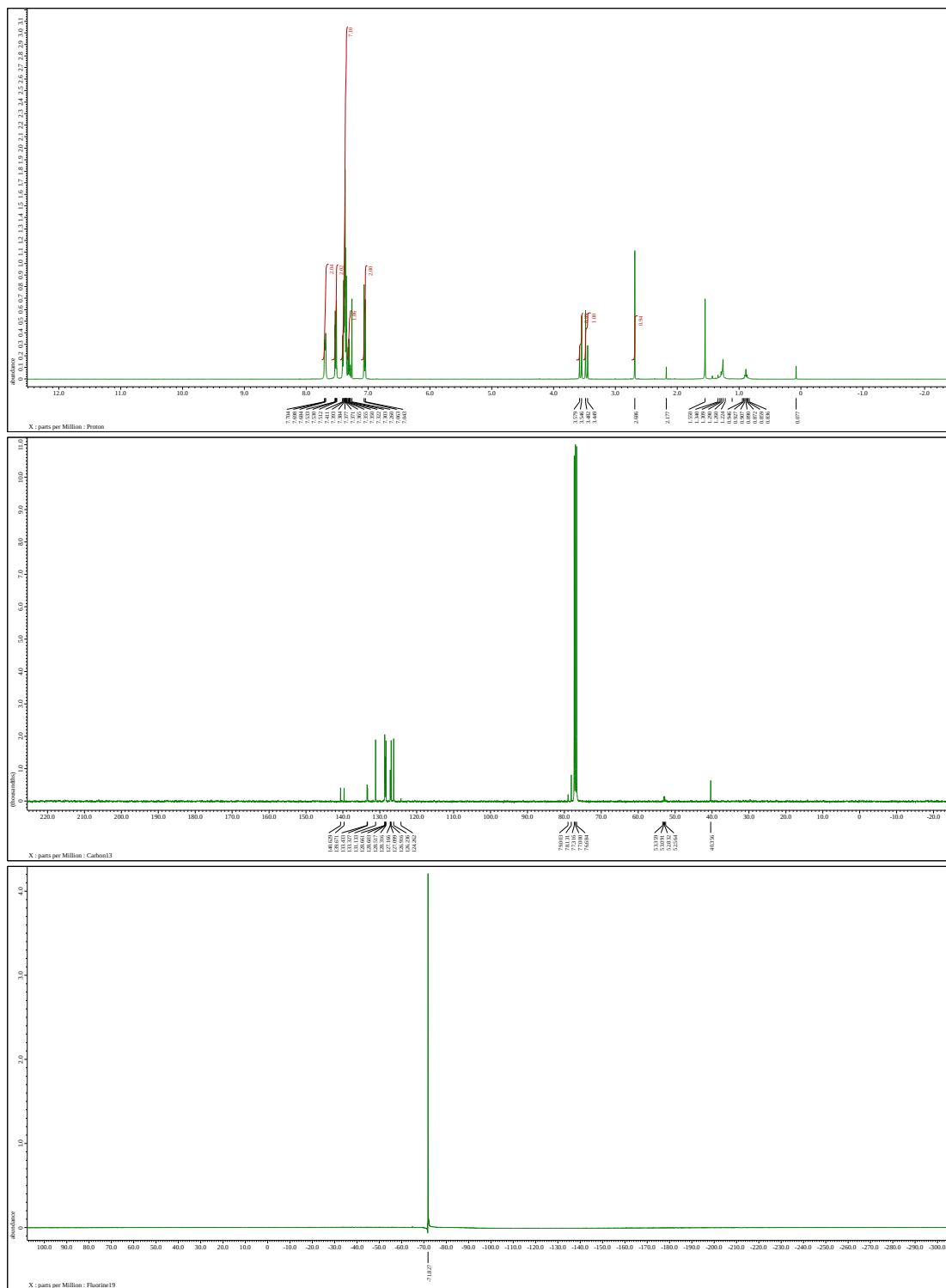
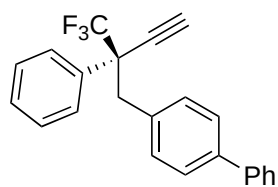
Supplementary Fig. 28: ^1H , ^{13}C , and ^{19}F NMR charts of **7ai**.



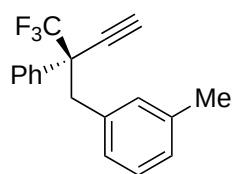
7aj



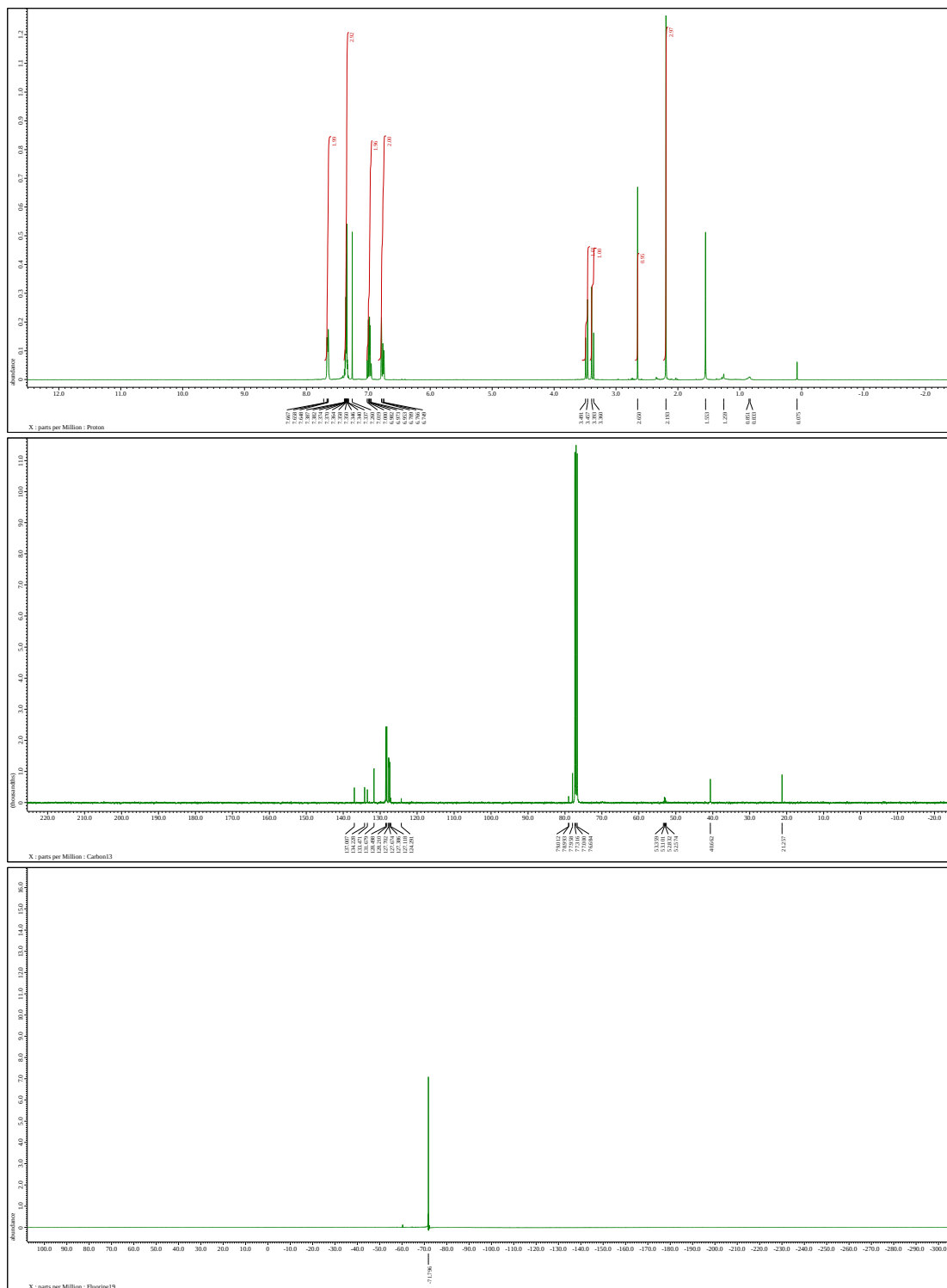
Supplementary Fig. 29: ^1H , ^{13}C , and ^{19}F NMR charts of **7aj.**



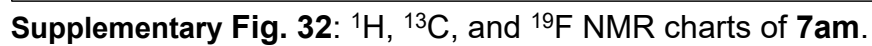
Supplementary Fig. 30: ¹H, ¹³C, and ¹⁹F NMR charts of **7ak.**

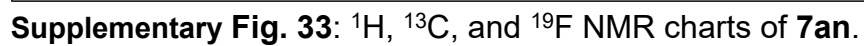


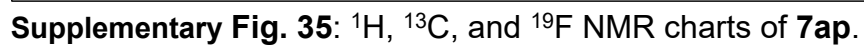
7al

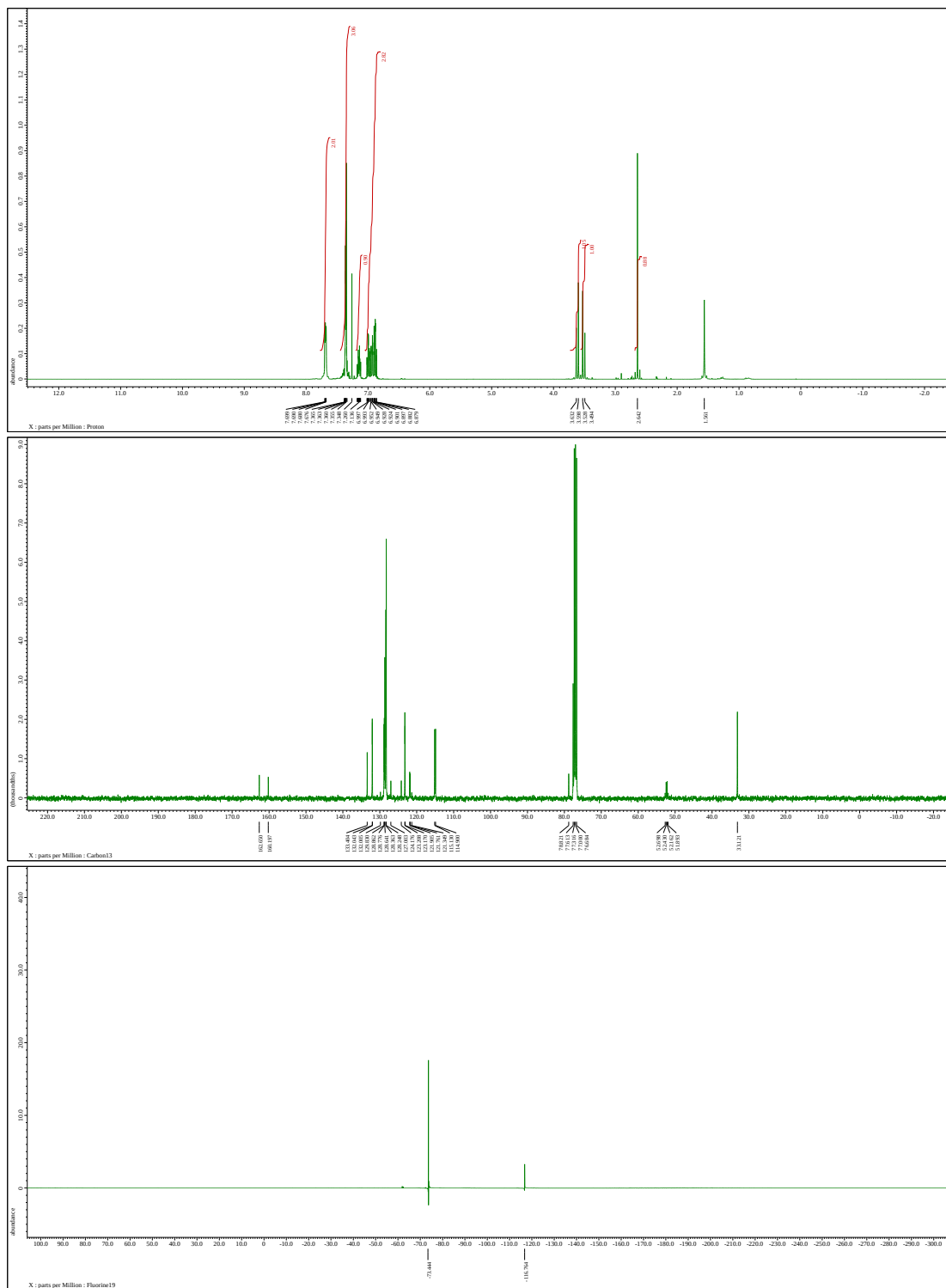
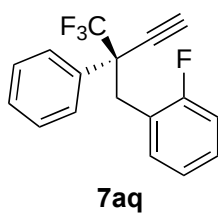


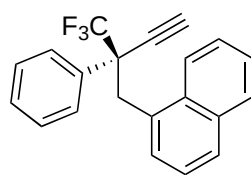
Supplementary Fig. 31: ¹H, ¹³C, and ¹⁹F NMR charts of **7al.**



