**Supporting Information**

# Ullmann-type *N*-Arylation of Anilines with Alkyl(aryl)sulfonium Salts

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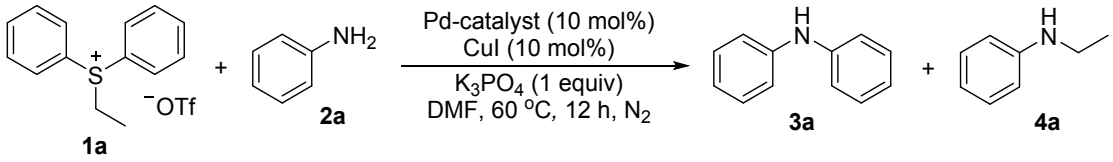
## 1. General Information.

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ on a 500 or 400 MHz (for $^1H$), 471 (for $^{19}F$), and 126 or 101 MHz (for $^{13}C$) spectrometer. All chemical shifts were reported in ppm relative to TMS (0 ppm for $^1H$ NMR) or $PhCF_3$ (-63.5 ppm for $^{19}F$ NMR) as an internal or external standard. The HPLC experiments were carried out on a Wufeng LC-100 II instrument (column: Shodex, C18, 5 μm, 4.6 × 250 mm), and the yields of product were determined by using the corresponding pure compound as an external standard. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. Melting points were measured and uncorrected. MS experiments were performed on a TOF-Q ESI instrument. Alkylphenysulfonium triflates (**1a**-**h**) were prepared according to the literatures.[1] Solvents were dried before use according to the literature.[2] Other reagents in the reactions were all purchased from the commercial sources and used without further purification.

## 2. Screening of the optimal reaction conditions for *N*-phenylation of aniline

**Table S1.** *N*-Phenylation of **2a** by **1a** in the presence of different catalysts.[a]

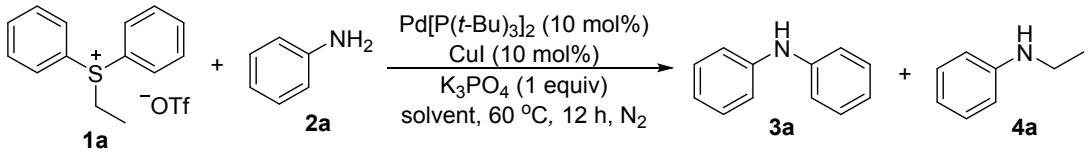



| Entry | Pd-catalyst | Yield (**3a**, %) | Yield (**4a**, %) |
|---|---|---|---|
| 1[b] | $Pd[P(t\text{-}Bu)_3]_2$ | trace | 41 |
| 2 | $Pd[P(t\text{-}Bu)_3]_2$ | 7 | 16 |
| 3 | $Pd(PPh_3)_4$ | 0 | 49 |
| 7 | $Pd(Pcy_3)_2$ | 0 | 57 |
| 4 | $Pd_2(dba)_3$ | trace | 43 |
| 5 | $Pd(PPh_3)_2Cl_2$ | 0 | 42 |
| 6 | $Pd(OAc)_2$ | 0 | 53 |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Pd-catalyst (0.02 mmol, 10 mol%), CuI (0.02 mmol, 10 mol%), $K_3PO_4$ (0.2 mmol), DMF (2 mL), 60 °C, $N_2$, 12 h. The yields were determined by HPLC (λ = 284 nm, water / methanol = 15 / 85 (v / v))

using diphenylamine (**3a**, $t_R$ = 5.31 min) and *N*-ethylaniline (**4a**, $t_R$ = 4.61 min) as external standards, respectively. [b] Without CuI.

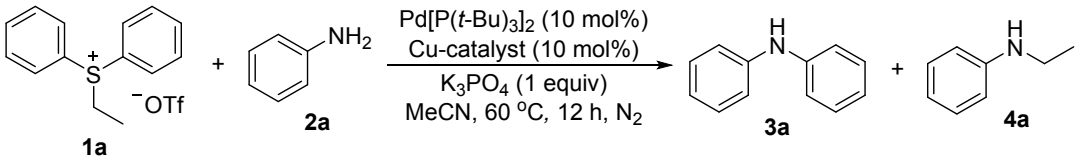
**Table S2.** The solvent effects on *N*-phenylation of aniline by **1a**.[a]




| Entry | solvent | Yield (**3a**, %) | Yield (**4a**, %) |
|---|---|---|---|
| 1 | DMF | 7 | 16 |
| 2 | Toluene | trace | 67 |
| 3 | 1,4-dioxane | 10 | 67 |
| 4 | NMP | 4 | 58 |
| 5 | THF | 3 | 60 |
| 6 | DCE | 2 | 42 |
| 7 | MeCN | 52 | 46 |
| 8 | PhCN | 2 | 44 |
| 9 | $MeNO_2$ (degassing) | 0 | 7 |
| 10 | DMSO | 0 | 41 |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), $Pd[P(t\text{-}Bu)_3]_2$ (0.02 mmol, 10 mol%), CuI (0.02 mmol, 10 mol%), $K_3PO_4$ (0.2 mmol), solvent (2 mL), 60 °C, $N_2$, 12 h. The yields were determined by HPLC (λ = 284 nm, water / methanol = 15 / 85 (v / v)) using diphenylamine (**3a**, $t_R$ = 5.31 min) and *N*-ethylaniline (**4a**, $t_R$ = 4.61 min) as external standards, respectively.

**Table S3.** *N*-Phenylation of **2a** by **1a** in the presence of different copper catalysts.[a]

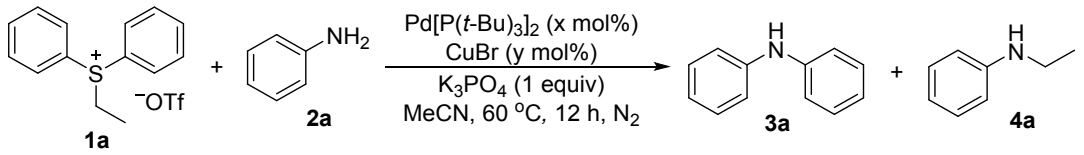



| Entry | Cu-catalyst | Yield (**3a**, %) | Yield (**4a**, %) |
|---|---|---|---|
| 1 | CuI | 52 | 46 |
| 2 | CuBr | 76 | 18 |
| 3 | CuCl | 52 | 22 |
| 4 | CuOAc | 62 | 17 |
| 5 | CuOTf | 57 | 11 |
| 6 | $CuCl_2$ | 58 | 32 |
| 7 | $Cu(OAc)_2$ | 56 | 20 |

| | | | |
|---|---|---|---|
| 8 | $Cu(acac)_2$ | 39 | 39 |
| 9 | CuSCN | 27 | 39 |
| 10 | CuCN | 57 | 17 |
| 11 | CuTc | 68 | 32 |
| 12 | $CuBr_2$ | 47 | 14 |
| 13 | Cu | 62 | 28 |
| 14 | $Cu(MeCN)_4PF_6$ | 57 | 15 |
| 15 | $Cu_2O$ | 65 | 28 |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Pd[P(*t*-$Bu_3)_2$] (0.02 mmol, 10 mol%), Cu-catalyst (0.02 mmol, 10 mol%), $K_3PO_4$ (0.2 mmol), MeCN (2 mL), 60 °C, $N_2$, 12 h. The yields were determined by HPLC (λ = 284 nm, water / methanol = 15 / 85 (v / v)) using diphenylamine (**3a**, $t_R$ = 5.31 min) and *N*-ethylaniline (**4a**, $t_R$ = 4.61 min) as external standards, respectively.

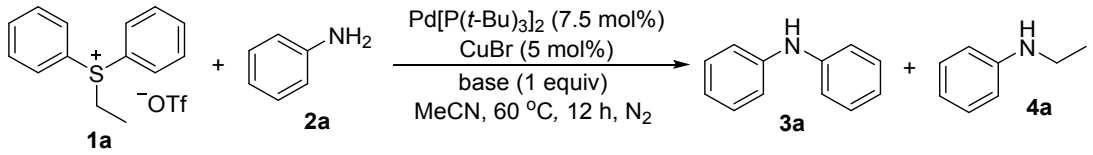
**Table S4.** *N*-Phenylation of **2a** by **1a** with different catalysts loadings.[a]




| Entry | x | y | Yield (**3a**, %) | Yield (**4a**, %) |
|---|---|---|---|---|
| 1 | 10 | 10 | 76 | 18 |
| 2 | 10 | 20 | 12 | 38 |
| 3 | 10 | 7.5 | 77 | 17 |
| 4 | 10 | 5 | 60 | 9 |
| 5 | 7.5 | 7.5 | 64 | 18 |
| 6 | 7.5 | 5 | 77 | 8 |
| 7 | 5 | 7.5 | 51 | 31 |
| 8 | 10 | 0 | 51 | 43 |
| 9 | 0 | 7.5 | trace | 59 |
| 10 | 0 | 0 | 0 | 43 |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Pd[P(*t*-$Bu_3)_2$] (x mol%), CuBr (y mol%), $K_3PO_4$ (0.2 mmol), MeCN (2 mL), 60 °C, $N_2$, 12 h. The yields were determined by HPLC (λ = 284 nm, water / methanol = 15 / 85 (v / v)) using diphenylamine (**3a**, $t_R$ = 5.31 min) and *N*-ethylaniline (**4a**, $t_R$ = 4.61 min) as external standards, respectively.

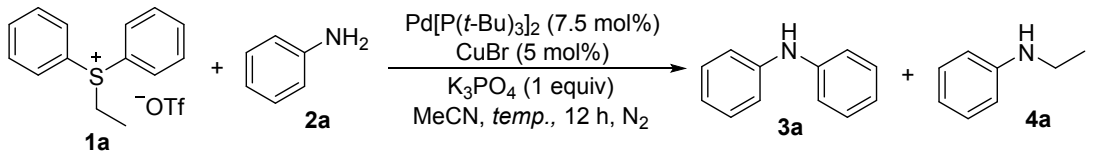
**Table S5.** *N*-Phenylation of **2a** by **1a** in the presence of different bases.[a]




| Entry | Base | Yield (**3a**, %) | Yield (**4a**, %) |
|---|---|---|---|
| 1 | $K_3PO_4$ | 77 | 8 |
| 2 | $K_2HPO_4$ | trace | 46 |
| 3 | $K_2CO_3$ | 51 | 29 |
| 4 | $Cs_2CO_3$ | 19 | 19 |
| 5 | $Na_2CO_3$ | 3 | 65 |
| 6 | $NaHCO_3$ | trace | 38 |
| 7 | DBU | trace | 48 |
| 8 | KOH | 30 | 26 |
| 9 | NaOAc | trace | 58 |
| 10 | KF | trace | 31 |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Pd[P(*t*-$Bu_3$)$_2$] (0.015 mmol, 7.5 mol%), CuBr (0.01 mmol, 5 mol%), base (0.2 mmol), MeCN (2 mL), 60 °C, $N_2$, 12 h. The yields were determined by HPLC (λ = 284 nm, water / methanol = 15 / 85 (v / v)) using diphenylamine (**3a**, $t_R$ = 5.31 min) and *N*-ethylaniline (**4a**, $t_R$ = 4.61 min) as external standards, respectively.

**Table S6.** *N*-Phenylation of **2a** by **1a** at different reaction temperatures.[a]

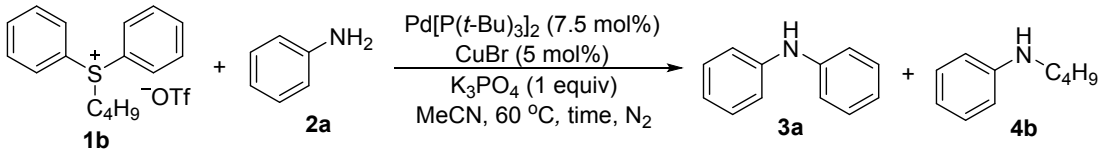



| Entry | *Temp.* | Yield (**3a**, %) | Yield (**4a**, %) |
|---|---|---|---|
| 1 | 40 | 41 | 21 |
| 2 | 50 | 66 | 31 |
| 3 | 60 | 77 | 8 |
| 4 | 70 | 51 | 19 |
| 5 | 80 | 43 | 26 |
| 6[b] | 60 | 94 | 4 |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), Pd[P(*t*-$Bu_3$)$_2$] (0.015 mmol, 7.5 mol%), CuBr (0.01 mmol, 5 mol%), $K_3PO_4$ (0.2 mmol), MeCN (2 mL), $N_2$, 12 h. The yields were determined by HPLC (λ = 284 nm, water / methanol = 15 / 85 (v / v)) using diphenylamine (**3a**, $t_R$ = 5.31 min) and *N*-ethylaniline (**4a**, $t_R$ = 4.61 min) as external standards, respectively. [b] Reaction conditions: **1a** (0.24 mmol), **2a** (0.2

mmol), Pd[P(*t*-Bu$_3$)$_2$] (0.015 mmol, 7.5 mol%), CuBr (0.01 mmol, 5 mol%), $K_3PO_4$ (0.24 mmol), MeCN (2 mL), $N_2$, 16 h.

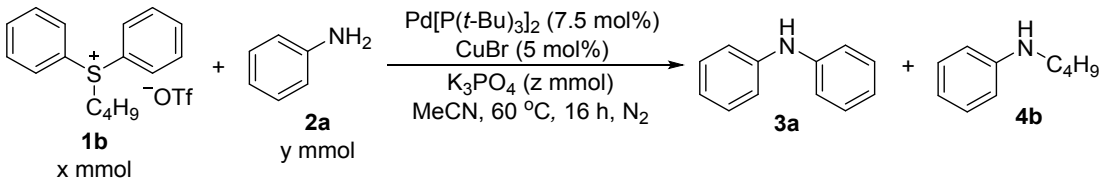
**Table S7.** N-Phenylation of **2a** by **1b** at different reaction times.[a]




| Entry | Time | Yield (**3a**, %) | Yield (**4b**, %) |
|---|---|---|---|
| 1 | 8 | 37 | trace |
| 2 | 12 | 89 | 6 |
| 3 | 16 | 93 | 7 |
| 4 | 20 | 87 | 4 |
| 5 | 24 | 66 | 4 |

[a] Reaction conditions: **1b** (0.3 mmol), **2a** (0.2 mmol), Pd[P(*t*-Bu$_3$)$_2$] (0.015 mmol, 7.5 mol%), CuBr (0.01 mmol, 5 mol%), $K_3PO_4$ (0.2 mmol), MeCN (2 mL), 60 °C, $N_2$. The yields were determined by HPLC (λ = 284 nm, water / methanol = 15 / 85 (v / v)) using diphenylamine (**3a**, $t_R$ = 5.31 min) and *N*-butylaniline (**4b**, $t_R$ = 5.85 min) as external standards, respectively.

**Table S8**. *N*-Phenylation of **2a** by **1a** with different reactant ratios.[a]



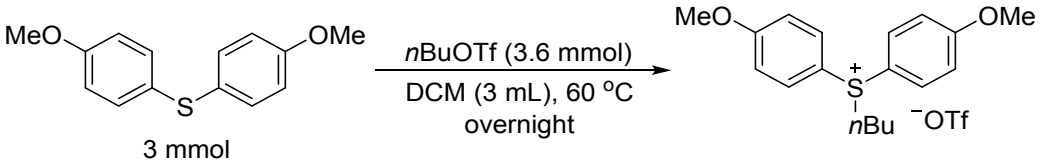

| Entry | x : y : z | Yield (**3a**, %) | Yield (**4b**, %) |
|---|---|---|---|
| 1 | 0.3 : 0.2 : 0.2 | 93 | 7 |
| 2 | 0.24 : 0.2 : 0.2 | 91 | 5 |
| 3 | 0.24 : 0.2 : 0.24 | >99 (94[b]) | 0 |
| 4 | 0.26 : 0.2 : 0.24 | >99 | 0 |
| 5 | 0.2 : 0.24 : 0.2 | 66 | 6 |
| 6 | 0.2 : 0.24 : 0.24 | 90 | 7 |
| 7[c] | 0.24 : 0.2 : 0.24 | 84 | 15 |
| 8[d] | 0.24 : 0.2 : 0.24 | 0 | 42 |
| 9[e] | 0.24 : 0.2 : 0.24 | 0 | 49 |

[a] Reaction conditions: **1b** (x mmol), **2a** (y mmol), Pd[P(*t*Bu)$_3$]$_2$ (0.015 mmol, 7.5 mol%), CuBr (0.01 mmol, 5 mol%), $K_3PO_4$ (z mmol), MeCN (2 mL), 60 °C, $N_2$, 16 h.

The yields were determined by HPLC (λ = 284 nm, water / methanol = 15 / 85 (v / v)) using diphenylamine (**3a**, $t_R$ = 5.31 min) and *N*-butylaniline (**4b**, $t_R$ = 5.85 min) as external standards, respectively. [b] Isolated yield. [c] Without CuBr. [d] Without $Pd[P(tBu)_3]_2$. [e] Without $Pd[P(tBu)_3]_2$ and CuBr.

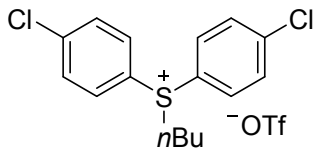
**3. Procedures for the synthesis of alkylarylsulfonium triflates (1i-u)**.

**3.1. Typical procedure for the synthesis of 1i and 1j**




A sealed tube was charged with butyl trifluoromethanesulfonate (0.74 g, 3.6 mmol), bis(4-methoxyphenyl)sulfane (0.74 g, 3.0 mmol) and DCM (3 mL) with vigorous stirring. The mixture was heated at 60 °C overnight, cooled to room temperature, and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using a mixture of dichloromethane / acetonitrile = 3 / 1 (v / v) as eluents to provide butylbis(4-methoxyphenyl)sulfonium trifluoromethanesulfonate (**1i**) as a light yellow oil (1.2 g, 90%). $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.93 (d, *J* = 9.1 Hz, 4H), 7.08 (d, *J* = 9.1 Hz, 4H), 4.00 (t, *J* = 7.5 Hz, 2H), 3.79 (s, 6H), 1.63 (m, 2H), 1.49 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.2 (s, 3F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 164.4, 132.5, 120.9 (q, *J* = 320.3 Hz), 117.0, 114.7, 55.9, 45.3, 26.6, 21.2, 13.4. IR (KBr): 3098, 3053, 2965, 2939, 2876, 2845, 1591, 1576, 1498, 1464, 1444, 1417, 1309, 1262, 1225, 1179, 1159, 1081, 1030, 835, 800, 756 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{18}H_{23}OS]^+$ ($[M]^+$): 303.1413; found: 303.1418.

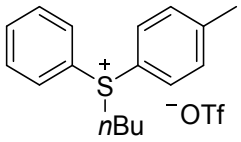
**Butylbis(4-chlorophenyl)sulfonium trifluoromethanesulfonate (1j)**




White solid (0.78 g, 57%), from bis(4-chlorophenyl)sulfane (0.48 g, 3 mmol) and butyl trifluoromethanesulfonate (0.74 g, 3.6 mmol). M.p. 100-102 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.07 (d, *J* = 8.6 Hz, 4 H), 7.64 (d, *J* = 8.6 Hz, 4H), 4.24 (t, *J* = 7.5 Hz, 2H), 1.71 (m, 2H), 1.56 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.2 (s, 3F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 142.1, 132.2, 132.0, 122.5,

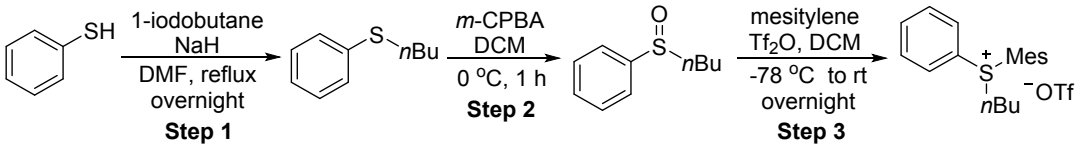
120.8 (q, $J$ = 320.6 Hz), 44.8, 26.6, 21.4, 13.4. IR (KBr): 3093, 3059, 3023, 2997, 2973, 2954, 2939, 2881, 1570, 1478, 1458, 1422, 1397, 1385, 1364, 1300, 1223, 1207, 1189, 1181, 1161, 1120, 1093, 1075, 1030, 1008, 922, 838, 829, 822, 802, 754, 745, 700 $cm^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{16}H_{17}Cl_2S]^+$ ($[M]^+$): 311.0423; found: 311.0421.

### 3.2. Typical procedure for the synthesis of 1k




To a stirred mixture of phenyl(*p*-tolyl)sulfane (3.0 mmol, 0.6 g) and butyl formate (6.0 mmol, 0.6 g) was added trifluoromethanesulfonic acid (1.5 mL) at 0 °C. The mixture was warmed to 20 °C for 10 h, poured into distilled water (20 mL), and extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of dichloromethane / acetonitrile = 3 / 1 (v / v) as eluents to give butyl(phenyl)(*p*-tolyl)sulfonium trifluoromethanesulfonate (**1k**) as an orange oil (0.43 g, 36%). $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.99 (dm, $J$ = 7.9 Hz, 2H), 7.90 (d, $J$ = 8.4 Hz, 2H), 7.71-7.64 (m, 3H), 7.48 (d, $J$ = 8.3 Hz, 2H), 4.19 (t, $J$ = 7.5 Hz, 2H), 2.43 (s, 3H), 1.70 (m, 2H), 1.56 (m, 2H), 0.92 (t, $J$ = 7.3 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.2 (s, 3F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 146.4, 134.5, 132.3, 131.5, 130.7, 130.4, 125.0, 120.9 (q, $J$ = 321.3 Hz), 120.5, 45.0, 26.6, 21.7, 21.3, 13.4. IR (KBr): 3090, 3062, 2964, 2935, 2876, 1593, 1494, 1479, 1467, 1447, 1424, 1405, 1384, 1260, 1224, 1157, 1103, 1082, 1030, 813, 755, 700. HRMS-ESI (m/z) calcd. for $[C_{17}H_{21}S]^+$ ($[M]^+$): 257.1358; found: 257.1354.

### 3.3. Typical procedure for the synthesis of 1l




**Step 1:** Under a nitrogen atmosphere, benzenethiol (4.1 mL, 40 mmol) was added slowly to a suspension of NaH (1.9 g, 48 mmol, 60% purity (in oil)) in DMF (40 mL) with vigorously stirring. The mixture was kept at room temperature for 10 minutes

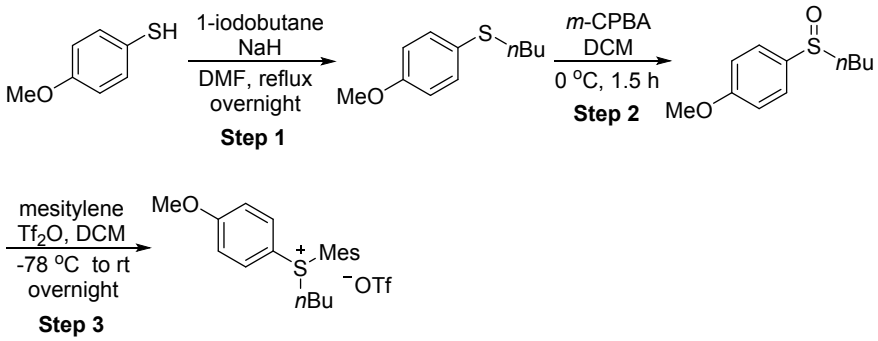
and 1-iodobutane (8.8 g, 48 mmol) was added. The resulting mixture was heated at reflux overnight, cooled to room temperature, quenched by a saturated aqueous solution of NaCl (200 mL), and extracted with ethyl acetate (3 × 80 mL). The extracts were washed with water, dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether as eluent to give butyl(phenyl)sulfane (6.6 g, 99%) as a colorless oil.

**Step 2:** To a solution of butyl(phenyl)sulfane (6.6 g, 40 mmol) in DCM (265 mL) was slowly added *m*-CPBA (8.9 g, 44 mmol, 85% purity) at 0 °C. The mixture was reacted at 0 °C for 1 h, neutralized with a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 100 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 5 / 1 (v / v) as eluents to afford (butylsulfinyl)benzene (6.5 g, 92%) as a light yellow oil.

**Step 3:** Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (24 mmol, 4.0 mL) was added slowly to a solution of (butylsulfinyl)benzene (3.6 g, 20 mmol) and mesitylene (7.2 g, 60 mmol) in DCM (200 mL) at -78 °C. The mixture was reacted at room temperature overnight, neutralized by a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM (10 mL) / diethyl ether (300 mL) system to afford butyl(mesityl)(phenyl)sulfonium trifluoromethanesulfonate (**1l**) as a white solid (5.7 g, 66%).

M.p.: 114-116 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.60 (m, 5H), 7.15 (s, 2H), 4.65 (m, 1H), 4.01 (m, 1H), 2.40 (m, 9H), 1.84 (m, 2H), 1.60 (m, 2H), 0.94 (t, $J$ = 7.0 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.2 (s, 3F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 147.1, 144.1, 132.8, 132.5, 131.2, 127.2, 125.3, 120.9 (q, $J$ = 321.3 Hz), 114.8, 42.6, 26.8, 21.6, 21.4, 21.2, 13.5. IR (KBr): 3093, 3070, 3011, 2970, 2941, 2879, 1600, 1479, 1468, 1458, 1446, 1418, 1401, 1383, 1276, 1255, 1223, 1185, 1157, 1103, 1030, 997, 917, 871, 860, 759, 741, 709, 685 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{19}H_{25}S]^+$ ($[M]^+$): 285.1671; found: 285.1671.

### 3.4. Typical procedure for the synthesis of 1m



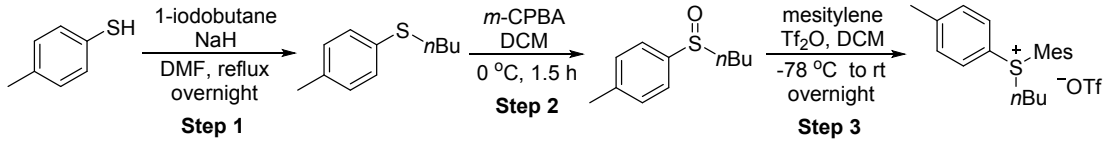

**Step 1:** Under a nitrogen atmosphere, 4-methoxybenzenethiol (2.8 g, 20 mmol) was added slowly to a suspension of NaH (0.96 g, 24 mmol, 60% purity) in DMF (20 mL) with vigorously stirring. The mixture was kept at room temperature for 10 minutes and 1-iodobutane (4.4 g, 24 mmol) was added. The resulting mixture was heated at reflux overnight, cooled to room temperature, quenched with a saturated aqueous solution of NaCl (50 mL), and extracted with ethyl acetate (3 × 40 mL). The extracts were washed with water, dried over anhydrous $Na_2SO_4$, and concentrated to dryness under reduced pressure. The crude product was used in the next step without further purification.

**Step 2:** To a solution of the crude product in DCM (130 mL) was slowly added *m*-CPBA (4.5 g, 22 mmol, 85% purity) at 0 °C. The mixture was stirred at 0 °C for 1.5 h, neutralized with a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduce pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 4 / 1 (v / v) as eluents to afford 1-(butylsulfinyl)-4-methoxybenzene as a light yellow oil (4.3 g, 100%).

**Step 3:** Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (12 mmol, 2.0 mL) was slowly added to a solution of 1-(butylsulfinyl)-4-methoxybenzene (2.1 g, 10 mmol) and mesitylene (3.6 g, 30 mmol) in DCM (100 mL) at -78 °C. The mixture was reacted at room temperature overnight, neutralized by a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of DCM / acetonitrile = 3 / 1 (v / v) as eluents to afford butyl(mesityl)(4-methoxyphenyl)sulfonium trifluoromethanesulfonate (**1m**) as a while solid (3.3 g, 71%).

M.p.: 73-76 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.53 (d, *J* = 9.0 Hz, 2H), 7.11 (s, 2H), 7.09 (d, *J* = 9.0 Hz, 2H), 4.48 (m, 1H), 3.98 (m, 1H), 3.83 (s, 3H), 2.41 (s, 6H), 2.36 (s, 3H), 1.78 (m, 1H), 1.60-1.54 (m, 3H), 0.92 (t, *J* = 6.9 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.2 (s, 3F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 162.9, 146.8, 143.8, 132.8, 129.3, 120.8 (q, *J* = 321.3 Hz), 116.8, 115.6, 114.3, 55.9, 42.4, 26.8, 21.5, 21.3, 21.1, 13.5. IR (KBr): 3088, 3052, 2961, 2935, 2877, 1601, 1492, 1465, 1455, 1418, 1401, 1382, 1298, 1276, 1257, 1224, 1188, 1159, 1149, 1100, 1083, 1030, 1013, 970, 919, 897, 860, 833, 808, 791, 754, 737, 716, 704, 696 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{20}H_{27}OS]^+$ ([M]$^+$): 315.1777; found: 315.1779.

### 3.5. Typical procedure for the synthesis of 1n



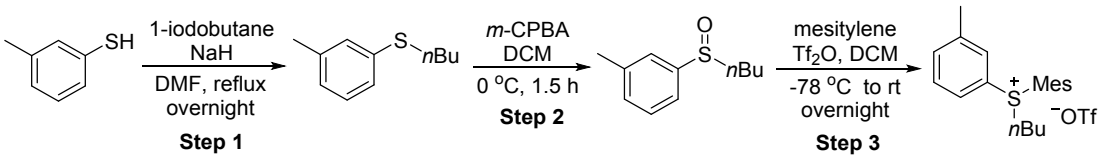

**Step 1:** Under a nitrogen atmosphere, a solution of 4-methylbenzenethiol (4.9 g, 40 mmol) in DMF (10 mL) was added slowly to a suspension of NaH (1.9 g, 48 mmol, 60% purity) in DMF (30 mL) with vigorously stirring. The mixture was kept at room temperature for 10 minutes and 1-iodobutane (8.8 g, 48 mmol) was added. The resulting mixture was heated at reflux overnight, cooled to room temperature, quenched with a saturated aqueous solution of NaCl (100 mL), and extracted with ethyl acetate (3 × 80 mL). The extracts were washed with water, dried over anhydrous $Na_2SO_4$, and concentrated to dryness under reduced pressure. The crude product was used in the next step without further purification.

**Step 2:** To a solution of the crude product in DCM (250 mL) was slowly added *m*-CPBA (8.9 g, 44 mmol, 85% purity) at 0 °C. The mixture was stirred at 0 °C for 1.5 h, neutralized with a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 5 / 1 (v / v) as eluents to afford 1-(butylsulfinyl)-4-methylbenzene as a colorless oil (7.0 g, 89%).

**Step 3:** Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (12 mmol, 2.0 mL) was slowly added to a solution of 1-(butylsulfinyl)-4-methylbenzene (2.0 g, 10 mmol) and mesitylene (3.6 g, 30 mmol) in DCM (100 mL) at -78 °C. The mixture

was reacted at room temperature overnight, neutralized by a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of DCM / acetonitrile = 3 / 1 (v / v) as eluents, following by crystallization from a system of DCM (5 mL) and $Et_2O$ (50 mL), to afford butyl(mesityl)(4-methylphenyl)sulfonium trifluoromethanesulfonate (**1n**) as a white solid (3.0 g, 67%). M.p.: 71-73 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.44 (d, $J$ = 8.3 Hz, 2H), 7.38 (d, $J$ = 8.3 Hz, 2H), 7.12 (s, 2H), 4.52 (m, 1H), 3.96 (m, 1H), 2.37-2.36 (m, 12H), 1.78 (m, 1H), 1.59-1.54 (m, 3H), 0.91 (t, $J$ = 6.9 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.2 (s, 3F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 146.9, 144.0, 143.6, 132.8, 131.9, 127.1, 121.5, 120.8 (q, $J$ = 321.2 Hz), 115.0, 42.4, 26.8, 21.6, 21.4, 21.3, 21.1, 13.5. IR (KBr): 3096, 3060, 3040, 2960, 2934, 2874, 1630, 1591, 1580, 1498, 1466, 1416, 1388, 1361, 1306, 1260, 1226, 1186, 1162, 1102, 1083, 1031, 1016, 849, 821, 800, 757, 739 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{20}H_{27}S]^+$ ($[M]^+$): 299.1828; found: 299.1824.

### 3.6. Typical procedure for the synthesis of 1o




**Step 1:** Under a nitrogen atmosphere, 3-methylbenzenethiol (1.9 g, 15 mmol) was added slowly to a suspension of NaH (0.72 g, 18 mmol, 60% purity) in DMF (15 mL) with vigorously stirring. The mixture was kept at room temperature for 10 minutes and 1-iodobutane (3.3 g, 18 mmol) was added. The resulting mixture was heated at reflux overnight, cooled to room temperature, quenched with a saturated aqueous solution of NaCl (50 mL), and extracted with ethyl acetate (3 × 40 mL). The extracts were washed with water, dried over anhydrous $Na_2SO_4$, and concentrated to dryness under reduced pressure. The crude product was used in the next step without further purification.

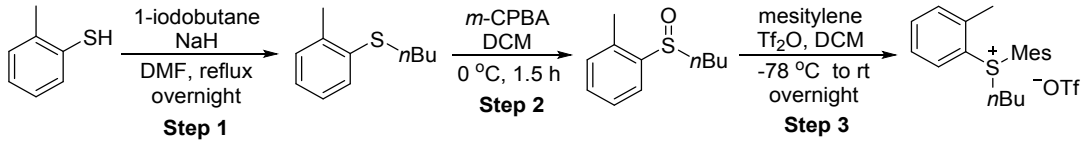
**Step 2:** To a solution of the crude product in DCM (95 mL) was slowly added *m*-CPBA (3.3 g, 16.5 mmol, 85% purity) at 0 °C. The mixture was stirred at 0 °C for 1.5 h, neutralized with a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and

concentrated to dryness under the reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 5 / 1 (v / v) as eluents to afford 1-(butylsulfinyl)-3-methylbenzene as a colorless oil (2.9 g, 99%).

**Step 3:** Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (6 mmol, 1.0 mL) was slowly added to a solution of 1-(butylsulfinyl)-3-methylbenzene (0.98 g, 5 mmol) and mesitylene (1.8 g, 15 mmol) in DCM (50 mL) was at -78 °C. The mixture was reacted at room temperature overnight, neutralized by a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from dichloromethane (5 mL) / diethyl ether (60 mL) system to afford butyl(mesityl)(*m*-tolyl)sulfonium trifluoromethanesulfonate (**1o**) as a white solid (1.3 g, 58%).

M.p.: 111-113 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.48-7.44 (m, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.15 (s, 2H), 4.65 (m, 1H), 4.01 (m, 1H), 2.43 (s, 3H), 2.41 (s, 6H), 2.40 (s, 3H), 1.83 (m, 1H), 1.66-1.55 (m, 3H), 0.95 (t, *J* = 7.2 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.2 (s, 3F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 146.9, 144.1, 142.2, 133.4, 132.8, 130.9, 127.3, 125.0, 124.1, 120.8 (q, *J* = 321.3 Hz), 115.0, 42.5, 26.8, 21.6, 21.4, 21.4, 21.2, 13.5. IR (KBr): 3091, 3060, 3023, 2965, 2941, 2879, 2870, 1599, 1573, 1475, 1457, 1413, 1384, 1362, 1283, 1255, 1222, 1172, 1154, 1099, 1076, 1031, 995, 916, 882, 862, 786, 753, 735, 709 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{20}H_{27}S]^+$ ([M]$^+$): 299.1828; found: 299.1823.

### 3.7. Typical procedure for the synthesis of 1p




**Step 1:** Under a nitrogen atmosphere, 2-methylbenzenethiol (1.9 g, 15 mmol) was added slowly to a suspension of NaH (0.72 g, 18 mmol, 60% purity) in DMF (15 mL) with vigorously stirring. The mixture was kept at room temperature for 10 minutes and 1-iodobutane (3.3 g, 18 mmol) was added. The resulting mixture was heated at reflux overnight, cooled to room temperature, quenched with a saturated aqueous solution of NaCl (50 mL), and extracted with ethyl acetate (3 × 40 mL). The extracts were washed with water, dried over anhydrous $Na_2SO_4$, and concentrated to dryness

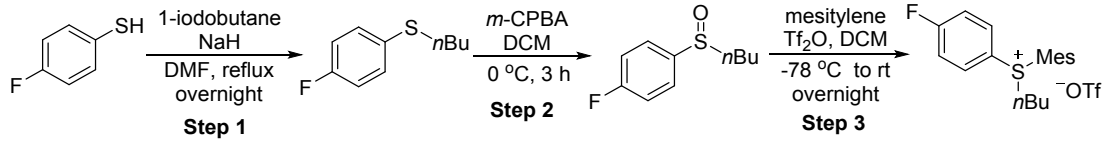
under reduced pressure. The crude product was used in the next step without further purification.

**Step 2:** To a solution of the crude product in DCM (95 mL) was slowly added *m*-CPBA (3.3 g, 16.5 mmol, 85% purity) at 0 °C. The mixture was reacted at 0 °C for 1.5 h, neutralized with a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 5 / 1 (v / v) as eluents to afford 1-(butylsulfinyl)-3-methylbenzene as a light yellow oil (1.3 g, 44%).

**Step 3:** Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (6 mmol, 1.0 mL) was added slowly to a solution of 1-(butylsulfinyl)-3-methylbenzene (0.98 g, 5 mmol) and mesitylene (1.8 g, 15 mmol) in DCM (50 mL) at -78 °C. The mixture was reacted at room temperature overnight, neutralized by a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of DCM / acetonitrile = 3 / 1 (v / v) as eluents, followed by crystallization from a system of DCM (5 mL) and *n*-hexane (50 mL), to afford butyl(mesityl)(o-tolyl)sulfonium trifluoromethanesulfonate (**1p**) as a white solid (1.0 g, 45%).

M.p.: 122-124 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.09 (d, $J$ = 7.8 Hz, 1H), 7.54 (m, 2H), 7.35 (d, $J$ = 7.2 Hz, 1H), 7.04 (s, 2H), 4.31 (m, 1H), 4.10 (m, 1H), 2.37 (s, 6H), 2.31 (s, 3H), 2.18 (s, 3H), 1.85 (m, 1H), 1.61-1.56 (m, 3H), 0.92 (t, $J$ = 6.6 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.2 (s, 3F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 146.4, 143.2, 138.8, 133.3, 132.9, 132.8, 129.4, 129.0, 122.5, 120.8 (q, $J$ = 321.3 Hz), 115.7, 40.6, 26.4, 21.7, 21.3, 20.9, 19.9, 13.5. IR (KBr): 3101, 3069, 3030, 2971, 2943, 2878, 1637, 1600, 1571, 1476, 1461, 1411, 1383, 1349, 1349, 1338, 1263, 1222, 1211, 1152, 1100, 1081, 1029, 870, 785, 765, 755, 715, 705 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{20}H_{27}S]^+$ ($[M]^+$): 299.1828; found: 299.1825.

### 3.8. Typical procedure for the synthesis of 1q



**Step 1:** Under a nitrogen atmosphere, a solution of 4-fluorobenzenethiol (5.1 g, 40 mmol) in DMF (10 mL) was added slowly to a suspension of NaH (0.5 g, 12 mmol, 60% purity) in DMF (30 mL) with vigorously stirring. The mixture was kept at room temperature for 10 minutes and 1-iodobutane (8.8 g, 48 mmol) was added. The resulting mixture was heated at reflux overnight, cooled to room temperature, quenched with a saturated aqueous solution of NaCl (100 mL), and extracted with ethyl acetate (3 × 80 mL). The extracts were washed with water, dried over anhydrous $Na_2SO_4$, and concentrated to dryness under reduced pressure. The crude product was used in the next step without further purification.

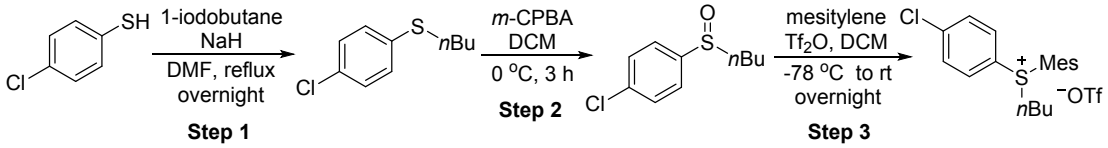
**Step 2**: To a solution of the crude product in DCM (265 mL) was slowly added *m*-CPBA (8.9 g, 44 mmol, 85% purity) at 0 °C. The mixture was reacted at 0 °C for 3 h, neutralized with a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 5 / 1 (v / v) as eluents to afford 1-(butylsulfinyl)-4-fluorobenzene as a colorless oil (8.0 g, 100%).

