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Supplementary information

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Room-temperature synthesis of *m*-benzyne

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1. General

Instrumentation.

^{1}H NMR and ^{13}C NMR spectra were obtained on a BRUKER AVANCE III HD 500 spectrometer. Samples were recorded at 300 K. Chemical shifts are expressed in δ (ppm) values. ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane (δ: 0.00 ppm for ^{1}H-NMR), $C(H/D)Cl_3$ (δ: 7.26 and 77.16 ppm for ^{1}H and ^{13}C NMR, respectively), CHD_2CN (δ: 1.94 and 118.3 for ^{1}H and ^{13}C NMR, respectively), $C(H/D)D_2SOCD_3$ (δ: 2.50 and 39.52 ppm for ^{1}H and ^{13}C NMR, respectively) as internal standards. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were recorded on a JASCO FT/IR-4700 spectrometer. Melting points were determined with a SRS MPA 100 OptiMelt automated melting point system and were uncorrected. ESI mass spectra were measured on a Bruker compact spectrometer. GC yields were determined on a Shimadzu GC-2025 spectrometer. X-ray data were collected at 93 K on a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix6000HE hybrid pixel array detector with CuKα radiation source. Yamazen medium pressure liquid chromatography (MPLC) system (EPCLC-W-Prep 2XY A-Type) was used for purification of products. The reaction temperature was controlled by thermostated water bath TGK Fine F-0010D or acetone/dry ice bath (–78°).

Materials

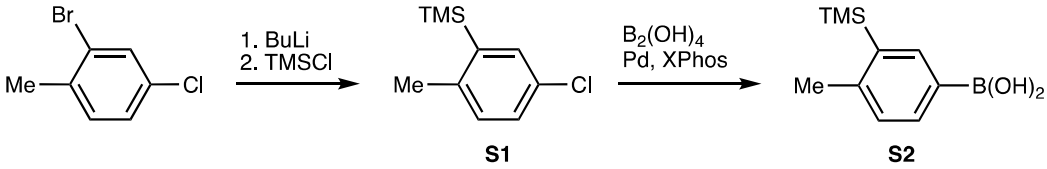
Unless otherwise noted, materials were purchased from Sigma-Aldrich Co. LLC., Wako Pure Chemical Industries, Ltd., FUJIFILM Wako Pure Chemical Co., Tokyo Kasei Industry Co. Ltd., and other commercial suppliers. All chemicals were used as received. Medium pressure liquid chromatography was performed using the disposable Hi-flash premium column from Yamazen Co., and thin-layer chromatography was carried out on 0.25 mm Merck silica gel plates (60F-254).

2. Experimental Details

2.1. Preparation of materials

4-Cyano-3-(trimethylsilyl)phenylboronic acid,[1] 2-methoxy-5-(trimethylsilyl)phenylboronic acid,[2,3] trimethyl[3-(tributylstannyl)phenyl]silane (**22**),[4] imino-λ^3-bromane **23**,[5] 4-(trimethylsilyl)benzonitrile,[6] 5,5-dimethyl-3-[(trimethylsilyl)oxy]cyclohex-2-en-1-one (**54**)[7] were prepared according to the reported procedure.

[4-Methyl-3-(trimethylsilyl)phenyl]boronic acid (S2)



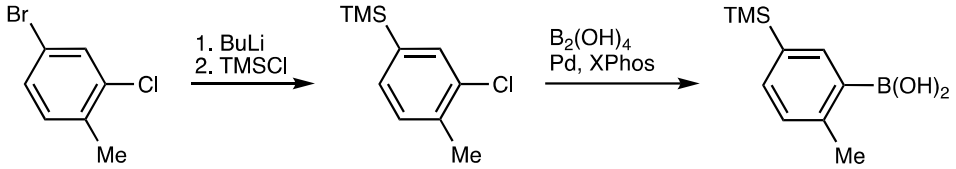
To a stirred solution of 2-bromo-4-chlorotoluene (0.66 mL, 5.0 mmol) in dry THF (10 mL) in a round-bottomed flask under an argon atmosphere was added BuLi (2.3 M in hexane, 2.2 mL, 5.1 mmol) at –78 °C. After 30 min, TMSCl (0.95 mL, 7.5 mmol) was added to the solution at –78 °C and stirring was continued at room temperature for 3 h. The reaction was quenched with saturated NH_4Cl aq. and extracted with Et_2O. The combined organic extract was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed in vacuo to give an oil, which was purified by silica gel chromatography (hexane), affording (5-chloro-2-methylphenyl)trimethylsilane (**S1**) in 94% yield (937 mg) as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.37 (d, *J* = 2.4 Hz, 1H), 7.21 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 2.41 (s, 3H), 0.32 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 141.7, 141.1, 134.0, 131.3 (2C), 129.0, 22.4, –0.22.

S2 was prepared according to the reported method.[8]

In a glass tube, a mixture of palladium(II) phenethylamine (7.6 mg, 0.010 mmol), dicyclohexyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphane (9.7 mg, 0.02 mmol), tetrahydroxydiboron (137.9 mg, 1.54 mmol), potassium acetate (294.6 mg, 3.0 mmol), and sodium *tert*-butoxide (1.5 mg, 0.016 mmol) was suspended in EtOH (10 mL) under argon atmosphere. Then, aryl chloride **S1** (202 mg, 1.02 mmol) was added and the mixture was heated to 80 °C for 19.5 h. After cooling to rt, the reaction mixture was filtered through a celite pad with AcOEt, and the filtrate was concentrated under reduced pressure. The residue was treated with 1 M HCl aq. and extracted it with AcOEt several times. The solution was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give arylboronic acid **S2** (193.5 mg, 91%) as an off-white solid. This solid was used for following transformations without further purification.

[4-Methyl-3-(trimethylsilyl)phenyl]boronic acid (**S2**): **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.36 (d, *J* = 1.3 Hz, 1H), 8.11 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 2.55 (s, 3H), 0.41 (s, 9H).

[2-Methyl-5-(trimethylsilyl)phenyl]boronic acid (S4)



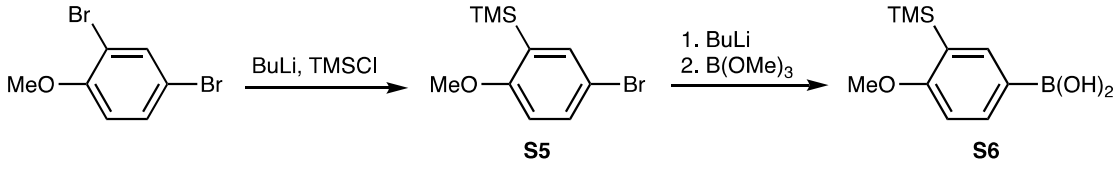
S3 **S4**

Synthesis of **S3** and **S4** was performed as described for **S2** starting with 4-bromo-2-chlorotoluene.

(3-Chloro-4-methylphenyl)trimethylsilane (**S3**): a colorless oil, 89% yield (883 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.44 (d, *J* = 1.0 Hz, 1H), 7.28 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 2.37 (s, 3H), 0.25 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 140.1, 136.6, 134.6, 133.9, 131.6, 130.8, 20.2, –1.05.

[2-Methyl-5-(trimethylsilyl)phenyl]boronic acid (**S4**): an off-white solid, 90% yield (187 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.45 (d, *J* = 1.4 Hz, 1H), 7.62 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 2.85 (s, 3H), 0.31 (s, 9H).

[4-Methoxy-3-(trimethylsilyl)phenyl]boronic acid (S6)

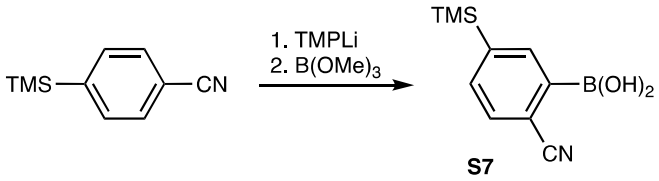


S5 **S6**

To a stirred solution of 2,4-dibromoanisole (665 mg, 2.5 mmol) and TMSCl (1.6 mL, 13 mmol) in dry THF (10 mL) in a round-bottomed flask under an argon atmosphere was added BuLi (2.3 M in hexane, 1.1 mL, 2.5 mmol) at –78°C. After 30 min, the resulting mixture was allowed to warm to room temperature and stirring was continued for 1 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic extract was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed in vacuo to give an oily residue. The residue was purified by silica chromatography (hexane), affording (5-bromo-2-methoxyphenyl)trimethylsilane (**S5**) in 65% yield (517 mg, 81% purity, containing a small amount of 2,4-bis(trimethylsilyl)anisole) as a colorless oil. Spectral data matched those reported in literature.[9] **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.41 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 0.25 (s, 9H).

To a stirred solution of **S5** (459 mg, 81% purity, 1.4 mmol) in dry THF (5.0 mL) was added BuLi (2.3 M in hexane, 0.62 mL, 5.1 mmol) in a round-bottomed flask under an argon atmosphere at –78°C. After 30 min, $B(OMe)_3$ (0.50 mL, 4.5 mmol) was added to the solution at –78 °C. The resulting mixture was allowed to warm to room temperature and stirring was continued for 1 h. The reaction was quenched with 1 M aqueous HCl and extracted with Et_2O. The combined organic extract was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed in vacuo to give an oily residue. The residue was purified by silica gel chromatography (hexane/AcOEt = 8:2), affording [4-methoxy-3-(trimethylsilyl)phenyl]boronic acid (**S6**) in 63% yield (204 mg) as a colorless solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.87 (d, *J* = 1.8 Hz, 1H), 7.83 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 0.28 (s, 9H).

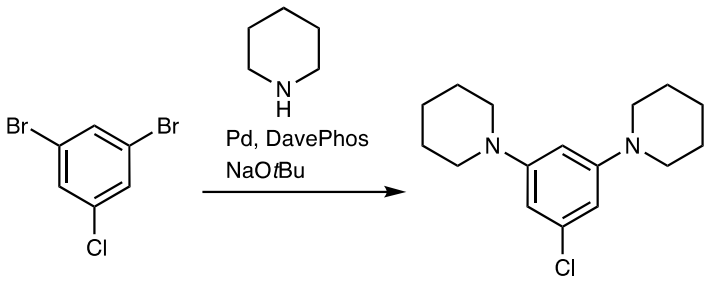
[2-Cyano-5-(trimethylsilyl)phenyl]boronic acid (S7)



S7

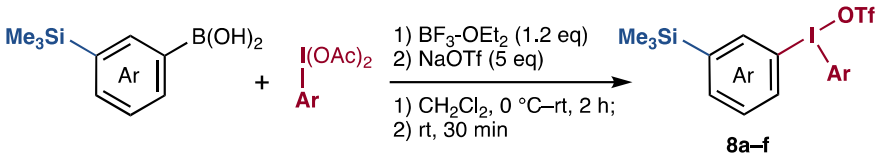
To a stirred solution of 4-(trimethylsilyl)benzonitrile (584 mg, 3.3 mmol) in dry THF (5.0 mL) was added freshly prepared TMPLi (1.5 M in THF, 2.4 mL, 3.7 mmol) in a round-bottomed flask under an argon atmosphere at –78°C. The mixture was warmed to 0 °C and stirred for 30 min. $B(OMe)_3$ (0.93 mL, 8.3 mmol) was added to the solution at –78 °C. The resulting mixture was allowed to warm to room temperature and stirring was continued for 1 h. The reaction was quenched with 1 M aqueous HCl and extracted with Et_2O. The combined organic extract was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed in vacuo to give an oily residue. The residue was purified by silica gel chromatography (hexane/AcOEt = 8:2), affording [4-methoxy-3-(trimethylsilyl)phenyl]boronic acid (**S7**) in 25% yield (179 mg) as a colorless solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.91 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 0.27 (s, 9H).

1,1'-(5-Chloro-1,3-phenylene)bispiperidine (67)



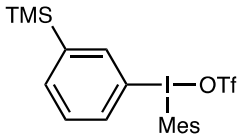
67 was synthesized by the reported method.[10] To a stirred solution of 1,3-dibromo-5-chlorobenzene (272 mg, 1.0 mmol), $Pd_2(dba)_3$ (18.2 mg, 0.020 mmol), DavePhos (23.4 mg, 0.060 mmol), and NaO*t*Bu (272 mg, 2.8 mmol) in DME (2.0 mL) in a Schlenk tube under an argon atmosphere was slowly added piperidine (0.24 mL, 2.4 mmol) and stirring was continued at 60°C for 4 days. After cooled to room temperature, the reaction mixture was diluted with ether (20 mL), filtered through celite, and evaporated. The residue was purified by silica gel chromatography (hexane/AcOEt = 100:0 to 81:19), affording 1,1'-(5-chloro-1,3-phenylene)bispiperidine (**67**) in 41% yield (116 mg) as a colorless solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 6.39 (d, *J* = 2.1 Hz, 2H), 6.34 (t, *J* = 2.1 Hz, 1H), 3.13–3.11 (m, 8H), 1.70–1.65 (m, 8H), 1.59–1.54 (m, 2H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 153.9, 135.4, 108.1, 103.3, 50.8, 25.9, 24.5. **mp:** 78–80 °C. **IR (ATR):** 2983, 2938, 2807, 1579, 1555, 1442, 1210, 1119, 992, 921, 800, 669 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** $[M+H]^+$ Calcd for $C_{16}H_{24}{}^{35}ClN_2$: 279.1623; Found 279.1619.

2.2 General procedure for the synthesis of λ^3-iodane precursors

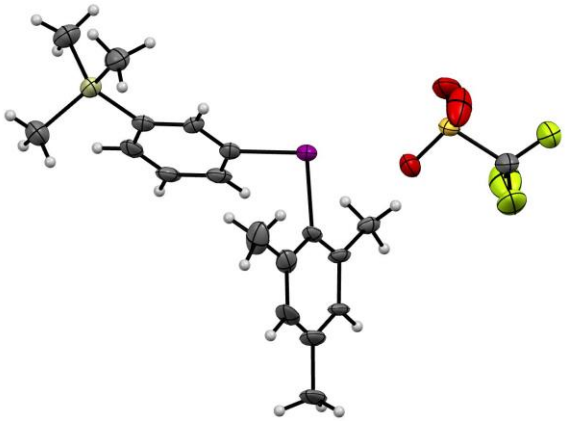


To a stirred solution of (diacetoxyiodo)arene (0.30 mmol) in CH_2Cl_2 (2.5 mL) in a round-bottomed flask were added BF_3•OEt_2 (38 μL, 0.30 mmol) and [3-(trimethylsilyl)aryl]boronic acid (0.25 mmol) was added at 0 °C and the mixture was stirred at room temperature under air. After 2 h, an aqueous solution of NaOTf (218 mg, 1.3 mmol) was added and stirred vigorously for 30 min. The product was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. After washing the residue with hexane and Et_2O by decantation, the pure product was obtained.

Mesityl[3-(trimethylsilyl)phenyl](trifluoromethanesulfonato)-λ^3-iodane (8a)

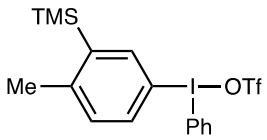


Following **General Procedure** (2.0 mmol scale) using [3-(trimethylsilyl)phenyl]boronic acid (**20**) and (diacetoxyiodo)mesitylene (**21**), the titled compound was obtained in 87% yield (954 mg) as a colorless solid. Recrystallization with (CH_2Cl_2-hexane) at room temperature gave **8a** as colorless prisms suitable for X-ray crystal analysis. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.78 (dd, *J* = 2.0, 0.7 Hz, 1H), 7.64 (ddd, *J* = 7.3, 1.0, 0.7 Hz, 1H), 7.55 (ddd, *J* = 8.2, 2.0, 1.0 Hz, 1H), 7.37 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.13 (s, 2H), 2.64 (s, 3H), 2.37 (s, 3H), 0.24 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 147.9, 144.8, 142.7, 137.2, 136.6, 132.5, 132.2, 130.6, 120.5 (q, $^1J_{C\text{-}F}$ = 320 Hz), 120.1, 113.1, 27.3, 21.3, –1.4. **mp:** 177–179 °C (dec.). **IR (ATR):** 3051, 2964, 2889, 1588, 1457, 1376, 1243, 1166, 1026, 842, 634, 517 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** $[M–OTf]^+$ Calcd for $C_{18}H_{24}ISi$: 395.0686; Found 395.0678. **Anal.** Calcd for $C_{19}H_{24}F_3IO_3SSi$: C, 41.92; H, 4.44; N 0.00. Found C, 41.80; H, 4.44; N, 0.00.

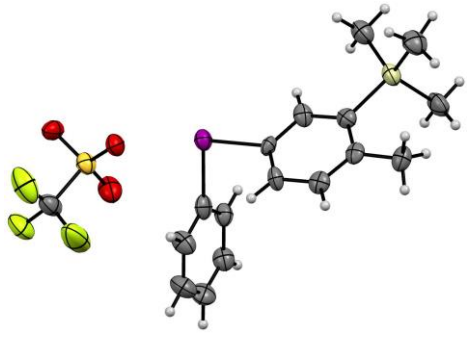


ORTEP drawing of **8a** with 50% ellipsoid probability (CCDC 2061582).

[4-Methyl-3-(trimethylsilyl)phenyl](phenyl)(trifluoromethanesulfonato)-λ^3-iodane (8b)

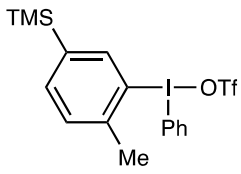


Following **General Procedure** using **S2** and (diacetoxyiodo)benzene, the titled compound was obtained in 65% yield (83.3 mg) as a colorless solid. Recrystallization with (CH_2Cl_2-hexane) at room temperature gave **8b** as colorless prisms suitable for X-ray crystal analysis. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.83 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.49–7.46 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 1H), 2.48 (s, 3H), 0.32 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 149.2, 146.1, 140.1, 135.5, 135.1, 134.1, 132.6, 132.5, 120.4 (q, $^1J_{C\text{-}F}$ = 320 Hz), 113.3, 111.1, 23.0, –0.5. **mp:** 129–132 °C (dec.). **IR (ATR):** 2960, 2899, 1472, 1445, 1283, 1222, 1161, 1024, 842, 738, 635, 516 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** $[M–OTf]^+$ Calcd for $C_{16}H_{20}ISi$: 367.0373; Found 367.0372. **Anal.** Calcd for $C_{17}H_{20}F_3IO_3SSi$: C, 39.54; H, 3.90; N 0.00. Found C, 39.55; H, 4.05; N, 0.00.

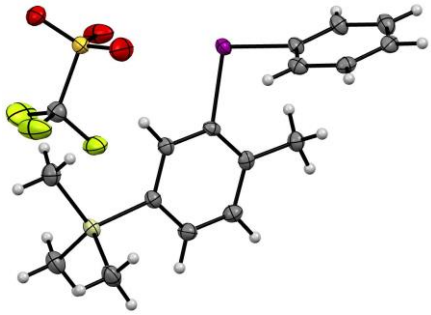


ORTEP drawing of **8b** with 50% ellipsoid probability (CCDC 2268762).

[2-Methyl-5-(trimethylsilyl)phenyl](phenyl)(trifluoromethanesulfonato)-λ^3-iodane (8c)

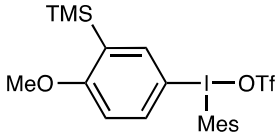


Following **General Procedure** using **S4** and (diacetoxyiodo)benzene, the titled compound was obtained in 73% yield (94.2 mg) as a colorless solid. Recrystallization with (CH_2Cl_2-hexane) at room temperature gave **8c** as colorless prisms suitable for X-ray crystal analysis. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.09 (d, *J* = 0.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.83 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.48–7.43 (m, 3H), 2.58 (s, 3H), 0.28 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 145.0, 142.0, 141.7, 138.6, 134.3, 132.5, 132.4, 132.2, 120.4 (q, $^1J_{C\text{-}F}$ = 320 Hz), 119.7, 112.5, 25.8, –1.2. **mp:** 137–141 °C (dec.). **IR (ATR):** 2962, 2881, 1441, 1248, 1157, 1027, 839, 748, 634, 517 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** [M–OTf]$^+$ Calcd for $C_{16}H_{20}ISi$: 367.0373; Found 367.0353. **Anal.** Calcd for $C_{17}H_{20}F_3IO_3SSi$: C, 39.54; H, 3.90; N 0.00. Found C, 39.46; H, 3.99; N, 0.00.



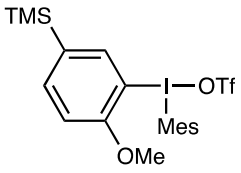
ORTEP drawing of **8c** with 50% ellipsoid probability (CCDC 2268732).