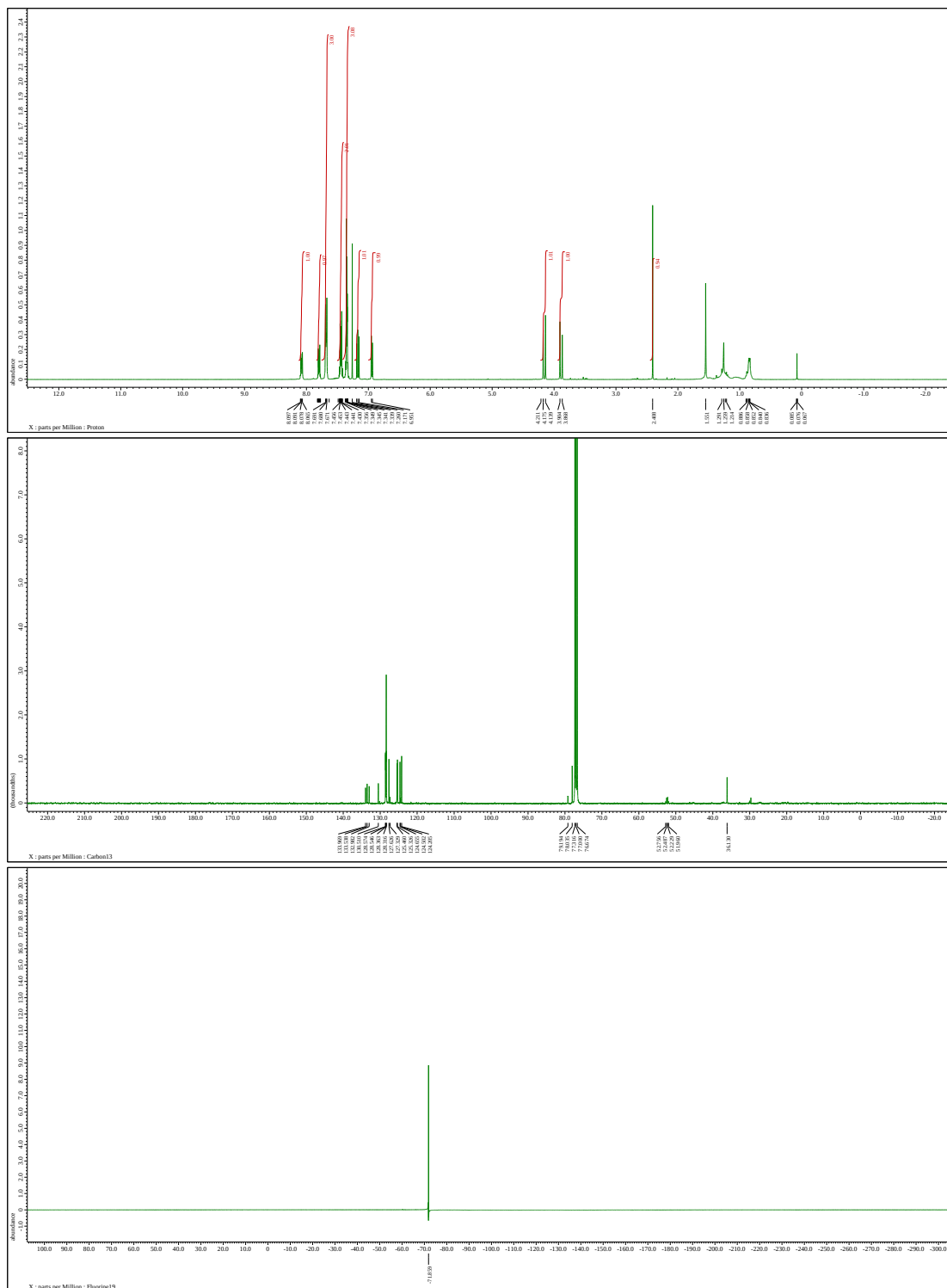




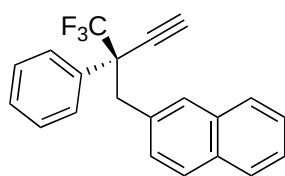




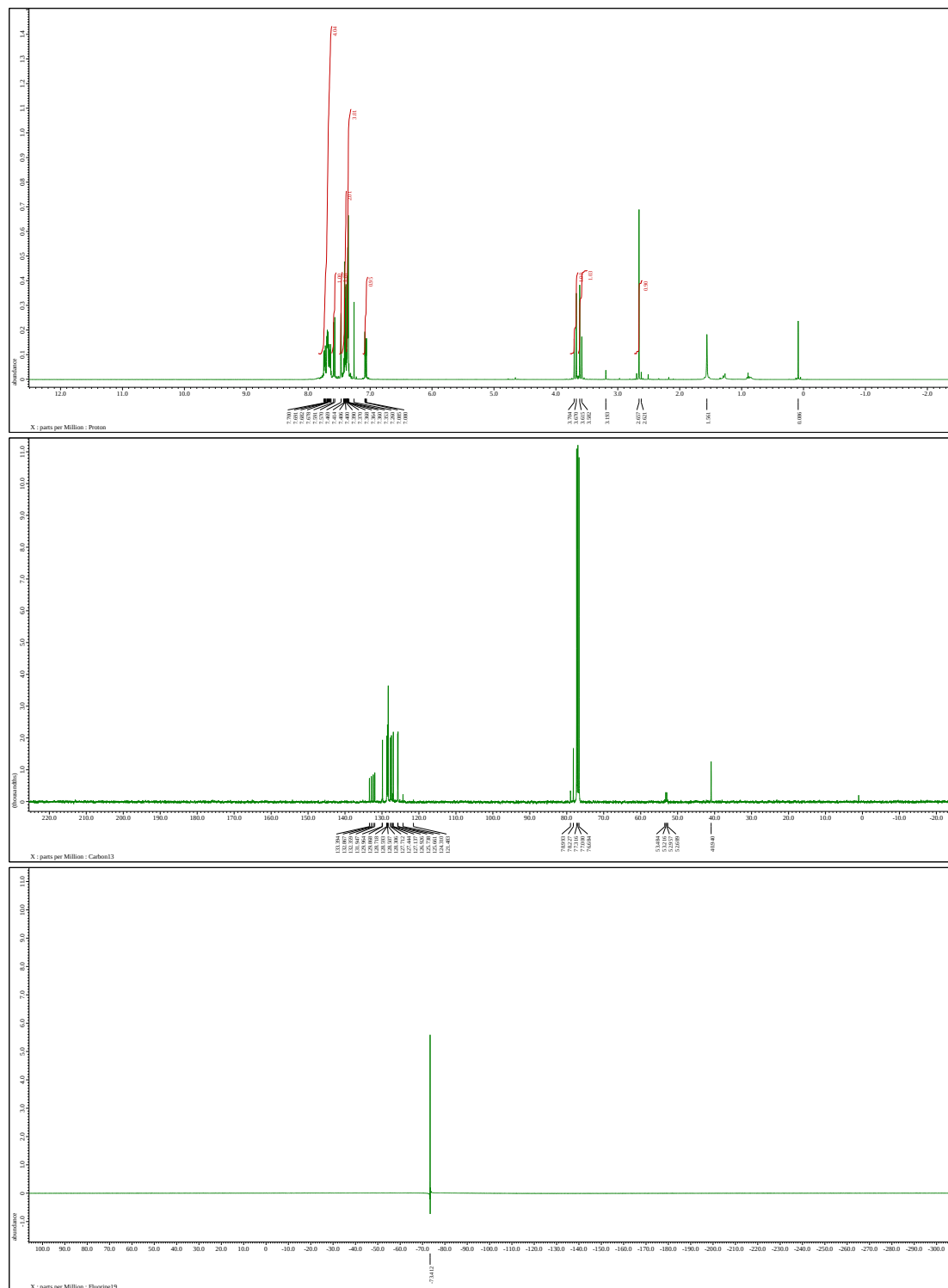
7ar



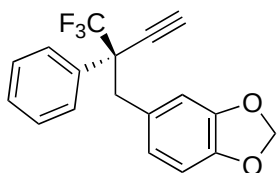
Supplementary Fig. 37: ¹H, ¹³C, and ¹⁹F NMR charts of **7ar.**



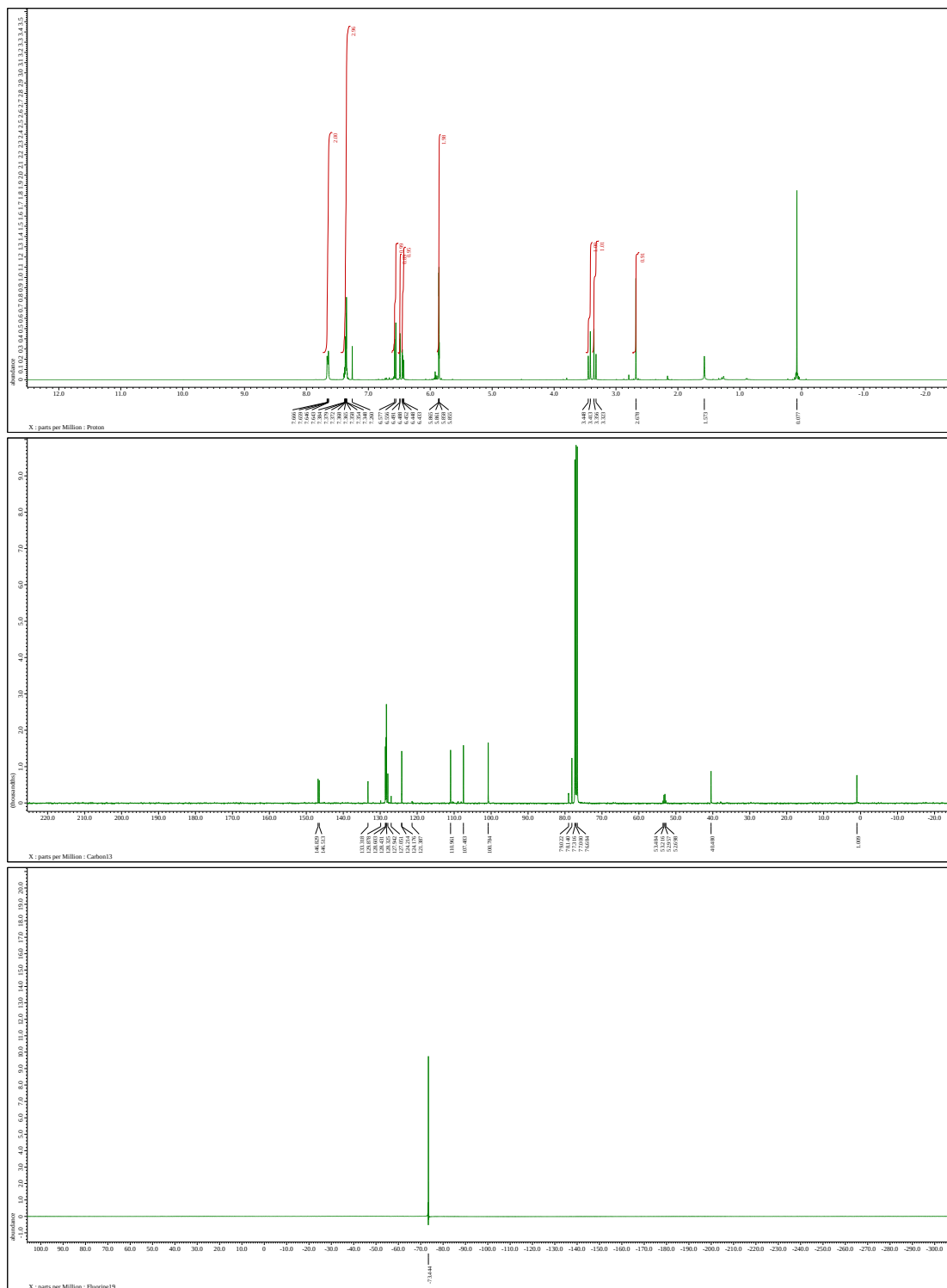
7as



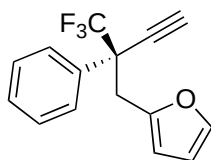
Supplementary Fig. 38: ^1H , ^{13}C , and ^{19}F NMR charts of **7as.**



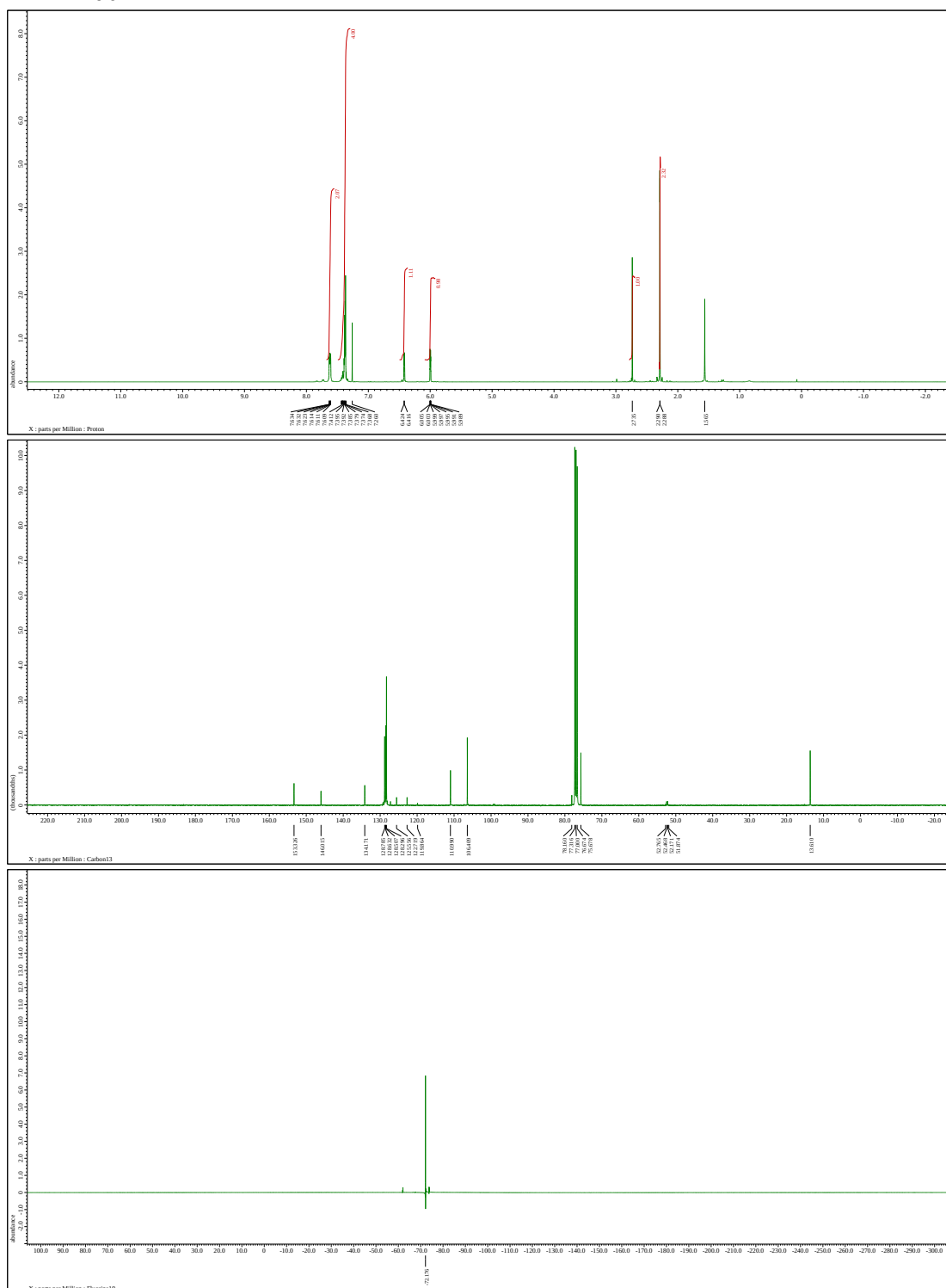
7at

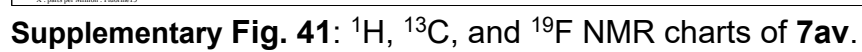


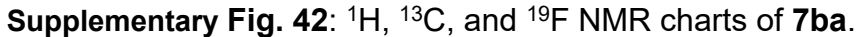
Supplementary Fig. 39: ¹H, ¹³C, and ¹⁹F NMR charts of **7at.**

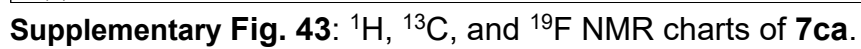


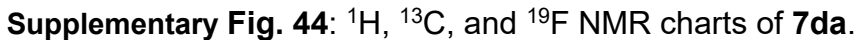
7au

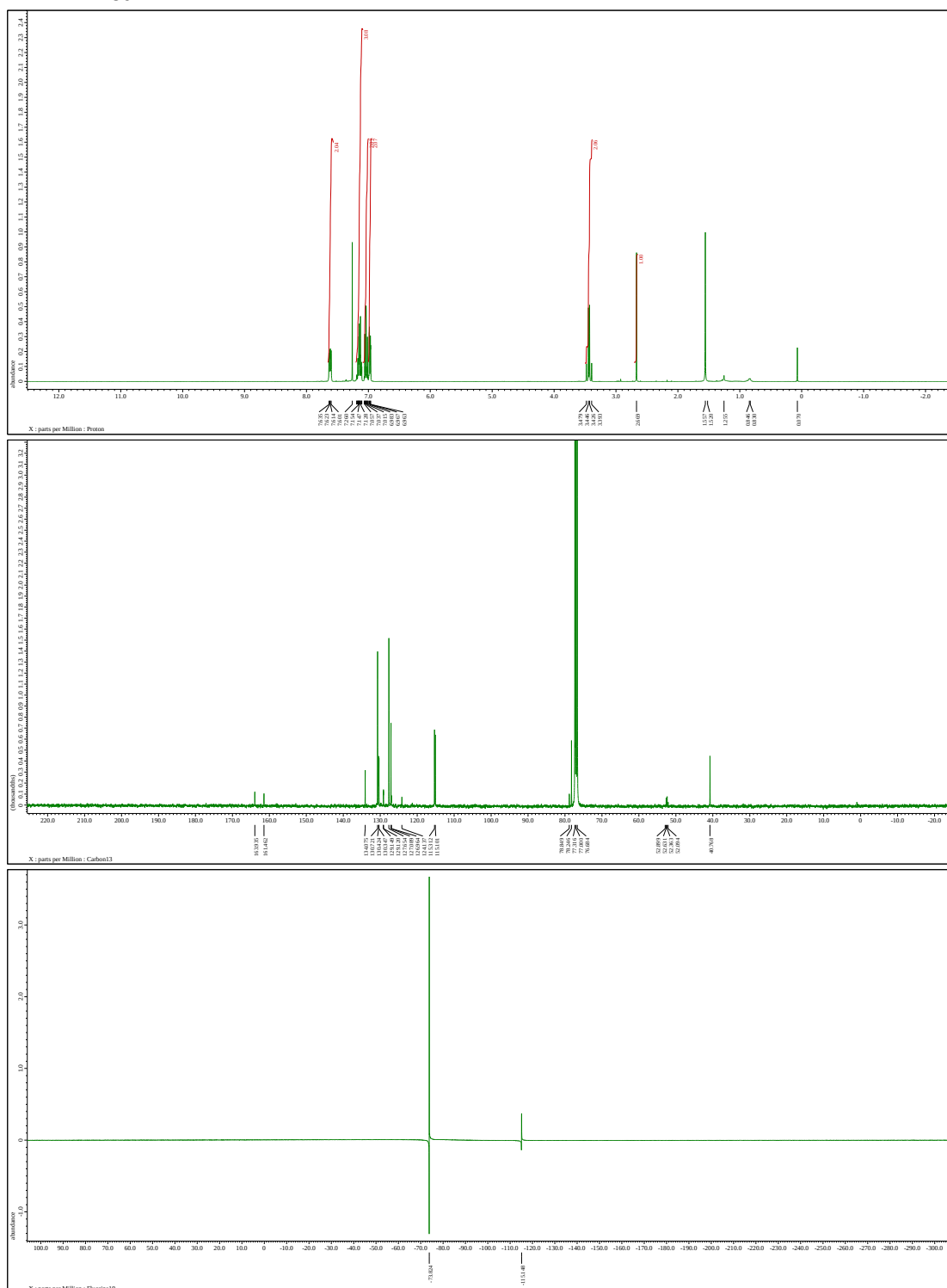
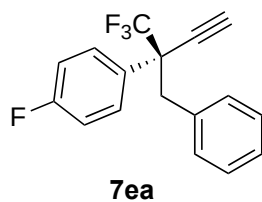




