Electronic Supplementary Information

In-situ generation and reactions of *p*-(trifluoromethyl)benzyl electrophiles: efficient access to *p*-(trifluoromethyl)benzyl compounds

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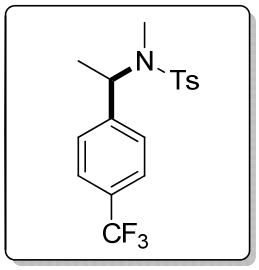
I. General Information

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. *N*,*N*-Dimethylformamide (DMF) was dried over calcium hydride and distilled before use. *p*-Quinone derivatives were purchased or synthesized according to the literature.[1] All reactions were carried out in the sealed tubes and monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The products were purified by flash column chromatography on silica gel (300−400 mesh). Melting points were uncorrected. NMR spectra were obtained on a Varian Inova 500 spectrometer (500 MHz for ^{1}H NMR; 125 MHz for ^{13}C NMR; 470 MHz for ^{19}F NMR). ^{1}H NMR and ^{13}C NMR were determined with TMS as the internal standard. ^{19}F NMR was determined with C_6H_5F as external reference. All chemical shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). Part of the mass spectra were idientified by GC-MS, by which gas chromatography was performed on a Hewlett Packard HP 6890 chromatograph with a HP5 column. Mass spectra were recorded on a AMD 402/3 mass spectrometer.

II. Procedures and Analytical Data for Compounds

Synthesis of (trifluoromethyl)benzylamines



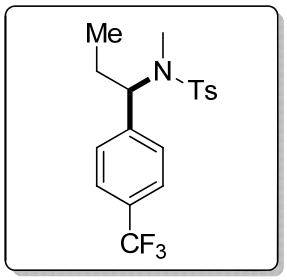
9a: *N*,4-dimethyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide

To the solution of *N*,4-dimethylbenzenesulfonamide **8a** (278 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) in DCE (1 mL) was added TMSCl (126 μL, 1 mmol) and $In(OTf)_3$ (141 mg, 0.25 mmol). Then, 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol) was added. After the reaction was finished as indicated by TLC (reaction time, 36 h), the resulting mixture was poured into water (20 mL) and extracted with DCM (CH_2Cl_2, 20 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1: 40) to afford **9a** (133 mg, 75%).

Colorless crystals, m.p. 40–41 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.29 (d, *J* = 7.0 Hz, 3H), 2.44

1 P. Camps, A. González, D. Muñoz-Torrero, M. Simon, A. Zúñiga, M. A. Martins, M. Font-Bardia, X. Solans, *Tetrahedron*, 2000, **56**, 8141.

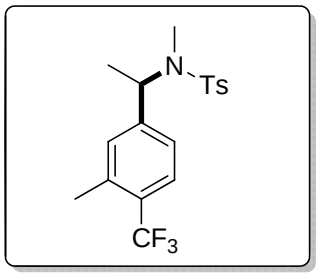
(s, 3H), 2.59 (s, 3H), 5.32 (q, J = 7.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.0, 21.4, 28.5, 54.4, 123.9 (CF_3, q, J = 270.6 Hz), 125.3 (q, J = 3.8 Hz), 126.9, 127.5, 129.4 (q, J = 32.3 Hz), 129.7, 136.7, 143.4, 144.2. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -64.5. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{18}F_3NNaO_2S$ $(M+Na)^+$ 380.0903. Found 380.0899.



9c: *N*,4-dimethyl-*N*-(1-(4-(trifluoromethyl)phenyl)propyl)benzenesulfonamide

Following the procedure for the synthesis of **9a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), *N*,4-dimethylbenzenesulfonamide **8a** (278 mg, 1.5 mmol) and heptan-4-one **7f** (140 μL, 1.5 mmol) gave **9c** (56 mg, 30%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 40). Reaction time 48 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.86 (t, J = 7.0 Hz, 3H), 1.69–1.76 (m, 1H), 1.91–1.97 (m, 1H), 2.41 (s, 3H), 2.64 (s, 3H), 5.05 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 11.2, 21.4, 23.6, 28.6, 61.1, 123.9 (CF_3, q, J = 270.6 Hz), 125.3 (q, J = 3.8 Hz), 127.0, 128.2, 129.5, 129.8 (q, J = 32.3 Hz), 137.1, 142.8, 143.2. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -64.6. **HRMS** (ESI-TOF) Calcd for $C_{18}H_{20}F_3NNaO_2S$ $(M+Na)^+$ 394.1059. Found 394.1065.

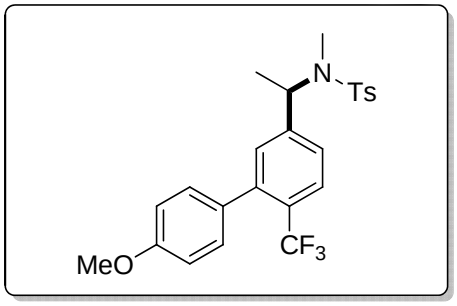


9d: *N*,4-dimethyl-*N*-(1-(3-methyl-4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide

Following the procedure for the synthesis of **9a**, the reaction of 3-methyl-4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5b** (330 mg, 1.25 mmol), *N*,4-dimethylbenzenesulfonamide **8a** (93 mg, 0.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9d** (90 mg, 49%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 40). Reaction time 48 h.

Colorless crystals, m.p. 99–100 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.29 (d, J = 7.0 Hz, 3H), 2.43 (s, 3H), 2.44 (s, 3H), 2.59 (s, 3H), 5.25 (q, J = 7.0 Hz, 1H), 7.16 (s, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.1, 19.3, 21.4, 28.6, 54.3, 124.2, 124.3 (CF_3, q, J = 272.0 Hz), 125.8 (q, J = 5.5 Hz),

127.0, 127.9 (q, J = 29.9 Hz), 129.7, 130.8, 136.7, 136.9, 143.3, 143.8. **HRMS** (ESI-TOF) Calcd for $C_{18}H_{20}F_3NNaO_2S$ $(M+Na)^+$ 394.1059. Found 394.1047.

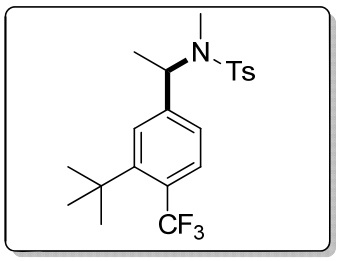


9e:

N-(1-(4'-methoxy-6-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)ethyl)-*N*,4-dimethylbenzenesulfonamid e

Following the procedure for the synthesis of **9a**, the reaction of 4'-methoxy-6-(trifluoromethyl)-6-((trimethylsilyl)oxy)-[1,1'-biphenyl]-3(6*H*)-one **5c** (178 mg, 0.5 mmol), *N*,4-dimethylbenzenesulfonamide **8a** (278 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9e** (123 mg, 53%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 60). Reaction time 48 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.31 (d, J = 7.0 Hz, 3H), 2.41 (s, 3H), 2.63 (s, 3H), 3.85 (s, 3H), 5.30 (q, J = 7.0 Hz, 1H), 6.93 (d, J = 8.5 Hz, 2H), 7.15 (s, 1H), 7.19 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.3, 21.5, 28.7, 54.4, 55.2, 113.1, 124.0 (CF_3, q, J = 272.0 Hz), 125.8, 126.3 (q, J = 5.3 Hz), 126.9, 127.7 (q, J = 29.6 Hz), 129.7, 129.9, 130.9, 131.8, 136.7, 141.3, 143.3, 143.5, 159.1. **HRMS** (ESI-TOF) Calcd for $C_{24}H_{24}F_3NNaO_3S$ $(M+Na)^+$ 486.1321. Found 486.1318.

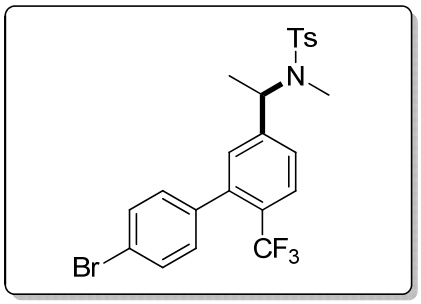


9f: *N*-(1-(3-(*tert*-butyl)-4-(trifluoromethyl)phenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide

Following the procedure for the synthesis of **9a**, the reaction of 3-(*tert*-butyl)-4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5d** (153 mg, 0.5 mmol), *N*,4-dimethylbenzenesulfonamide **8a** (278 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9f** (95 mg, 46%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 40). Reaction time 72 h.

Colorless crystals, m.p. 100–101 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.34 (d, J = 7.0 Hz, 3H), 1.40 (s, 9H), 2.43 (s, 3H), 2.61 (s, 3H), 5.29 (q, J = 7.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.58 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.5, 21.4, 28.6, 31.8 (q, J = 2.8 Hz), 36.5, 54.6, 124.2, 124.7 (CF_3, q, J = 272.0

Hz), 126.9, 127.2 (q, J = 29.9 Hz), 128.0, 128.4 (q, J = 7.4 Hz), 129.7, 136.9, 143.3, 143.5, 149.4. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{26}F_3NNaO_2S$ $(M+Na)^+$ 436.1529. Found 436.1510.

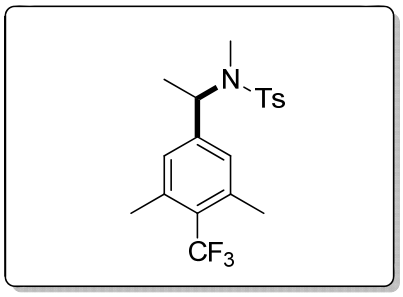


9g:

N-(1-(4'-bromo-6-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide

Following the procedure for the synthesis of **9a**, the reaction of 4'-bromo-6-(trifluoromethyl)-6-((trimethylsilyl)oxy)-[1,1'-biphenyl]-3(6*H*)-one **5e** (202 mg, 0.5 mmol), *N*,4-dimethylbenzenesulfonamide **8a** (278 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9g** (102 mg, 40%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 40). Reaction time 48 h.

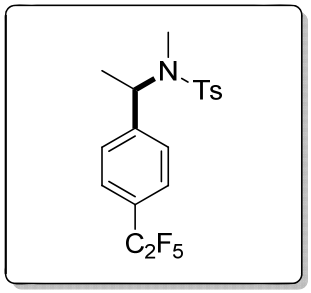
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.31 (d, J = 7.0 Hz, 3H), 2.41 (s, 3H), 2.63 (s, 3H), 5.31 (q, J = 7.0 Hz, 1H), 7.12 (s, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.3, 21.5, 28.6, 54.3, 122.0, 123.8 (CF_3, q, J = 272.0 Hz), 126.3, 126.4 (q, J = 5.3 Hz), 126.9, 127.5 (q, J = 29.6 Hz), 129.7, 130.5, 130.9, 136.6, 138.3, 140.2, 143.4, 143.8. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{21}BrF_3NNaO_2S$ $(M+Na)^+$ 534.0321. Found 534.0334.



9h: *N*-(1-(3,5-dimethyl-4-(trifluoromethyl)phenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide

To the solution of *N*,4-dimethylbenzenesulfonamide **8a** (278 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) in DCE (1 mL) was added TMSCl (126 μL, 1 mmol) and $In(OTf)_3$ (141 mg, 0.25 mmol). Then, the mixture was heated to 45 ℃ and 3,5-dimethyl-4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5f** (139 mg, 0.5 mmol) was added. After the reaction was finished as indicated by TLC (reaction time, 15 h), the resulting mixture was poured into water (20 mL) and extracted with DCM (CH_2Cl_2, 20 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1: 40) to afford **9h** (60 mg, 31%).

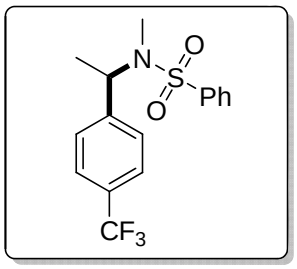
Colorless crystals, m.p. 131–132 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.28 (d, *J* = 7.0 Hz, 3H), 2.41 (s, 3H), 2.42 (s, 3H), 2.44 (s, 3H), 2.60 (s, 3H), 5.18 (q, *J* = 7.0 Hz, 1H), 6.92 (s, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.3, 21.4, 21.5 (q, *J* = 4.0 Hz), 28.7, 54.2, 126.0 (CF_3, q, *J* = 267.6 Hz), 126.7 (q, *J* = 29.9 Hz), 127.1, 128.9, 129.7, 137.1, 137.5 (q, *J* = 1.9 Hz), 142.6, 143.3. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -56.1. **HRMS** (ESI-TOF) Calcd for $C_{19}H_{22}F_3NNaO_2S$ $(M+Na)^+$ 408.1216. Found 408.1222.



9i: *N*,4-dimethyl-*N*-(1-(4-(perfluoroethyl)phenyl)ethyl)benzenesulfonamide

Following the procedure for the synthesis of **9a**, the reaction of 4-(perfluoroethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5g** (150 mg, 0.5 mmol), *N*,4-dimethylbenzenesulfonamide **8a** (278 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9i** (107 mg, 53%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 40). Reaction time 36 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.29 (d, *J* = 7.0 Hz, 3H), 2.44 (s, 3H), 2.60 (s, 3H), 5.33 (q, *J* = 7.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.0, 21.4, 28.5, 54.4, 113.5 (qt, J_1 = 253.1 Hz, J_2 = 38.6 Hz), 119.1 (tq, J_1 = 249.4 Hz, J_2 = 39.4 Hz), 126.5 (t, *J* = 6.3 Hz), 126.9, 127.5, 127.8 (t, *J* = 23.9 Hz), 129.7, 136.7, 143.4, 144.4. **HRMS** (ESI-TOF) Calcd for $C_{18}H_{18}F_5NNaO_2S$ $(M+Na)^+$ 430.0871. Found 430.0889.

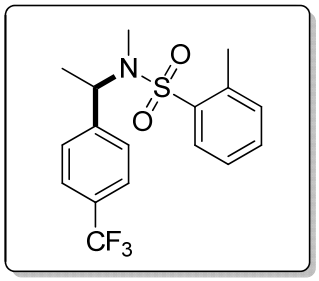


9j: *N*-methyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide

Following the procedure for the synthesis of **9a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), *N*-methylbenzenesulfonamide **8b** (257 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9j** (130 mg, 76%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 40). Reaction time 36 h.

Colorless crystals, m.p. 85–86 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.30 (d, *J* = 7.0 Hz, 3H), 2.61 (s, 3H), 5.33 (q, *J* = 7.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.53–7.63 (m, 5H), 7.86 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.1, 28.5, 54.5, 123.9 (CF_3, q, *J* = 270.6 Hz), 125.4 (q, *J* =

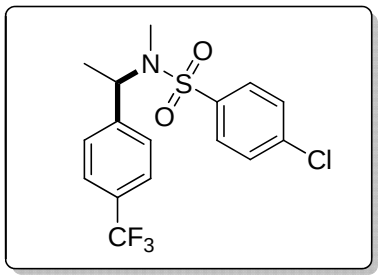
3.8 Hz), 126.9, 127.5, 129.2, 129.8 (q, J = 32.1 Hz), 132.6, 139.7, 143.9. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{16}F_3NNaO_2S$ $(M+Na)^+$ 366.0746. Found 366.0735.



9k: *N*,2-dimethyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide

Following the procedure for the synthesis of **9a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), *N*,2-dimethylbenzenesulfonamide **8c** (277 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9k** (114 mg, 64%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 40). Reaction time 48 h.

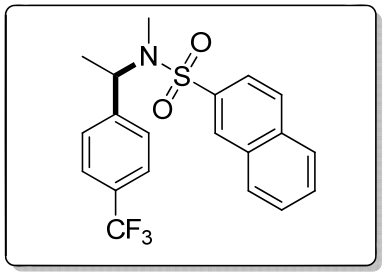
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.50 (d, J = 7.0 Hz, 3H), 2.62 (s, 6H), 5.22 (q, J = 7.0 Hz, 1H), 7.34 (m, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 7.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.7, 20.4, 28.2, 53.9, 123.9 (CF_3, q, J = 270.6 Hz), 125.3 (q, J = 3.8 Hz), 126.1, 127.7, 129.8 (q, J = 32.1 Hz), 130.0, 132.7, 132.8, 137.4, 137.7, 143.7. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{18}F_3NNaO_2S$ $(M+Na)^+$ 380.0903. Found 380.0907.



9l: 4-chloro-*N*-methyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide

Following the procedure for the synthesis of **9a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), 4-chloro-*N*-methylbenzenesulfonamide **8d** (307 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9l** (143 mg, 76%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 40). Reaction time 36 h.

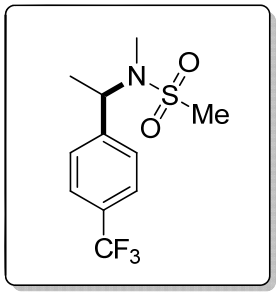
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.32 (d, J = 7.0 Hz, 3H), 2.61 (s, 3H), 5.33 (q, J = 7.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.2, 28.5, 54.6, 123.9 (CF_3, q, J = 270.6 Hz), 125.4 (q, J = 3.8 Hz), 127.5, 128.4, 129.4, 129.8 (q, J = 32.1 Hz), 138.3, 139.0, 143.8. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{15}ClF_3NNaO_2S$ $(M+Na)^+$ 400.0356. Found 400.0346.



9m: *N*-methyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)naphthalene-2-sulfonamide

Following the procedure for the synthesis of **9a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), *N*-methylnaphthalene-2-sulfonamide **8e** (331 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9m** (126 mg, 64%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 40). Reaction time 48 h.

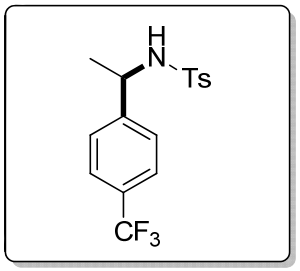
Colorless crystals, m.p. 126–127 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.31 (d, *J* = 7.0 Hz, 3H), 2.65 (s, 3H), 5.41 (q, *J* = 7.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.60–7.67 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.97 (t, *J* = 8.0 Hz, 2H), 8.43 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.3, 28.6, 54.5, 122.3, 123.9 (CF_3, q, *J* = 270.5 Hz), 125.4 (q, *J* = 3.8 Hz), 127.5, 127.6, 127.9, 128.3, 128.8, 129.1, 129.5, 129.8 (q, *J* = 32.1 Hz), 132.2, 134.7, 136.7, 144.0. **HRMS** (ESI-TOF) Calcd for $C_{20}H_{18}F_3NNaO_2S$ $(M+Na)^+$ 416.0903. Found 416.0901.



9n: *N*-methyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)methanesulfonamide

Following the procedure for the synthesis of **9a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), *N*-methylmethanesulfonamide **8f** (164 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9n** (118 mg, 84%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 24). Reaction time 36 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.62 (d, *J* = 7.0 Hz, 3H), 2.67 (s, 3H), 2.87 (s, 3H), 5.31 (q, *J* = 7.0 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 16.3, 28.3, 38.5, 54.4, 123.9 (CF_3, q, *J* = 270.6 Hz), 125.5 (q, *J* = 3.8 Hz), 127.6, 129.9 (q, *J* = 32.1 Hz), 143.7. **HRMS** (ESI-TOF) Calcd for $C_{11}H_{14}F_3NNaO_2S$ $(M+Na)^+$ 304.0590. Found 304.0584.

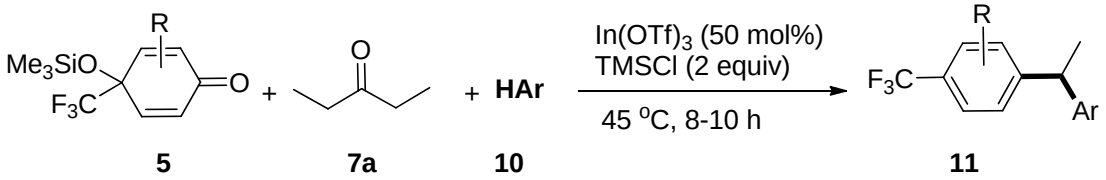


9o: 4-methyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide

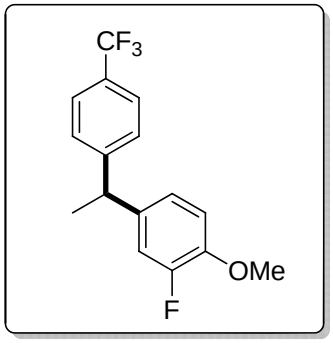
Following the procedure for the synthesis of **9a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), 4-methylbenzenesulfonamide **8g** (256 mg, 1.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **9o** (45 mg, 26%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 15). Reaction time 36 h. Some 4-methyl-*N*-(3-(3-oxopentan-2-yl)-4-(trifluoromethyl)phenyl) benzenesulfonamide,[2] which has been reported previously by us can't be isolated from 9o.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.42 (d, *J* = 7.0 Hz, 3H), 2.31 (s, 3H), 4.55 (q, *J* = 7.0 Hz, 1H), 5.82 (d, *J* = 7.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H). **HRMS** (ESI-TOF) Calcd for $C_{16}H_{17}F_3NO_2S$ $(M+H)^+$ 344.0927. Found 344.0930.

Synthesis of unsymmetrical trifluoromethylateddiarylmethanes



5 **7a** **10** **11**

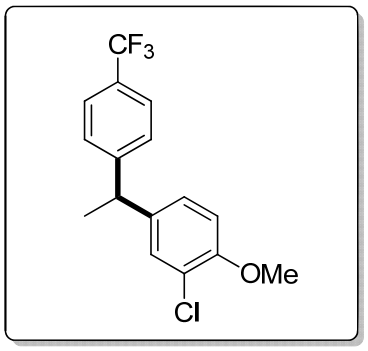


11a: 2-fluoro-1-methoxy-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

To the solution of 1-fluoro-2-methoxybenzene **10a** (57 μL, 0.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) in DCE (1 mL) was added TMSCl (126 μL, 1 mmol) and $In(OTf)_3$ (141 mg, 0.25 mmol) at 45 ℃. Then, 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (250 mg, 1.0 mmol) was added. After the reaction was finished as indicated by TLC (reaction time, 8 h), the resulting mixture was poured into water (20 mL) and extracted with DCM (CH_2Cl_2, 20 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1: 240) to afford **11a** (128 mg, 86%).

2 J. Dong, L. Shi, L. Pan, X. Xu, Q. Liu, *Sci. Rep.*, 2016, **6**, 26957.

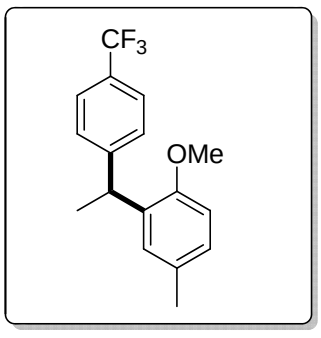
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.60 (d, *J* = 7.0 Hz, 3H), 3.84 (s, 3H), 4.13 (q, *J* = 7.0 Hz, 1H), 6.86–6.93 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.6, 43.7, 56.2, 113.3, 115.3 (d, *J* = 18.3 Hz), 123.0 (d, *J* = 3.4 Hz), 124.2 (CF_3, q, *J* = 272.0 Hz), 125.4 (q, *J* = 3.8 Hz), 127.8, 128.5 (q, *J* = 32.1 Hz), 138.3 (d, *J* = 5.5 Hz), 146.0 (d, *J* = 10.6 Hz), 150.1, 152.3 (d, *J* = 244.5 Hz). MS (70 eV): *m/z* (%): 298.1 (39) [M^+], 283.1 (100) [$M^+ - CH_3$], 283.1 (6) [$M^+ - 2\ CH_3$]; MS (70 eV): calcd for $C_{16}H_{14}F_4O$: 298.0981, found 298.1.



11b: 2-chloro-1-methoxy-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (250 mg, 1.0 mmol), 1-chloro-2-methoxybenzene **10b** (64 μL, 0.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11b** (113 mg, 72%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 240). Reaction time 8 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.59 (d, *J* = 7.0 Hz, 3H), 3.84 (s, 3H), 4.11 (q, *J* = 7.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.21 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.5, 43.6, 56.0, 112.0, 122.3, 123.1 (CF_3, q, *J* = 272.0 Hz), 125.3 (q, *J* = 3.5 Hz), 126.7, 127.8, 128.4 (q, *J* = 32.1 Hz), 129.2, 138.4, 150.1, 153.4. MS (70 eV): *m/z* (%): 316.1 (13) [M^+], 314.1 (37) [M^+], 301.1 (33) [$M^+ - CH_3$], 299.1 (100) [$M^+ - CH_3$]; MS (70 eV): calcd for $C_{16}H_{14}ClF_3O$: 314.0685, found 314.1.

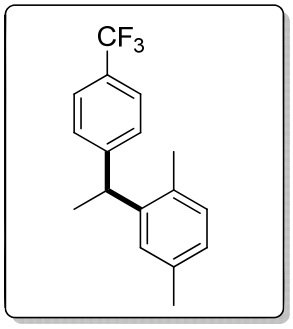


11c: 1-methoxy-4-methyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), 1-methoxy-4-methylbenzene **10c** (126 μL, 1.0 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11c** (102 mg, 70%) after purification by column chromatography on silica gel (EtOAc/PE =

1: 240). Reaction time 8 h.

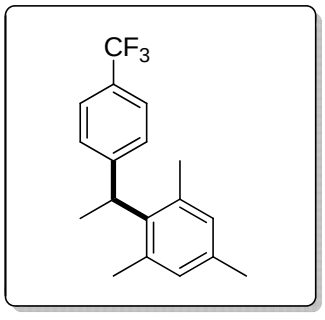
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.57 (d, *J* = 7.5 Hz, 3H), 2.27 (s, 3H), 3.71 (s, 3H), 4.56 (q, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 20.6, 20.7, 37.4, 55.5, 110.6, 124.8 (CF_3, q, *J* = 270.1 Hz), 124.9 (q, *J* = 3.6 Hz), 127.7, 127.8 (q, *J* = 32.3 Hz), 127.9, 128.1, 129.7, 133.4, 150.7, 154.7. MS (70 eV): *m/z* (%): 294.2 (88) [M^+], 279.1 (100) [$M^+ - CH_3$]; MS (70 eV): calcd for $C_{17}H_{17}F_3O$: 294.1231, found 294.2.



11d: 1,4-dimethyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), p-xylene **10d** (124 μL, 1.0 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11d** (97 mg, 70%) after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 10 h.

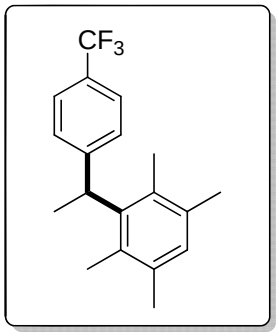
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.60 (d, *J* = 7.5 Hz, 3H), 2.15 (s, 3H), 2.32 (s, 3H), 4.33 (q, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 7.06 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 19.3, 21.2, 21.9, 40.9, 124.9 (CF_3, q, *J* = 270.1 Hz), 125.2 (q, *J* = 3.6 Hz), 127.1, 127.3, 127.9, 128.3 (q, *J* = 32.3 Hz), 130.5, 132.8, 135.5, 142.6, 150.5. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -64.2. MS (70 eV): *m/z* (%): 278.1 (44) [M^+], 263.1 (100) [$M^+ - CH_3$]; MS (70 eV): calcd for $C_{17}H_{17}F_3$: 278.1282, found 278.1.