Mesityl[4-methoxy-3-(trimethylsilyl)phenyl](trifluoromethanesulfonato)-λ^3-iodane (8d)



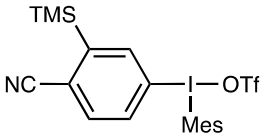
Following **General Procedure** (0.37 mmol scale) using **S2** and (diacetoxyiodo)mesitylene (**16**), the titled compound was obtained in 70% yield (148 mg) as a colorless solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.77 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.53 (d, *J* = 2.5 Hz, 1H), 7.09 (s, 2H), 6.84 (d, *J* = 8.9 Hz, 1H), 3.82 (s, 3H), 2.66 (s, 6H), 2.34 (s, 3H), 0.21 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 166.8, 144.4, 142.4, 139.7, 136.9, 135.1, 130.4, 121.0, 120.5 (q, $^1J_{C\text{-}F}$ = 320 Hz), 113.7, 101.4, 55.7, 27.2, 21.2, –1.4. **mp:** 198–201 °C (dec.). **IR (ATR):** 2959, 2908, 2850, 1572, 1466, 1376, 1243, 1165, 1025, 844, 635, 518 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** [M–OTf]$^+$ Calcd for $C_{19}H_{26}IOSi$: 425.0792; Found 425.0787. **Anal.** Calcd for $C_{20}H_{26}F_3IO_4SSi$: C, 41.82; H, 4.56; N 0.00. Found C, 41.77; H, 4.49; N, 0.00.

Mesityl[2-methoxy-5-(trimethylsilyl)phenyl](trifluoromethanesulfonato)-λ^3-iodane (8d')



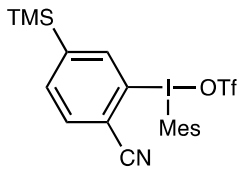
Following **General Procedure** (0.50 mmol scale) using **S2** and (diacetoxyiodo)mesitylene (**16**), the titled compound was obtained in 86% yield (246 mg) as a colorless solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.61 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.14 (s, 2H), 7.11 (d, *J* = 1.3 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 3.98 (s, 3H), 2.62 (s, 6H), 2.38 (s, 3H), 0.14 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 156.7, 144.7, 143.2, 138.8, 137.7, 136.2, 130.4, 120.6 (q, $^1J_{C\text{-}F}$ = 320 Hz), 118.1, 112.8, 100.8, 57.1, 27.0, 21.2, –1.3. **mp:** 166–171 °C (dec.). **IR (ATR):** 2958, 2919, 1578, 1487, 1455, 1376, 1242, 1157, 1028, 843, 634, 515 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** [M–OTf]$^+$ Calcd for $C_{19}H_{26}IOSi$ 425.0792; Found 425.0796. **Anal.** Calcd for $C_{20}H_{26}F_3IO_4SSi$: C, 41.82; H, 4.56; N 0.00. Found C, 41.42; H, 4.47; N, 0.00.

[4-Cyano-3-(trimethylsilyl)phenyl](mesityl)(trifluoromethanesulfonato)-λ^3-iodane (8e)



To a stirred solution of (diacetoxyiodo)mesitylene (**21**, 438 mg, 1.2 mmol) in CH_2Cl_2 (5.0 mL), BF_3•OEt_2 (150 μL, 1.2 mmol) and 4-cyano-3-(trimethylsilyl)phenylboronic acid (111 mg, 0.50 mmol) was added at 0 °C and the mixture was stirred at room temperature. After 15 h, an aqueous solution of NaOTf (218 mg, 1.3 mmol) was added and stirred vigorously for 30 min. The product was extracted with CH_2Cl_2 for three times. The combined organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give an oily residue. After washing the residue with hexane and Et_2O by decantation, pure **8e** was obtained in 42% yield (123 mg) as a colorless solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.84 (d, *J* = 2.0 Hz, 1H), 7.70 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.15 (s, 2H), 2.62 (s, 6H), 2.38 (s, 3H), 0.36 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 150.6, 150.0, 142.8, 138.0, 136.3, 132.8, 130.5, 120.6, 120.4, 120.2 (q, $^1J_{C\text{-}F}$ = 319 Hz), 118.1, 117.1, 27.3, 21.3, –1.7. **mp:** 206–207 °C (dec.). **IR (ATR):** 2974, 2962, 2908, 2225, 1449, 1238, 1165, 1024, 839, 634, 518 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** [M–OTf]$^+$ Calcd for $C_{19}H_{23}INSi$: 420.0639; Found 420.0639. **Anal.** Calcd for $C_{20}H_{23}F_3INO_3SSi$: C, 42.18; H, 4.07; N 2.46. Found C, 42.10; H, 4.13; N, 2.47.

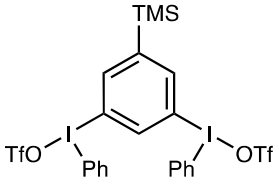
[2-Cyano-5-(trimethylsilyl)phenyl](mesityl)(trifluoromethanesulfonato)-λ^3-iodane (8f)



To a stirred solution of (diacetoxyiodo)mesitylene (**21**, 596 mg, 1.6 mmol) in CH_2Cl_2 (5.0 mL), BF_3•OEt_2 (0.21 mL, 1.6 mmol) and **S7** (179 mg, 0.82 mmol) was added at 0 °C and the mixture was stirred at room temperature. After 15 h, an aqueous solution of sodium triflate (704 mg, 4.1 mmol) was

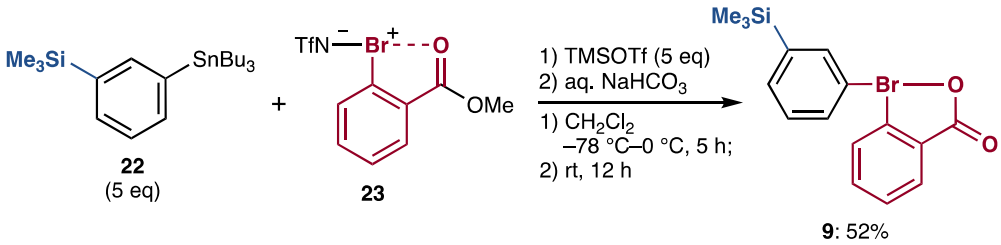
added and stirred vigorously for 30 min. The product was extracted with CH_2Cl_2 for three times. The combined organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give an oily residue. After washing the residue with hexane and Et_2O by decantation, pure **8f** was obtained in 11% yield (53 mg) as a colorless solid. **^{1}H NMR (500 MHz, CD_3CN):** δ = 8.19 (d, *J* = 0.5 Hz, 1H), 7.97 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.23 (s, 2H), 2.63 (s, 6H), 2.34 (s, 3H), 0.27 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, CD_3CN):** δ = 154.3, 146.3, 144.0, 142.8, 138.9, 136.5, 131.7, 121.9, 115.2, 27.2, 21.0, –1.8. **mp:** 154–156 °C (dec.). **IR (ATR):** 2958, 2229, 1450, 1240, 1159, 1026, 834, 632, 517 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** $[M–OTf]^+$ Calcd for $C_{19}H_{23}INSi$: 420.0639; Found 420.0639.

3,5-[Bis(phenyl(triflato)-λ^3-iodanyl)]phenyl(trimethyl)silane (59)



To a stirred solution of [5-(trimethylsilyl)-1,3-phenylene]diboronic acid and (diacetoxyiodo)benzene (274 mg, 0.85 mmol) in CH_2Cl_2 (5.0 mL) in a round-bottomed flask under an argon atmosphere was added BF_3•OEt_2 (0.11 mL, 0.88 mmol) at –78 °C. The resulting mixture was allowed to warm to room temperature and stirring was continued for 15 h. The mixture was cooled to 0 °C, to which was added TMSOTf (0.15 mL, 0.85 mL) and stirred for 5 min. The solvent was removed in vacuo and the residue was washed with Et_2O by decantation, affording pure **59** in 55% yield (234 mg) as a colorless solid. **^{1}H NMR (500 MHz, DMSO-*d*$_6$):** δ = 9.14 (t, *J* = 1.5 Hz, 1H), 8.60–8.59 (m, 2H), 8.24 (t, *J* = 8.2 Hz, 4H), 7.68 (t, *J* = 7.5 Hz, 2H), 7.55–7.52 (m, 4H), 0.36 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, DMSO-*d*$_6$):** δ = 150.3, 141.9, 140.3, 137.1, 135.2, 132.4, 132.0, 120.7 (q, $^1J_{C\text{-}F}$ = 322 Hz), 117.0, –1.6. **mp:** 228–235 °C (dec.). **IR (ATR):** 3189, 1471, 1223, 1025, 847, 735, 634, 517 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** $[M–2OTf]^{2+}$ Calcd for $C_{21}H_{22}I_2Si$: 277.9785; Found 277.9790.

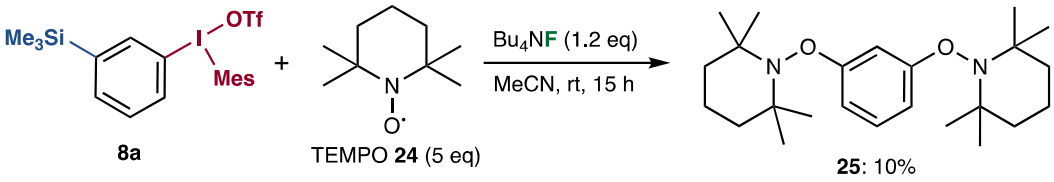
2.3 Synthesis of diaryl-λ^3-bromane 9



To a stirred solution of **22** (90.5 mg, 0.25 mmol) and **23** (531.1 mg, 1.21 mmol) in dichloromethane (5.0 mL) in a round-bottomed flask under an argon atmosphere was added TMSOTf (0.25 mL, 1.4 mmol) at –78 °C and the mixture was gradually warmed to room temperature for 5 h (monitored by

TLC). The solvent was removed under reduced pressure to give an oil, to which were added acetonitrile (5 mL) and saturated $NaHCO_3$ aq. (5 mL) and the mixture was stirred vigorously for 12 h. Water (5 mL) was added, and the product was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give an oil. After washing with hexane and Et_2O by decantation, the pure 1-[3-(trimethylsilyl)phenyl]-1,2-benzbromoxol-3-(1*H*)-one (**9**) was obtained in 52% yield (45 mg) as a colorless solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.55 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.95 (ddd, *J* = 7.2, 1.2, 0.6 Hz, 1H), 7.84 (dd, *J* = 2.0, 0.6 Hz, 1H), 7.75 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1H), 7.70 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.61 (ddd, *J* = 7.5, 7.2, 0.6 Hz, 1H), 7.44 (ddd, *J* = 8.6, 7.2, 2.0 Hz, 1H), 6.69 (ddd, *J* = 8.6, 0.6 Hz, 1H), 0.35 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 165.7, 148.6, 138.6, 137.3, 135.8, 134.6, 133.1, 133.0, 132.9, 132.2, 131.2, 126.2, 120.8, –1.2. **mp:** 106–109 °C (dec.). **IR (ATR):** 3044, 2957, 1604, 1352, 1248, 1117, 983, 838, 748, 683 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** $[M+Na]^+$ Calcd for $C_{16}H_{17}{}^{79}BrNaO_2Si$: 371.0073; Found 371.0074.

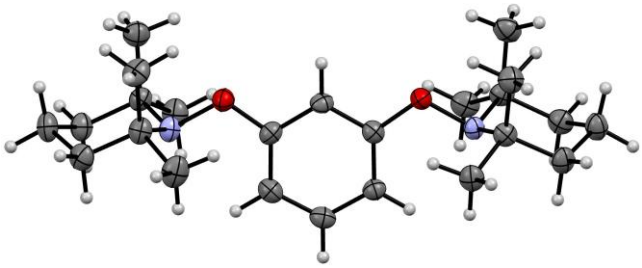
2.4. Trapping of *m*-benzyne (2) in the presence of 24



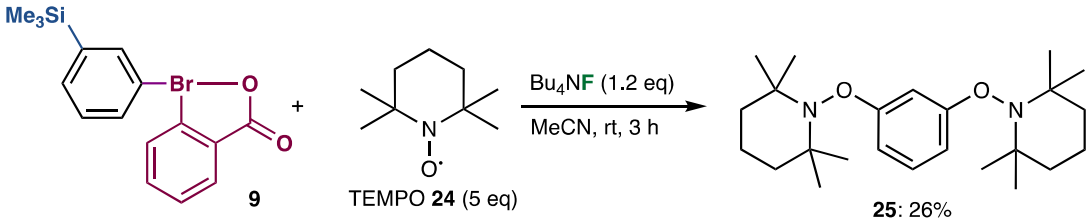
With 8a: To a stirred solution of **8a** (54.9 mg, 0.10 mmol) and **24** (78.8 mg, 0.50 mmol) in dry acetonitrile (1.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 60 μL, 0.060 mmol) at room temperature and the mixture was stirred for 15 h. After concentration of the reaction mixture under reduced pressure, the yield of **25** (15%) was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard.

0.25 mmmol scale experiment for isolation of 25: To a stirred solution of **8a** (136 mg, 0.25 mmol) and TEMPO (**24**, 195 mg, 1.25 mmol) in dry acetonitrile (2.5 mL) in a round-bottomed flask under an argon atmosphere was slowly added TBAF in THF (1 M, 0.30 mL, 0.30 mmol) at room temperature and the mixture was stirred for 15 h. After the complete consumption of **8a** (confirmed by ^{1}H NMR), the reaction mixture was concentrated under reduced pressure to give an oil, to which was added an excess amount of methanol. The mixture was kept in a freezer (–27 °C) overnight, then the supernatant was removed by decantation and the resulting precipitate was dried under high vacuum, affording 1,3-bis[(2',2',6',6'-tetramethylpiperidin-1'-yl)oxy]benzene (**25**) (10 mg, 10%) as an off-white solid. Slow evaporation of ($CHCl_3$-hexane) at room temperature gave **25** as colorless prisms suitable for X-ray

crystal analysis. *NOTE*: this compound is not stable on silica and decomposes on the TLC plate. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.12 (br s, 1H), 7.00 (t, *J* = 8.1 Hz, 1H), 6.61 (br d, *J* = 7.4 Hz, 2H), 1.68–1.53 (m, 10H), 1.42–1.39 (m, 2H), 1.22 (s, 12H), 1.02 (s, 12H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 164.7, 128.3, 105.8, 100.8, 60.3, 40.0, 32.8, 20.6, 17.3. **mp:** 127–133 °C (dec.). **IR (ATR):** 2970, 2929, 1604, 1601, 1591, 1484, 1107, 986, 969, 841, 779 cm^{-1}. **HRMS (ESI, positive ion mode) *m/z*:** $[M+H]^+$ Calcd for $C_{24}H_{41}N_2O_2$ 389.3163; Found 389.3164.



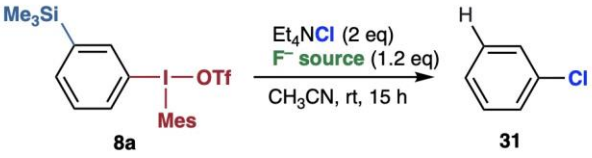
ORTEP drawing of **25** with 50% ellipsoid probability (CCDC 2061583).



With 9: To a stirred solution of **9** (2.3 mg, 6.6 μmol) and **24** (4.9 mg, 0.031 mmol) in dry acetonitrile (0.30 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 7.9 μL, 7.9 μmol) at room temperature and the mixture was stirred for 3 h. After the complete consumption of **9** (confirmed by TLC), the reaction mixture was concentrated under reduced pressure, **25** was obtained in 26% yield, which was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard.

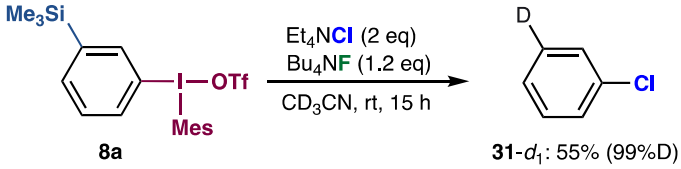
2.5. Trapping of 2 in the presence of chloride ion in acetonitrile

Table S1. Reactions with various fluoride sources.



Entry	Fluoride	GC yield (%)
1	TBAF in THF	66
2	TBAF • $3H_2O$	66
3	TBAT	41
4	KF	0
5	CsF	35

2.6. Trapping of 2 in the presence of chloride ion in acetonitrile-d_3



To a stirred solution of **8a** (13.6 mg, 0.050 mmol) and Et_4NCl (8.5 mg, 0.051 mmol) in dry acetonitrile (1.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 30 μL, 0.030 mmol) at room temperature and the mixture was stirred for 15 h. After the complete consumption of **8a** (confirmed by ^{1}H NMR), **31**-d_1 was obtained in 55% yield (>99%D). The yield of the product **31**-d_1 was determined by ^{1}H NMR with *p*-dimethoxybenzene as an internal standard and the deuterium content was determined by an integral ratio between *p*-proton and a sum of *o*- and *m*-protons (vide infra).

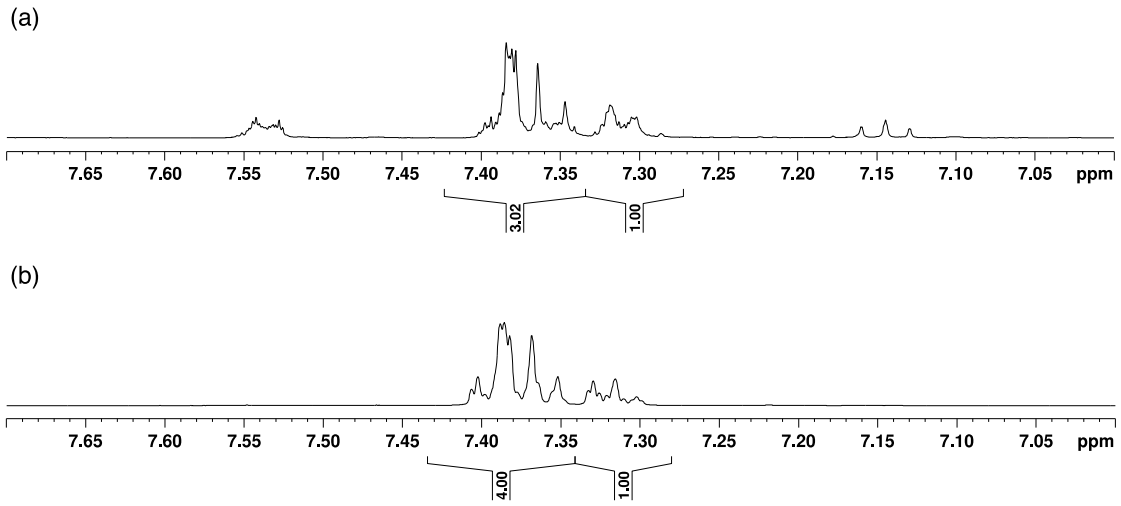


Figure S1. ^{1}H NMR spectra of (a) the reaction mixture and (b) an authentic sample of **31** (CD_3CN).

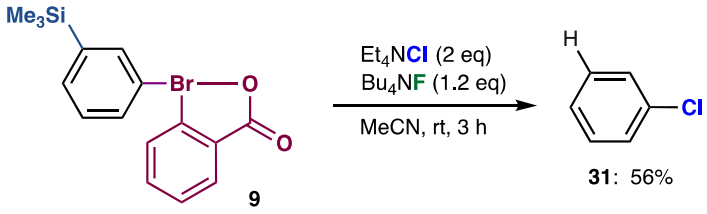
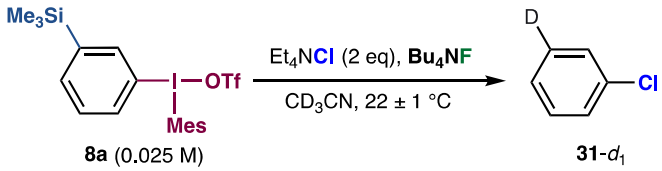


Figure S2. Trapping of **2** in the presence of chloride ion in acetonitrile with **9**.

To a stirred solution of **9** (8.7 mg, 0.025 mmol) and Et_4NCl (8.4 mg, 0.051 mmol) in dry acetonitrile (0.50 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 30 µL, 0.030 mmol) at room temperature and the mixture was stirred for 15 h. After the complete consumption of **9** (confirmed by TLC), **31** was obtained in 56% yield. The yield was determined by GC analysis using capillary column SH-Rtx-5 (0.25 mm x 30 m, 70 °C to 270 °C) with 1,3,5-triisopropylbenzene as an internal standard. The GC retention time of product was consistent with that of an authentic sample of **31**.