**Step 3:** Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (12 mmol, 2.0 mL) were slowly added to a solution of 1-(butylsulfinyl)-4-fluorobenzene (2.0 g, 10 mmol) and mesitylene (3.6 g, 30 mmol) in DCM (100 mL) at -78 °C. The mixture was reacted at room temperature overnight, neutralized by a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of DCM / acetonitrile = 3 / 1 (v / v) as eluents, followed by crystallization from a system of DCM (5 mL) and $Et_2O$ (50 mL), to give butyl(4-fluorophenyl)(mesityl)sulfonium trifluoromethanesulfonate (**1q**) as a white solid (3.2 g, 71%).

M.p.: 78-80 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.67 (m, 2H), 7.31 (t, *J* = 8.4 Hz, 2H), 7.15 (s, 2H), 4.62 (m, 1H), 4.02 (m, 1H), 2.41 (s, 6H), 2.39 (s, 3H), 1.81 (m, 1H), 1.62-1.53 (m, 3H), 0.94 (t, *J* = 7.0 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.3 (s, 3F), -104.8 (m, 1F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 164.8 (d, *J* = 256.7 Hz), 147.2, 144.0, 132.9, 130.0 (d, *J* = 10.1 Hz), 120.8 (q, *J* = 320.0 Hz), 120.4 (d, *J* = 3.78 Hz), 118.7 (d, *J* = 22.7 Hz), 114.7, 42.8, 26.7, 21.5, 21.4, 21.1, 13.4. IR (KBr): 3107, 3068,

3031, 2960, 2877, 1598, 1590, 1496, 1467, 1420, 1405, 1389, 1344, 1277, 1253, 1224, 1158, 1111, 1102, 1084, 1029, 1008, 968, 931, 865, 852, 841, 810, 756 $cm^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{19}H_{24}FS]^+$ ($[M]^+$): 303.1577; found: 303.1582.

### 3.9. Typical procedure for the synthesis of 1r




**Step 1:** Under a nitrogen atmosphere, a solution of 4-chlorobenzenethiol (2.9 g, 20 mmol) in DMF (5 mL) was added slowly to a suspension of NaH (0.96 g, 24 mmol, 60% purity) in DMF (15 mL) with vigorously stirring. The mixture was kept at room temperature for 10 minutes and 1-iodobutane (4.4 g, 24 mmol) was added. The resulting mixture was heated at reflux overnight, cooled to room temperature, quenched with a saturated aqueous solution of NaCl (50 mL), and extracted with ethyl acetate (3 × 40 mL). The extracts were washed with water, dried over anhydrous $Na_2SO_4$, and concentrated to dryness under reduced pressure. The crude product was used in the next step without further purification.

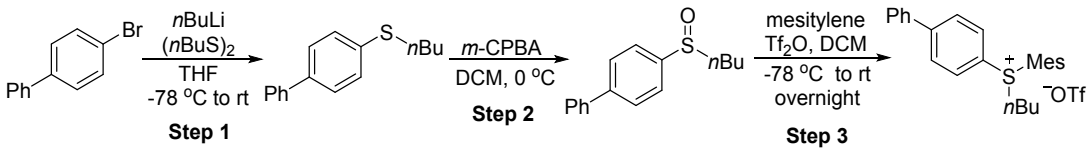
**Step 2:** To a solution of the crude product in DCM (130 mL) was slowly added *m*-CPBA (4.5 g, 22 mmol, 85% purity) at 0 °C. The mixture was stirred at 0 °C for 3 h, neutralized with a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 30 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 5 / 1 (v / v) as eluents to afford 1-(butylsulfinyl)-4-chlorobenzene as a colorless oil (3.9 g, 90%).

**Step 3:** Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (12 mmol, 2.0 mL) was added slowly to a solution of 1-(butylsulfinyl)-4-chlorobenzene (2.2 g, 10 mmol) and mesitylene (3.6 g, 30 mmol) in DCM (100 mL) at -78 °C. The mixture was reacted at room temperature overnight, neutralized by a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 30 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of DCM / acetonitrile = 3 / 1 (v / v) as eluents, followed by crystallization

from a combination of DCM (5 mL) and $Et_2O$ (50 mL), to afford butyl(4-chlorophenyl)(mesityl)sulfonium trifluoromethanesulfonate (**1r**) as a white solid (3.5 g, 75%).

M.p.: 110-112 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.58 (dm, $J$ = 9.1 Hz, 2H), 7.55 (dm, $J$ = 9.1 Hz, 2H), 7.14 (s, 2H), 4.57 (m, 1H), 4.00 (m, 1H), 2.38 (s, 6H), 2.37 (s, 3H), 1.78 (m, 1H), 1.59-1.52 (m, 3H), 0.91 (t, $J$ = 7.1 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.3 (s, 3F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 147.3, 144.1, 139.4, 132.9, 131.4, 128.8, 123.7, 120.8 (q, $J$ = 321.3 Hz), 114.5, 42.8, 26.7, 21.6, 21.4, 21.2, 13.5. IR (KBr): 3095, 3064, 3004, 2960, 2936, 2878, 1631, 1601, 1574, 1477, 1466, 1417, 1394, 1385, 1362, 1277, 1257, 1232, 1224, 1182, 1155, 1117, 1092, 1031, 1007, 919, 858, 826, 815, 791, 754, 748, 736, 719, 704, 694 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{19}H_{24}ClS]^+$ ($[M]^+$): 319.1282; found: 319.1278.

### 3.10. Typical procedure for the synthesis of 1s




**Step 1:** Under a nitrogen atmosphere, *n*-BuLi (2.5 M in pentane, 4.2 mL, 10.5 mmol) was added dropwise to a solution of 4-bromo-1,1'-biphenyl (2.3 g, 10 mmol) in THF (70 mL) at -78 ºC. After 30 min, ($n$BuS)$_2$ (1.20 g, 5.5 mmol) was added dropwise. The mixture was kept at -78 ºC for 30 min, warmed to 0 ºC for 1 h, and reacted at room temperature for 4 h. The reaction mixture was quenched with brine (100 mL) and extracted with DCM (2 × 40 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel using petroleum ether as eluent to afford crude [1,1'-biphenyl]-4-yl(butyl)sulfane.

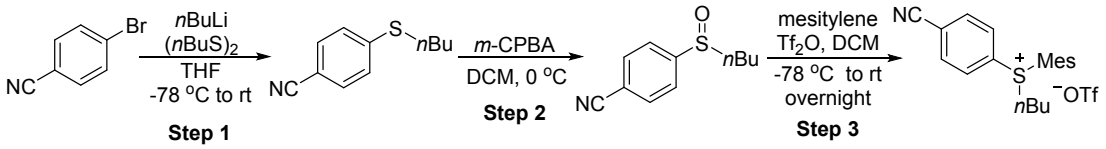
**Step 2:** To a solution of the crude [1,1'-biphenyl]-4-yl(butyl)sulfane in DCM (65 mL) was slowly added *m*-CPBA (2.2 g, 11 mmol, 85% purity) at 0 °C. The mixture was stirred at 0 °C for 1.5 h, neutralized with a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 5 / 1 (v / v) as eluents to afford 4-(butylsulfinyl)-1,1'-biphenyl

as a white solid (2.2 g, 84%).

**Step 3:** Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (6 mmol, 1.0 mL) was slowly added to a solution of 4-(butylsulfinyl)-1,1'-biphenyl (1.3 g, 5 mmol) and mesitylene (1.8 g, 15 mmol) in DCM (50 mL) at -78 °C. The mixture was reacted at room temperature overnight, neutralized by a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of DCM / acetonitrile = 3 / 1 (v / v) as eluents, followed by crystallization from a combination of DCM (5 mL) and $Et_2O$ (50 mL), to afford [1,1'-biphenyl]-4-yl(butyl)(mesityl)sulfonium trifluoromethanesulfonate **(1s)** as a colorless oil (2.0 g, 78%).

$^1$H NMR ($CDCl_3$, 500 MHz) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.44 (m, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.15 (s, 2H), 4.64 (m, 1H), 4.04 (m, 1H), 2.43 (s, 6H), 2.39 (s, 3H), 1.83 (m, 1H), 1.62-1.59 (m, 3H), 0.94 (t, *J* = 6.8 Hz, 3H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -78.2 (s, 3F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 147.1, 145.5, 144.1, 138.2, 132.9, 129.6, 129.2, 128.9, 127.7, 127.3, 123.4, 120.9 (q, *J* = 321.3 Hz), 114.8, 42.6, 26.8, 21.6, 21.4, 21.2, 13.5. IR (KBr): 3061, 3032, 2964, 2936, 2876, 1600, 1561, 1481, 1458, 1399, 1386, 1262, 1223, 1153, 1102, 1079, 1030, 1004, 839, 765, 738, 714, 699 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{25}H_{29}S]^+$ ($[M]^+$): 361.1984; found: 361.1993.

### 3.11. Typical procedure for the synthesis of 1t




**Step 1:** Under a nitrogen atmosphere, *n*-BuLi (2.5 M in pentane, 4.2 mL, 10.5 mmol) was added dropwise to a solution of 1-bromo-4-isocyanobenzene (1.8 g, 10 mmol) in THF (70 mL) at -78 ºC. After 1 h, ($n$BuS)$_2$ (1.20 g, 5.5 mmol) was dropwise added. The mixture was kept at -78 ºC for 30 min, warmed to 0 ºC for 1 h, and reacted at room temperature for 2 h. The reaction mixture was quenched with brine (100 mL) and extracted with DCM (2 × 40 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue

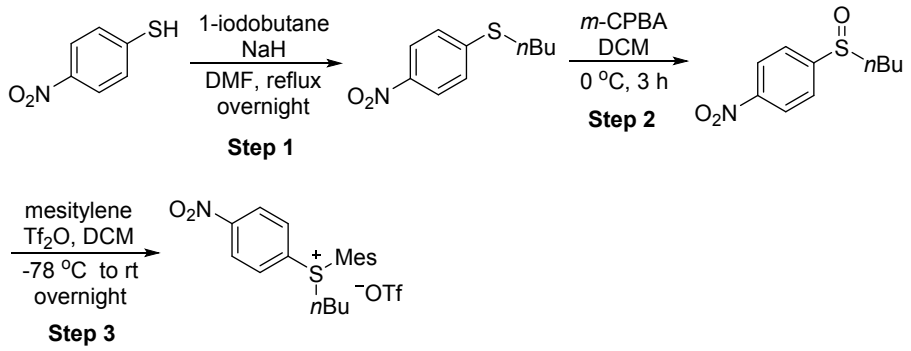
was purified by flash column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 10 / 1 (v / v) as eluents to afford crude 4-(butylthio)benzonitrile.

**Step 2:** To a solution of the crude 4-(butylthio)benzonitrile in DCM (65 mL) was slowly added *m*-CPBA (2.0 g, 10 mmol, 85% purity) at 0 °C. The mixture was stirred at 0 °C for 1.5 h, neutralized with a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 2 / 1 (v / v) as eluents to afford 4-(butylsulfinyl)benzonitrile as a yellow oil (1.2 g, 58%).

**Step 3:** Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (6 mmol, 1.0 mL) was slowly added to a solution of 4-(butylsulfinyl)benzonitrile (1.0 g, 5 mmol) and mesitylene (1.8 g, 15 mmol) in DCM (50 mL) at -78 °C. The mixture was reacted at room temperature overnight, neutralized by a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of DCM / acetonitrile = 3 / 1 (v / v) as eluents, followed by crystallization from a combination of DCM (5 mL) and $Et_2O$ (50 mL), to afford butyl(4-cyanophenyl)(mesityl)sulfonium trifluoromethanesulfonate **(1t)** as a white solid (1.3 g, 55%). *Note*: the product was found to slowly decompose at room temperature in organic solutions (e.g. $CDCl_3$).

M.p.: 113-115 °C. $^1$H NMR ($CD_3CN$, 500 MHz) δ 8.01 (d, $J$ = 8.5 Hz, 2H), 7.74 (d, $J$ = 8.5 Hz, 2H), 7.30 (s, 2H), 4.33 (m, 1H), 4.07 (m, 1H), 2.42 (s, 3H), 2.38 (s, 6H), 1.84 (m, 1H), 1.69 (m, 1H), 1.58 (m, 2H), 0.99 (t, $J$ = 7.3 Hz, 3H). $^{19}$F NMR ($CD_3CN$, 471 MHz) δ -79.3 (s, 3F). $^{13}$C NMR ($CD_3CN$, 126 MHz) δ 148.2, 145.1, 135.0, 133.2, 131.7, 128.9, 121.8 (q, $J$ = 320.5 Hz), 117.5, 116.7, 115.1, 43.3, 27.2, 21.8, 21.1, 21.0, 13.1. IR (KBr): 3097, 3069, 3042, 3013, 2965, 2940, 2878, 2233, 1599, 1570, 1492, 1469, 1460, 1403, 1384, 1365, 1264, 1224, 1157, 1128, 1104, 1086, 1032, 1015, 922, 861, 853, 836, 818, 793, 754, 740 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{20}H_{24}NS]^+$ ($[M]^+$): 310.1624; found: 310.1624.

### 3.12. Typical procedure for the synthesis of 1u



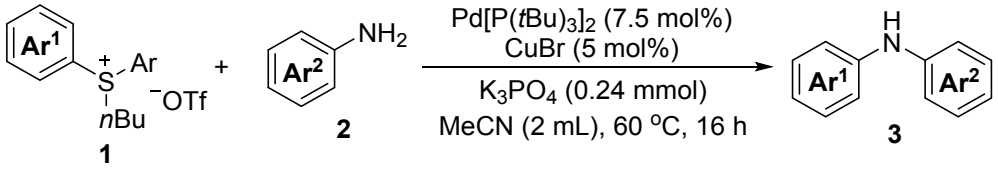

**Step 1:** Under a nitrogen atmosphere, a solution of 4-nitrobenzenethiol (0.82 g, 5 mmol) in DMF (2 mL) was added slowly to a suspension of NaH (0.24 g, 6 mmol, 60% purity) in DMF (3 mL) with vigorously stirring. The mixture was kept at room temperature for 10 minutes and 1-iodobutane (1.1 g, 6 mmol) was added. The resulting mixture was heated at reflux overnight, cooled to room temperature, quenched with a saturated aqueous solution of NaCl (20 mL), and extracted with ethyl acetate (3 × 20 mL). The extracts were washed with water, dried over anhydrous $Na_2SO_4$, and concentrated to dryness under reduced pressure. The crude product was used in the next step without further purification.

**Step 2:** To a solution of the crude product in DCM (50 mL) was slowly added *m*-CPBA (1.2 g, 6 mmol, 85% purity) at 0 °C. The mixture was stirred at 0 °C for 3 h, neutralized with a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether / ethyl acetate = 3 / 1 (v / v) as eluents to afford 1-(butylsulfinyl)-4-nitrobenzene as a yellow oil (0.91 g, 80%).

**Step 3:** Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (3.6 mmol, 0.61 mL) was added slowly to a solution of 1-(butylsulfinyl)-4-nitrobenzene (0.68 g, 3 mmol) and mesitylene (1.1 g, 9 mmol) in DCM (30 mL) at -78 °C. The mixture was reacted at room temperature overnight, neutralized by a saturated aqueous solution of $NaHCO_3$, and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated to dryness under reduced pressure. The residue was purified by crystallization from a combination of DCM (5 mL) and $Et_2O$ (100 mL) to afford butyl(mesityl)(4-nitrophenyl)sulfonium trifluoromethanesulfonate **(1u)** as a white solid (1.3 g, 90%). *Note*: the product was found to slowly decompose at room temperature in organic solutions (e.g. $CDCl_3$).

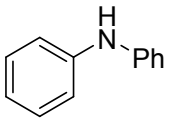
M.p.: 125-127 °C. $^1$H NMR ($CD_3CN$, 500 MHz) δ 8.41 (dm, $J$ = 9.2 Hz, 2H), 7.78 (d, $J$ = 9.2 Hz, 2H), 7.28 (s, 2H), 4.34 (m, 1H), 4.08 (m, 1H), 2.40 (s, 3H), 2.37 (s, 6H), 1.87-1.78 (m, 1H), 1.72-1.63 (m, 1H), 1.57 (m, 2H), 0.96 (t, $J$ = 7.3 Hz, 3H). $^{19}$F NMR ($CD_3CN$, 471 MHz) δ -79.3 (s, 3F). $^{13}$C NMR ($CD_3CN$, 126 MHz) δ 150.2, 147.6, 144.6, 132.7, 132.6, 129.0, 125.6, 121.2 (q, $J$ = 320.4 Hz), 114.5, 43.0, 26.6, 21.2, 20.5, 20.5, 12.6. IR (KBr): 3119, 3080, 3062, 3035, 3015, 2960, 2932, 2876, 1606, 1600, 1581, 1533, 1481, 1459, 1402, 1381, 1357, 1346, 1258, 1238, 1223, 1187, 1153, 1144, 1114, 1106, 1085, 1030, 1009, 975, 918, 864, 853, 825, 754, 741, 728, 707, 700 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{19}H_{24}NO_2S]^+$ ($[M]^+$): 330.1522; found: 330.1530.

**4. General procedure for *N*-arylation of anilines with arylsulfonium triflates**.



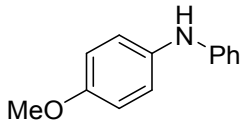

In a nitrogen-filled glove box, a sealed tube was charge with $K_3PO_4$ (50.9 mg, 0.24 mmol), CuBr (1.4 mg, 0.01 mmol), Pd[P($t$Bu)$_3$]$_2$ (7.7 mg, 0.015 mmol), aniline (**2**, 0.2 mmol) and MeCN (1 mL) with vigorous stirring. Then, arylbutylsulfonium salts (**1**, 0.24 mmol) was added, followed by MeCN (1 mL). The mixture was reacted at 60 °C for 16 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product (**3**).

**Diphenylamine (3a)** [3]



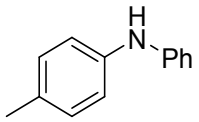

White solid (31.7 mg from **1b** (94.1 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 94%; 29.0 mg from **1l** (104.2 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 86%), a mixture of petroleum ether/ethyl acetate = 100/0 to 40/1 (v/v) as eluents for column chromatography. M.p.: 52-54 °C. $^1$H NMR ($CDCl_3$, 500 MHz,) δ 7.30 (t, $J$ = 7.7 Hz, 4H), 7.10 (d, $J$ = 8.0 Hz, 4H), 6.96 (t, $J$ = 7.3 Hz, 2H), 5.71 (brs, 1H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 143.2, 129.4, 121.1, 117.9.

**4-Methoxy-*N*-phenylaniline (3b)** [3]



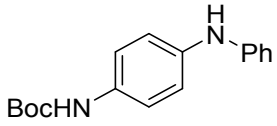

Gray solid (33.4 mg from **1b** (94.1 mg, 0.24 mmol) and **2b** (24.6 mg, 0.2 mmol), 84%; 35.2 mg from **1i** (108.5 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 88%; 30.2 mg from **1m** (111.4 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 76%), a mixture of petroleum ether/ethyl acetate = 100/0 to 40/1 (v/v) as eluents for column chromatography. M.p.: 104-106 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.24 (tm, *J* = 7.9 Hz, 2H), 7.09 (dm, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 2H), 6.89 (dm, *J* = 8.8 Hz, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 5.34 (brs, 1H), 3.82 (s, 3H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 155.3, 145.2, 135.8, 129.4, 122.2, 119.6, 115.7, 114.7, 55.6.

**4-Methyl-*N*-phenylaniline (3c)** [3]



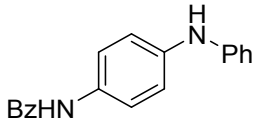

Yellow solid (34.4 mg from **1b** (94.1 mg, 0.24 mmol) and **2c** (21.4 mg, 0.2 mmol), 94%; 27.8 mg from **1n** (107.5 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 76%). M.p.: 87-89 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.22 (m, 2H), 7.07 (d, *J* = 8.2, 2H), 7.00-6.98 (m, 4H), 6.87 (d, *J* = 7.4 Hz, 1H), 5.57 (brs, 1H), 2.29 (s, 3H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 144.0, 140.4, 131.0, 129.9, 129.4, 120.3, 119.0, 116.9, 20.7.

***Tert*-Butyl (4-(phenylamino)phenyl)carbamate (3d)** [3]



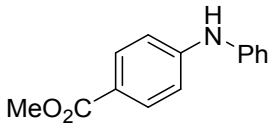

Light yellow solid (49.2 mg from **1b** (94.1 mg, 0.24 mmol) and **2d** (41.7 mg, 0.2 mmol), 87%), a mixture of petroleum ether/ethyl acetate = 20/1 to 5/1 (v/v) as eluents for column chromatography. M.p.: 129-131 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.25-7.20 (m, 4H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.47 (brs, 1H), 5.27 (brs, 1H), 1.51 (s, 9H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 153.2, 144.1, 138.5, 132.4, 129.4, 120.4, 120.3, 119.9, 116.7, 80.4, 28.4.

***N*-(4-(Phenylamino)phenyl)benzamide (3e)** [4]



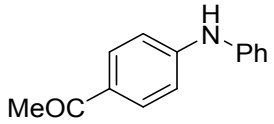

Yellow solid (50.2 mg from **1b** (94.1 mg, 0.24 mmol) and **2e** (42.4 mg, 0.2 mmol), 87%), a mixture of petroleum ether/ethyl acetate = 20/1 to 2/1 (v/v) as eluents for column chromatography. M.p.: 176-178 °C. $^1$H NMR (500 MHz, acetone-$d_6$) δ 9.40 (brs, 1H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.33 (brs, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H). $^{13}$C NMR (126 MHz, acetone-$d_6$) δ 165.0, 144.4, 139.7, 135.7, 132.7, 131.2, 129.1, 128.3, 127.3, 121.5, 119.6, 118.2, 116.5.

**Methyl 4-(phenylamino)benzoate (3f)** [5]



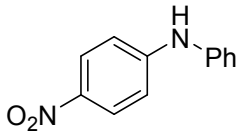

White solid (43.8 mg from **1b** (94.1 mg, 0.24 mmol) and **2f** (30.2 mg, 0.2 mmol), 96%), a mixture of petroleum ether/ethyl acetate = 40/1 to 20/1 (v/v) as eluents for column chromatography. M.p.: 113-115 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.09 (brs, 1H), 3.88 (s, 3H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 167.0, 148.1, 140.9, 131.5, 129.5, 123.1, 121.1, 120.5, 114.6, 51.7.

**1-(4-(Phenylamino)phenyl)ethan-1-one (3g)** [5]



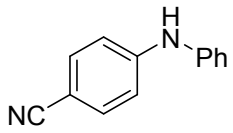

White solid (41.5 mg from **1b** (94.1 mg, 0.24 mmol) and **2g** (27.0 mg, 0.2 mmol), 98%), a mixture of petroleum ether/ethyl acetate = 40/1 to 20/1 (v/v) as eluents for column chromatography. M.p.: 104-106 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.34 (tm, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.24 (brs, 1H), 2.53 (s, 3H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 196.5, 148.5, 140.7, 130.7, 129.5, 129.0, 123.4, 120.7, 114.4, 26.2.

**4-Nitro-*N*-phenylaniline (3h)** [5]



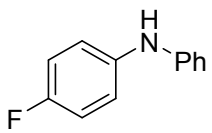
Yellow solid (39.4 mg from **1b** (94.1 mg, 0.24 mmol) and **2h** (27.6 mg, 0.2 mmol), 92%; 33.2 mg from **1u** (114.9 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol) at 40 °C, 78%), a mixture of petroleum ether/ethyl acetate = 20/1 to 5/1 (v/v) as eluents for column chromatography. M.p.: 134-136 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.11 (d, *J* = 9.2 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 9.2 Hz, 2H), 6.39 (brs, 1H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 150.3, 139.7, 139.6, 129.8, 126.3, 124.7, 122.0, 113.7.

**4-(Phenylamino)benzonitrile (3i)** [5]



Yellow solid (38.1 mg from **1b** (94.1 mg, 0.24 mmol) and **2i** (23.6 mg, 0.2 mmol), 98%; 20.4 mg from **1t** (110.2 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 53%; 27.9 mg from **1t** (110.2 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol) at 40 °C, 72%; 24.6 mg from **1t** (110.2 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol) at room temperature, 63%), a mixture of petroleum ether/ethyl acetate = 40/1 to 10/1 (v/v) as eluents for column chromatography. M.p.: 98-100 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.47 (d, *J* = 8.8 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.17 (brs, 1H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 148.1, 140.1, 133.8, 129.7, 124.0, 121.3, 120.0, 114.9, 101.4.

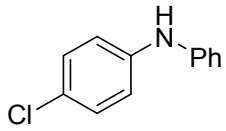
**4-Fluoro-*N*-phenylaniline (3j)** [5]



Yellow oil (36.2 mg from **1b** (94.1 mg, 0.24 mmol) and **2j** (22.2 mg, 0.2 mmol), 97%; 18.7 mg from **1q** (108.5 mg, 0.24 mmol) and **2a** (0.2 mmol), 50%), a mixture of petroleum ether/ethyl acetate = 100/0 to 40/1 (v/v) as eluents for column chromatography. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.27 (t, *J* = 7.8 Hz, 2H), 7.06 (m, 2H),

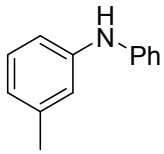
7.02-6.98 (m, 4H), 6.92 (t, $J$ = 7.4 Hz, 1H), 5.18 (brs, 1H). $^{19}$F NMR ($CDCl_3$, 471 MHz) δ -122.0 (m, 1F). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 158.1 (d, $J$ = 240.2 Hz), 144.0, 139.0 (d, $J$ = 2.5 Hz), 129.4, 120.6, 120.6, 116.8, 116.0 (d, $J$ = 22.5 Hz).

**4-Chloro-*N*-phenylaniline (3k)** [3]



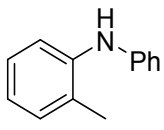

Yellow solid (34.0 mg from **1b** (94.1 mg, 0.24 mmol) and **2k** (25.5 mg, 0.2 mmol), 84%; 28.6 mg from **1j** (110.4 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 70%; 14.0 mg from **1r** (112.3 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 34%; 28.2 mg from **1r** (112.3 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol) at 40 °C, 69%), a mixture of petroleum ether/ethyl acetate = 100/0 to 40/1 (v/v) as eluents for column chromatography. M.p.: 74-76 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.29 (t, $J$ = 7.9 Hz, 2H), 7.22 (dm, $J$ = 8.8 Hz, 2H), 7.06 (d, $J$ = 7.7 Hz, 2H), 7.01-6.96 (m, 3H), 5.67 (brs, 1H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 142.7, 141.9, 129.5, 129.3, 125.5, 121.5, 118.8, 118.1.

**3-Methyl-*N*-phenylaniline (3n)** [6]



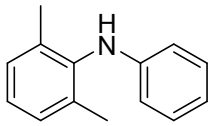

Colorless oil (31.9 mg from **1b** (94.1 mg, 0.24 mmol) and **2n** (21.4 mg, 0.2 mmol), 87%; 27.8 mg from **1o** (107.5 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 76%), a mixture of petroleum ether/ethyl acetate = 100/0 to 40/1 (v/v) as eluents for column chromatography. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.25 (t, $J$ = 7.8 Hz, 2H), 7.14 (tm, $J$ = 7.5 Hz, 1H), 7.05 (dm, $J$ = 7.9 Hz, 2H), 6.91 (t, $J$ = 7.4 Hz, 1H), 6.88-6.87 (m, 2H), 6.75 (d, $J$ = 7.4 Hz, 1H), 5.63 (brs, 1H), 2.30 (s, 3H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 143.3, 143.1, 139.3, 129.4, 129.2, 121.9, 120.9, 118.6, 117.9, 115.0, 21.6.

**2-Methyl-*N*-phenylaniline (3o)** [5]



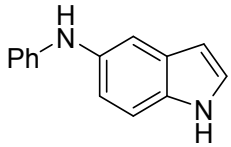
Colorless oil (30.5 mg from **1b** (94.1 mg, 0.24 mmol) and **2o** (21.4 mg, 0.2 mmol), 83%; 30.7 mg from **1p** (107.5 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 84%), a mixture of petroleum ether/ethyl acetate = 100/0 to 40/1 (v/v) as eluents for column chromatography. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.17-7.14 (m, 3H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.87-6.83 (m, 3H), 6.81 (t, *J* = 7.4 Hz, 1H), 5.27 (s, 1H), 2.17 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.1, 141.3, 131.0, 129.4, 128.4, 126.8, 122.1, 120.5, 118.9, 117.5, 17.9.

**2,6-Dimethyl-*N*-phenylaniline (3p)** [5]



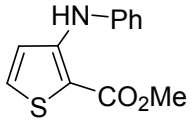
Light yellow oil (24.7 mg from **1b** (94.1 mg, 0.24 mmol) and **2p** (24.2 mg, 0.2 mmol), 63%), a mixture of petroleum ether/ethyl acetate = 100/0 to 40/1 (v/v) as eluents for column chromatography. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.18-7.13 (m, 4H), 7.09 (m, 1H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 2H), 5.19 (brs, 1H), 2.23 (s, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 146.3, 138.3, 135.9, 129.3, 128.6, 125.8, 118.2, 113.6, 18.4.

***N*-Phenyl-1*H*-indol-5-amine (3q)** [7]



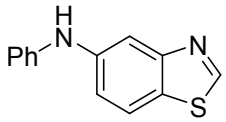
Light yellow solid, (27.9 mg from **1b** (94.1 mg, 0.24 mmol) and **2q** (26.4 mg, 0.2 mmol), 67%; 18.7 mg from **1b** (94.1 mg, 0.24 mmol), $K_3PO_4$ (101.8 mg, 0.48 mmol) and **2q** (26.4 mg, 0.2 mmol), 45%), a mixture of petroleum ether/ethyl acetate = 40/1 to 5/1 (v/v) as eluents for column chromatography. M.p.: 99-101 $^o$C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.09 (brs, 1H), 7.44 (d, *J* = 1.7 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.23-7.20 (m, 3H), 7.05 (dd, *J* = 8.5 Hz, *J* = 2.0 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.49 (t, *J* = 2.0 Hz, 1H), 5.62 (brs, 1H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 146.3, 135.3, 132.7, 129.3, 128.7, 124.9, 119.1, 118.4, 115.4, 113.2, 111.6, 102.5.

**Methyl 3-(phenylamino)thiophene-2-carboxylate (3r)** [8]



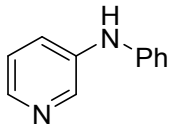
White solid (42.5 mg from **1b** (94.1 mg, 0.24 mmol) and **2r** (31.4 mg, 0.2 mmol), 91%), a mixture of petroleum ether/ethyl acetate = 80/1 to 40/1 (v/v) as eluents for column chromatography. M.p.: 66-68 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.79 (brs, 1H), 7.36 (d, *J* = 5.5 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 5.5 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 3.87 (s, 3H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 165.2, 151.5, 141.5, 131.8, 129.4, 123.1, 120.3, 117.9, 102.9, 51.4.

**_N_-Phenylbenzo[*d*]thiazol-5-amine (3s)**



Light yellow solid (27.6 mg from **1b** (94.1 mg, 0.24 mmol) and **2s** (30.0 mg, 0.2 mmol), 61%), a mixture of petroleum ether/ethyl acetate = 20/1 to 5/1 (v/v) as eluents for column chromatography. M.p.: 151-153 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.96 (s, 1H), 7.85 (d, *J* = 1.8 H, 1H), 7.79 (d, *J* =8.6 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.19 (dd, *J* = 8.7 Hz, 1.9 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.97 (t, *J* =7.3 Hz, 1H), 5.95 (brs, 1H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 154.9, 154.8, 142.9, 142.4, 129.5, 125.9, 122.2, 121.5, 118.1, 118.1, 111.0. IR (KBr): 3314, 3179, 3104, 3077, 3062, 3032, 2922, 2850, 1594, 1518, 1496, 1467, 1448, 1429, 1407, 1332, 1323, 1316, 1304, 1272, 1244, 1226, 1175, 1156, 1143, 1075, 1027, 947, 870, 862, 838, 807, 781, 749, 706 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{13}H_{11}N_2S]^+$ ([M + H]): 227.0637; found: 227.0642.

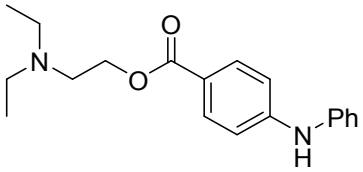
**_N_-Phenylpyridin-3-amine (3t)** [9]



Light yellow solid (8.4 mg from **1b** (94.1 mg, 0.24 mmol) and **2t** (18.8 mg, 0.2 mmol), 25%; 18.0 mg from **1b** (94.1 mg, 0.24 mmol) and **2t** (18.8 mg, 0.2 mmol) at 80 °C, 53%), a mixture of petroleum ether/ethyl acetate = 40/1 to 5/1 (v/v) as eluents for column chromatography. $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.38 (s, 1H), 8.16 (s, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.17 (m, 1H), 7.08 (d, *J* = 7.7 Hz,

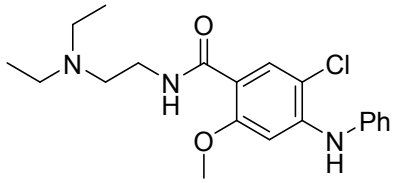
2H), 6.99 (t, $J$ = 7.4 Hz, 1H), 5.89 (brs, 1H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 142.0, 141.9, 140.2, 139.9, 129.6, 123.7, 123.4, 122.1, 118.4.

**2-(Diethylamino)ethyl 4-(phenylamino)benzoate (3u)**



Light yellow oil (34.6 mg from **1b** (94.1 mg, 0.24 mmol) and **2u** (47.2 mg, 0.2 mmol), 55%), a mixture of dicholromethane/acetonitrile = 5/1 to 3/1 (v/v) as eluents for column chromatography. $^1$H NMR ($CD_3CN$, 500 MHz) δ 7.88 (d, $J$ = 8.7 Hz, 2H), 7.34 (t, $J$ = 7.8 Hz, 2H), 7.25 (brs, 1H), 7.21 (d, $J$ = 7.9 Hz, 2H), 7.07-7.03 (m, 3H), 4.45 (t, $J$ = 5.3 Hz, 2H), 3.26 (t, $J$ = 5.3 Hz, 2H), 3.05 (q, $J$ = 7.2 Hz, 4H), 1.21 (t, $J$ = 7.2 Hz, 6H). $^{13}$C NMR ($CD_3CN$, 126 MHz) δ 165.8, 149.1, 141.2, 131.5, 129.4, 122.7, 120.1, 119.6, 114.2, 59.8, 51.2, 48.1, 9.3. IR (KBr): 3492, 3355, 3060, 2985, 2918, 2850, 1708, 1611, 1592, 1527, 1498, 1473, 1451, 1384 1275, 1174, 1110, 1036, 849, 767, 756, 696 cm$^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{19}H_{25}N_2O_2]^+$ ([M + H]): 313.1911; found: 313.1904.

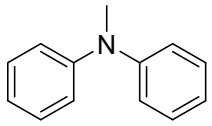
**5-Chloro-*N*-(2-(diethylamino)ethyl)-2-methoxy-4-(phenylamino)benzamide (3v)**



White solid (31.8 mg from **1b** (94.1 mg, 0.24 mmol) and **2v** (59.9 mg, 0.2 mmol), 42%), a mixture of dicholromethane/acetonitrile/$Et_3N$ = 5/1/0 to 3/1/0.03 (v/v/v) as eluents for column chromatography. M.p.: 83-85 $^o$C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.24 (brs, 1H), 8.21 (s, 1H), 7.38 (t, $J$ = 7.8 Hz, 2H), 7.23 (d, $J$ = 7.9 Hz, 2H), 7.14 (t, $J$ = 7.4 Hz, 1H), 6.74 (s, 1H), 6.37 (brs, 1H), 3.79 (s, 3H), 3.50 (q, $J$ = 5.7 Hz, 2H), 2.63 (t, $J$ = 5.9 Hz, 2H), 2.57 (q, $J$ = 7.1 Hz, 4H), 1.04 (t, $J$ = 7.1 Hz, 6H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 164.2, 157.5, 143.9, 140.2, 133.0, 129.7, 124.2, 121.9, 113.6, 112.8, 96.8, 56.0, 51.6, 46.8, 37.5, 12.0. IR (KBr): 3371, 3248, 3047, 3003, 2969, 2935, 2872, 2810, 1633, 1612, 1590, 1564, 1538, 1512, 1463, 1453, 1429, 1407, 1384, 1346, 1322, 1297, 1267, 1239, 1204, 1172, 1139, 1083, 1066, 1053, 1028, 1002, 924,

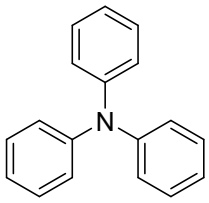
842, 823, 776, 736, 694 $cm^{-1}$. HRMS-ESI (m/z) calcd. for $[C_{20}H_{27}ClN_3O_2]^+$ ([M + H]): 376.1786; found: 376.1792.

*N*-Methyl-*N*-phenylaniline (**3w**) [6]



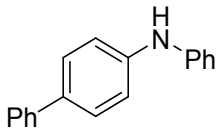
Yellow oil (19.7 mg from **1b** (94.1 mg, 0.24 mmol) and **2w** (21.4 mg, 0.2 mmol) at 80 °C for 16 h, 54%; 27.7 mg from **1b** (94.1 mg, 0.24 mmol) and **2w** (21.4 mg, 0.2 mmol) at 80 °C for 24 h, 76%), petroleum ether as eluent for column chromatography. $^1H$ NMR ($CDCl_3$, 400 MHz) δ 7.29 (tm, *J* = 8.0 Hz, 4H), 7.04 (d, *J* = 8.6 Hz, 4H), 6.97 (t, *J* = 7.3 Hz, 2H), 3.33 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 101 MHz) δ 149.1, 129.2, 121.3, 120.5, 40.3.

Triphenylamine (**3x**)



In a nitrogen-filled glove box, a sealed tube was charge with $K_3PO_4$ (50.9 mg, 0.24 mmol), CuBr (1 .4 mg, 0.01 mmol), $Pd[P(tBu)_3]_2$ (7.7 mg, 0.015 mmol), diphenylamine (**3a**, 33.8 mg, 0.2 mmol), and MeCN (1 mL) with vigorous stirring. Then, diphenylbutylsulfonium triflate (94.1 mg, 0.24 mmol) was added, followed by MeCN (1 mL). The mixture was reacted at 80 °C for 24 h. The yield of **3x** (5%) was determined by HPLC (λ = 284 nm, water / methanol = 15 / 85 (v / v)) using pure triphenylamine (R = 14.44 min) as an external standard.

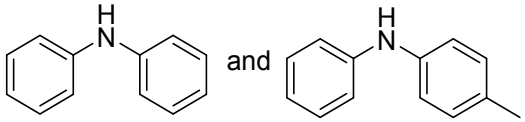
***N*-Phenyl-[1,1'-biphenyl]-4-amine (3y)** [9]



White solid (25.6 mg from **1s** (122.4 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 52%; 30.2 mg from **1s** (122.4 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol) at 40 °C,

62%), a mixture of petroleum ether/ethyl acetate = 100/0 to 40/1 (v/v) as eluents for column chromatography. M.p.: 111-113 °C. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.34-7.30 (m, 3H), 7.15 (m, 4H), 6.98 (t, *J* = 7.4 Hz, 1H), 5.79 (brs, 1H). $^{13}$C NMR ($CDCl_3$, 126 MHz) δ 142.9, 142.6, 140.9, 133.8, 129.4, 128.8, 128.0, 126.6, 126.6, 121.3, 118.1, 117.8.