11e: 1,3,5-trimethyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), mesitylene **10e** (140 μL, 1.0 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11e** (112 mg, 77%) after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 10 h.

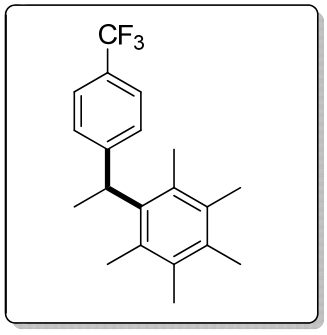
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.67 (d, *J* = 7.0 Hz, 3H), 2.09 (s, 6H), 2.25 (s, 3H), 4.63 (q, *J* = 7.0 Hz, 1H), 6.83 (s, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 16.7, 20.7, 21.0, 37.9, 124.8 (CF_3, q, *J* = 270.1 Hz), 125.0 (q, *J* = 3.6 Hz), 127.1, 127.6 (q, *J* = 32.1 Hz), 130.1, 135.8, 136.3, 139.1, 149.8. MS (70 eV): *m/z* (%): 292.2 (46) [M^+], 277.2 (100) [$M^+ - CH_3$], 262.1 (10) [$M^+ - 2\ CH_3$]; MS (70 eV): calcd for $C_{18}H_{19}F_3$: 292.1439, found 292.2.



11f: 1,2,4,5-tetramethyl-3-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), 1,2,4,5-tetramethylbenzene **10f** (134 mg, 1.0 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11f** (109 mg, 71%) after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 10 h.

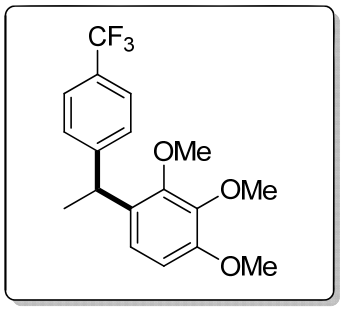
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.69 (d, *J* = 7.0 Hz, 3H), 1.99 (s, 6H), 2.20 (s, 6H), 4.74 (q, *J* = 7.0 Hz, 1H), 6.91 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 16.7, 17.1, 19.0, 20.8, 38.4, 124.8 (CF_3, q, *J* = 270.1 Hz), 125.0 (q, *J* = 3.6 Hz), 126.8, 127.4 (q, *J* = 32.3 Hz), 130.4, 131.0, 132.5, 142.1, 150.4. MS (70 eV): *m/z* (%): 306.2 (85) [M^+], 291.2 (100) [$M^+ - CH_3$], 276.1 (11) [$M^+ - 2\ CH_3$]; MS (70 eV): calcd for $C_{19}H_{21}F_3$: 306.1595, found 306.2.



11g: 1,2,3,4,5-pentamethyl-6-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), 1,2,3,4,5-pentamethylbenzene **10g** (148 mg, 1.0 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11g** (115 mg, 72%) after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 10 h.

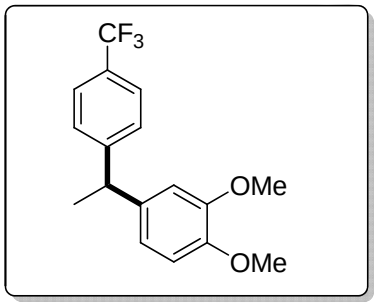
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.70 (d, *J* = 7.0 Hz, 3H), 2.05 (s, 6H), 2.20 (s, 6H), 2.26 (s, 3H), 4.77 (q, *J* = 7.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 16.9, 17.1, 17.6, 17.8, 38.7, 124.8 (CF_3, q, *J* = 270.1 Hz), 125.0 (q, *J* = 3.6 Hz), 126.7, 127.3 (q, *J* = 32.1 Hz), 132.1, 133.4, 139.6, 150.8. MS (70 eV): *m/z* (%): 320.2 (87) [M^+], 305.2 (100) [$M^+ - CH_3$], 290.1 (7) [$M^+ - 2\ CH_3$], 275.1 (21) [$M^+ - 3\ CH_3$]; MS (70 eV): calcd for $C_{20}H_{23}F_3$: 320.1752, found 320.2.



11h: 1,2,3-trimethoxy-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), 1,2,3-trimethoxybenzene **10h** (168 mg, 1.0 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11h** (90 mg, 53%) and little unidentified compounds after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 8 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.57 (d, *J* = 7.0 Hz, 3H), 3.62 (s, 3H), 3.84 (s, 6H), 4.49 (q, *J* = 7.0 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.3, 37.9, 55.9, 60.5, 60.6, 106.9, 121.6, 124.7 (CF_3, q, *J* = 270.1 Hz), 125.1 (q, *J* = 3.6 Hz), 127.8, 127.9 (q, *J* = 32.3 Hz), 131.2, 142.3, 151.2, 151.4, 152.4. MS (70 eV): *m/z* (%): 340.2 (92) [M^+], 325.1 (100) [$M^+ - CH_3$], 310.1 (6) [$M^+ - 2\ CH_3$]; HR-MS (70 eV): calcd for $C_{18}H_{19}F_3O_3$: 340.1286, found 340.2.

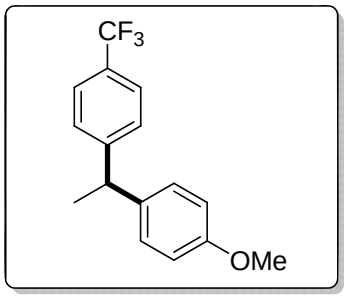


11i: 1,2-dimethoxy-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (150 mg, 0.6 mmol), 1,2-dimethoxy benzene **10i** (64 μL, 0.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11i** (79 mg, 51%) and little unidentified compounds after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 8 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.63 (d, *J* = 7.0 Hz, 3H), 3.82 (s, 3H), 3.84 (s, 3H), 4.13 (q, *J* = 7.0 Hz, 1H), 6.69 (s, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz,

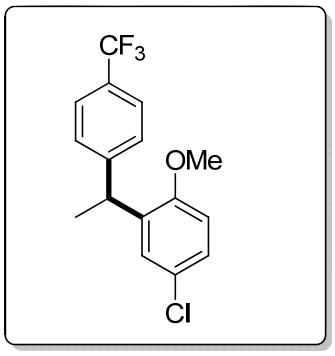
1H), 7.31 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H). MS (70 eV): *m/z* (%): 310.1 (57) [M^+], 295.1 (100) [$M^+ - CH_3$], 280.1 (4) [$M^+ - 2\ CH_3$]; MS (70 eV): calcd for $C_{17}H_{17}F_3O_2$: 310.1181, found 310.1.



11j: 1-methoxy-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), anisole **10j** (108 μL, 1.0 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11j** (57 mg, 41%) and little unidentified compounds after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 8 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.62 (d, J = 7.0 Hz, 3H), 3.77 (s, 3H), 4.15 (q, J = 7.0 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H). MS (70 eV): *m/z* (%): 280.1 (72) [M^+], 265.1 (100) [$M^+ - CH_3$]; MS (70 eV): calcd for $C_{16}H_{15}F_3O$: 280.1075, found 280.1.

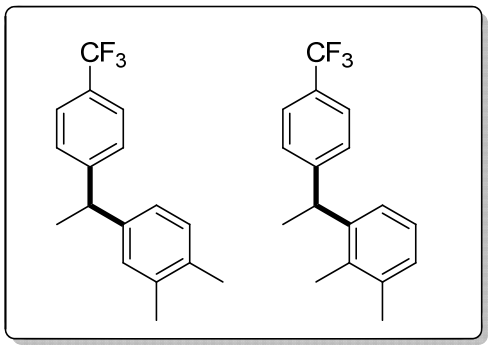


11k: 4-chloro-1-methoxy-2-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (250 mg, 1.0 mmol), p-xylene **10k** (62 μL, 0.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11k** (57 mg, 36%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 240). Reaction time 8 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.55 (d, J = 7.5 Hz, 3H), 3.72 (s, 3H), 4.54 (q, J = 7.5 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 7.13–7.16 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 20.5, 37.5, 55.6, 111.8, 124.9 (CF_3, q, J = 270.1 Hz), 125.1 (q, J = 3.6 Hz), 125.5, 127.1, 127.5, 127.8, 128.2 (q, J = 32.3 Hz), 135.4, 149.8, 150.4. MS (70 eV): *m/z* (%): 316.1 (18) [M^+], 314.1 (54) [M^+], 301.1 (14) [$M^+ - CH_3$], 299.1 (43) [$M^+ - CH_3$], 159.1 (100) [$M^+ - C_8H_8ClO$]; MS (70 eV): calcd for

$C_{16}H_{14}ClF_3O$: 314.0685, found 314.1.



11l: 1,2-dimethyl-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

11l': 1,2-dimethyl-3-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), o-xylene **10l** (120 μL, 1.0 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11l/l'** (91 mg, 66%) after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 10 h.

Colorless viscous liquid, **11l/11l' =** 20/3.

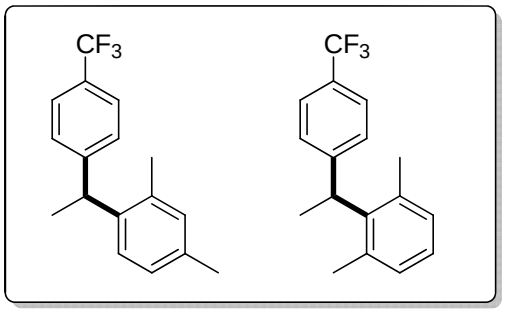
^{1}H NMR (500 MHz, $CDCl_3$):

11l, δ 1.61 (d, *J* = 7.0 Hz, 3H), 2.21 (s, 6H), 4.12 (q, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.97 (s, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H).

11l', δ 1.60 (d, *J* = 7.0 Hz, 3H), 2.09 (s, 3H), 2.26 (s, 3H), 4.42 (q, *J* = 7.0 Hz, 1H), 7.05 (m, 1H), 7.11 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 15.1, 19.3, 19.9, 20.9, 21.6, 22.2, 41.2, 44.3, 124.9 (CF_3, q, *J* = 270.1 Hz), 124.5, 124.8, 125.3 (q, *J* = 3.6 Hz), 125.4, 127.8, 127.9, 128.2 (q, *J* = 32.1 Hz), 128.9, 129.8, 134.6, 136.7, 137.1, 142.6, 142.8, 150.7.

MS (70 eV): *m/z* (%): 278.1 (39) [M^+], 263.1 (100) [$M^+ - CH_3$], 248.1 (18) [$M^+ - 2\ CH_3$]; MS (70 eV): calcd for $C_{17}H_{17}F_3$: 278.1282, found 278.1.



11m: 2,4-dimethyl-1-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

11m': 1,3-dimethyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), m-xylene **10m** (123 μL, 1.0 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11m/m'** (94 mg, 68%) after purification by column chromatography on silica gel using petroleum ether as eluant.

Reaction time 10 h.

Colorless viscous liquid, **11m/11m' =** 20/1.

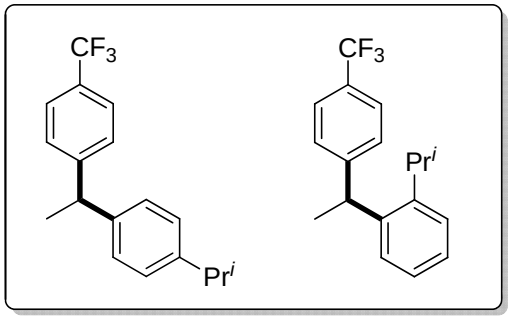
^{1}H NMR (500 MHz, $CDCl_3$):

11m, δ 1.59 (d, *J* = 7.0 Hz, 3H), 2.16 (s, 3H), 2.29 (s, 3H), 4.31 (q, *J* = 7.0 Hz, 1H), 6.96 (s, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 2H).

11m', δ 1.68 (d, *J* = 7.0 Hz, 3H), 2.09 (s, 3H), 2.26 (s, 3H), 4.67 (q, *J* = 7.0 Hz, 1H), 6.99–7.05 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 16.5, 19.6, 20.9, 21.1, 21.9, 38.2, 40.6, 124.9 (CF_3, q, *J* = 270.1 Hz), 125.1 (q, *J* = 3.6 Hz), 125.2 (q, *J* = 3.6 Hz), 126.4, 126.5, 126.8, 127.1, 127.9, 128.3 (q, *J* = 32.1 Hz), 131.4, 135.8, 135.9, 136.4, 139.9, 142.1, 149.5, 150.6.

MS (70 eV): *m/z* (%): 278.2 (40) [M^+], 263.2 (100) [$M^+ - CH_3$], 248.1 (17) [$M^+ - 2\ CH_3$]; MS (70 eV): calcd for $C_{17}H_{17}F_3$: 278.1282, found 278.2.



11n: 1-isopropyl-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

11n': 1-isopropyl-2-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5a** (125 mg, 0.5 mmol), cumene **10n** (140 μL, 1.0 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11n/n'** (73 mg, 50%) after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 10 h.

Colorless viscous liquid, **11n/11n' =** 20/1.

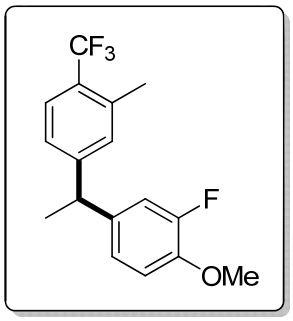
^{1}H NMR (500 MHz, $CDCl_3$):

11n, δ 1.22 (d, *J* = 6.5 Hz, 6H), 1.64 (d, *J* = 7.0 Hz,, 3H), 2.87 (m, 1H), 4.16 (q, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H).

11n', δ 1.07 (d, *J* = 6.5 Hz, 6H), 1.64 (d, *J* = 7.0 Hz,, 3H), 3.18 (m, 1H), 4.53 (q, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.18–7.29 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 21.7 (2), 22.4, 23.9, 24.0, 33.6, 34.1, 44.3, 44.7, 124.8 (CF_3, q, *J* = 270.1 Hz), 125.3 (q, *J* = 3.6 Hz), 125.8 (CF_3, q, *J* = 270.1 Hz), 126.5, 127.4, 127.9, 128.4 (q, *J* = 32.1 Hz), 141.5, 142.5, 145.1, 146.5, 149.1, 150.7, 150.9.

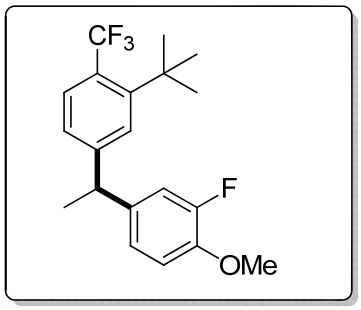
MS (70 eV): *m/z* (%): 292.2 (37) [M^+], 277.2 (100) [$M^+ - CH_3$]; MS (70 eV): calcd for $C_{18}H_{19}F_3$: 292.1439, found 292.2.



11o: 2-fluoro-1-methoxy-4-(1-(3-methyl-4-(trifluoromethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 3-methyl-4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5b** (264 mg, 1.0 mmol), 1-fluoro-2-methoxybenzene **10a** (57 μL, 0.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11o** (89 mg, 57%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 240). Reaction time 8 h.

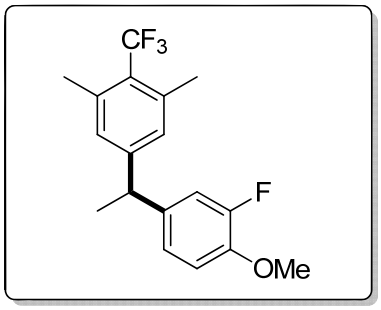
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.59 (d, *J* = 7.5 Hz, 3H), 2.43 (s, 3H), 3.85 (s, 3H), 4.07 (q, *J* = 7.5 Hz, 1H), 6.86–6.93 (m, 3H), 7.08 (d, *J* = 8.5 Hz, 1H), 7.09 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 19.3 (q, *J* = 1.8 Hz), 21.5, 43.5, 56.2, 113.2, 115.2 (d, *J* = 18.3 Hz), 122.9 (d, *J* = 3.4 Hz), 124.5 (CF_3, q, *J* = 272.0 Hz), 124.6, 125.9 (q, *J* = 3.8 Hz), 126.8 (q, *J* = 32.1 Hz), 131.0, 136.7, 138.4 (d, *J* = 5.5 Hz), 145.9 (d, *J* = 10.6 Hz), 149.8, 152.2 (d, *J* = 244.3 Hz). MS (70 eV): *m/z* (%): 312.2 (31) [M^+], 297.2 (100) [$M^+ - CH_3$], 282.1 (8) [$M^+ - 2\ CH_3$]; MS (70 eV): calcd for $C_{17}H_{16}F_4O$: 312.1137, found 312.2.



11p: 2-(*tert*-butyl)-4-(1-(3-fluoro-4-methoxyphenyl)ethyl)-1-(trifluoromethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 3-(tert-butyl)-4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5d** (306 mg, 1.0 mmol), 1-fluoro-2-methoxybenzene **10a** (57 μL, 0.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11p** (90 mg, 51%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 240). Reaction time 8 h.

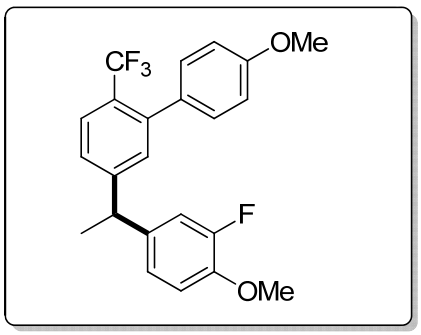
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.42 (s, 9H), 1.61 (d, *J* = 7.0 Hz, 3H), 3.86 (s, 3H), 4.10 (q, *J* = 7.0 Hz, 1H), 6.88–6.94 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.7, 31.9 (q, *J* = 3.3 Hz), 36.5, 43.9, 56.2, 113.3, 115.3 (d, *J* = 18.3 Hz), 122.9 (d, *J* = 3.4 Hz), 124.6, 125.4 (CF_3, q, *J* = 272.0 Hz), 125.9 (q, *J* = 32.1 Hz), 128.2, 128.5(q, *J* = 3.8 Hz), 138.5 (d, *J* = 5.5 Hz), 145.9 (d, *J* = 10.6 Hz), 149.3, 149.5, 152.3 (d, *J* = 244.3 Hz). MS (70 eV): *m/z* (%): 354.2 (35) [M^+], 339.2 (100) [$M^+ - CH_3$]; MS (70 eV): calcd for $C_{20}H_{22}F_4O$: 354.1607, found 354.2.



11q: 5-(1-(3-fluoro-4-methoxyphenyl)ethyl)-1,3-dimethyl-2-(trifluoromethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 3,5-dimethyl-4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5f** (278 mg, 1.0 mmol), 1-fluoro-2-methoxybenzene **10a** (57 μL, 0.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11q** (78 mg, 48%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 240). Reaction time 8 h.

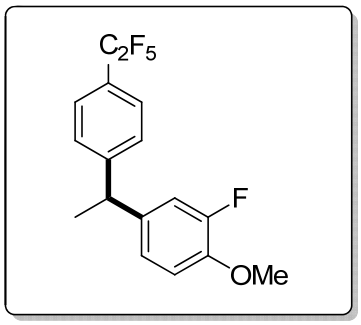
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.57 (d, *J* = 7.0 Hz, 3H), 2.43 (s, 6H), 3.85 (s, 3H), 4.00 (q, *J* = 7.0 Hz, 1H), 6.86–6.93 (m, 5H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.5, 21.6 (q, *J* = 4.0 Hz), 43.3, 56.2, 113.3, 115.2 (d, *J* = 18.3 Hz), 122.9 (d, *J* = 3.4 Hz), 125.5 (q, *J* = 28.3 Hz), 125.7 (CF_3, q, *J* = 272.0 Hz), 129.2, 137.6 (q, *J* = 1.9 Hz), 138.5 (d, *J* = 5.5 Hz), 145.9 (d, *J* = 10.6 Hz), 148.7, 152.2 (d, *J* = 244.3 Hz). MS (70 eV): *m/z* (%): 326.2 (31) [M^+], 311.1 (100) [$M^+ - CH_3$]; MS (70 eV): calcd for $C_{18}H_{18}F_4O$: 326.1294, found 326.2.



11r: 5-(1-(3-fluoro-4-methoxyphenyl)ethyl)-4'-methoxy-2-(trifluoromethyl)-1,1'-biphenyl

Following the procedure for the synthesis of **11a**, the reaction of 4'-methoxy-6-(trifluoromethyl)-6-((trimethylsilyl)oxy)-[1,1'-biphenyl]-3(6H)-one **5c** (356 mg, 1.0 mmol), 1-fluoro-2-methoxybenzene **10a** (57 μL, 0.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11r** (81 mg, 48%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 240). Reaction time 8 h.

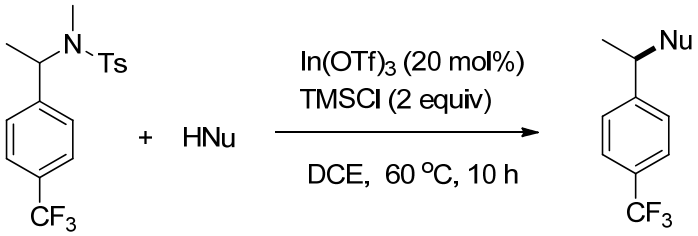
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.62 (d, *J* = 7.0 Hz, 3H), 3.84 (s, 3H), 3.85 (s, 3H), 4.13 (q, *J* = 7.0 Hz, 1H), 6.86–6.95 (m, 5H), 7.14 (s, 1H), 7.23–7.25 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.6, 43.6, 56.2, 56.3, 113.1, 113.3, 115.3 (d, *J* = 18.3 Hz), 122.9 (d, *J* = 3.4 Hz), 124.2 (CF_3, q, *J* = 272.0 Hz), 126.1, 126.3 (q, *J* = 3.8 Hz), 126.6 (q, *J* = 32.1 Hz), 130.1, 131.4, 132.2, 138.3 (d, *J* = 5.5 Hz), 141.3, 146.0 (d, *J* = 10.6 Hz), 149.6, 152.3 (d, *J* = 244.3 Hz), 159.1. MS (70 eV): *m/z* (%): 404.1 (65) [M^+], 389.1 (100) [$M^+ - CH_3$], 374.0 (2) [$M^+ - 2\ CH_3$]; MS (70 eV): calcd for $C_{23}H_{20}F_4O_2$: 404.1399, found 404.1.



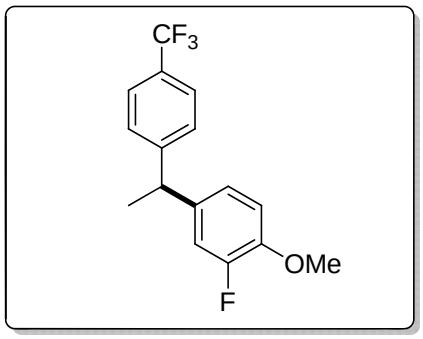
11s: 2-fluoro-1-methoxy-4-(1-(4-(perfluoroethyl)phenyl)ethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of 4-(perfluoroethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dienone **5g** (300 mg, 1.0 mmol), 1-fluoro-2-methoxybenzene **10a** (57 μL, 0.5 mmol) and pentan-3-one **7a** (157 μL, 1.5 mmol) gave **11s** (115 mg, 57%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 240). Reaction time 8 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.61 (d, J = 7.5 Hz, 3H), 3.85 (s, 3H), 4.14 (q, J = 7.5 Hz, 1H), 6.87–6.94 (m, 3H), 7.31 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.6, 43.7, 56.2, 113.3, 113.5 (qt, J_1 = 253.1 Hz, J_2 = 38.6 Hz), 115.3 (d, J = 18.3 Hz), 119.1 (tq, J_1 = 249.4 Hz, J_2 = 39.4 Hz), 123.0 (d, J = 3.4 Hz), 126.5 (t, J = 15.8 Hz), 126.6 (t, J = 5.6 Hz), 127.8, 138.3 (d, J = 5.5 Hz), 146.1 (d, J = 10.6 Hz), 150.3, 152.3 (d, J = 244.5 Hz). MS (70 eV): *m/z* (%): 348.1 (36) [M^+], 333.1 (100) [$M^+ - CH_3$], 318.1 (2) [$M^+ - 2\ CH_3$]; MS (70 eV): calcd for $C_{17}H_{14}F_6O$: 404.1399, found 348.1.



9a **11** or **12**

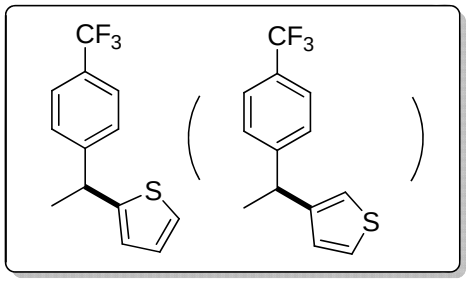


11a: 2-fluoro-1-methoxy-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

To the solution of *N*,4-dimethyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide **9a** (358 mg, 1.0 mmol) in DCE (1 mL) was added TMSCl (126 μL, 1 mmol) and $In(OTf)_3$ (56 mg, 0.1 mmol) at 60 ℃. Then, 1-fluoro-2-methoxybenzene **10a** (57 μL, 0.5 mmol) was added. After the reaction was finished as indicated by TLC (reaction time, 10 h), the resulting mixture was

poured into water (20 mL) and extracted with DCM (CH_2Cl_2, 20 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1: 240) to afford **11a** (134 mg, 90%).

Please see the analytic data of **11a**, **11b**, **11d** and **11e** in page S9-12.



11t: 2-(1-(4-(trifluoromethyl)phenyl)ethyl)thiophene

11t': 3-(1-(4-(trifluoromethyl)phenyl)ethyl)thiophene

Following the procedure for the synthesis of **11a**, the reaction of *N*,4-dimethyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide **9a** (179 mg, 0.5 mmol) and thiophene **10t** (82 μL, 1.0 mmol) gave **11t/t'** (81 mg, 63%) after purification by column chromatography on silica gel (EtOAc/PE = 1: 240). Reaction time 10 h.

Colorless viscous liquid, **11t/11t' =** 2/1.

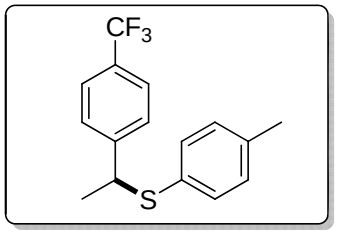
^{1}H NMR (500 MHz, $CDCl_3$):

11t, δ 1.71 (d, *J* = 7.5 Hz, 3H), 4.40 (q, *J* = 7.5 Hz, 1H), 6.81 (dd, *J* = 5.0 Hz, 1H), 6.93 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 1H), 7.17 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H).