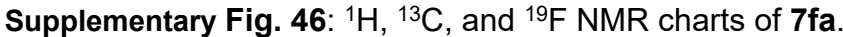


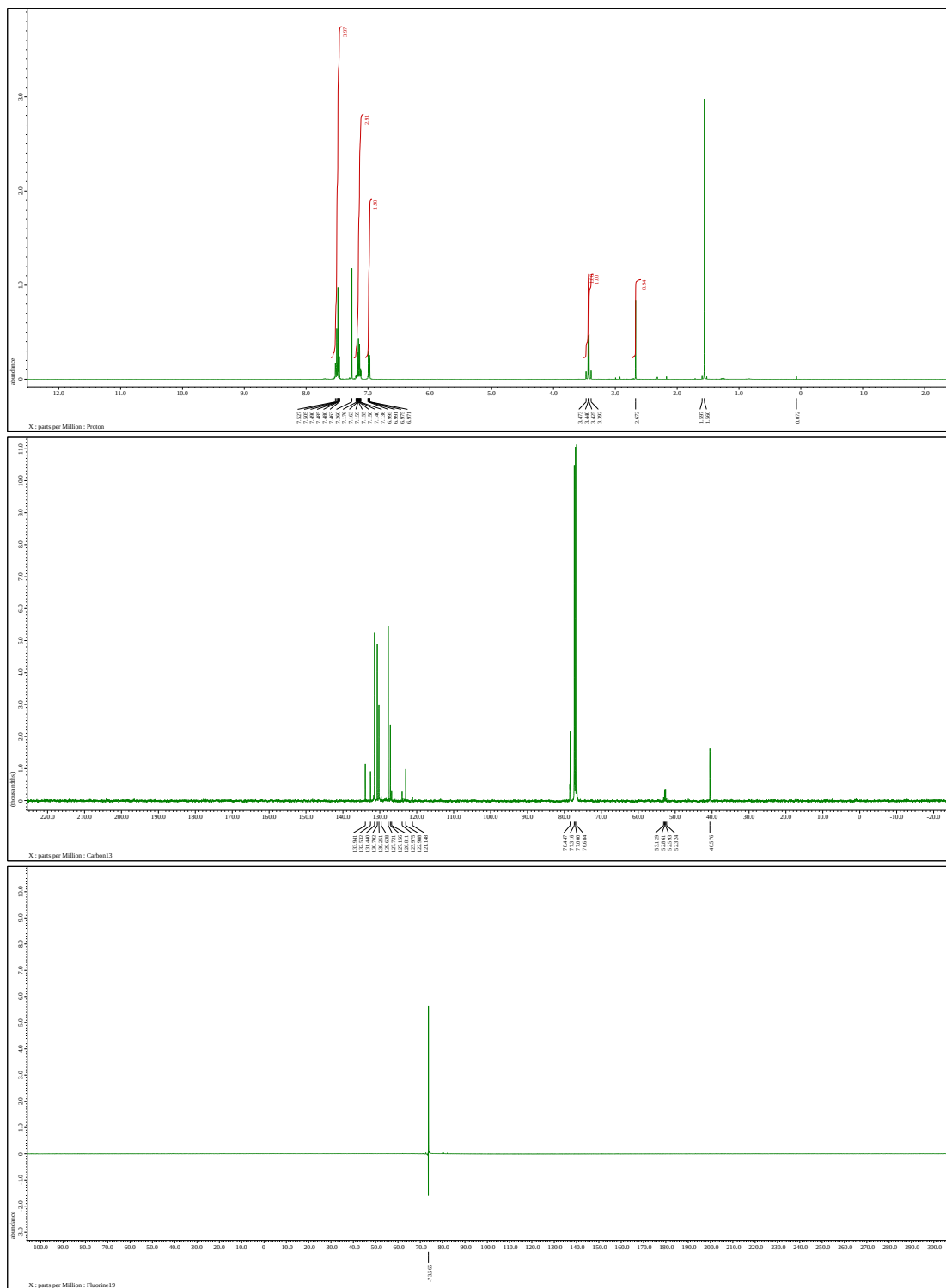
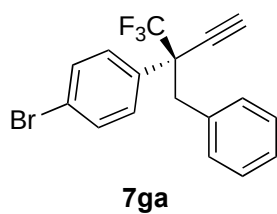




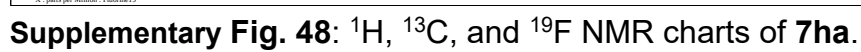


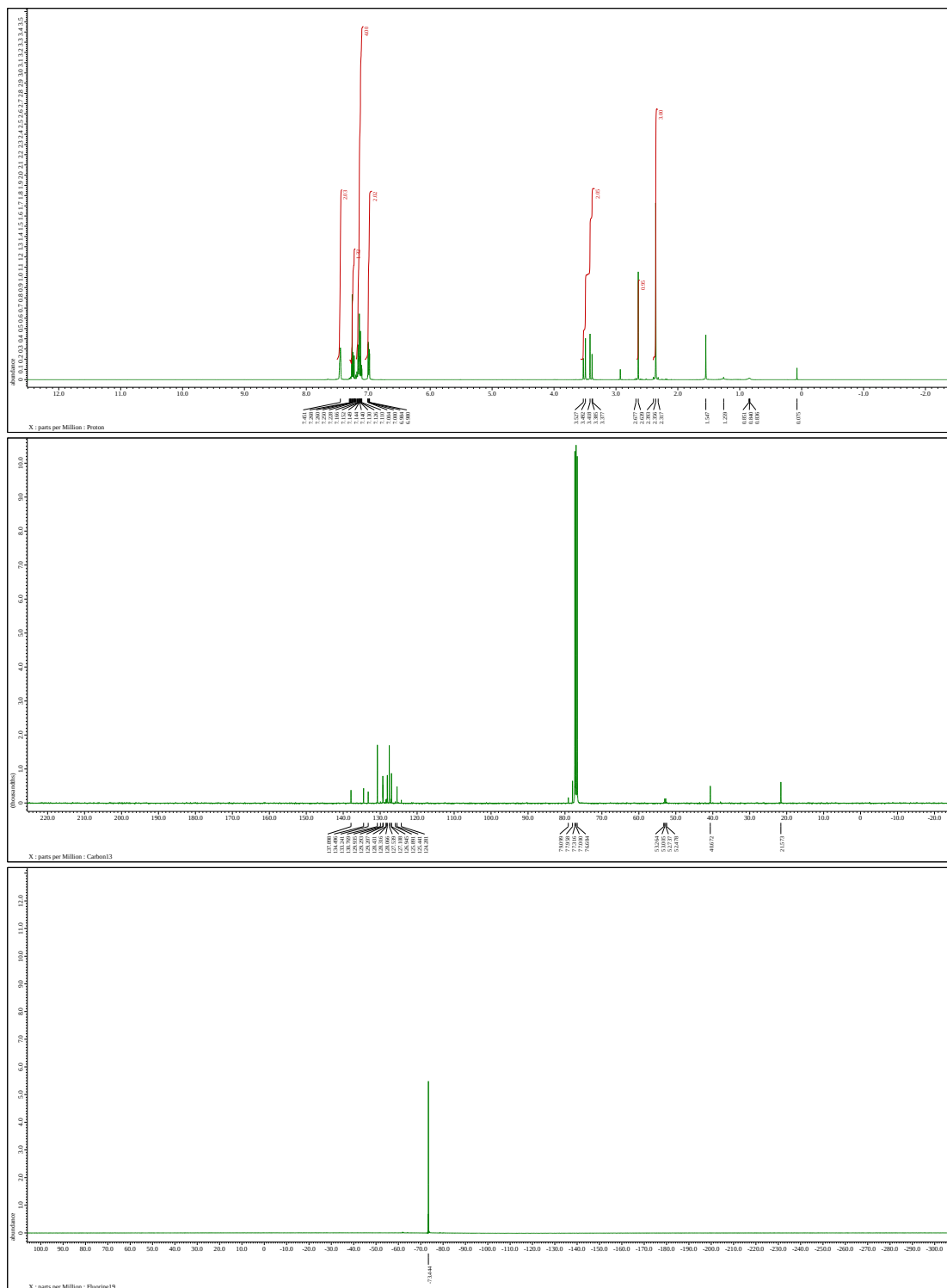
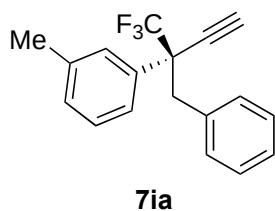
Supplementary Fig. 45: ^1H , ^{13}C , and ^{19}F NMR charts of **7ea**.



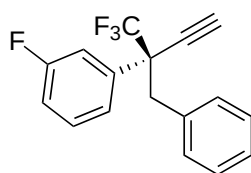


Supplementary Fig. 47: ^1H , ^{13}C , and ^{19}F NMR charts of **7ga**.

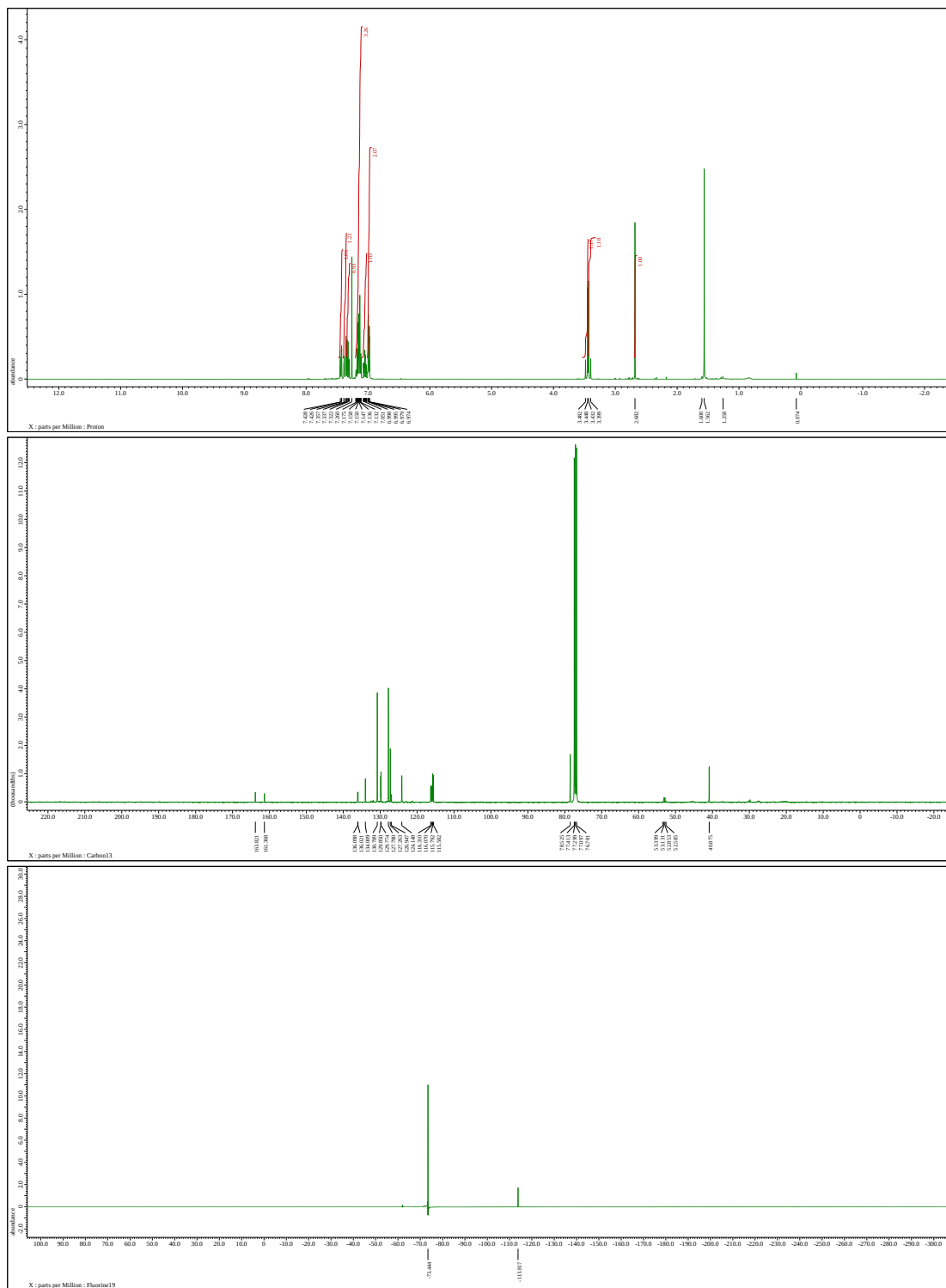


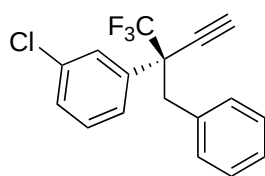


Supplementary Fig. 49: ^1H , ^{13}C , and ^{19}F NMR charts of **7ia.**

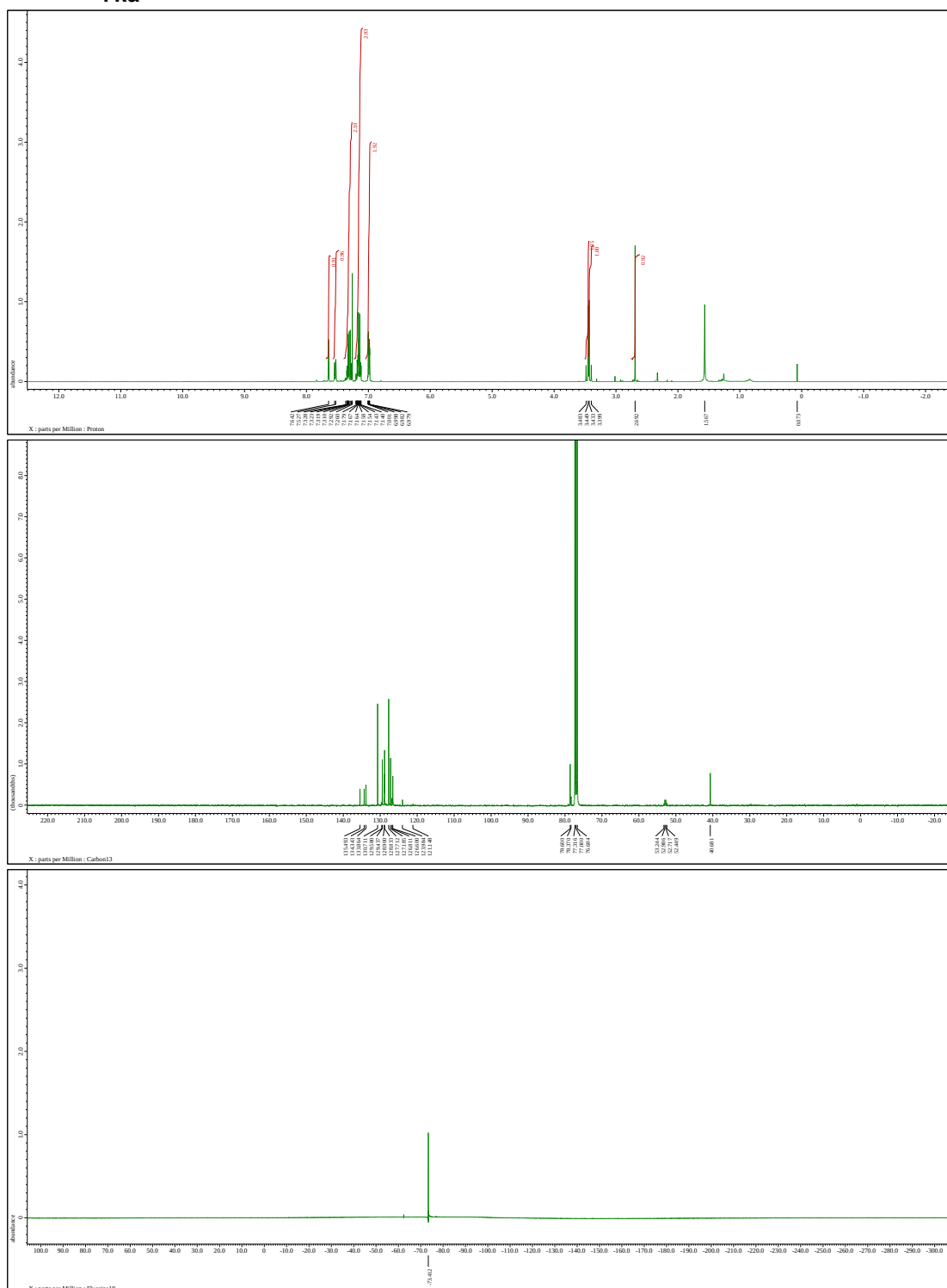


7ja

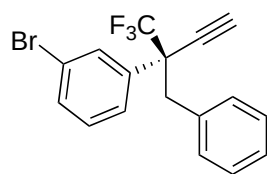




7ka



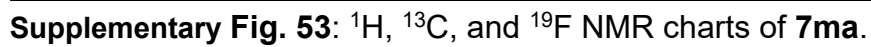
Supplementary Fig. 51: ^1H , ^{13}C , and ^{19}F NMR charts of **7ka**.