2.7. Rate measurements for the reaction of 8a and chloride ion in the presence of a various amount of TBAF in CD_3CN



8a (54.5 mg, 0.10 mmol), Et_4NCl (33.5 mg, 0.20 mmol), and *p*-dimethoxybenzene (an internal standard, 14.0 mg, 0.10 mmol) were dissolved in CD_3CN (4.0 mL) and the mixture was aliquoted into

four NMR tubes. TBAF in THF (1 M, 15/30/60/150 μL, 0.015/0.030/0.060/0.15 mmol) was added to each tube. ^{1}H NMR spectra were measured at 15, 35, 65, 95, 125, and 185 min after addition of TBAF. The concentration of **8a** at each time was determined by ^{1}H NMR with *p*-dimethoxybenzene as an internal standard.

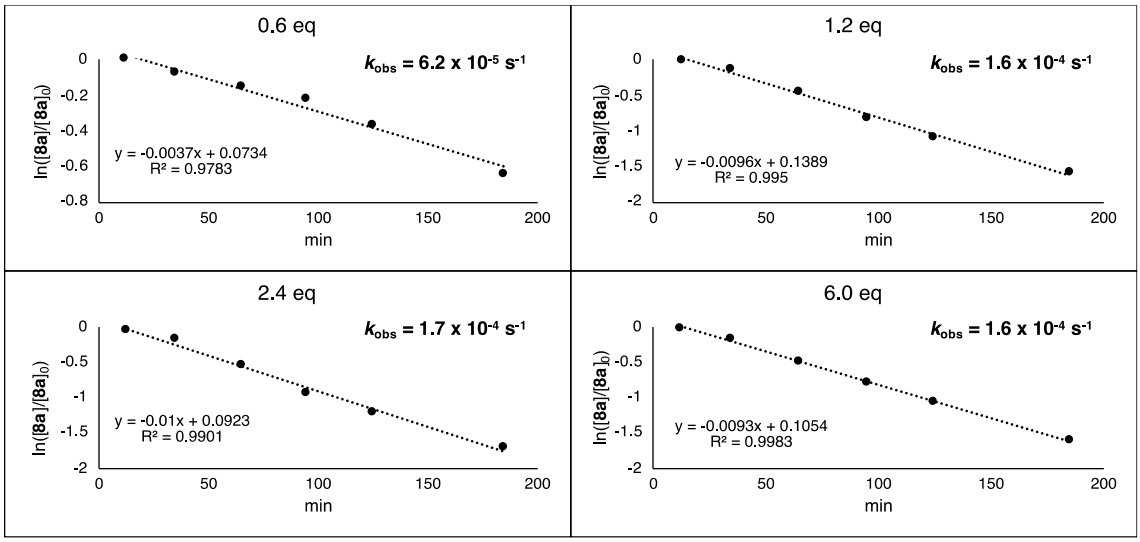
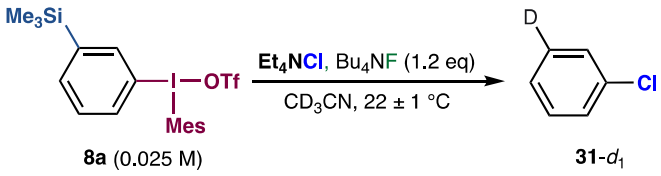


Figure S3. Rate measurements for the reaction of **8a** with chloride ion (2 equiv.) in the presence of a various amount of TBAF.

2.8. Rate measurements for the reaction of 8a and chloride ion in the presence of a various amount of Et_4NCl in CD_3CN



8a (0.025 M) **31**-d_1

8a (13.5/13.6/13.6 mg, 0.25/0.25/0.25 mmol), Et_4NCl (4.4/8.5/20.5 mg, 0.027/0.051/0.124 mmol), and *p*-dimethoxybenzene (an internal standard, 3.7/3.6/3.6 mg, 0.027/0.026/0.026 mmol) were dissolved in CD_3CN (1.0 mL) and each mixture was transferred into an NMR tube. TBAF (1 M in THF, 30 μL, 0.030 mmol) was added to each tube. ^{1}H NMR spectra were measured at 15, 30, 60, 120, and 180 min after addition of TBAF. The concentration of **8a** at each time was determined by ^{1}H NMR with *p*-dimethoxybenzene as an internal standard. The results are shown below.

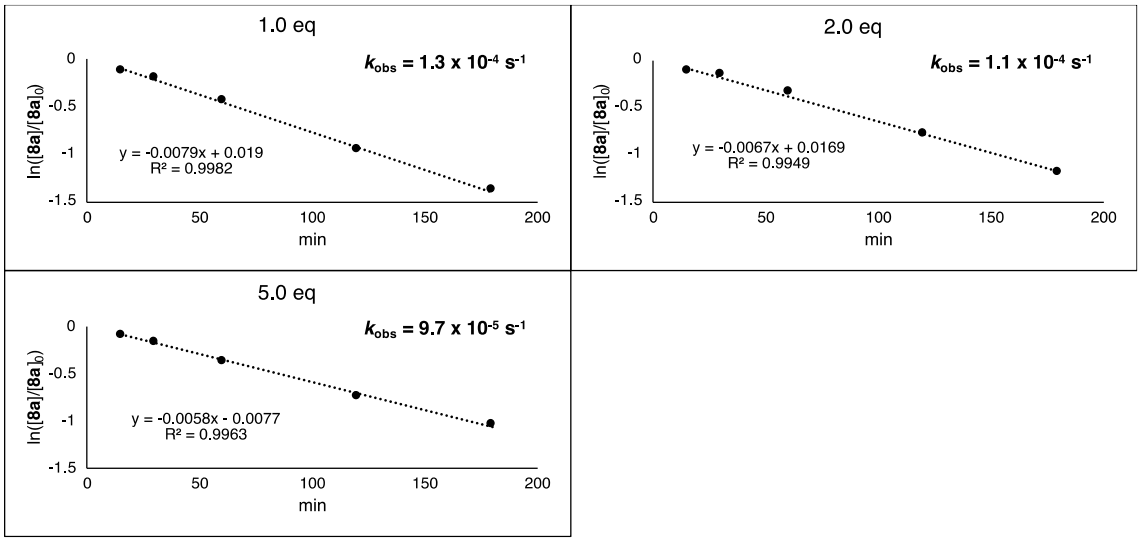
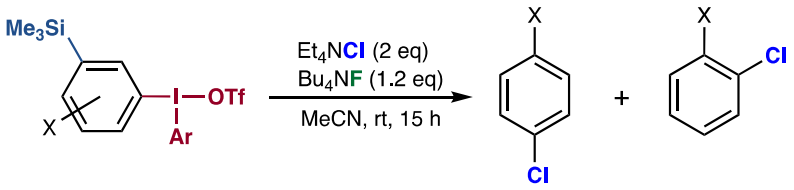
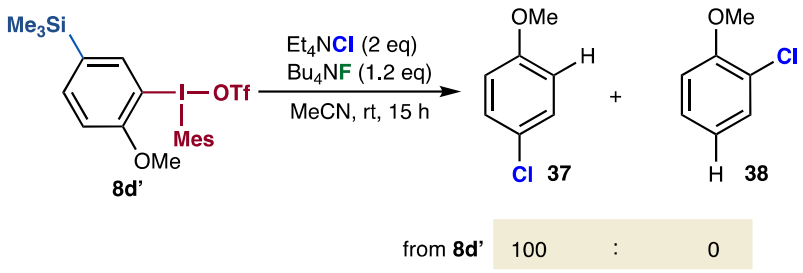


Figure S4. Rate measurements for the reaction of **8a** with a various amount of chloride ion in the presence of TBAF (1.2 equiv.).

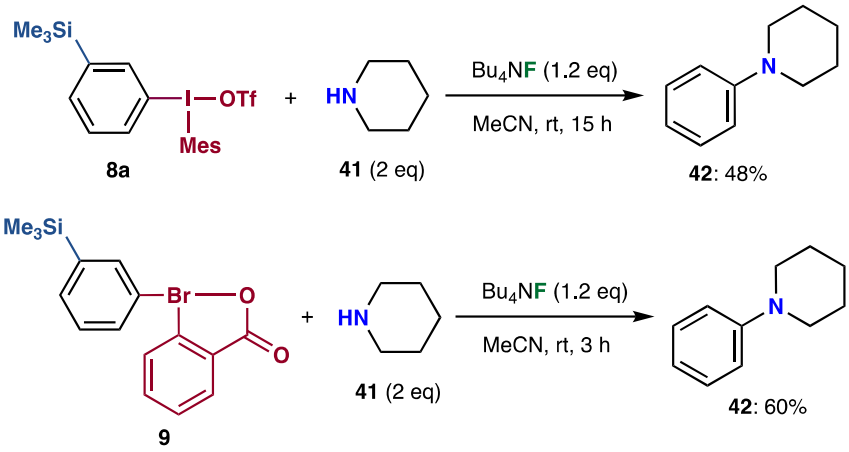
2.9. General procedure for trapping of substituted *m*-benzynes in the presence of chloride ion



To a stirred solution of the precursor (0.025 mmol) and Et_4NCl (8.3 mg, 0.050 mmol) in dry acetonitrile (1.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 30 μL, 0.030 mmol) at room temperature and the mixture was stirred for 15 h. After the complete consumption of the precursor (confirmed by ^{1}H NMR), a mixture of *o*/*p*-substituted chloroarenes was obtained. The yield of chloroarene was determined by GC analysis using capillary column SH-Rtx-5 (0.25 mm x 30 m, 40 °C to 250 °C) with 1,3,5-triisopropylbenzene as an internal standard. The GC retention times of products were consistent with those of authentic samples. These results are summarized in the main text (Figure 3c) and below. Diaryl-λ^3-iodane **8d'** reacts much slower than other 3-(trimethylsilyl)aryl-λ^3-iodanes **8a–8f**, probably due to the intramolecular coordination of *ortho* methoxy group to the iodine(III) center. The selective formation of **37** supported the formation of *m*-aryne under the reaction conditions.



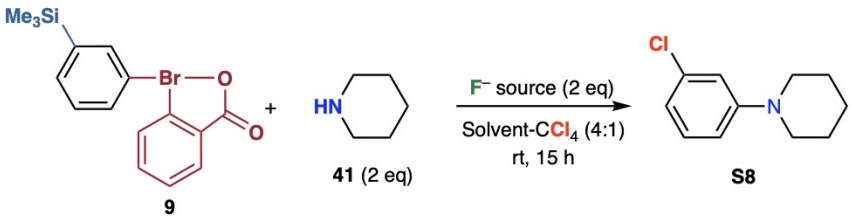
2.10. Trapping of 2 in the presence of piperidine 41



With 8a: To a stirred solution of **8a** (55.4 mg, 0.10 mmol) and **41** (15 µL, 13 mg, 0.15 mmol) in dry acetonitrile (2.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 0.12 mL, 0.12 mmol) at room temperature and the mixture was stirred for 15 h. After the complete consumption of **8a** (confirmed by ^{1}H NMR), the solvent was removed in vacuo and the residue was purified by silica gel chromatography (hexane/AcOEt = 100:0 to 79:21), affording *N*-phenylpiperidine (**42**) in 48% yield (7.9 mg) as a colorless oil. Spectral data were consistent with those reported in literature.[11] **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.27–7.22 (m, 2H), 6.95–6.93 (m, 2H), 6.83–6.80 (m, 1H), 3.16–3.14 (m, 4H), 1.73–1.69 (m, 4H), 1.59–1.55 (m, 2H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 152.4, 129.1, 119.3, 116.7, 50.8, 26.0, 24.5.

With 9: To a stirred solution of **9** (7.0 mg, 0.020 mmol) and **41** (4.0 µL, 3.4 mg, 0.040 mmol) in dry acetonitrile (0.50 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 24 µL, 0.024 mmol) at room temperature and the mixture was stirred for 3 h. After the complete consumption of **9** (confirmed by TLC), the solvent was removed in vacuo and the residue was purified by silica gel chromatography (hexane/AcOEt = 100:0 to 79:21), affording **41** in 60% yield (1.9 mg) as a colorless oil.

Table S2. Trapping of 2 in the presence of 41 and carbon tetrachloride.



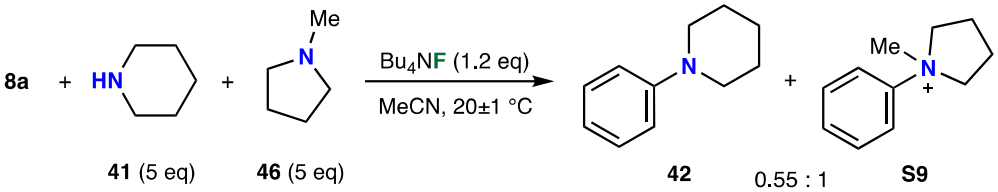
Entry	Fluoride	Solvent	^{1}H NMR yield (%)
1	TBAT	*t*-BuCN	42
2	TBAT	THF	25
3	TBAT	CH_2Cl_2	8
4	KF + 18-crown-6	*t*-BuCN	50
5	CsF + 18-crown-6	*t*-BuCN	43

Use of dry fluoride ion sources and non-acidic *t*-BuCN as a co-solvent was effective in improving the yield of chlorine-trapped product **S8**. TBAT: tetrabutylammonium difluorotriphenylsilicate.

General procedure for the trapping of 2 in the presence of 41 and carbon tetrachloride.

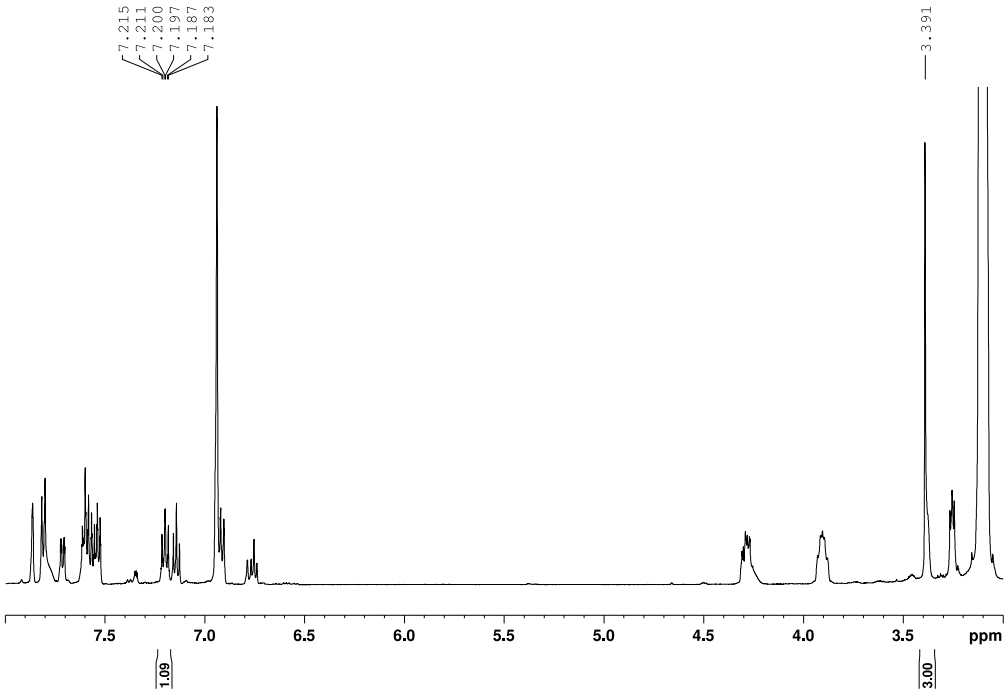
To a solution of **9** (7.0 mg, 0.020 mmol), **41** (4.0 μL, 3.4 mg, 0.040 mmol), KF (2.3 mg, 0.040 mmol), and 18-crown-6 (10.0 mg, 0.038 mmol) in pivalonitrile (0.40 mL) in a Schlenk tube under an argon atmosphere was slowly added carbon tetrachloride (0.10 mL) at room temperature and the mixture was stirred for 3 h. After the complete consumption of **9** (confirmed by TLC), the solvent was removed in vacuo and the residue was purified by PTLC (hexane/AcOEt = 9:1), affording 1-(3-chlorophenyl)piperidine (**S8**) in 46% yield (1.8 mg) as a colorless oil. Spectral data were consistent with those reported in literature.[12] **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.14 (dd, *J* = 8.4, 7.8 Hz, 1H), 6.87 (dd, *J* = 2.3, 1.9 Hz, 1H), 6.79 (ddd, *J* = 8.4, 2.3, 0.8 Hz, 1H), 6.76 (ddd, *J* = 7.8, 1.9, 0.8 Hz, 1H), 3.17–3.15 (m, 4H), 1.71–1.67 (m, 4H), 1.61–1.56 (m, 2H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 153.3, 135.0, 130.0, 118.7, 116.1, 114.4, 50.3, 25.8, 24.4.

2.11. Measurement of Mayr's electrophilicity parameter *E* with a diffusion-clock method.

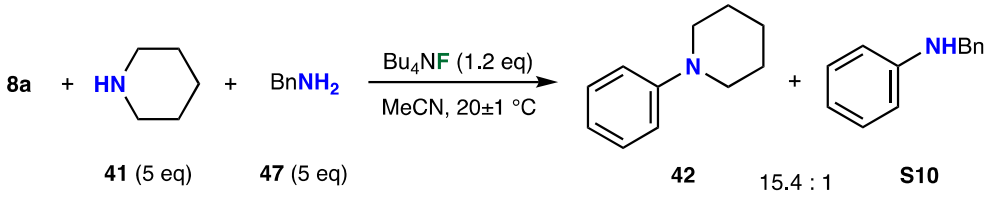


41 (5 eq) **46** (5 eq) **42** 0.55 : 1 **S9**

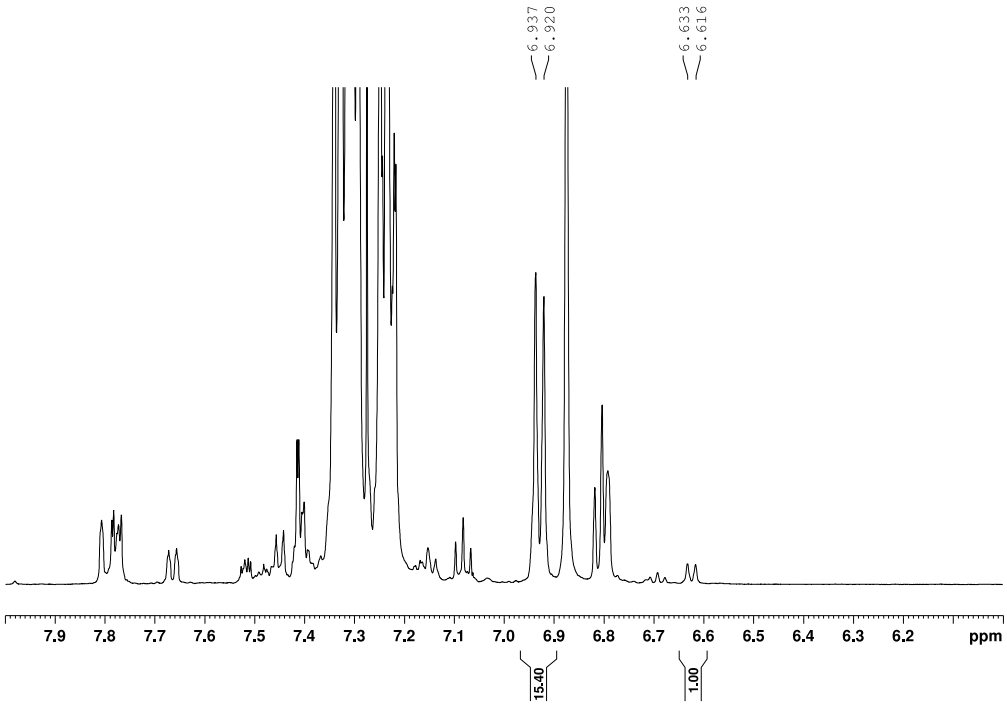
Representative procedure. 41 and 46: To a stirred solution of **8a** (26.9 mg, 0.050 mmol), **41** (25 µL, 22 mg, 0.25 mmol), and **46** (27 µL, 22 mg, 0.25 mmol) in dry acetonitrile (1.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 60 µL, 0.060 mmol) at room temperature and the mixture was stirred for 15 h at 20 °C. After the complete consumption of **8a** (confirmed by ^{1}H NMR), the solvent was removed in vacuo and the residue was dissolved in CD_3CN. The ratio of **42** and **S9** (0.55:1) was determined by ^{1}H NMR. ^{1}H NMR data of **42** was consistent with those of an authentic sample. ^{1}H NMR data of **S9** was consistent with that reported in the literature.[13] For compound **S9**, comparison of characteristic ^{1}H NMR peaks in the reaction mixture was carried out. In reference 13, ^{1}H NMR data of compound **S9-OTf** was reported to be: **^{1}H NMR (500 MHz, CD_3CN):** δ = 7.71 (2 H, d, *J* = 7.7 Hz), 7.66–7.54 (3H, m), 4.15 (2H, ddd, *J* = 7.0, 4.8, 2.7 Hz), 3.90 (2H, dt, *J* = 12.2, 6.5 Hz), 3.34 (3H, s), 2.29 (4H, ddd, *J* = 13.3, 7.0, 4.2 Hz).