11t', δ 1.64 (d, *J* = 7.5 Hz, 3H), 4.22 (q, *J* = 7.5 Hz, 1H), 6.85 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 1H), 6.99 (dd, *J* = 5.0 Hz, 1H), 7.25 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 22.0, 23.1, 40.5, 40.6, 120.2, 123.1 (CF_3, q, *J* = 270.1 Hz), 123.2 (CF_3, q, *J* = 270.1 Hz), 123.8, 123.9, 125.3 (q, *J* = 3.6 Hz), 125.4 (q, *J* = 3.6 Hz), 125.8, 126.7, 127.5, 127.6, 128.6 (q, *J* = 32.3 Hz), 128.7 (q, *J* = 32.3 Hz), 146.0, 149.2, 150.0, 150.3.

MS (70 eV): *m/z* (%): 256.0 (44) [M^+], 241.0 (100) [$M^+ - CH_3$]; MS (70 eV): calcd for $C_{13}H_{11}F_3S$: 256.0534, found 256.0.

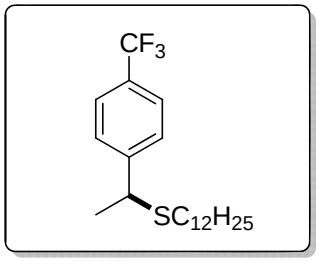


12a: *p*-tolyl(1-(4-(trifluoromethyl)phenyl)ethyl)sulfane

Following the procedure for the synthesis of **11a**, the reaction of *N*,4-dimethyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide **9a** (179 mg, 0.5 mmol) and 4-methylbenzenethiol **10u** (124 mg, 1.0 mmol) gave **12a** (124 mg, 84%) after purification by

column chromatography on silica gel using petroleum ether as eluant. Reaction time 10 h.

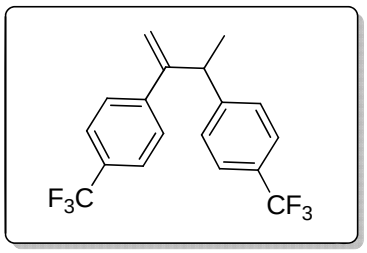
Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.60 (d, *J* = 7.0 Hz, 3H), 2.28 (s, 3H), 4.27 (q, *J* = 7.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.1, 21.8, 47.9, 124.8 (CF_3, q, *J* = 270.1 Hz), 125.2 (q, *J* = 3.6 Hz), 127.6, 129.1 (q, *J* = 32.3 Hz), 129.6, 130.4, 137.8, 147.6. MS (70 eV): *m/z* (%): 296.1 (38) [M^+], 173.1 (100) [$M^+ - C_7H_7S$]; MS (70 eV): calcd for $C_{16}H_{15}F_3S$: 296.0847, found 296.1.



12b: dodecyl(1-(4-(trifluoromethyl)phenyl)ethyl)sulfane

Following the procedure for the synthesis of **11a**, the reaction of *N*,4-dimethyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide **9a** (179 mg, 0.5 mmol) and dodecane-1-thiol **10v** (240 μL, 1.0 mmol) gave **12b** (114 mg, 61%) after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 10 h.

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.22–1.32 (m, 18H), 1.46–1.49 (m, 2H), 1.56 (d, *J* = 7.0 Hz, 3H), 2.23–2.35 (m, 2H), 3.98 (q, *J* = 7.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.1, 22.5, 22.7, 28.9, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6 (2), 31.3, 31.9, 43.7, 124.1 (CF_3, q, *J* = 270.1 Hz), 125.4 (q, *J* = 3.6 Hz), 127.5, 129.1 (q, *J* = 32.3 Hz), 148.5. MS (70 eV): *m/z* (%): 374.2 (2) [M^+], 201.2 (74) [$M^+ - C_9H_8F_3$], 173.1 (100) [$M^+ - C_{12}H_{25}S$]; MS (70 eV): calcd for $C_{21}H_{33}F_3S$: 374.2255, found 374.2.

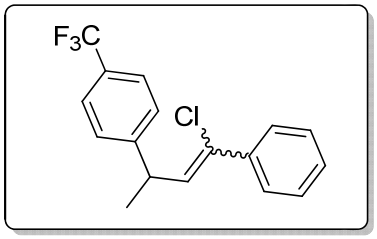


13: 4,4'-(but-1-ene-2,3-diyl)bis((trifluoromethyl)benzene)

To the solution of *N*,4-dimethyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide **9a** (179 mg, 0.5 mmol) in DCE (1 mL) was added TMSCl (126 μL, 1 mmol) and $In(OTf)_3$ (56 mg, 0.1 mmol) at 80 ℃. After the reaction was finished as indicated by TLC (reaction time, 10 h), the resulting mixture was poured into water (20 mL) and extracted with DCM (CH_2Cl_2, 20 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1: 240) to afford **13** (159 mg, 93%).

Colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.49 (d, *J* = 7.0 Hz, 3H), 3.73 (q, *J* = 7.0

Hz, 1H), 6.44 (d, *J* = 2.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 20.8, 42.5, 123.8 (CF_3, q, *J* = 270.6 Hz), 124.6 (CF_3, q, *J* = 270.6 Hz), 125.5 (q, *J* = 3.8 Hz), 126.3, 127.6, 128.1, 128.8 (q, *J* = 32.1 Hz), 129.1 (q, *J* = 32.1 Hz), 136.7, 140.7, 149.1. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -64.4, -64.3. MS (70 eV): *m/z* (%): 344.1 (31) [M^+], 329.1 (32) [$M^+ - CH_3$], 275.1 (100) [$M^+ - CF_3$]; MS (70 eV): calcd for $C_{18}H_{14}F_6$: 344.1000, found 344.1.



15: (*E*)-1-(4-chloro-4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)benzene

15': (*Z*)-1-(4-chloro-4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)benzene

Following the procedure for the synthesis of **11a**, the reaction of *N*,4-dimethyl-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide **9a** (358 mg, 1.0 mmol) and ethynylbenzene **14** (55 μL, 0.5 mmol) gave **15/15'** (67 mg, 43%) after purification by column chromatography on silica gel using petroleum ether as eluant. Reaction time 10 h.

Colorless viscous liquid, **15/15' =** 1/0.8.

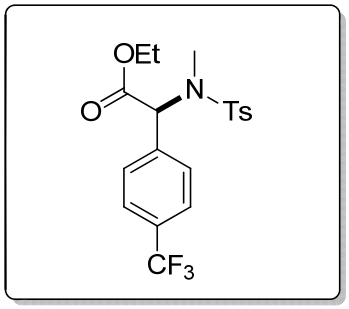
^{1}H NMR (500 MHz, $CDCl_3$):

15, δ 1.37 (d, *J* = 7.0 Hz, 3H), 3.63 (m, 1H), 6.10 (d, *J* = 10.5 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.31–7.39 (m, 4H), 7.56 (d, *J* = 8.0 Hz, 4H).

15', δ 1.49 (d, *J* = 7.0Hz, 3H), 4.23 (m, 1H), 6.21 (d, *J* = 9.0 Hz, 1H), 7.31–7.39 (m, 5H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 20.8, 22.3, 39.5, 39.6, 123.8 (CF_3, q, *J* = 270.1 Hz), 124.6 (CF_3, q, *J* = 270.1 Hz), 125.5 (q, *J* = 3.6 Hz), 125.6 (q, *J* = 3.6 Hz), 126.5, 127.1, 127.4, 128.3, 128.4, 128.5, 128.7, 128.9, 131.0, 131.1, 132.7, 133.1, 136.9, 137.7, 148.8, 148.9.

MS (70 eV): *m/z* (%): 312.1 (33) [M^+], 310.1 (100) [M^+], 297.0 (21) [$M^+ - CH_3$], 295.0 (65) [$M^+ - CH_3$]; MS (70 eV): calcd for $C_{17}H_{14}ClF_3$: 310.0736, found 310.1.



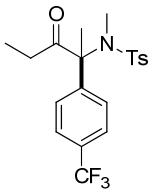
17: ethyl 2-(*N*,4-dimethylphenylsulfonamido)-2-(4-(trifluoromethyl)phenyl)acetate

To the solution of ethyl 2-(4-(trifluoromethyl)-4-((trimethylsilyl)oxy)cyclohexa-2,5-dien-1-ylidene)acetate **16** (160 mg, 0.5 mmol) and *N*,4-dimethylbenzenesulfonamide **8a** (278 mg, 1.5 mmol) in DCE (1 mL) was added TMSCl (126 μL, 1 mmol) and $In(OTf)_3$ (28 mg, 0.05 mmol) at 25 ℃. After the reaction

was finished as indicated by TLC (reaction time, 18 h), the resulting mixture was poured into water (20 mL) and extracted with DCM (CH_2Cl_2, 20 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1: 15) to afford **17** (83 mg, 40%).

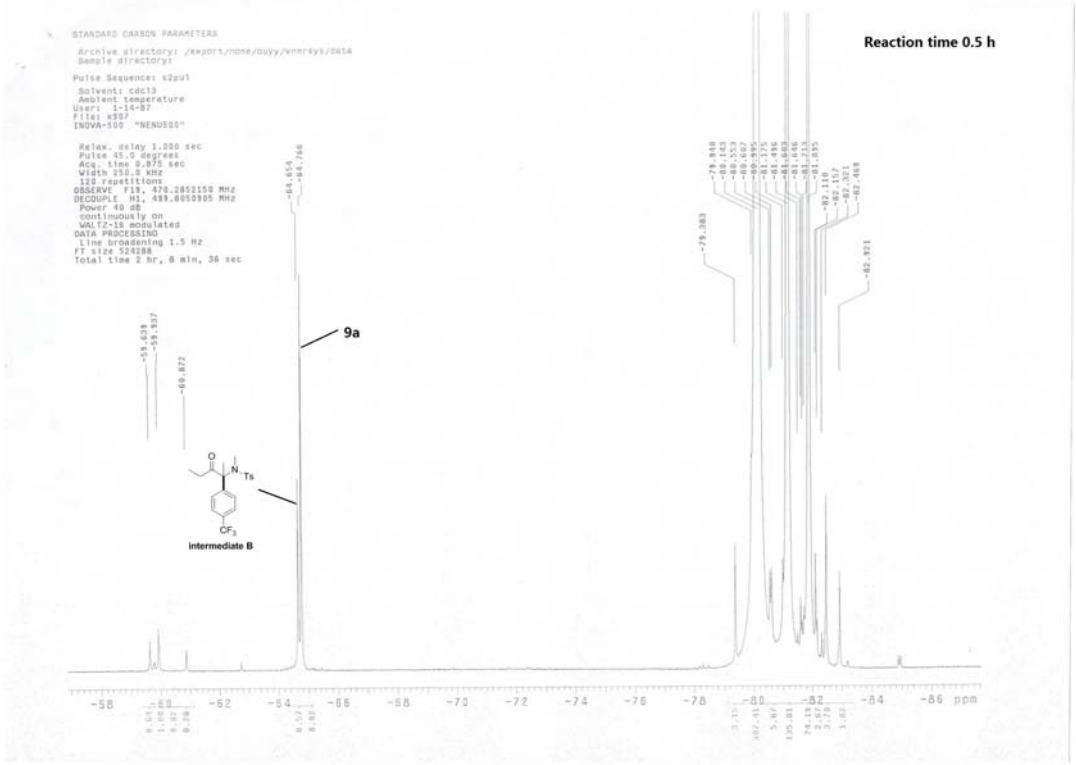
Colorless crystals, m.p. 89–90 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.17 (m, 3H), 2.45 (s, 3H), 2.76 (s, 3H), 4.03–4.12 (m, 2H), 5.92 (s, 1H), 7.33 (d, *J* = 7.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 7.0 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 13.9, 21.5, 30.9, 61.6, 61.9, 123.7 (CF_3, q, *J* = 270.3 Hz), 125.7 (q, *J* = 3.8 Hz), 127.3, 128.9, 129.6, 130.8 (q, *J* = 32.3 Hz), 135.9, 137.9, 143.7, 168.9. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -64.7. **HRMS** (ESI-TOF) Calcd for $C_{19}H_{20}F_3NNaO_4S$ $(M+Na)^+$ 438.0957. Found 438.0955.

III. Mechanism Study



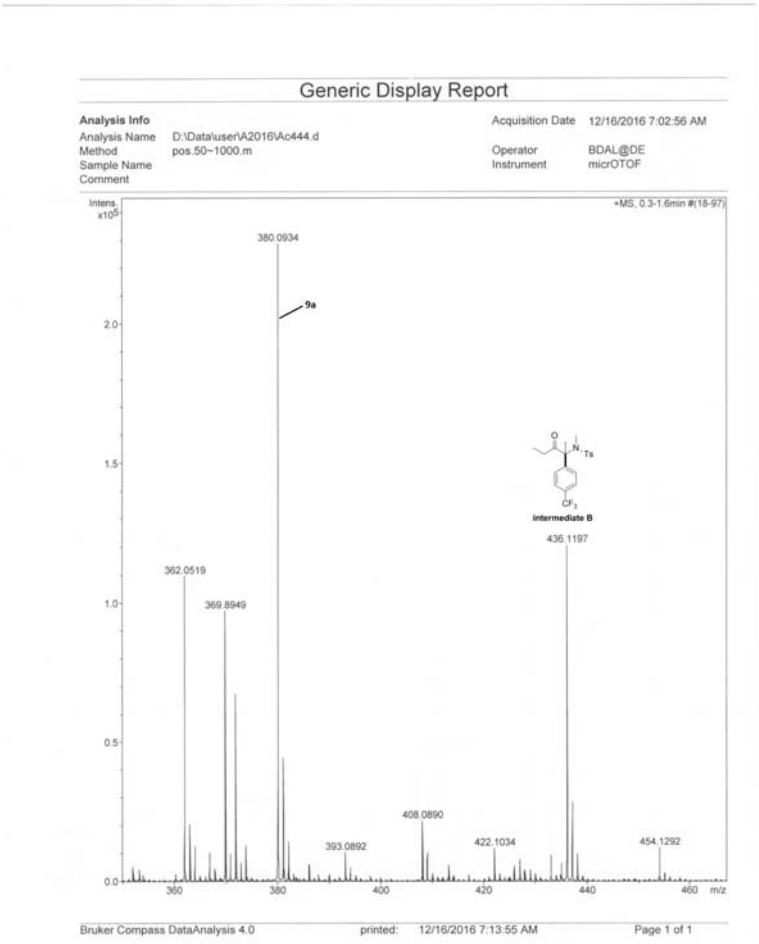
intermediate B

(a) ^{19}F NMR monitoring reaction of **5a**, **7a**, and **8a** (0.5 h)



(b) HRMS (ESI-TOF) spectrum of intermediate **B** in the reaction mixture.

HRMS (ESI-TOF) Calcd for $C_{20}H_{22}F_3NNaO_3S$ $(M+Na)^+$ 436.1165. Found 436.1197

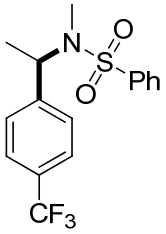


IV . Crystal Data and OPTEP Drawings

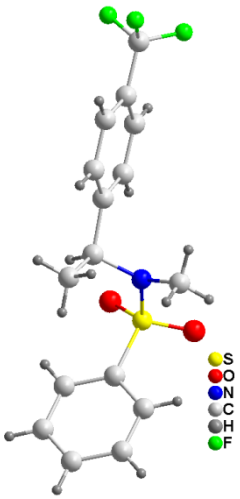
Single-crystal X-ray diffraction data was collected at room temperature on a Oxford Diffraction Gemini R Ultra diffractometer, the X-ray generator using Mo-Kα (λ = 0.71073 Å) radiation with a ω scan technique. The crystal structures were solved by direct method of SHELXS-97[3] and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined anisotropic. CCDC deposition number: 1479295 (**9j**). Data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

(1) Crystal data and OPTEP drawing of compound **9j**

ORTEP drawing:



9j



Crystal data:

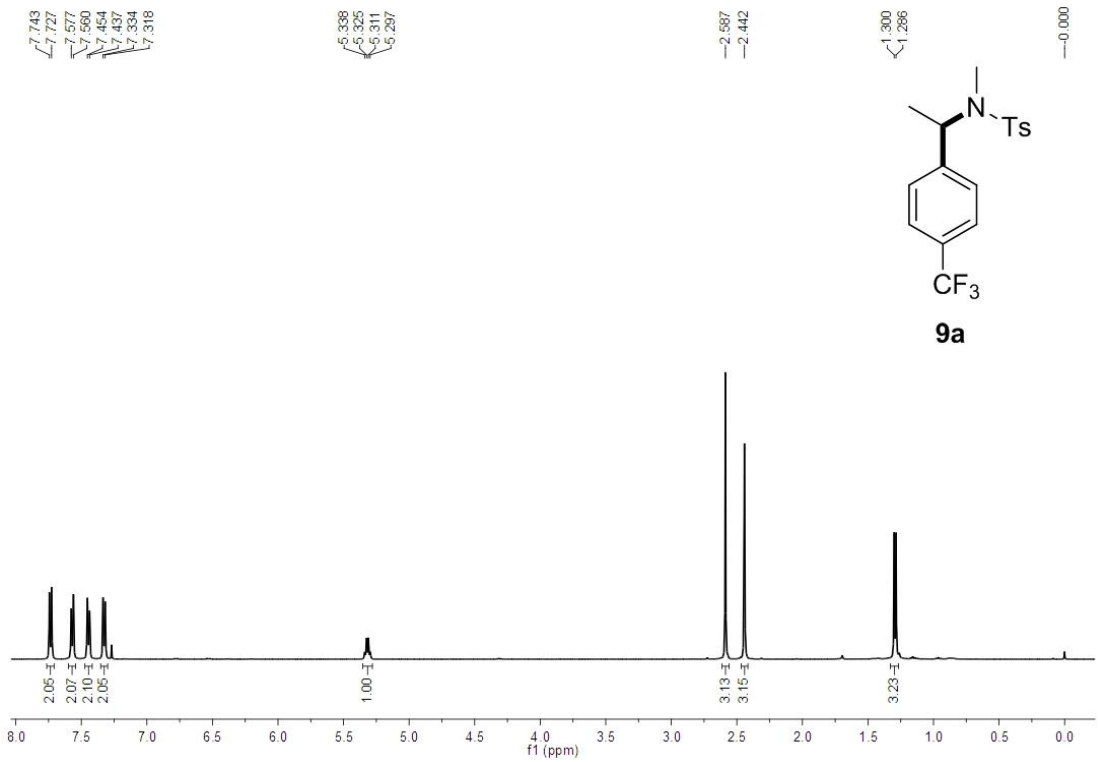
Empirical formula	$C_{16}H_{16}F_3NO_2S$
Formula weight	343.36
Crystal system	Monoclinic
Space group	P 1 21/n 1
a (Å)	8.5653(13)
b (Å)	10.5123(16)
c (Å)	17.819(3)
α (deg)	90
β (deg)	94.319(3)
γ (deg)	90
Volume (Å^3)	1599.9(4)
Z	4
Calculated density (mg/m^3)	1.425

3 G. M. Sheldrick, *SHELXS-97*, *Programs for X-ray Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1997.

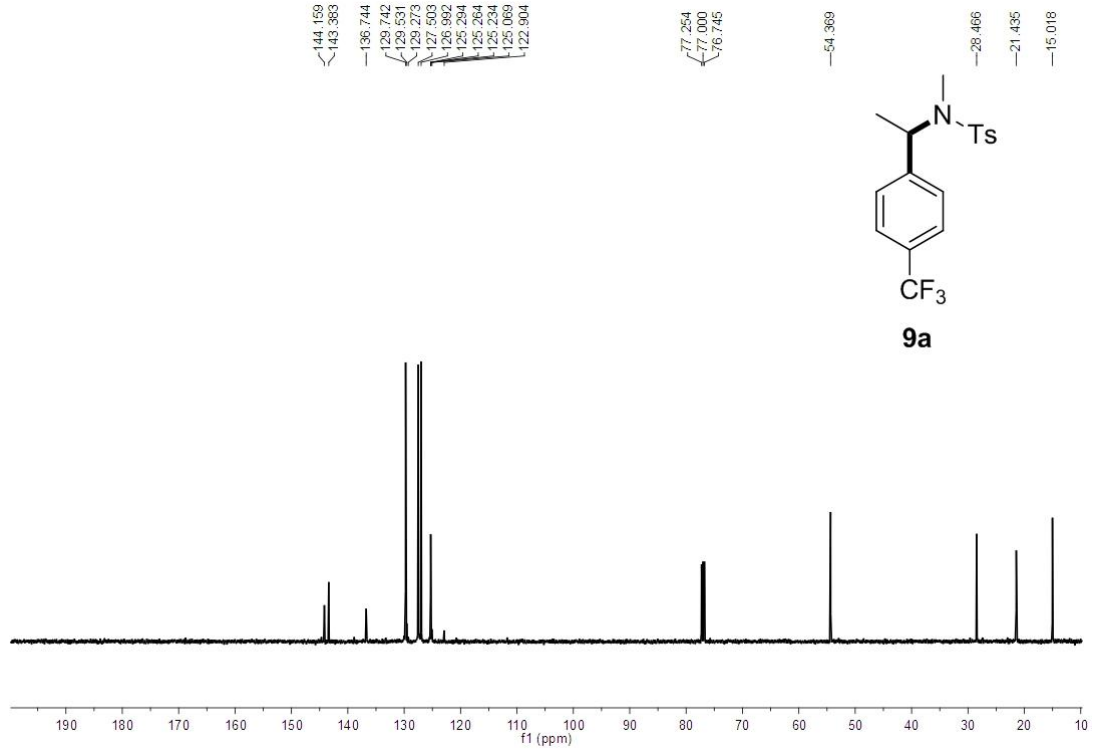
Absorption coefficient (mm^{-1})	0.241
F(000)	712
Theta range for data collection (deg)	0.995 to 26.037
Reflections collected/unique	9833/3136
Goodness-of-fit on F^2	1.007
Final R indices [$I > 2\sigma(I)$]	R1=0.063, WR2 =0.162
R indices (all data)	R1=0.064, WR2 =0.180

V. Copies of ^{1}H NMR , ^{13}C NMR and ^{19}F NMR Spectra

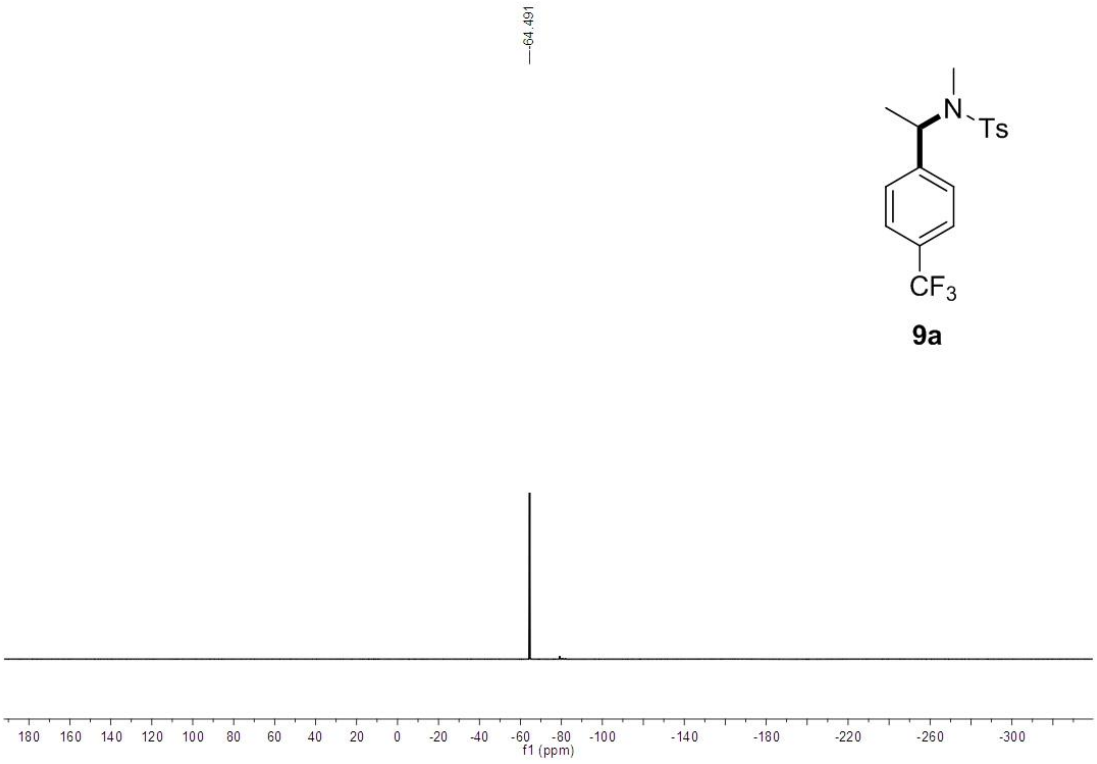
^{1}H NMR (500 MHz, $CDCl_3$) for **9a**



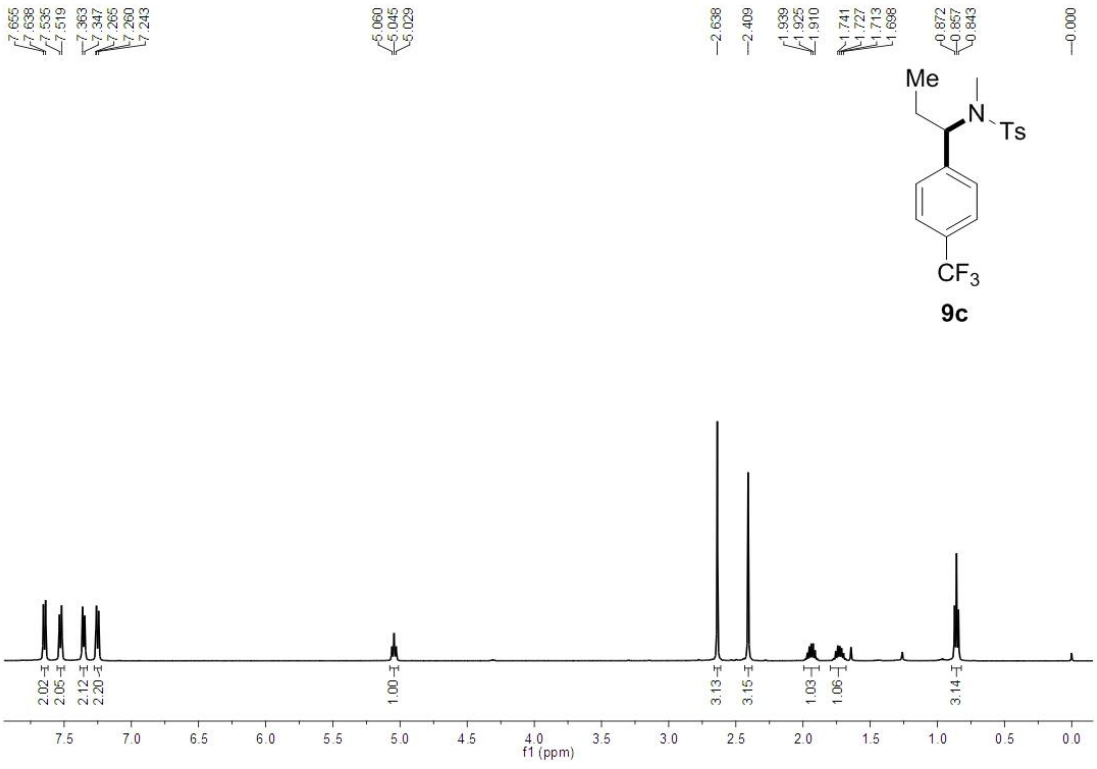
^{13}C NMR (125 MHz, $CDCl_3$) for **9a**