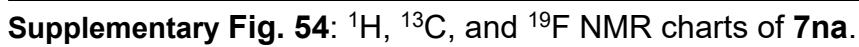


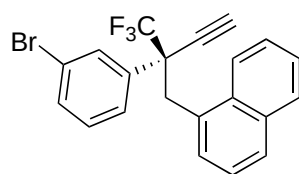
7la



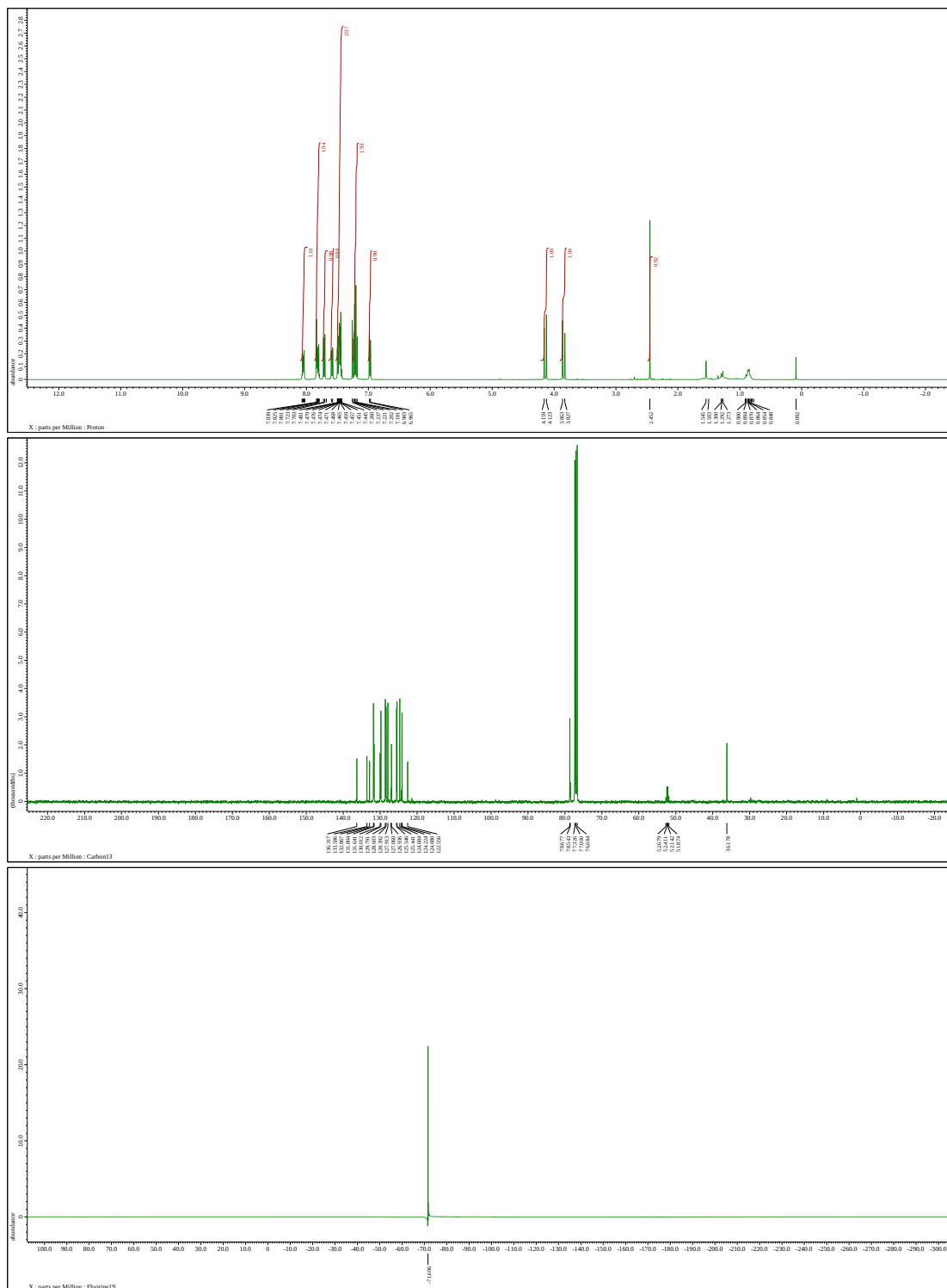
Supplementary Fig. 52: ¹H, ¹³C, and ¹⁹F NMR charts of 7la.



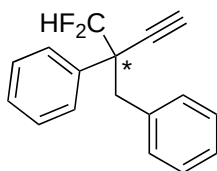




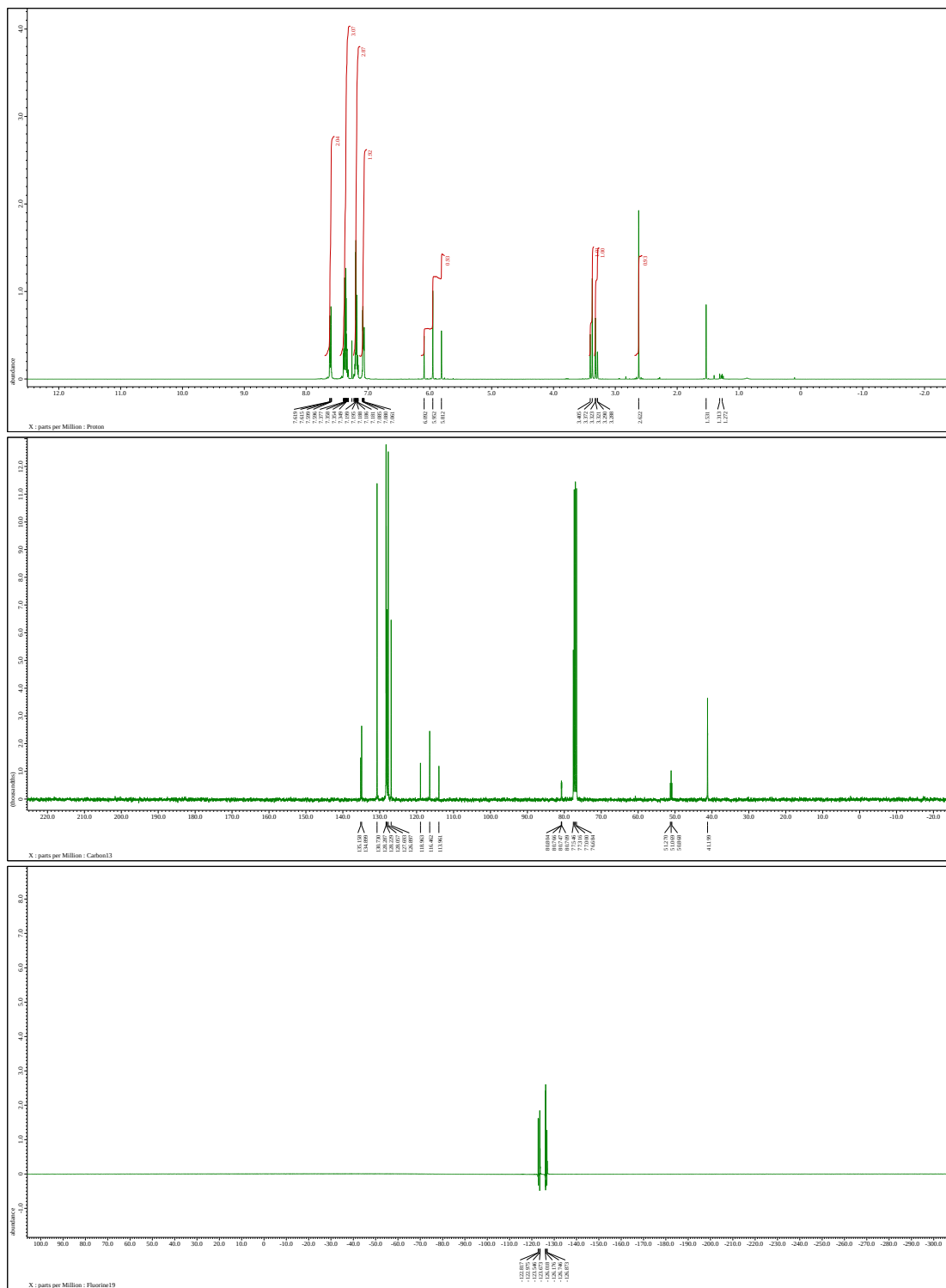
7lr



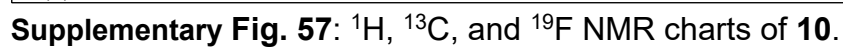
Supplementary Fig. 55: ¹H, ¹³C, and ¹⁹F NMR charts of **7lr.**

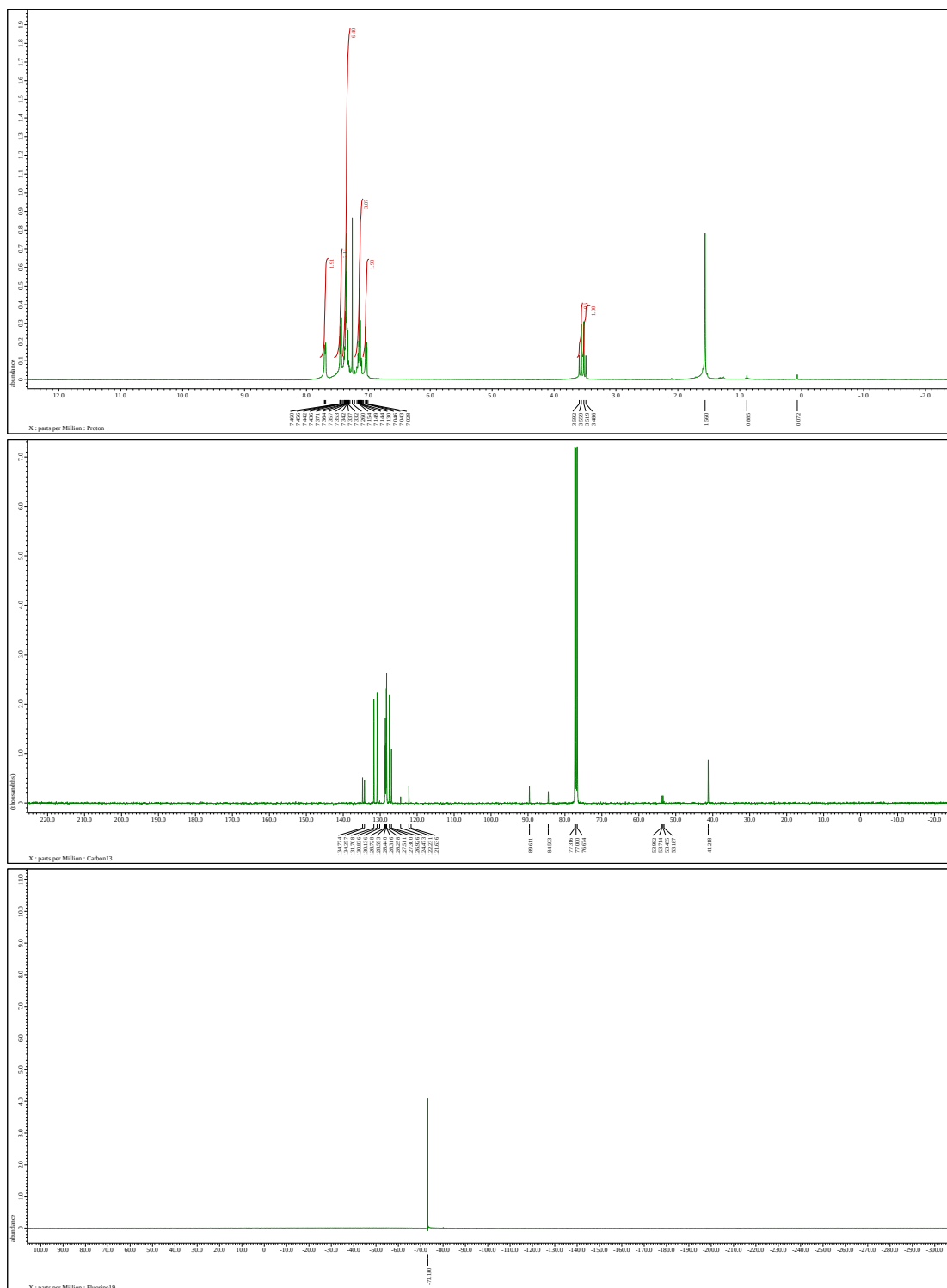
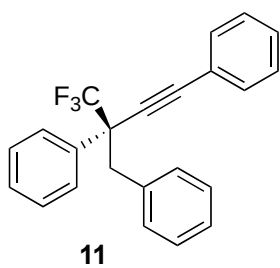


9

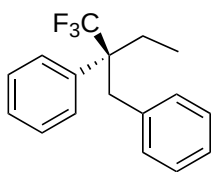


Supplementary Fig. 56: ^1H , ^{13}C , and ^{19}F NMR charts of **9**.

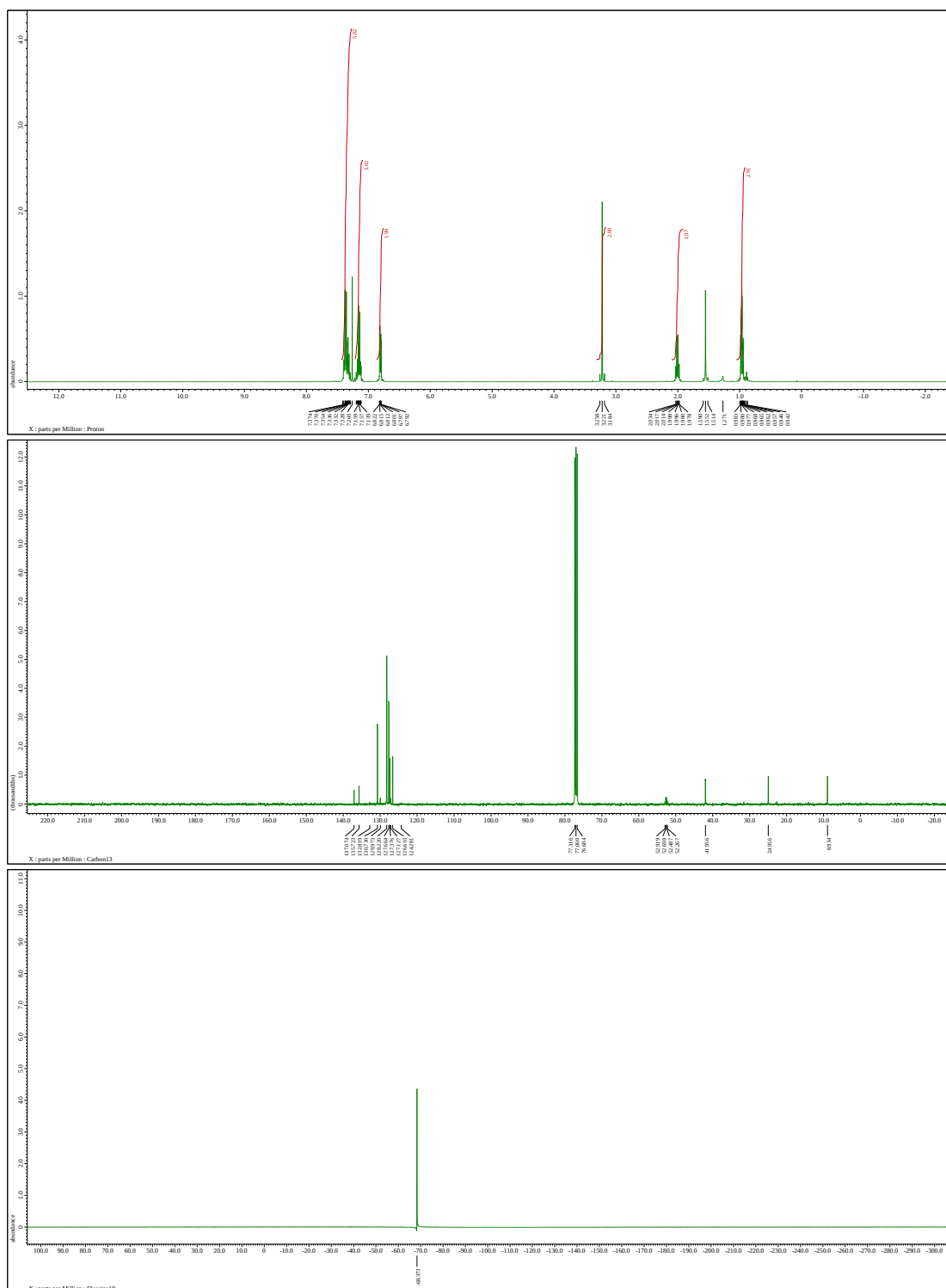




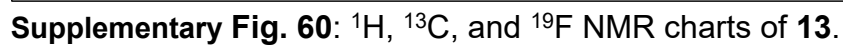
Supplementary Fig. 58: ¹H, ¹³C, and ¹⁹F NMR charts of **11**.



12



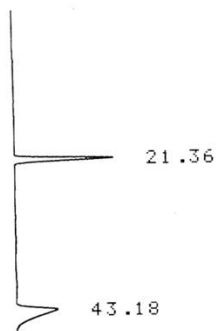
Supplementary Fig. 59: ^1H , ^{13}C , and ^{19}F NMR charts of **12**.



1.23: HPLC charts

5 (racemate)

CH. 1 C.S 1.25 ATT 5 OFFS 0 00/00/00 03:25



0J-H
1% P₄OH
0.5 mL/mL
220 nm

D-2500

00/00/00 03:25

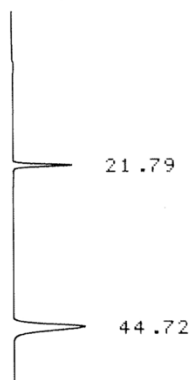
METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	21.36	111322	46.050	BB
2	43.18	130422	53.950	BB
TOTAL		241744	100.000	
PEAK REJ :		0		

5 (chiral)

CH. 1 C.S 1.25 ATT 2 OFFS 0 00/00/00 02:29



0J-H
1% P₄OH
0.5 mL/mL
220 nm

D-2500

00/00/00 02:29

METHOD: TAG: 2 CH: 1

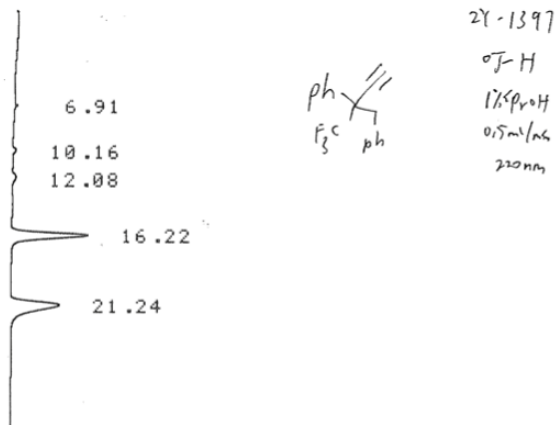
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	21.79	6518	26.234	BB
2	44.72	18328	73.766	BB
TOTAL		24846	100.000	
PEAK REJ :		0		

Supplementary Fig. 61: HPLC charts of 5.