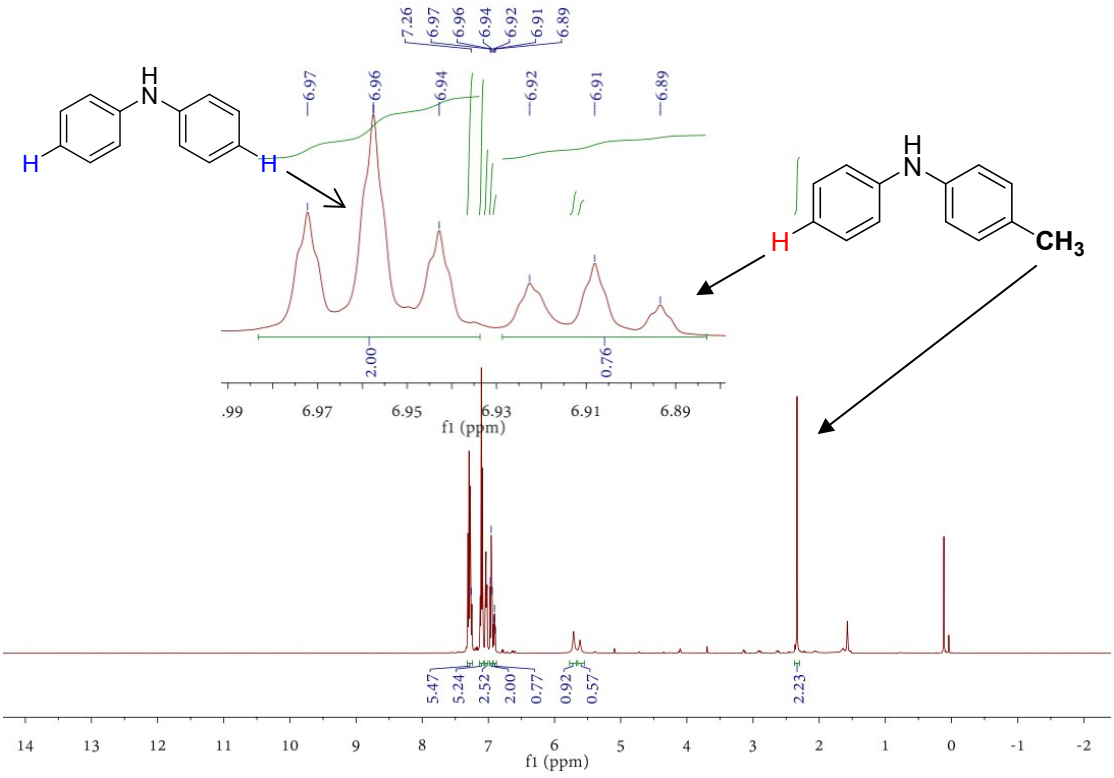
**A mixture of diphenylamine (3a) and 4-methyl-*N*-phenylaniline (3c)**



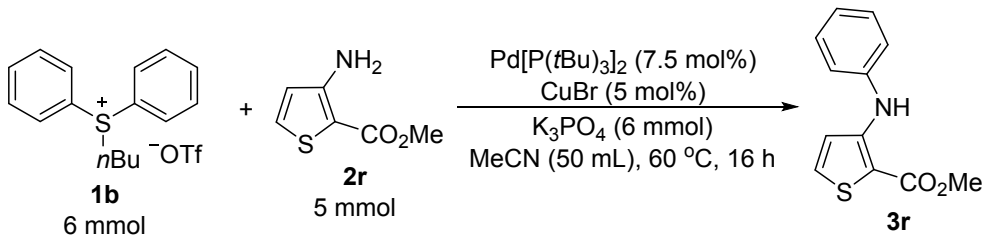

97% (**3a**/**3c** = 1.3/1)

Yellow oil (33.8 mg from **1k** (97.5 mg, 0.24 mmol) and **2a** (18.6 mg, 0.2 mmol), 97%, the ratio of **3a** and **3c** is 1.3 : 1, which was determined by $^1$H NMR spectroscopy), a mixture of petroleum ether/ethyl acetate = 100/0 to 40/1 (v/v) as eluents for column chromatography.

**The $^1$H NMR spectrum of the mixture of 3a and 3c**

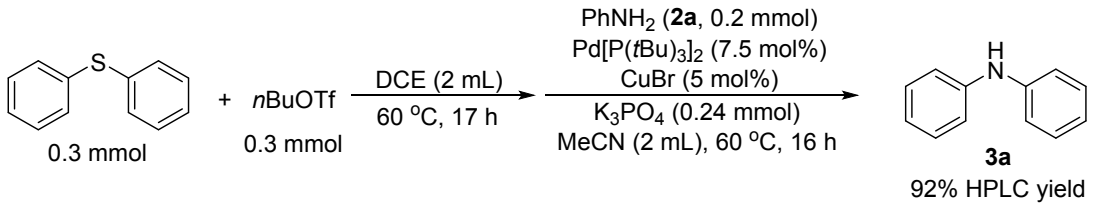



**A scale-up synthesis of 3r**

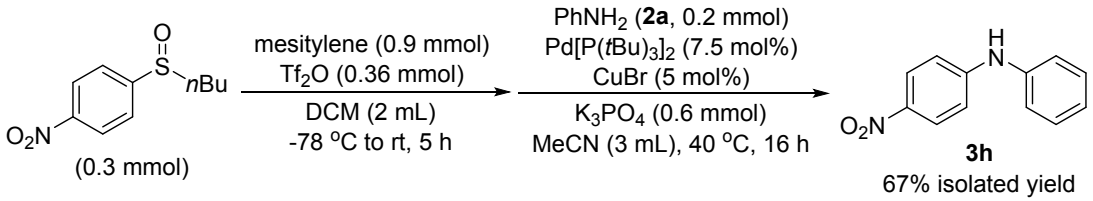



In a nitrogen-filled glove box, a sealed round-bottom flask (100 mL) was charge with $K_3PO_4$ (1.27 g, 6 mmol), CuBr (35 mg, 0.25 mmol), $Pd[P(tBu)_3]_2$ (192.5 mg, 0.375 mmol), methyl 3-aminothiophene-2-carboxylate (**2r**, 785 mg, 5 mmol) and MeCN (45 mL) with vigorous stirring. Then, butyldiphenylsulfonium trifluoromethanesulfonate (**1b**, 2.35 g, 6 mmol) was added, followed by MeCN (5 mL). The mixture was reacted at 60 °C for 16 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate = 80/1 to 40/1 (v/v) as eluents to give methyl 3-(phenylamino)thiophene-2-carboxylate (**3r**) as a white solid (1.12 g, 96%).

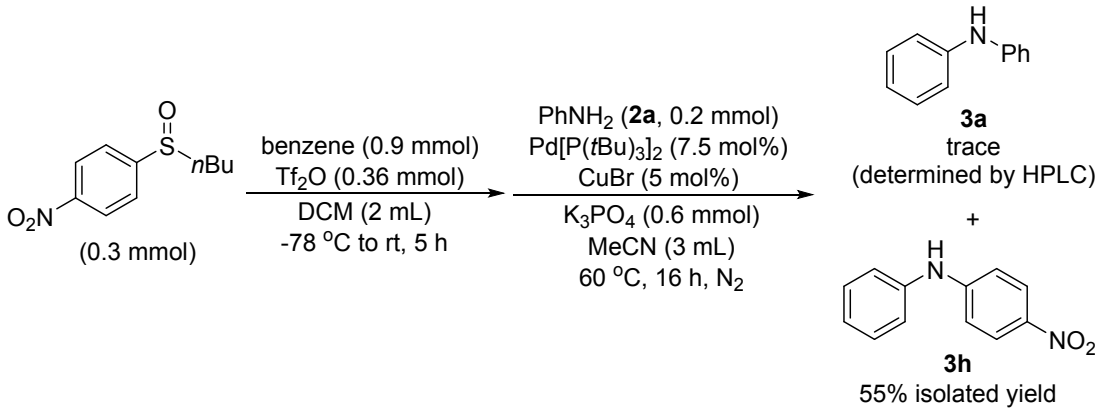
**Procedures for one-pot *N*-arylation of 2a**




A sealed tube was charged with butyl trifluoromethanesulfonate (61.7 mg, 0.3 mmol), diphenylsulfane (55.9 mg, 0.3 mmol) and DCE (2 mL) with vigorous stirring. The mixture was heated at 60 °C for 17 h, cooled to room temperature, and concentrated to dryness under reduced pressure. The crude diphenyl(butyl)sulfonium triflate (**1b**) was dissolved in MeCN (1 mL) and added to a mixture of $K_3PO_4$ (50.9 mg, 0.24 mmol), CuBr (1.4 mg, 0.01 mmol), $Pd[P(tBu)_3]_2$ (7.7 mg, 0.015 mmol), aniline (**2a**, 0.2 mmol) and MeCN (1 mL) with vigorous stirring under a nitrogen atmosphere. The mixture was reacted at 60 °C for 16 h. The yield of product **3a** was determined by HPLC ($\lambda$ = 284 nm, water / methanol = 15 / 85 (v / v)) using diphenylamine ($t_R$ = 5.31 min) as an external standard.




Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (60.5 μL, 0.36 mmol) was added to a solution of 1-(butylsulfinyl)-4-nitrobenzene (68.1 mg, 0.3 mmol) and mesitylene (108 mg, 0.9 mmol) in DCM (2 mL) at -78 °C. The mixture was reacted at room temperature for 5 h and concentrated to dryness under reduced pressure. The crude bu-tyl(mesityl)(4-nitrophenyl)sulfonium triflate (**1u**) was dissolved in MeCN (2 mL) and added to a mixture of $K_3PO_4$ (127.2 mg, 0.6 mmol), CuBr (1.4 mg, 0.01 mmol), Pd[P(*t*Bu)$_3$]$_2$ (7.7 mg, 0.015 mmol), aniline (**2a**, 0.2 mmol) and MeCN (1 mL) with vigorous stirring under a nitrogen atmosphere. The mixture was reacted at 40 °C for 16 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate = 20/1 to 5/1 (v/v) as eluents to give the desired product (**3h**, 28.7 mg, 67%).




Under a nitrogen atmosphere, trifluoromethanesulfonic anhydride (60.5 μL, 0.36 mmol) was added to a solution of 1-(butylsulfinyl)-4-nitrobenzene (68.1 mg, 0.3 mmol) and benzene (70.2 mg, 0.9 mmol) in DCM (2 mL) at -78 °C. The mixture was reacted at room temperature for 5 h and concentrated to dryness under reduced pressure. The crude butyl(4-nitrophenyl)(phenyl)sulfonium triflate was dissolved in MeCN (2 mL) and added to a mixture of $K_3PO_4$ (127.2 mg, 0.6 mmol), CuBr (1.4 mg, 0.01 mmol), Pd[P(*t*Bu)$_3$]$_2$ (7.7 mg, 0.015 mmol), aniline (**2a**, 0.2 mmol) and MeCN (1

mL) with vigorous stirring under a nitrogen atmosphere. The mixture was reacted at 60 °C for 16 h and then detected by HPLC using diphenylamine (**3a**) as an external standard ($t_R$ = 5.86 min, λ = 284 nm, water/methanol = 15/85 (v/v)). The result showed formation of **3a** in a trace amount (< 1%). Next, the reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using a mixture of petroleum ether/ethyl acetate = 20/1 to 5/1 (v/v) as eluents to afford 23.7 mg of **3h** (55%).

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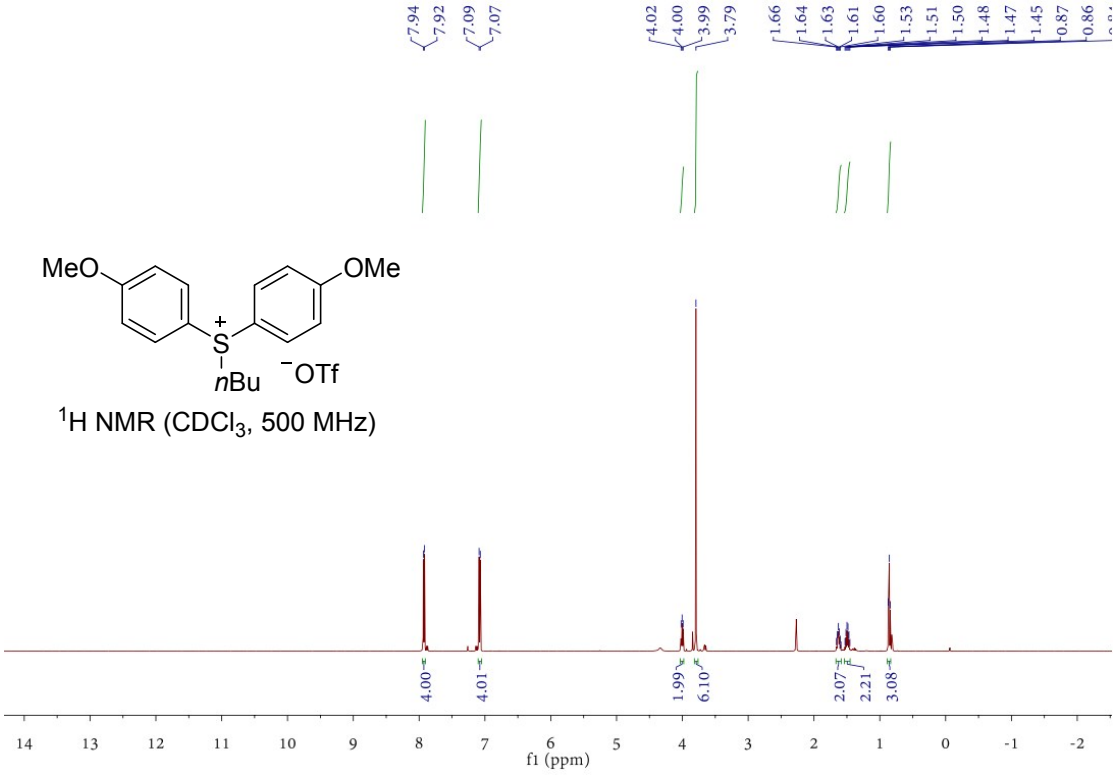
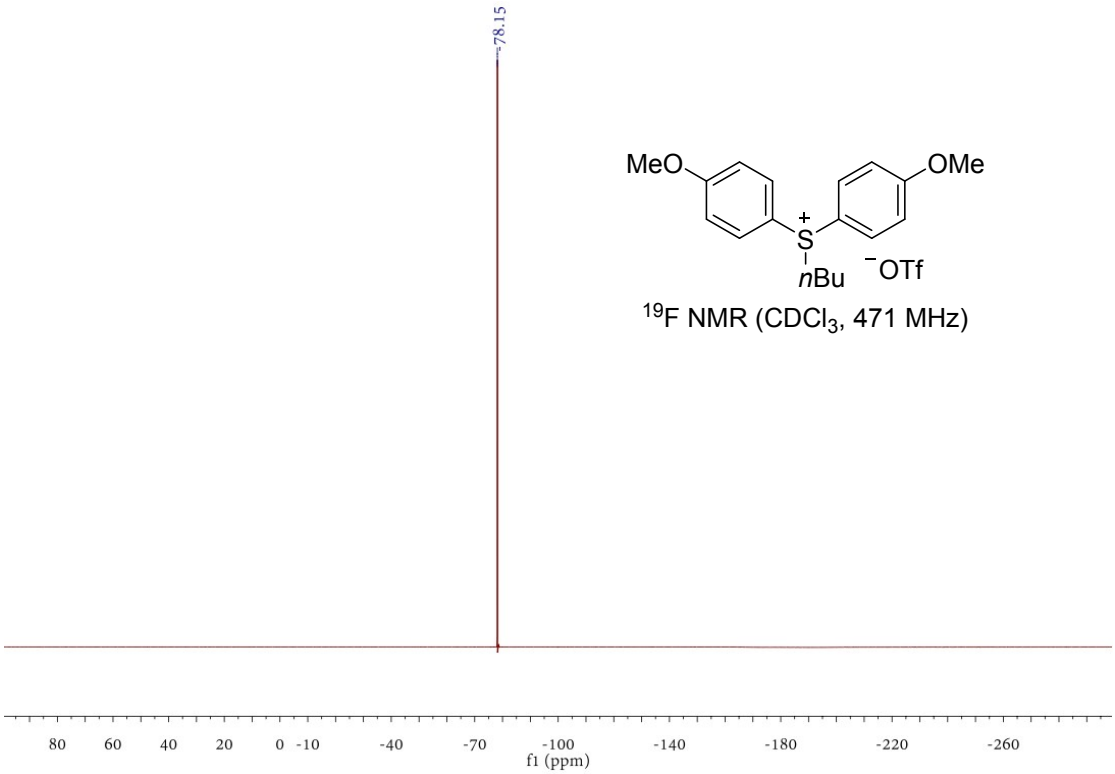
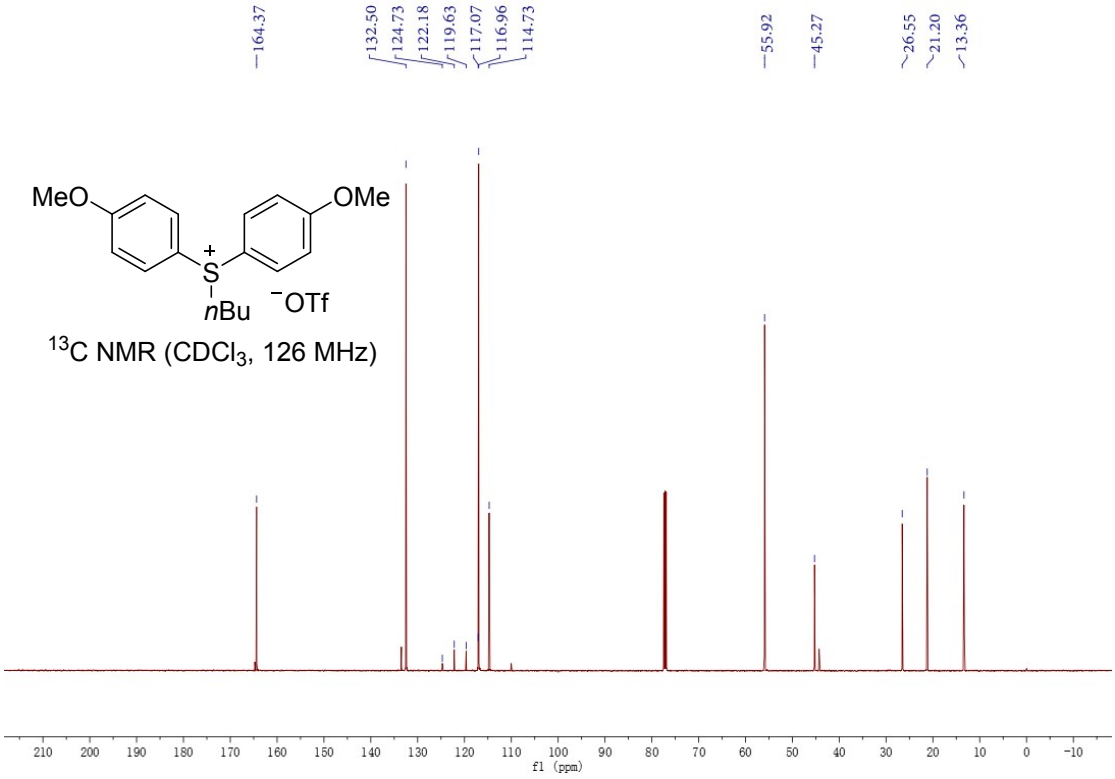
## 5. NMR spectra of the products



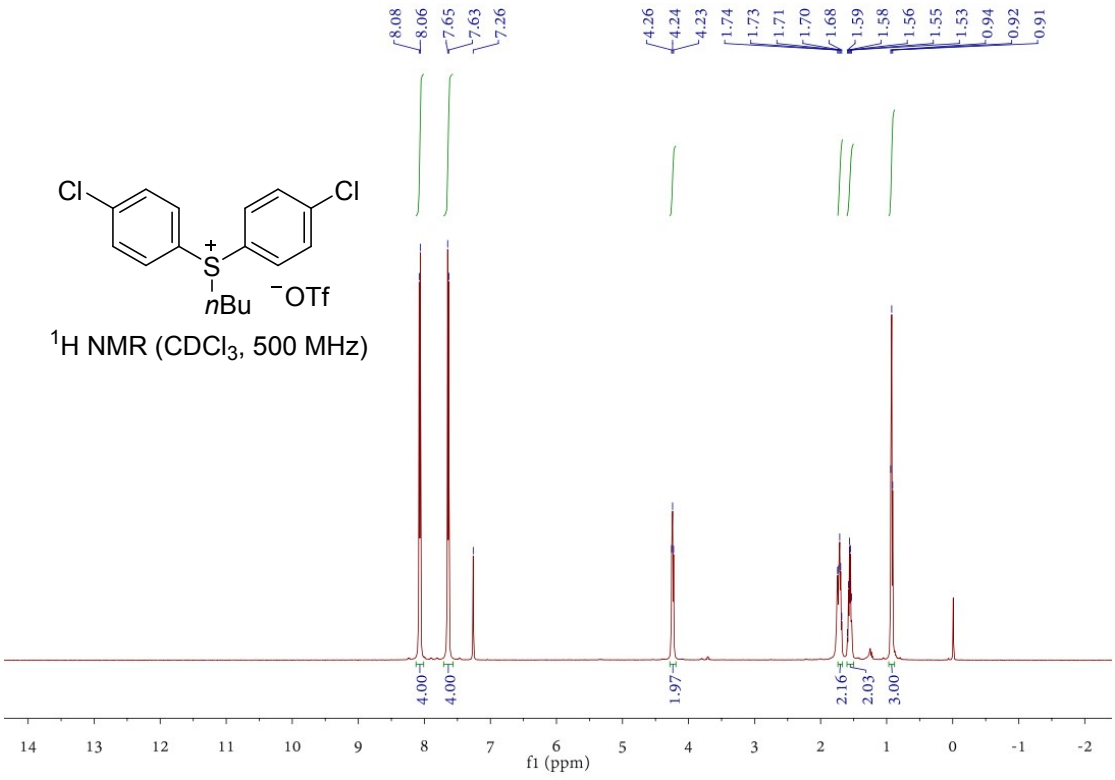

$^{1}$H NMR ($CDCl_3$, 500 MHz)



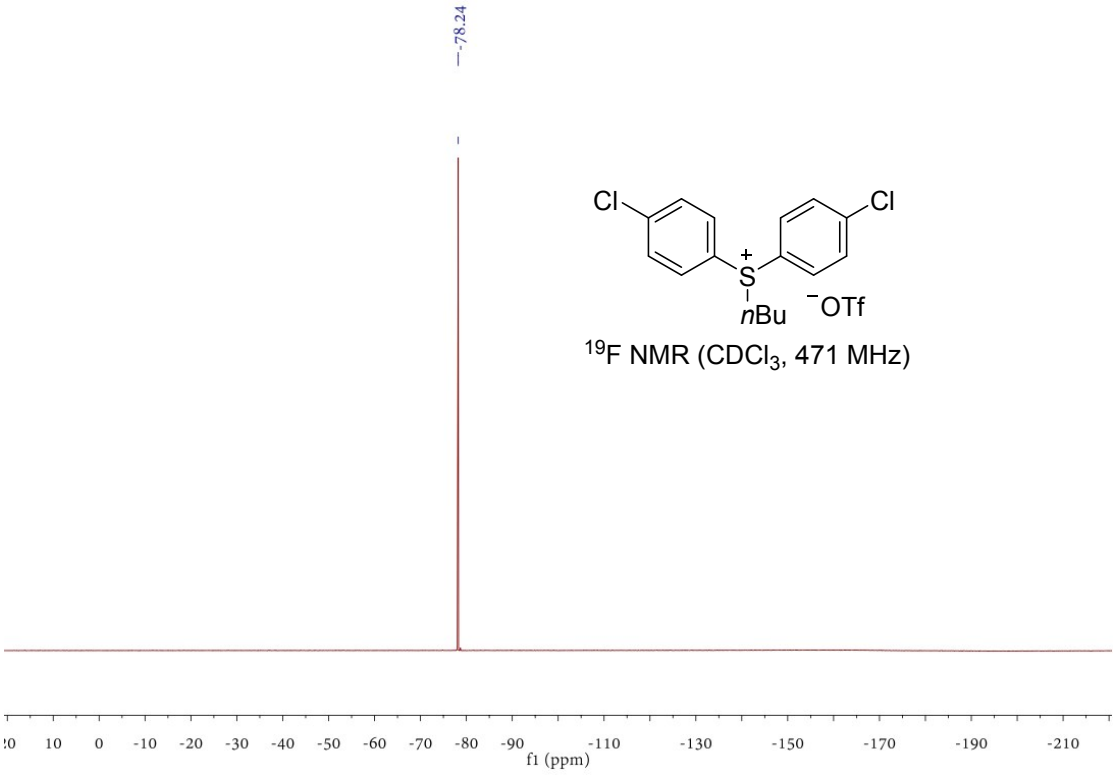

$^{19}$F NMR ($CDCl_3$, 471 MHz)




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




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

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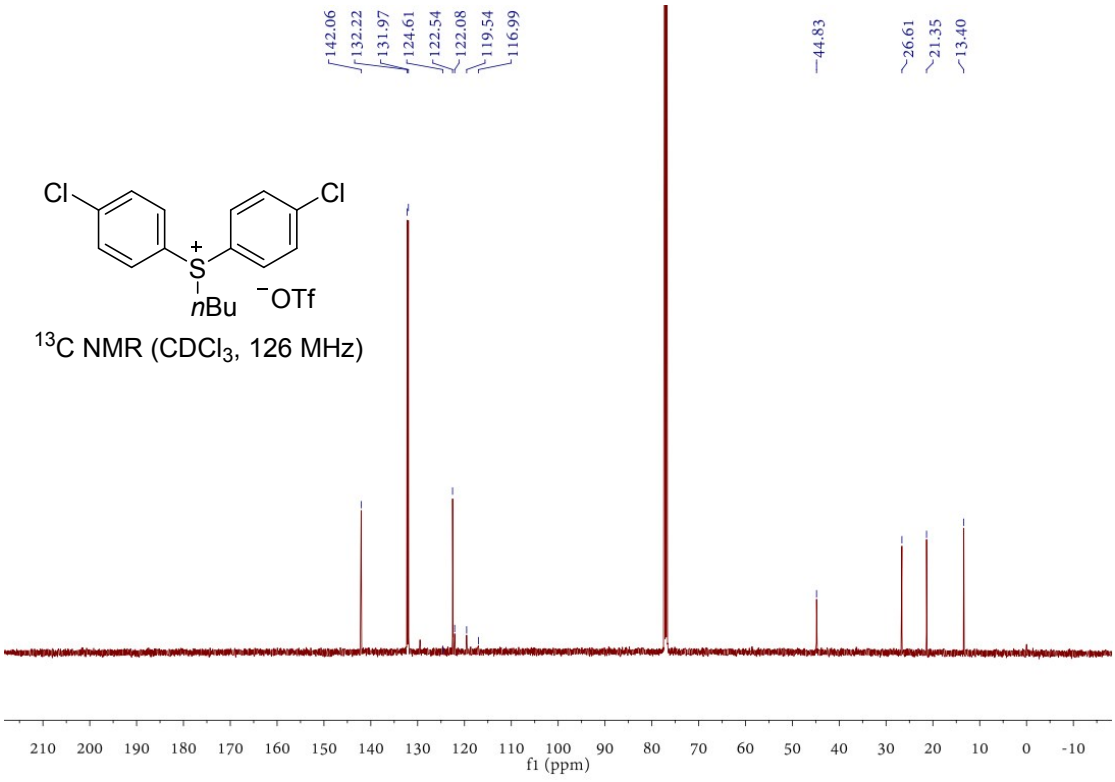


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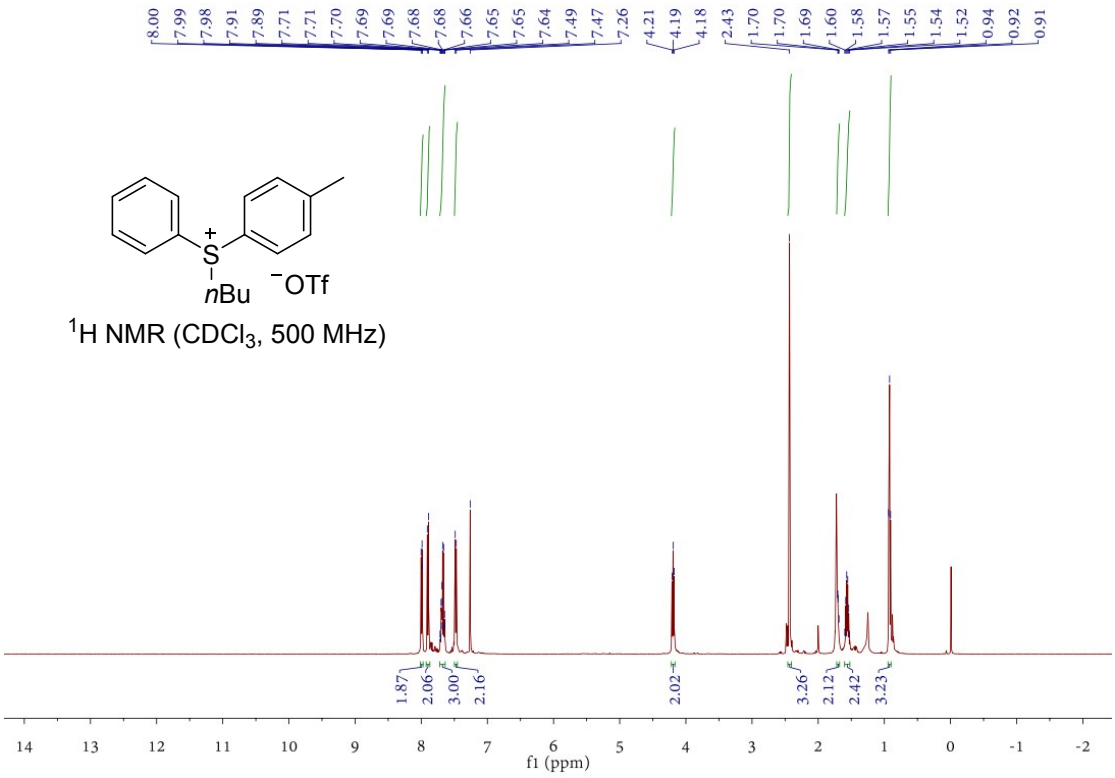





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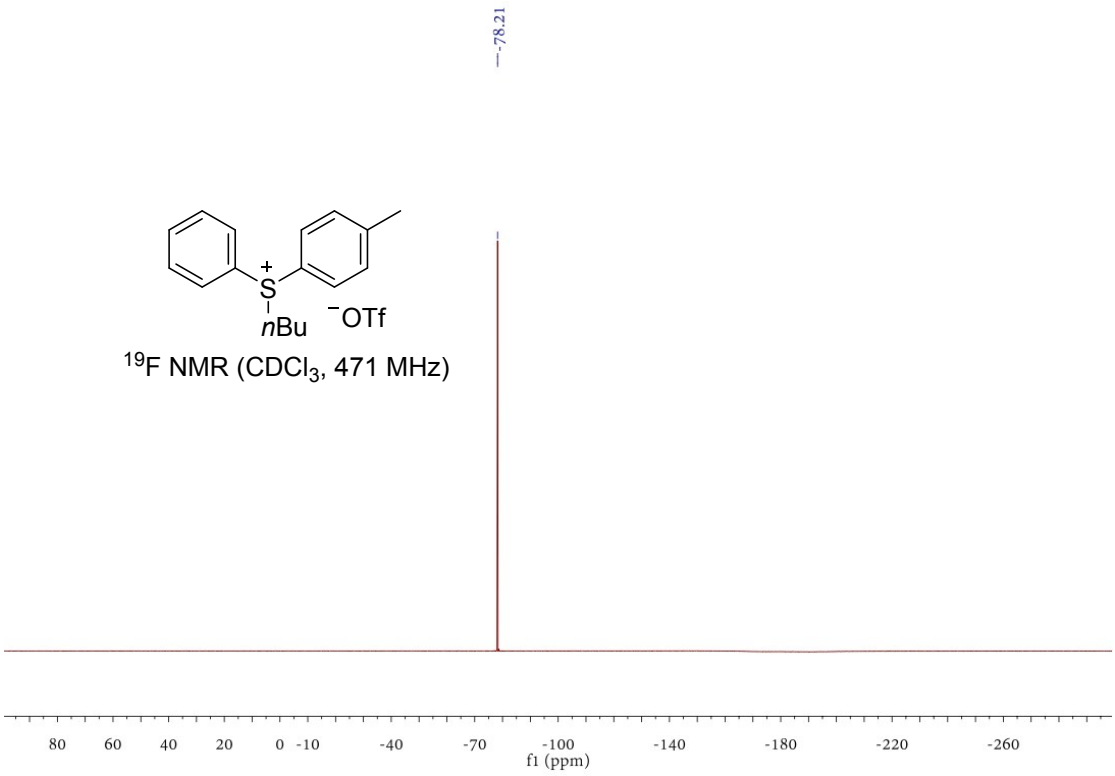
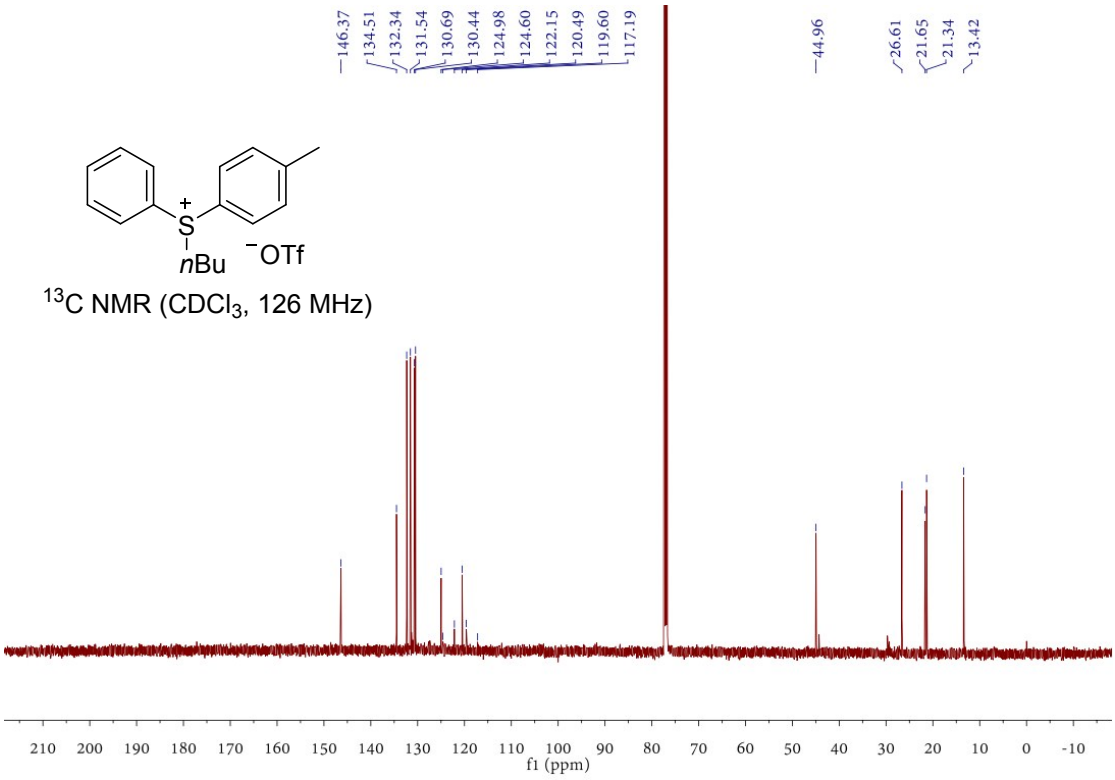


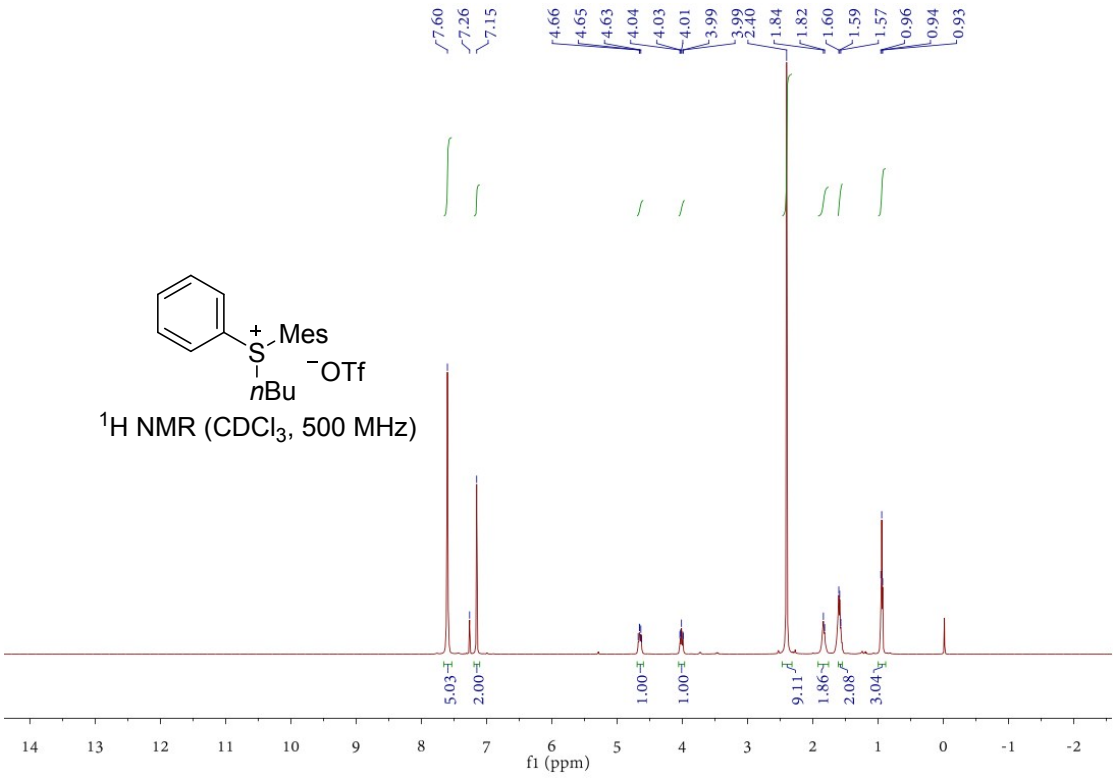




$^{19}$F NMR ($CDCl_3$, 471 MHz)




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

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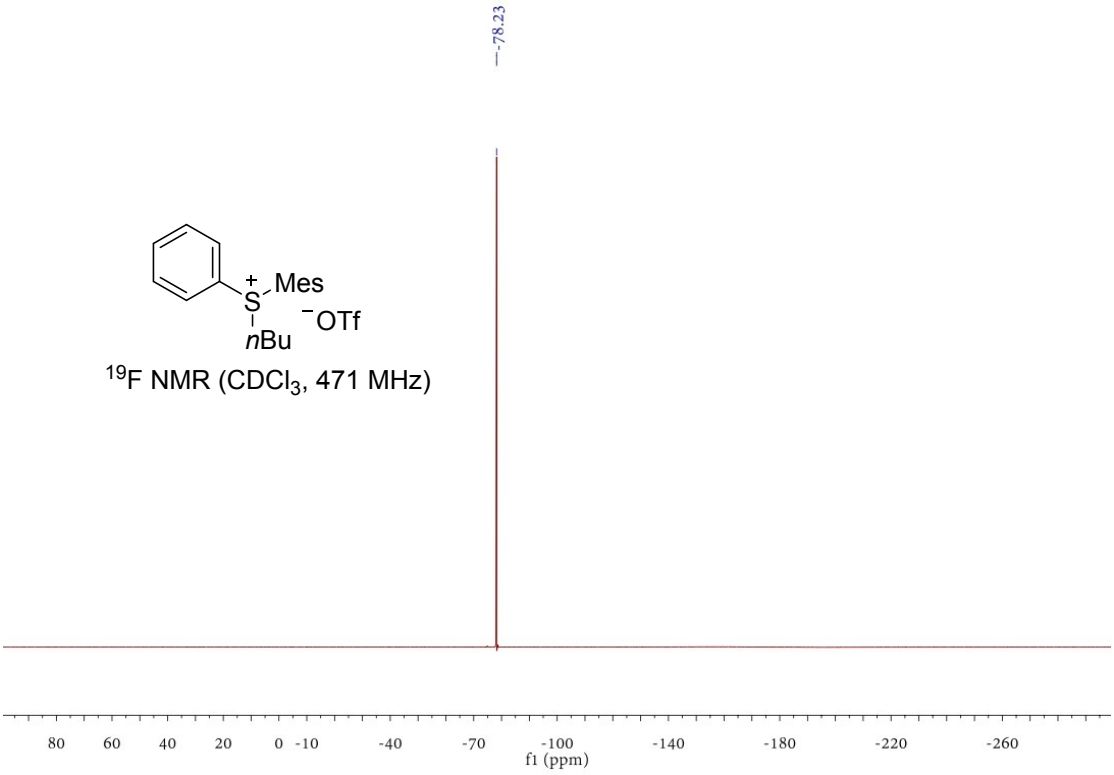