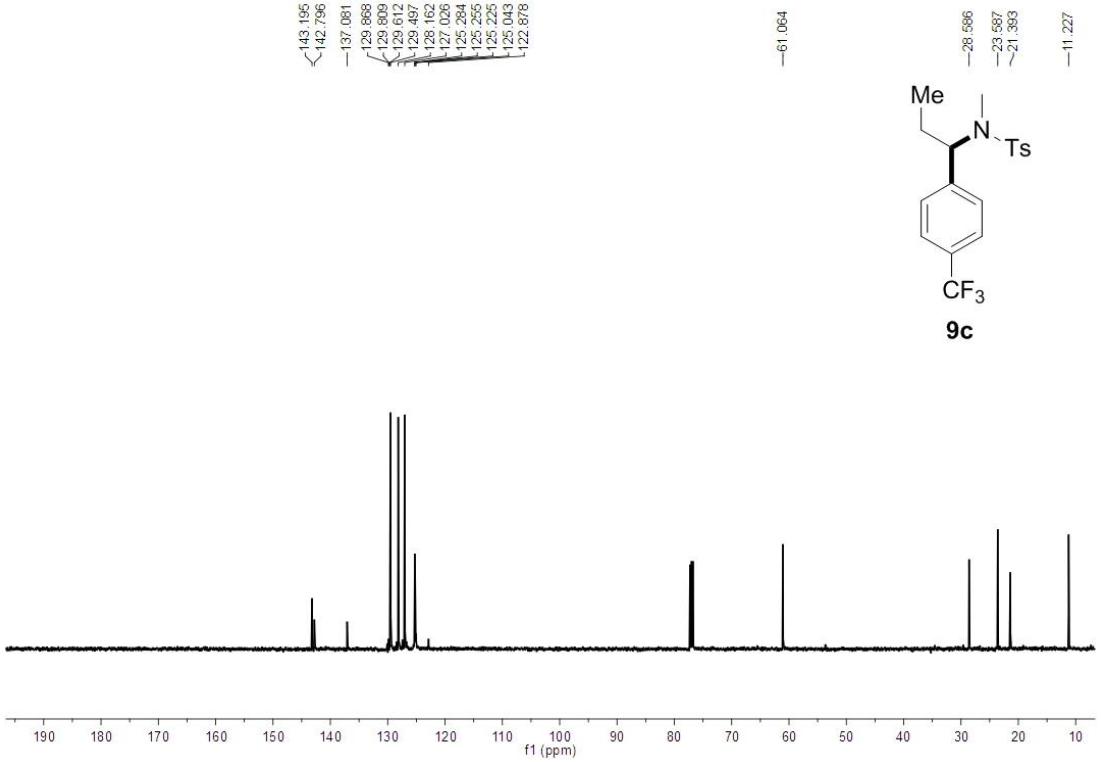
^{19}F NMR (470 MHz, $CDCl_3$) for **9a**



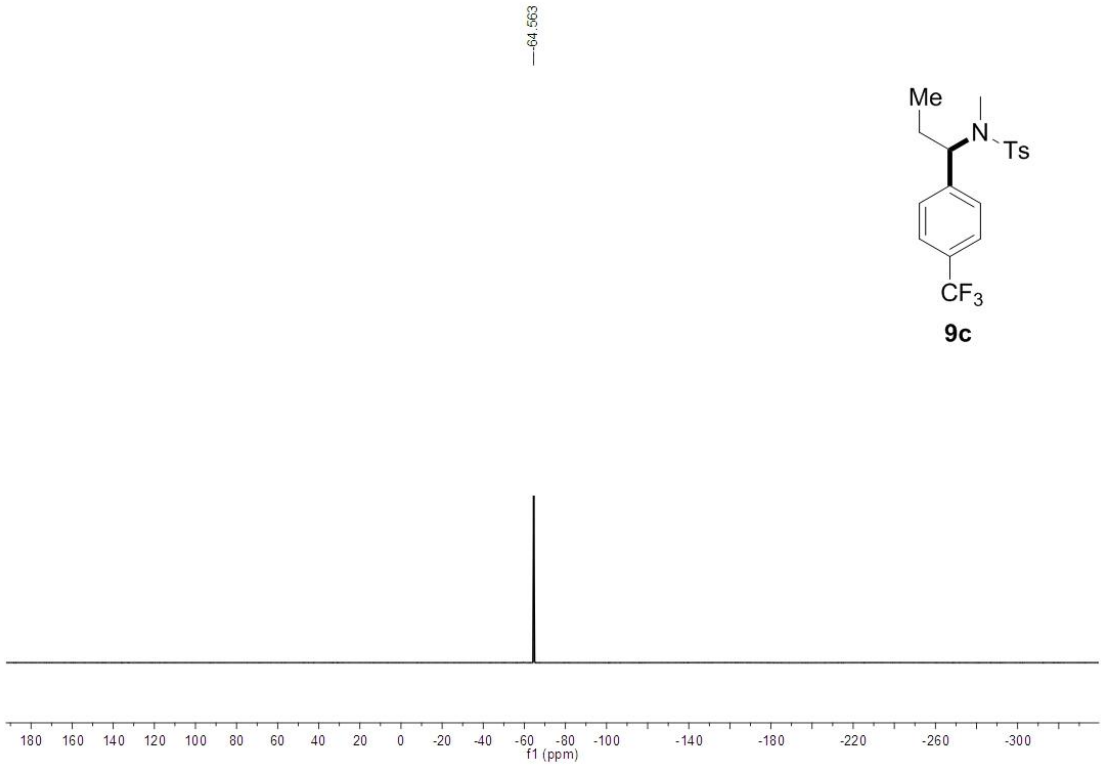
^{1}H NMR (500 MHz, $CDCl_3$) for **9c**



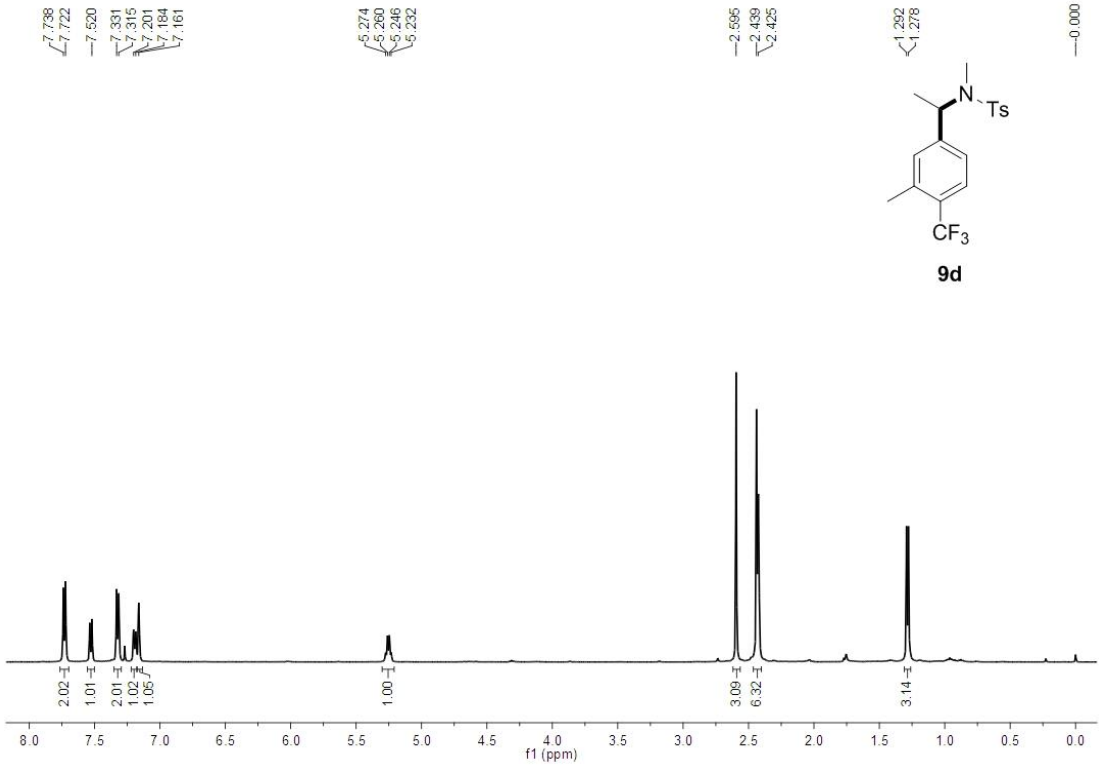
^{13}C NMR (125 MHz, $CDCl_3$) for **9c**



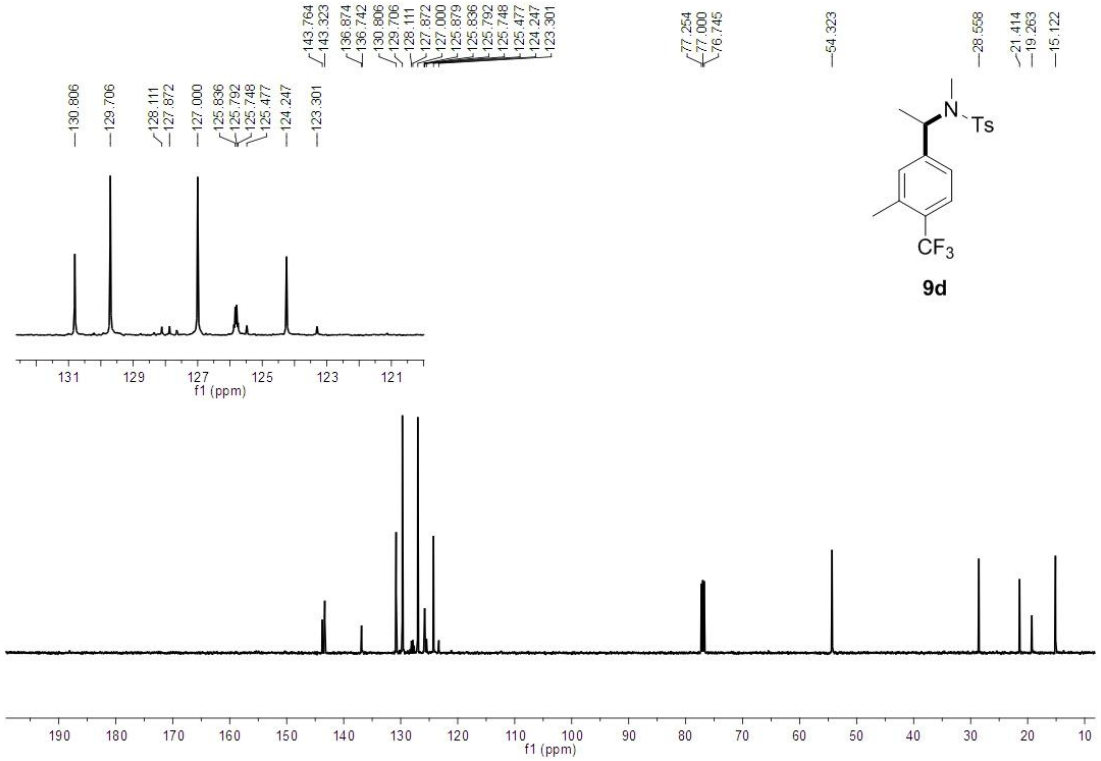
^{19}F NMR (470 MHz, $CDCl_3$) for **9c**



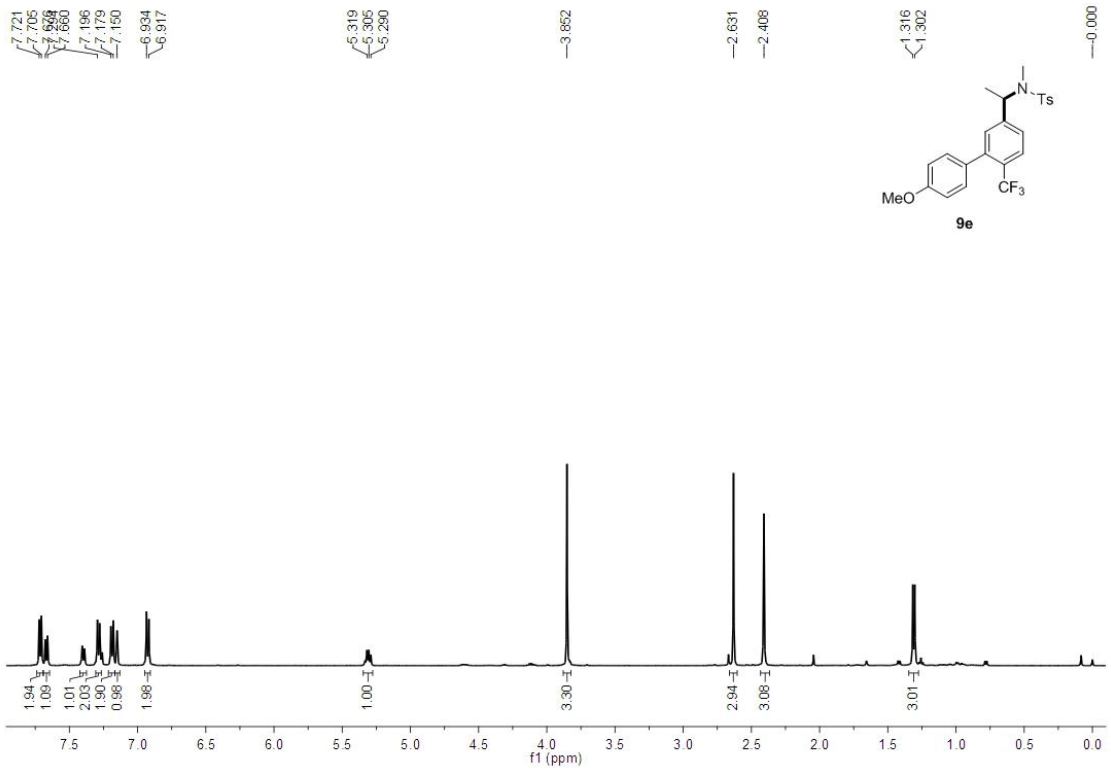
^{1}H NMR (500 MHz, $CDCl_3$) for **9d**



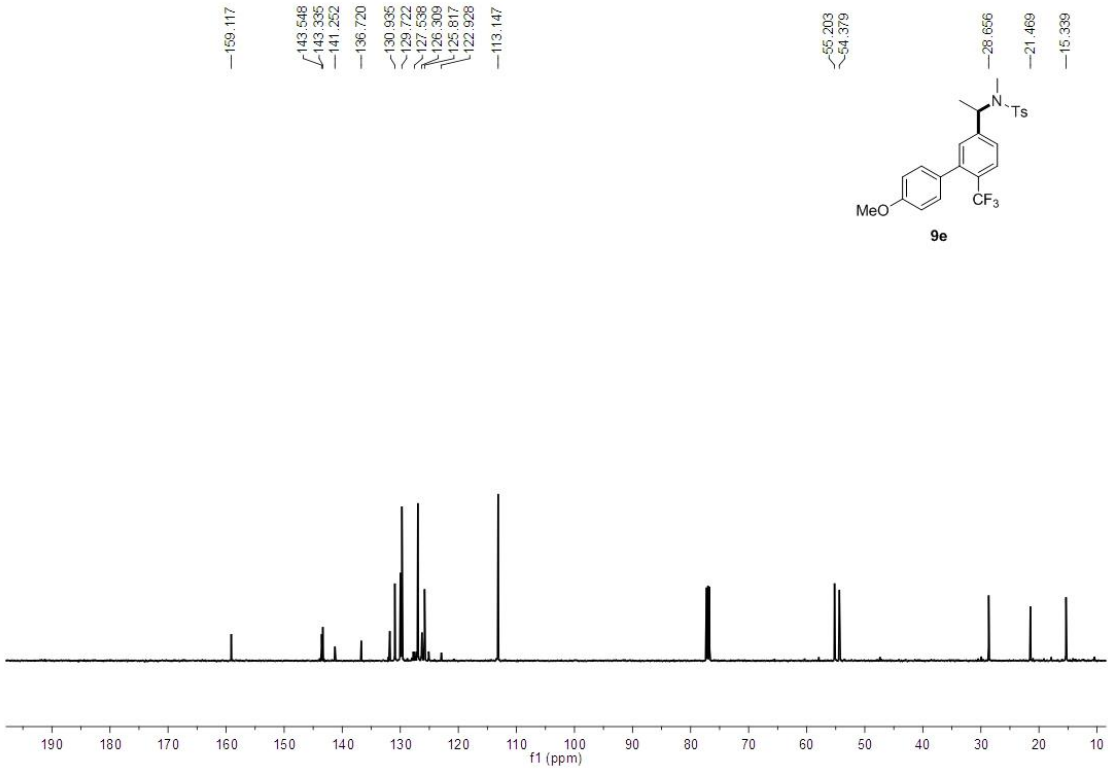
^{13}C NMR (125 MHz, $CDCl_3$) for **9d**



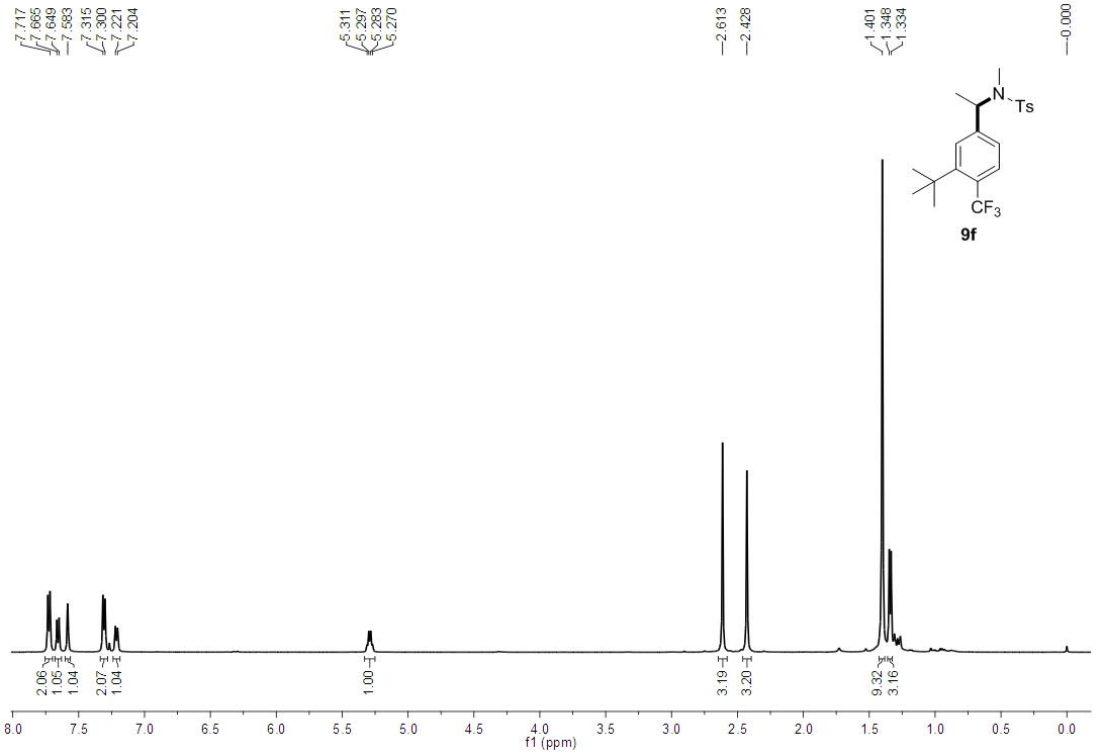
^{1}H NMR (500 MHz, $CDCl_3$) for **9e**



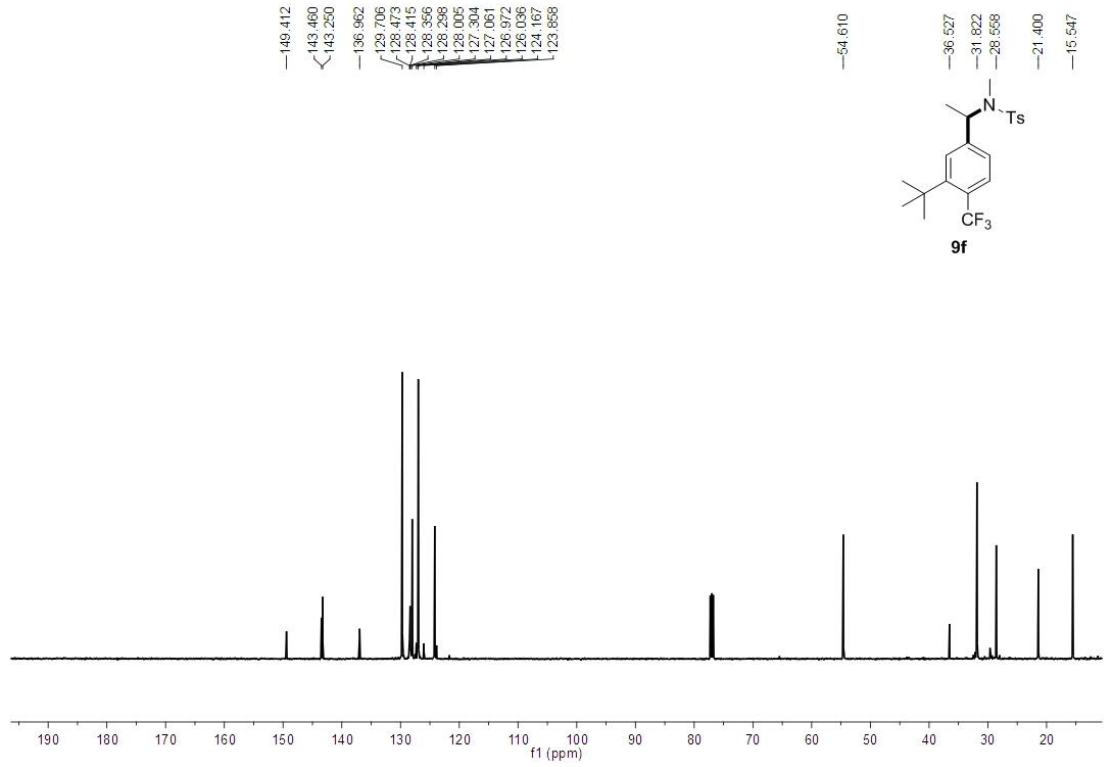
^{13}C NMR (125 MHz, $CDCl_3$) for **9e**



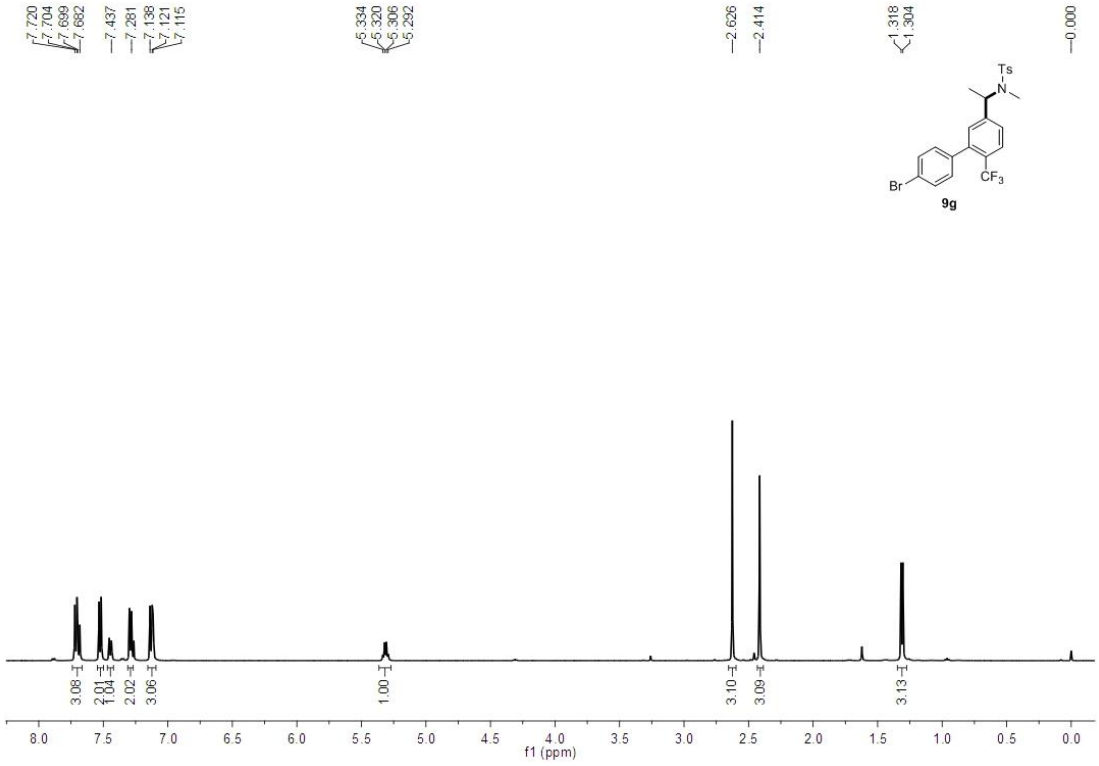
^{1}H NMR (500 MHz, $CDCl_3$) for **9f**



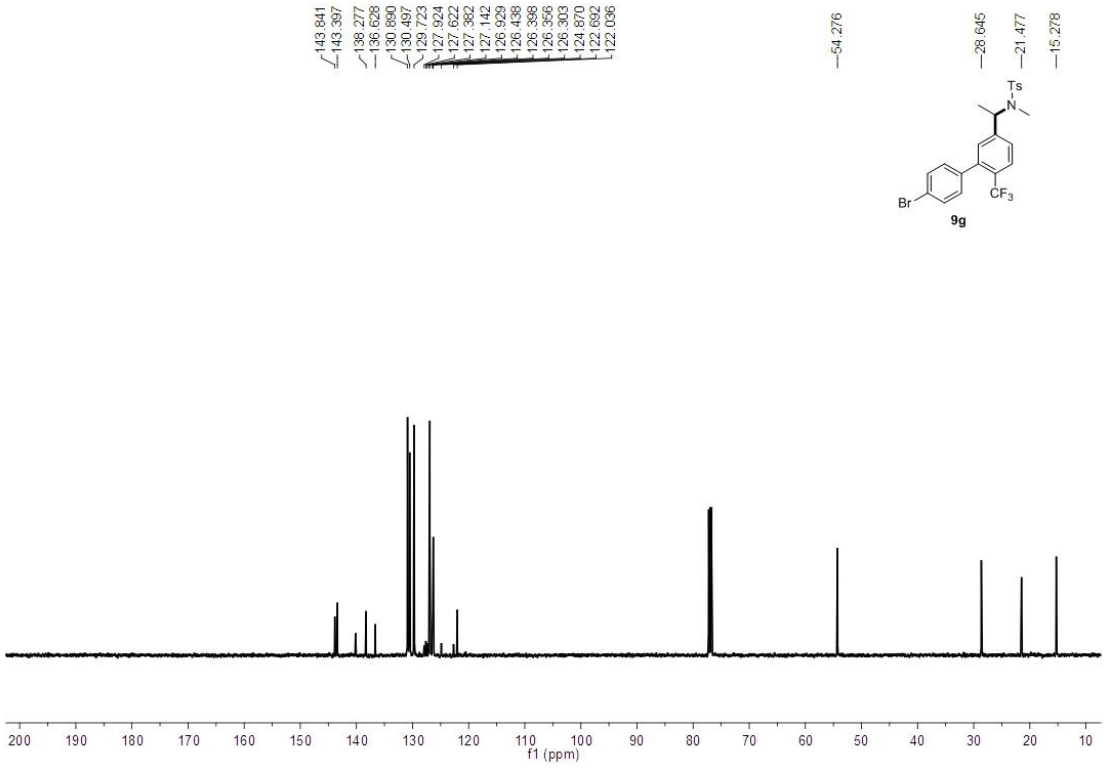
^{13}C NMR (125 MHz, $CDCl_3$) for **9f**