7aa (racemate)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:21



D-2500

00/00/00 00:21

METHOD:

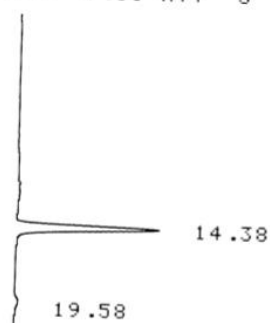
TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
4	16.22	20010	49.260	BB
5	21.24	20611	50.740	BB
TOTAL		40621	100.000	
PEAK REJ :		1200		

7aa (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:22



D-2500

00/00/00 00:22

METHOD:

TAG: 2 CH: 1

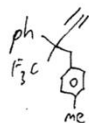
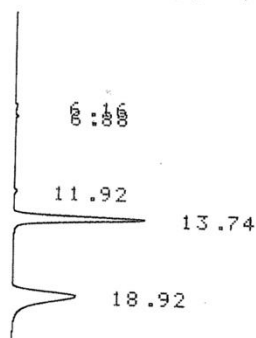
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.38	29864	97.002	BB
2	19.58	923	2.998	BB
TOTAL		30787	100.000	
PEAK REJ :		0		

Supplementary Fig. 62: HPLC charts of 7aa.

7ab (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 04:12
2Y-1442



0J-H
1% iPrOH
0.5m/min
220nm

D-2500

00/00/00 04:12

METHOD:

TAG: 3 CH: 1

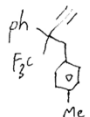
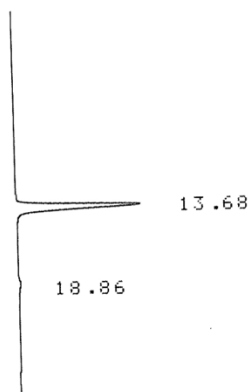
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
4	13.74	54065	50.596	BB
5	18.92	52792	49.404	BB
TOTAL				

PEAK REJ : 106857 100.000
700

7ab (chiral)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 08:01
2Y-1443



0J-H
1% iPrOH
0.5m/min
220nm

D-2500

00/00/00 08:01

METHOD:

TAG: 6 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

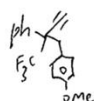
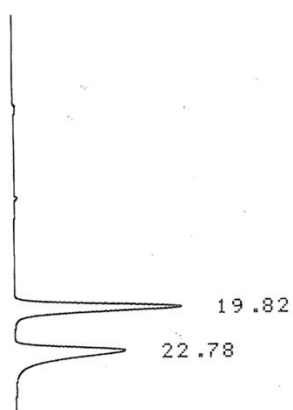
NO.	RT	AREA	CONC	BC
1	13.68	48405	97.242	BB
2	18.86	1373	2.758	BB
TOTAL				

PEAK REJ : 49778 100.000
0

Supplementary Fig. 63: HPLC charts of 7ab.

7ac (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 01:19



ZY-1471
0J-11
10% PrOH
0.5 ml/min
220nm

D-2500

00/00/00 01:19

METHOD: TAG: 3 CH: 1

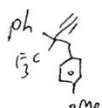
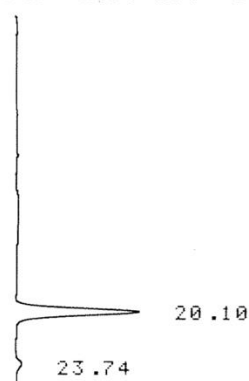
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.82	101021	50.795	BB
2	22.78	97857	49.205	BB
TOTAL		198878	100.000	

PEAK REJ : 0

7ac (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 03:10



ZY-1472
0J-11
10% PrOH
0.5 ml/min
220nm

D-2500

00/00/00 03:10

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

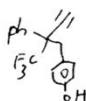
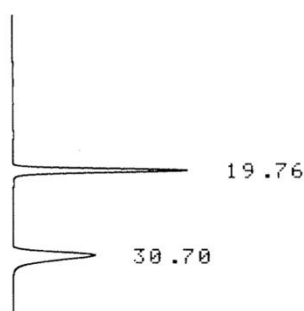
NO.	RT	AREA	CONC	BC
1	20.10	35227	96.136	BB
2	23.74	1416	3.864	BB
TOTAL		36643	100.000	

PEAK REJ : 0

Supplementary Fig. 64: HPLC charts of 7ac.

7ad (racemate)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 04:12



2(-1647)
0J-H
20% PrOH
0.5m/min
120nm

D-2500

00/00/00 04:12

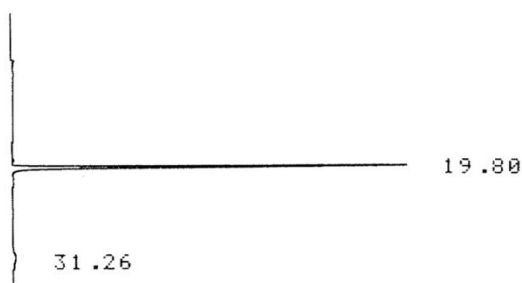
METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.76	47549	50.141	BB
2	30.70	47281	49.859	BB
TOTAL		94830	100.000	
PEAK REJ :		0		

7ad (chiral)

CH. 1 C.S 1.25 ATT 4 OFFS 0 00/00/00 00:01



2(-1648)
0J-H
20% PrOH
0.5m/min
120nm

D-2500

00/00/00 00:01

METHOD: TAG: 1 CH: 1

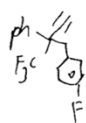
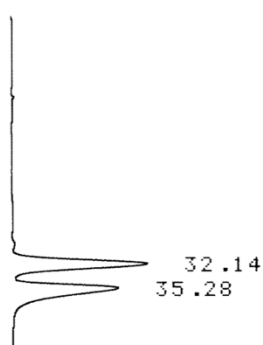
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.80	71668	95.999	BB
2	31.26	2987	4.001	BB
TOTAL		74655	100.000	
PEAK REJ :		0		

Supplementary Fig. 65: HPLC charts of 7ad.

7ae (racemate)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 00:56



24-1767
0J-H
0.3ml/min
1% iPrOH
220nm

D-2500

00/00/00 00:56

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	32.14	82872	50.214	BB
2	35.28	82166	49.786	BB

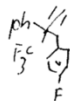
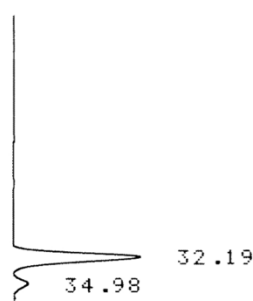
TOTAL

165038 100.000

PEAK REJ : 0

7ae (chiral)

CH. 1 C.S 1.25 ATT 2 OFFS 0 00/00/00 00:42



24-1763
0J-H
0.3ml/min
1% iPrOH
220nm

D-2500

00/00/00 00:42

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	32.19	36704	95.833	BB
2	34.98	1596	4.167	BB

TOTAL

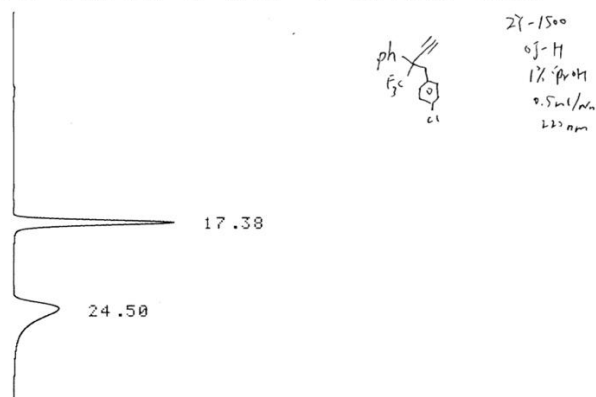
38300 100.000

PEAK REJ : 0

Supplementary Fig. 66: HPLC charts of 7ae.

7af (racemate)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:00



D-2500

00/00/00 00:00

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	17.38	45384	51.277	BB
2	24.50	43123	48.723	BB

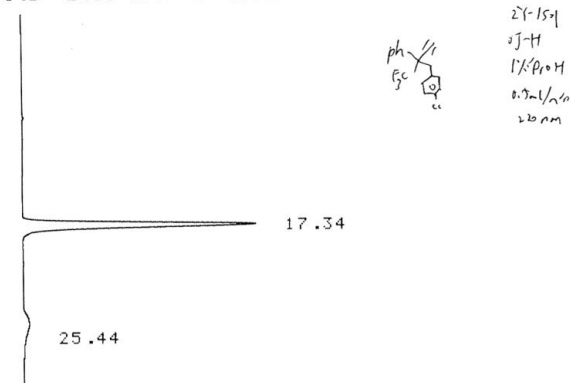
TOTAL 88507 100.000

PEAK REJ :

0

7af (chiral)

CH. 1 C.S 2.50 ATT 2 OFFS 0 00/00/00 01:28



D-2500

00/00/00 01:28

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	17.34	35915	95.094	BB
2	25.44	1853	4.906	BB

TOTAL 37768 100.000

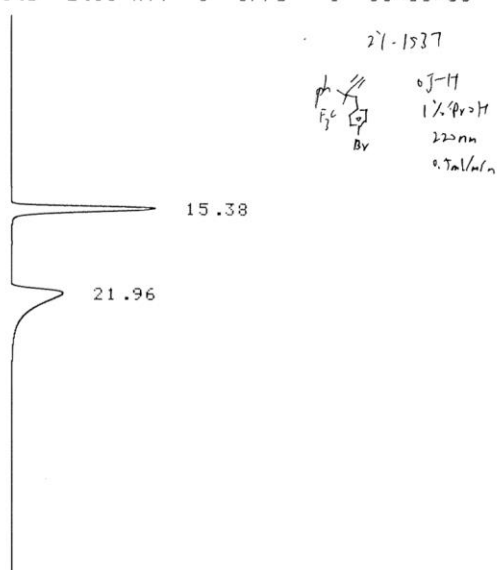
PEAK REJ :

0

Supplementary Fig. 67: HPLC charts of 7af.

7ag (racemate)

CH. 1 C.S 2.50 ATT 6 OFFS 0 00/00/00 01:57



D-2500

00/00/00 01:57

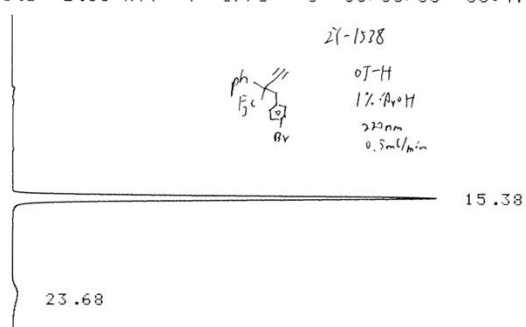
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.38	343806	47.005	BB
2	21.96	387618	52.995	BB
TOTAL		731424	100.000	
PEAK REJ :		0		

7ag (chiral)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 03:47



D-2500

00/00/00 03:47

METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

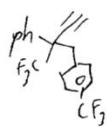
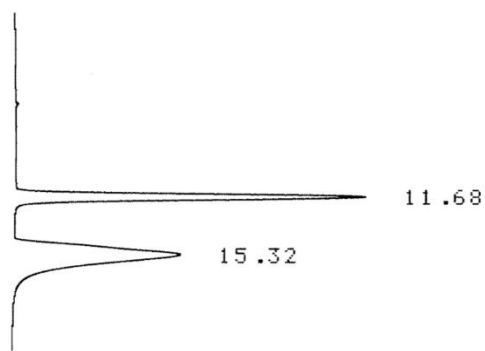
NO.	RT	AREA	CONC	BC
1	15.38	227544	97.027	BB
2	23.68	6972	2.973	BB
TOTAL		234516	100.000	
PEAK REJ :		0		

Supplementary Fig. 68: HPLC charts of 7ag.

7ah (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 00:09

2Y-1512



OT-H
1% AcOH
0.5 mL/min
220 nm

D-2500

00/00/00 00:09

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.68	144051	53.995	BB
2	15.32	122736	46.005	BB

TOTAL

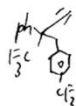
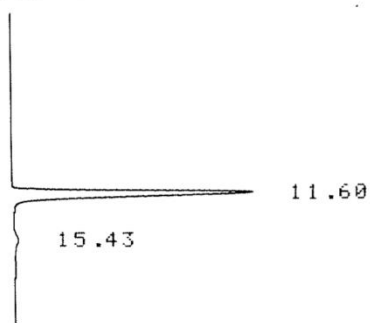
266787 100.000

PEAK REJ : 0

7ah (chiral)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 00:34

2Y-1513



OT-H
1% AcOH
0.5 mL/min
220 nm

D-2500

00/00/00 00:34

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.60	91516	95.737	BB
2	15.43	4075	4.263	BB

TOTAL

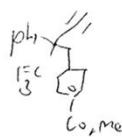
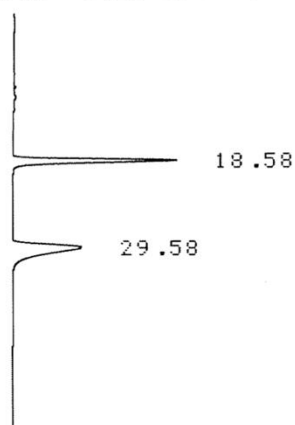
95591 100.000

PEAK REJ : 0

Supplementary Fig. 69: HPLC charts of 7ah.

7ai (racemate)

CH. 1 C.5 1.25 ATT 4 OFFS . 0 00/00/00 00:44



27-1655
07-14
10% Ph₄OH
0.5 ml/min
270nm

D-2500

00/00/00 00:44

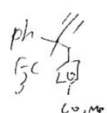
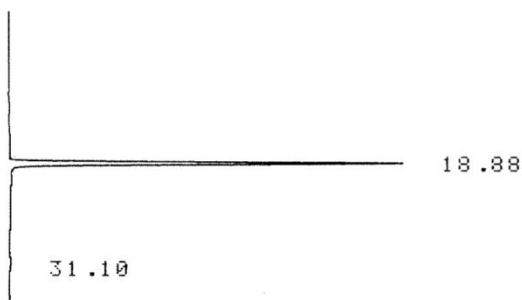
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	18.58	87848	50.612	BB
2	29.58	85724	49.388	BB
TOTAL		173572	100.000	
PEAK REJ :		0		

7ai (chiral)

CH. 1 C.5 1.25 ATT 4 OFFS . 0 00/00/00 03:09



27-1656
07-14
10% Ph₄OH
0.5 ml/min
270nm

D-2500

00/00/00 03:09

METHOD: TAG: 3 CH: 1

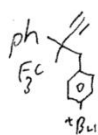
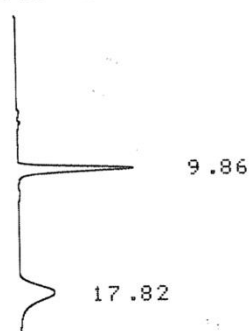
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	18.88	133304	97.798	BB
2	31.10	3002	2.202	BB
TOTAL		136306	100.000	
PEAK REJ :		0		

Supplementary Fig. 70: HPLC charts of 7ai.

7aj (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 00:58
2Y-1449



0J-H
1% PhOH
0.5 ml/min
220 nm

D-2500

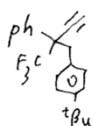
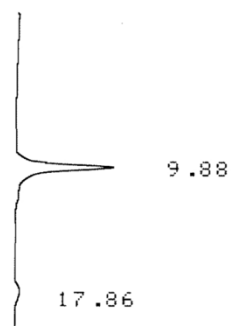
00/00/00 00:58

METHOD: TAG: 2 CH: 1
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	9.86	42994	52.497	BB
2	17.82	38904	47.503	BB
TOTAL		81898	100.000	
PEAK REJ :		0		

7aj (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:28



2Y-1449
0J-H
1% PhOH
0.5 ml/min
220 nm

D-2500

00/00/00 00:28

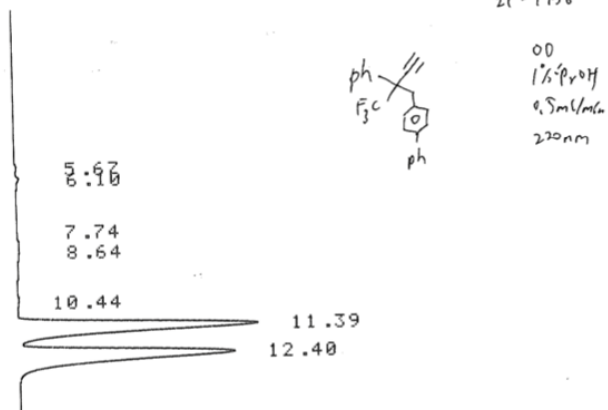
METHOD: TAG: 1 CH: 1
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	9.88	29071	91.802	BB
2	17.86	2596	8.198	BB
TOTAL		31667	100.000	
PEAK REJ :		0		

Supplementary Fig. 71: HPLC charts of 7aj.