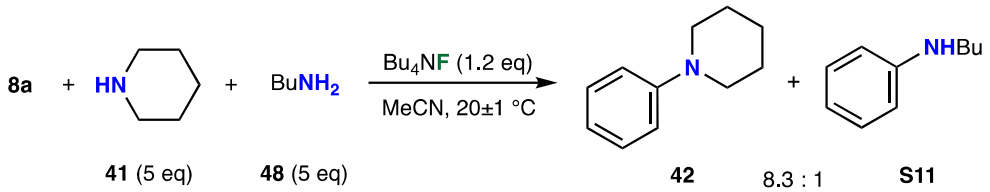
^{1}H NMR spectrum (500 MHz, CD_3CN) of the reaction mixture of **8a** with **41** and **46**.



41 and 47: The ratio of **42** and **S10** (15.4:1) was determined by ^{1}H NMR ($CDCl_3$). Spectral data were consistent with those reported in literature.[11,14,15] For compound **S10**, comparison of characteristic ^{1}H NMR peaks in the reaction mixture was carried out. In reference 14, ^{1}H NMR data of compound **S10:** **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.37 (m, 4H), 7.28 (m, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 2H), 4.33 (s, 2H), 4.04 (br s, 1H).

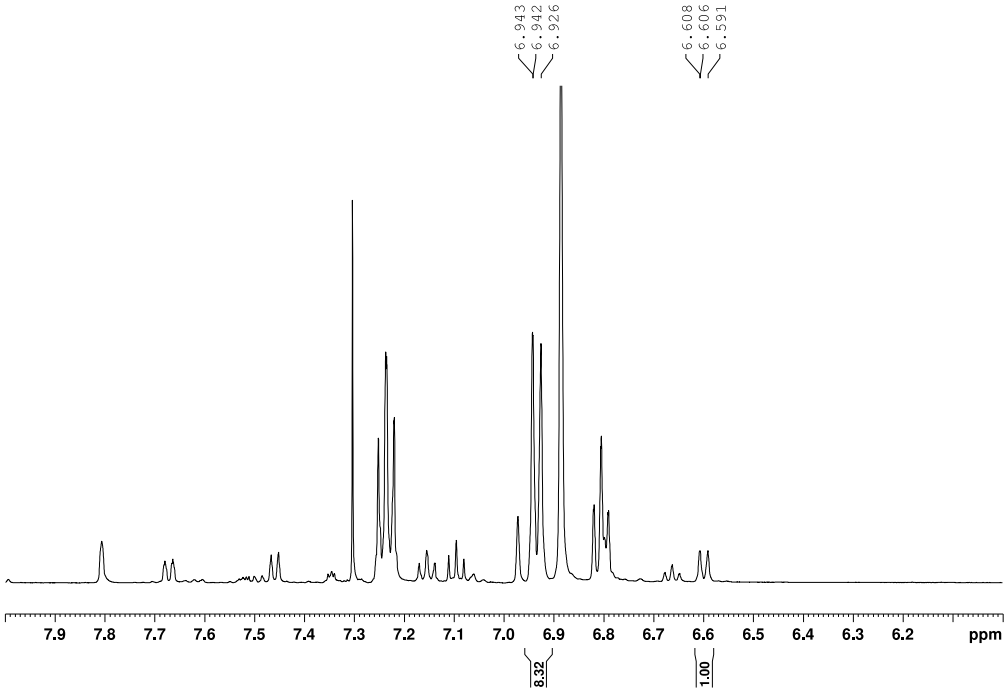


^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the reaction mixture of **8a** with **41** and **47**.



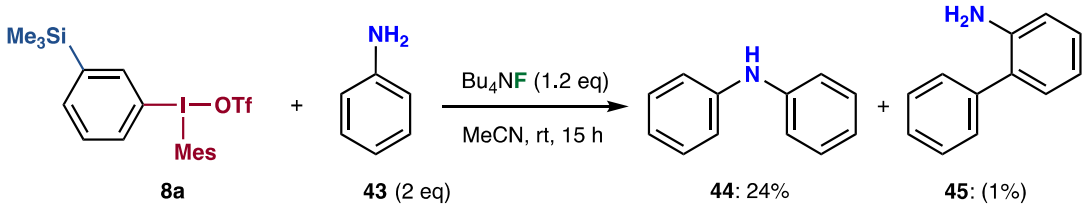
41 and 48: The ratio of **42** and **S11** (8.3:1) was determined by ^{1}H NMR ($CDCl_3$). Spectral data were

consistent with those reported in literature.[11,14] For compound **S11**, comparison of characteristic ^{1}H NMR peaks in the reaction mixture was carried out. In reference 14, ^{1}H NMR data of compound **S11:** **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.20 (td, *J* = 7.4, 1.7 Hz, 2H), 6.72 (td, *J* = 7.2, 1.0 Hz, 1H), 6.64 (dd, *J* = 7.5, 0.9 Hz, 2H), 3.62 (br s, 1H), 3.15 (t, *J* = 6.9 Hz, 2H), 1.65 (quintet, *J* = 7.2 Hz, 2H), 1.48 (sextet, *J* = 7.3 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the reaction mixture of **8a** with **41** and **48**.

2.12. Trapping of 2 in the presence of 43

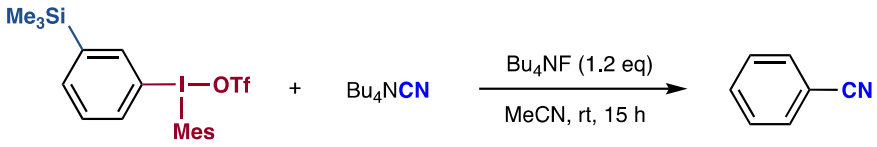


To a stirred solution of **8a** (54.3 mg, 0.10 mmol) and **43** (18 µL, 18 mg, 0.20 mmol) in dry acetonitrile (2.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 0.12 mL, 0.12 mmol) at room temperature and the mixture was stirred for 15 h. After the complete consumption of **8a** (confirmed by ^{1}H NMR), the solvent was removed in vacuo and the residue was purified by silica gel chromatography (hexane/AcOEt = 8:2), affording diphenylamine (**44**) in 24% yield (4.0 mg) as a yellow solid. Spectral data were consistent with those reported in literature.[16] **^{1}H**

NMR (500 MHz, $CDCl_3$): δ = 7.28–7.25 (m, 4H), 7.08–7.06 (m, 4H), 6.94–6.91 (m, 2H), 5.69 (br s, 1H). **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$):** δ = 143.3, 129.5, 121.2, 118.0.

2-Amino-1,1'-biphenyl (**45**)[17] was obtained in 1% yield. The yield was determined by GC analysis using capillary column SH-Rtx-5 (0.25 mm x 30 m, 70 °C to 270 °C) with 1,3,5-trimethoxybenzene as an internal standard. The GC retention time of product was consistent with that of an authentic sample of **45**.

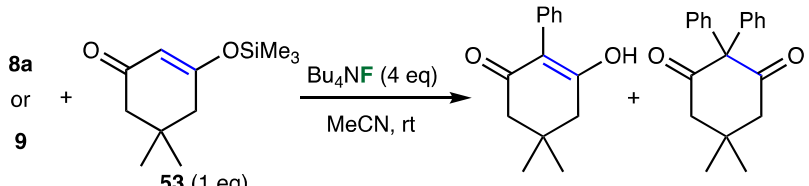
2.13. Trapping of 2 in the presence of 45



8a **51** (2 eq) **52**: (43%)

To a stirred solution of **8a** (27.2 mg, 0.050 mmol) and **51** (26.1 mg, 0.097 mmol) in dry acetonitrile (1.0 mL) in a Schlenk tube under argon atmosphere was slowly added TBAF in THF (1 M, 60 µL, 0.060 mmol) at room temperature and the mixture was stirred for 15 h. After the complete consumption of **8a** (confirmed by ^1H NMR), benzonitrile (**52**) was obtained in 43% yield. The yield was determined by GC analysis using capillary column SH-Rtx-5 (0.25 mm x 30 m, 70 °C to 200 °C) with *o*-dichlorobenzene as an internal standard. The GC retention time of product was consistent with that of an authentic sample of **52**.

2.14. Trapping of 2 in the presence of 53



53 (1 eq)

with **8a** (15 h): **54**: 44% [54%] **55**: 7%
with **9** (3 h): **54**: 54% **55**: 8%

With 8a: To a stirred solution of **8a** (54.2 mg, 0.10 mmol) and **53** (20.8 mg, 0.98 mmol) in dry acetonitrile (2.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 0.40 mL, 0.40 mmol) at room temperature and the mixture was stirred for 15 h. After the complete consumption of **8a** (confirmed by ^1H NMR), saturated NH_4Cl aq. (5 mL) was added and extracted with Et_2O (3 x 10 mL). The combined organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give an oily residue. **54** was obtained in 54% yield, which was determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard. The residue

was purified by silica gel chromatography (hexane/AcOEt = 1:1), affording 2-phenyl-3-hydroxy-5,5-dimethylcyclohex-2-en-1-one (**54**) in 44% yield (4.0 mg) as a colorless solid and 5,5-dimethyl-2,2-diphenylcyclohexane-1,3-dione (**55**) in 7% yield (1.0 mg, including small impurities) as a colorless solid. Spectral data were consistent with those reported in the literatures.

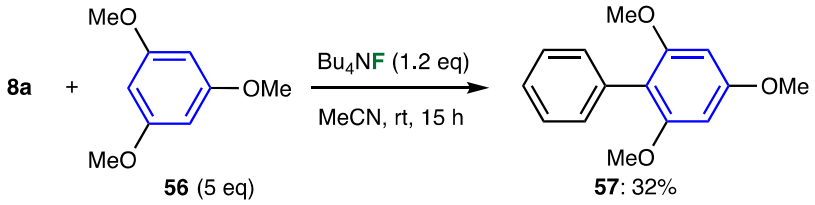
54:[18] **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.47–7.43 (m, 2H), 7.38–7.34 (m, 1H), 7.22–7.20 (m, 2H), 2.49 (s, 2H), 2.39 (s, 2H), 1.17 (s, 6H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 196.6, 168.9, 130.9, 130.8, 129.6, 128.5, 117.1, 51.0, 41.8, 31.9, 28.5.

55:[19] **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.37–7.34 (m, 6H), 6.84–6.82 (m, 4H), 2.75 (s, 4H), 1.11 (s, 6H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 207.1, 137.6, 129.7, 128.8, 128.1, 53.2, 31.4, 28.7, 27.4.

EI-MS *m/z* (relative intensity): 292 (55%, M^+), 194 (58), 165 (100), 83 (80).

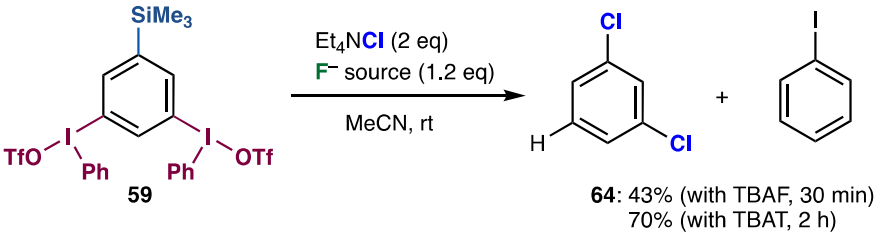
With 9: To a stirred solution of **9** (8.72 mg, 0.025 mmol) and **53** (5.27 mg, 0.025 mmol) in dry acetonitrile (1.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 0.10 mL, 0.10 mmol) at room temperature and the mixture was stirred for 3 h. After the complete consumption of **9** (confirmed by TLC), following the same procedure as above, affording **54** as a colorless solid in 54% yield (2.9 mg) and **55** as a colorless solid in 8% yield (0.3 mg, including small impurities).

2.15. Trapping of 2 in the presence of 56.



To a stirred solution of **8a** (54.4 mg, 0.10 mmol) and **56** (84.0 mg, 0.50 mmol) in dry acetonitrile (2.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 0.12 mL, 0.12 mmol) at room temperature and the mixture was stirred for 15 h. After the complete consumption of **8a** (confirmed by ^{1}H NMR), the solvent was removed in vacuo and the residue was purified by preparative TLC (hexane/AcOEt = 8:2), affording 2,4,6-trimethoxy-1,1'-biphenyl (**57**) in 32% yield (7.8 mg) as a colorless solid. Spectral data were consistent with those reported in literature.[20] **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.40–7.37 (m, 2H), 7.33–7.26 (m, 3H), 6.23 (s, 2H), 3.86 (s, 3H), 3.72 (s, 6H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 160.6, 158.5, 134.2, 131.3, 127.8, 126.6, 112.7, 91.1, 56.0, 55.5.

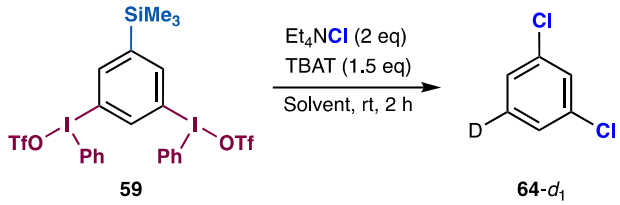
2.16. Fluorolysis of 59 in the presence of Et_4NCl



With TBAF: To a stirred solution of **59** (25.6 mg, 0.030 mmol) and Et_4NCl (10.6 mg, 0.064 mmol) in dry acetonitrile (1.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 36 μL, 0.036 mmol) at room temperature and the mixture was stirred for 30 min. After the complete consumption of **59** (confirmed by ^{1}H NMR), **64** was obtained in 43%. The yields were determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard and the deuterium contents were determined either by ^{1}H NMR or GC-MS. ^{1}H NMR spectrum was consistent with that of an authentic sample of **64**.[21] **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.48 (br s, 1H), 7.35–7.34 (m, 3H). **EI-MS *m/z* (relative intensity):** 150 (10%, M^+), 148 (64, M^+), 146 (100, M^+), 111 (36), 75 (26), 50 (13).

With TBAT: A solution of **59** (17.1 mg, 0.020 mmol), Et_4NCl (8.8 mg, 0.053 mmol) and TBAT (12.7 mg, 0.024 mmol) in dry acetonitrile (1.0 mL) in a Schlenk tube under an argon atmosphere was stirred for 2 h at room temperature. After the complete consumption of **59** (confirmed by ^{1}H NMR), **64** was obtained in 70%. The yields were determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard and the deuterium contents were determined either by ^{1}H NMR or GC-MS. ^{1}H NMR spectrum was consistent with that of an authentic sample of **64**.

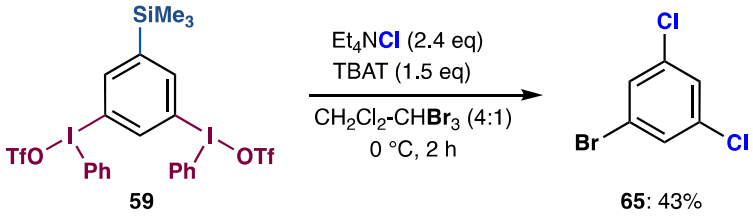
Table S3. Fluorolysis of 59 in the presence of Et_4NCl and deuterated solvents.



Entry	Solvent	yield (%)[a]	%D[b]
1	MeCN	70	0
2	CD_3CN	47	33
3	MeCN : D_2O = 100 : 1	47	55
4	CD_3CN : D_2O = 100 : 1	50	80
5[c]	MeCN : D_2O = 10 : 1	37	91
6[c]	CD_3CN : D_2O = 10 : 1	40	96
7[d]	CD_3CN : D_2O = 10 : 1	20	95

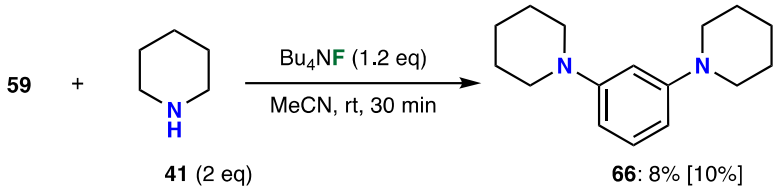
[a] Determined by ^{1}H-NMR. [b] Determined by GC-MS. [c] Run for 48 h. [d] Run with TBAF (1.5 eq)

2. 17. Fluorolysis of 59 in the presence of Et_4NCl and bromoform



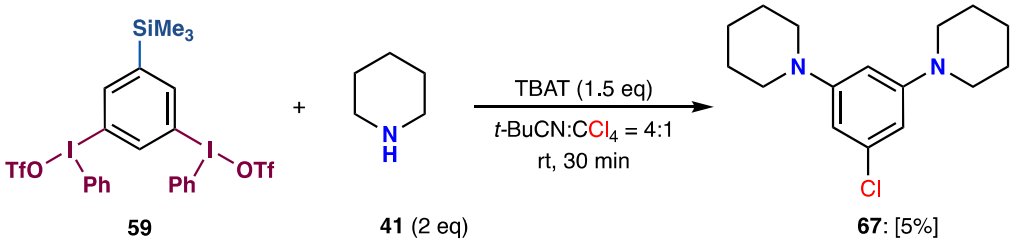
A solution of **59** (8.6 mg, 0.010 mmol), Et_4NCl (4.0 mg, 0.024 mmol) and TBAT (8.1 mg, 0.015 mmol) in dry dichloromethane (0.40 mL) and bromoform (0.10 mL) in a Schlenk tube under an argon atmosphere was stirred for 2 h at 0 °C. After the complete consumption of **59** (confirmed by ^{1}H NMR), **65** was obtained in 43%. The yield was determined by GC analysis using capillary column SH-Rtx-5 (0.25 mm x 30 m, 70 °C to 200 °C) with 1,3,5-trimethoxybenzene as an internal standard. The GC retention time and spectral data of product were consistent with that of an authentic sample of **65**.[22] **EI-MS *m/z* (relative intensity):** 228 (45%, M^+), 226 (100, M^+), 224 (60, M^+), 147 (30), 145 (46), 109 (27), 75 (23), 74 (37), 73 (13).

2.17. Fluorolysis of 59 in the presence of 41



To a stirred solution of **59** (21.3 mg, 0.025 mmol) and **41** (5.0 µL, 4.3 mg, 0.050 mmol) in dry acetonitrile (1.0 mL) in a Schlenk tube under an argon atmosphere was slowly added TBAF in THF (1 M, 30 µL, 0.030 mmol) at room temperature and the mixture was stirred for 15 h. After the complete consumption of **59** (confirmed by ^{1}H NMR), the yield of **66** (10%) was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard. The solvent was removed in vacuo and the residue was purified by silica gel chromatography (hexane/AcOEt = 97:3 to 77:23), affording 1,3-di(piperidin-1-yl)benzene (**66**) in 8% yield (0.5 mg) as a colorless oil. Spectral data were consistent with those reported in literature.[23] *NOTE*: this compound was readily oxidized on the TLC plate. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.11 (t, *J* = 8.1 Hz, 1H), 6.55 (t, *J* = 2.3 Hz, 1H), 6.46 (dd, *J* = 8.1, 2.3 Hz, 2H), 3.14–3.11 (m, 8H), 1.72–1.68 (m, 8H), 1.60–1.52 (m, 4H, overlapped with H_2O). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$):** δ = 153.5, 129.4, 108.7, 106.1, 51.3, 26.2, 24.5.

2.18. Fluorolysis of 59 in the presence of 41 and carbon tetrachloride



A solution of **59** (8.5 mg, 0.010 mmol), **41** (2.0 µL, 4.3 mg, 0.020 mmol), and TBAT (8.1 mg, 0.015 mmol) in pivalonitrile (0.40 mL) and carbon tetrachloride (0.10 mL) in a Schlenk tube under an argon atmosphere was stirred for 30 min. After the complete consumption of **59** (confirmed by ^{1}H NMR), the yield of **67** (5%) was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard. Spectral data were consistent with those of authentic sample of **67** according to the reported procedure (see section 2.1).