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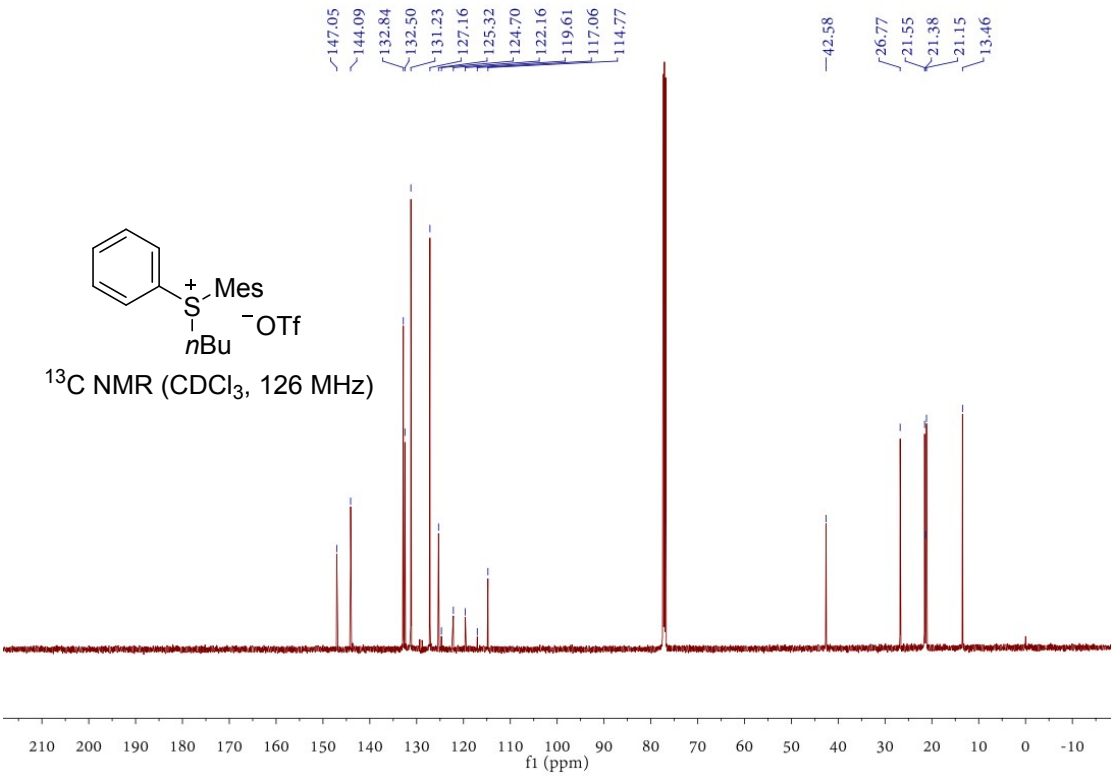


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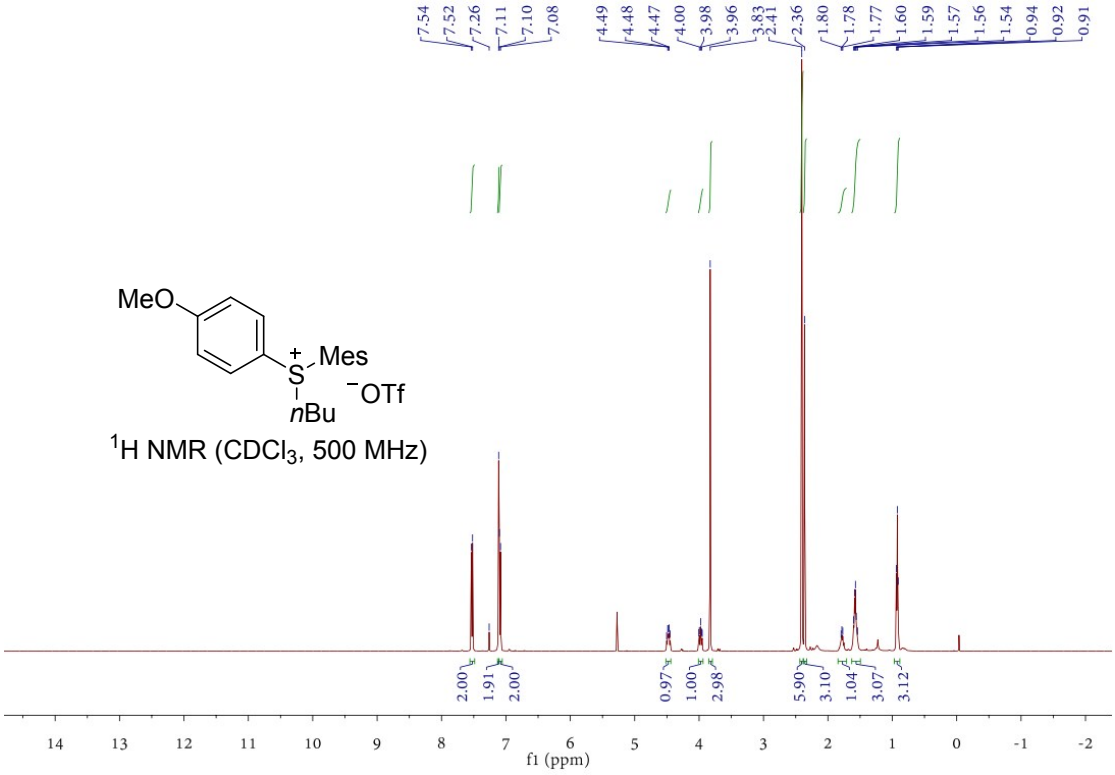


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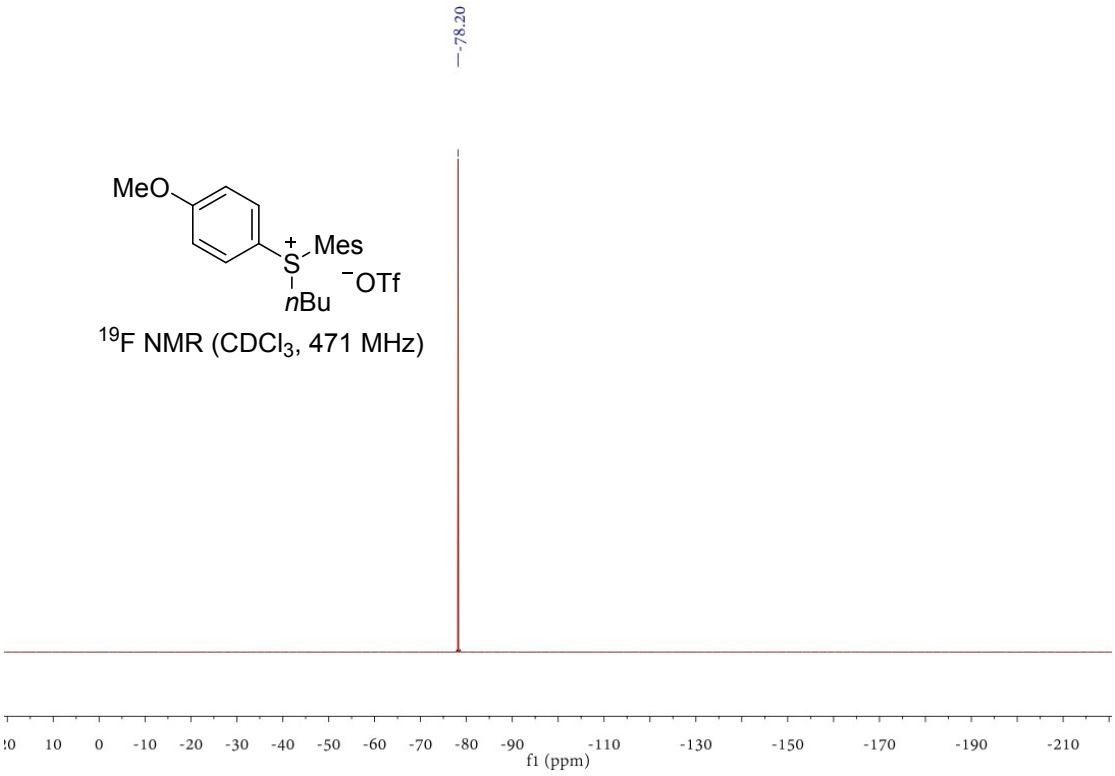


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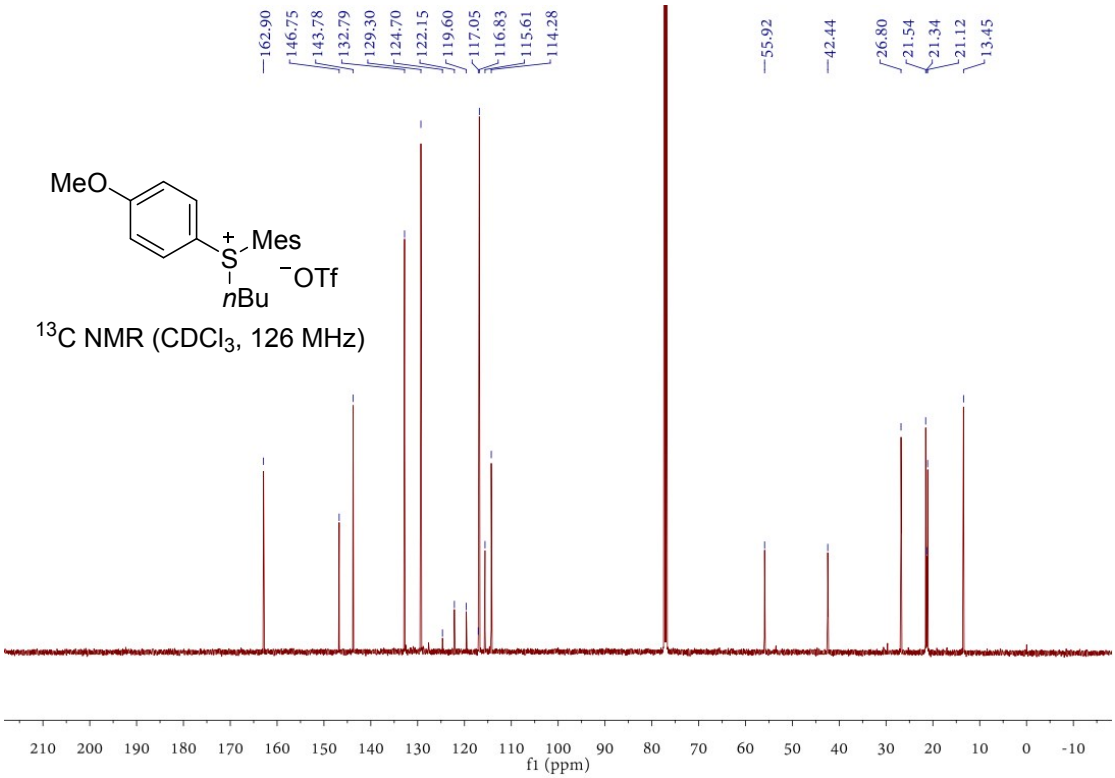


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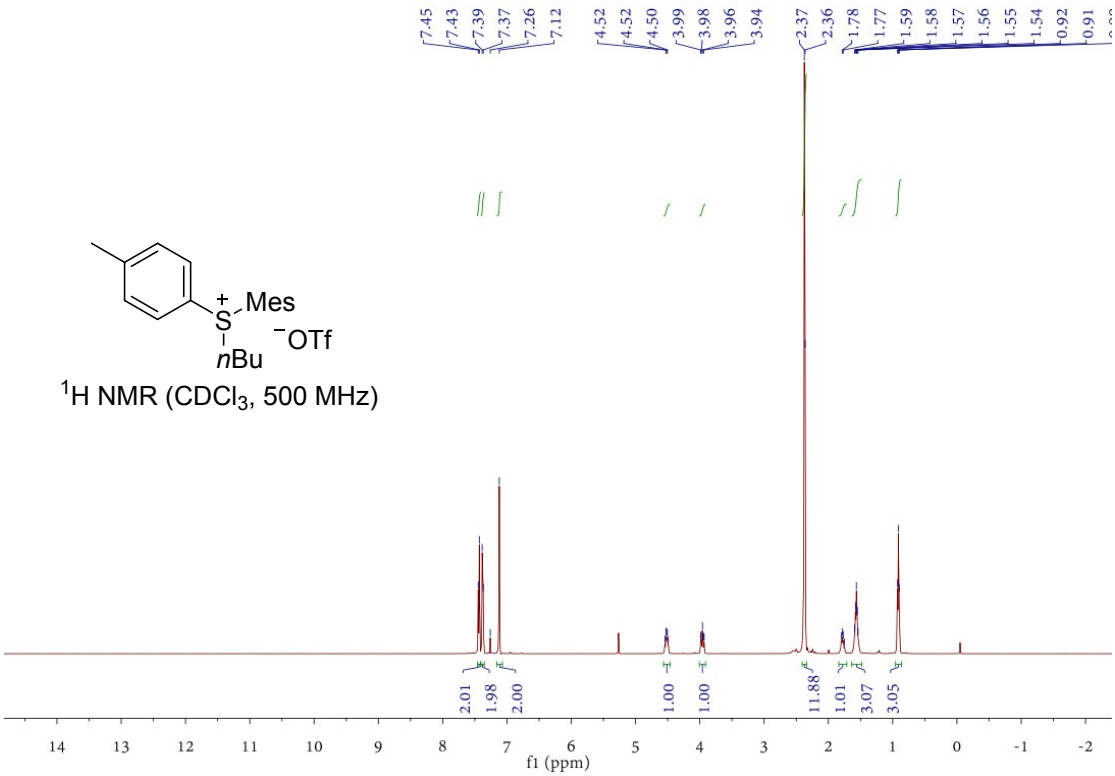
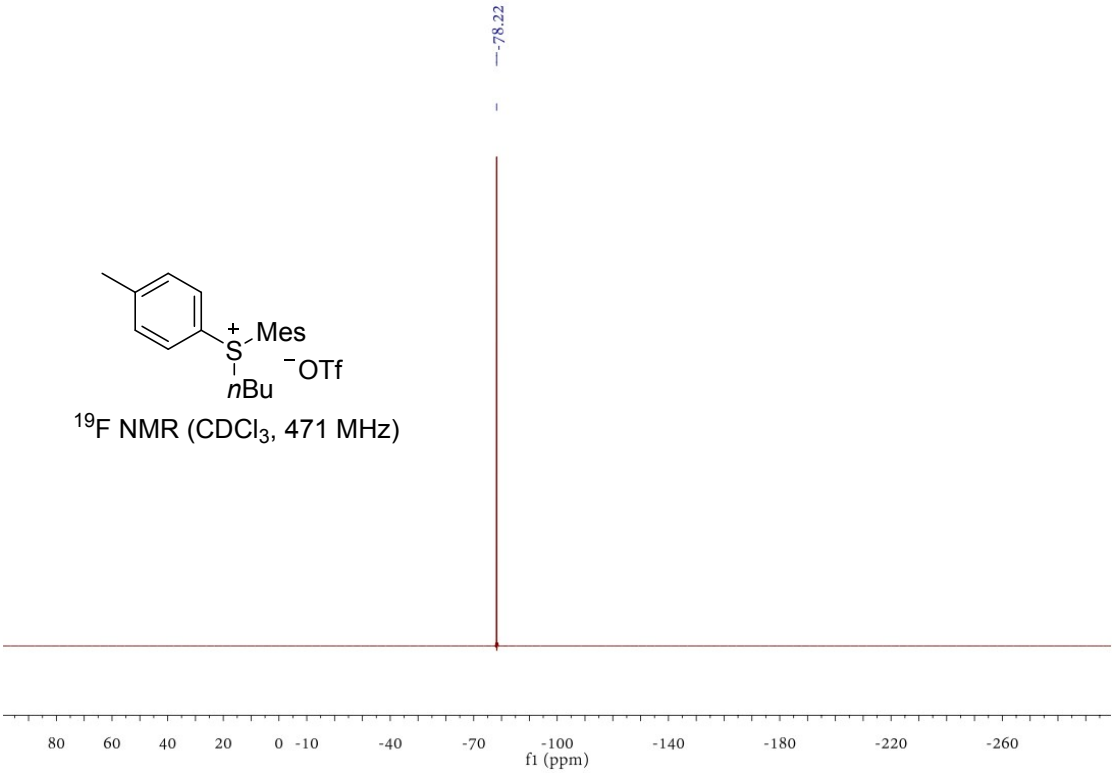



$^{1}$H NMR ($CDCl_3$, 500 MHz)

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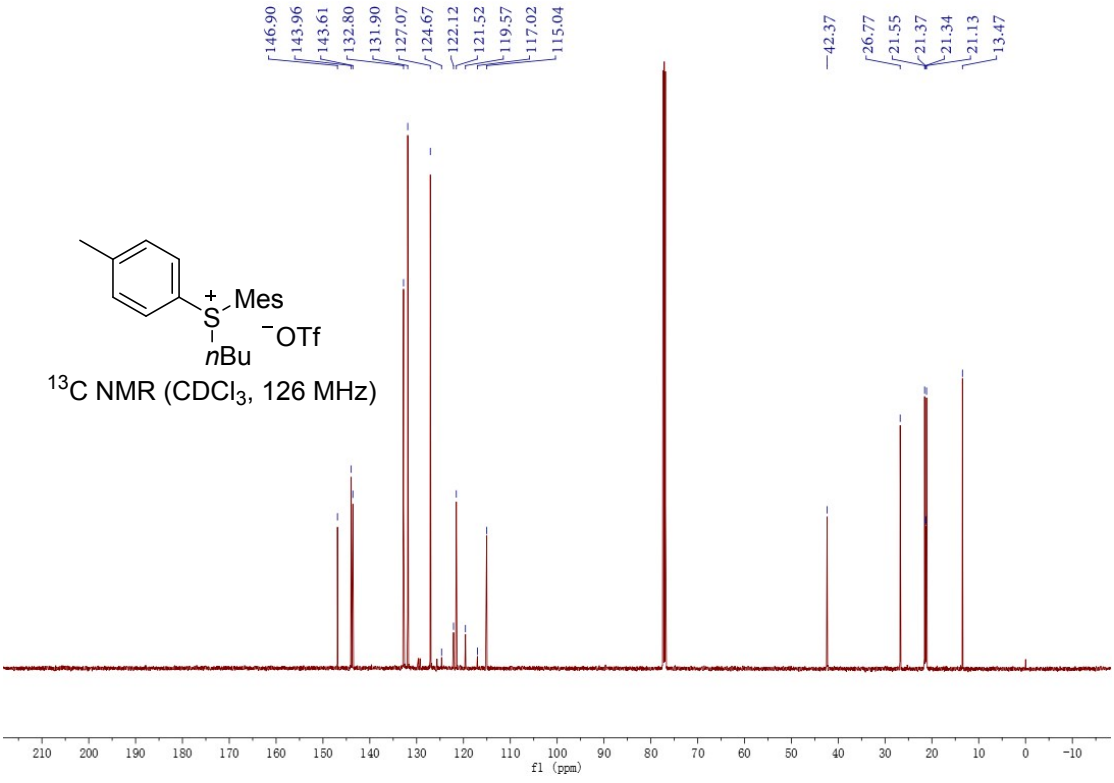
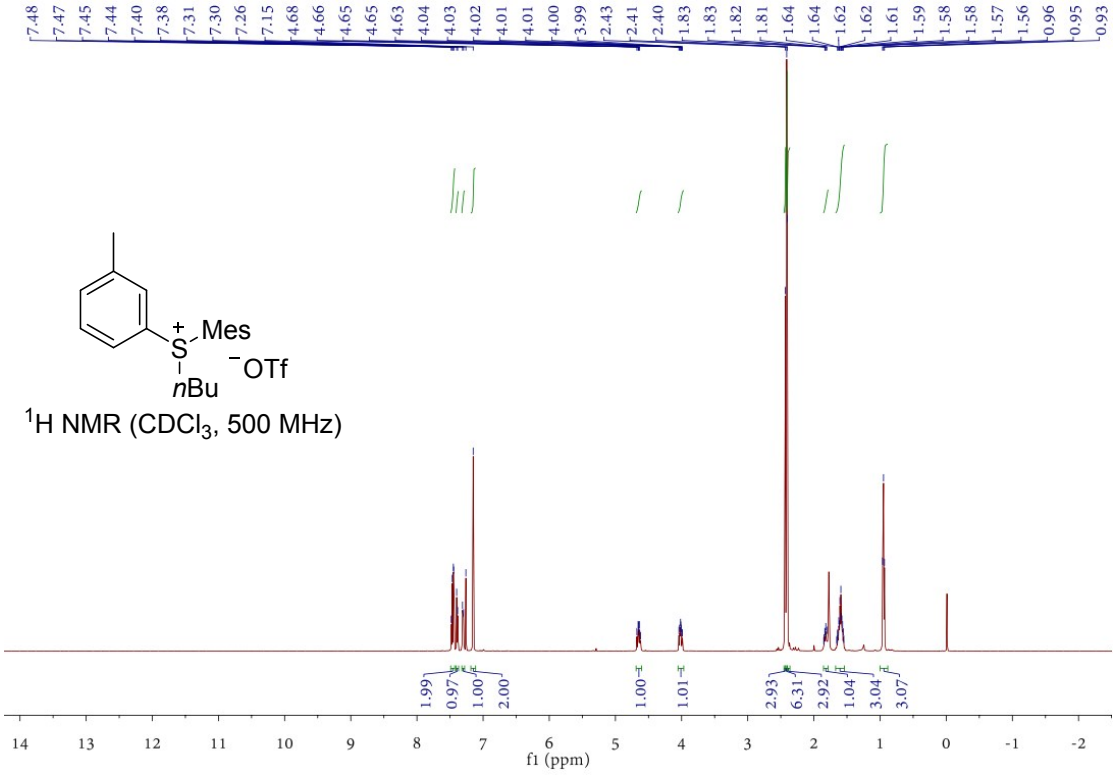



$^{13}$C NMR ($CDCl_3$, 126 MHz)







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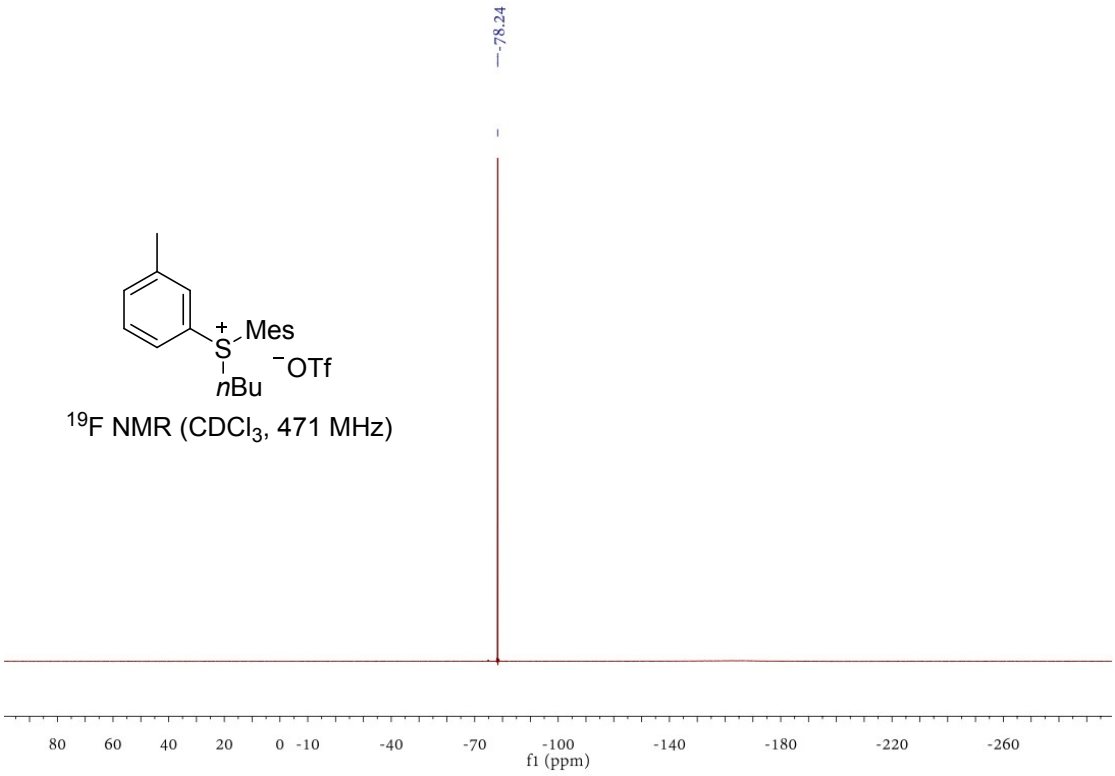





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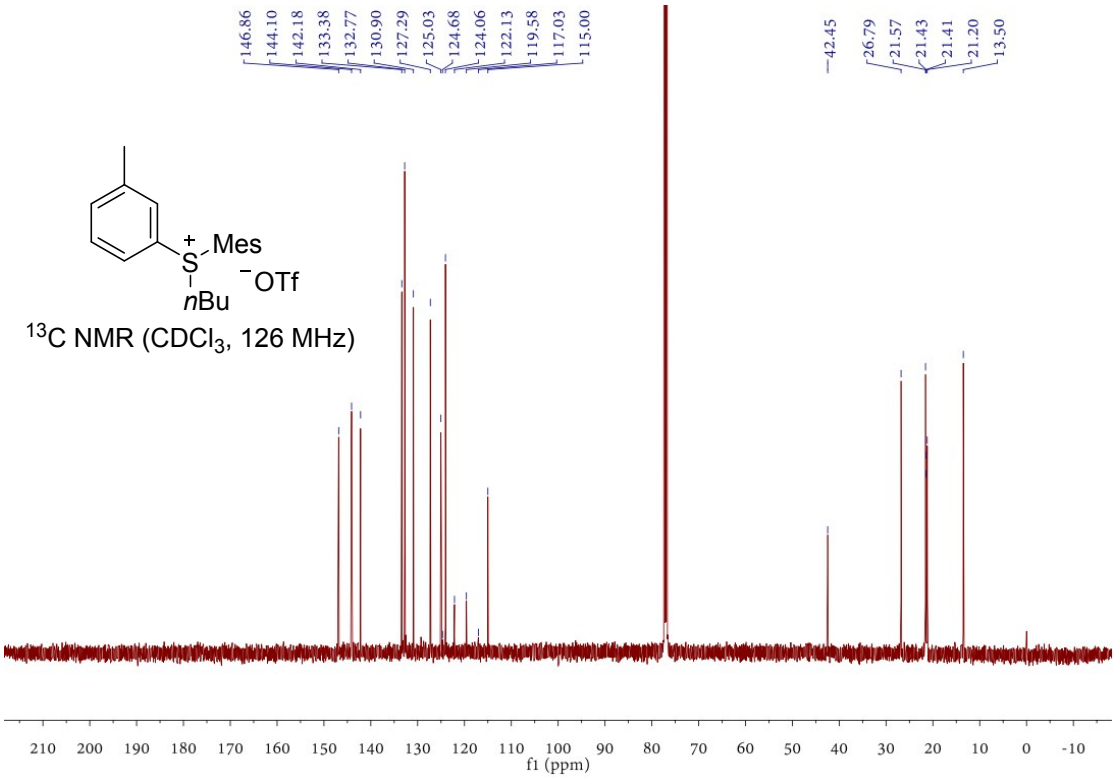


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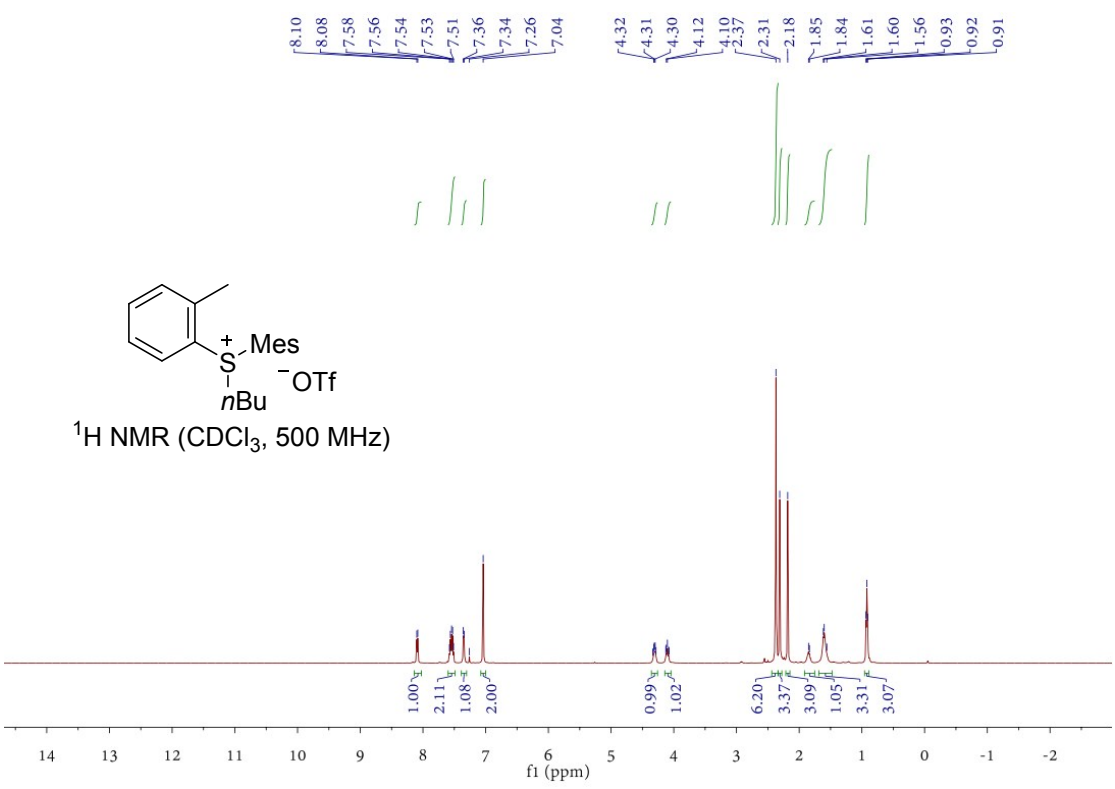


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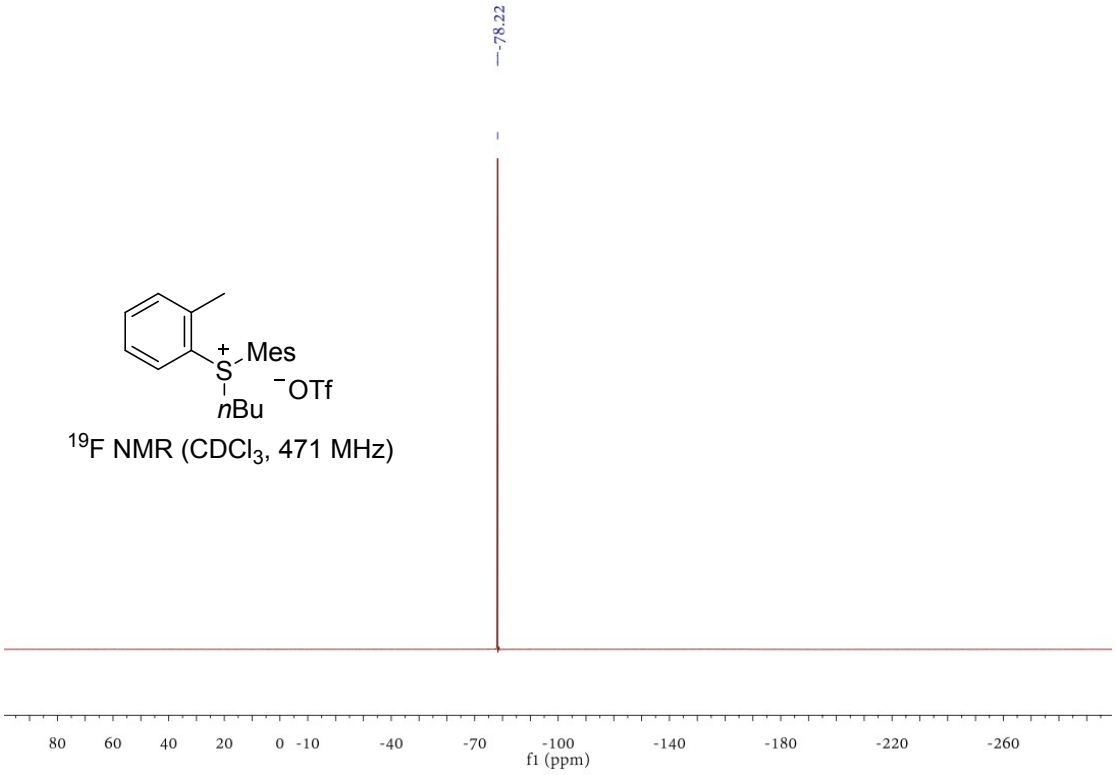


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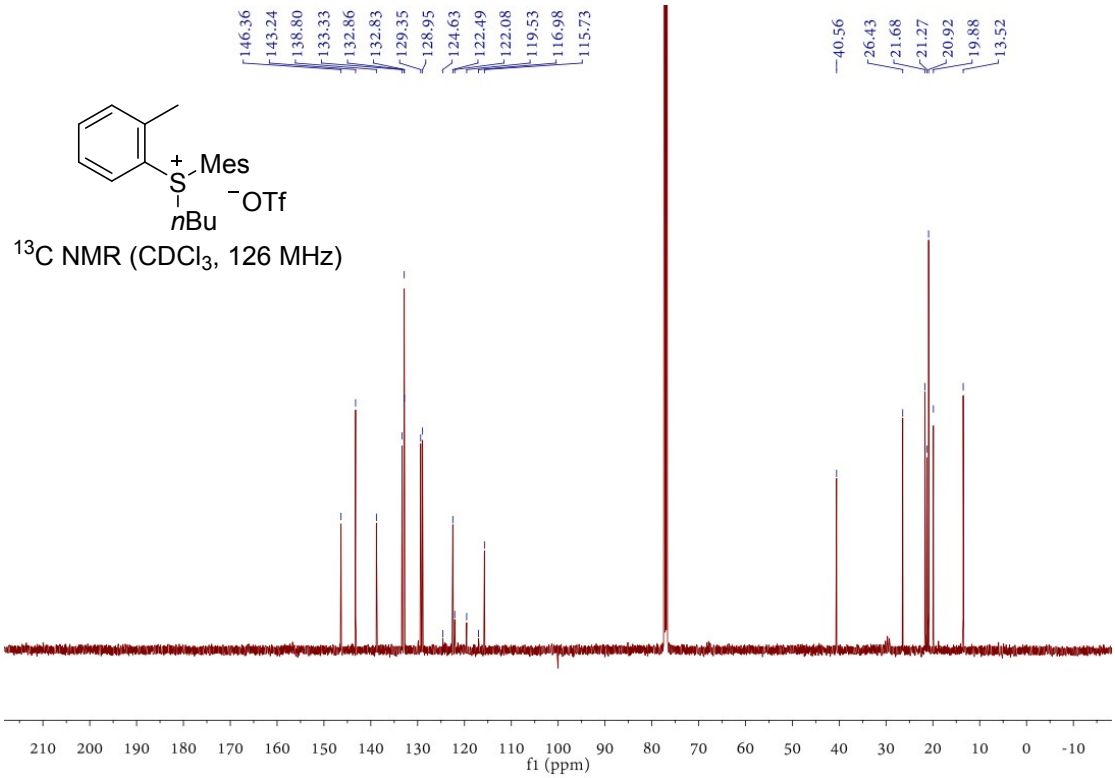


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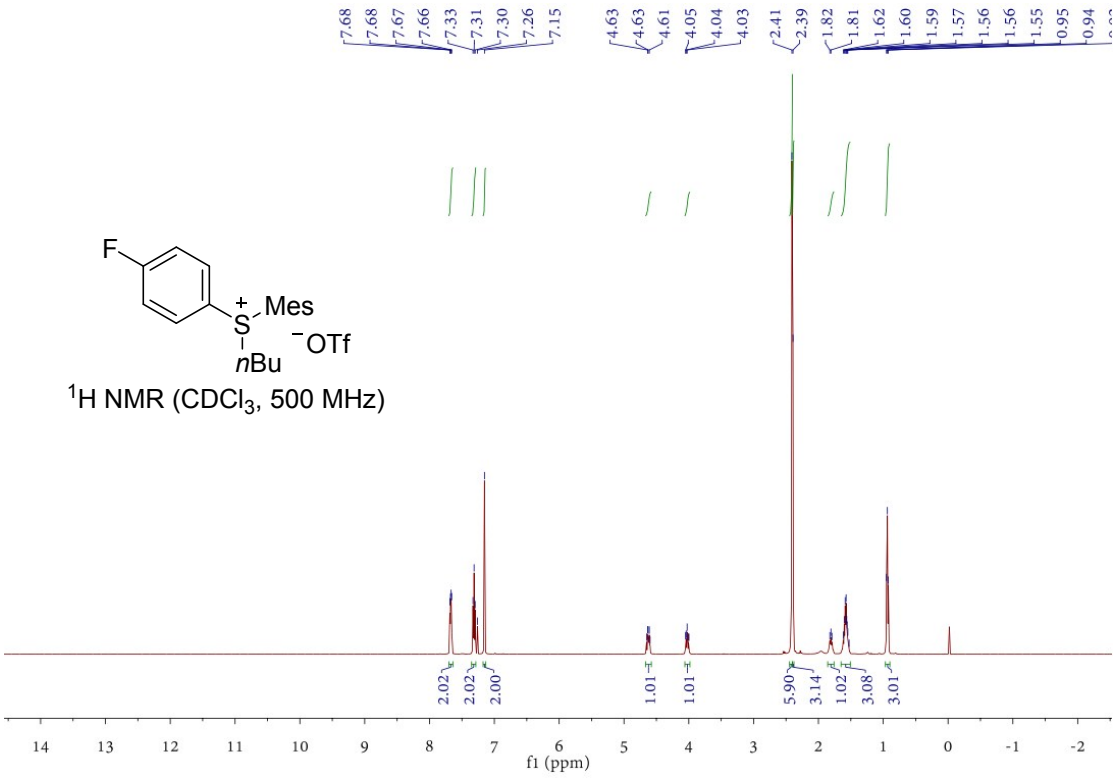


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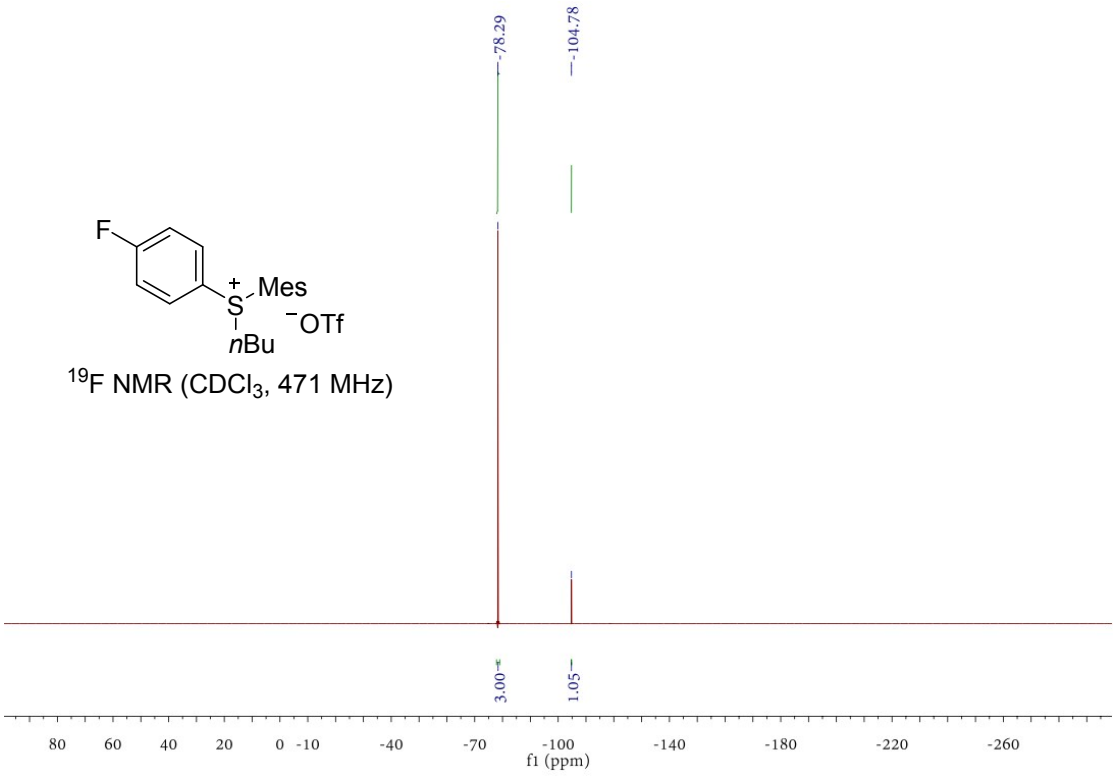