7ak (racemate)

CH. 1 C.S 5.00 ATT 5 OFFS 0 00/00/00 01:55
27-145



D-2500

00/00/00 01:55

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
6	11.39	205520	48.976	BU
7	12.40	214118	51.024	VB

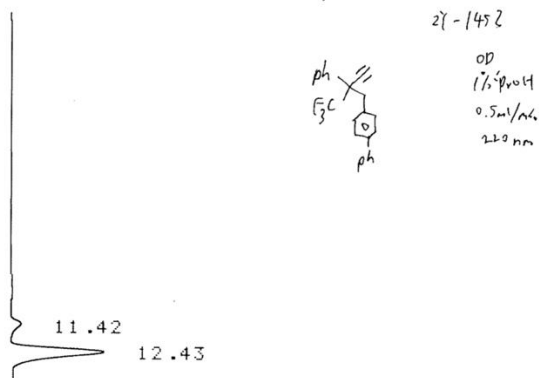
TOTAL 419638 100.000

PEAK REJ : 3500

7ak (chiral)

CH. 1 C.S 5.00 ATT 3 OFFS 0 00/00/00 02:23

27-147



D-2500

00/00/00 02:23

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.42	1818	8.681	BB
2	12.43	19125	91.319	BB

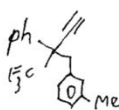
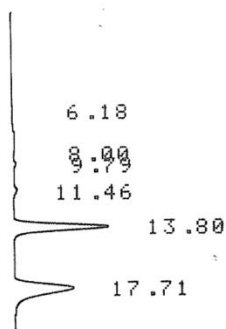
TOTAL 20943 100.000

PEAK REJ : 0

Supplementary Fig. 72: HPLC charts of 7ak.

7al (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 07:31
27-1444



0J-H
1% PrOH
0.5 ml/min
220 nm

D-2500

00/00/00 07:31

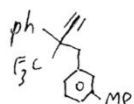
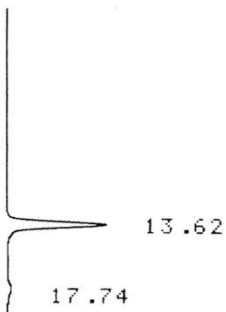
METHOD: TAG: 5 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
5	13.80	41647	49.819	BB
6	17.71	41950	50.181	BB
TOTAL		83597	100.000	
PEAK REJ :		1600		

7al (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:35
27-1445



0J-H
1% PrOH
0.5 ml/min
220 nm

D-2500

00/00/00 00:35

METHOD: TAG: 2 CH: 1

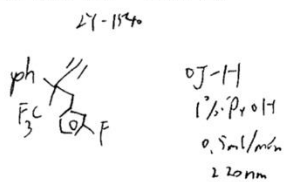
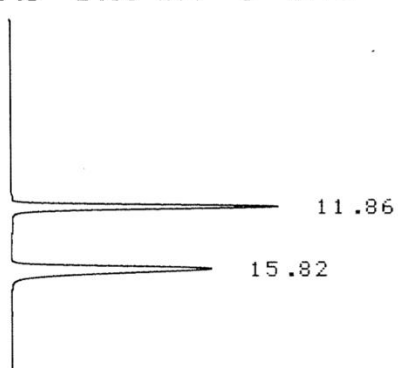
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.62	20157	95.080	BB
2	17.74	1043	4.920	BB
TOTAL		21200	100.000	
PEAK REJ :		0		

Supplementary Fig. 73: HPLC charts of 7al.

7am (racemate)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:10



D-2500

00/00/00 00:10

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.86	40194	45.931	BB
2	15.82	47316	54.069	BB

TOTAL

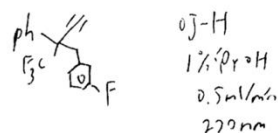
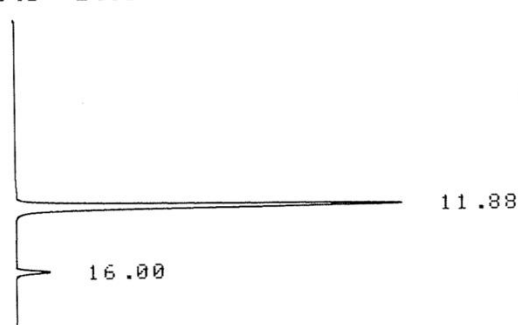
87510 100.000

PEAK REJ :

0

7am (chiral)

CH. 1 C.S 2.50 ATT 2 OFFS 0 00/00/00 00:21



D-2500

00/00/00 00:21

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.88	26913	94.931	BB
2	16.00	1437	5.069	BB

TOTAL

28350 100.000

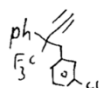
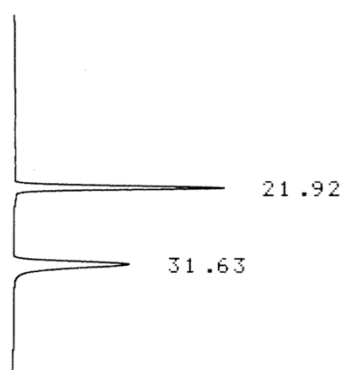
PEAK REJ :

0

Supplementary Fig. 74: HPLC charts of 7am.

7an (racemate)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 01:45



27-1604

07-11
1% PhOH
0.5ml/min
220nm

D-2500

00/00/00 01:45

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	21.92	54946	49.620	BB
2	31.63	55788	50.380	BB

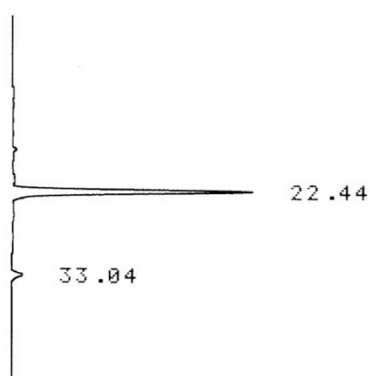
TOTAL

110734 100.000

PEAK REJ : 0

7an (chiral)

CH. 1 C.S 1.25 ATT 2 OFFS 0 00/00/00 00:04



27-1605

07-11
1% PhOH
0.5ml/min
220nm

D-2500

00/00/00 00:04

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	22.44	31052	95.642	BB
2	33.04	1415	4.358	BB

TOTAL

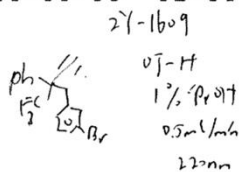
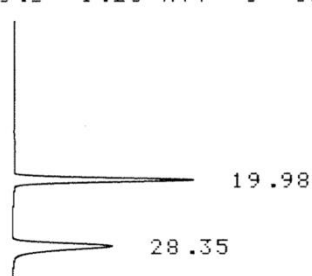
32467 100.000

PEAK REJ : 0

Supplementary Fig. 75: HPLC charts of 7an.

7ao (racemate)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 02:55



D-2500

00/00/00 02:55

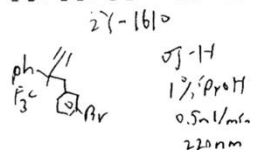
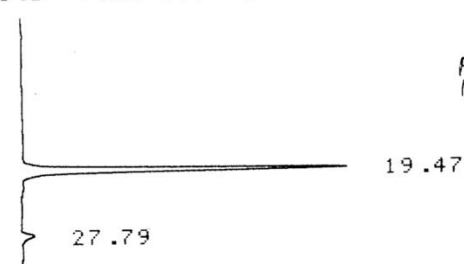
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.98	48335	51.028	BB
2	28.35	46387	48.972	BB
TOTAL		94722	100.000	
PEAK REJ :		0		

7ao (chiral)

CH. 1 C.S 1.25 ATT 2 OFFS 0 00/00/00 01:47



D-2500

00/00/00 01:47

METHOD: TAG: 4 CH: 1

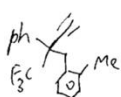
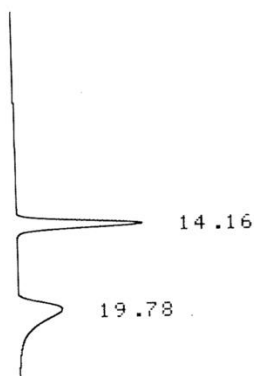
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.47	41257	96.682	BB
2	27.79	1416	3.318	BB
TOTAL		42673	100.000	
PEAK REJ :		0		

Supplementary Fig. 76: HPLC charts of 7ao.

7ap (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 00:37
27-1446



0J-H
1% PhOH
0.5mL/min
220nm

D-2500

00/00/00 00:37

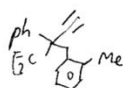
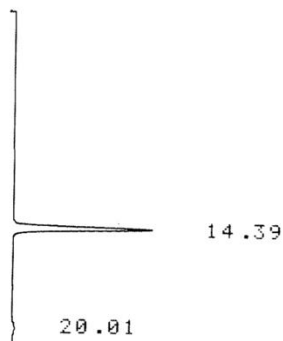
METHOD: TAG: 2 CH: 1
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.16	67756	52.148	BB
2	19.78	62173	47.852	BB
TOTAL		129929	100.000	

PEAK REJ : 0

7ap (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:00
27-1447



0J-H
1% PhOH
0.5mL/min
220nm

D-2500

00/00/00 00:00

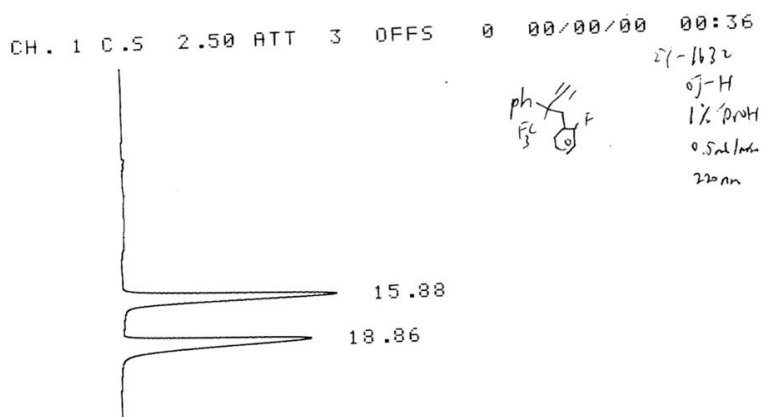
METHOD: TAG: 1 CH: 1
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.39	20469	95.085	BB
2	20.01	1058	4.915	BB
TOTAL		21527	100.000	

PEAK REJ : 0

Supplementary Fig. 77: HPLC charts of 7ap.

7aq (racemate)



D-2500

00/00/00 00:36

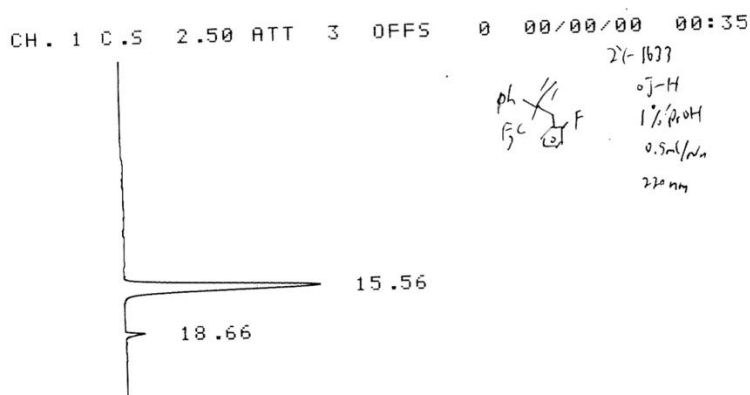
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.88	59573	48.618	BB
2	18.86	62961	51.382	BB
TOTAL		122534	100.000	

PEAK REJ : 0

7aq (chiral)



D-2500

00/00/00 00:35

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

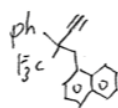
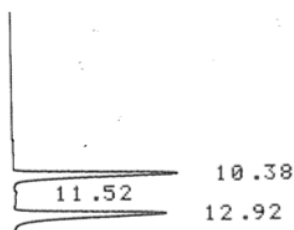
NO.	RT	AREA	CONC	BC
1	15.56	51528	96.512	BB
2	18.66	1862	3.488	BB
TOTAL		53390	100.000	

PEAK REJ : 0

Supplementary Fig. 78: HPLC charts of 7aq.

7ar (racemate)

CH. 1 C.S 2.50 ATT 6 OFFS 0 00/00/00 03:24
27-1451



00
1% iPrOH
0.5 mL/min
220 nm

D-2500

00/00/00 03:24

METHOD:

TAG:

5 CH: 1

FILE: 0 CALC-METHOD: AREA%

TABLE: 0 CONC: AREA

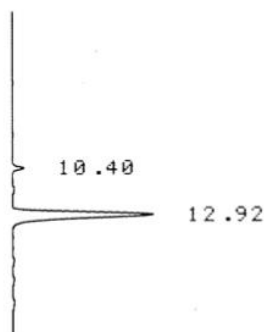
NO.	RT	AREA	CONC	BC
1	10.38	220533	47.754	BB
3	12.92	241279	52.246	BB
TOTAL		461812	100.000	

PEAK REJ :

3500

7ar (chiral)

CH. 1 C.S 2.50 ATT 6 OFFS 0 00/00/00 01:16



00
1% iPrOH
0.5 mL/min
220 nm

D-2500

00/00/00 01:16

METHOD:

TAG:

2 CH: 1

FILE: 0 CALC-METHOD: AREA%

TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	10.40	12167	4.633	BB
2	12.92	250443	95.367	BB
TOTAL		262610	100.000	

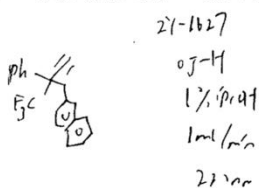
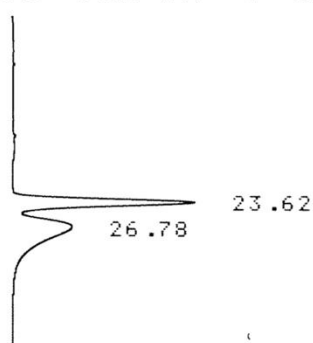
PEAK REJ :

0

Supplementary Fig. 79: HPLC charts of 7ar.

7as (racemate)

CH. 1 C.S 1.25 ATT 4 OFFS 0 00/00/00 02:24



D-2500

00/00/00 02:24

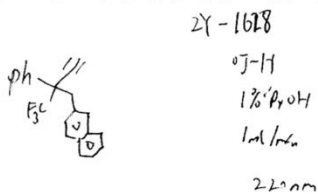
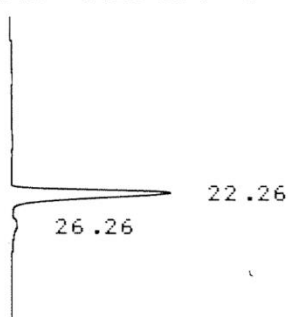
METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	23.62	183168	52.127	BU
2	26.78	168223	47.873	UB
TOTAL		351391	100.000	
PEAK REJ :		0		

7as (chiral)

CH. 1 C.S 1.25 ATT 6 OFFS 0 00/00/00 01:06



D-2500

00/00/00 01:06

METHOD: TAG: 2 CH: 1

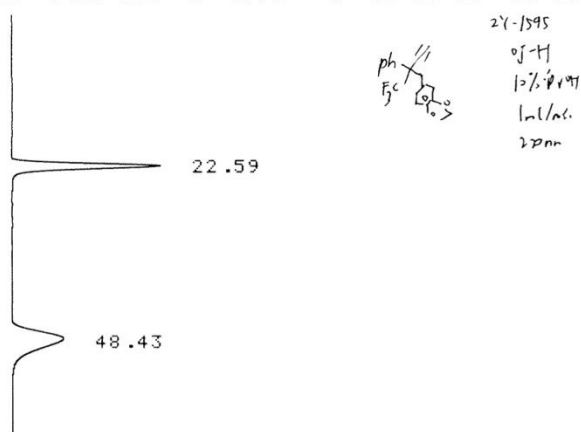
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	22.26	670761	97.442	BB
2	26.26	17608	2.558	BB
TOTAL		688369	100.000	
PEAK REJ :		0		

Supplementary Fig. 80: HPLC charts of 7as.

7at (racemate)

CH. 1 C.S 1.25 ATT 2 OFFS 0 00/00/00 03:15



D-2500

00/00/00 03:15

METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	22.59	37910	50.827	BB
2	48.43	36676	49.173	BB

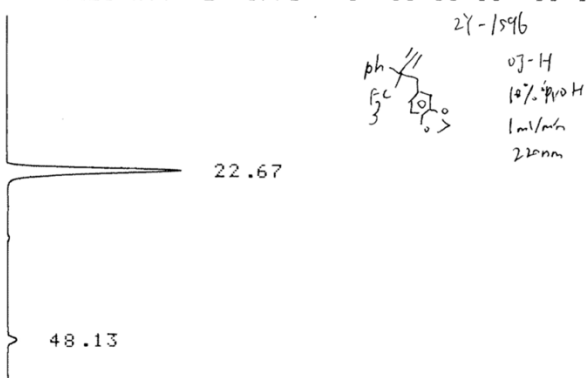
TOTAL 74586 100.000

PEAK REJ :

0

7at (chiral)

CH. 1 C.S 1.25 ATT 2 OFFS 0 00/00/00 00:01



D-2500

00/00/00 00:01

METHOD: TAG: 1 CH 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	22.67	34983	95.329	BB
2	48.13	1714	4.671	BB

TOTAL 36697 100.000

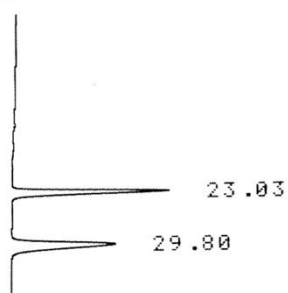
PEAK REJ :

0

Supplementary Fig. 81: HPLC charts of 7at.