3. Computational Details

All calculations were carried with the Gaussian 16 program package (Revision C.01).[24] Structure optimizations were carried out at the CCSD(T) level in the gas phase using the cc-pVDZ basis set in C_s symmetry. The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum (no imaginary frequency). The contribution analyses were performed with the Hirshfeld method using the Multiwfn program.[25]

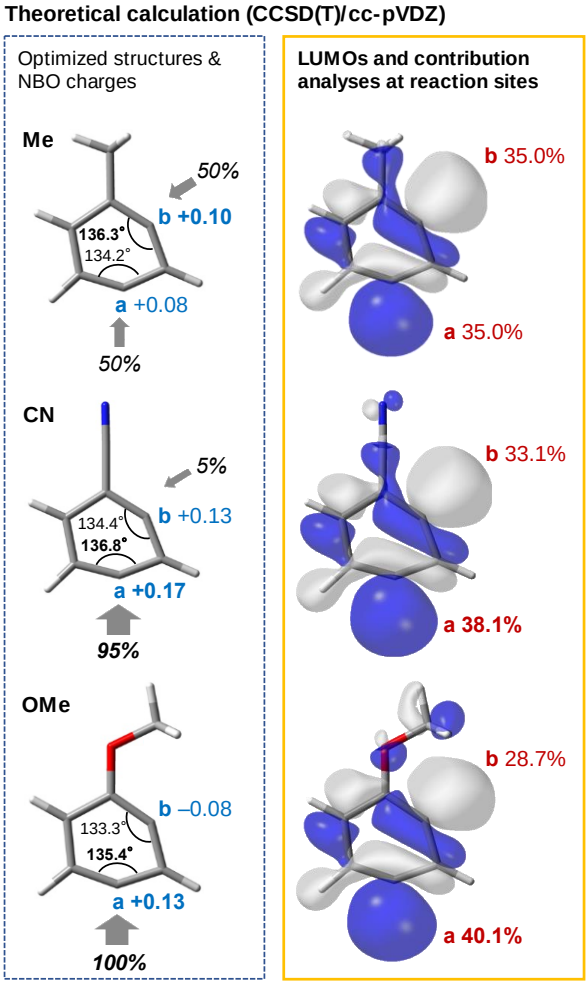
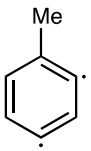


Figure S5. Optimized structures, NBO charges and contribution analyses at reaction sites of LUMOs of substituted *m*-benzynes.

Optimized structures



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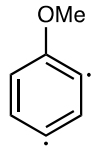
0 1

C	0.00000000	0.86257100	0.00000000
C	-1.12887300	0.03479800	0.00000000

C	-1.37069200	-1.33075200	0.00000000
C	-0.06425700	-1.81609000	0.00000000
C	1.19341100	-1.21753000	0.00000000
C	1.25218200	0.19705700	0.00000000
H	-2.31789800	-1.87530300	0.00000000
H	2.10012400	-1.83513400	0.00000000
H	2.20590400	0.74896000	0.00000000
C	-0.13092800	2.37827100	0.00000000
H	0.86697200	2.85242900	0.00000000
H	-0.68007900	2.72954400	0.89317000
H	-0.68007900	2.72954400	-0.89317000



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0 1

C	0.00000000	0.51835400	0.00000000
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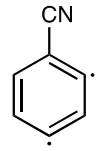
C	-0.35499100	-2.02538400	0.00000000
C	1.02810300	-1.91390500	0.00000000
C	1.93960800	-0.85882900	0.00000000
C	1.41702600	0.45090800	0.00000000
H	-0.98365700	-2.91886400	0.00000000
H	3.01803900	-1.05766400	0.00000000
H	2.03410600	1.36075500	0.00000000
O	-0.58430000	1.75712800	0.00000000
C	-2.01192400	1.73396400	0.00000000
H	-2.33531900	2.78763400	0.00000000
H	-2.40226600	1.21979900	0.90071100
H	-2.40226600	1.21979900	-0.90071100



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0 1

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C	1.49107800	-1.51305800	0.00000000
C	0.22194300	-2.06969800	0.00000000

C	-1.09250300	-1.60387900	0.00000000
C	-1.27744600	-0.20544900	0.00000000
H	2.47551700	-1.98584600	0.00000000
H	-1.93365800	-2.30675000	0.00000000
H	-2.26452300	0.27859700	0.00000000
C	-0.06432100	1.99102800	0.00000000
N	-0.06432100	3.17037600	0.00000000

4. References

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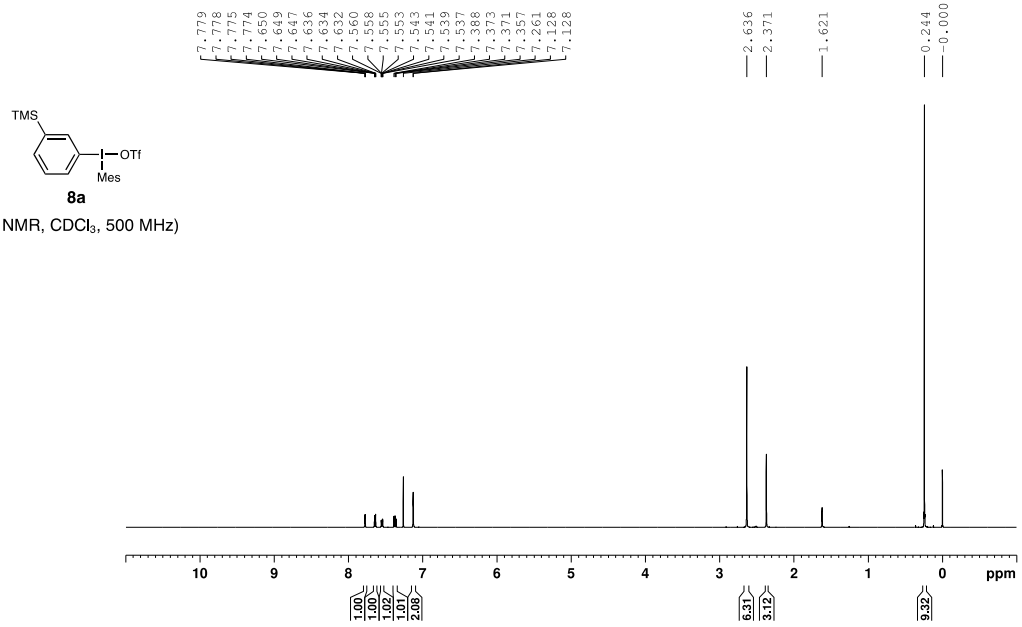
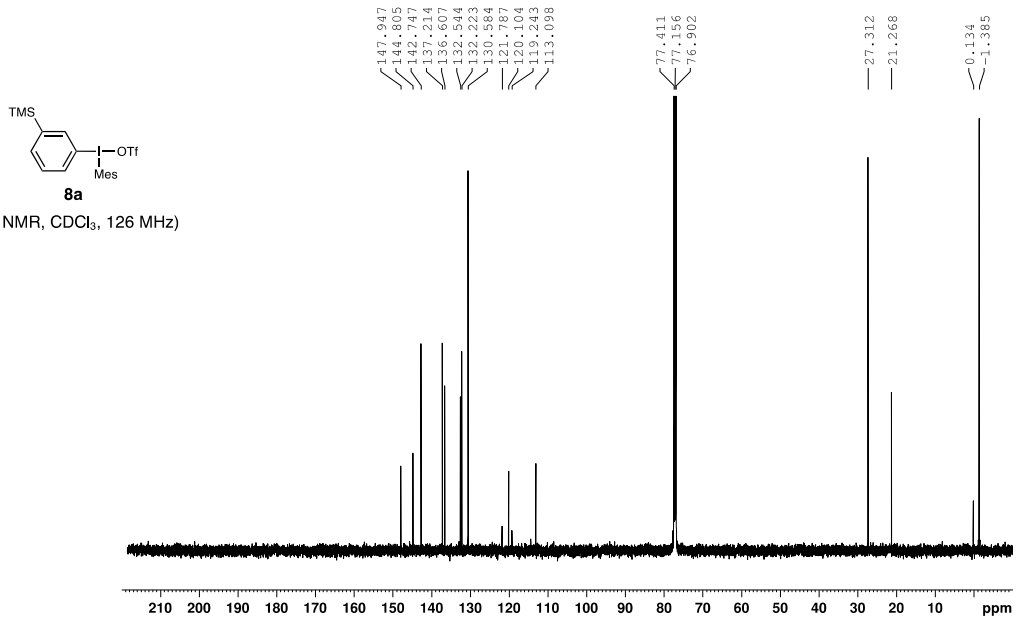
5. NMR spectra



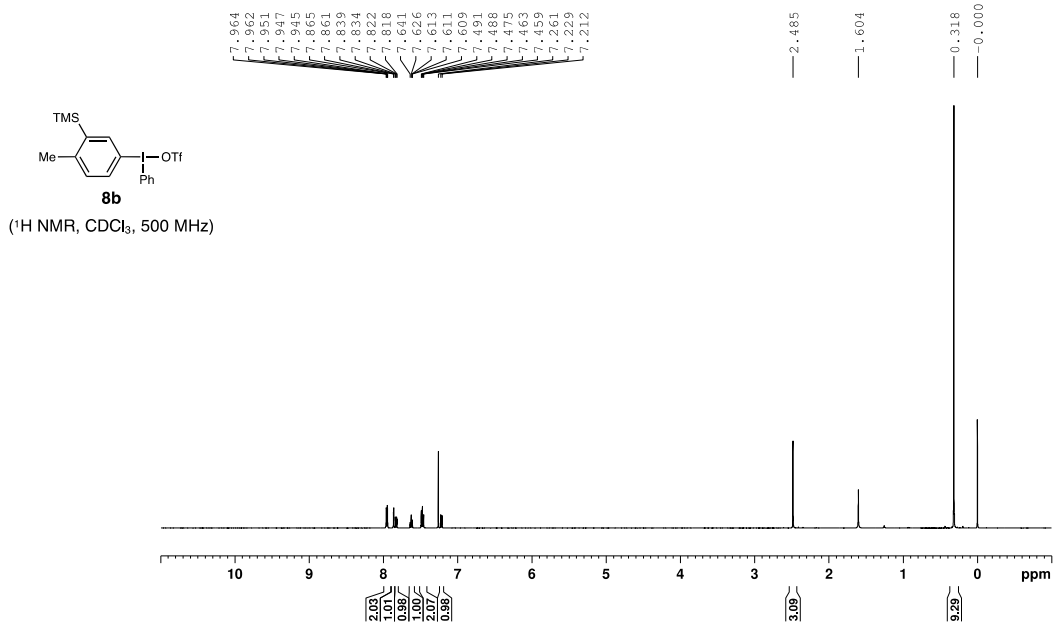
8a

(^{1}H NMR, $CDCl_3$, 500 MHz)



8a

(^{13}C NMR, $CDCl_3$, 126 MHz)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OTf
Ph
8b
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7.951
7.947
7.945
7.865
7.861
7.839
7.834
7.822
7.818
7.641
7.626
7.613
7.611
7.609
7.491
7.488
7.475
7.463
7.459
7.261
7.229
7.212
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1.604
0.318
-0.000
10
9
8
7
6
5
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ppm
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1.01
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1.00
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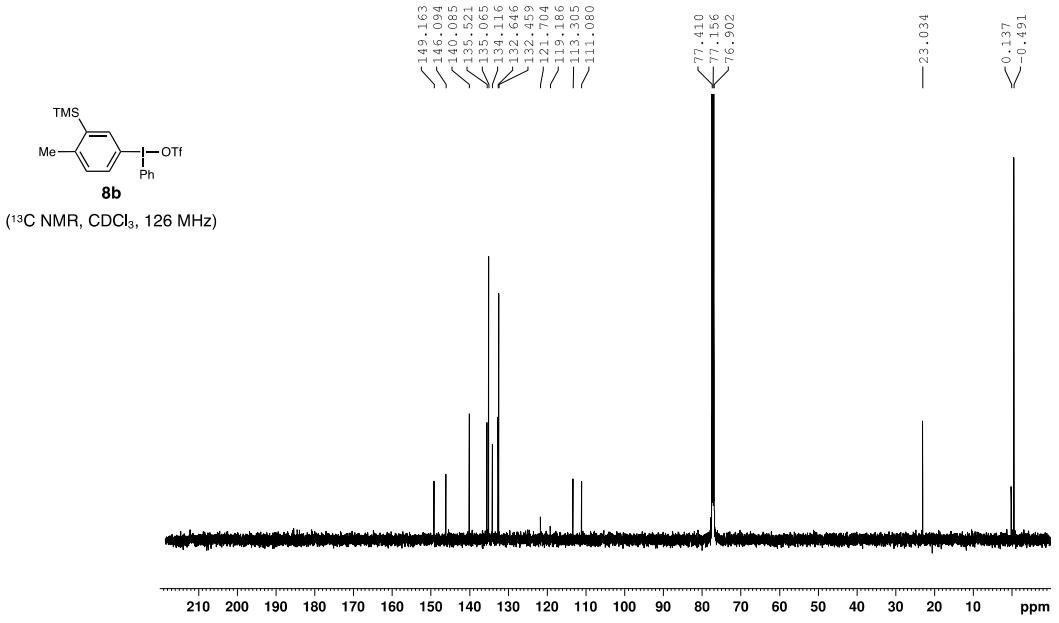
0.98
3.09
9.29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Me
I
OTf
Ph
8b
(13C NMR, CDCl3, 126 MHz)
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140.085
135.521
135.065
134.116
132.646
132.459
121.704
119.186
113.305
111.080
77.410
77.156
76.902
23.034
0.137
-0.491
210
200
190
180
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150
140
130
120
110
100
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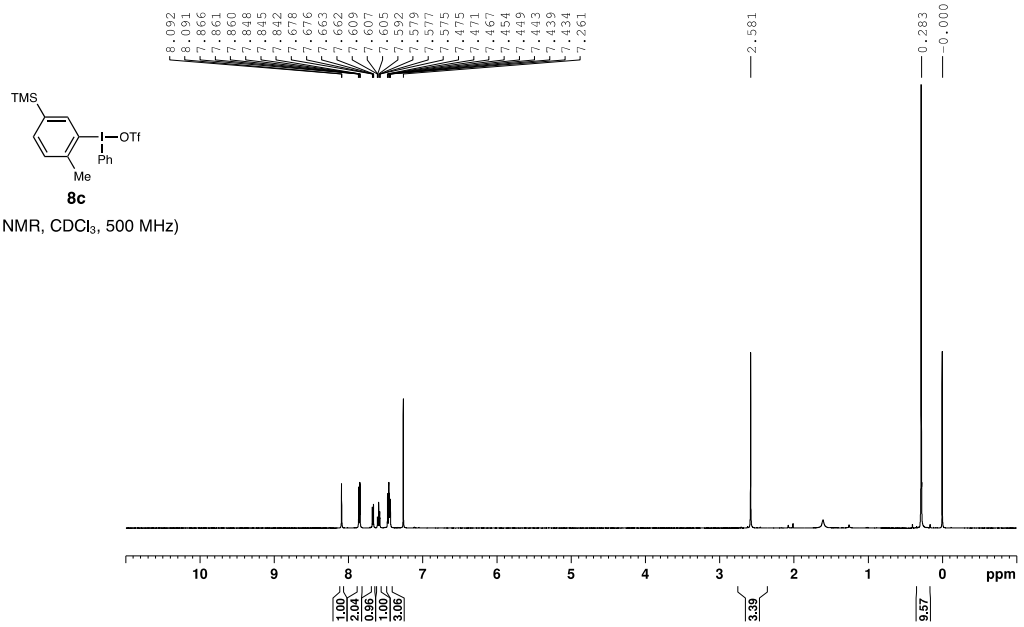
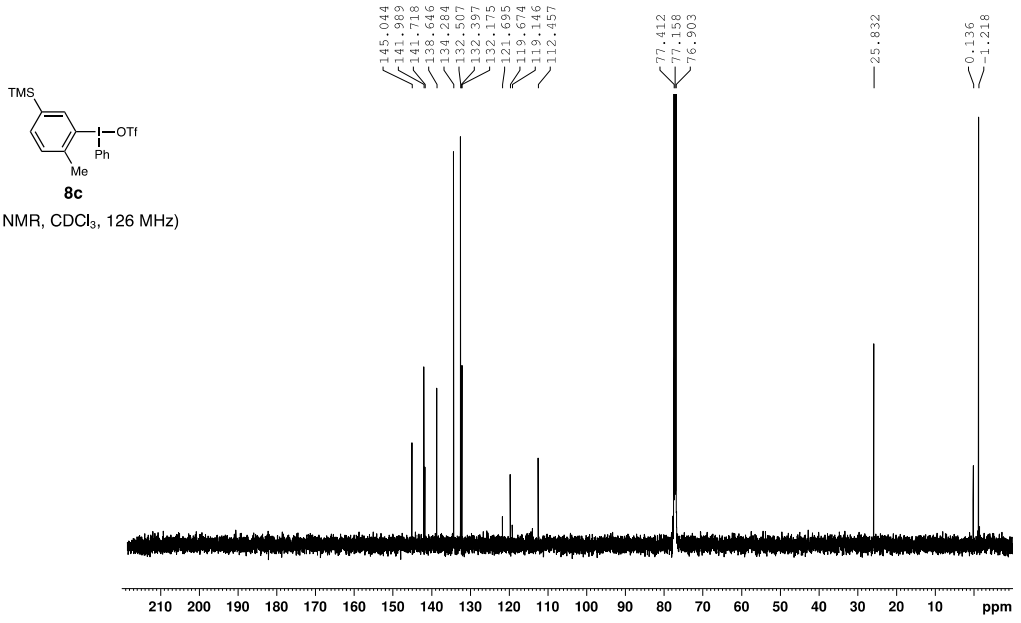
80
70
60
50
40
30
20
10
ppm



8c

(^{1}H NMR, $CDCl_3$, 500 MHz)



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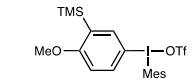
(^{13}C NMR, $CDCl_3$, 126 MHz)



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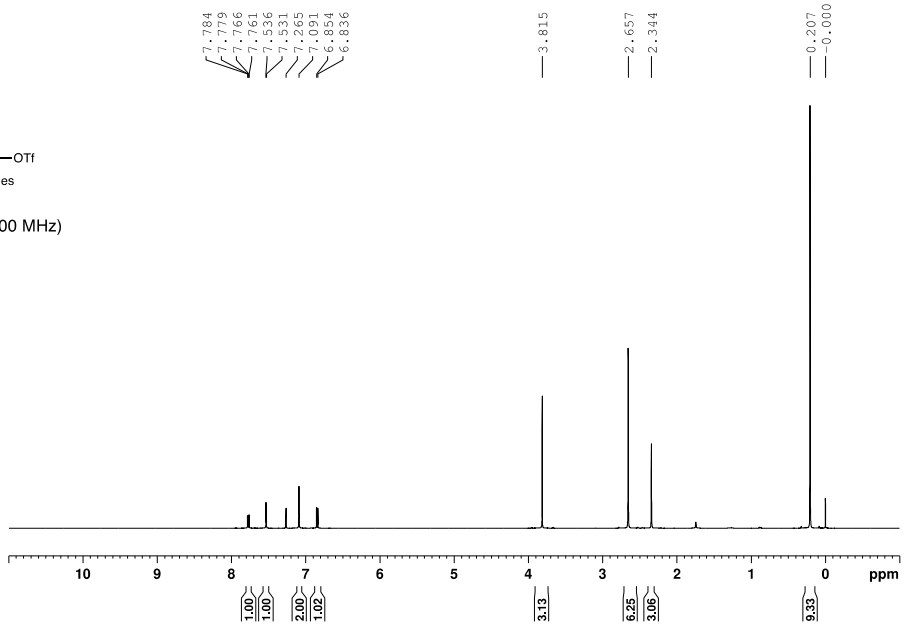