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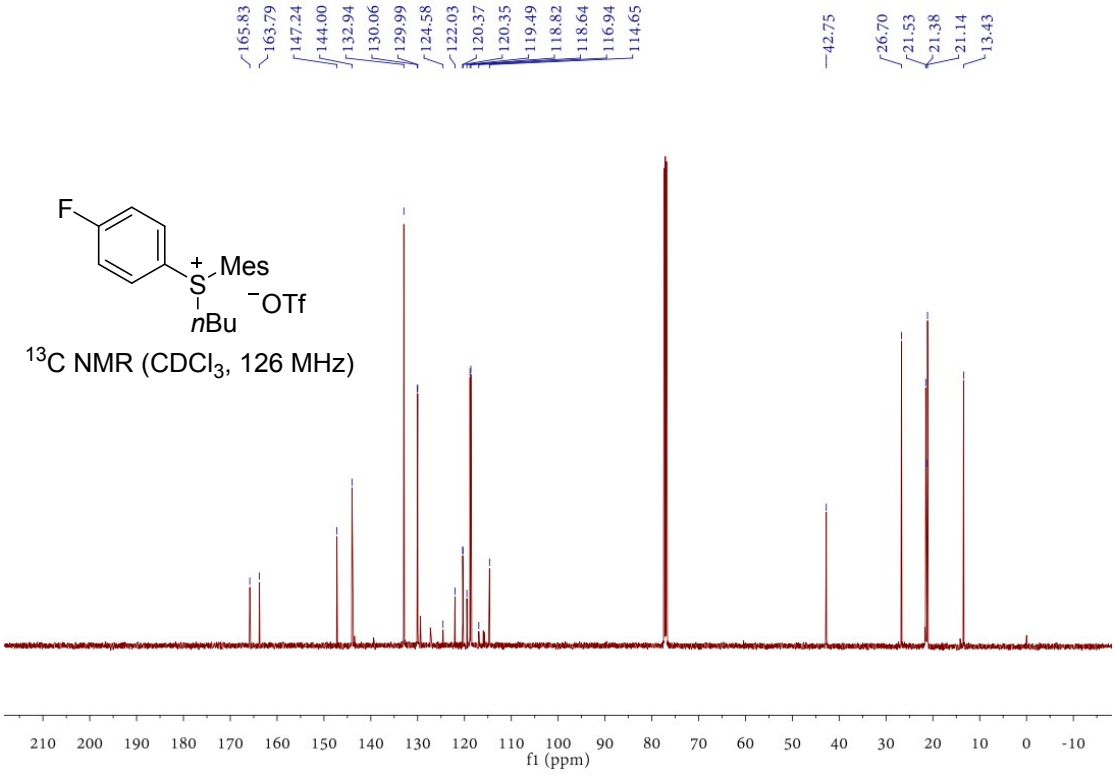


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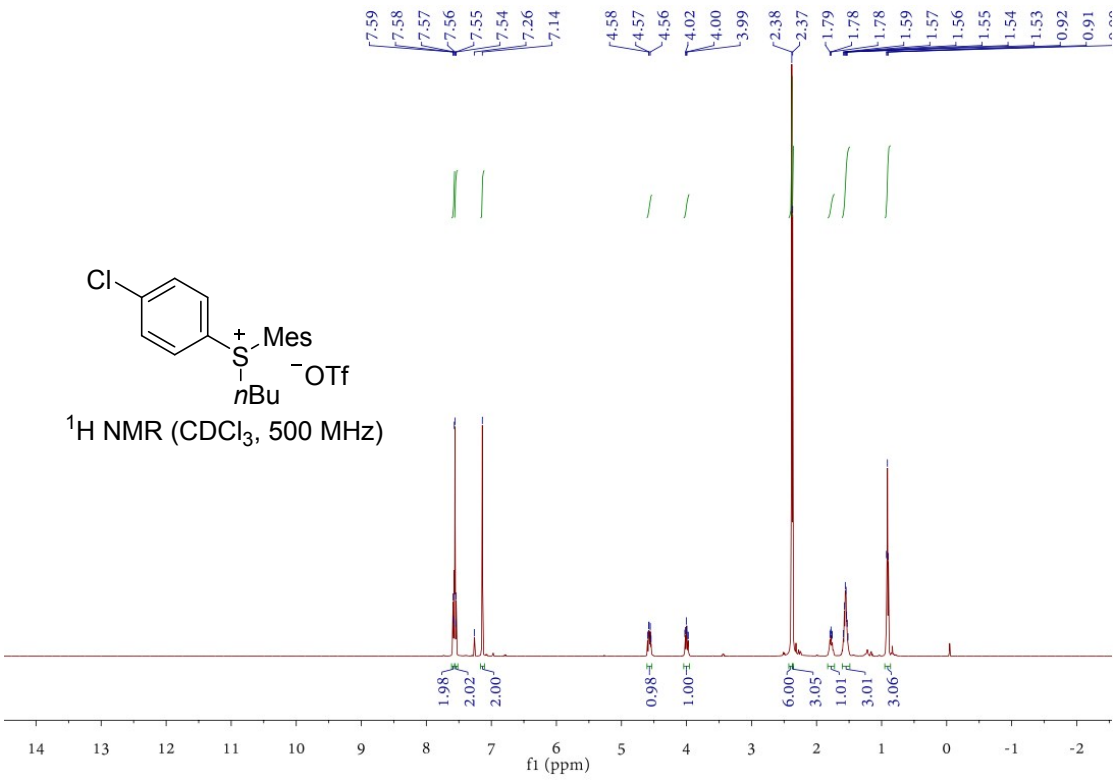


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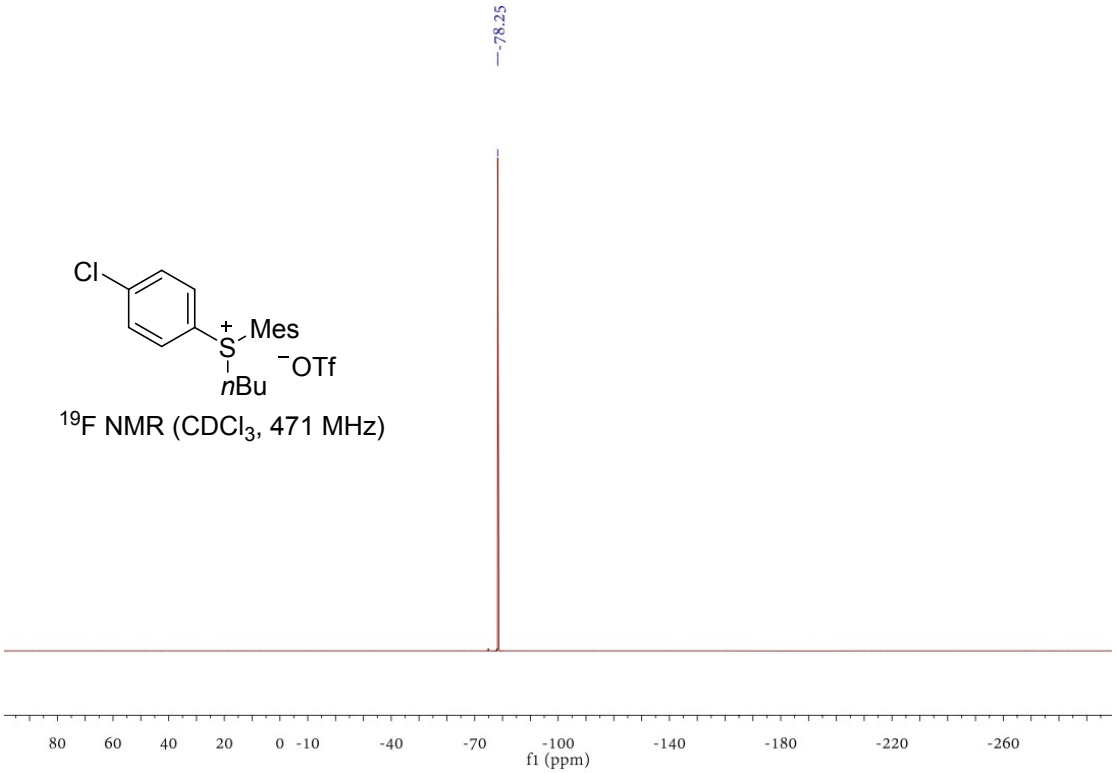


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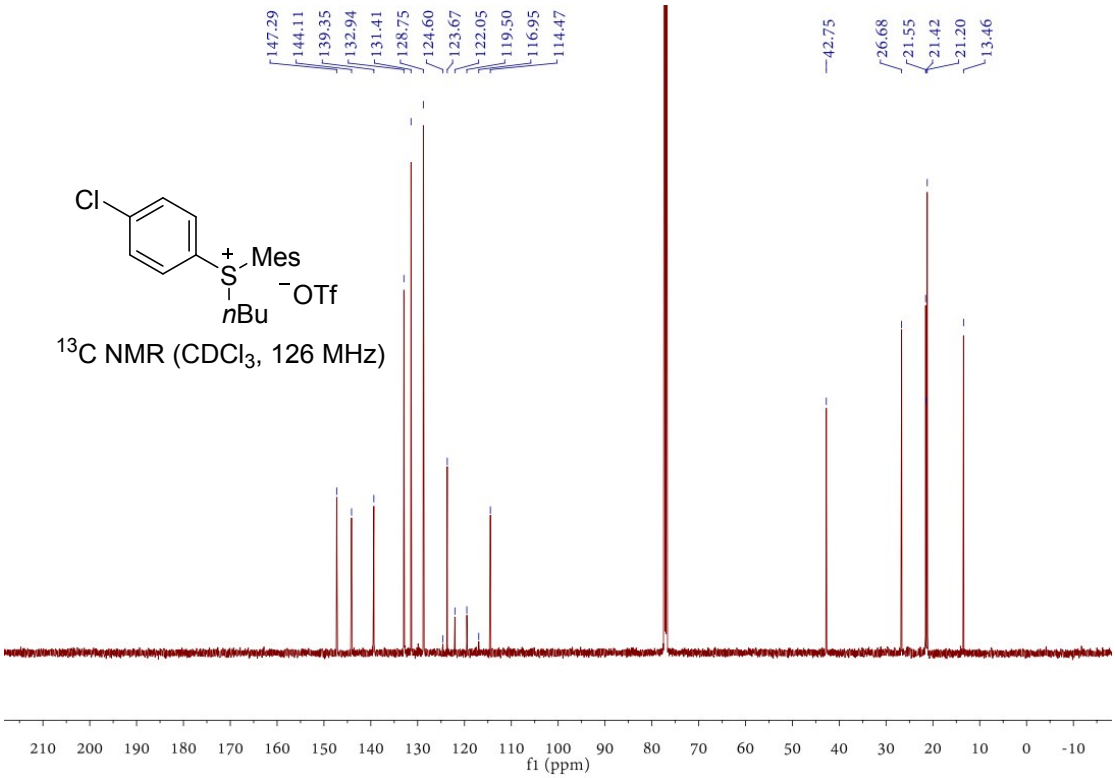


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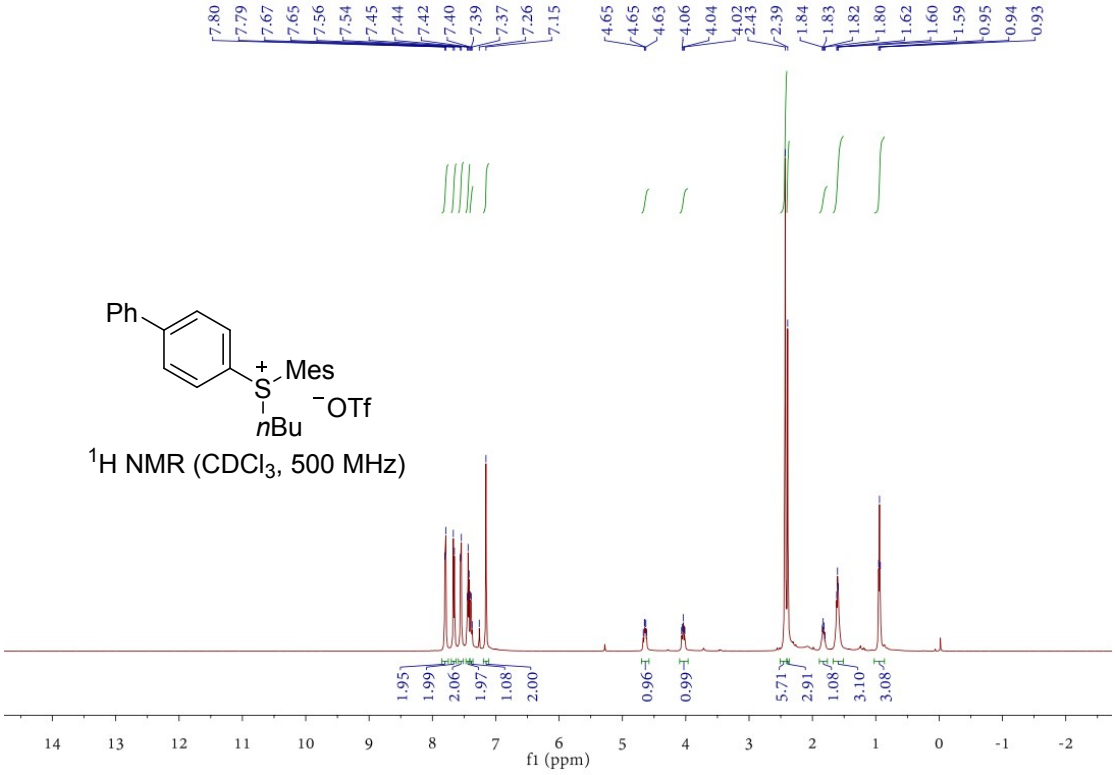





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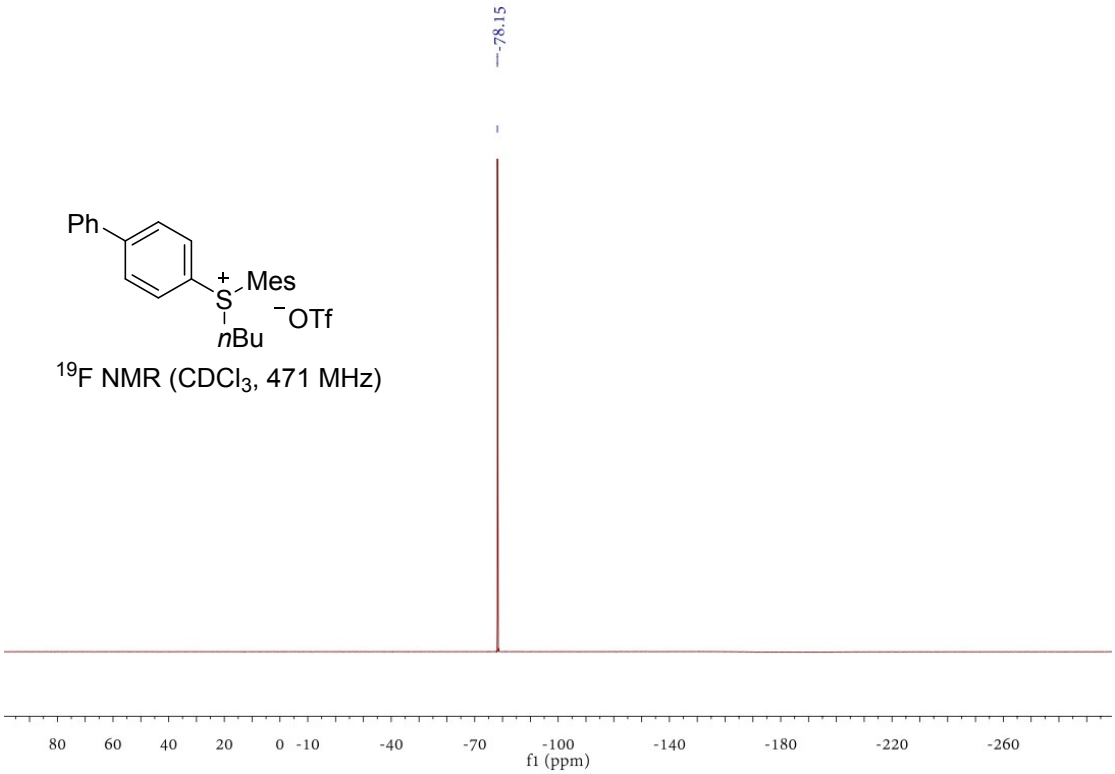





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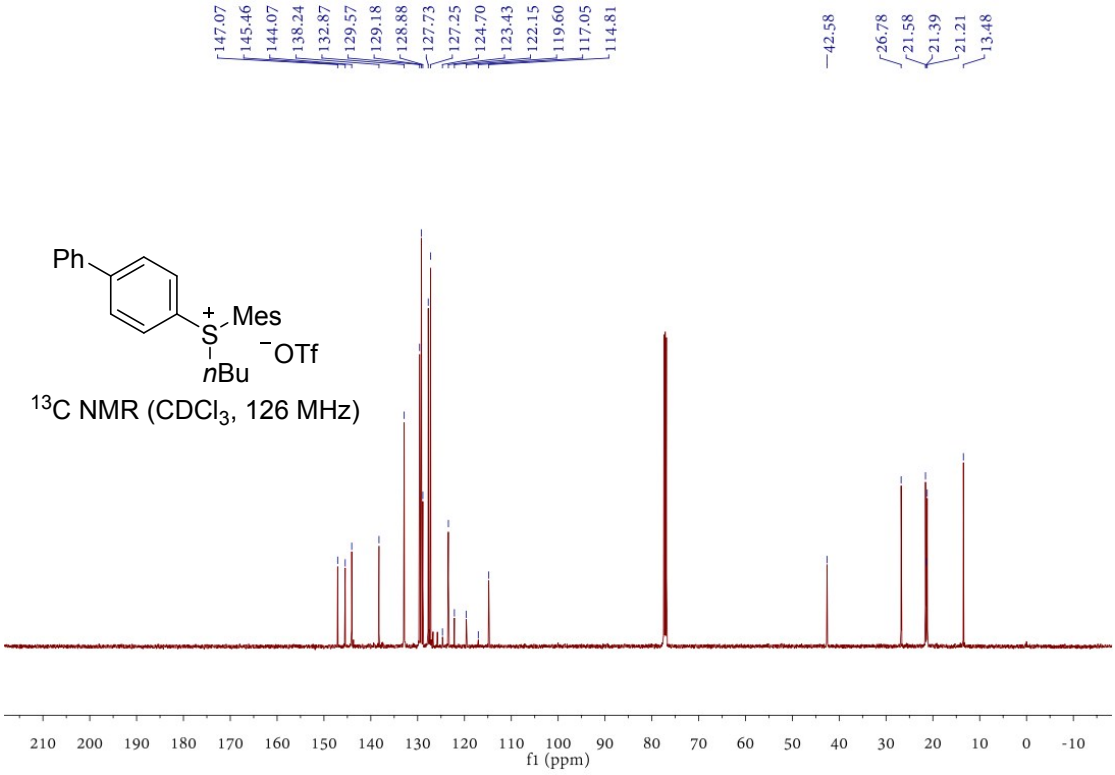
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144.07
138.24
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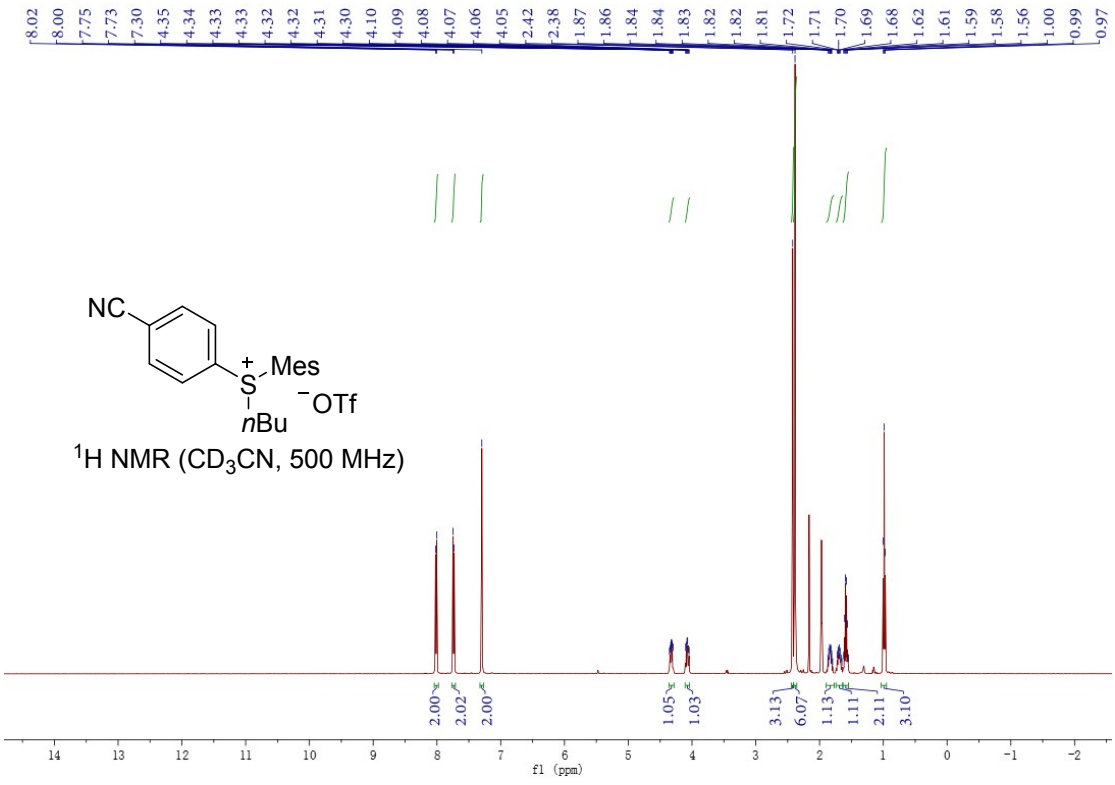
129.57
129.18
128.88
127.73
127.25
124.70
123.43
122.15
119.60
117.05
114.81
42.58
26.78
21.58
21.39
21.21
13.48
Ph
Mes
OTf
nBu
13C NMR (CDCl3, 126 MHz)
f1 (ppm)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8.00
7.75
7.73
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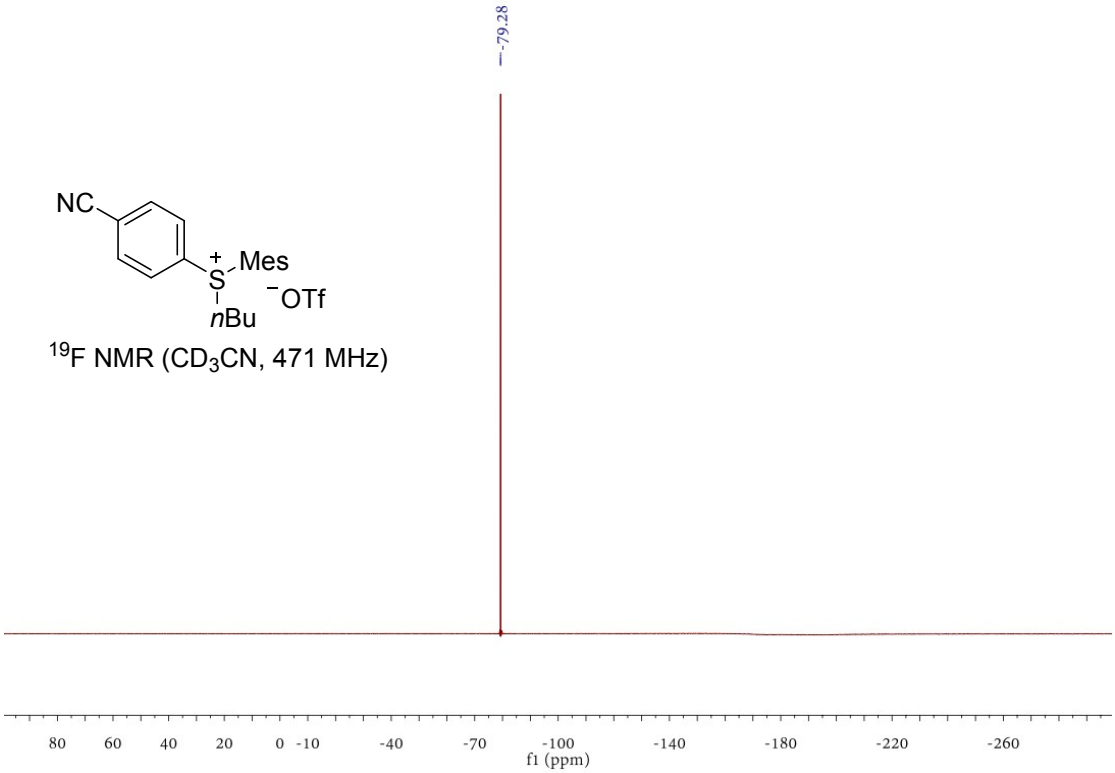
4.32
4.32
4.31
4.30
4.10
4.09
4.08
4.07
4.06
4.05
2.42
2.38
1.87
1.86
1.84
1.84
1.83
1.82
1.82
1.81
1.72
1.71
1.70
1.69
1.68
1.62
1.61
1.59
1.58
1.56
1.00
0.99
0.97
NC
Mes
OTf
nBu
1H NMR (CD3CN, 500 MHz)
2.00
2.02
2.00
1.05
1.03
3.13
6.07
1.13
1.11
2.11
3.10
f1 (ppm)







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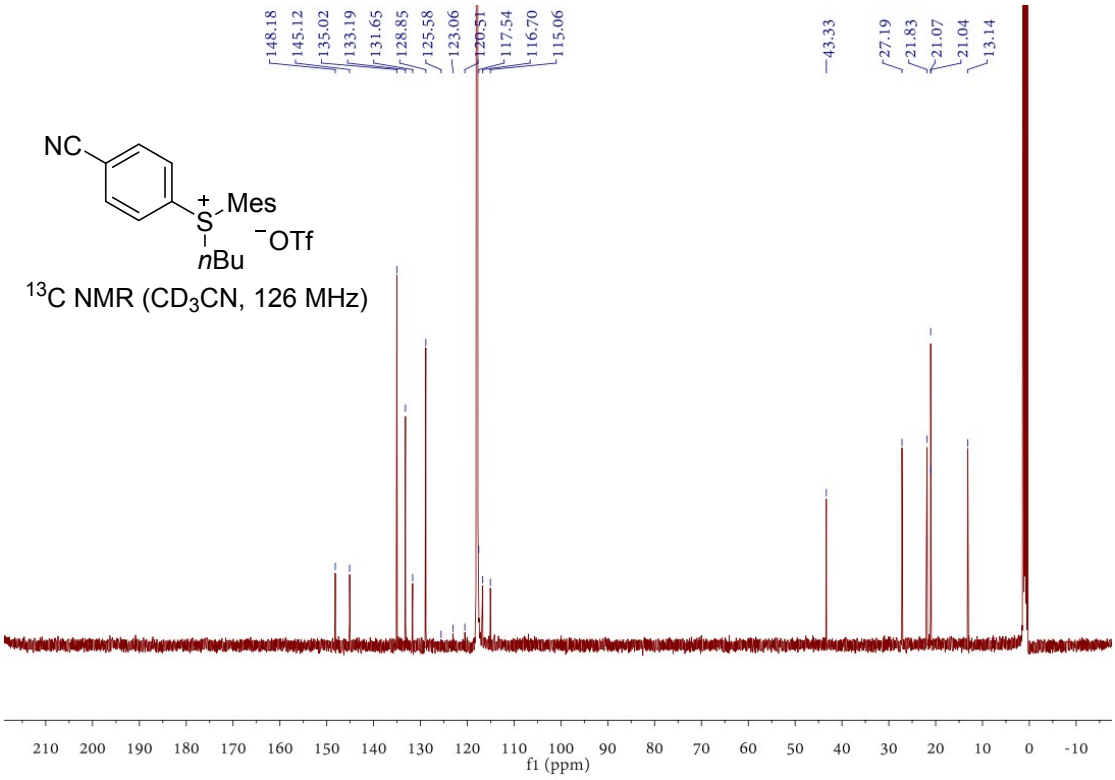
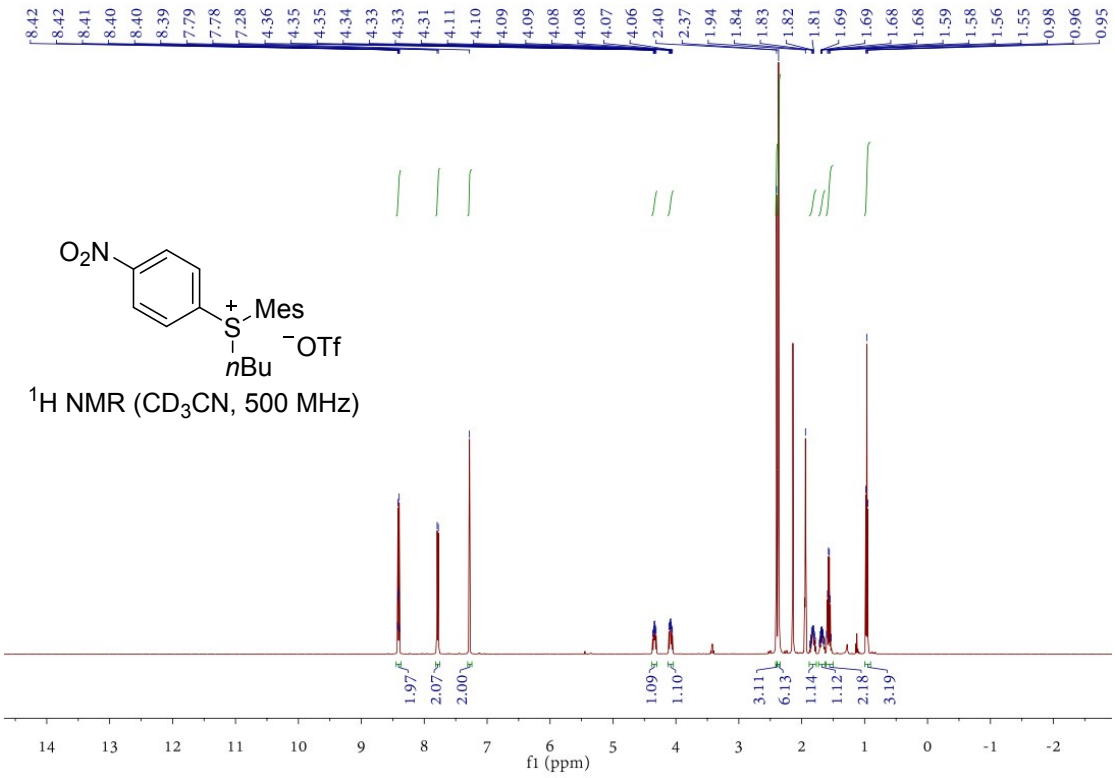


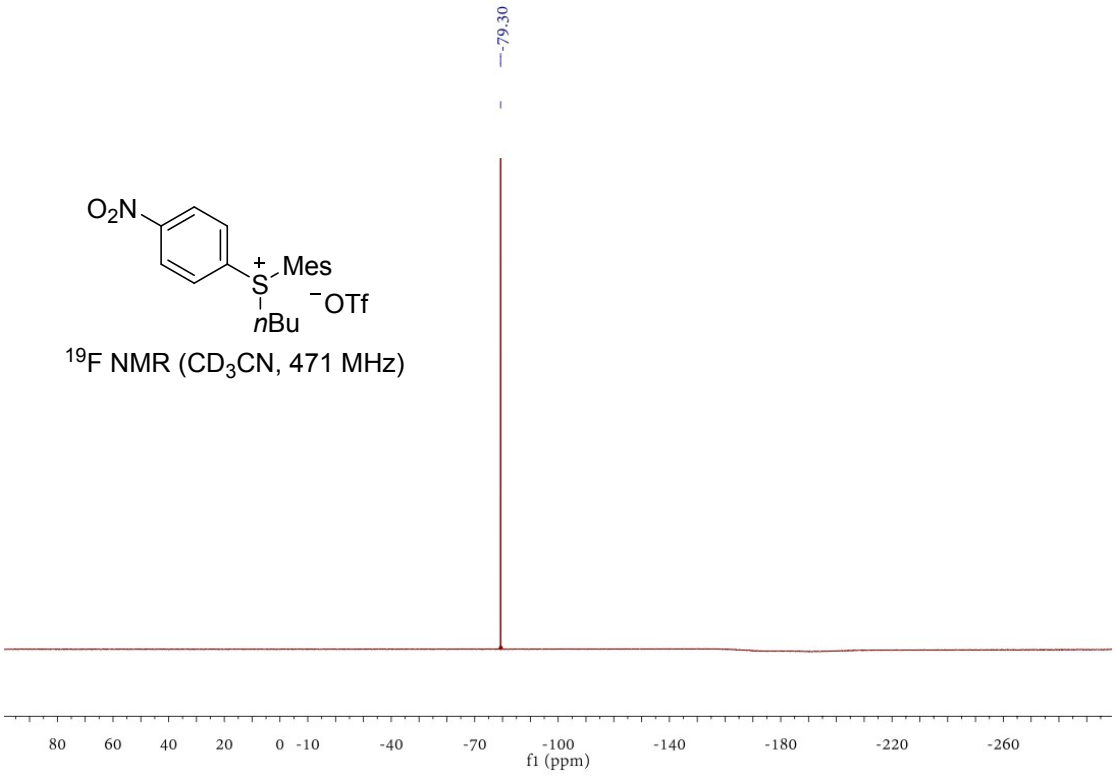




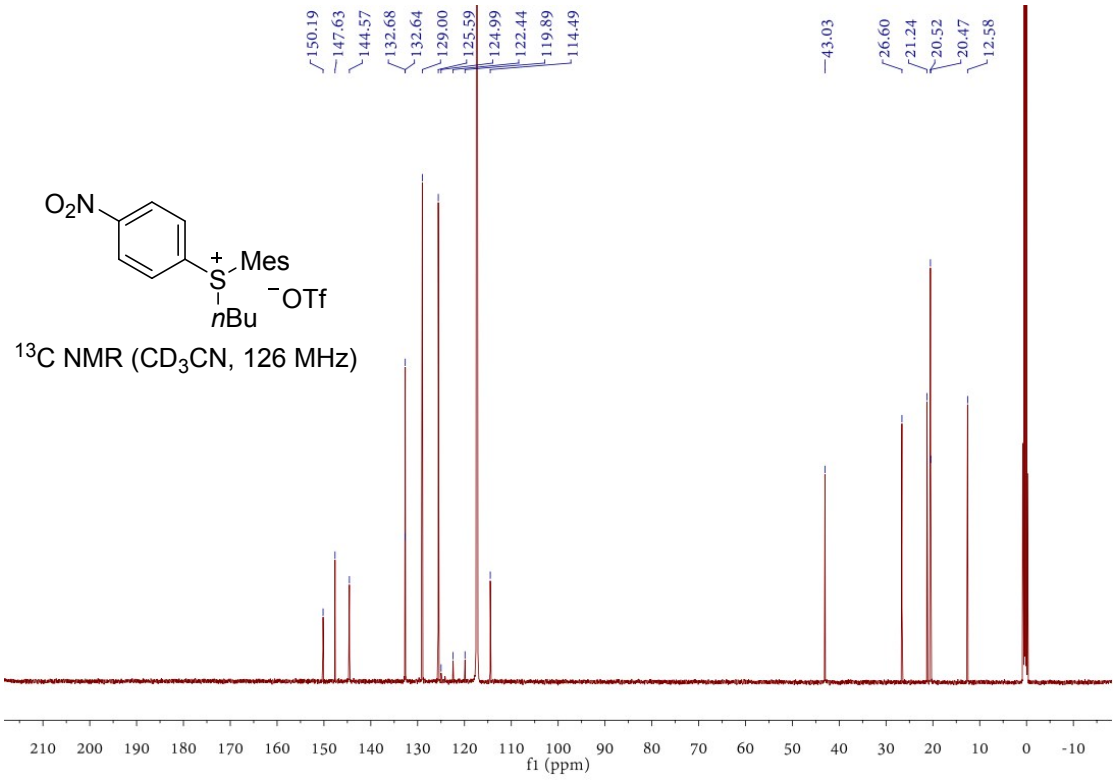
$^{13}$C NMR ($CD_3CN$, 126 MHz)



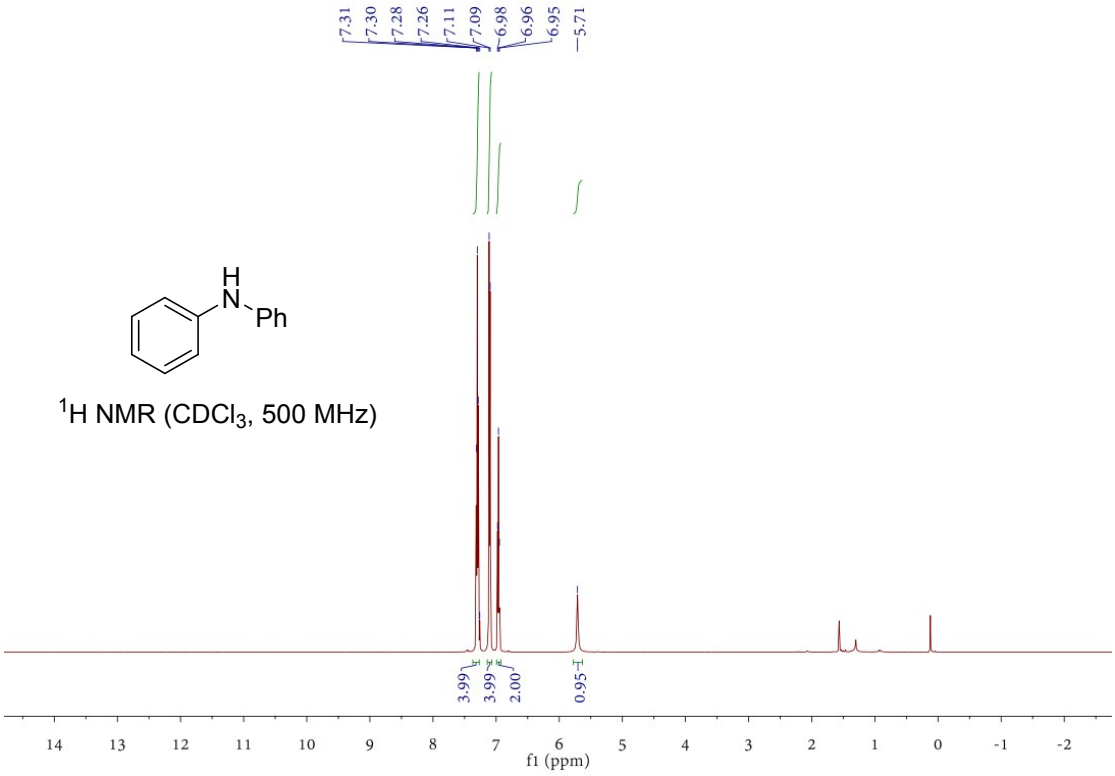

$^{1}$H NMR ($CD_3CN$, 500 MHz)