7au (racemate)

CH. 1 C.S 1.25 ATT 5 OFFS 0 00/00/00 00:16



27-1607
05-H
1% PhOH
0.5m/min
22nm

D-2500

00/00/00 00:16

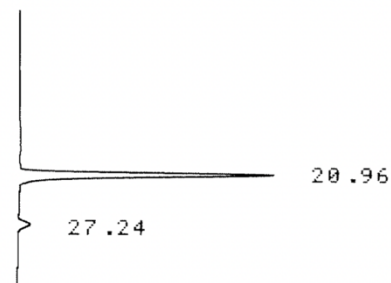
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	23.03	183632	49.752	BB
2	29.80	185463	50.248	BB
TOTAL		369095	100.000	
PEAK REJ :		0		

7au (chiral)

CH. 1 C.S 1.25 ATT 2 OFFS 0 00/00/00 00:38



27-1608
05-H
1% PhOH
0.5m/min
22nm

D-2500

00/00/00 00:38

METHOD: TAG: 2 CH: 1

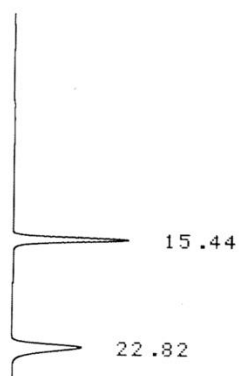
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	20.96	39608	94.960	BB
2	27.24	2102	5.040	BB
TOTAL		41710	100.000	
PEAK REJ :		0		

Supplementary Fig. 82: HPLC charts of 7au.

7av (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 00:00



21-1449
0J-H
1% AcOH
220nm
0.5ml/min

D-2500

00/00/00 00:00

METHOD: TAG: 1 CH: 1

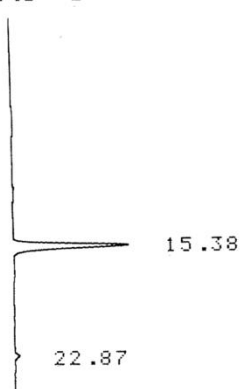
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.44	44780	50.247	BB
2	22.82	44340	49.753	BB

TOTAL 89120 100.000
PEAK REJ : 0

7av (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 08:23



21-1486
0J-H
1% AcOH
220nm
0.5ml/min

D-2500

00/00/00 08:23

METHOD: TAG: 6 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

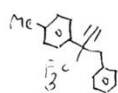
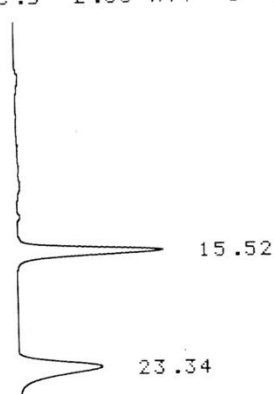
NO.	RT	AREA	CONC	BC
1	15.38	22707	97.192	BB
2	22.87	656	2.808	BB

TOTAL 23363 100.000
PEAK REJ : 0

Supplementary Fig. 83: HPLC charts of 7av.

7ba (racemate)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:59



27-1467

0J-14

1% PVA

0.5 ml/min

220 nm

D-2500

00/00/00 00:59

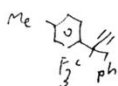
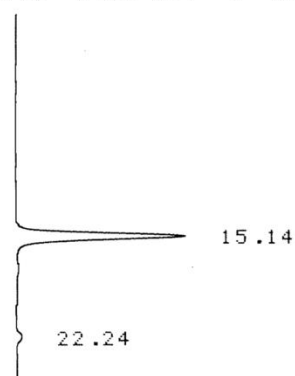
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.52	40652	49.590	BB
2	23.34	41325	50.410	BB
TOTAL		81977	100.000	
PEAK REJ :		0		

7ba (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 01:53



27-1468

0J-14

1% PVA

0.5 ml/min

220 nm

D-2500

00/00/00 01:53

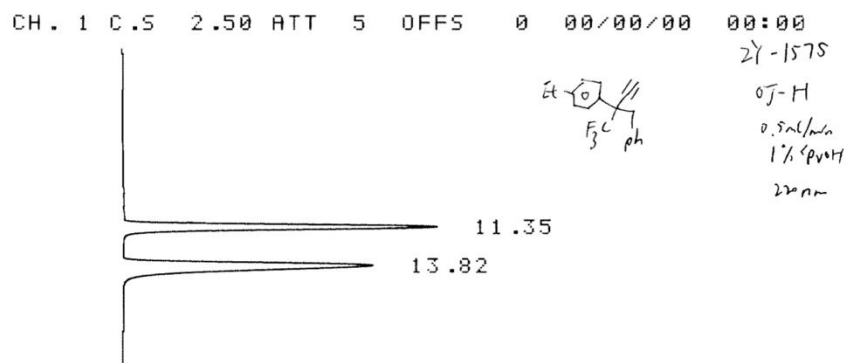
METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.14	44533	95.012	BB
2	22.24	2338	4.988	BB
TOTAL		46871	100.000	
PEAK REJ :		0		

Supplementary Fig. 84: HPLC charts of 7ba.

7ca (racemate)



D-2500 00/00/00 00:00

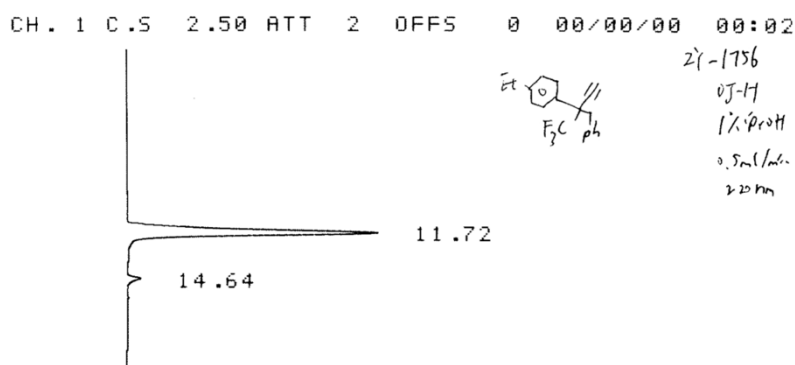
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.35	234656	46.948	BB
2	13.82	265160	53.052	BB
TOTAL		499816	100.000	

PEAK REJ : 0

7ca (chiral)



D-2500 00/00/00 00:02

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

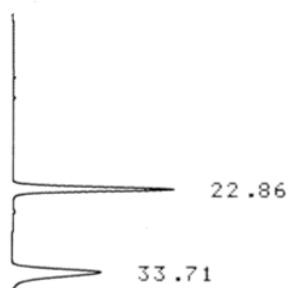
NO.	RT	AREA	CONC	BC
1	11.72	17448	94.826	BB
2	14.64	952	5.174	BB
TOTAL		18400	100.000	

PEAK REJ : 0

Supplementary Fig. 85: HPLC charts of 7ca.

7da (racemate)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 02:01



D-2500

00/00/00 02:01

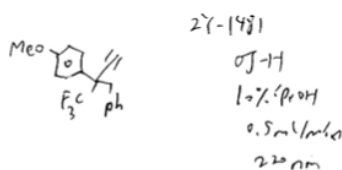
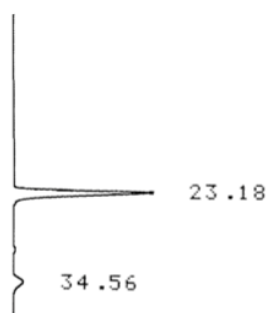
METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	22.86	52779	50.450	BB
2	33.71	51838	49.550	BB
TOTAL		104617	100.000	
PEAK REJ :		0		

7da (chiral)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 01:25



D-2500

00/00/00 01:25

METHOD: TAG: 3 CH: 1

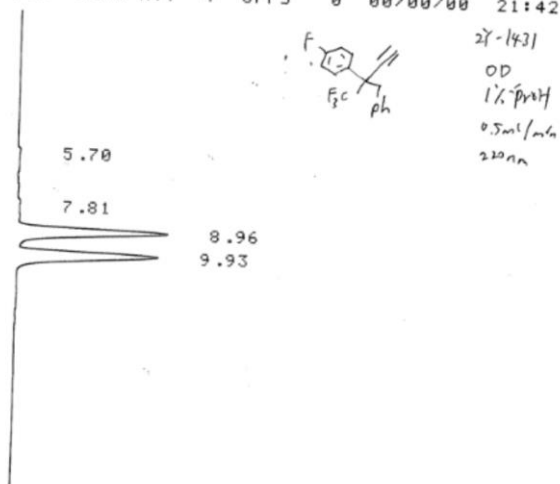
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	23.18	53632	95.361	BB
2	34.56	2609	4.639	BB
TOTAL		56241	100.000	
PEAK REJ :		0		

Supplementary Fig. 86: HPLC charts of 7da.

7ea (racemate)

CH. 1 C.S 5.00 ATT 4 OFFS 0 00/00/00 21:42



D-2500

00/00/00 21:42

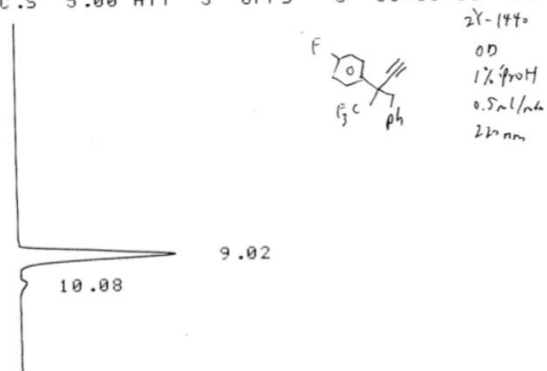
METHOD: TAG: 4 CH: 1
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
3	8.96	62309	50.026	BU
4	9.93	62243	49.974	UB

TOTAL
PEAK REJ : 124552 100.000
500

7ea (chiral)

CH. 1 C.S 5.00 ATT 3 OFFS 0 00/00/00 02:16



D-2500

00/00/00 02:16

METHOD: TAG: 3 CH: 1
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

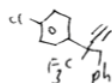
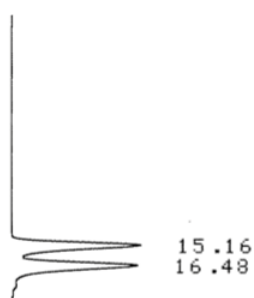
NO.	RT	AREA	CONC	BC
1	9.02	33123	97.198	BB
2	10.08	955	2.802	TBB

TOTAL
PEAK REJ : 34078 100.000
0

Supplementary Fig. 87: HPLC charts of 7ea.

7fa (racemate)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:00



27-1456
0J-H
1% PrOH
0.5 ml/min
220 nm

D-2500

00/00/00 00:00

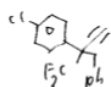
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.16	35691	48.019	BU
2	16.48	38636	51.981	UB
TOTAL		74327	100.000	
PEAK REJ :		0		

7fa (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:25



27-1459
0J-H
1% PrOH
0.5 ml/min
220 nm

D-2500

00/00/00 00:25

METHOD: TAG: 2 CH: 1

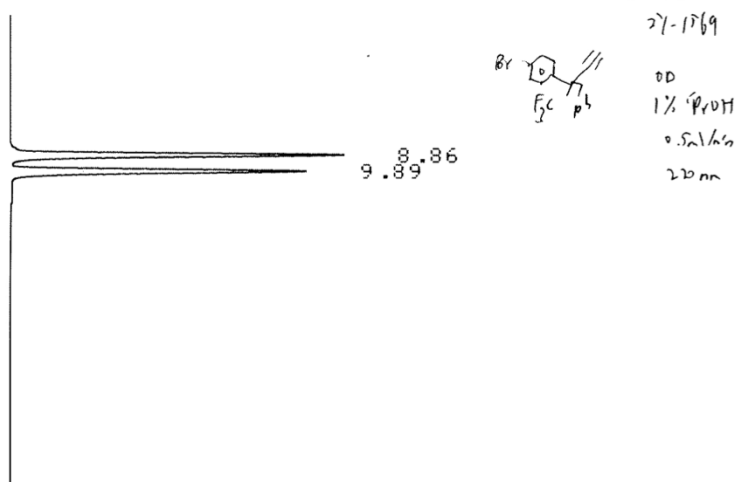
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.18	23828	94.951	BU
2	16.55	1267	5.049	UB
TOTAL		25095	100.000	
PEAK REJ :		0		

Supplementary Fig. 88: HPLC charts of 7fa.

7ga (racemate)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 01:43



D-2500

00/00/00 01:43

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	8.86	43906	51.060	BB
2	9.89	42083	48.940	BB

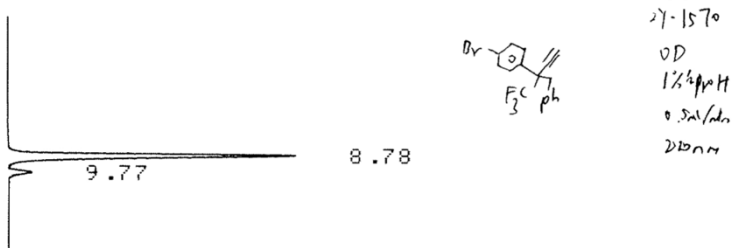
TOTAL

85989 100.000

PEAK REJ : 0

7ga (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:59



D-2500

00/00/00 00:59

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	8.78	36849	95.983	BB
2	9.77	1542	4.017	BB

TOTAL

38391 100.000

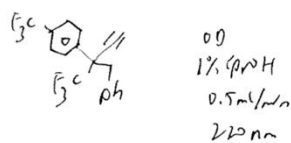
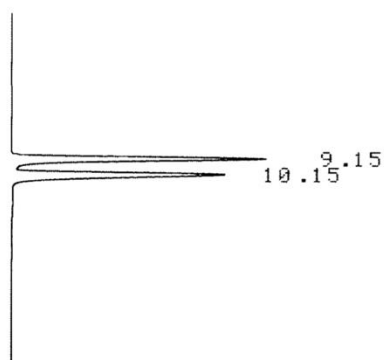
PEAK REJ : 0

Supplementary Fig. 89: HPLC charts of 7ga.

S115

7ha (racemate)

CH. 1 C.S 2.50 ATT 5 OFFS 0 00/00/00 00:46
27-177



D-2500

00/00/00 00:46

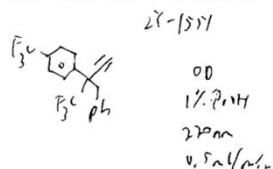
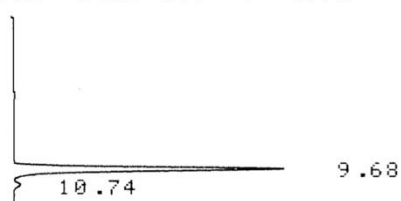
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	9.15	152182	50.672	BU
2	10.15	148144	49.328	UB
TOTAL		300326	100.000	
PEAK REJ :		0		

7ha (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 01:16



D-2500

00/00/00 01:16

METHOD: TAG: 1 CH: 1

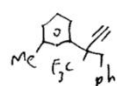
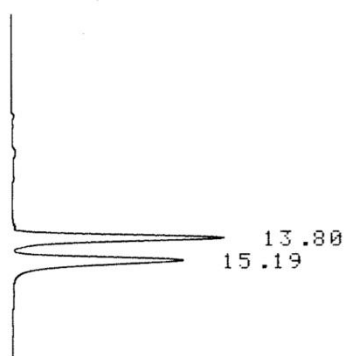
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	9.68	32244	96.447	BB
2	10.74	1188	3.553	BB
TOTAL		33432	100.000	
PEAK REJ :		0		

Supplementary Fig. 90: HPLC charts of 7ha.

7ia (racemate)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:46



27-15.7
0.7-H
1% β -OH
0.5 mL/min
220 nm

D-2500

00/00/00 00:46

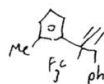
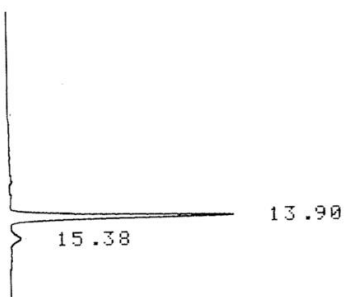
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.80	47133	50.424	BU
2	15.19	46341	49.576	UB
TOTAL		93474	100.000	
PEAK REJ :		0		

7ia (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 03:02



27-15.8
0.7-H
0.5 mL/min
1% β -OH
220 nm

D-2500

00/00/00 03:02

METHOD: TAG: 3 CH: 1

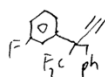
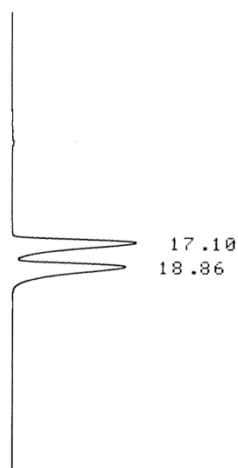
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.90	23758	94.635	BB
2	15.38	1347	5.365	BB
TOTAL		25105	100.000	
PEAK REJ :		0		

Supplementary Fig. 91: HPLC charts of 7ia.