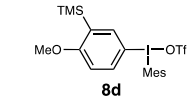

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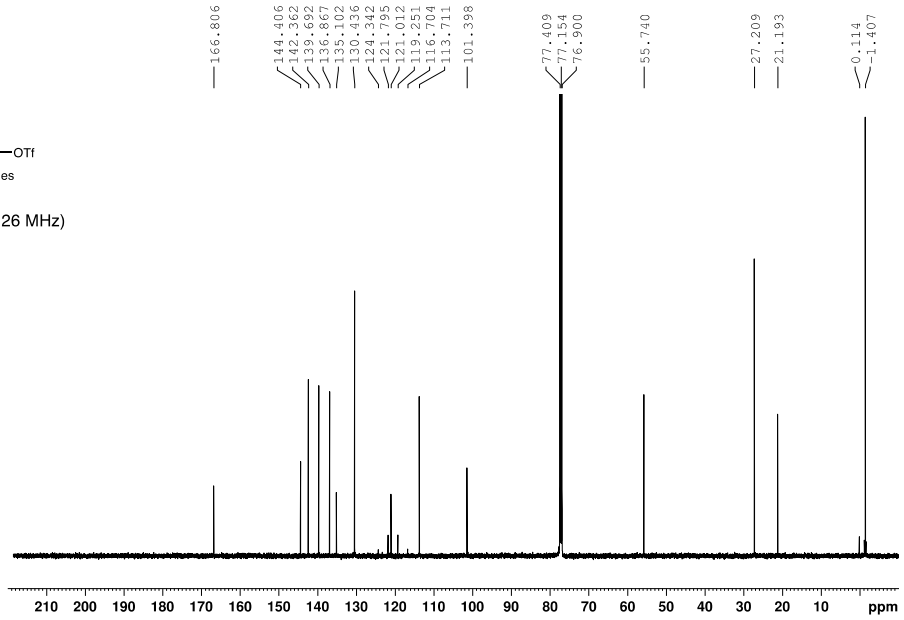

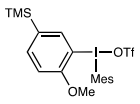

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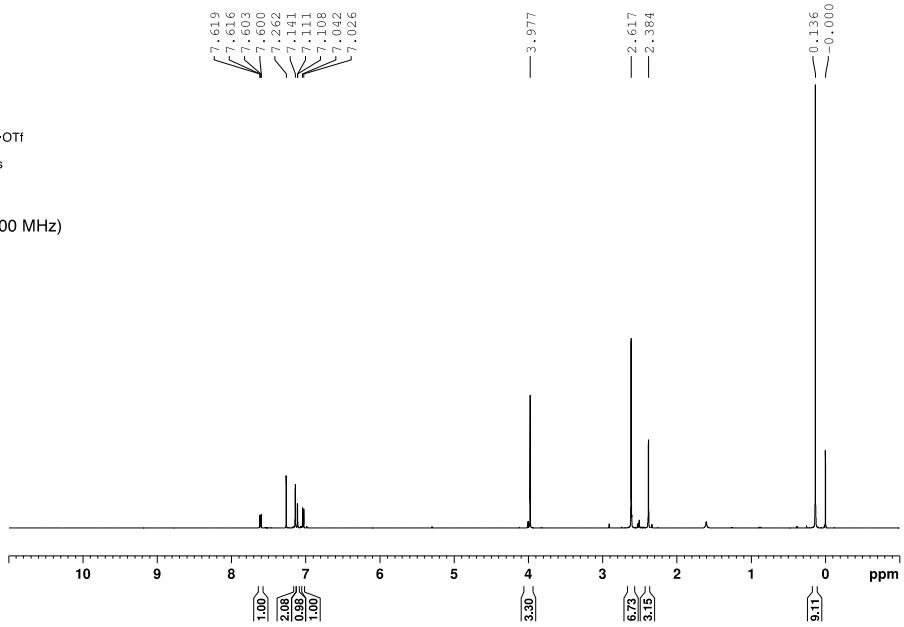
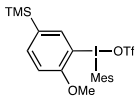
(^{1}H NMR, $CDCl_3$, 500 MHz)





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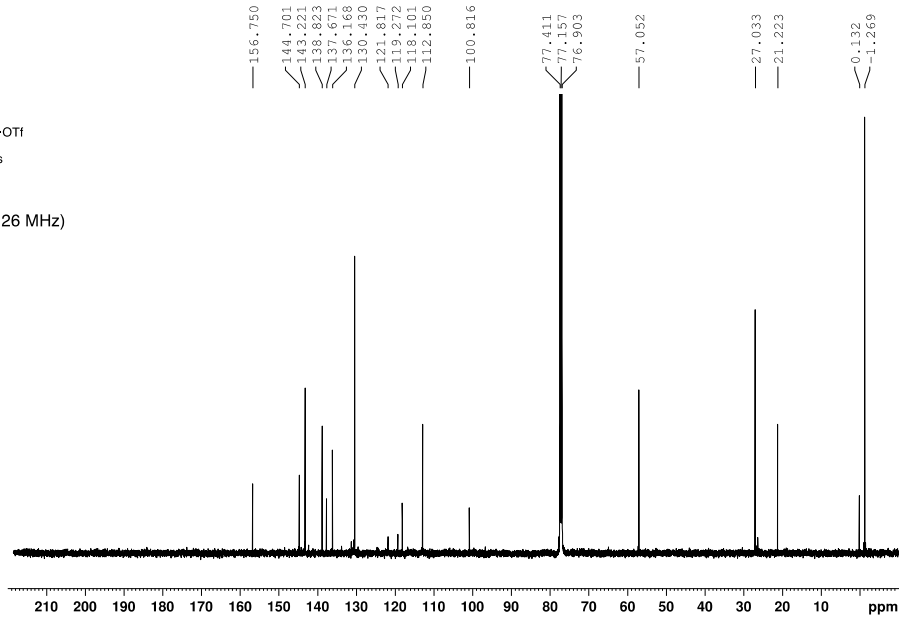

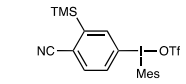

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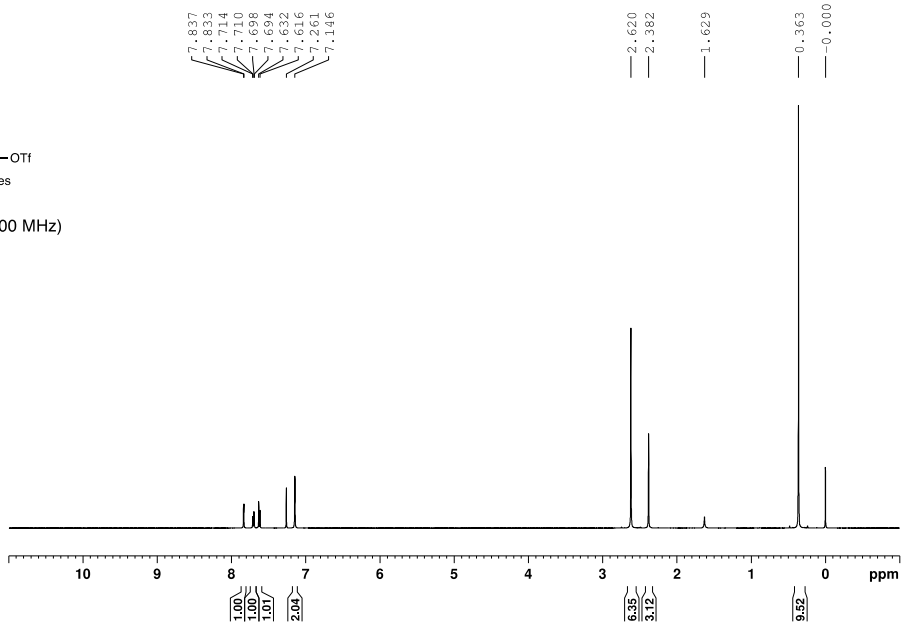
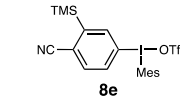
(^{1}H NMR, $CDCl_3$, 500 MHz)





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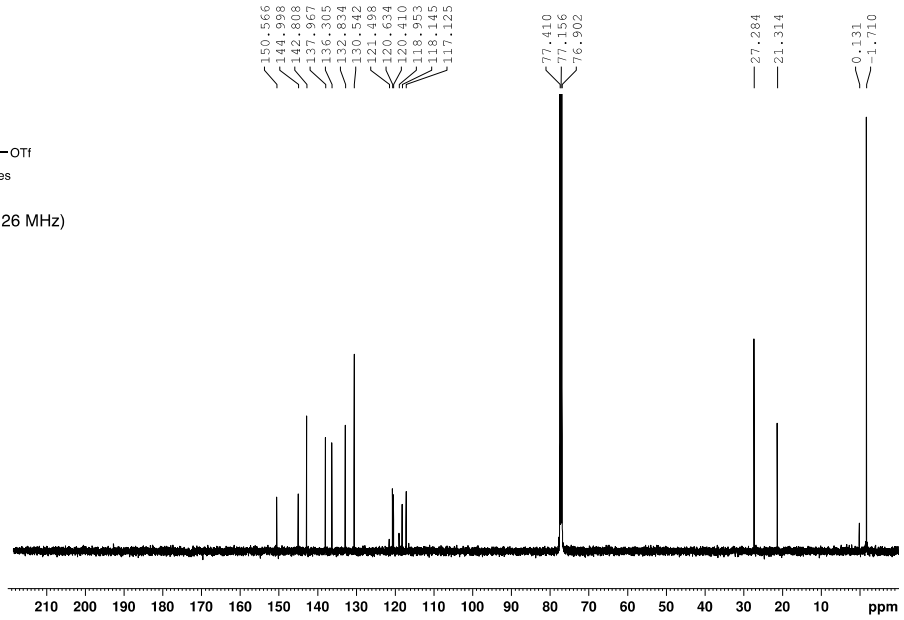

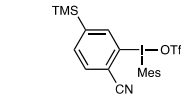

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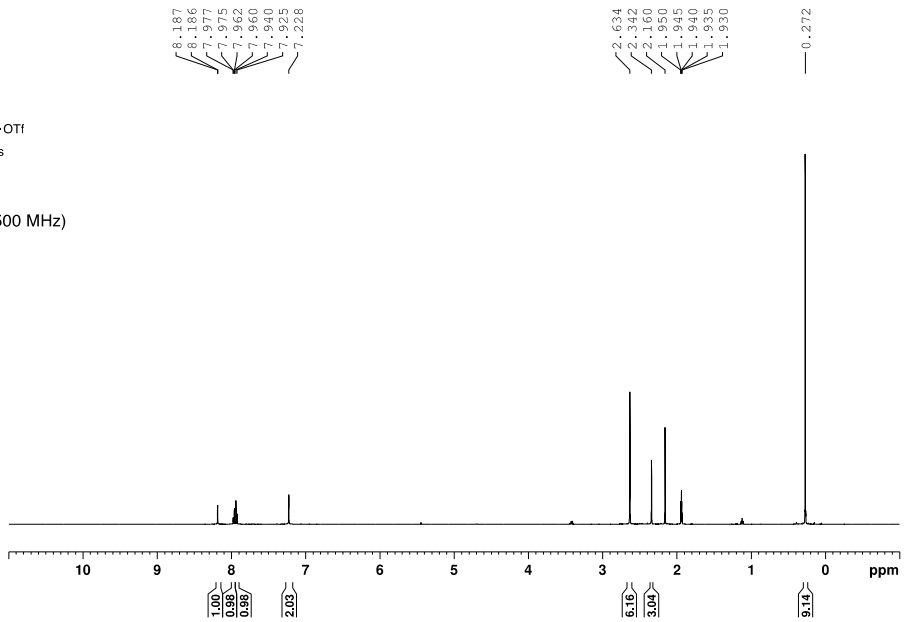
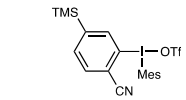
(^{1}H NMR, CD_3CN, 500 MHz)





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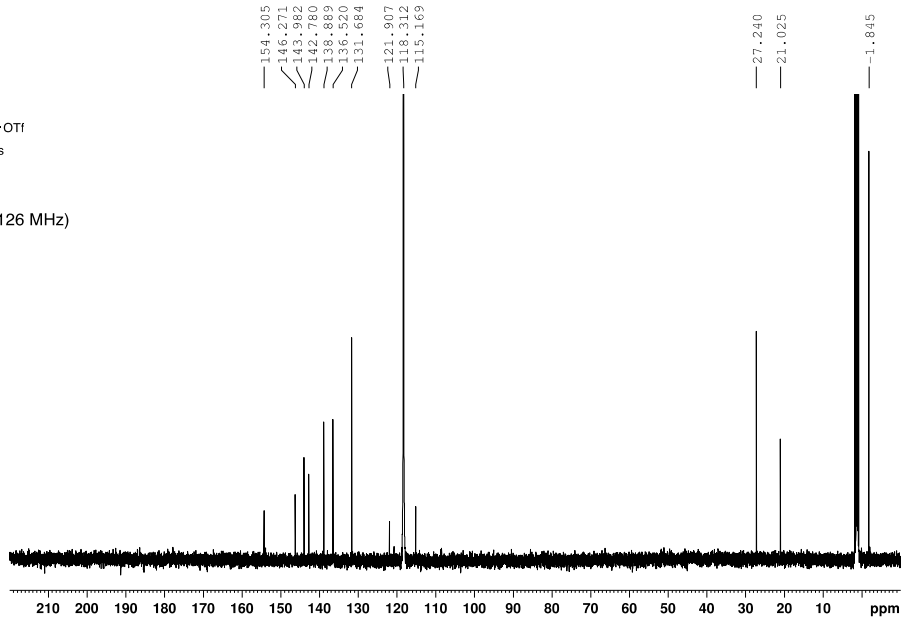

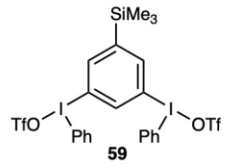

59

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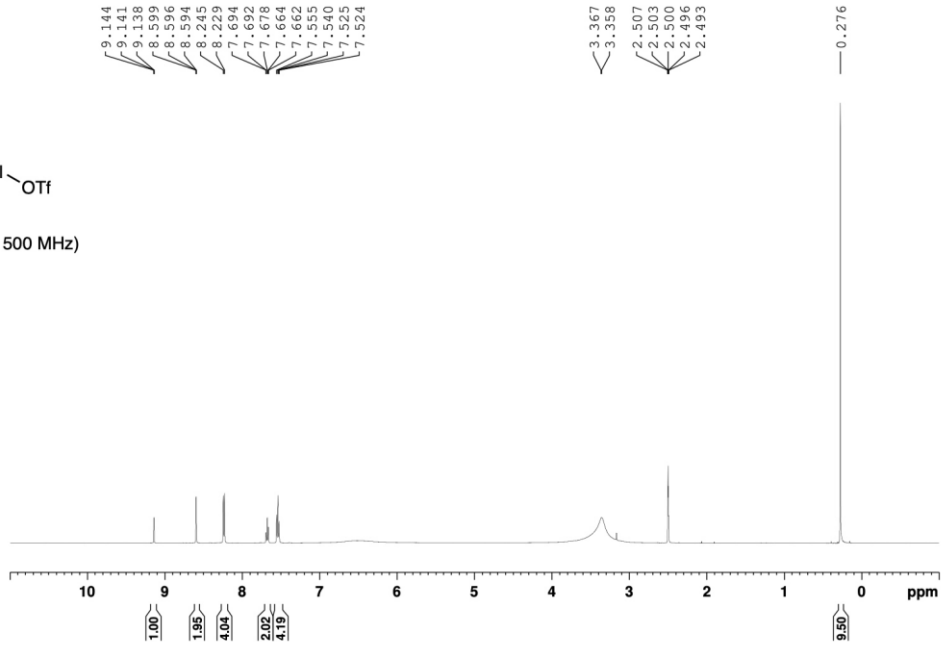

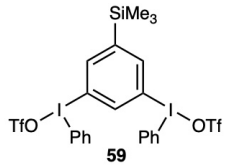

59

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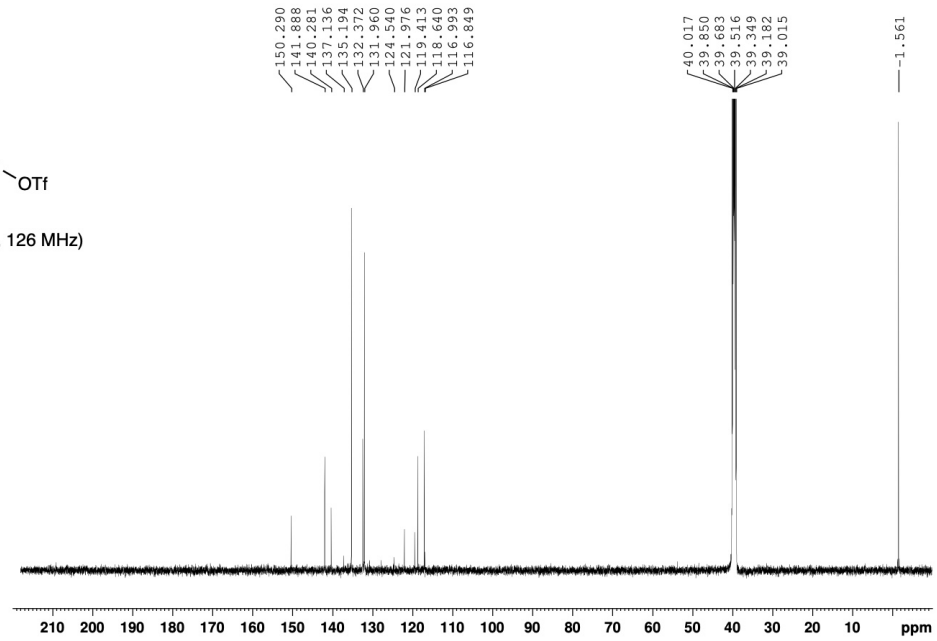