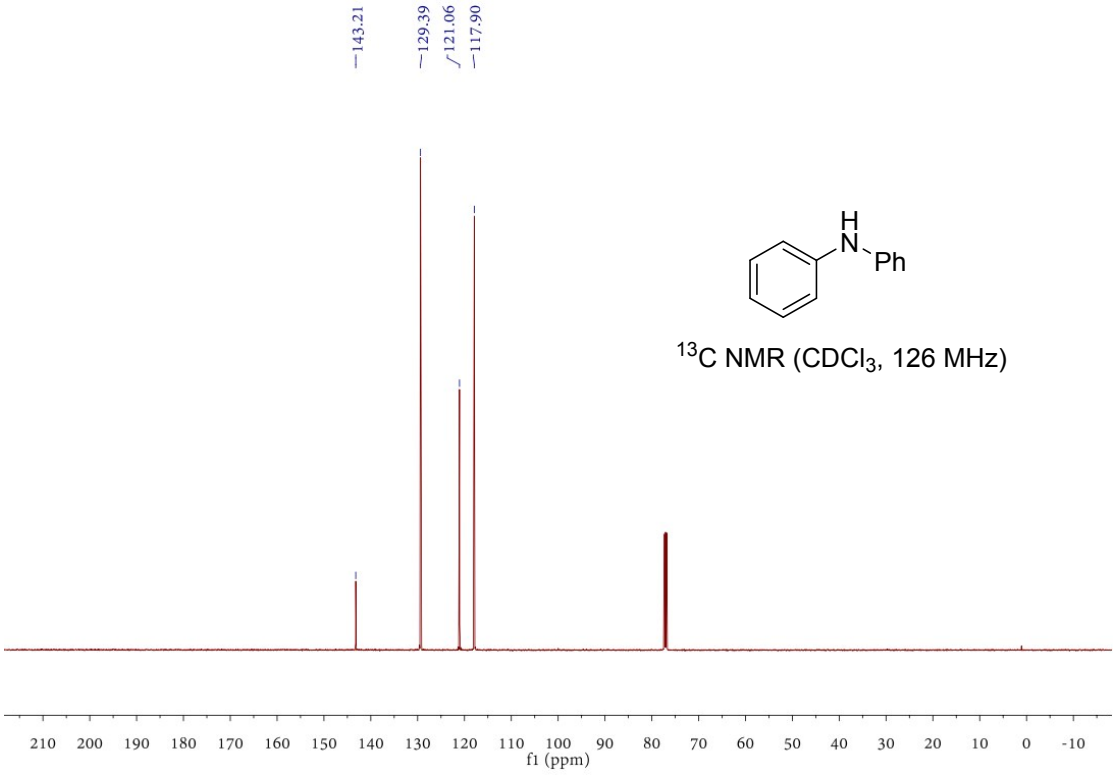

$^{19}$F NMR ($CD_3CN$, 471 MHz)



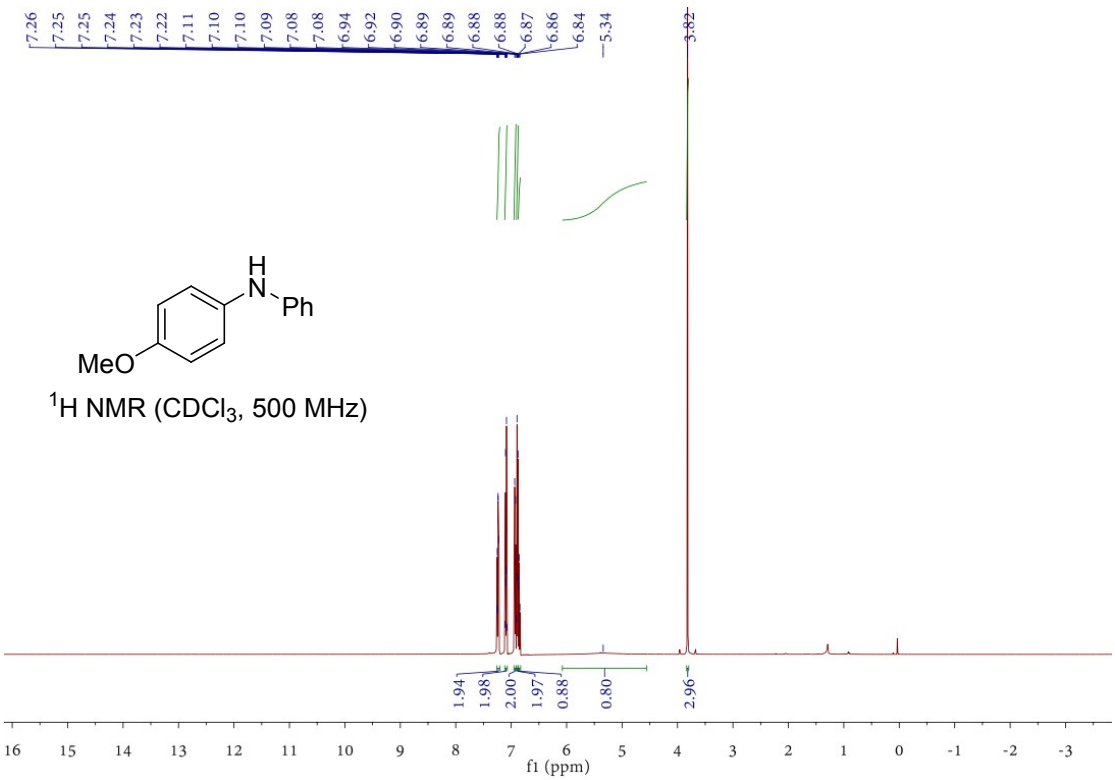

$^{13}$C NMR ($CD_3CN$, 126 MHz)



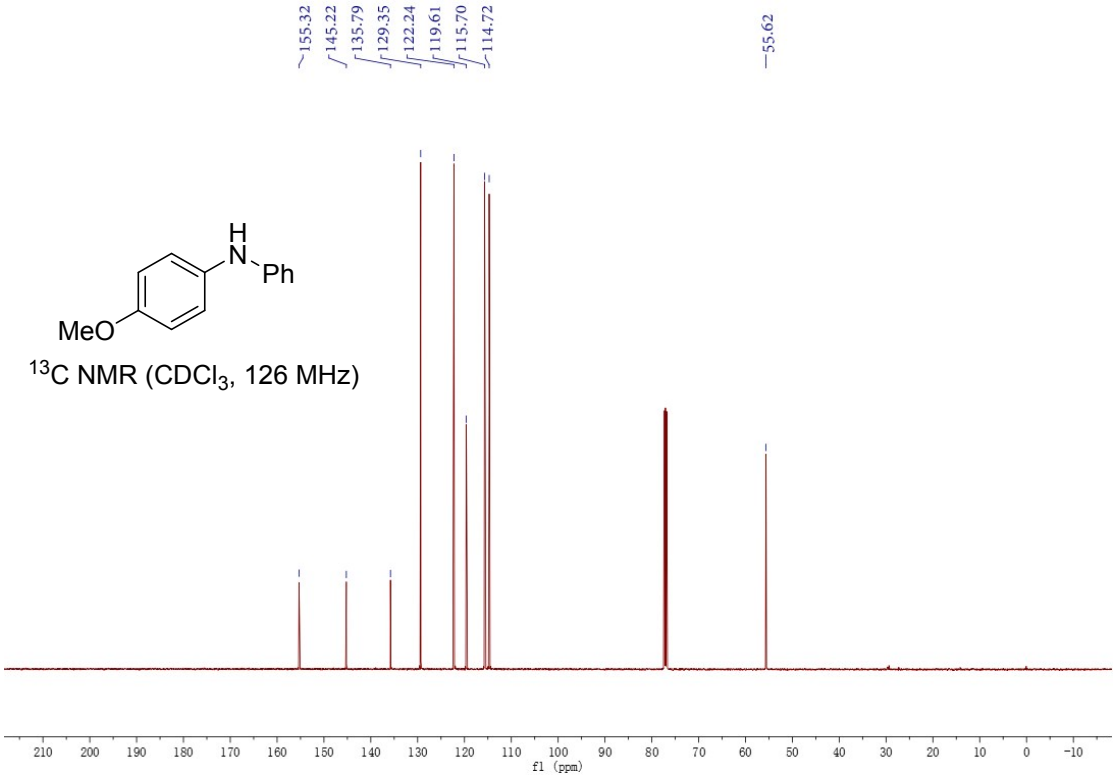

$^{1}$H NMR ($CDCl_3$, 500 MHz)



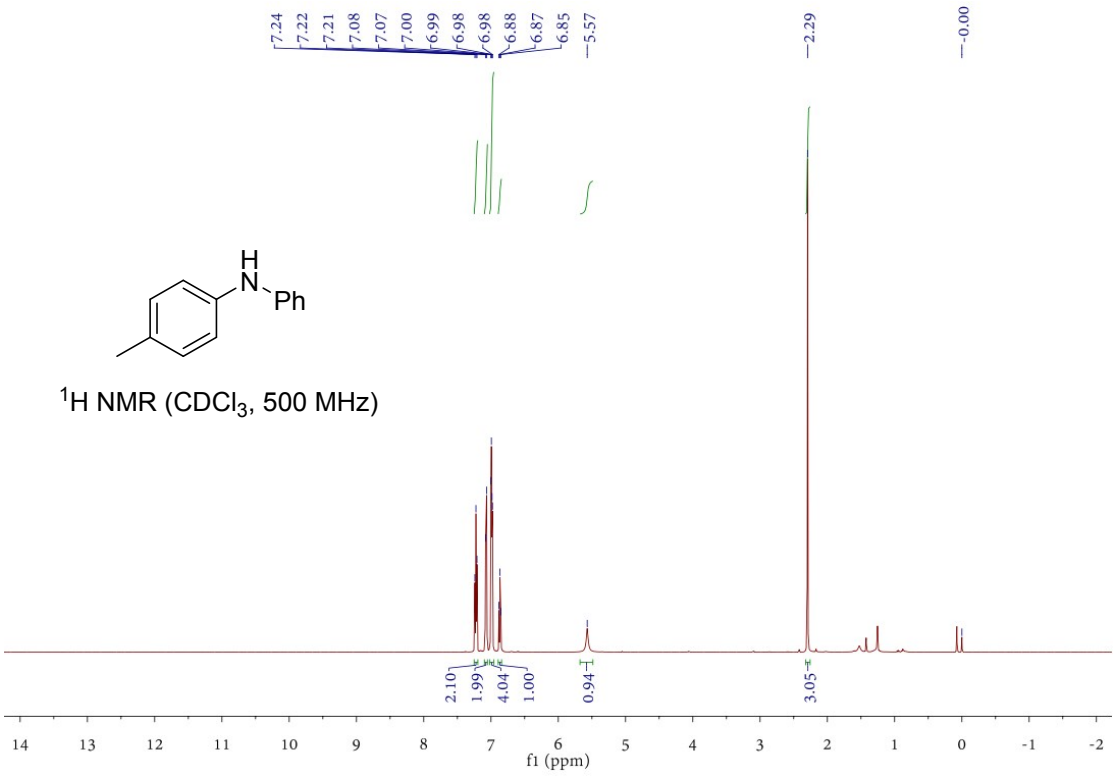

$^{13}$C NMR ($CDCl_3$, 126 MHz)



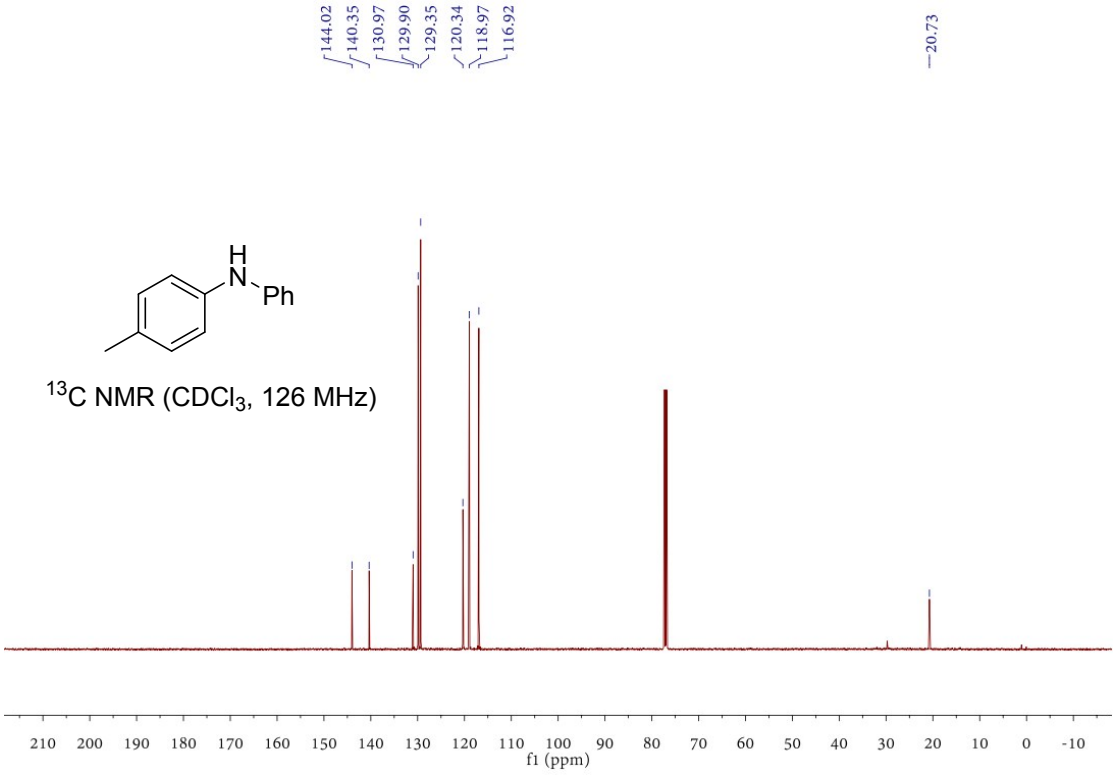

$^{1}$H NMR ($CDCl_3$, 500 MHz)



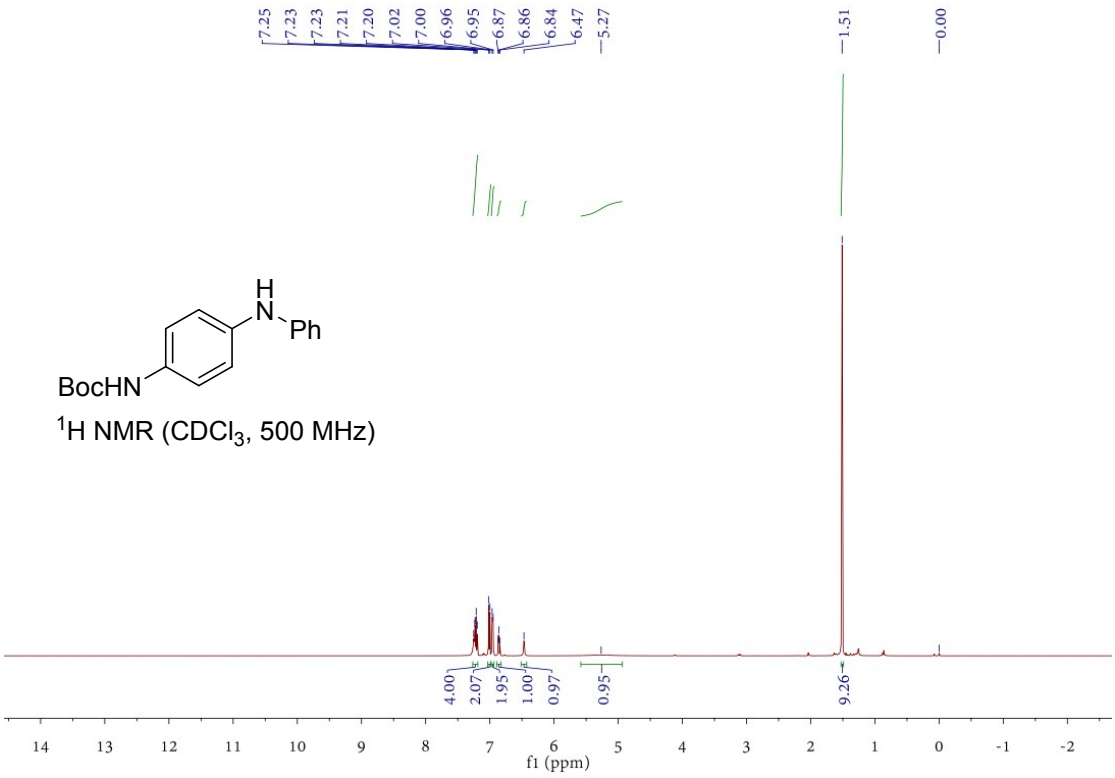

$^{13}C$ NMR ($CDCl_3$, 126 MHz)



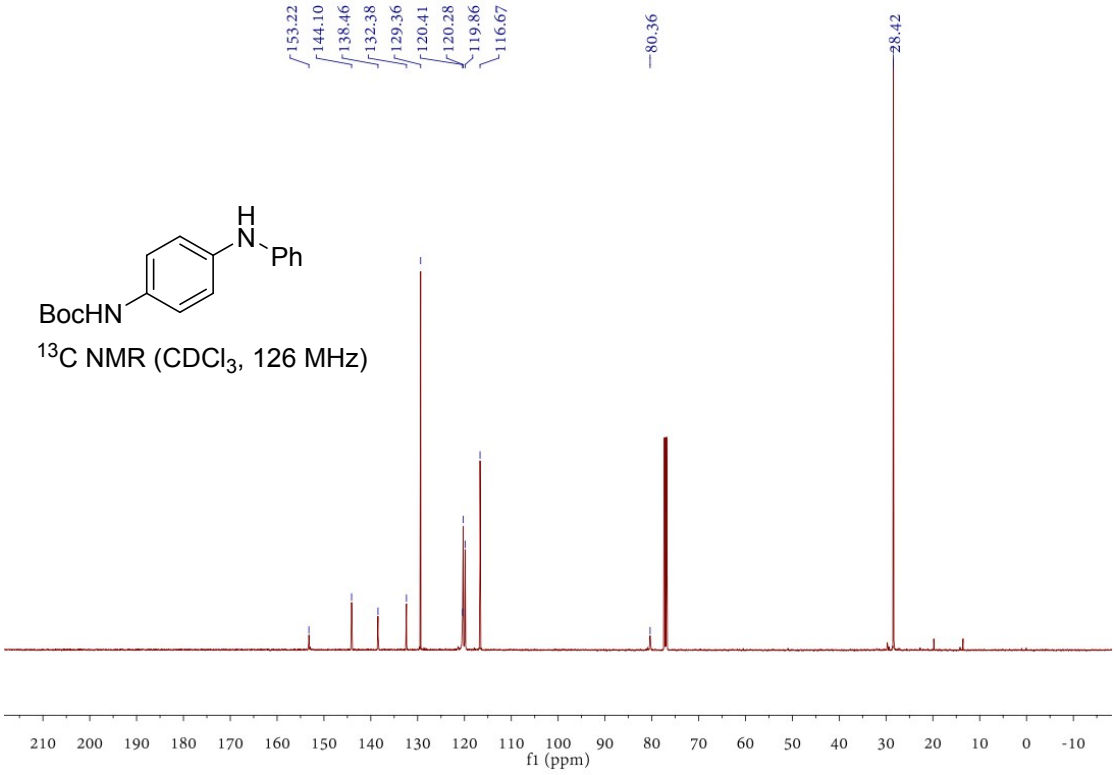

$^{1}H$ NMR ($CDCl_3$, 500 MHz)



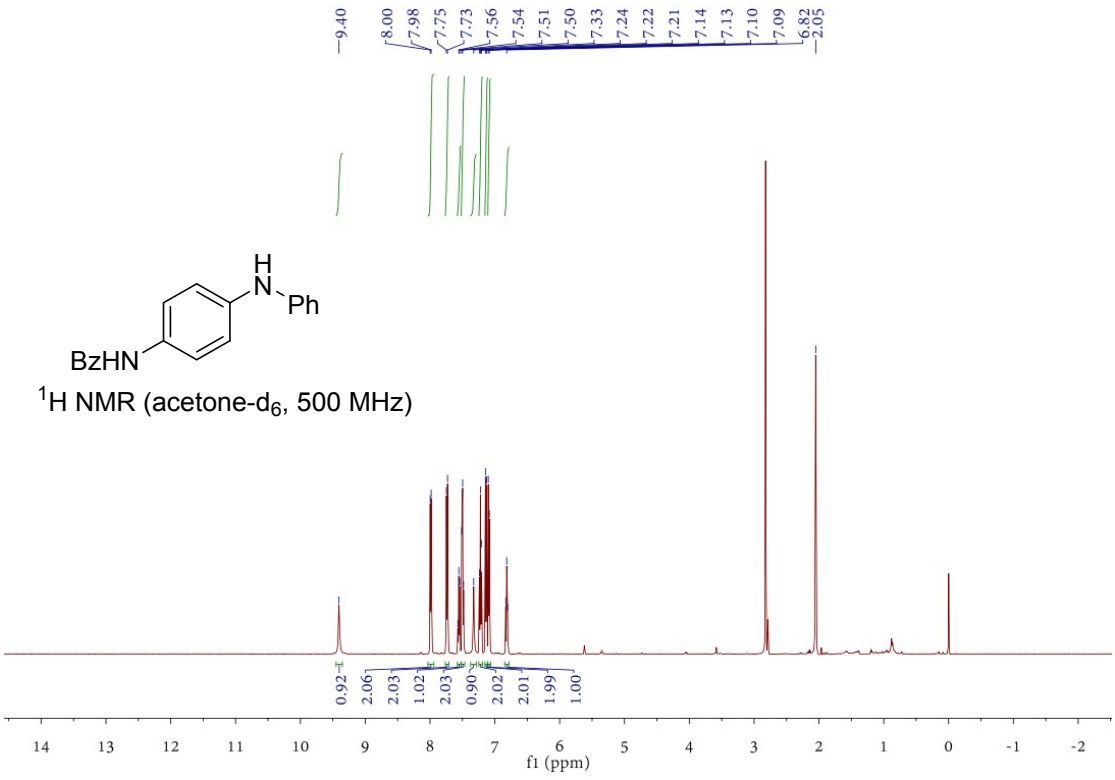

$^{13}C$ NMR ($CDCl_3$, 126 MHz)



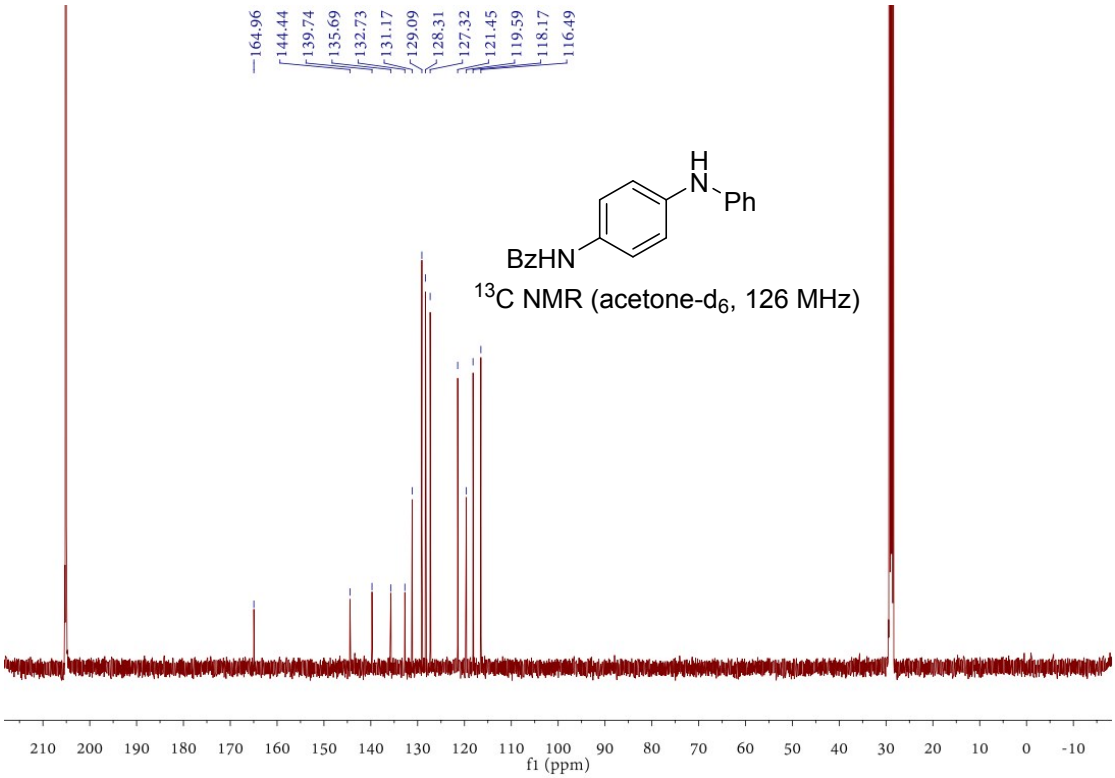

$^{1}H$ NMR ($CDCl_3$, 500 MHz)



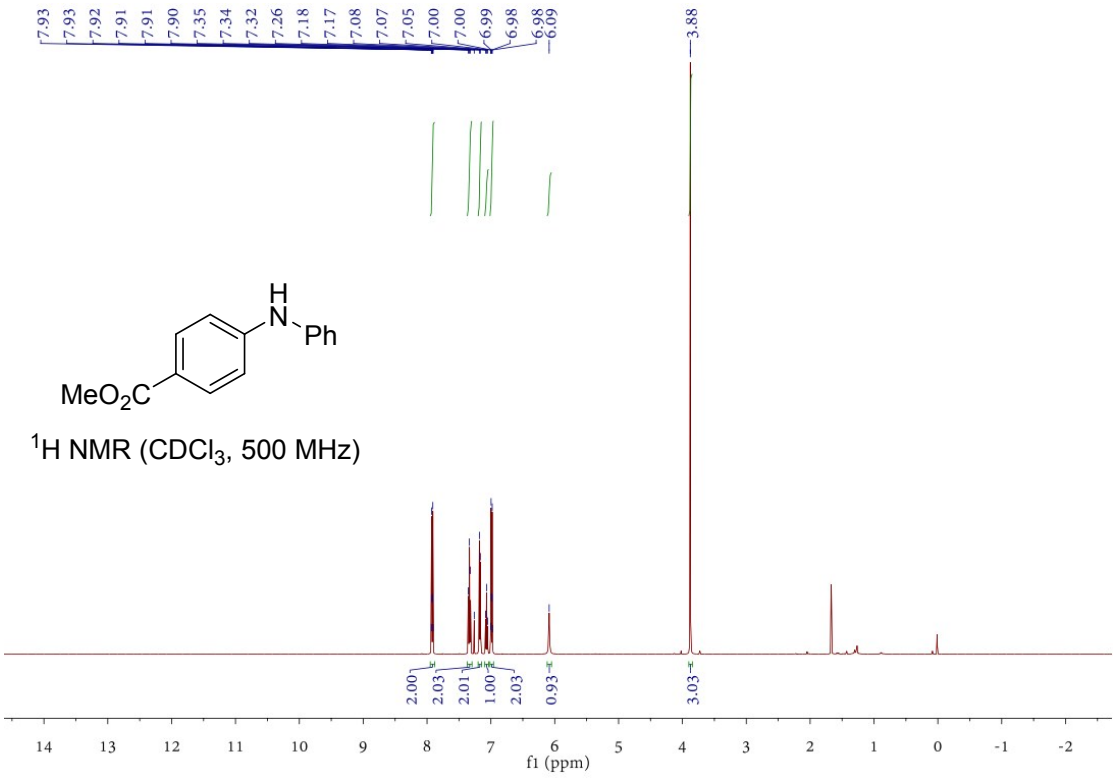

$^{13}C$ NMR ($CDCl_3$, 126 MHz)



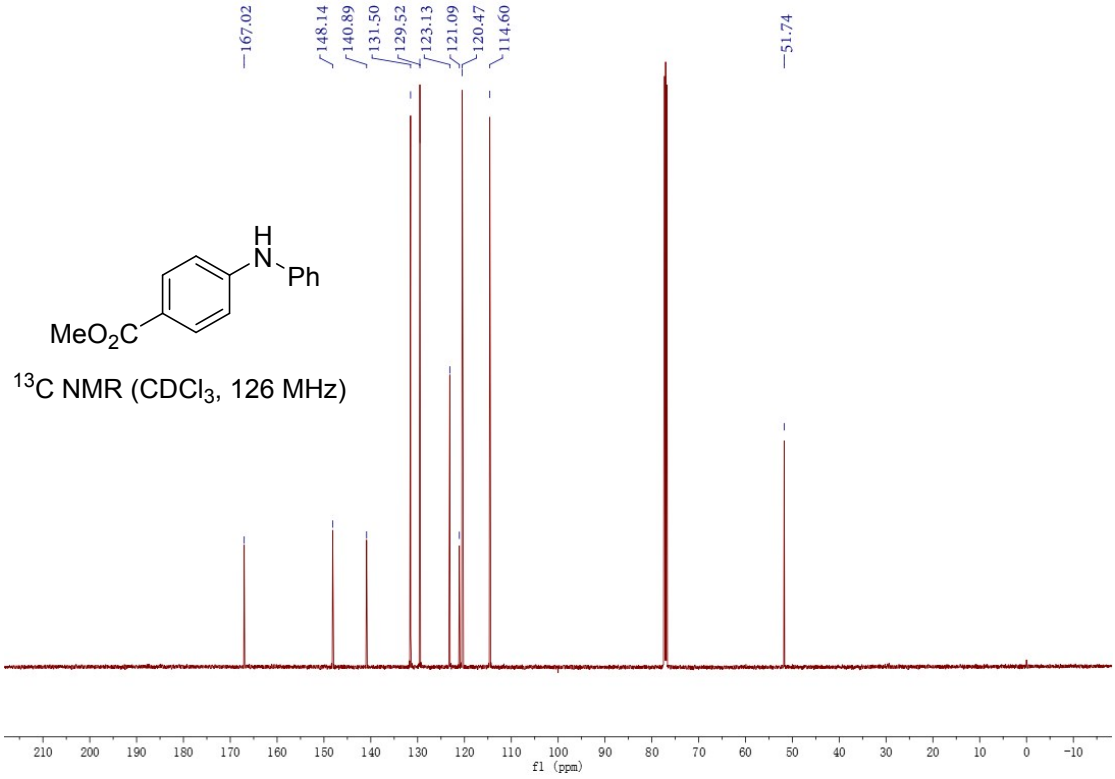

$^{1}H$ NMR (acetone-$d_6$, 500 MHz)

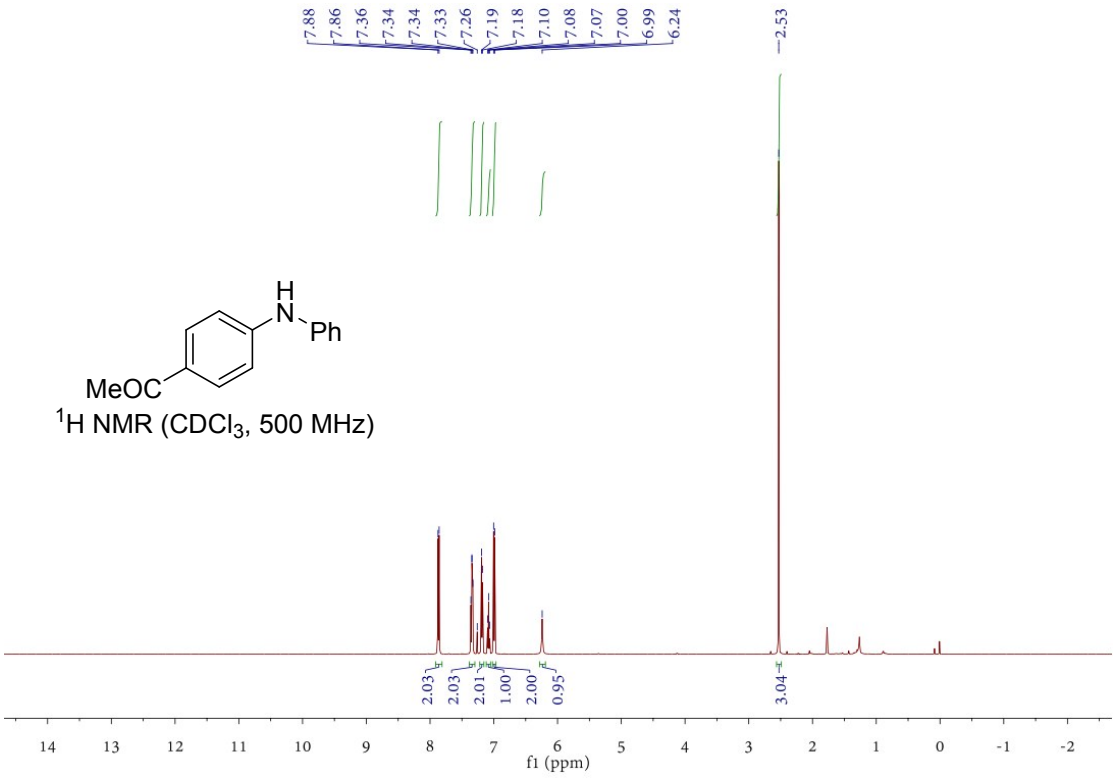


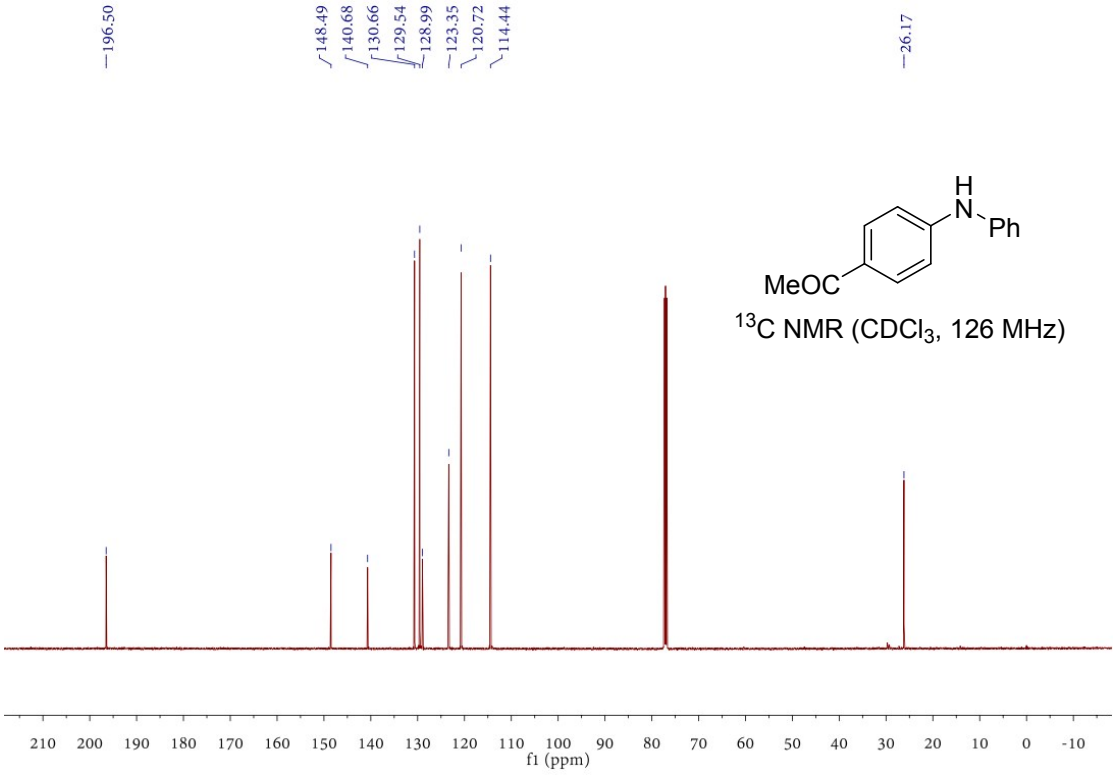

$^{13}$C NMR (acetone-$d_6$, 126 MHz)



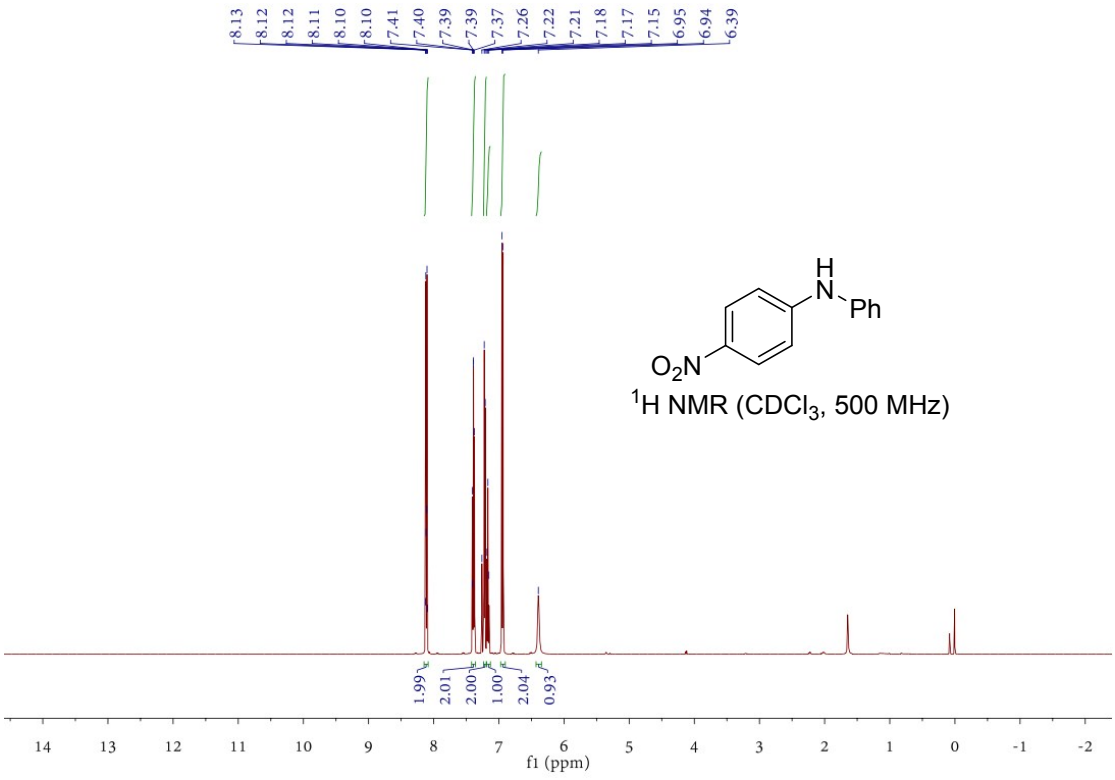

$^{1}$H NMR ($CDCl_3$, 500 MHz)


167.02
148.14
140.89
131.50
129.52
123.13
121.09
120.47
114.60
51.74
H
N
Ph
MeO2C
13C NMR (CDCl3, 126 MHz)
f1 (ppm)

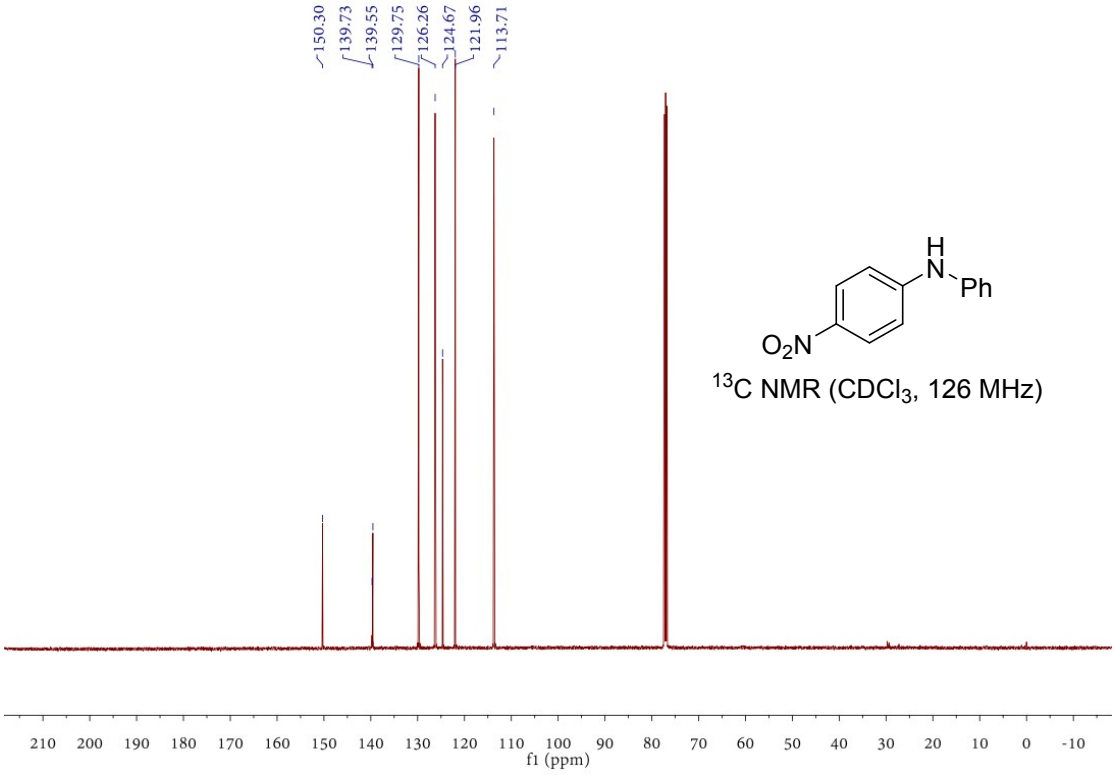

7.88
7.86
7.36
7.34
7.34
7.33
7.26
7.19
7.18
7.10
7.08
7.07
7.00
6.99
6.24
2.53
H
N
Ph
MeOC
1H NMR (CDCl3, 500 MHz)
2.03
2.03
2.01
1.00
2.00
0.95
3.04
f1 (ppm)