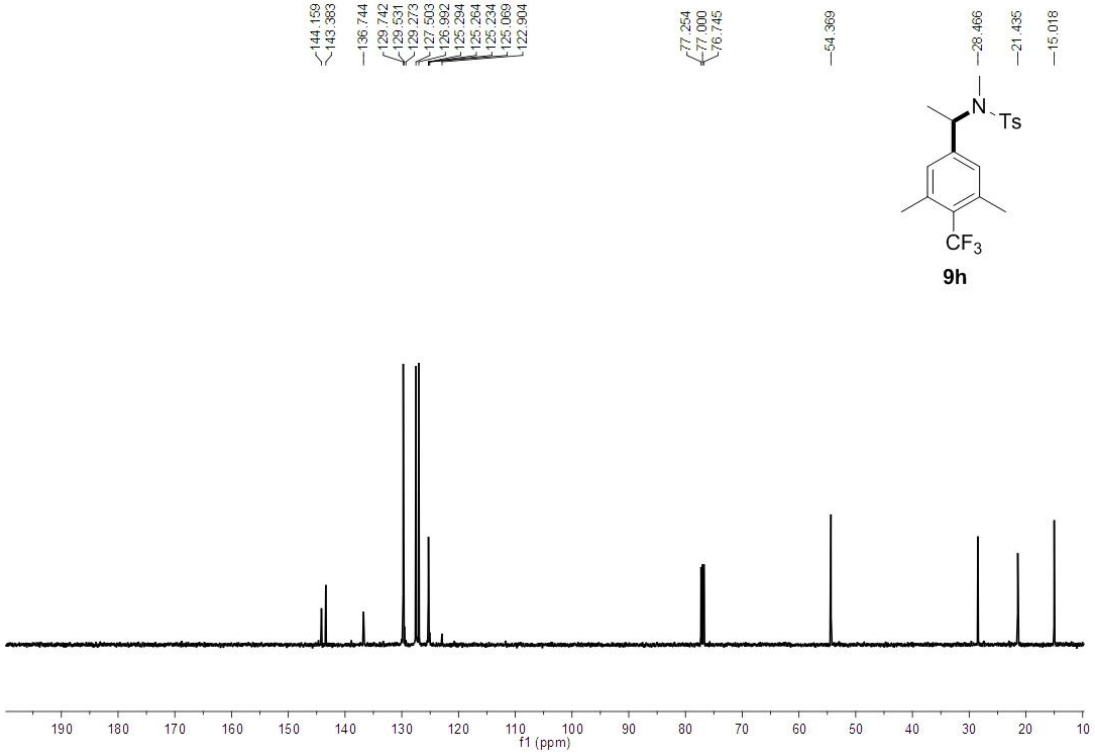
^{1}H NMR (500 MHz, $CDCl_3$) for **9g**



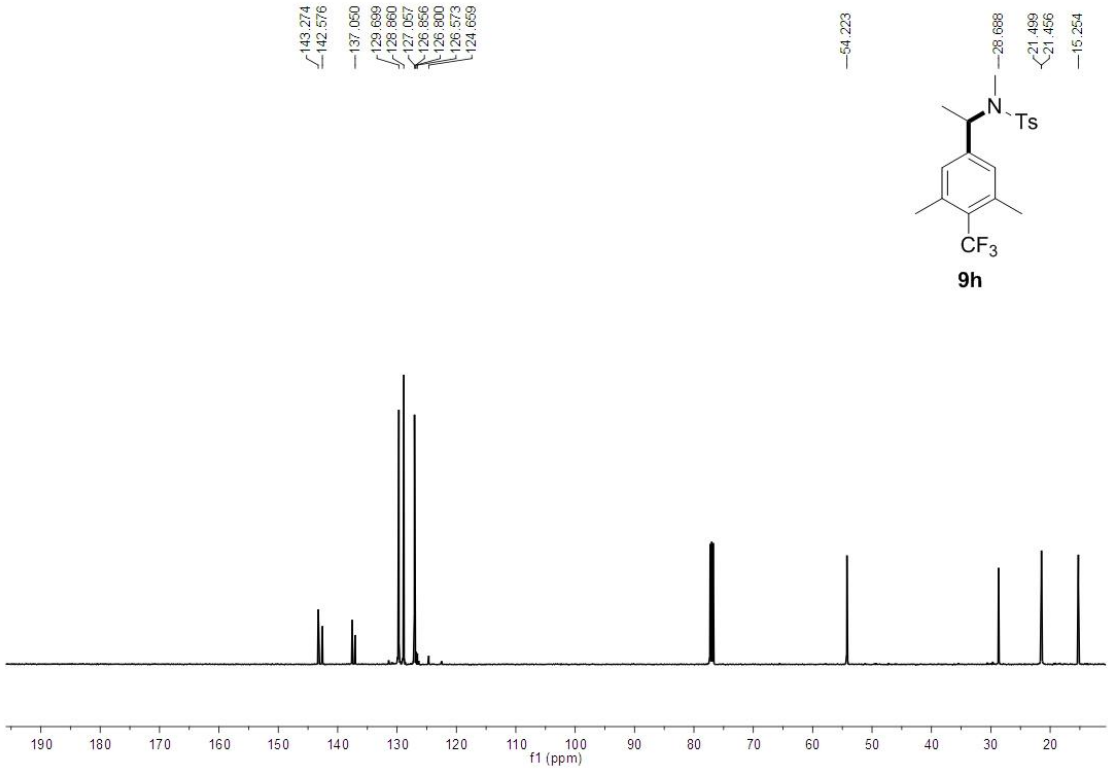
^{13}C NMR (125 MHz, $CDCl_3$) for **9g**



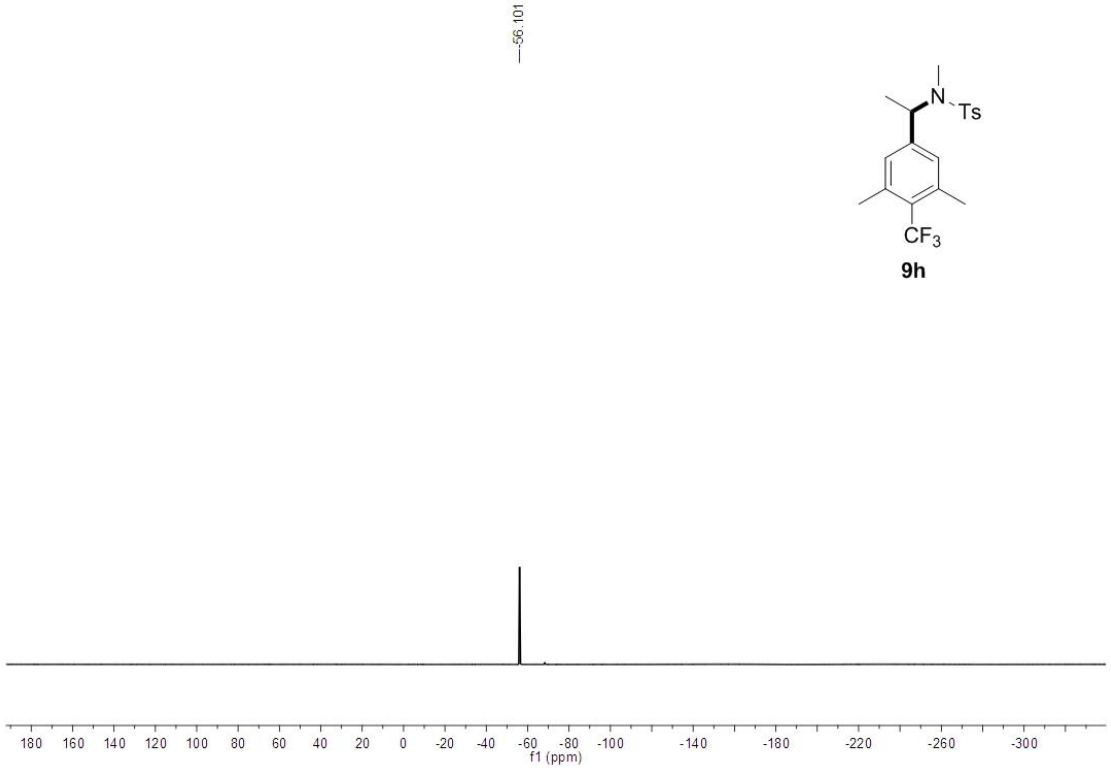
^{1}H NMR (500 MHz, $CDCl_3$) for **9h**



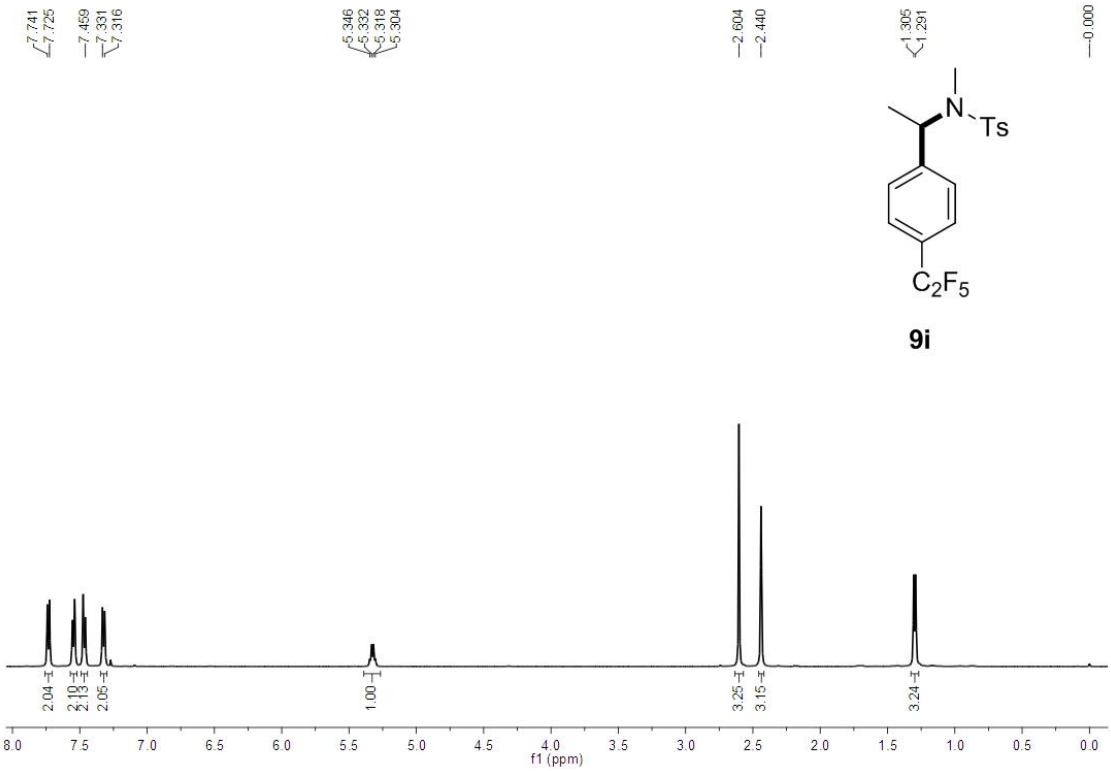
^{13}C NMR (125 MHz, $CDCl_3$) for **9h**



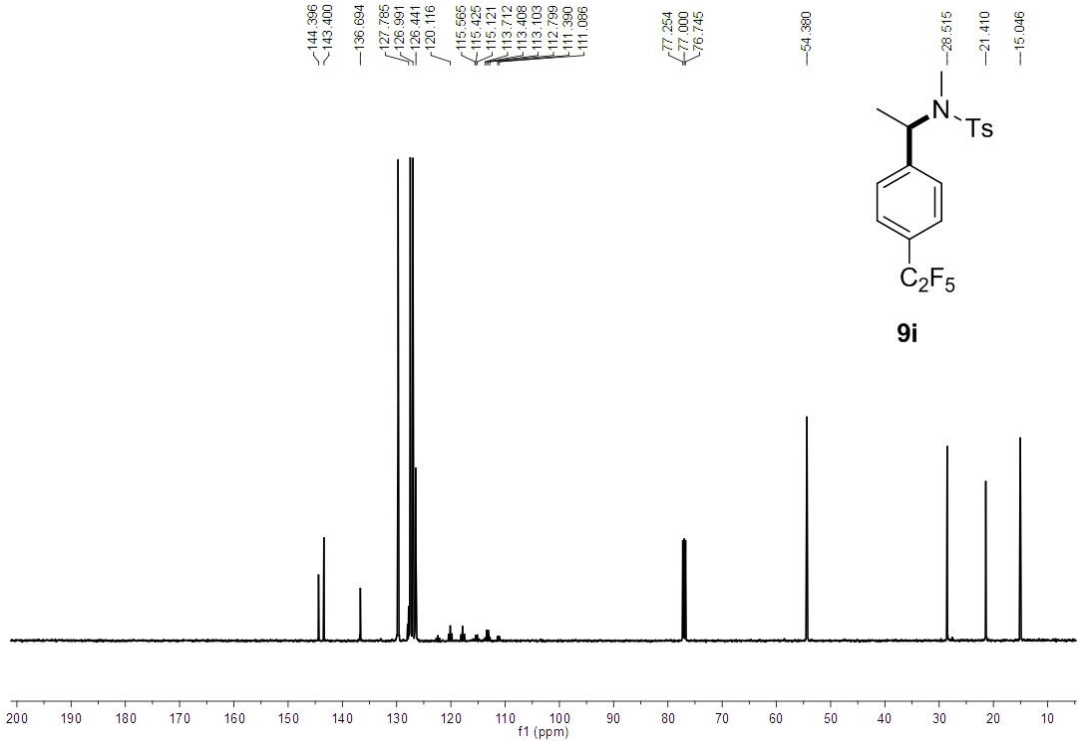
^{19}F NMR (470 MHz, $CDCl_3$) for **9h**



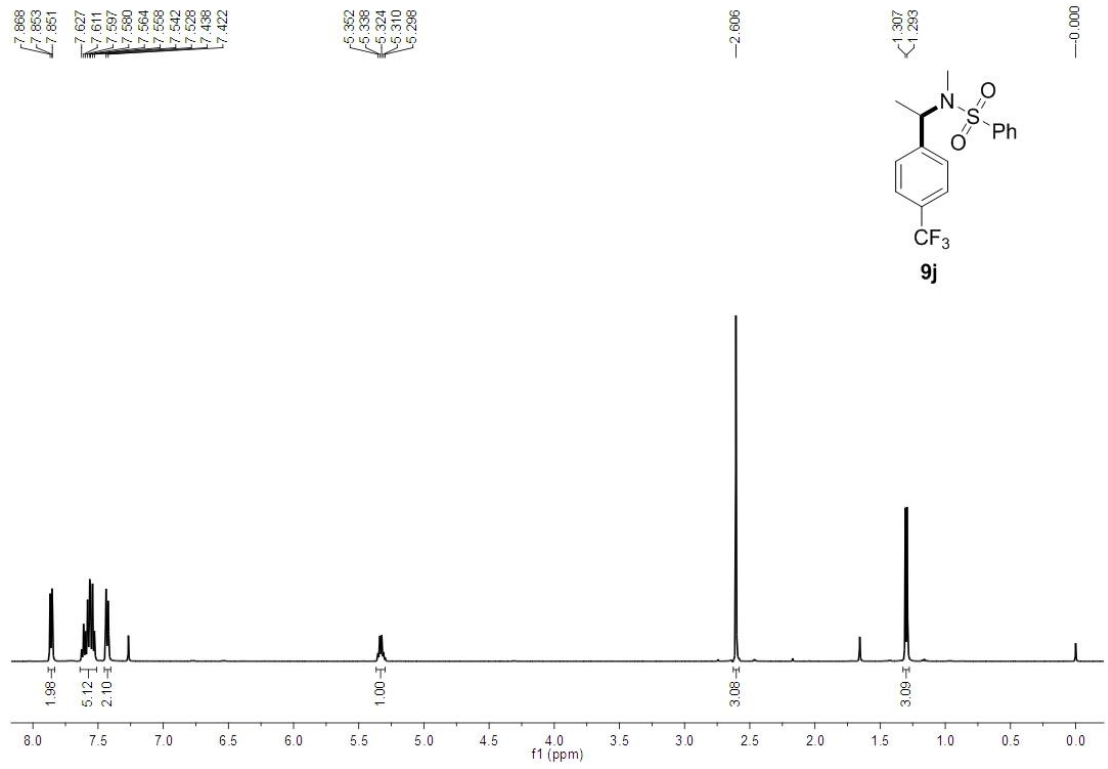
^{1}H NMR (500 MHz, $CDCl_3$) for **9i**



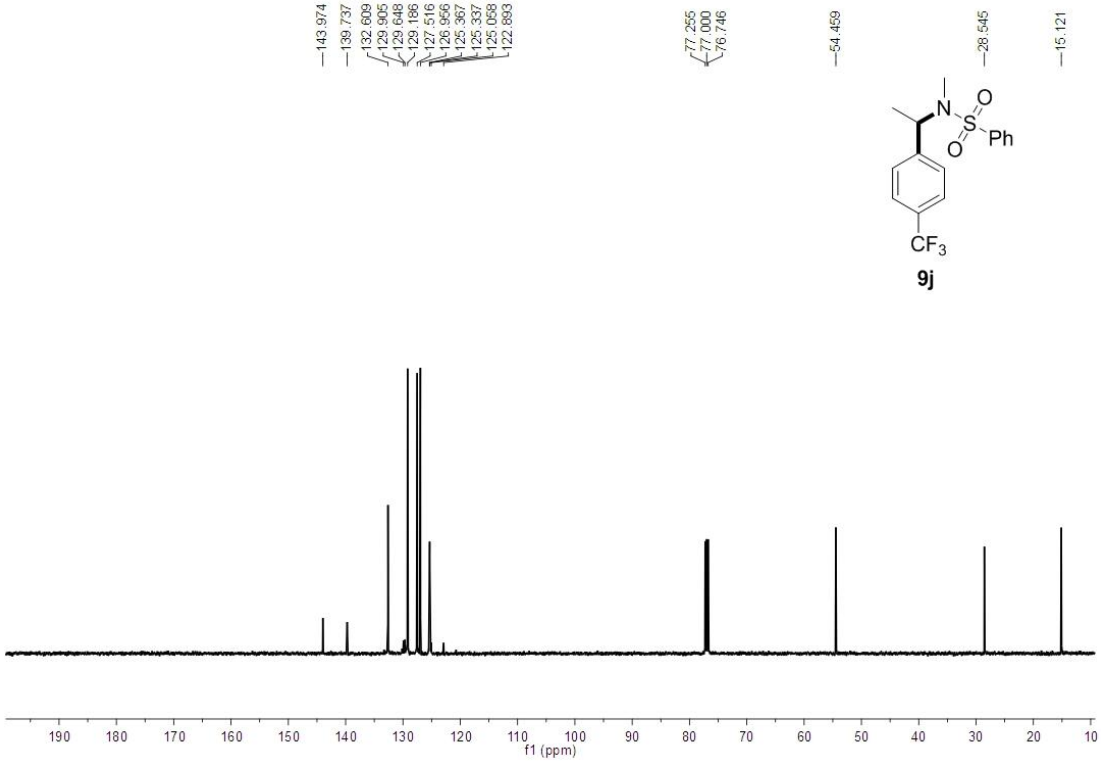
^{13}C NMR (125 MHz, $CDCl_3$) for **9i**



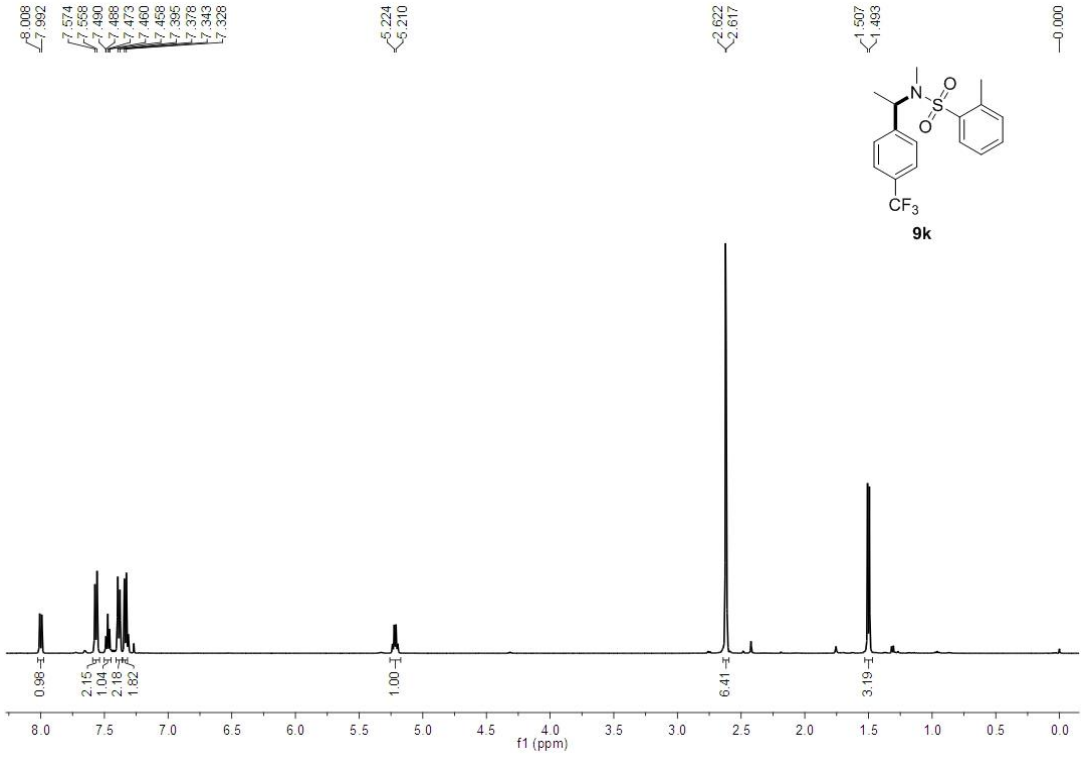
^{1}H NMR (500 MHz, $CDCl_3$) for **9j**



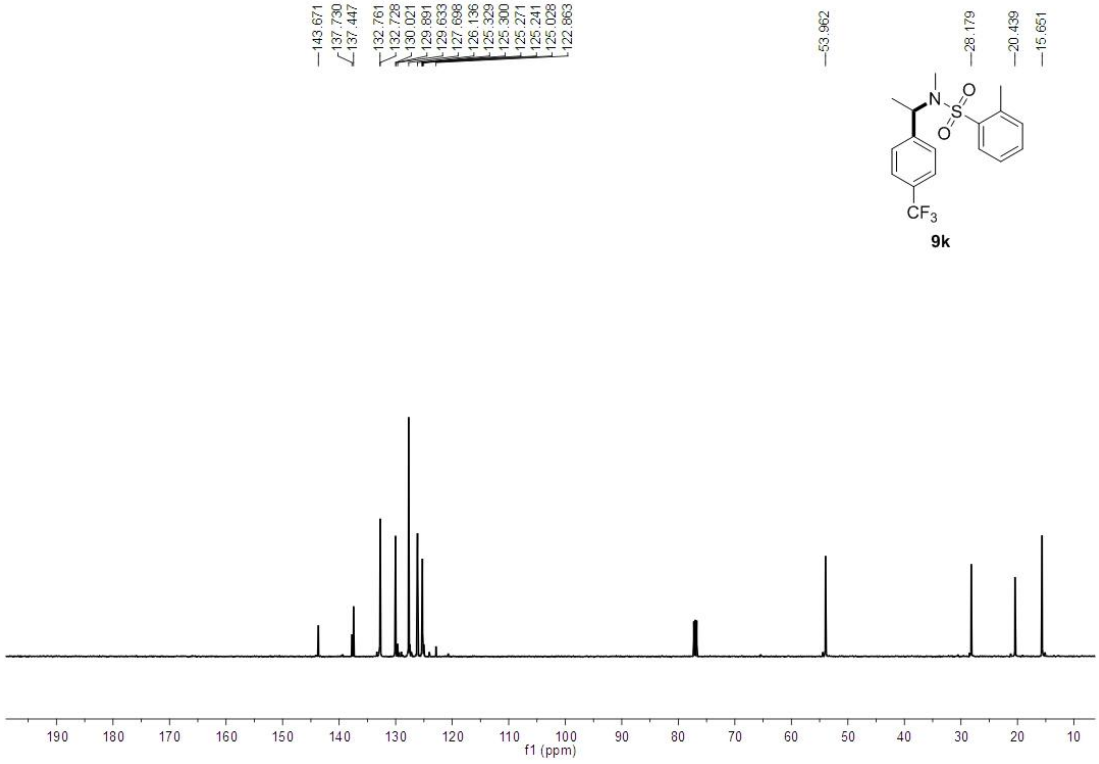
^{13}C NMR (125 MHz, $CDCl_3$) for **9j**



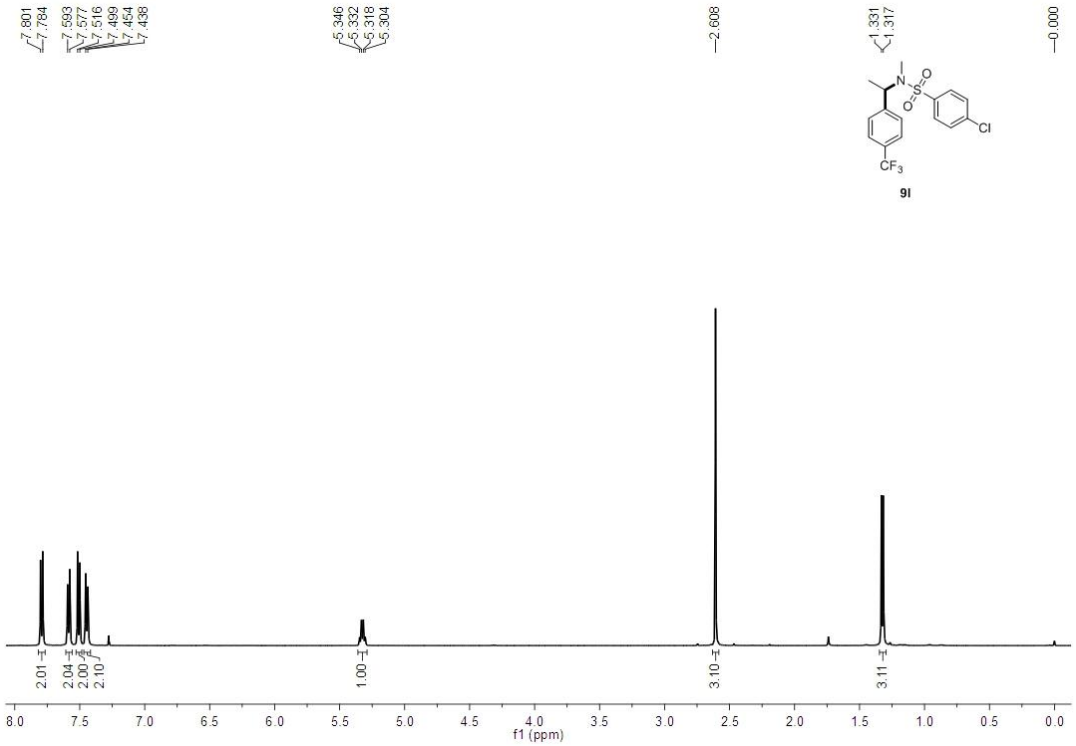
^{1}H NMR (500 MHz, $CDCl_3$) for **9k**