7ja (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 03:43



27-1544
00
100% hexane
0.5m/min
220nm

D-2500

00/00/00 03:43

METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

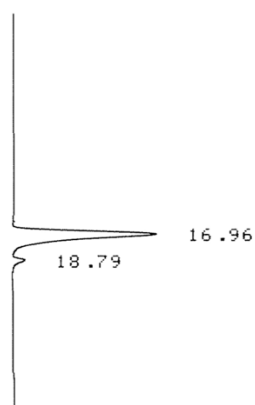
NO.	RT	AREA	CONC	BC
1	17.10	106167	49.215	BU
2	18.86	109552	50.785	UB

TOTAL 215719 100.000

PEAK REJ : 0

7ja (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 00:44



27-1545
00
100% hexane
0.5m/min
220nm

D-2500

00/00/00 00:44

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	16.96	55783	95.432	BB
2	18.79	2670	4.568	BB

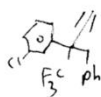
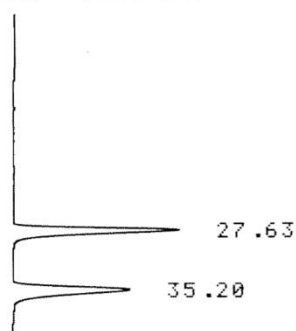
TOTAL 58453 100.000

PEAK REJ : 0

Supplementary Fig. 92: HPLC charts of 7ja.

7ka (racemate)

CH. 1 C.S 1.25 ATT 4 OFFS 0 00/00/00 01:05



27-1600
0J-H
1% p_rOH
0.5 ml/min
220 nm

D-2500

00/00/00 01:05

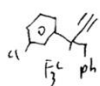
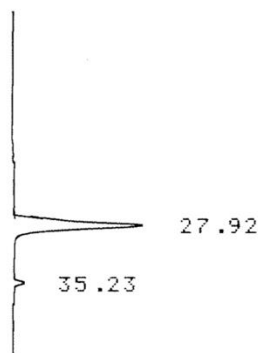
METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	27.63	134497	51.212	BB
2	35.20	128130	48.788	BB
TOTAL		262627	100.000	
PEAK REJ :		0		

7ka (chiral)

CH. 1 C.S 1.25 ATT 4 OFFS 0 00/00/00 00:17



27-1601
0J-H
1% p_rOH
0.5 ml/min
220 nm

D-2500

00/00/00 00:17

METHOD: TAG: 1 CH: 1

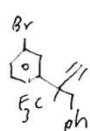
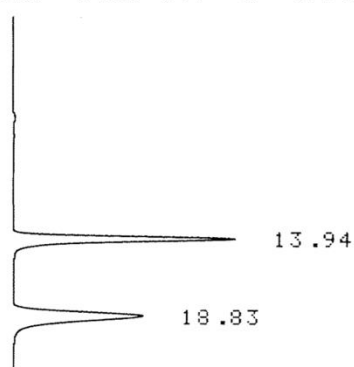
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	27.92	147598	97.300	BB
2	35.23	4096	2.700	BB
TOTAL		151694	100.000	
PEAK REJ :		0		

Supplementary Fig. 93: HPLC charts of 7ka.

7la (racemate)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 01:02



27-1493
0J-17
1% PhOH
0.5 mL/min
220 nm

D-2500

00/00/00 01:02

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.94	43268	51.048	BB
2	18.83	41492	48.952	BB

TOTAL

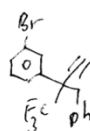
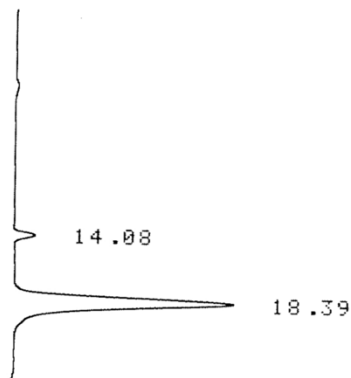
84760 100.000

PEAK REJ :

0

7la (chiral)

CH. 1 C.S 2.50 ATT 2 OFFS 0 00/00/00 02:28



27-1494
0J-H
1% PhOH
0.5 mL/min
220 nm

D-2500

00/00/00 02:28

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.08	2145	5.120	BB
2	18.39	39748	94.880	BB

TOTAL

41893 100.000

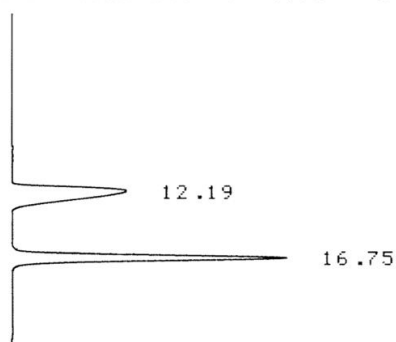
PEAK REJ :

0

Supplementary Fig. 94: HPLC charts of 7la.

7ma (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 01:28



27-1614
07-H
1% / 0.1H
0.5mL/mL
22.0m

D-2500

00/00/00 01:28

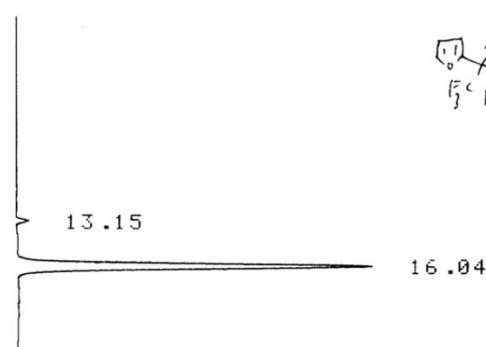
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	12.19	111003	46.790	BB
2	16.75	126236	53.210	BB
TOTAL		237239	100.000	
PEAK REJ :		0		

7ma (chiral)

CH. 1 C.S 2.50 ATT 2 OFFS 0 00/00/00 04:54



27-1615
07-H
1% / 0.1H
0.5mL/mL
22.0m

D-2500

00/00/00 04:54

METHOD: TAG: 3 CH: 1

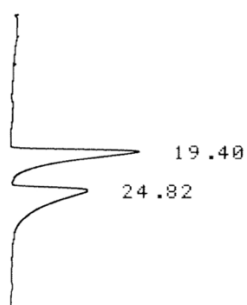
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.15	616	1.882	BB
2	16.04	32107	98.118	BB
TOTAL		32723	100.000	
PEAK REJ :		0		

Supplementary Fig. 95: HPLC charts of 7ma.

7na (racemate)

CH. 1 C.5 1.25 ATT 4 OFFS 0 00/00/00 00:05



2X-1577
0J-H
100% hexane
1.25/1.25
220nm

D-2500

00/00/00 00:05

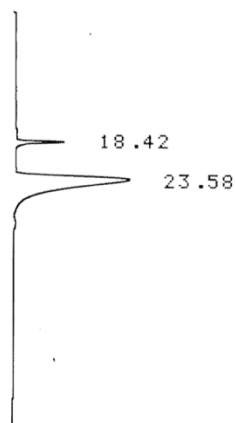
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.40	230428	55.847	BB
2	24.82	182180	44.153	BB
TOTAL		412608	100.000	
PEAK REJ :		0		

7na (chiral)

CH. 1 C.5 1.25 ATT 2 OFFS 0 00/00/00 02:43



2X-1578
0J-H
100% hexane
1.25/1.25
220nm

D-2500

00/00/00 02:43

METHOD: TAG: 2 CH: 1

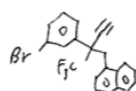
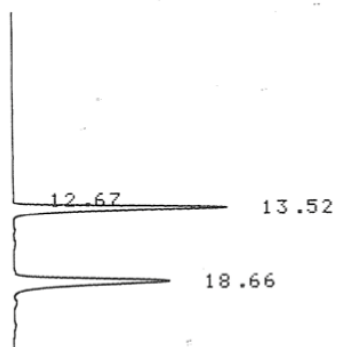
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	18.42	2494	5.083	BB
2	23.58	46571	94.917	BB
TOTAL		49065	100.000	
PEAK REJ :		0		

Supplementary Fig. 96: HPLC charts of 7na.

71r (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 00:43
27-1459



00
1% PrOH
0.5 mL/min
250 nm

D-2500

00/00/00 00:43

METHOD: TAG: 2 CH: 1

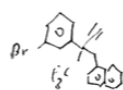
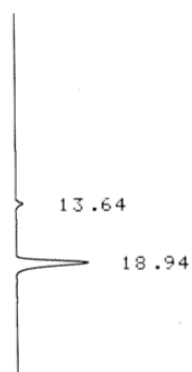
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
2	13.52	84006	49.898	BB
3	18.66	84348	50.102	BB
TOTAL		168354	100.000	
PEAK REJ :		800		

71r (chiral)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 01:00

27-1467



00
1% PrOH
0.5 mL/min
250 nm

D-2500

00/00/00 01:00

METHOD: TAG: 1 CH: 1

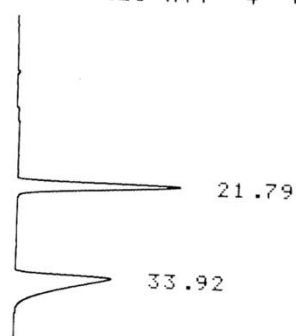
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.64	1684	4.439	BB
2	18.94	36255	95.561	BB
TOTAL		37939	100.000	
PEAK REJ :		0		

Supplementary Fig. 97: HPLC charts of 71r.

9 (racemate)

CH. 1 C.S 1.25 ATT 4 OFFS 0 00/00/00 04:45
27-1558



oJ-H
1% p₂OH
1 ml/min
220 nm

D-2500

00/00/00 04:45

METHOD:

TAG: 5 CH: 1

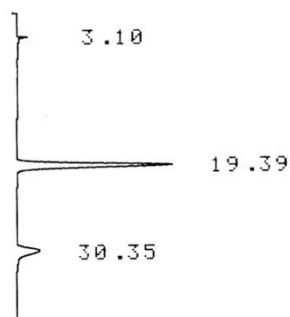
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	21.79	156554	46.727	BB
2	33.92	178488	53.273	BB
TOTAL				

PEAK REJ : 335042 100.000
0

9 (chiral)

CH. 1 C.S 1.25 ATT 2 OFFS 0 00/00/00 00:29



oJ-H
1% p₂OH
1 ml/min
220 nm

D-2500

00/00/00 00:29

METHOD:

TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

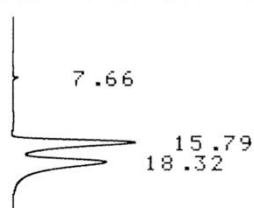
NO.	RT	AREA	CONC	BC
2	19.39	19866	81.532	BB
3	30.35	4500	18.468	BB
TOTAL				

PEAK REJ : 24366 100.000
400

Supplementary Fig. 98: HPLC charts of 9.

10 (racemate)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 02:08



2Y-1645
0J-H
100% hexane
0.5 ml/min
220 nm

D-2500

00/00/00 02:08

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
2	15.79	59580	51.112	BV
3	18.32	56988	48.888	VB

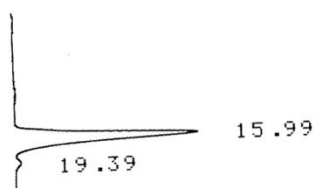
TOTAL

116568 100.000

PEAK REJ : 600

10 (chiral)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 01:15



2Y-1651
0J-H
100% hexane
0.5 ml/min
220 nm

D-2500

00/00/00 01:15

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	15.99	122008	96.492	BB
2	19.39	4435	3.508	BB

TOTAL

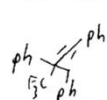
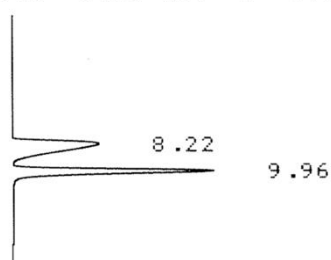
126443 100.000

PEAK REJ : 0

Supplementary Fig. 99: HPLC charts of 10.

11 (racemate)

CH. 1 C.S 2.50 ATT 5 OFFS 0 00/00/00 01:56



27-1641
0.5-H
1% PhOH
0.5ml/min
220nm

D-2500

00/00/00 01:56

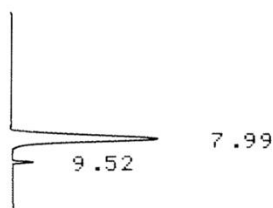
METHOD: TAG: 5 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	8.22	123622	48.472	BB
2	9.96	131417	51.528	BB
TOTAL		255039	100.000	
PEAK REJ :		0		

11 (chiral)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 07:27



27-1644
0.5-H
1% PhOH
0.5ml/min
220nm

D-2500

00/00/00 07:27

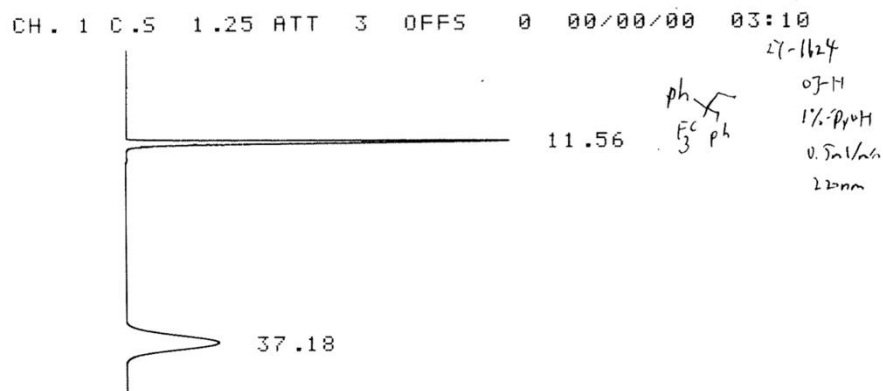
METHOD: TAG: 13 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	7.99	82751	96.389	BB
2	9.52	3100	3.611	BB
TOTAL		85851	100.000	
PEAK REJ :		0		

Supplementary Fig. 100: HPLC charts of 11.

12 (racemate)



D-2500

00/00/00 03:10

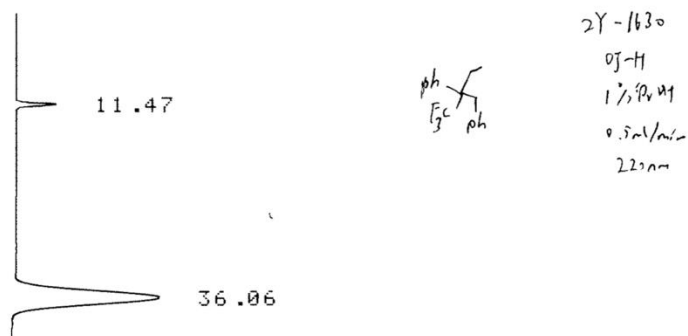
METHOD: TAG: 7 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.56	73777	47.572	BB
2	37.18	81308	52.428	BB
TOTAL		155085	100.000	
PEAK REJ :		0		

12 (chiral)

CH. 1 C.S 1.25 ATT 3 OFFS 0 00/00/00 00:11



D-2500

00/00/00 00:11

METHOD: TAG: 1 CH: 1

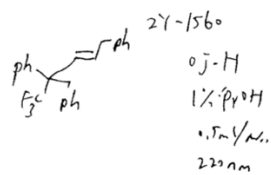
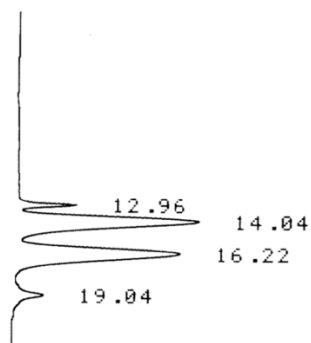
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.47	5916	4.170	BB
2	36.06	135966	95.830	BB
TOTAL		141882	100.000	
PEAK REJ :		0		

Supplementary Fig. 101: HPLC charts of 12.

13 (racemate)

CH. 1 C.S 2.50 ATT 4 OFFS 0 00/00/00 00:11



D-2500

00/00/00 00:11

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	12.96	17121	4.871	BU
2	14.04	159155	45.278	UU
3	16.22	156901	44.637	UB
4	19.04	18327	5.214	BB

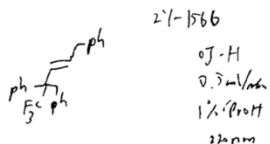
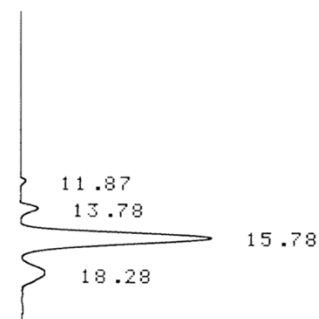
TOTAL

351504 100.000

PEAK REJ : 0

13 (chiral)

CH. 1 C.S 2.50 ATT 3 OFFS 0 00/00/00 01:38



D-2500

00/00/00 01:38

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
2	11.87	481	0.409	BB
3	13.78	4356	3.706	BB
4	15.78	100761	85.710	BB
5	18.28	11962	10.175	BB

TOTAL

117560 100.000

PEAK REJ : 0

Supplementary Fig. 102: HPLC charts of 13.

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