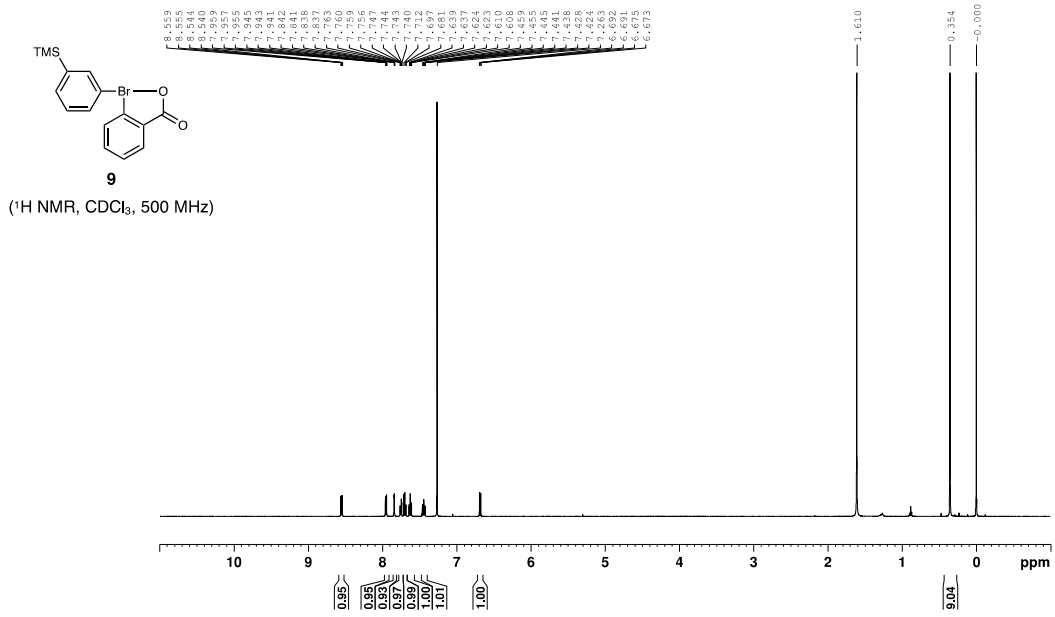
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9
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8.544
8.540
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7.955
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7.841
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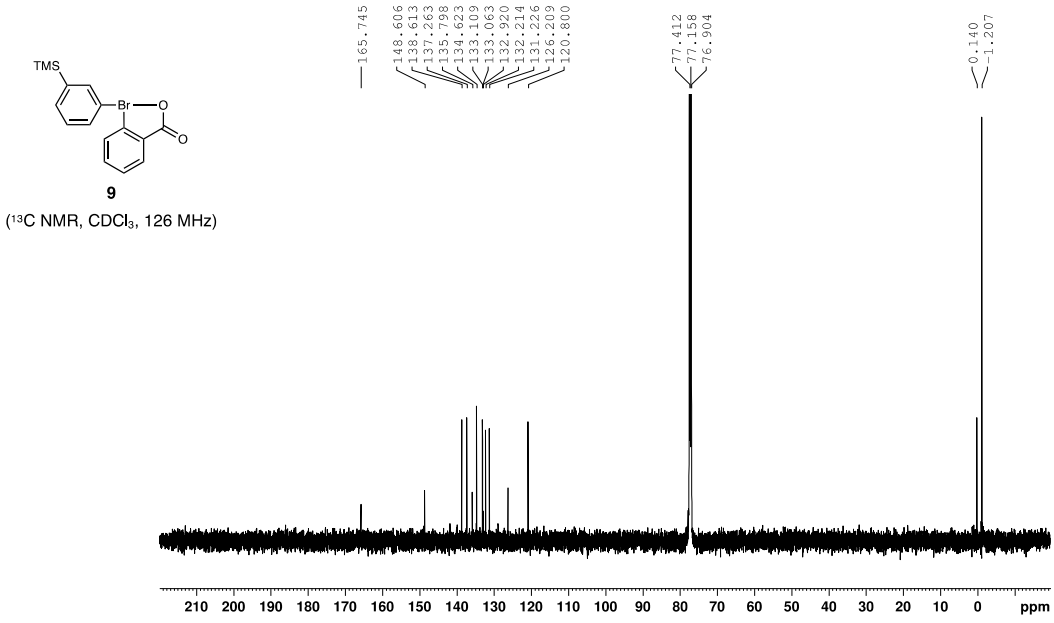
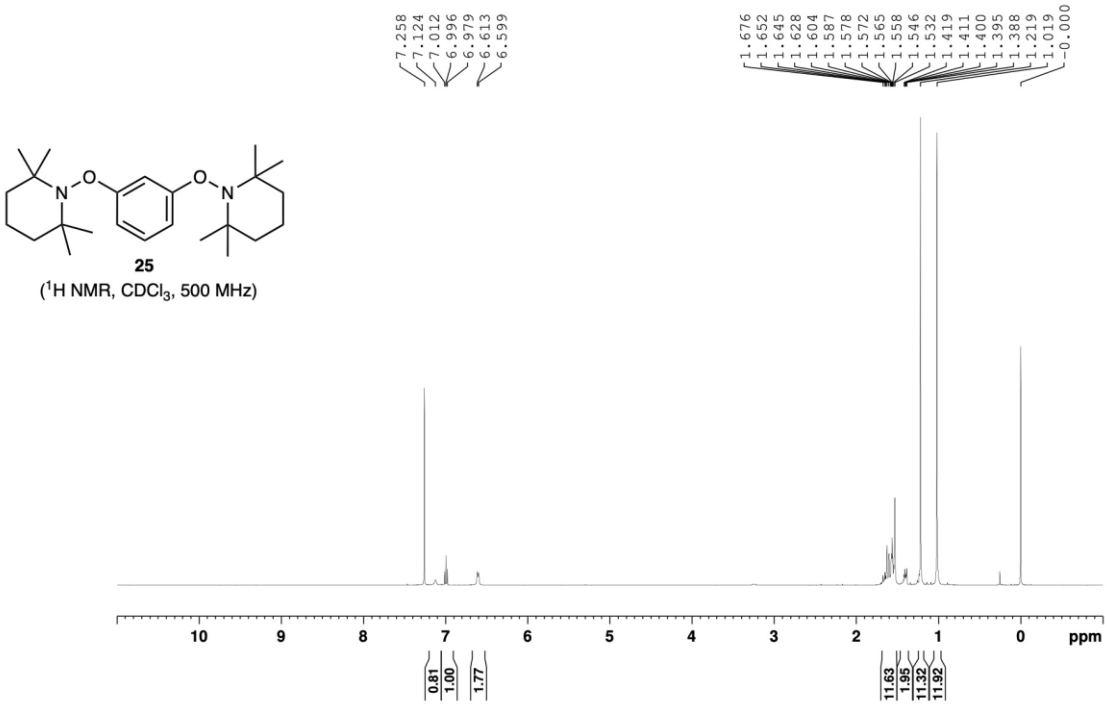
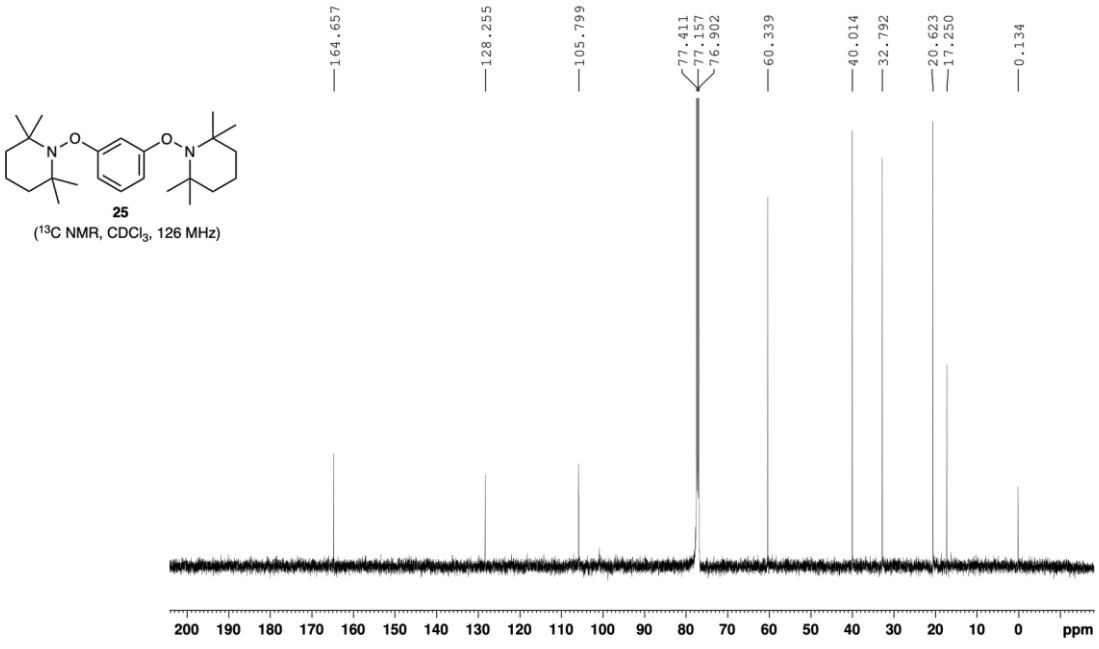
7.763
7.760
7.759
7.756
7.747
7.744
7.743
7.740
7.712
7.697
7.681
7.639
7.637
7.624
7.623
7.610
7.608
7.459
7.455
7.445
7.441
7.438
7.428
7.424
7.263
6.692
6.691
6.675
6.673
1.610
0.354
-0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
0.95
0.99
0.93
0.97
0.99
1.00
1.01
1.00
9.04


TMS
Br
O
O
9
(13C NMR, CDCl3, 126 MHz)
165.745
148.606
138.613
137.263
135.798
134.623
133.109
133.063
132.920
132.214
131.226
126.209
120.800
77.412
77.158
76.904
0.140
-1.207
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



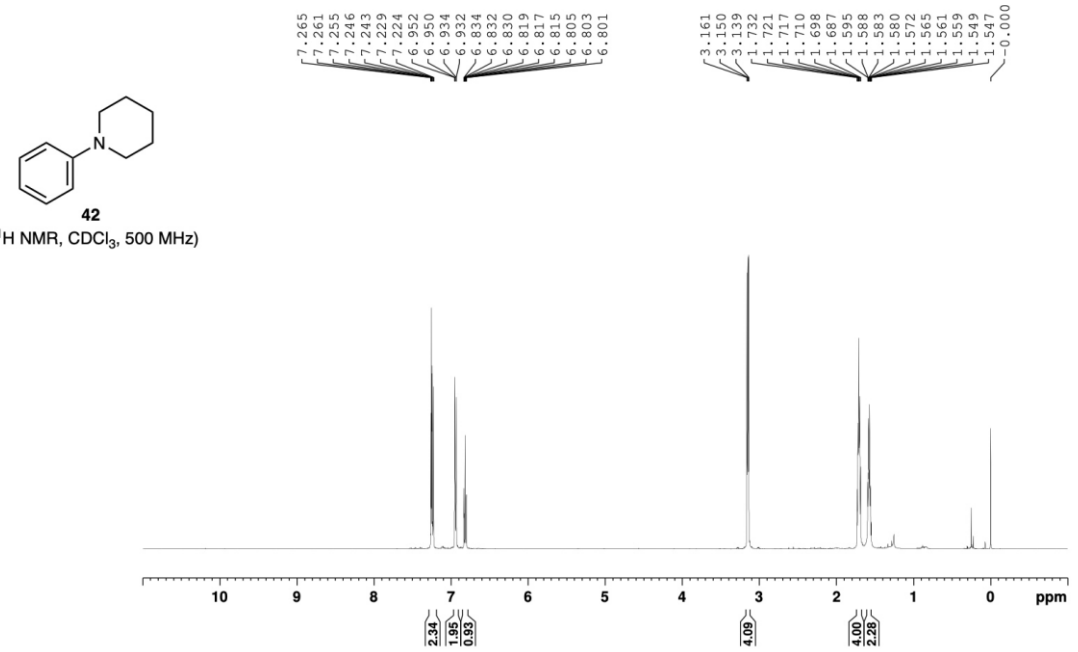
25

(^{1}H NMR, $CDCl_3$, 500 MHz)



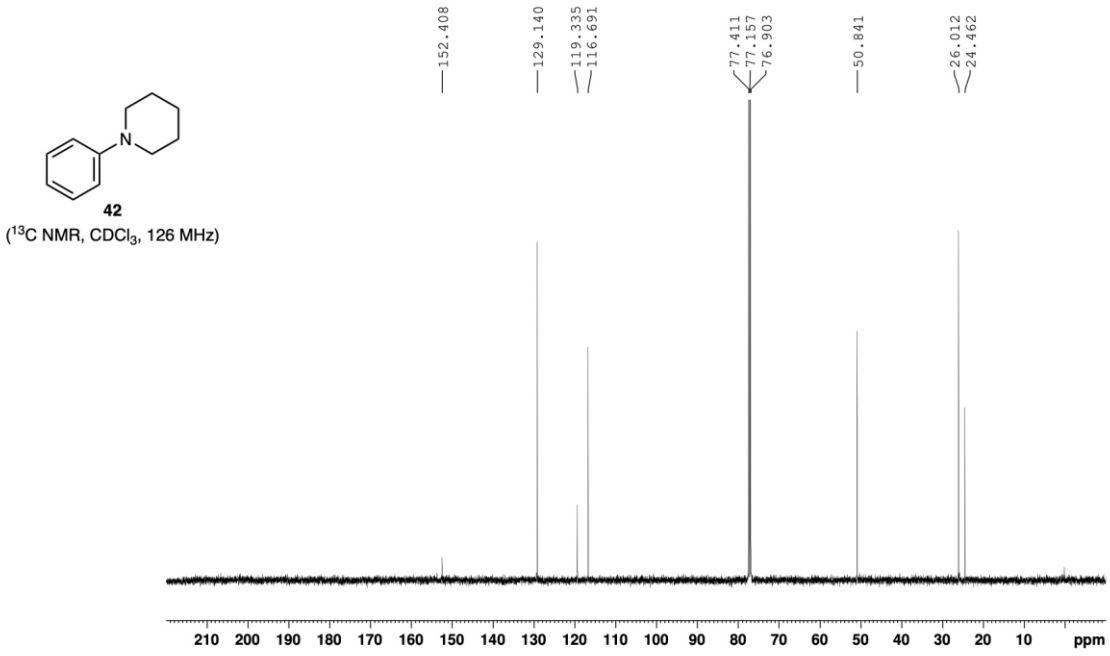
25

(^{13}C NMR, $CDCl_3$, 126 MHz)



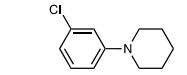
42

(^{1}H NMR, $CDCl_3$, 500 MHz)



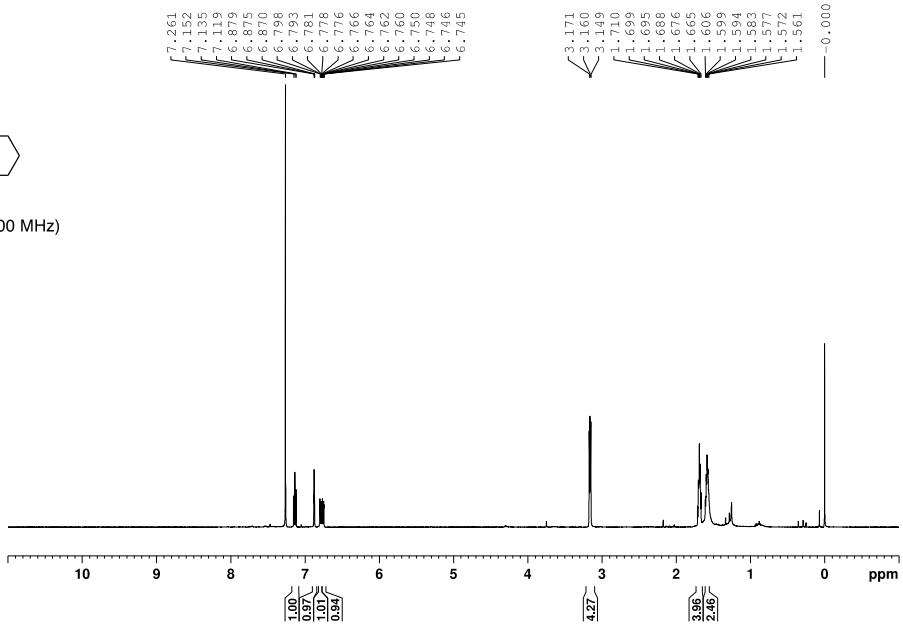
42

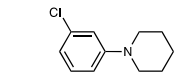
(^{13}C NMR, $CDCl_3$, 126 MHz)



S8

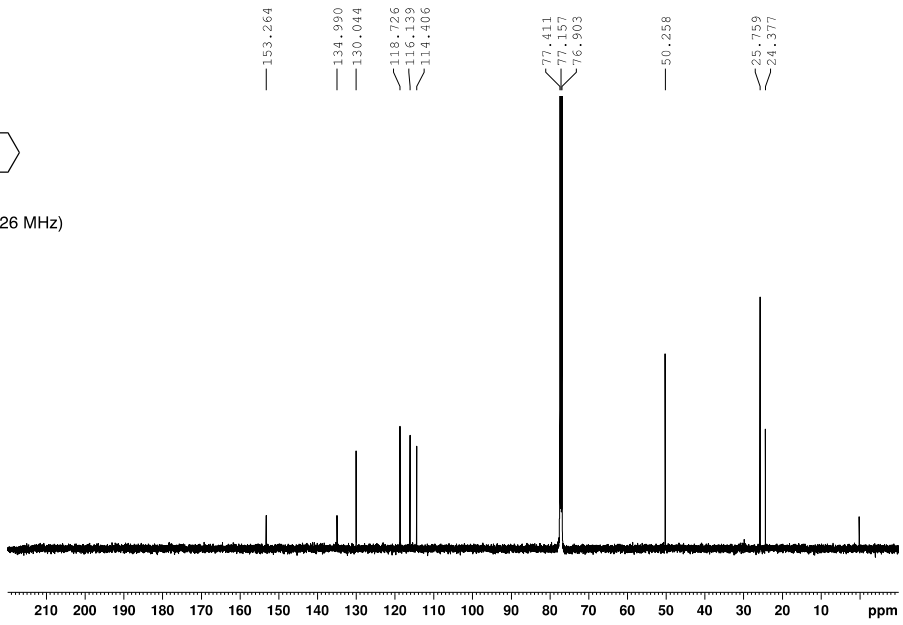
(^{1}H NMR, $CDCl_3$, 500 MHz)

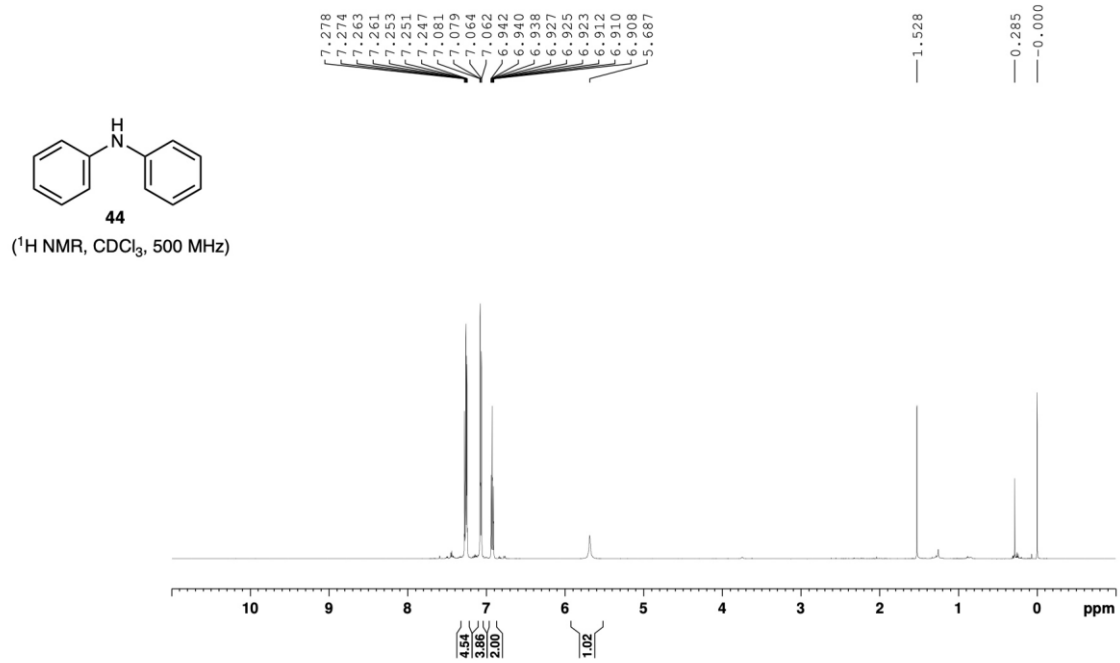




S8

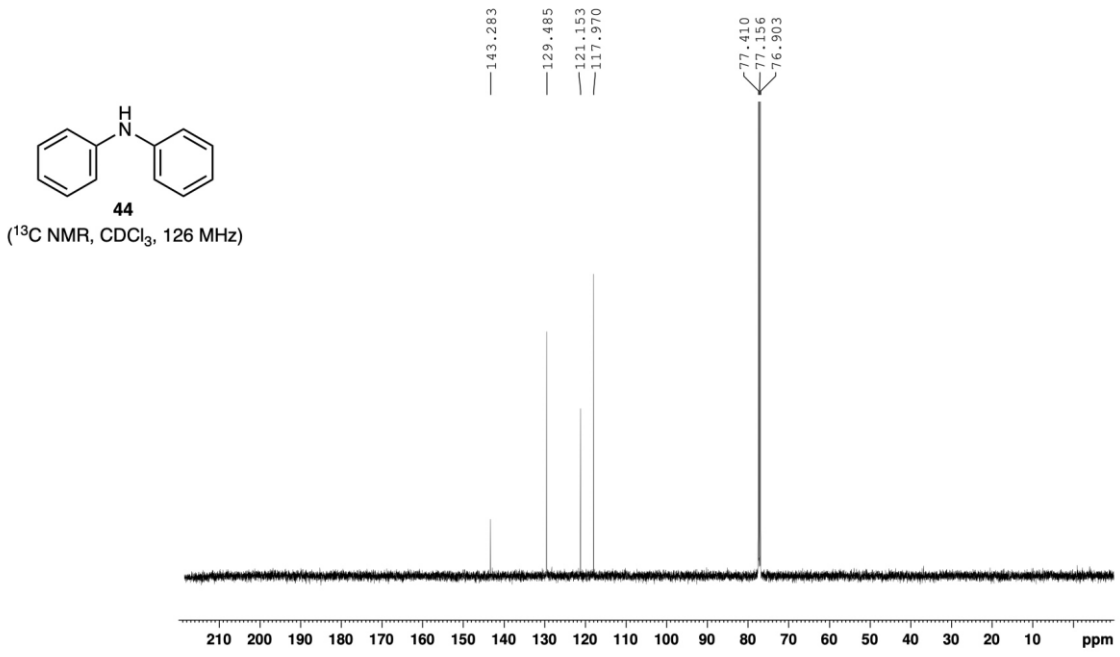
(^{13}C NMR, $CDCl_3$, 126 MHz)





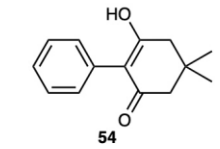
44

(^{1}H NMR, $CDCl_3$, 500 MHz)