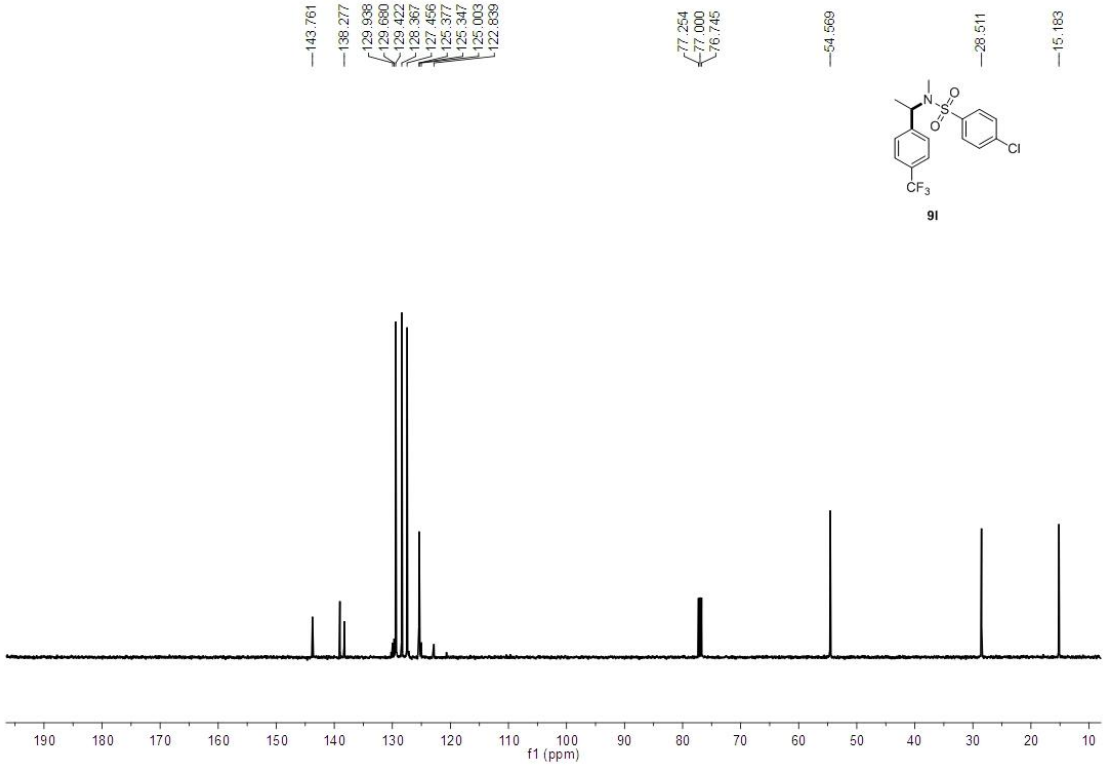
^{13}C NMR (125 MHz, $CDCl_3$) for **9k**



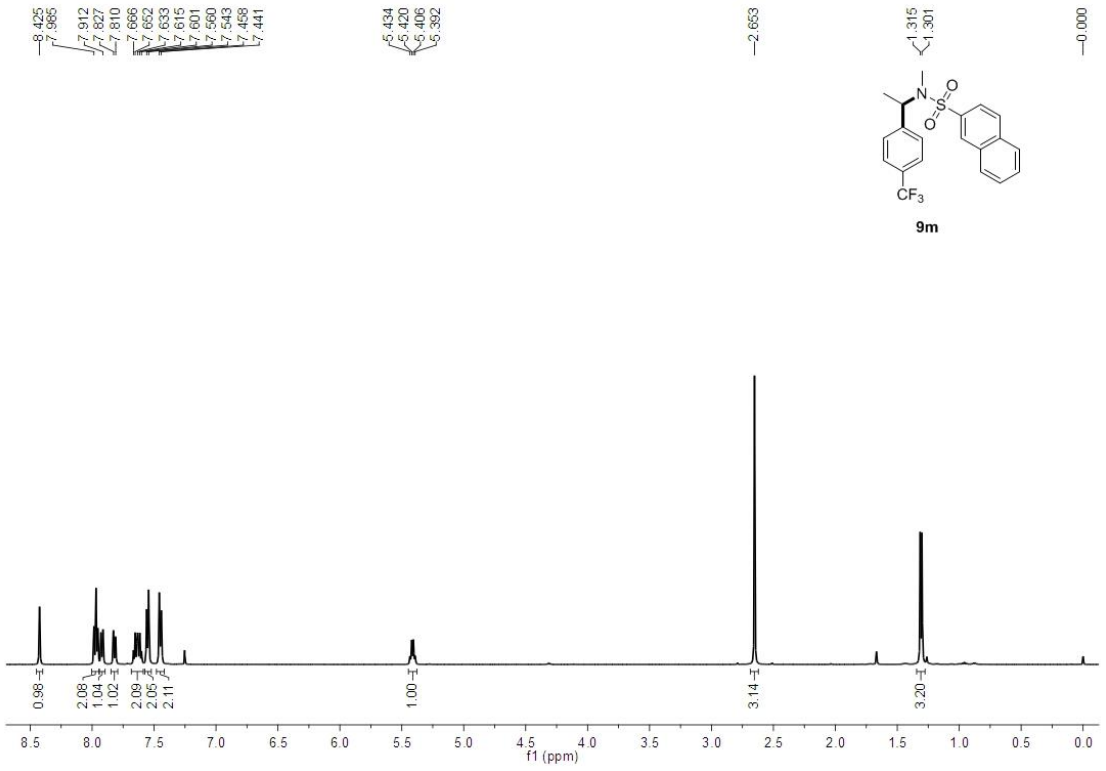
^{1}H NMR (500 MHz, $CDCl_3$) for **9l**



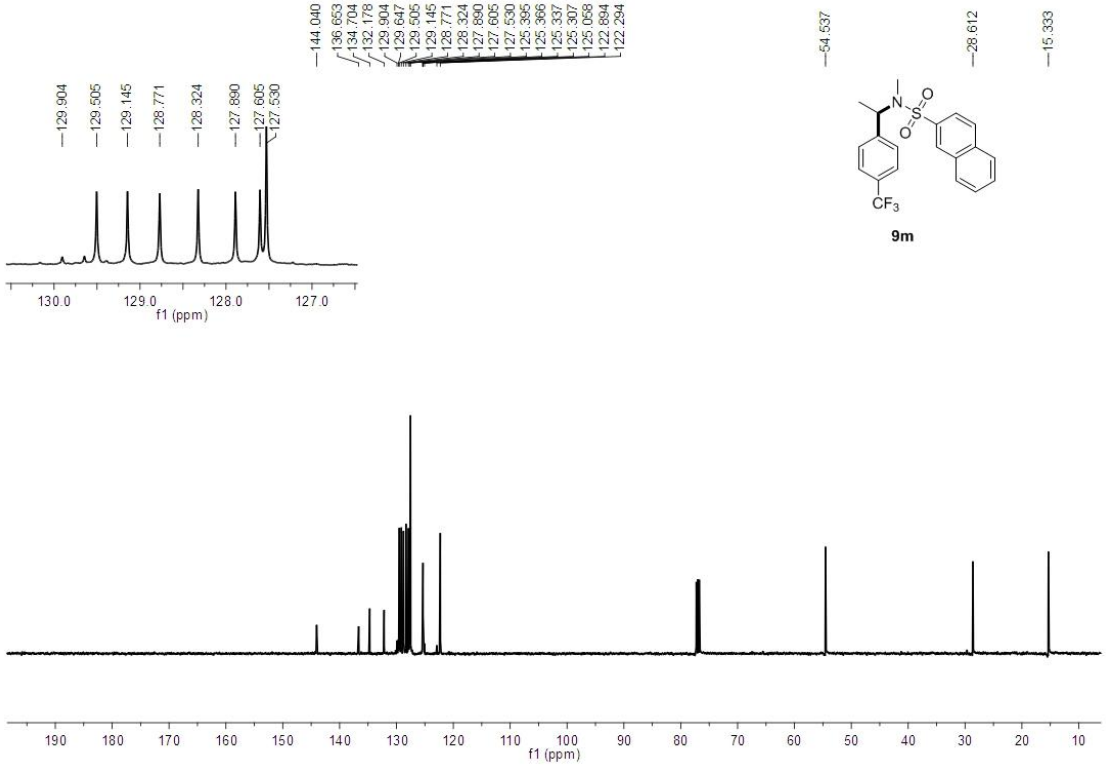
^{13}C NMR (125 MHz, $CDCl_3$) for **9l**



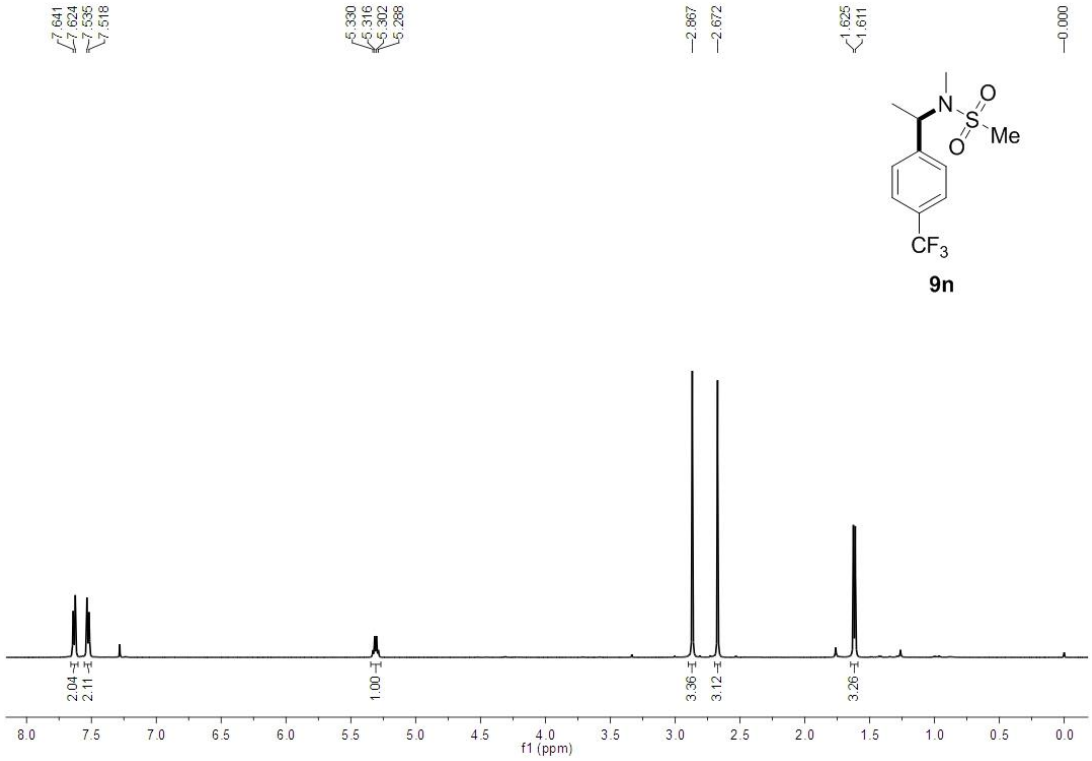
^{1}H NMR (500 MHz, $CDCl_3$) for **9m**



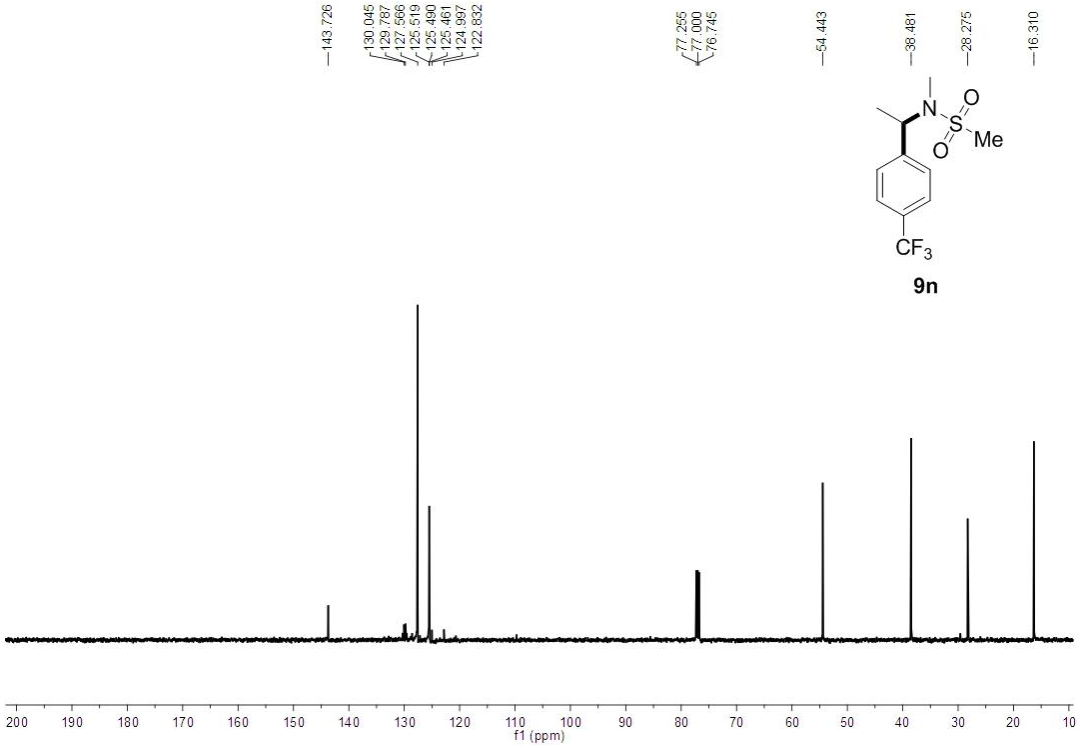
^{13}C NMR (125 MHz, $CDCl_3$) for **9m**



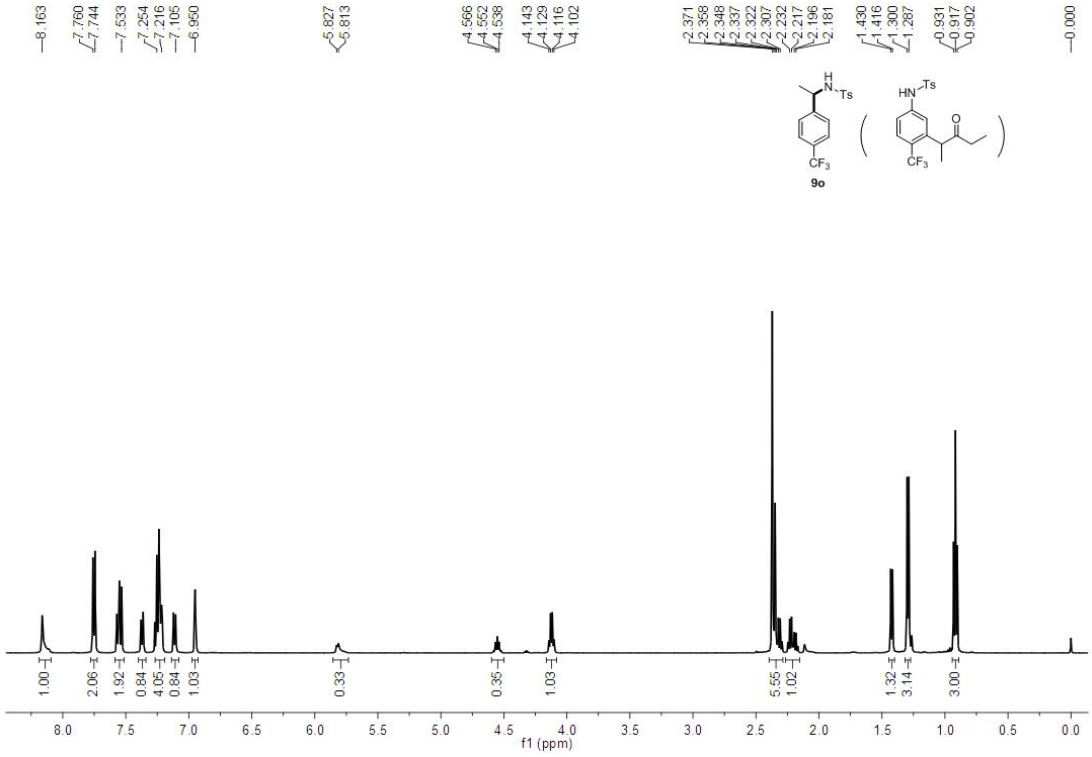
^{1}H NMR (500 MHz, $CDCl_3$) for **9n**



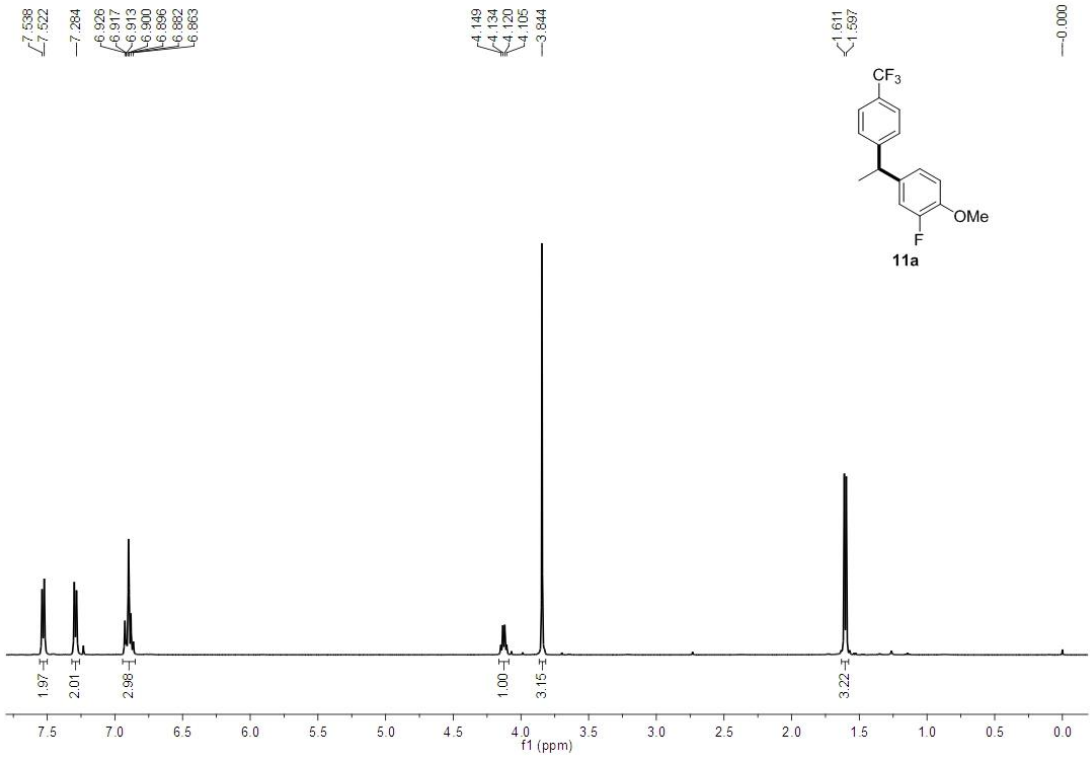
^{13}C NMR (125 MHz, $CDCl_3$) for **9n**



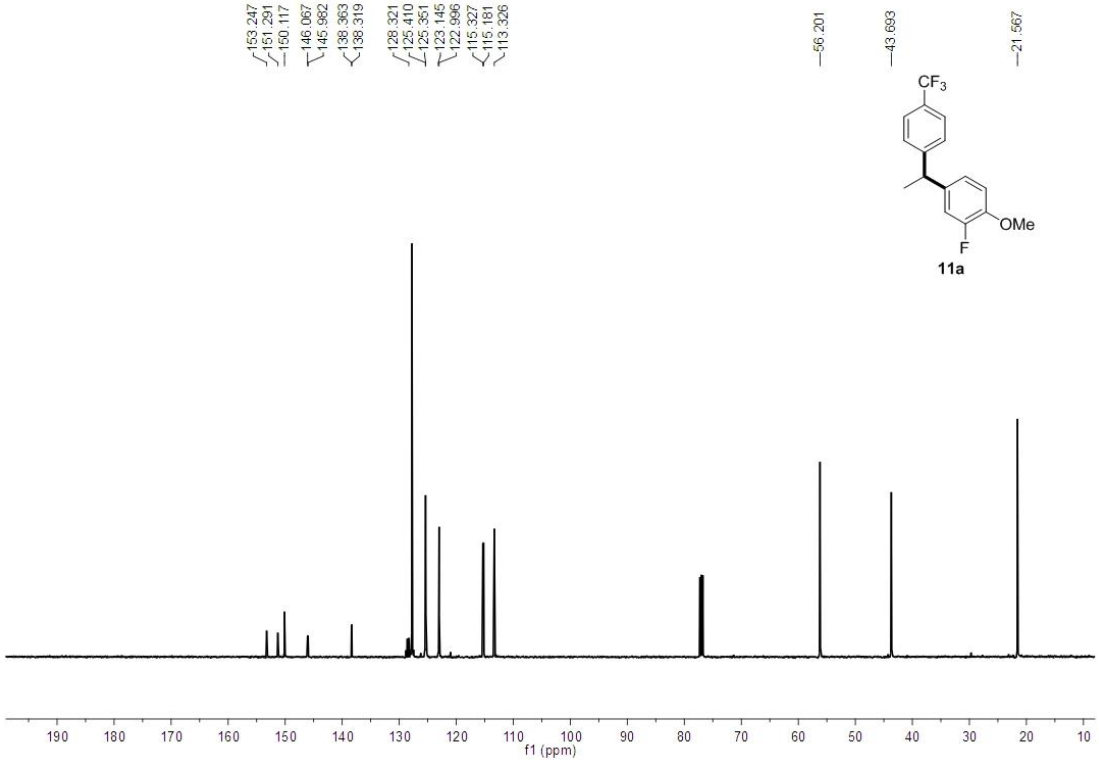
^{1}H NMR (500 MHz, $CDCl_3$) for **9o**



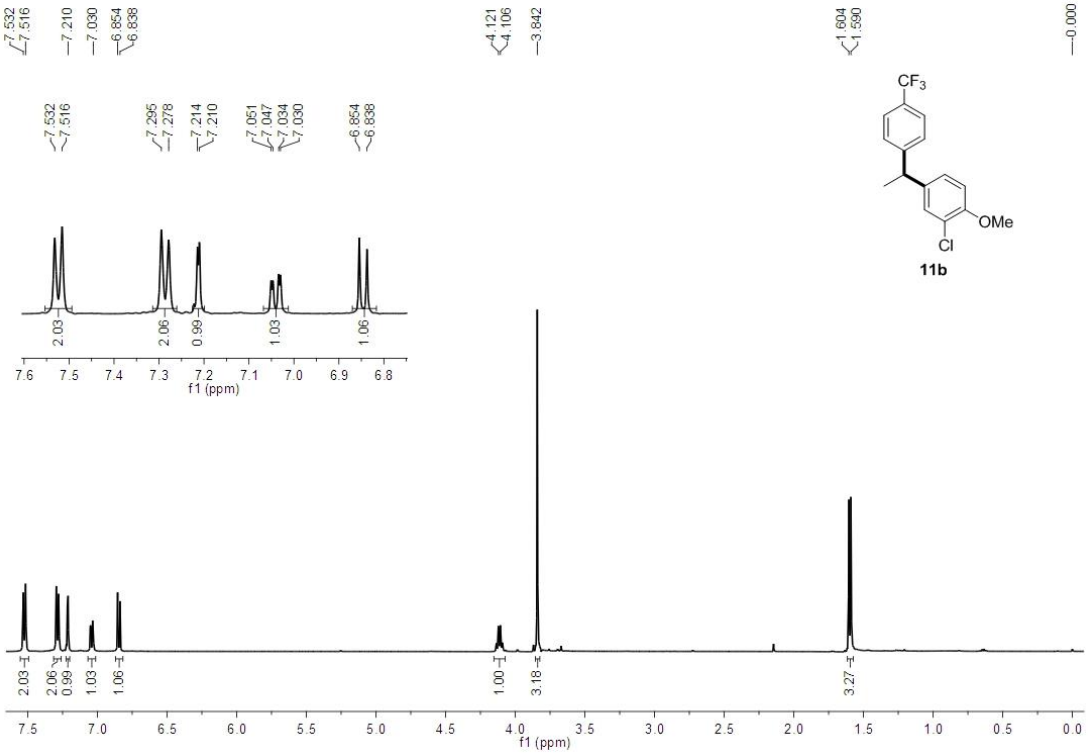
^{1}H NMR (500 MHz, $CDCl_3$) for **11a**



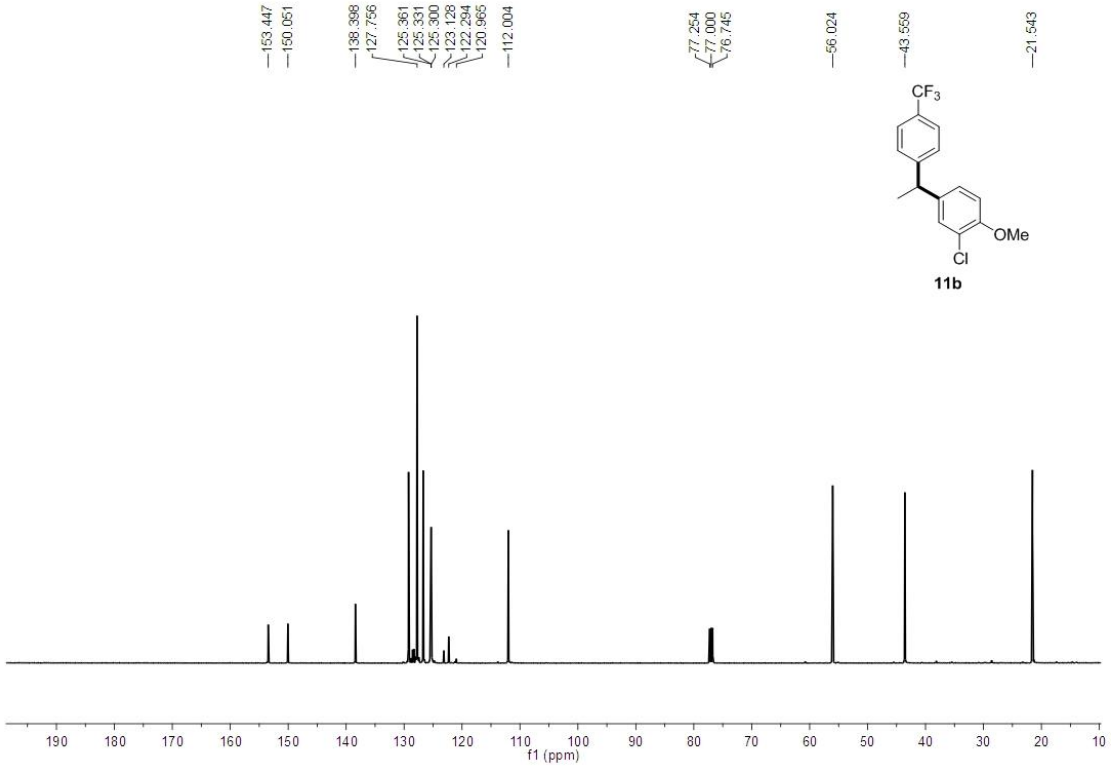
^{13}C NMR (125 MHz, $CDCl_3$) for **11a**