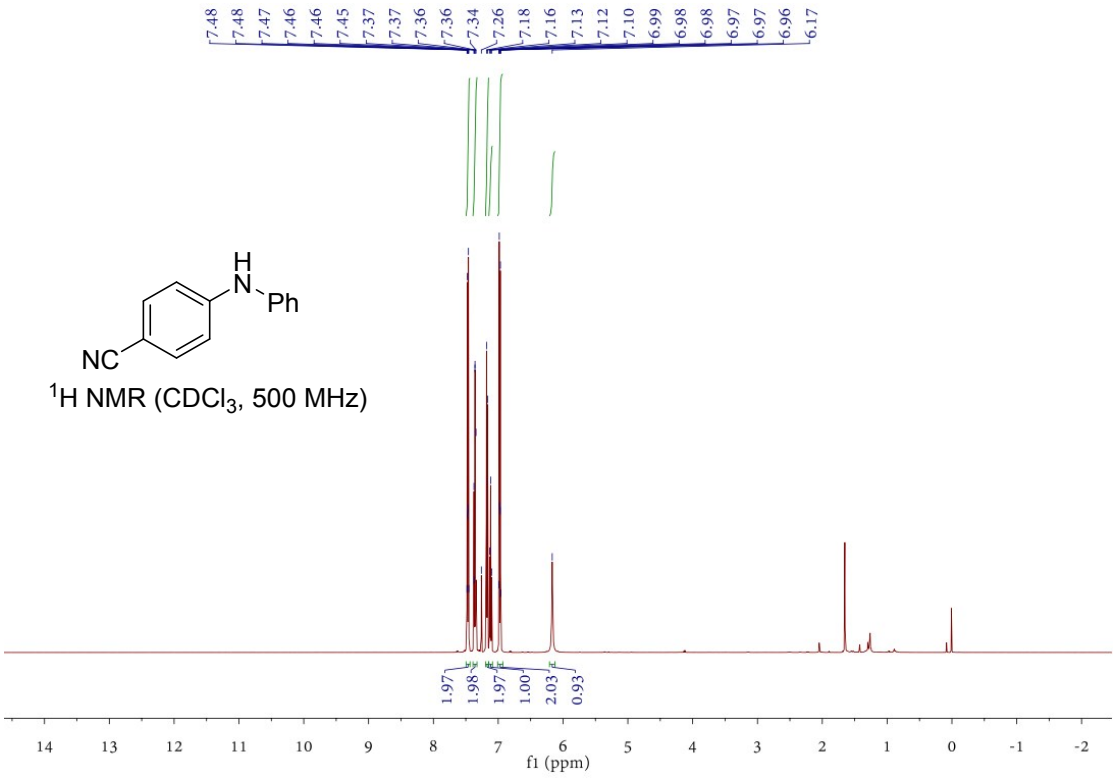

$^{13}C$ NMR ($CDCl_3$, 126 MHz)



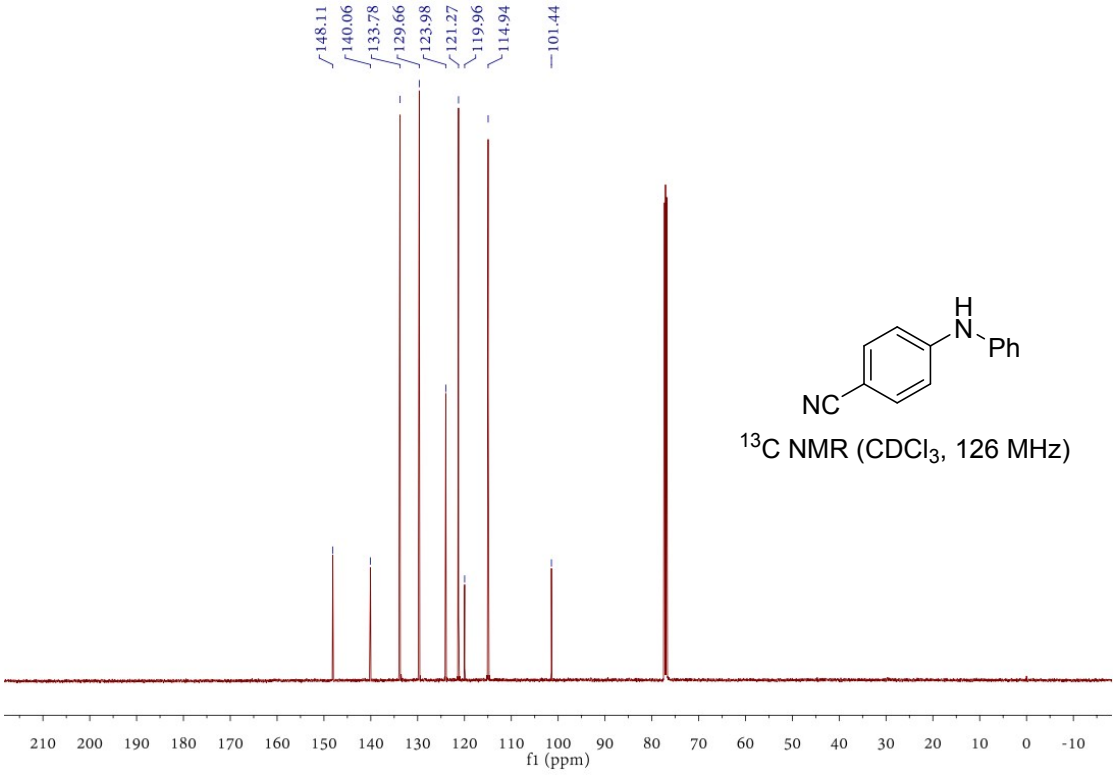

$^{1}H$ NMR ($CDCl_3$, 500 MHz)




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



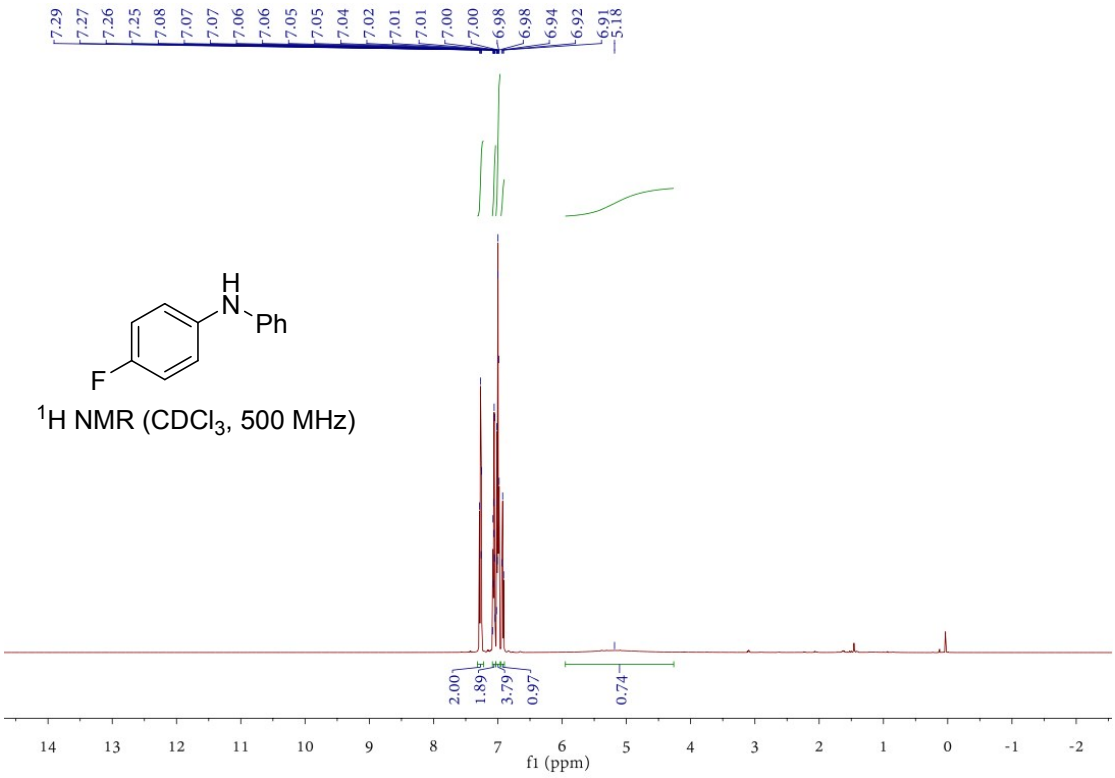

$^{1}$H NMR ($CDCl_3$, 500 MHz)







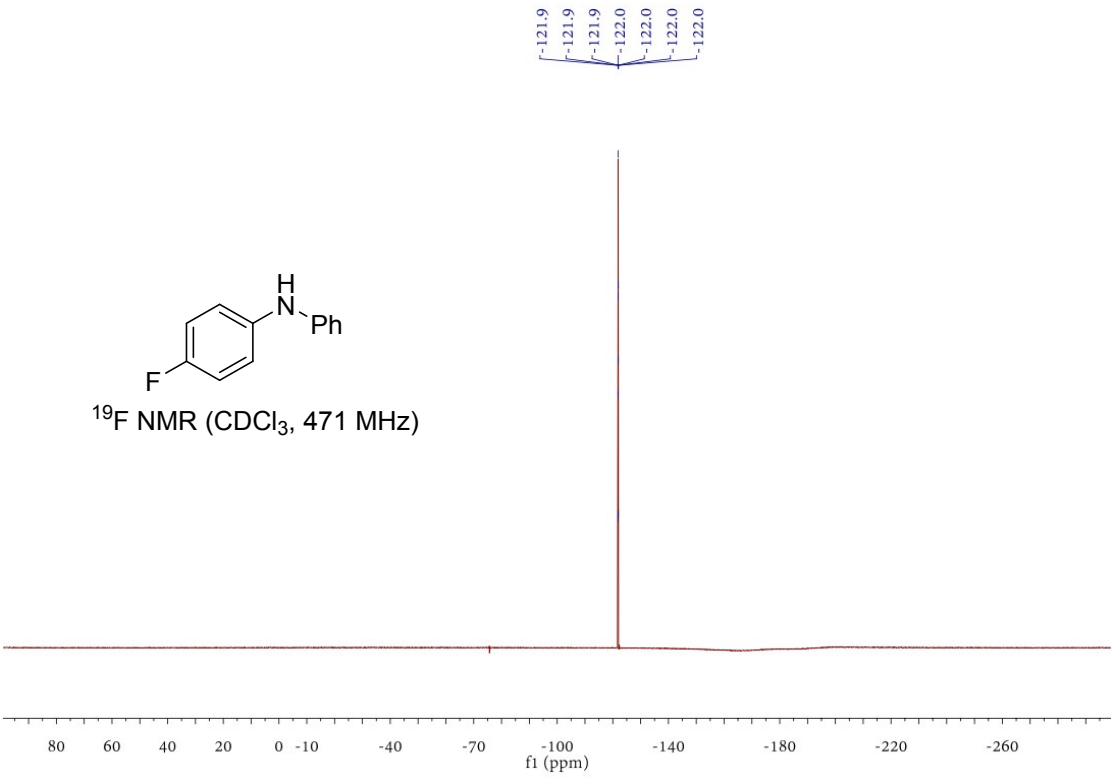
$^{13}C$ NMR ($CDCl_3$, 126 MHz)



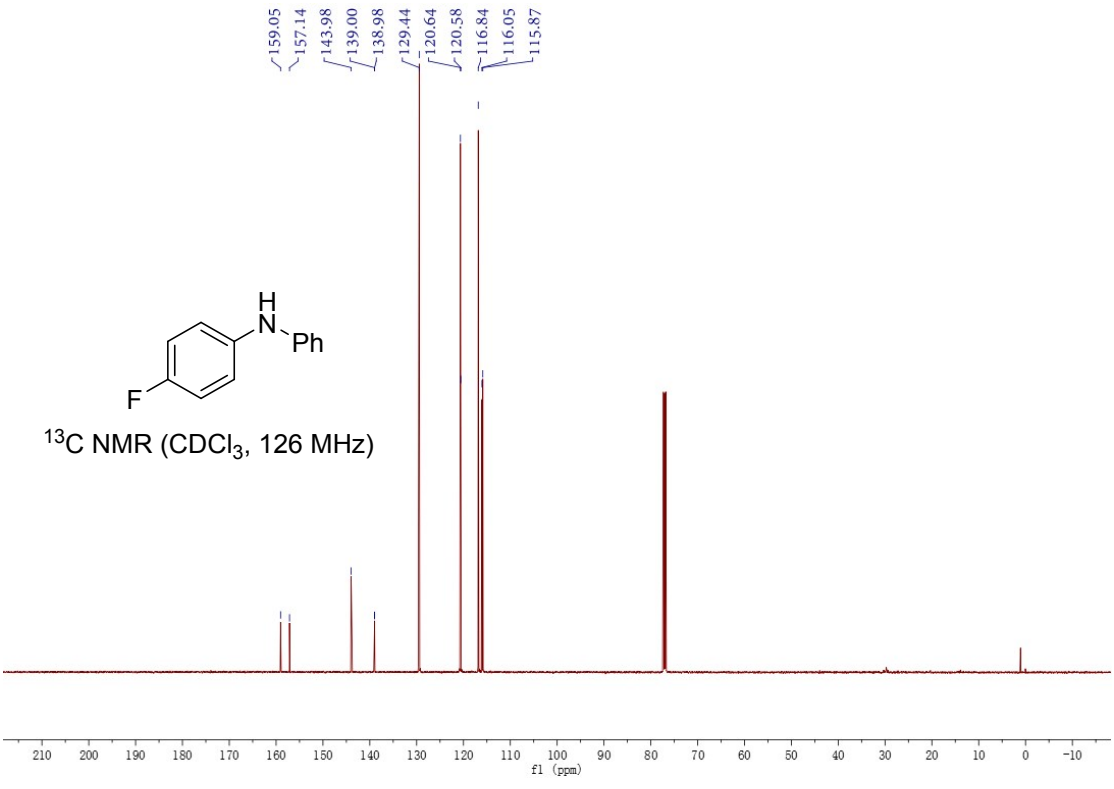




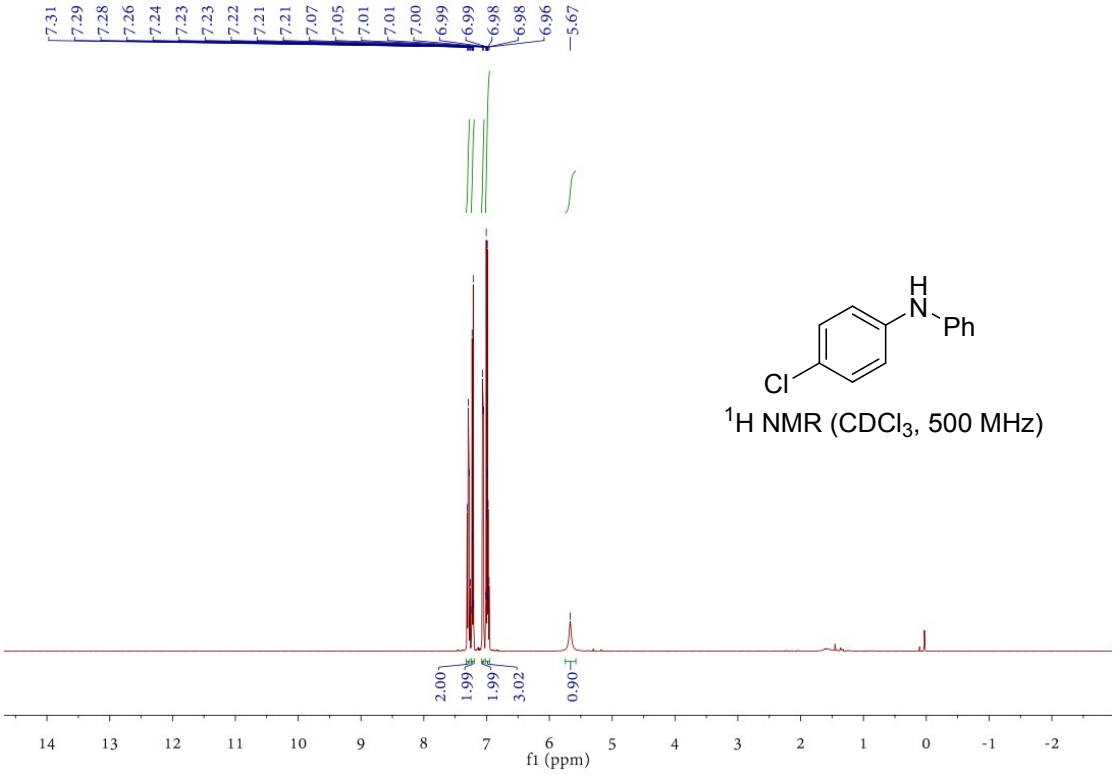
$^{1}H$ NMR ($CDCl_3$, 500 MHz)




$^{19}$F NMR ($CDCl_3$, 471 MHz)



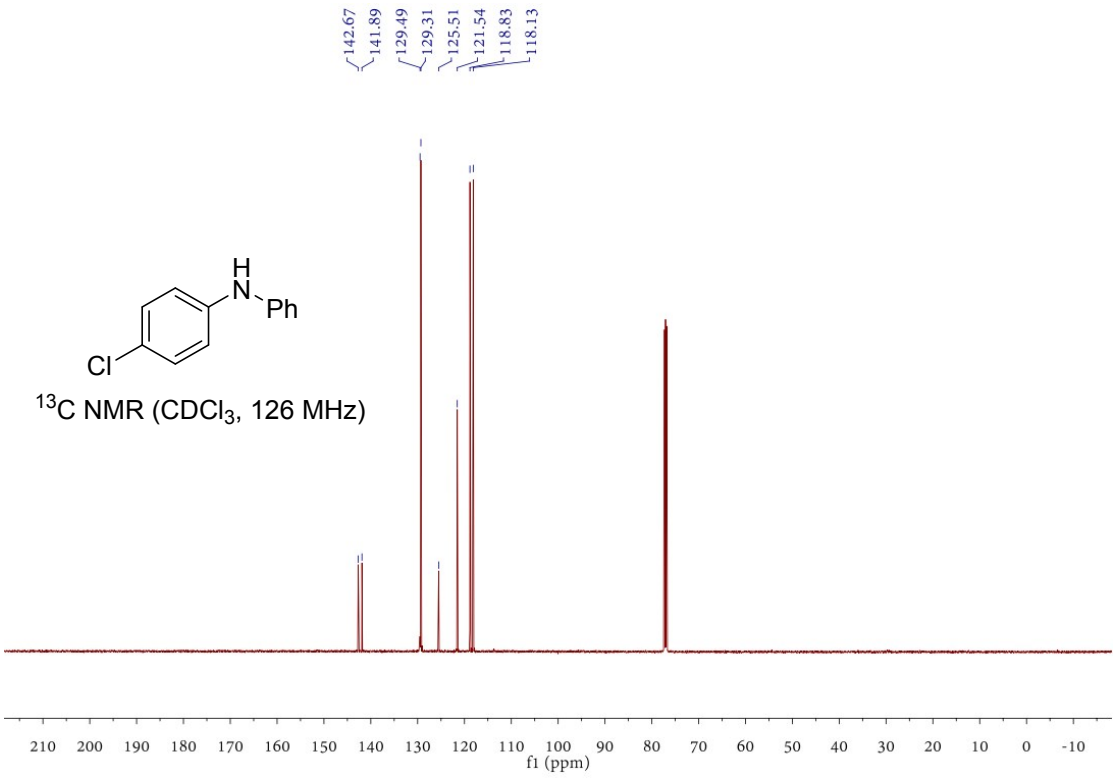

$^{13}$C NMR ($CDCl_3$, 126 MHz)







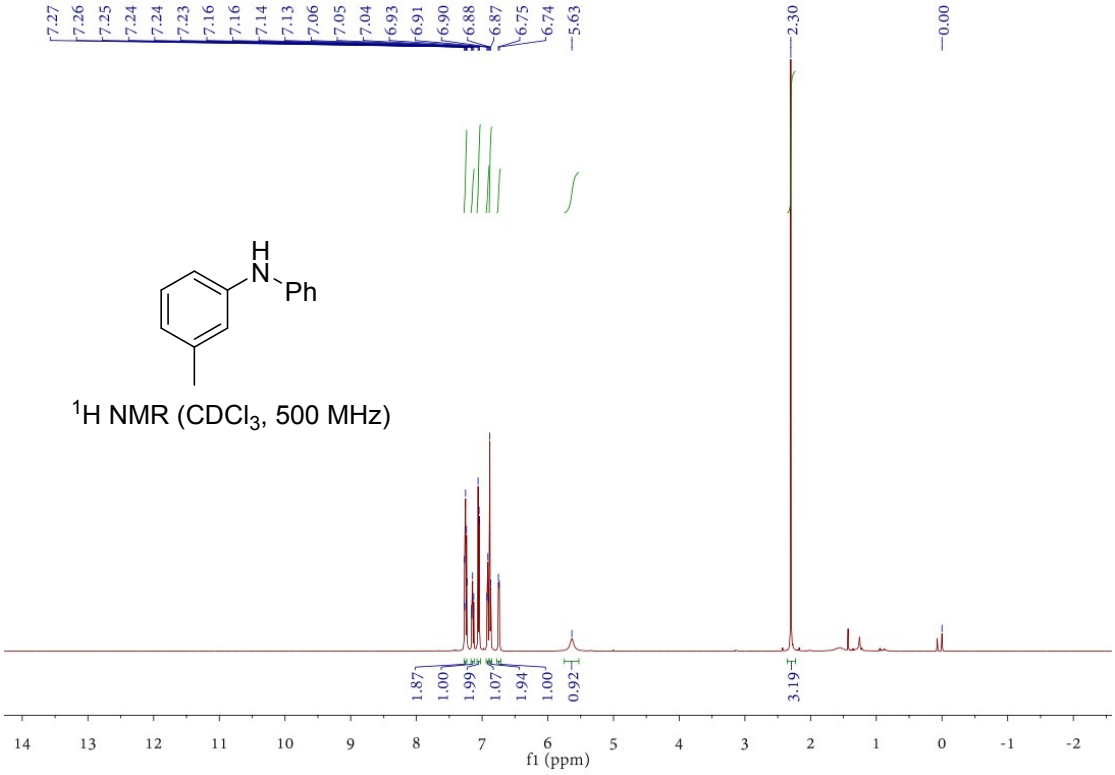
$^{1}$H NMR ($CDCl_3$, 500 MHz)



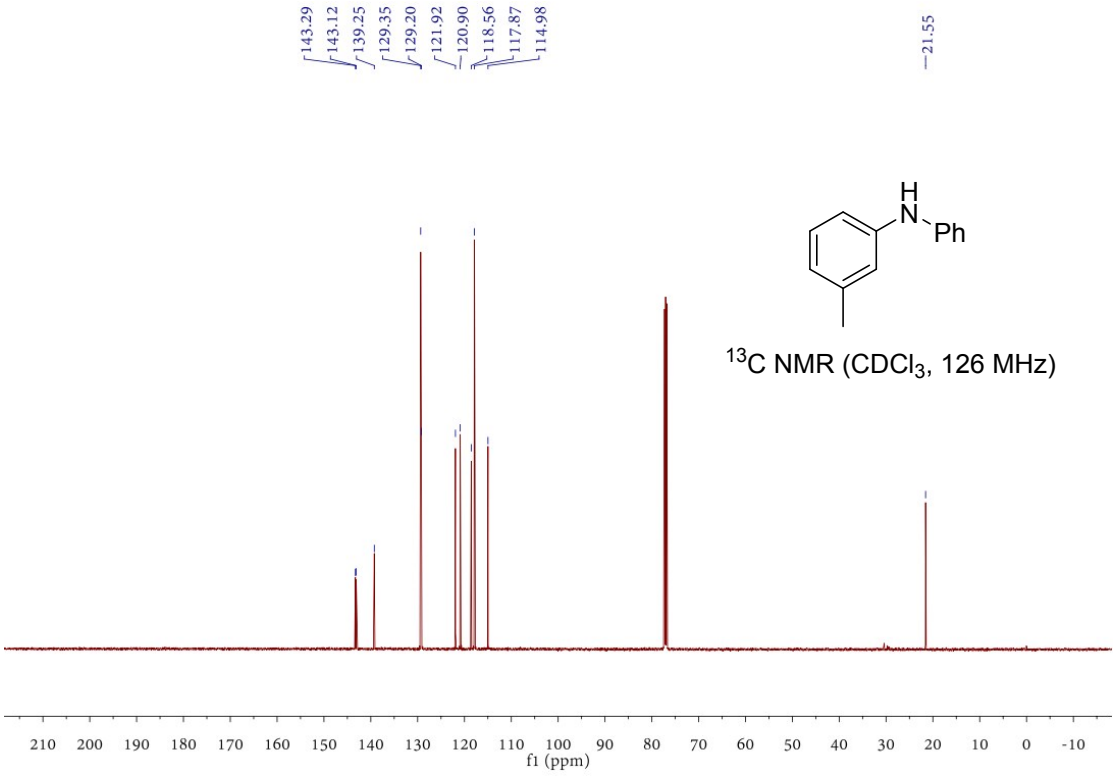




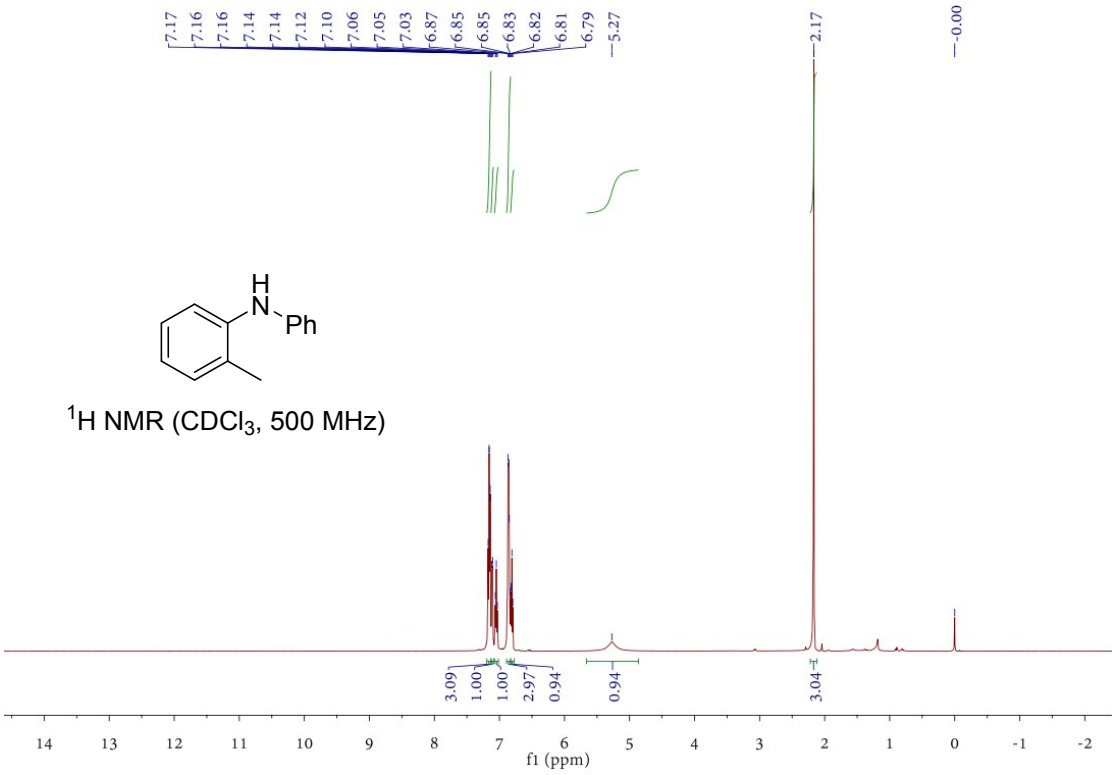
$^{13}$C NMR ($CDCl_3$, 126 MHz)



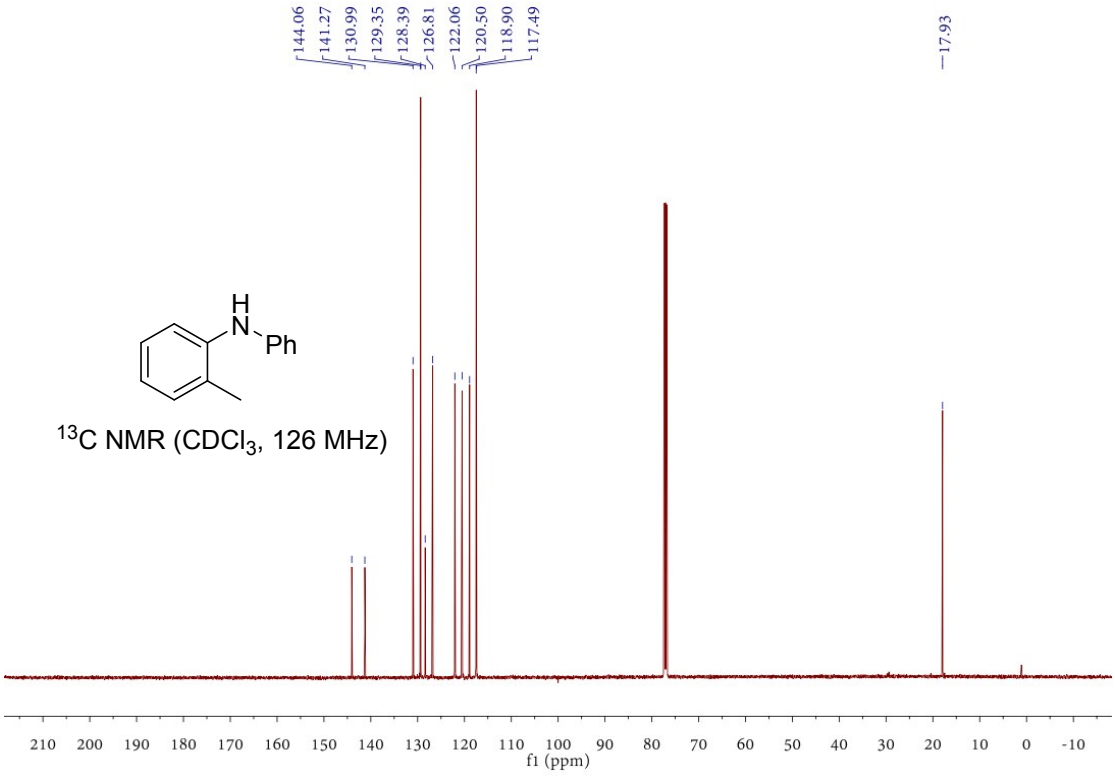

$^{1}$H NMR ($CDCl_3$, 500 MHz)



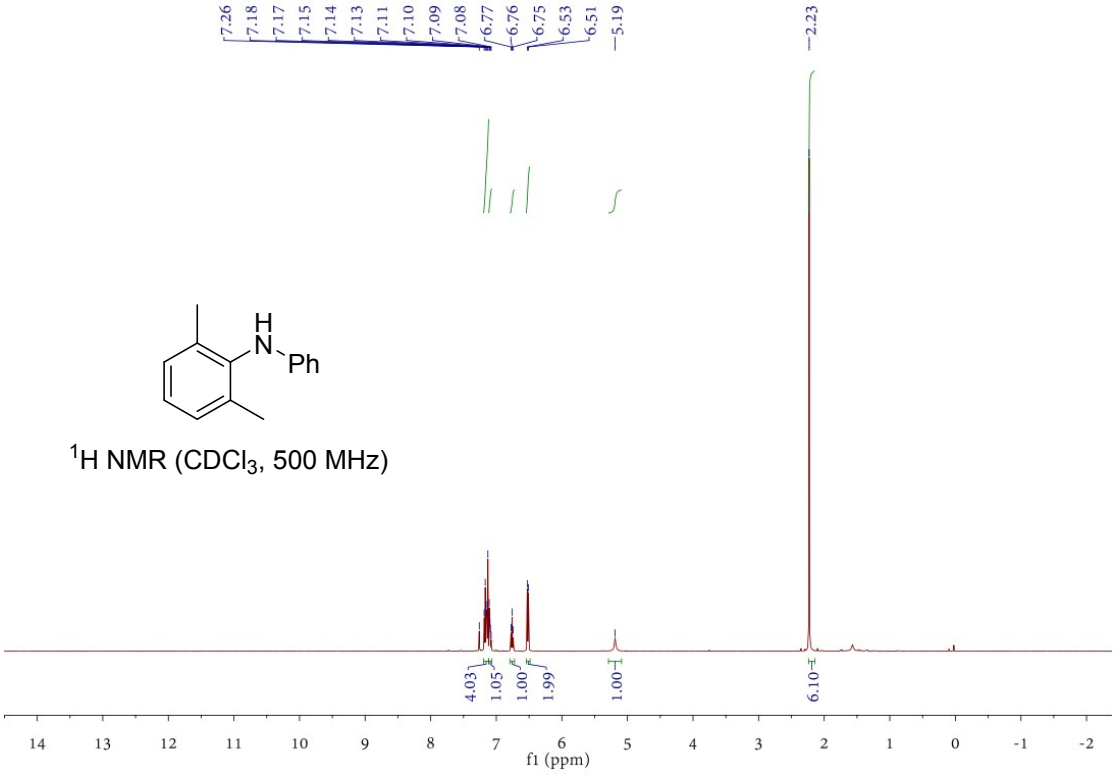

$^{13}$C NMR ($CDCl_3$, 126 MHz)



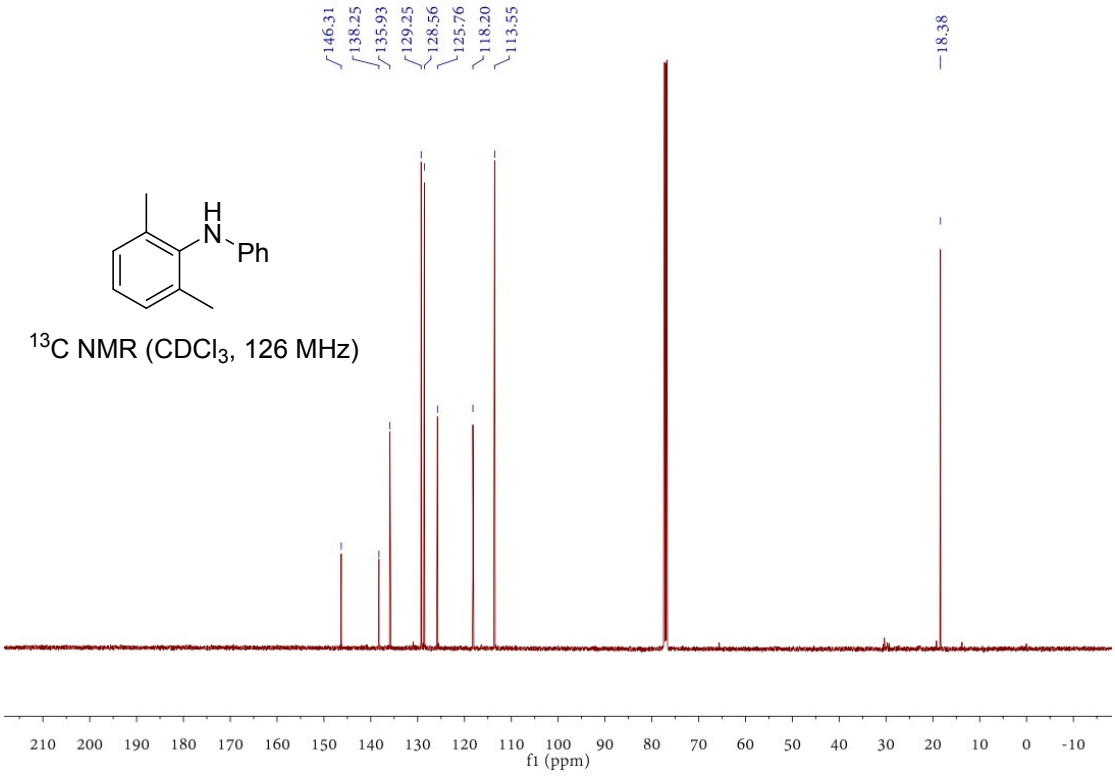

$^{1}$H NMR ($CDCl_3$, 500 MHz)



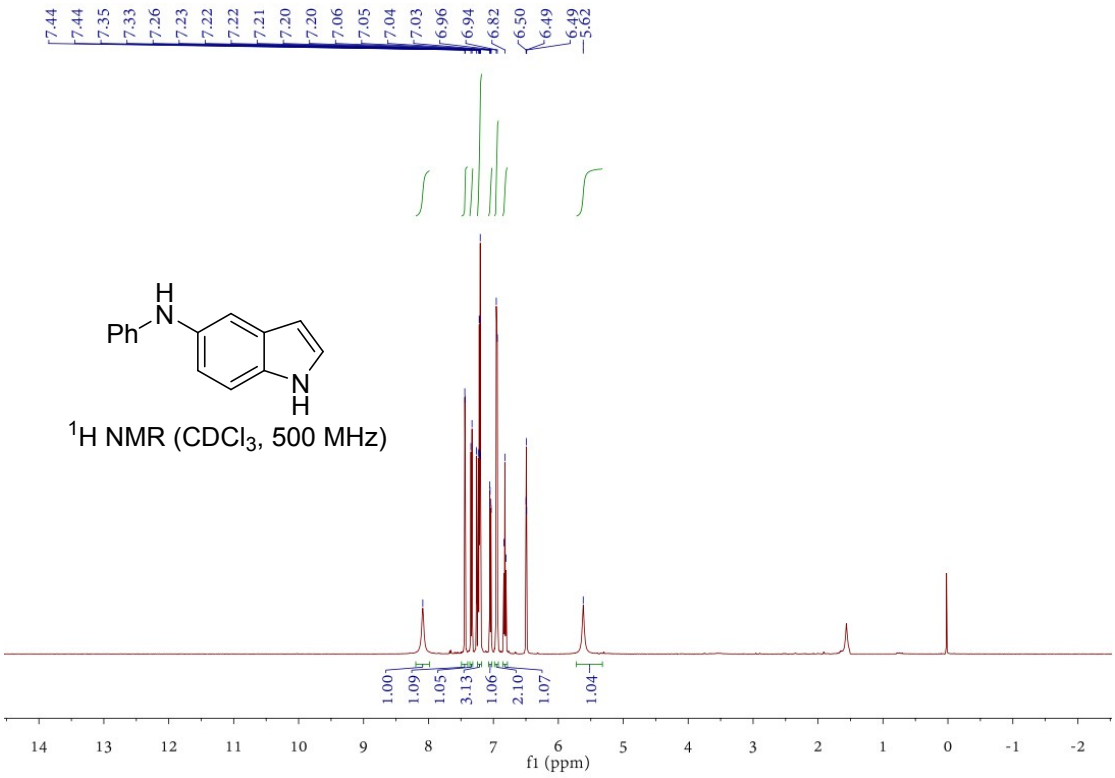

$^{13}$C NMR ($CDCl_3$, 126 MHz)