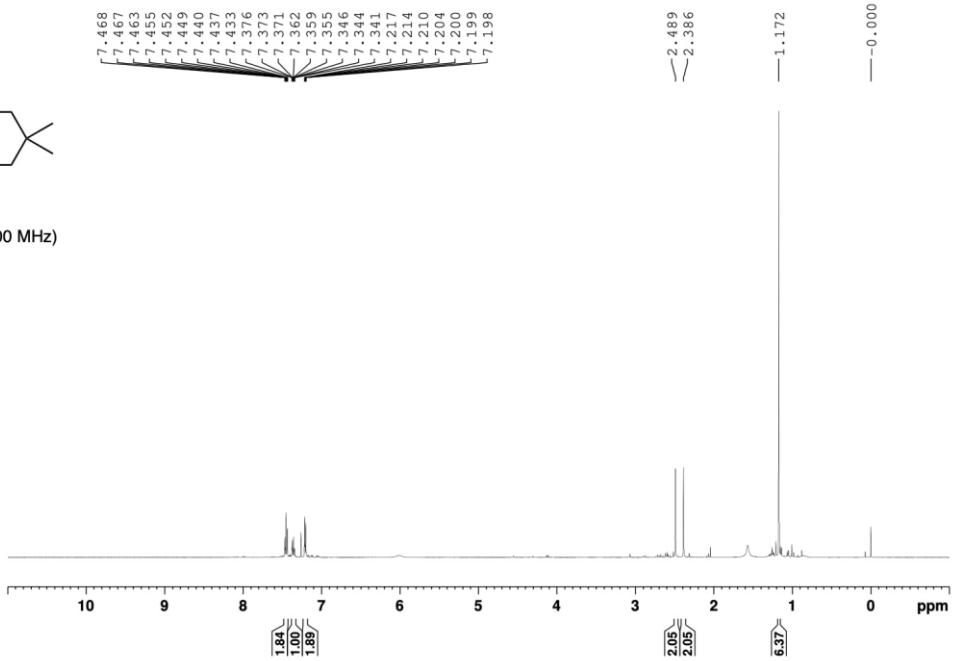
44

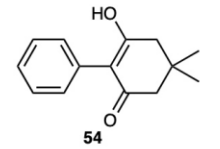
(^{13}C NMR, $CDCl_3$, 126 MHz)



54

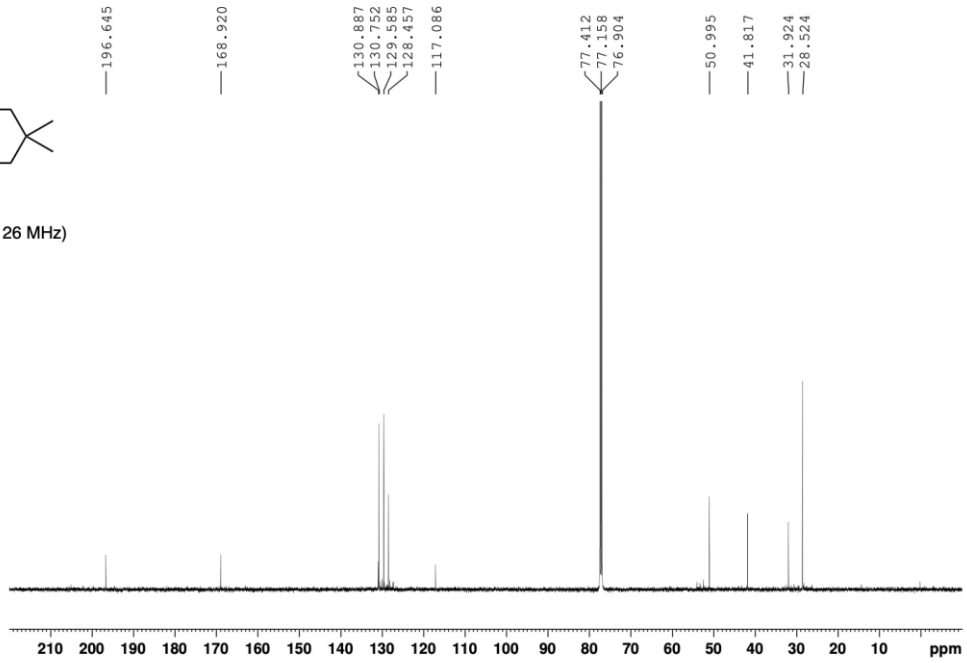
(^{1}H NMR, $CDCl_3$, 500 MHz)

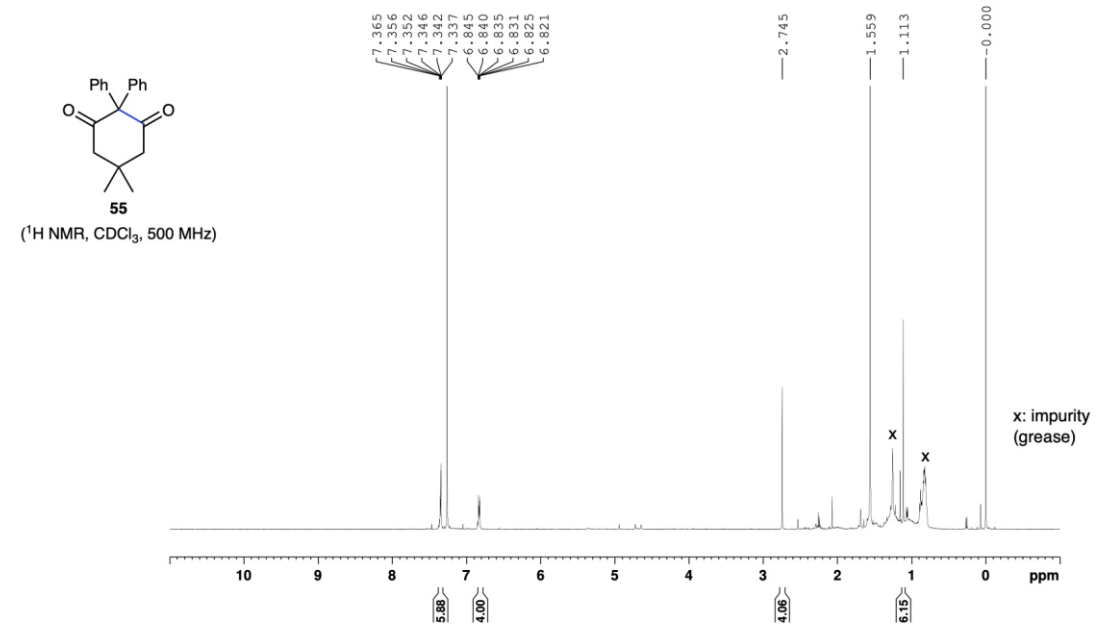


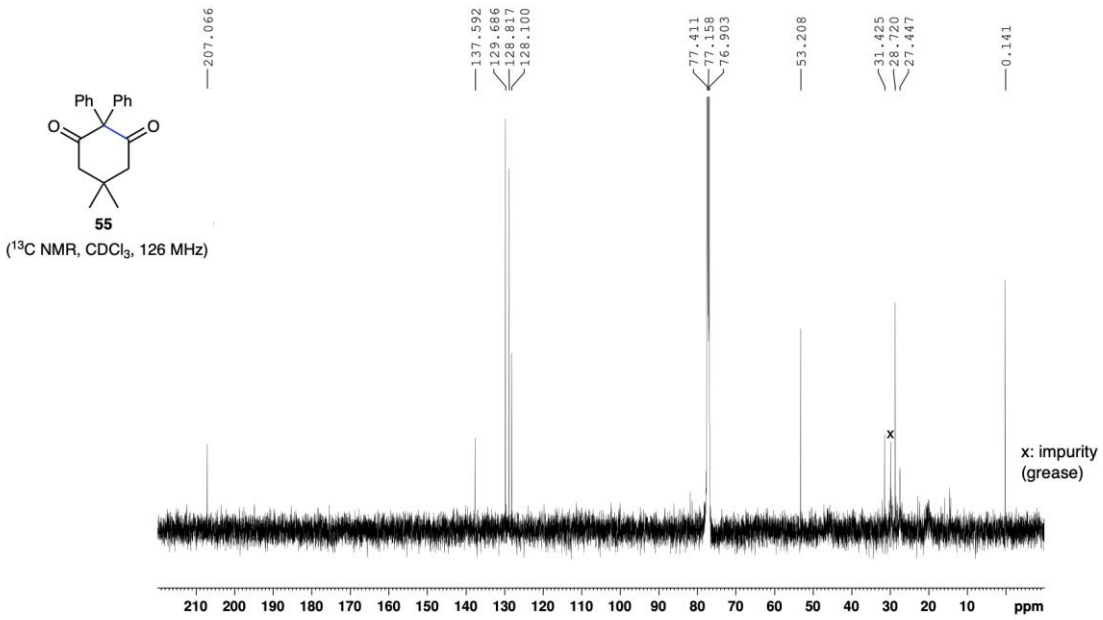


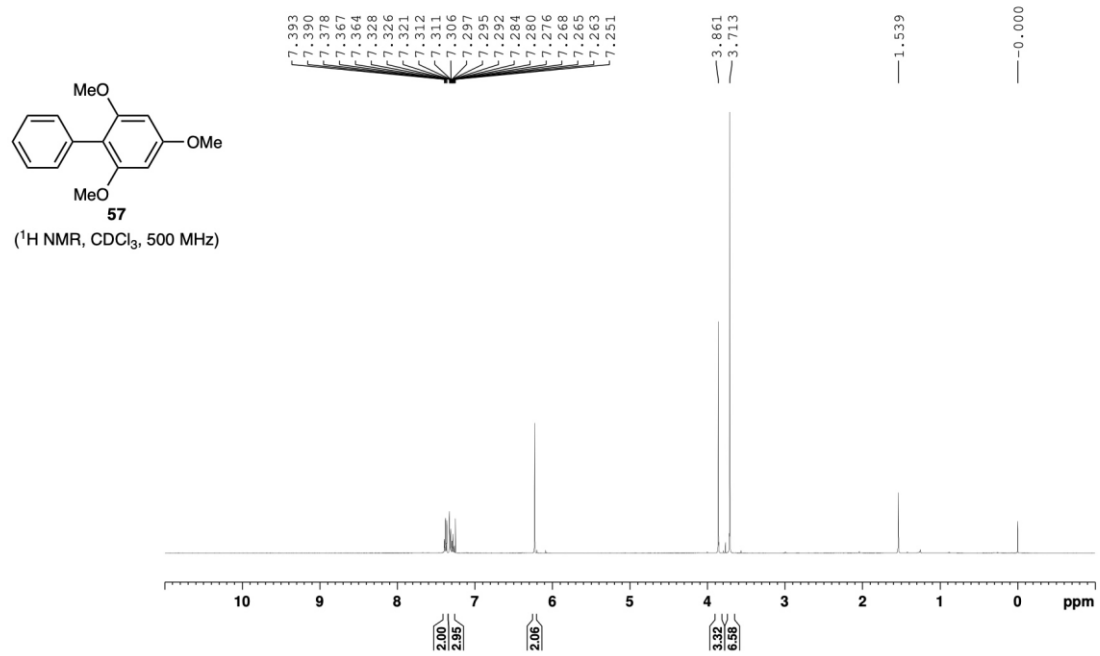
54

(^{13}C NMR, $CDCl_3$, 126 MHz)



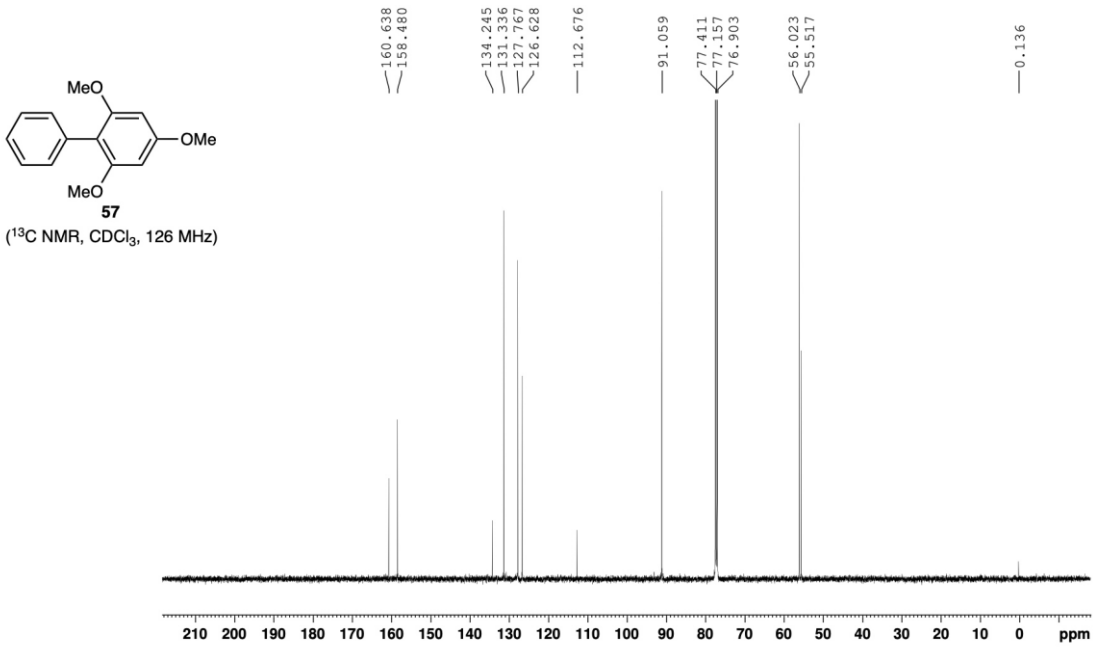

Ph
Ph
O
O
55
(1H NMR, CDCl3, 500 MHz)
7.365
7.356
7.352
7.346
7.342
7.337
6.845
6.840
6.835
6.831
6.825
6.821
2.745
1.559
1.113
0.000
x: impurity
(grease)
x
x
10
9
8
7
6
5
4
3
2
1
0
ppm
5.88
4.00
4.06
6.15


Ph
Ph
O
O
55
(13C NMR, CDCl3, 126 MHz)
207.066
137.592
129.686
128.817
128.100
77.411
77.158
76.903
53.208
31.425
28.720
27.447
0.141
x: impurity
(grease)
x
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



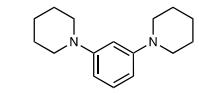
57

(^{1}H NMR, $CDCl_3$, 500 MHz)



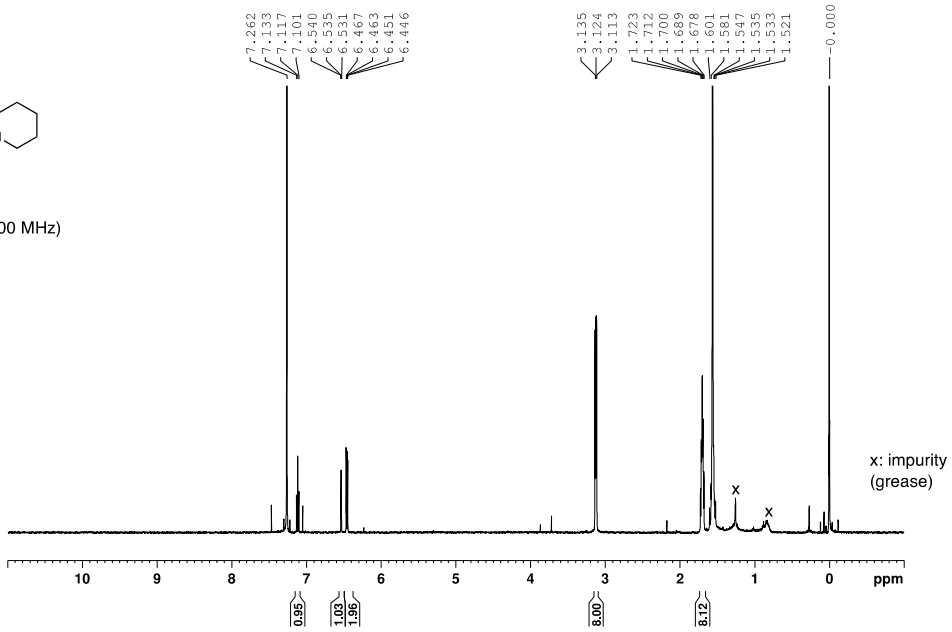
57

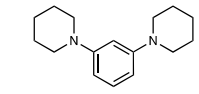
(^{13}C NMR, $CDCl_3$, 126 MHz)



66

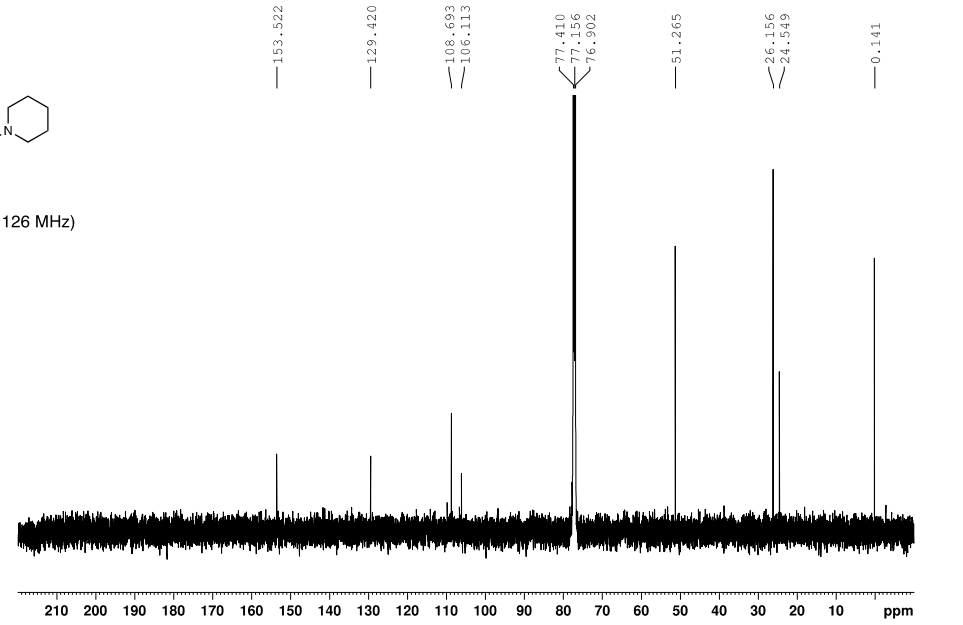
(^{1}H NMR, $CDCl_3$, 500 MHz)

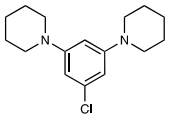




66

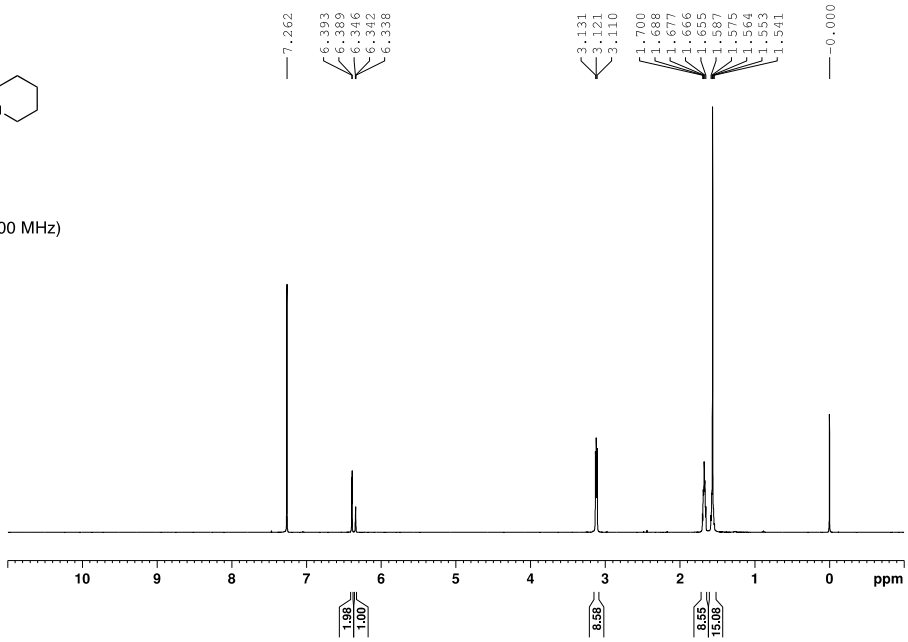
(^{13}C NMR, $CDCl_3$, 126 MHz)

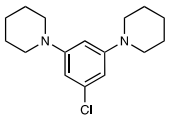




67

(^{1}H NMR, $CDCl_3$, 500 MHz)





67

(^{13}C NMR, $CDCl_3$, 126 MHz)