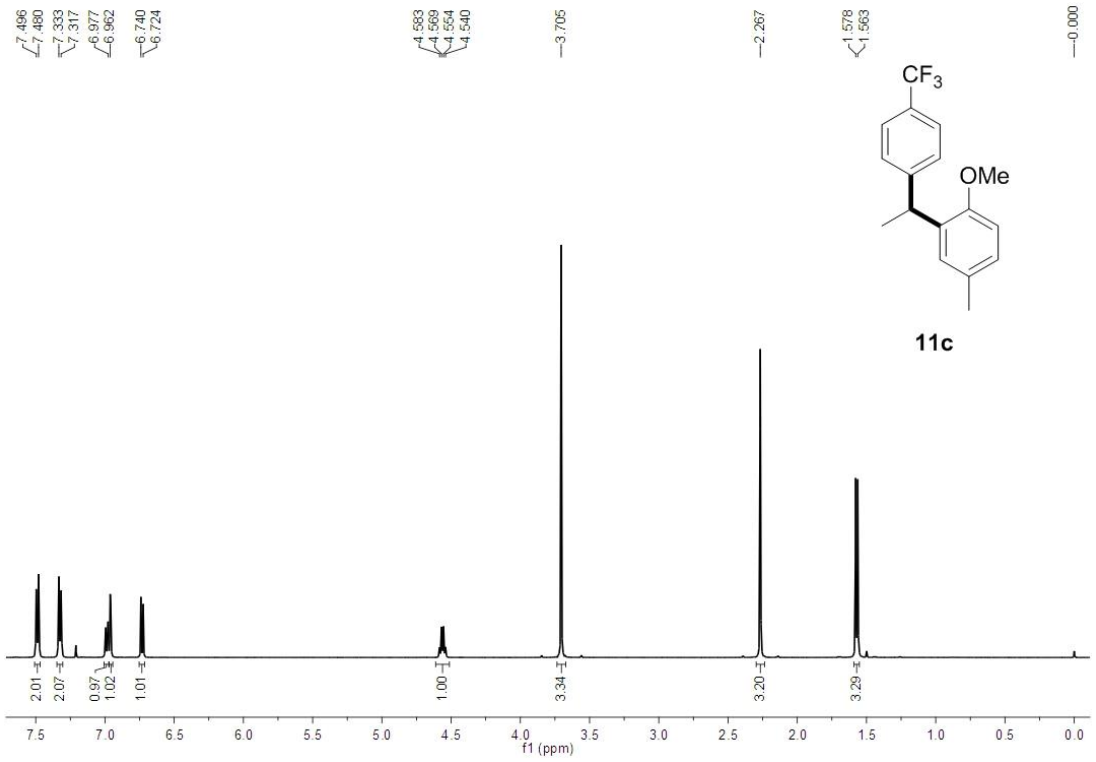
^{1}H NMR (500 MHz, $CDCl_3$) for **11b**



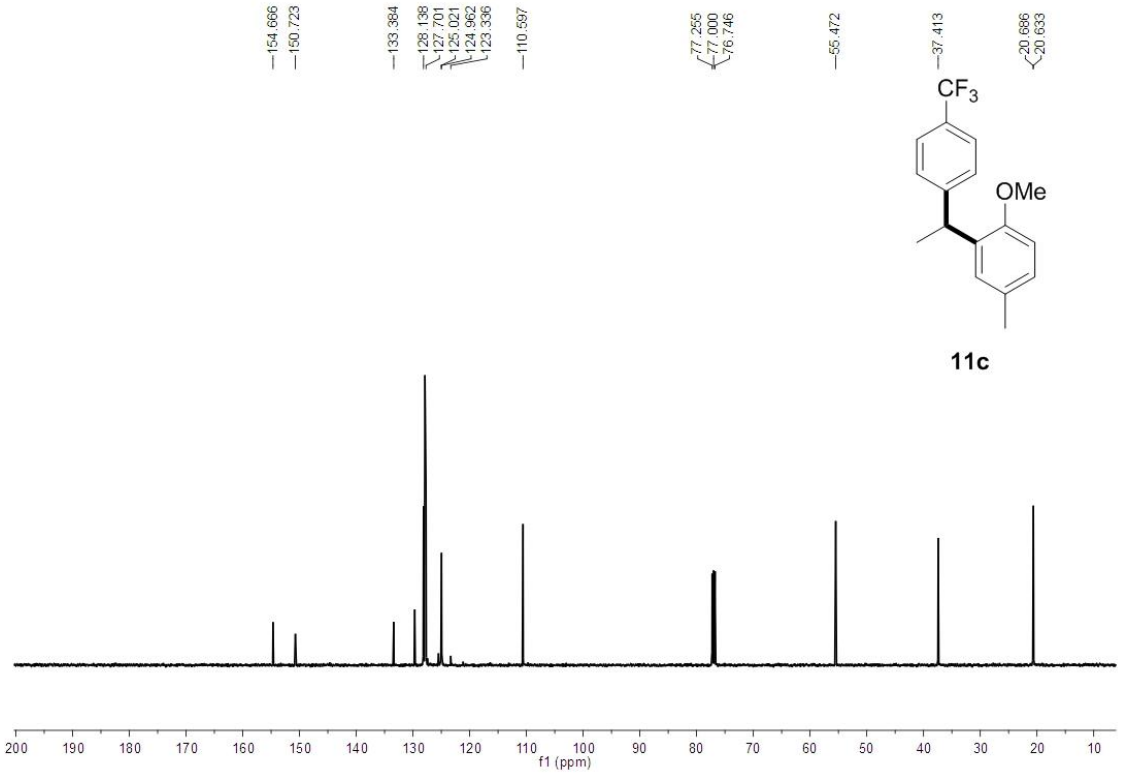
^{13}C NMR (125 MHz, $CDCl_3$) for **11b**



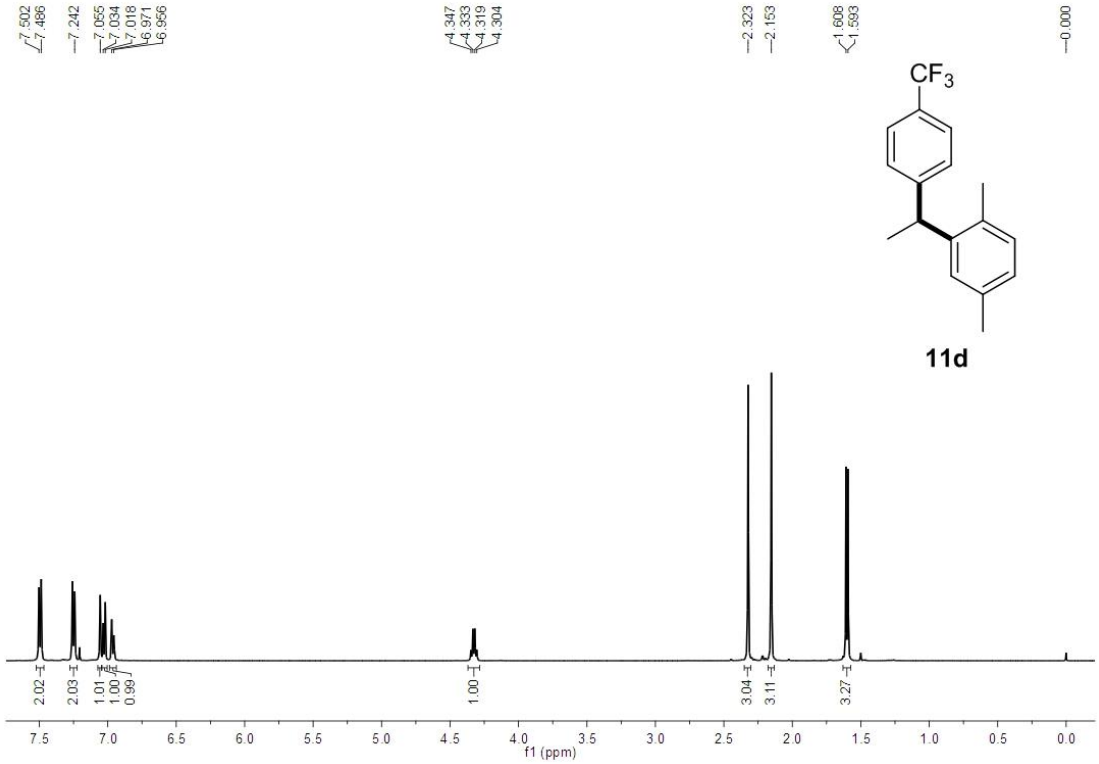
^{1}H NMR (500 MHz, $CDCl_3$) for **11c**



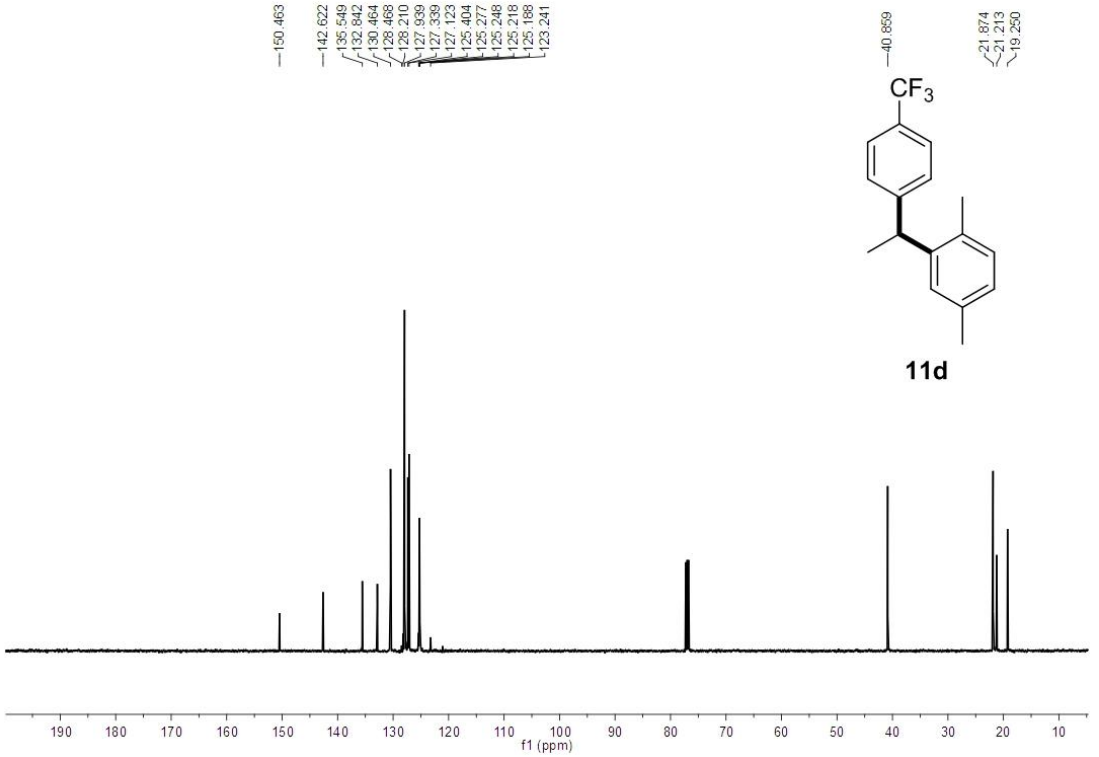
^{13}C NMR (125 MHz, $CDCl_3$) for **11c**



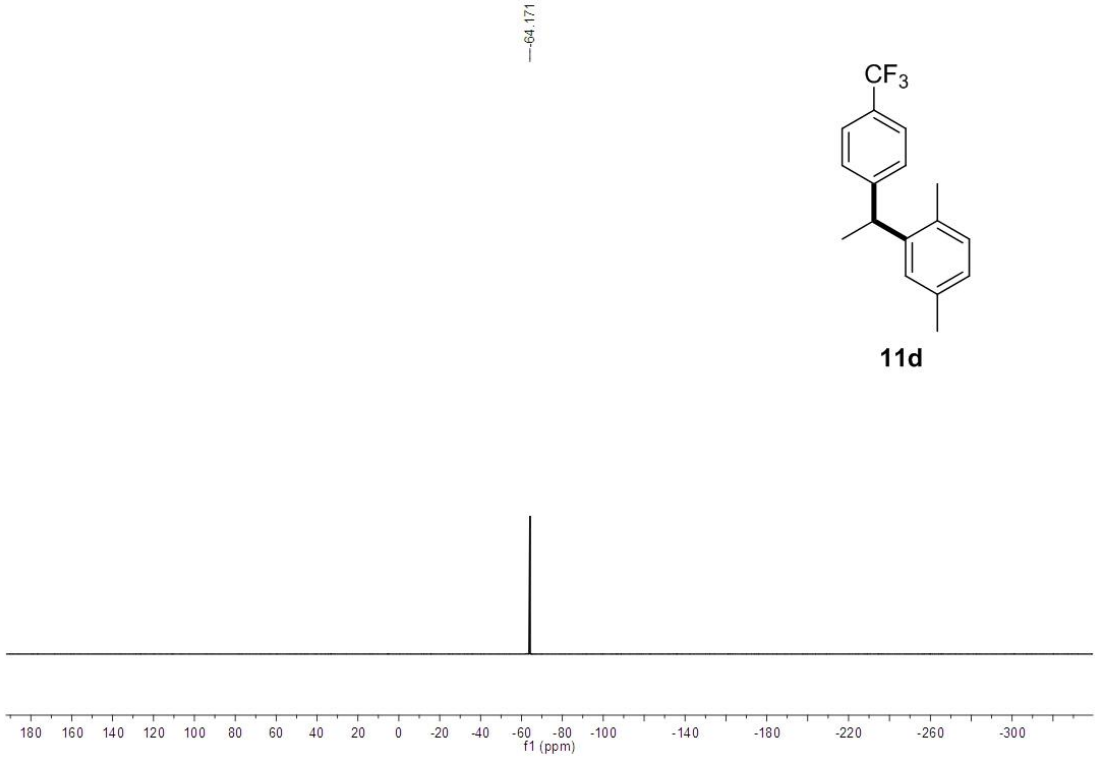
^{1}H NMR (500 MHz, $CDCl_3$) for **11d**



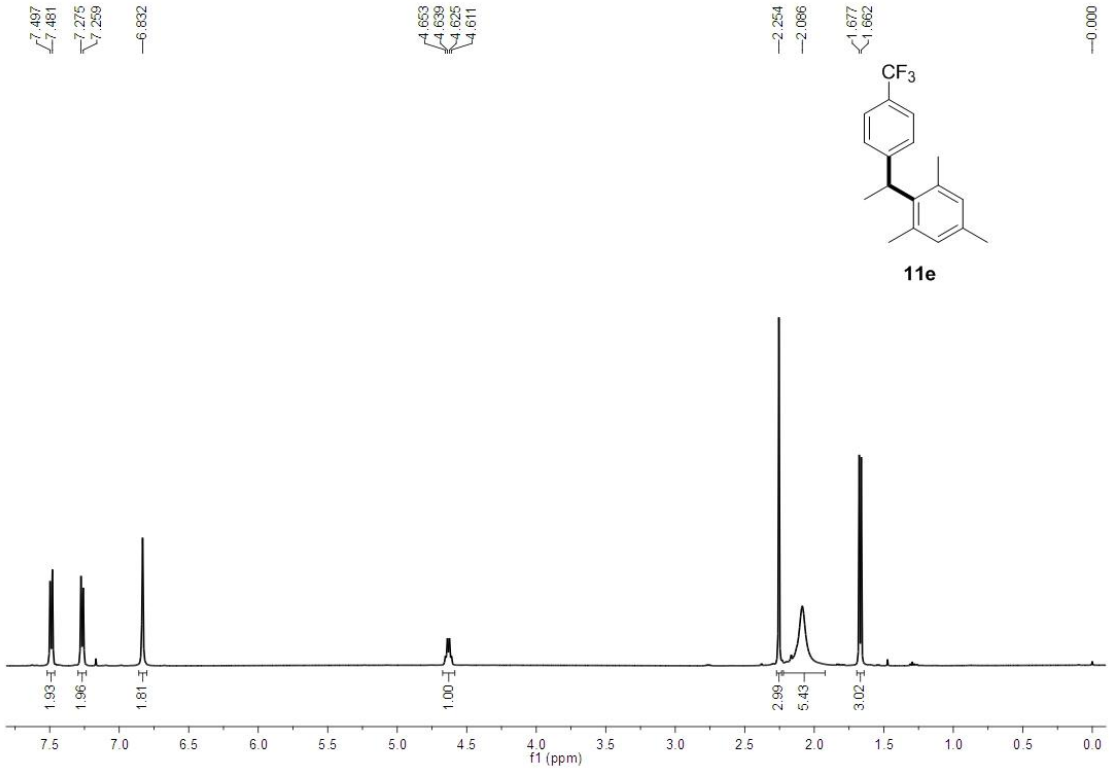
^{13}C NMR (125 MHz, $CDCl_3$) for **11d**



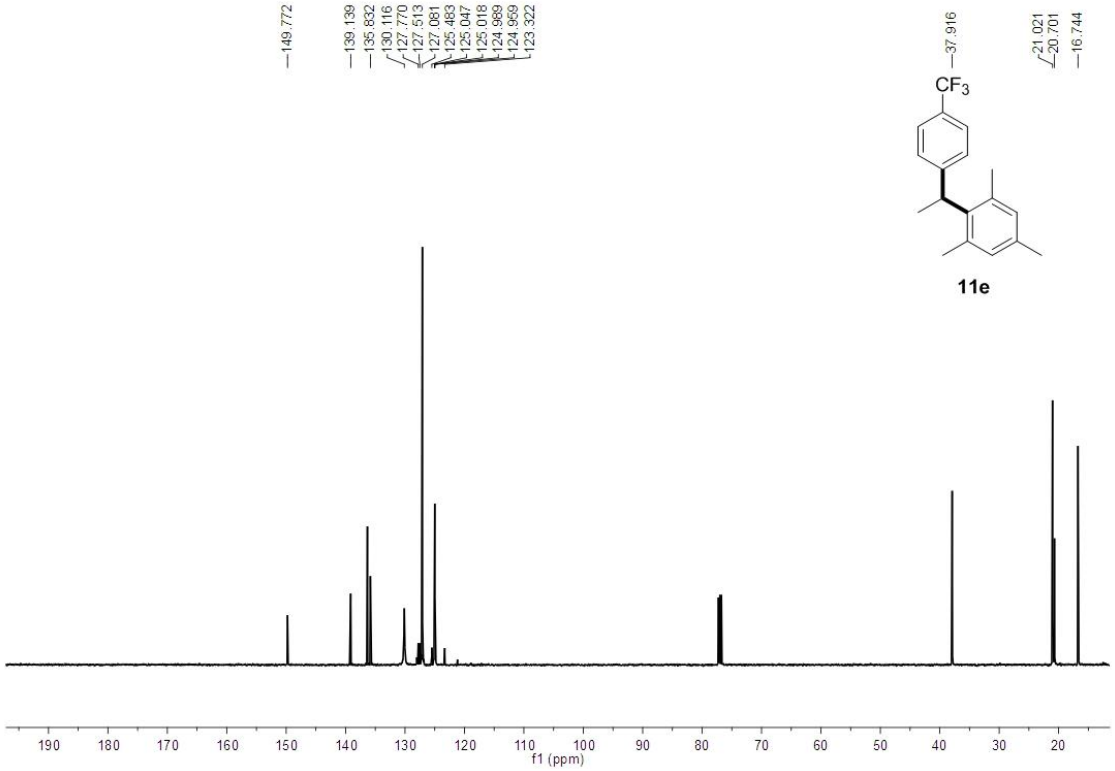
^{19}F NMR (470 MHz, $CDCl_3$) for **11d**



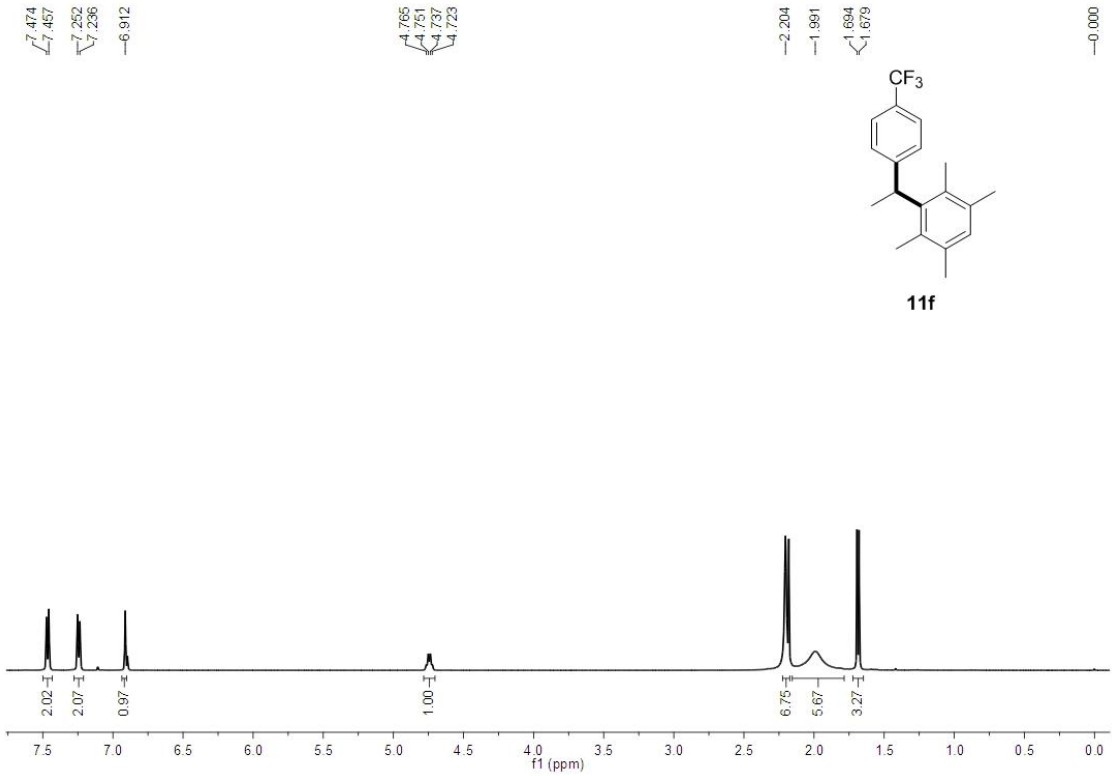
^{1}H NMR (500 MHz, $CDCl_3$) for **11e**



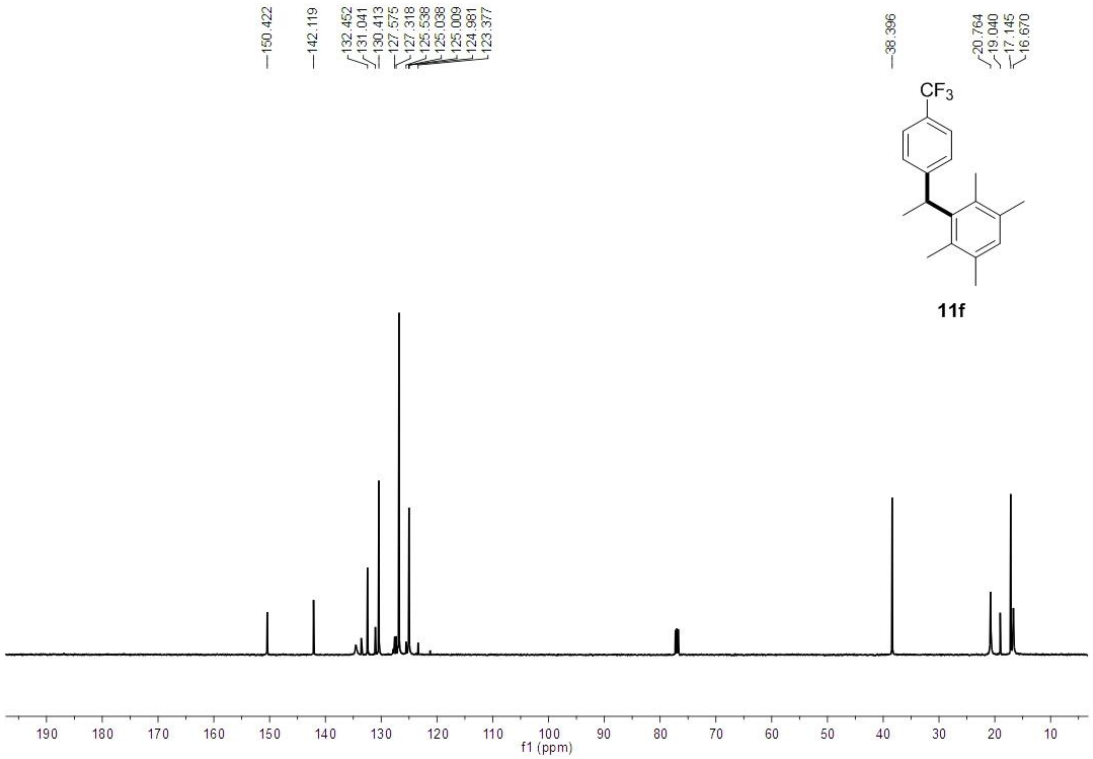
^{13}C NMR (125 MHz, $CDCl_3$) for **11e**