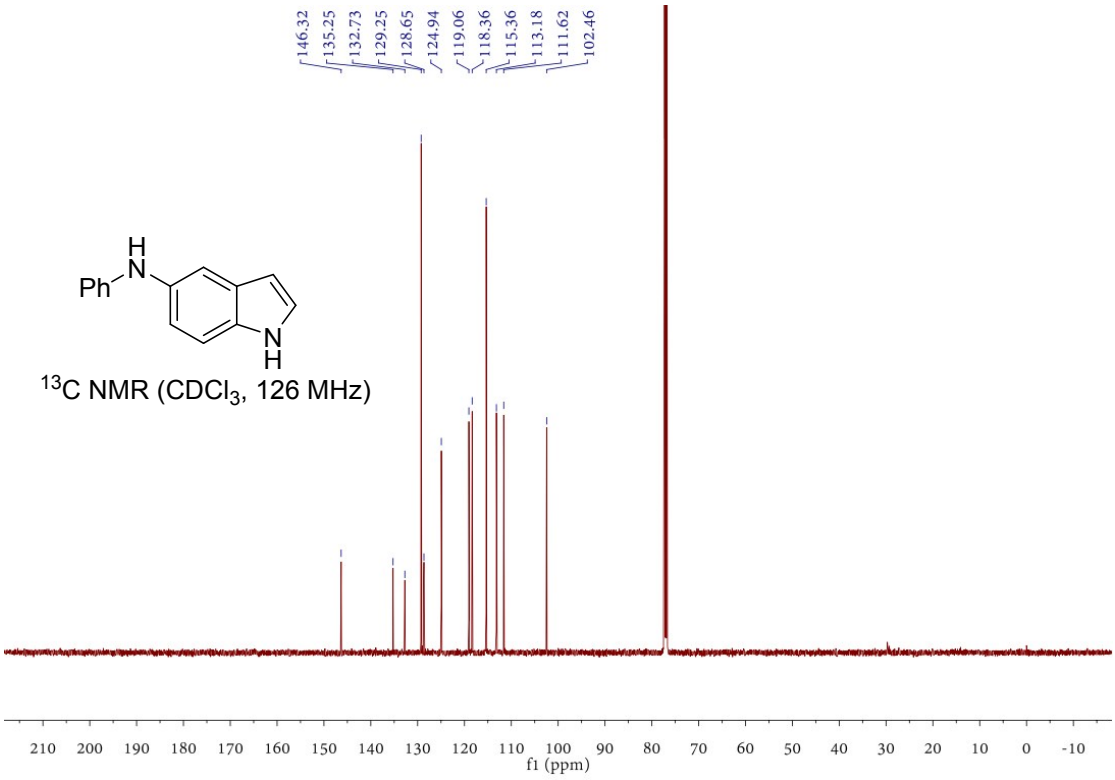

$^{1}$H NMR ($CDCl_3$, 500 MHz)



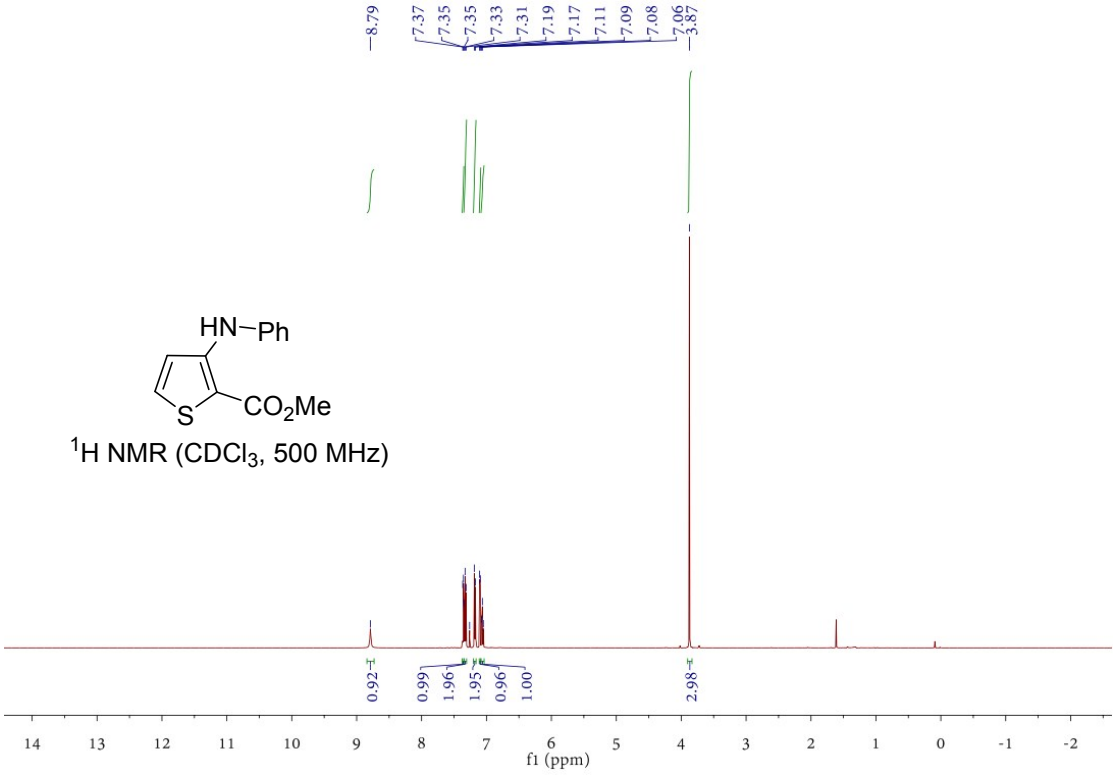

$^{13}$C NMR ($CDCl_3$, 126 MHz)



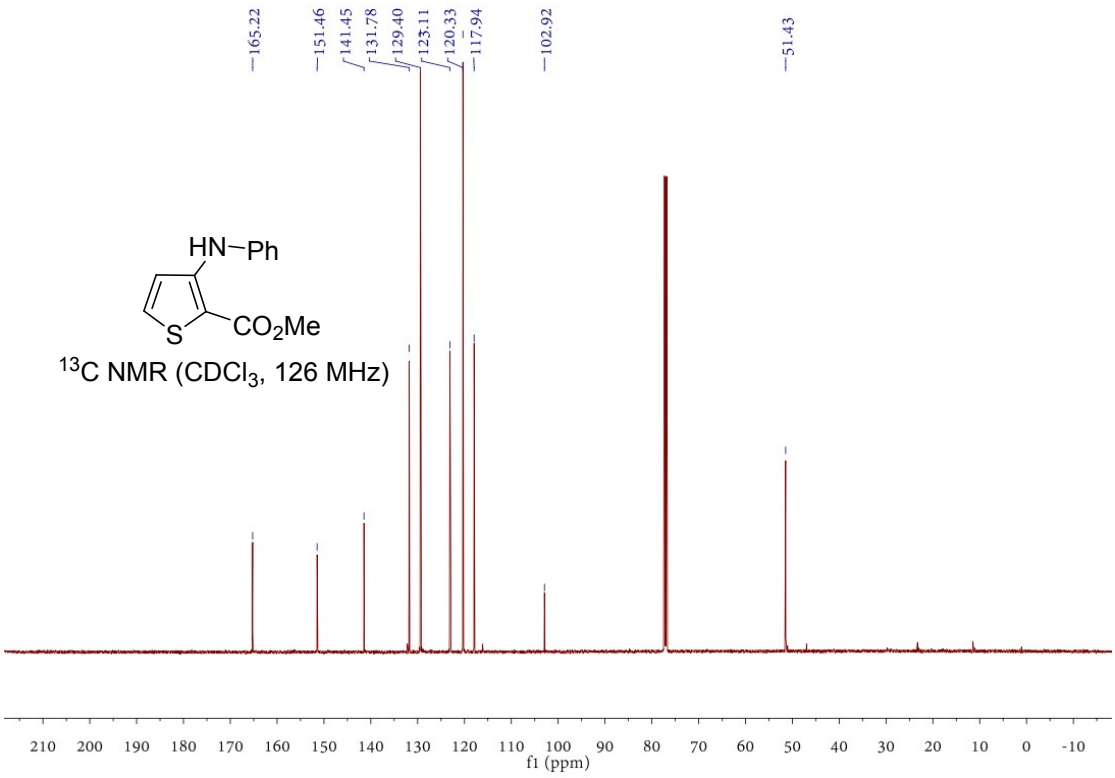

$^{1}$H NMR ($CDCl_3$, 500 MHz)



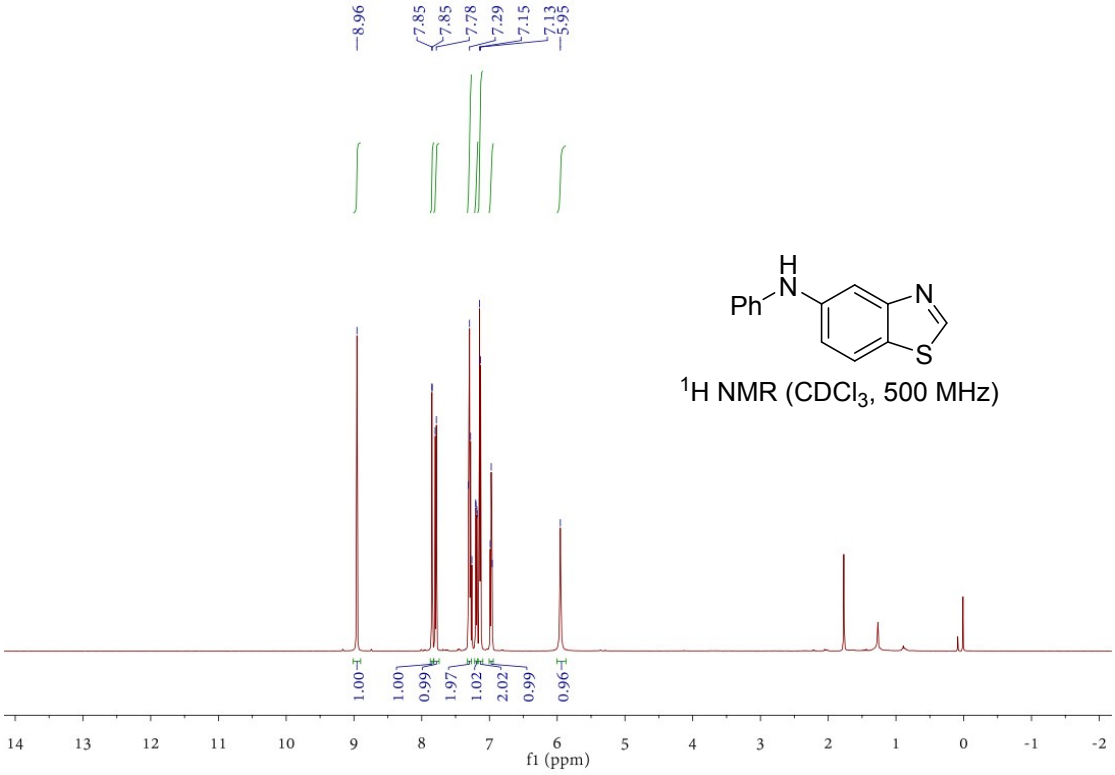

$^{13}$C NMR ($CDCl_3$, 126 MHz)




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



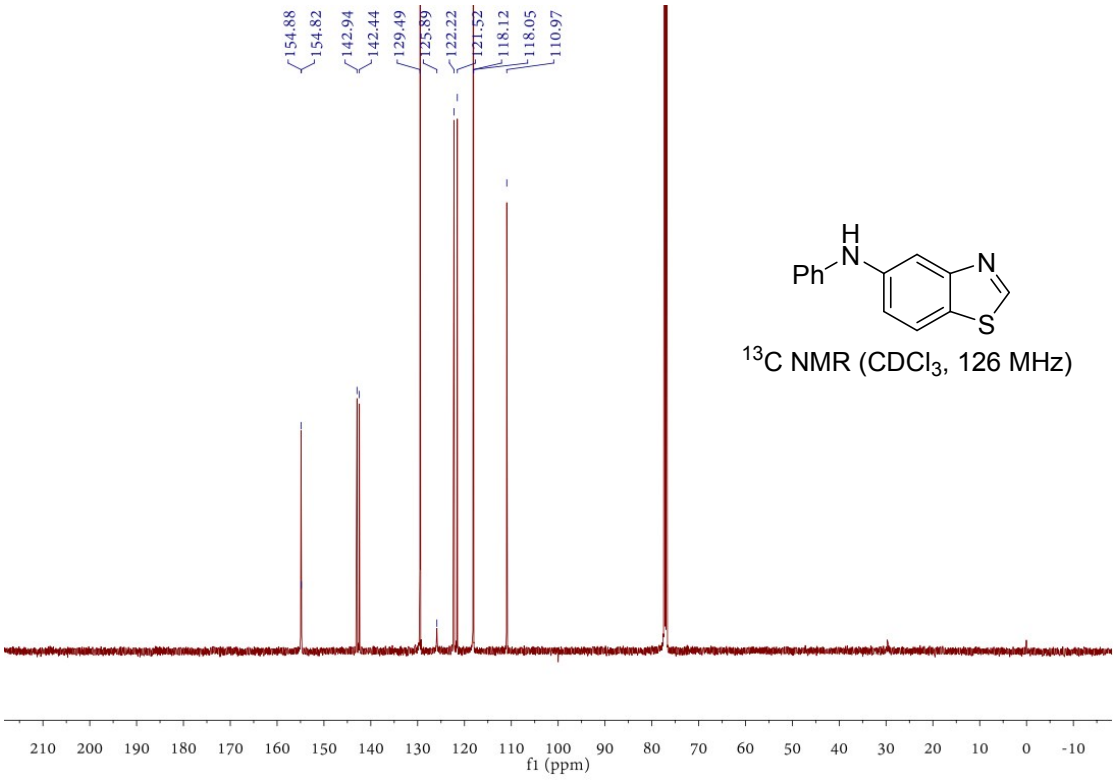

$^{13}$C NMR ($CDCl_3$, 126 MHz)







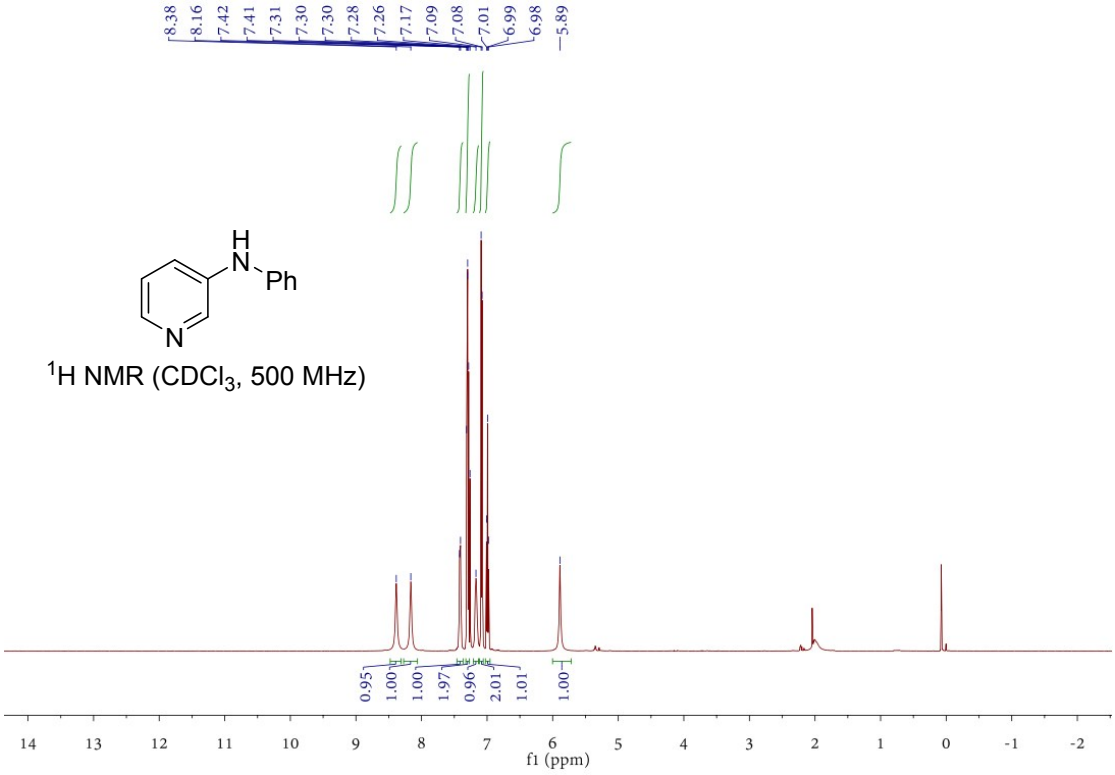
$^{1}$H NMR ($CDCl_3$, 500 MHz)



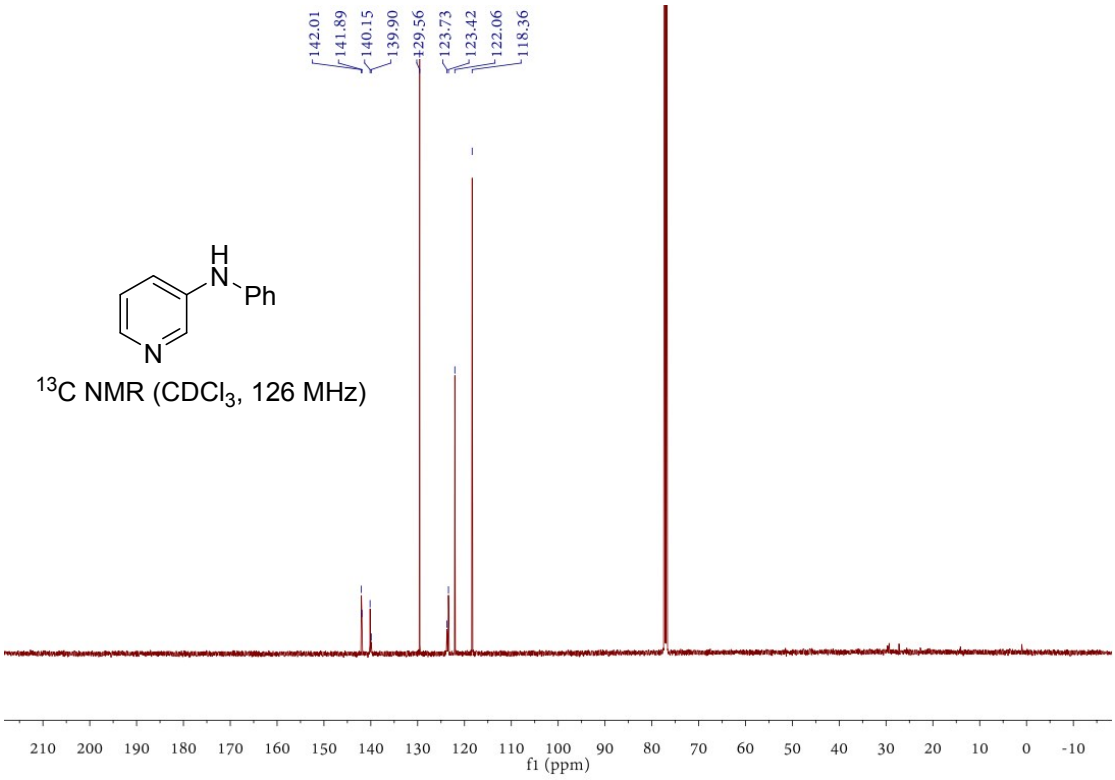




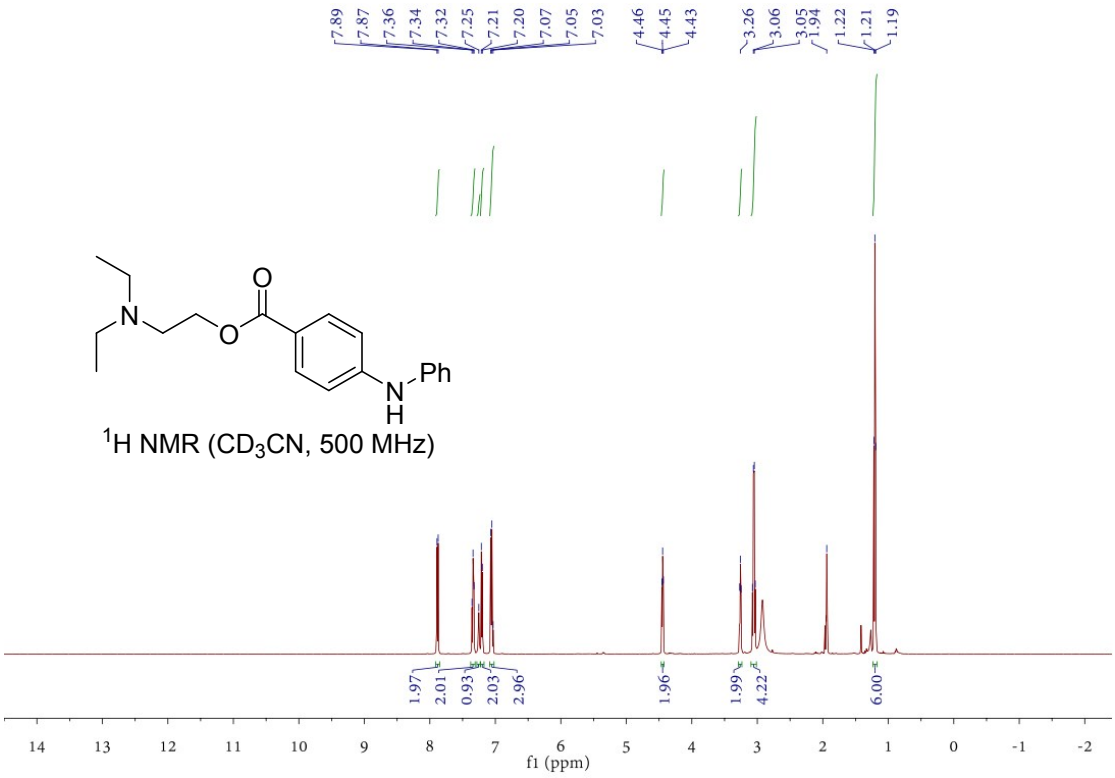
$^{13}$C NMR ($CDCl_3$, 126 MHz)



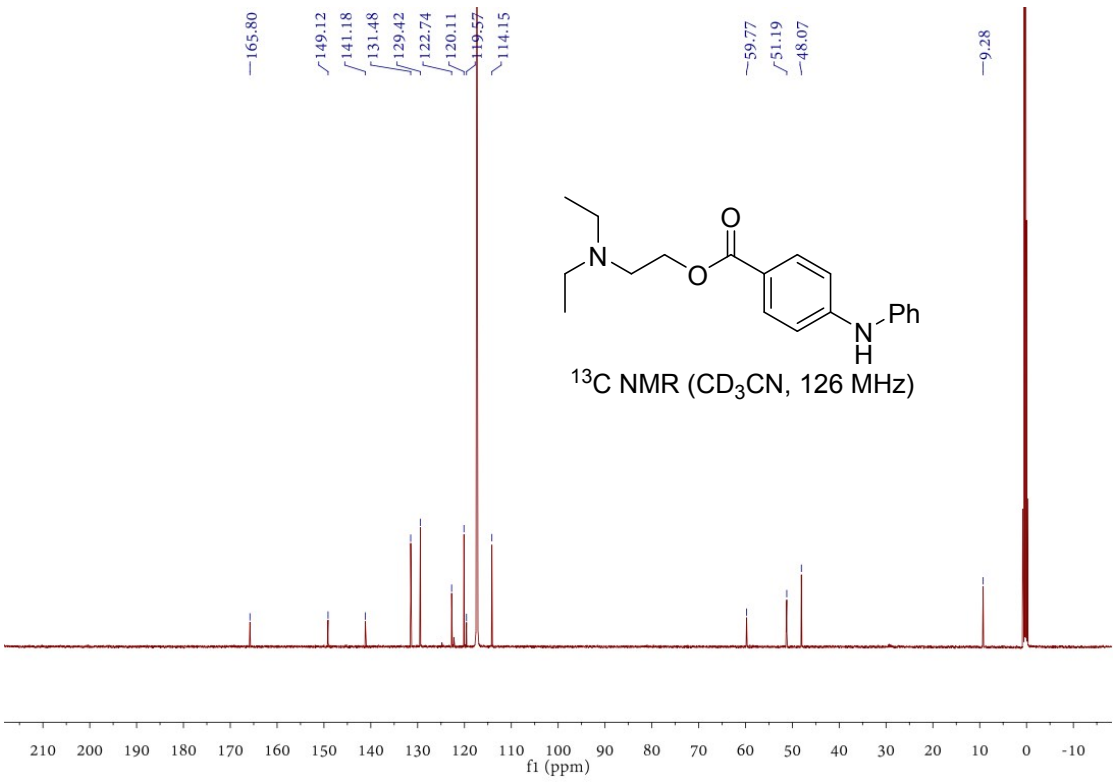

$^{1}$H NMR ($CDCl_3$, 500 MHz)



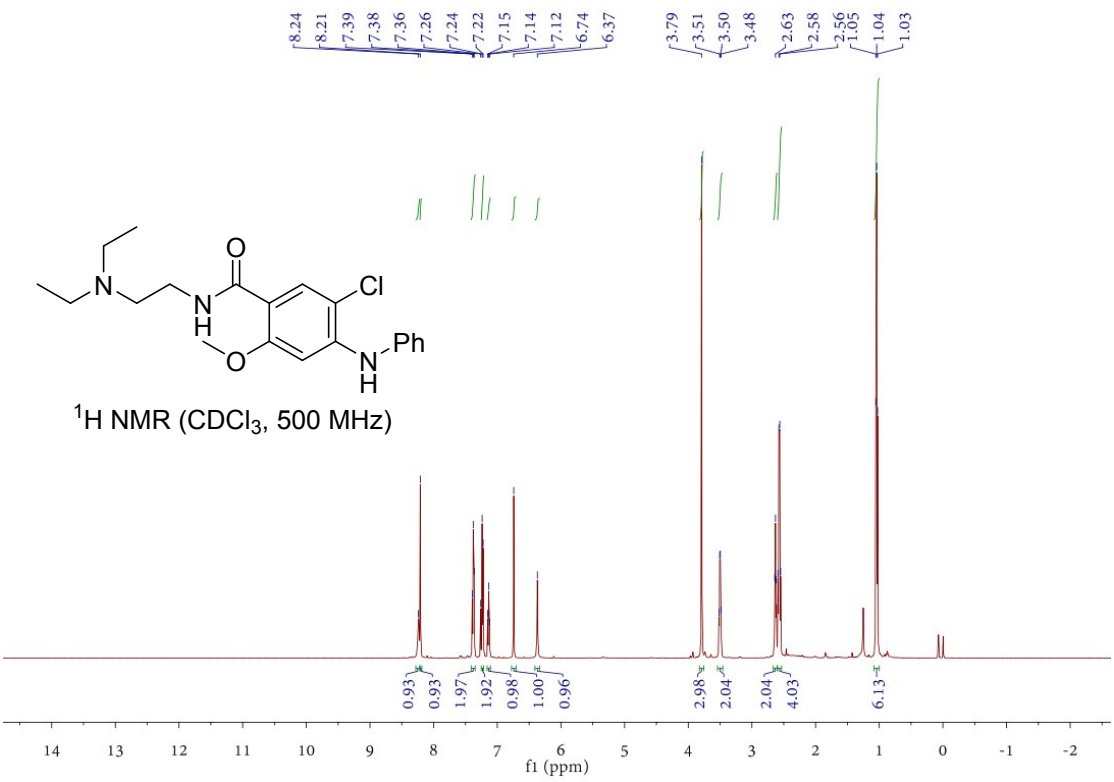

$^{13}$C NMR ($CDCl_3$, 126 MHz)



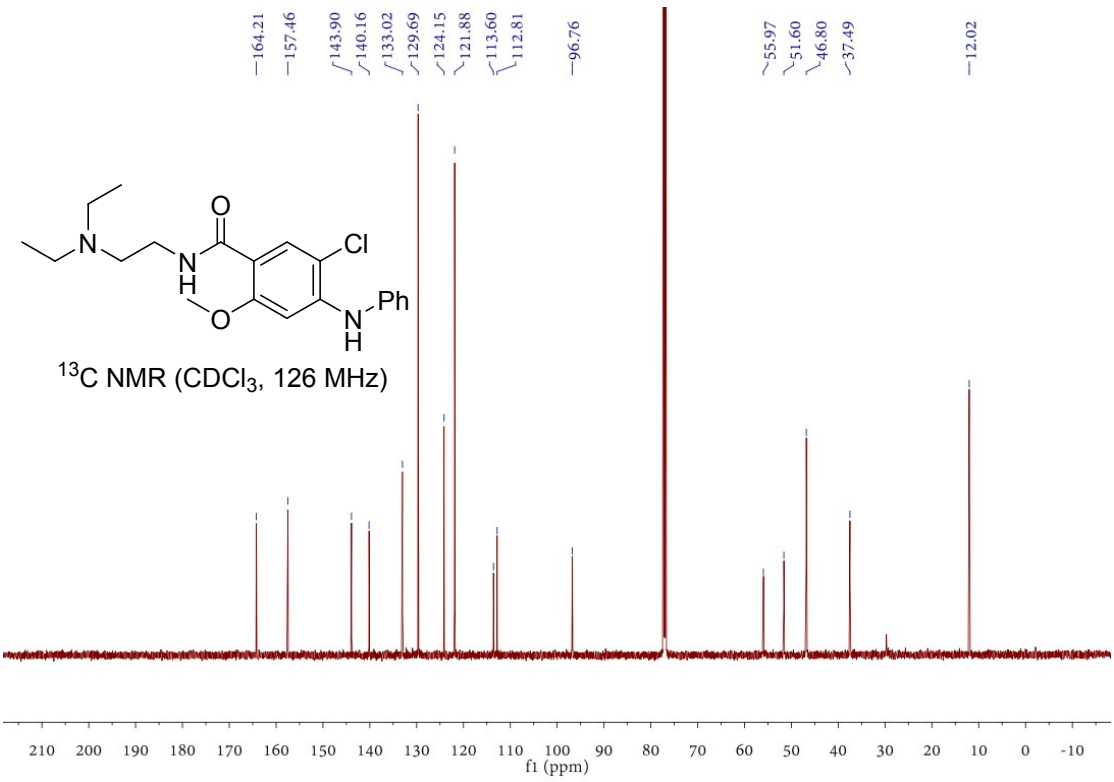

$^{1}$H NMR ($CD_3CN$, 500 MHz)



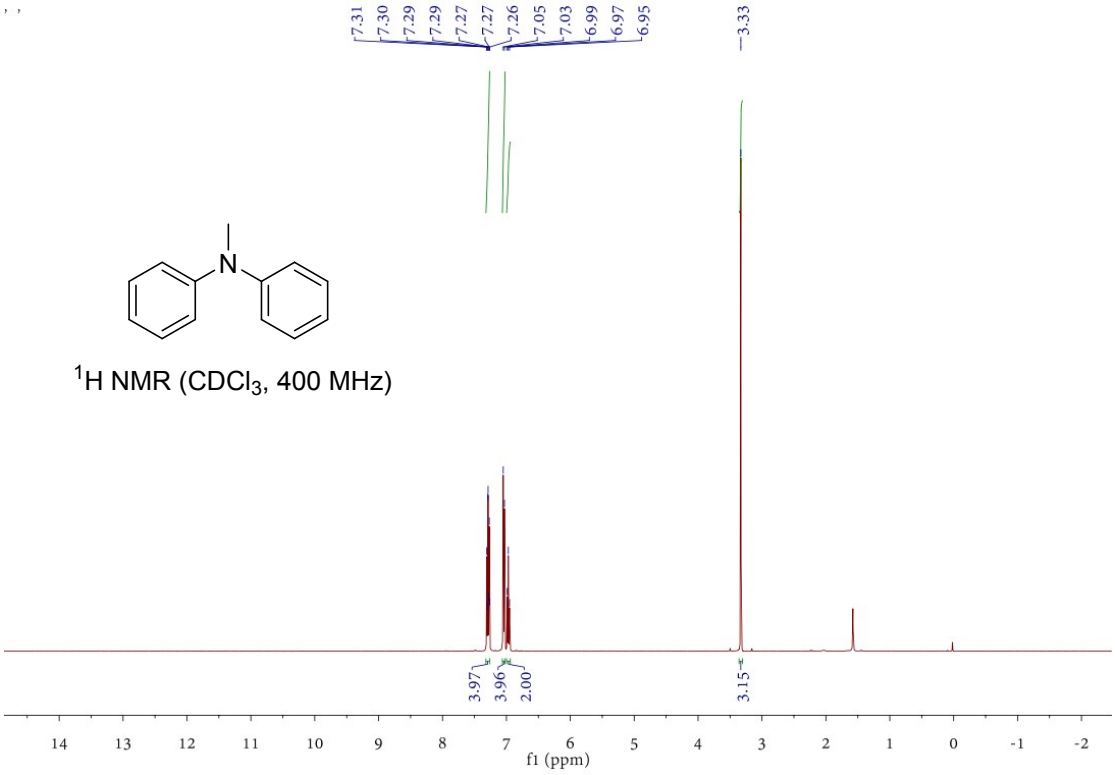

$^{13}$C NMR ($CD_3CN$, 126 MHz)



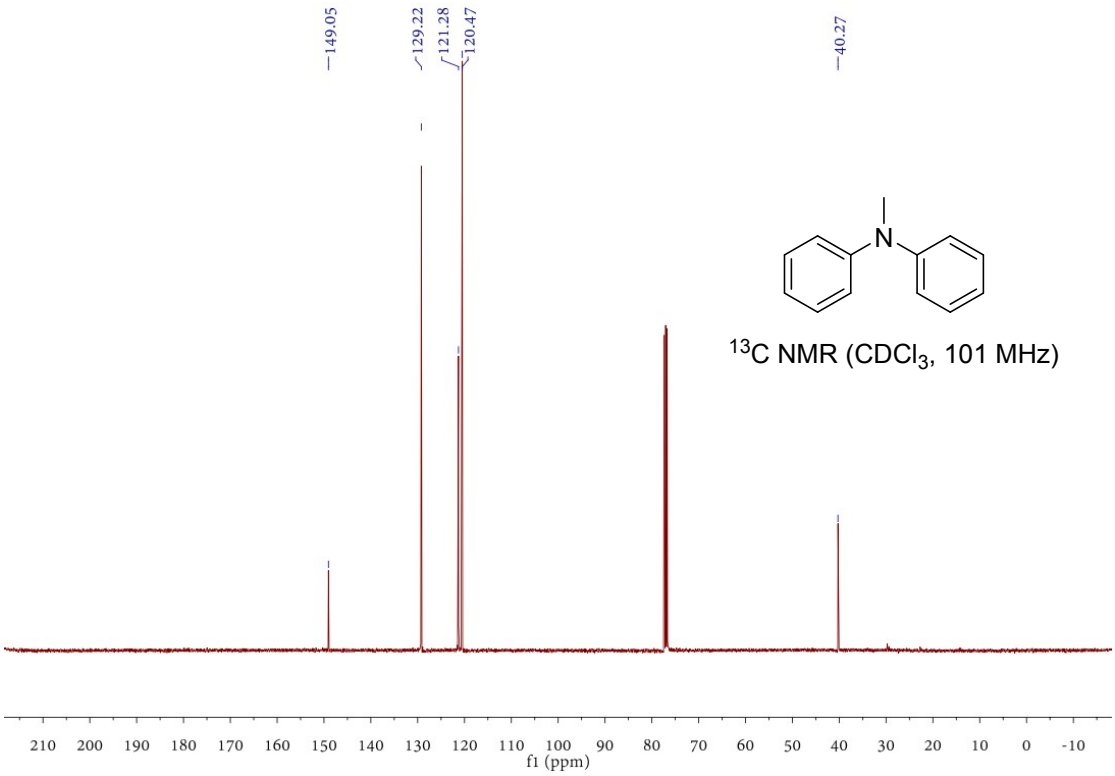

$^{1}$H NMR ($CDCl_3$, 500 MHz)



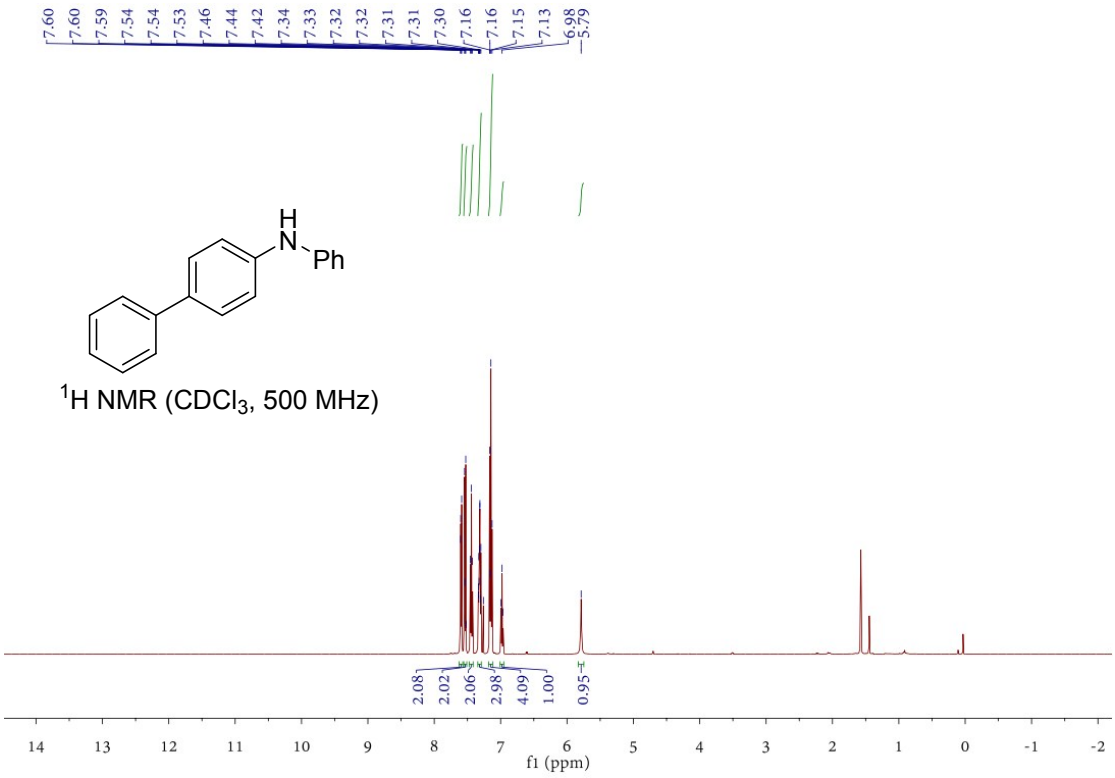

$^{13}$C NMR ($CDCl_3$, 126 MHz)



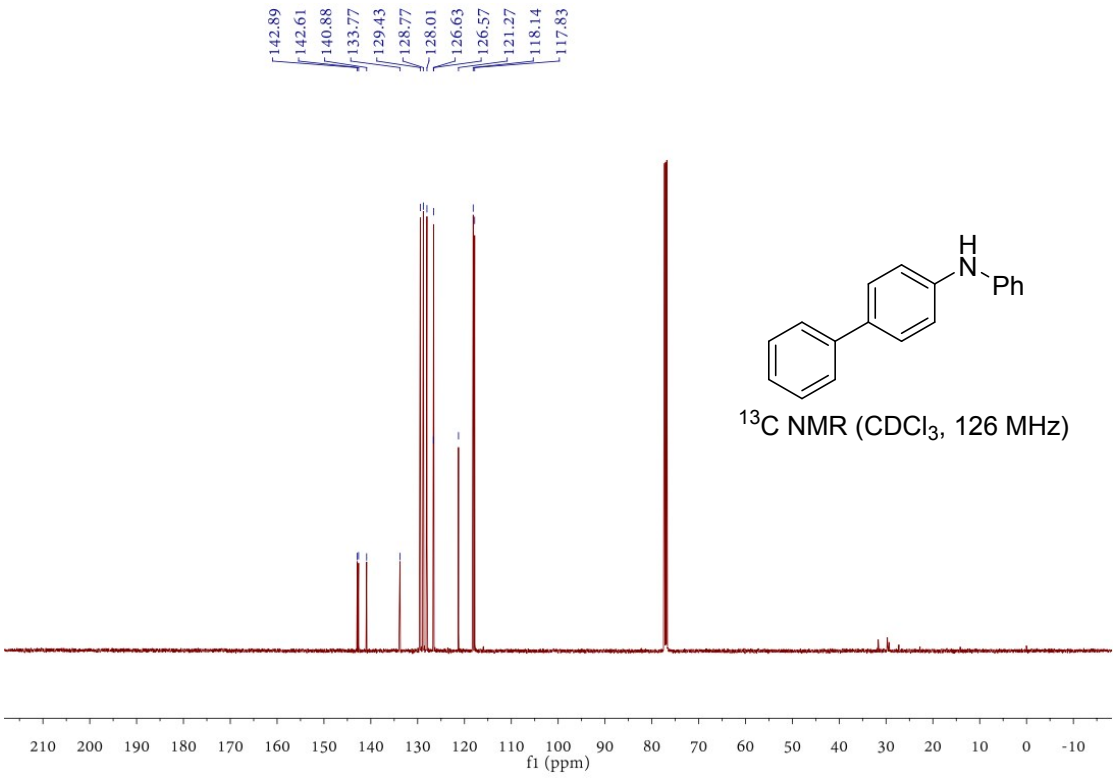

$^{1}$H NMR ($CDCl_3$, 400 MHz)




$^{13}$C NMR ($CDCl_3$, 101 MHz)




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




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