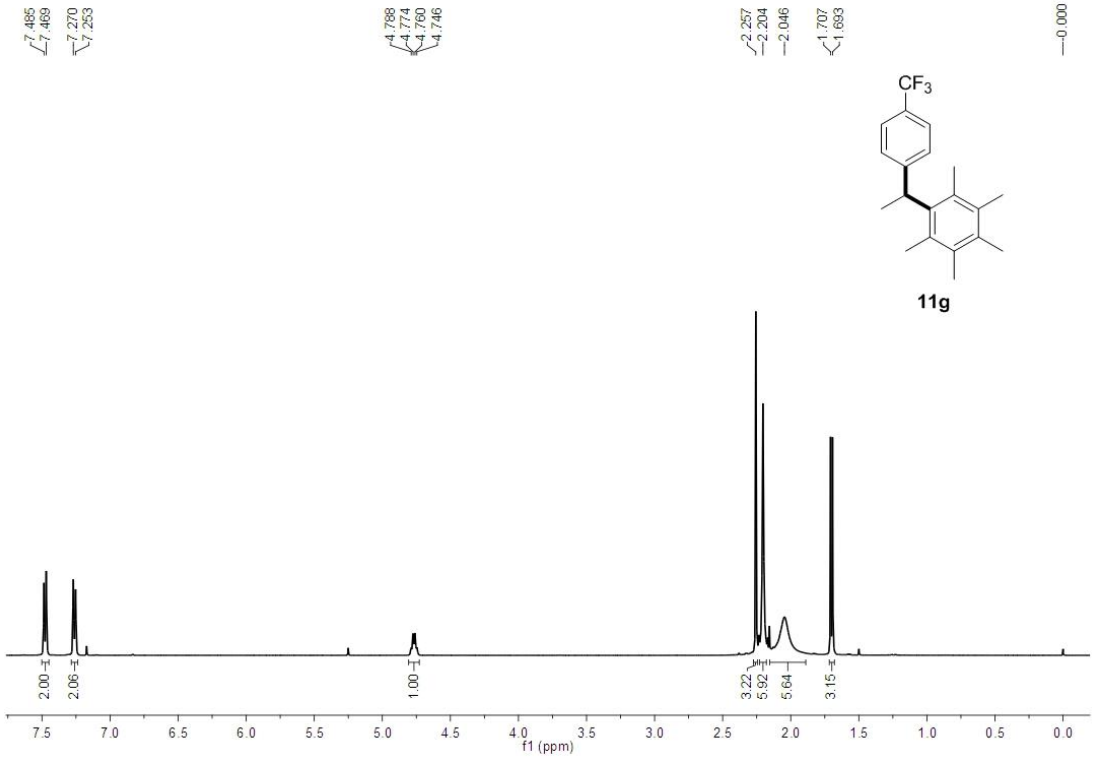
^{1}H NMR (500 MHz, $CDCl_3$) for **11f**



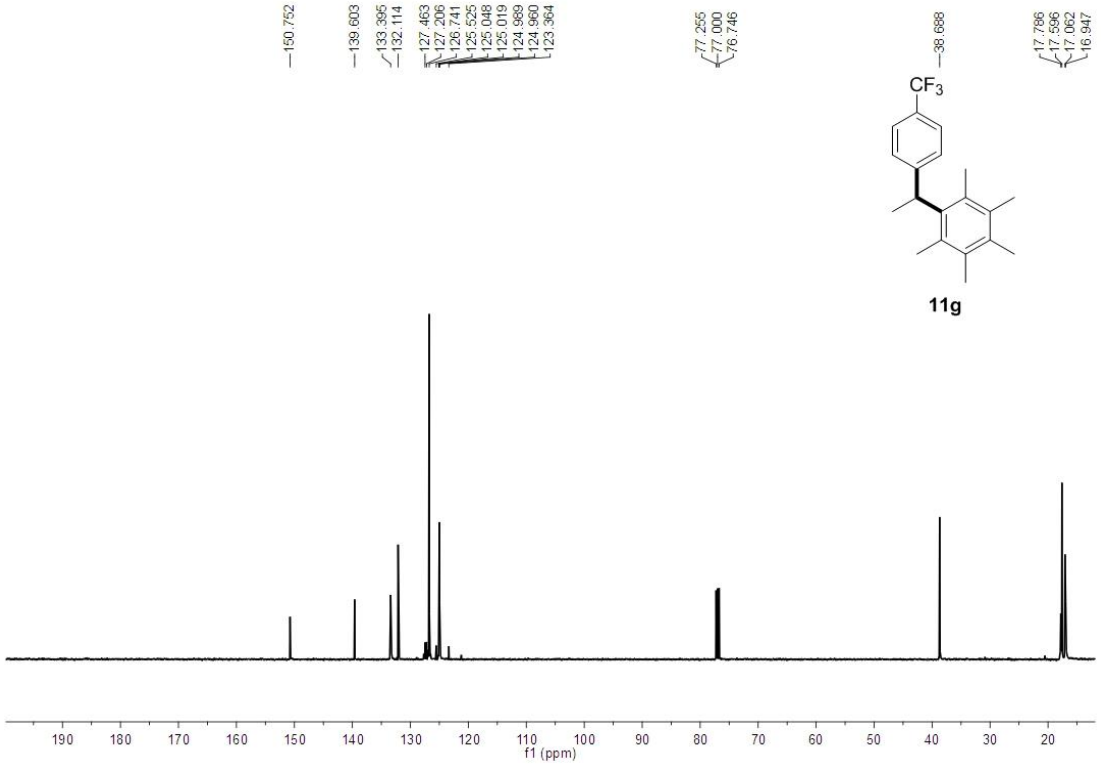
^{13}C NMR (125 MHz, $CDCl_3$) for **11f**



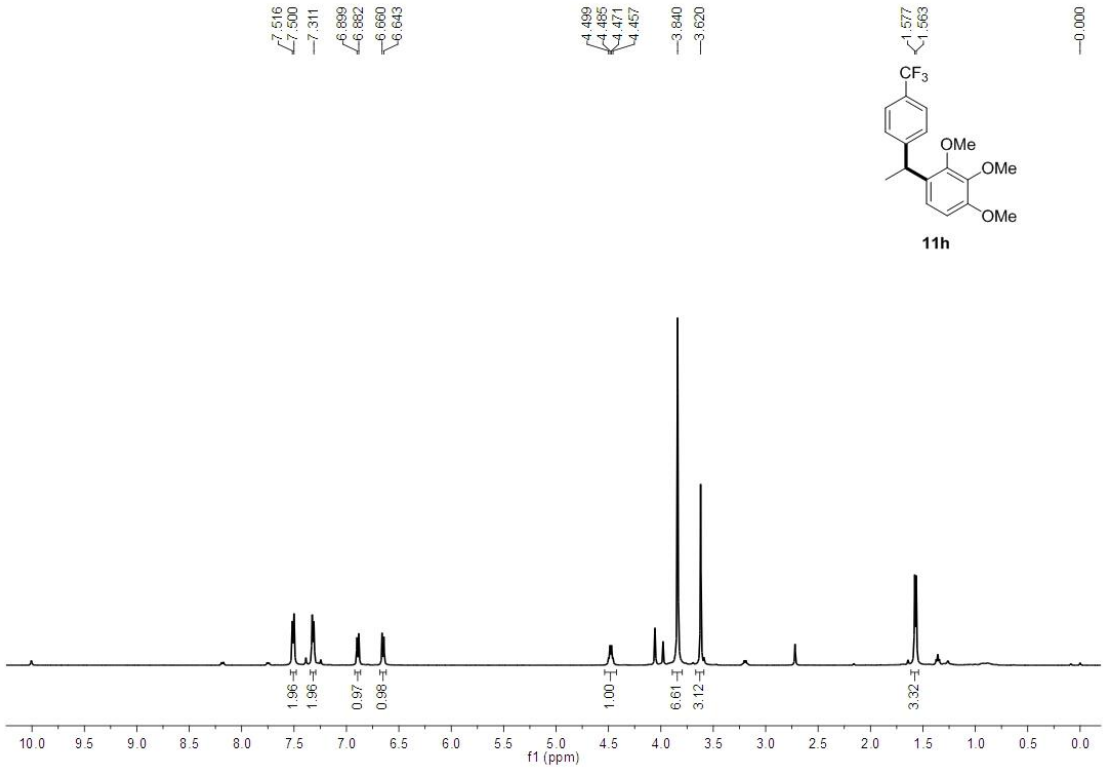
^{1}H NMR (500 MHz, $CDCl_3$) for **11g**



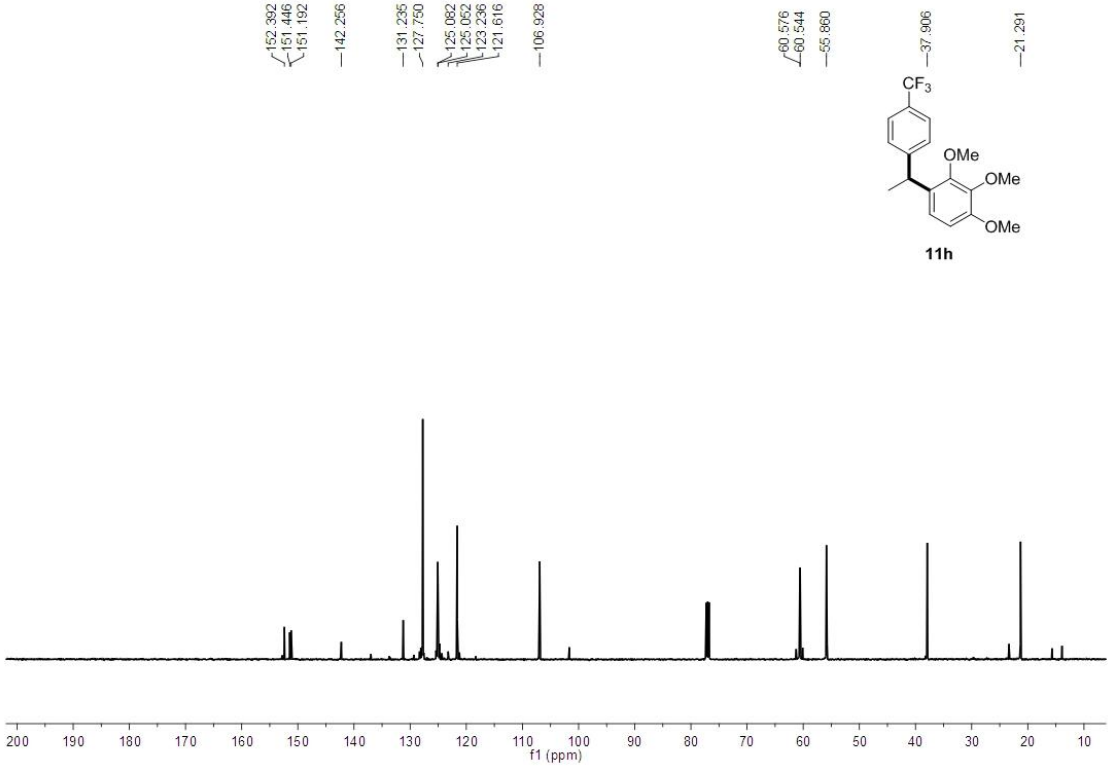
^{13}C NMR (125 MHz, $CDCl_3$) for **11g**



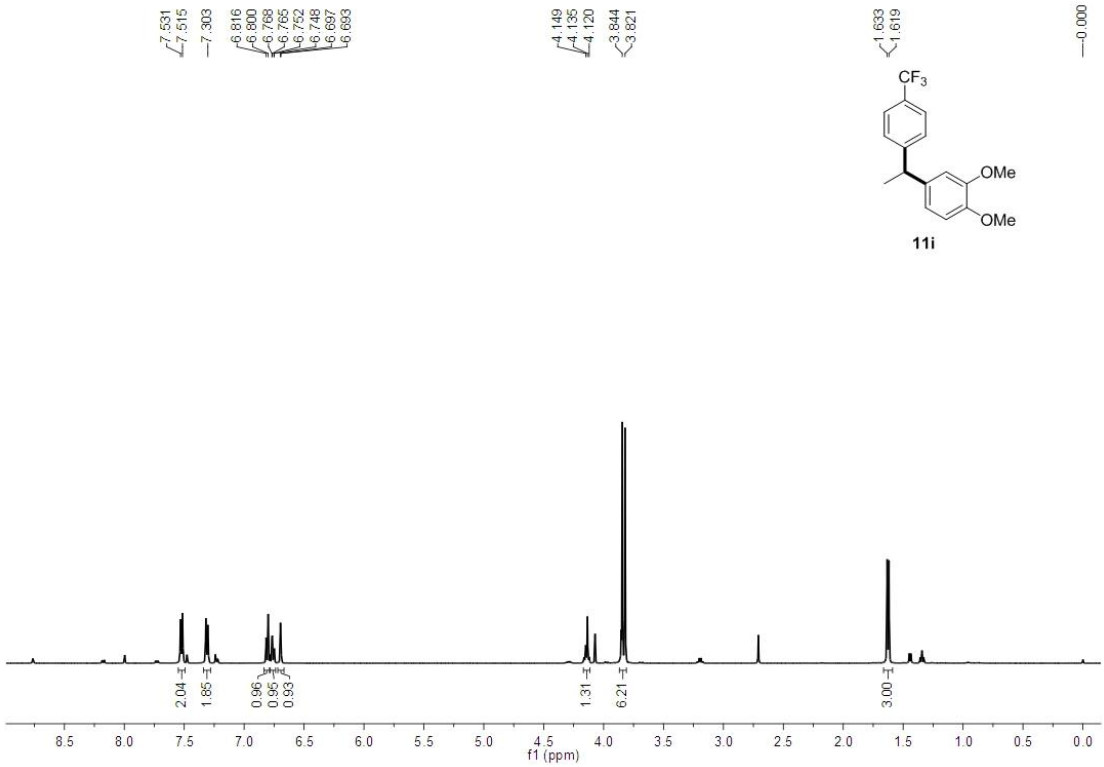
^{1}H NMR (500 MHz, $CDCl_3$) for **11h**



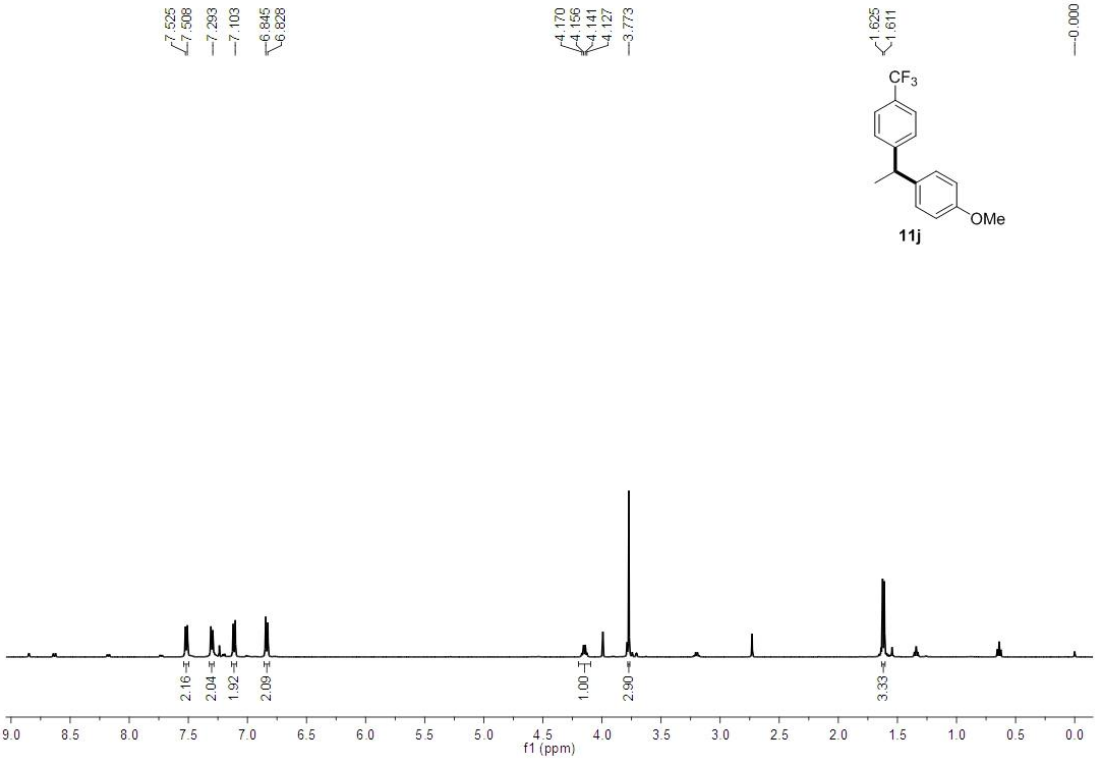
^{13}C NMR (125 MHz, $CDCl_3$) for **11h**



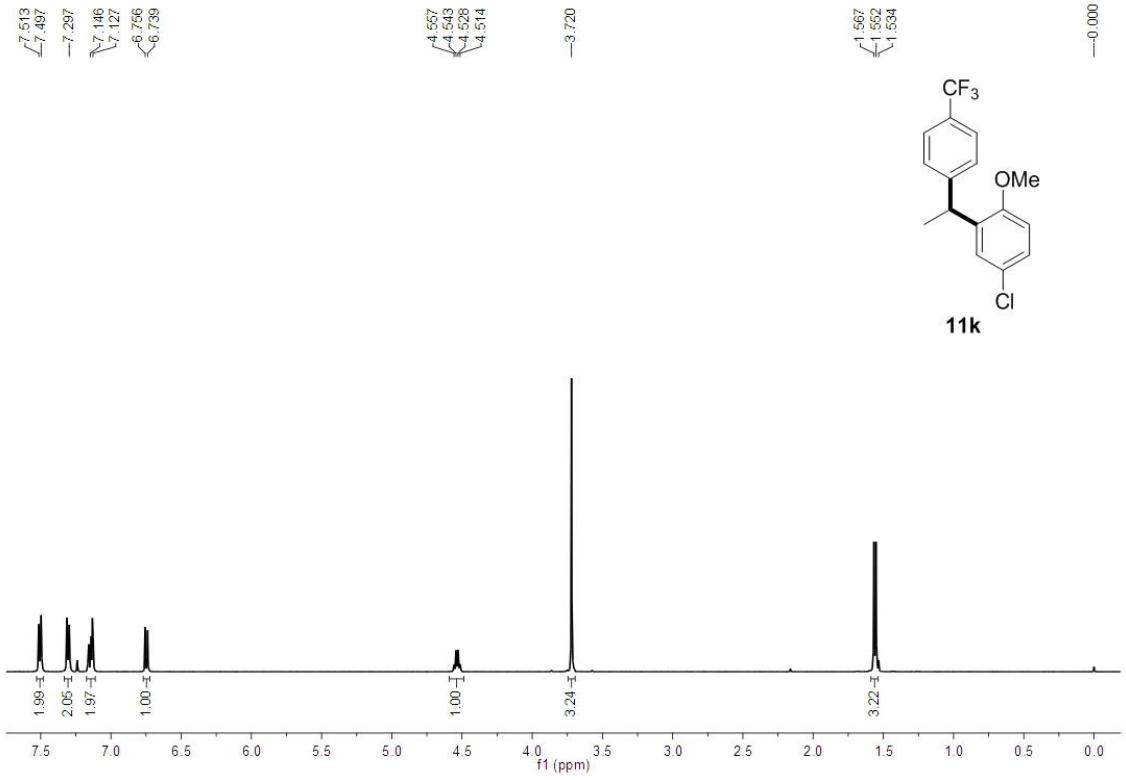
^{1}H NMR (500 MHz, $CDCl_3$) for **11i**



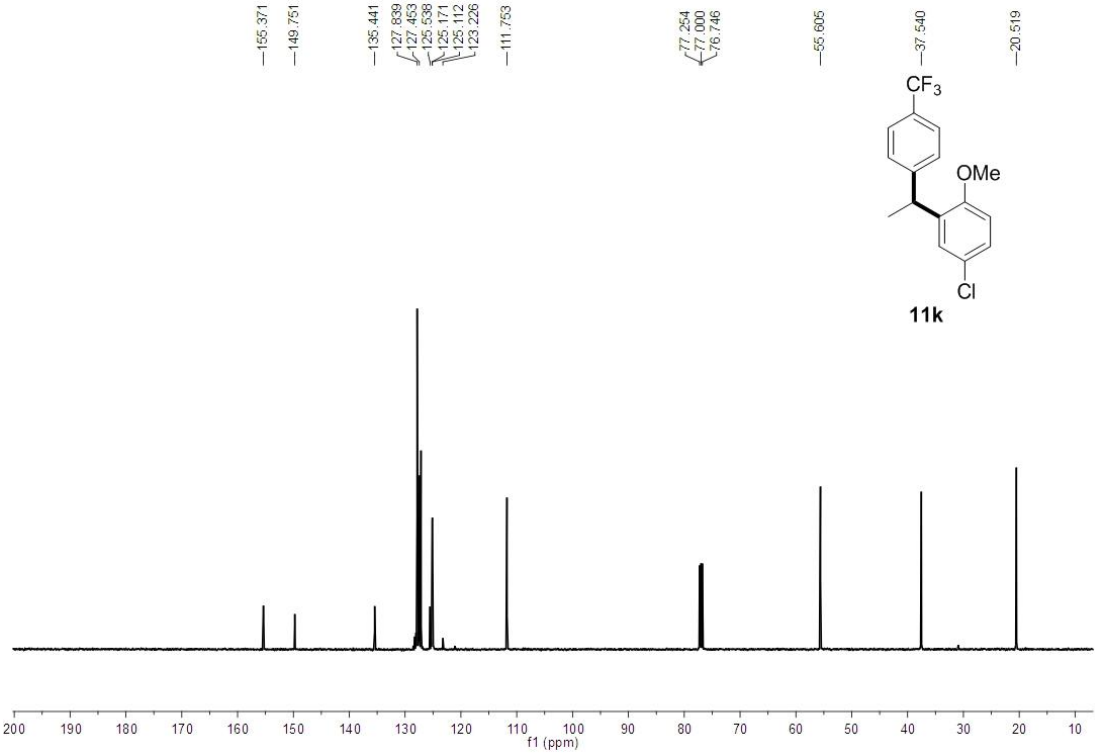
^{1}H NMR (500 MHz, $CDCl_3$) for **11j**



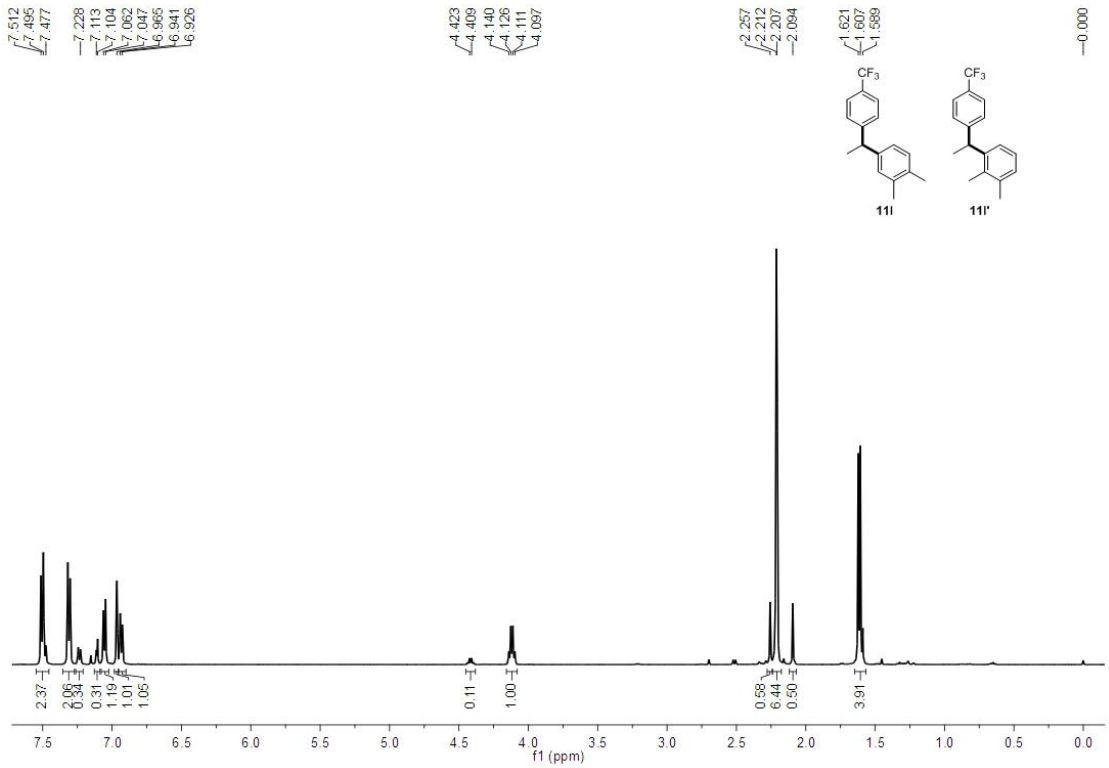
^{1}H NMR (500 MHz, $CDCl_3$) for **11k**



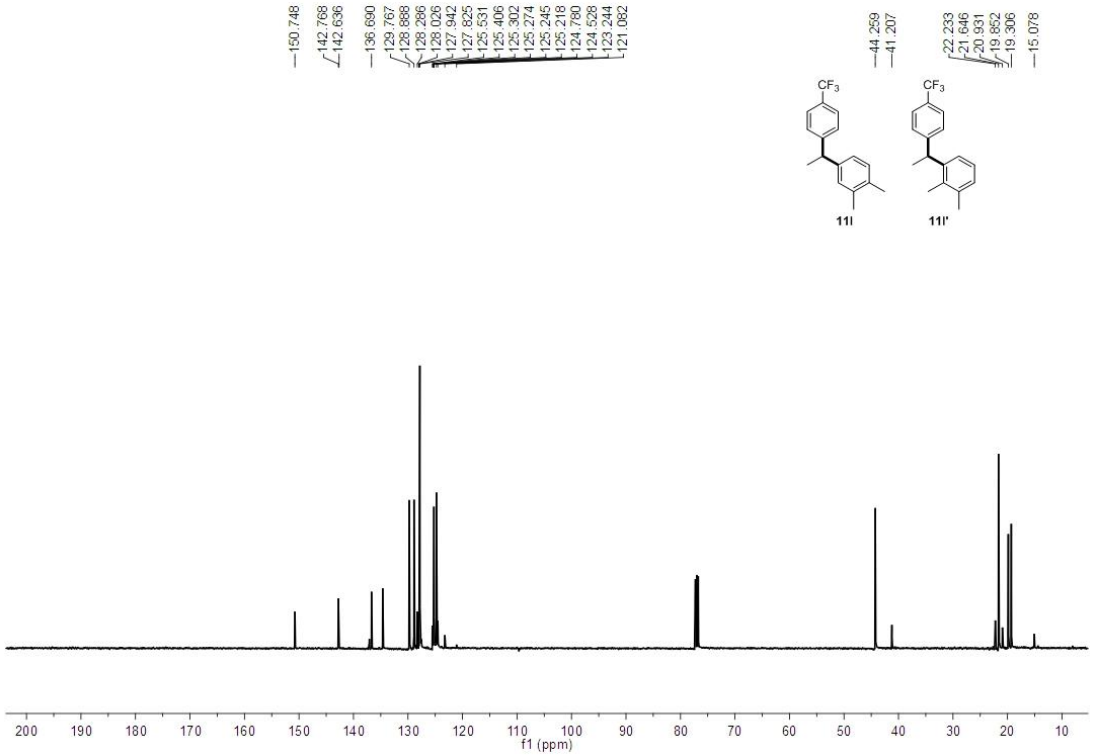
^{13}C NMR (125 MHz, $CDCl_3$) for **11k**



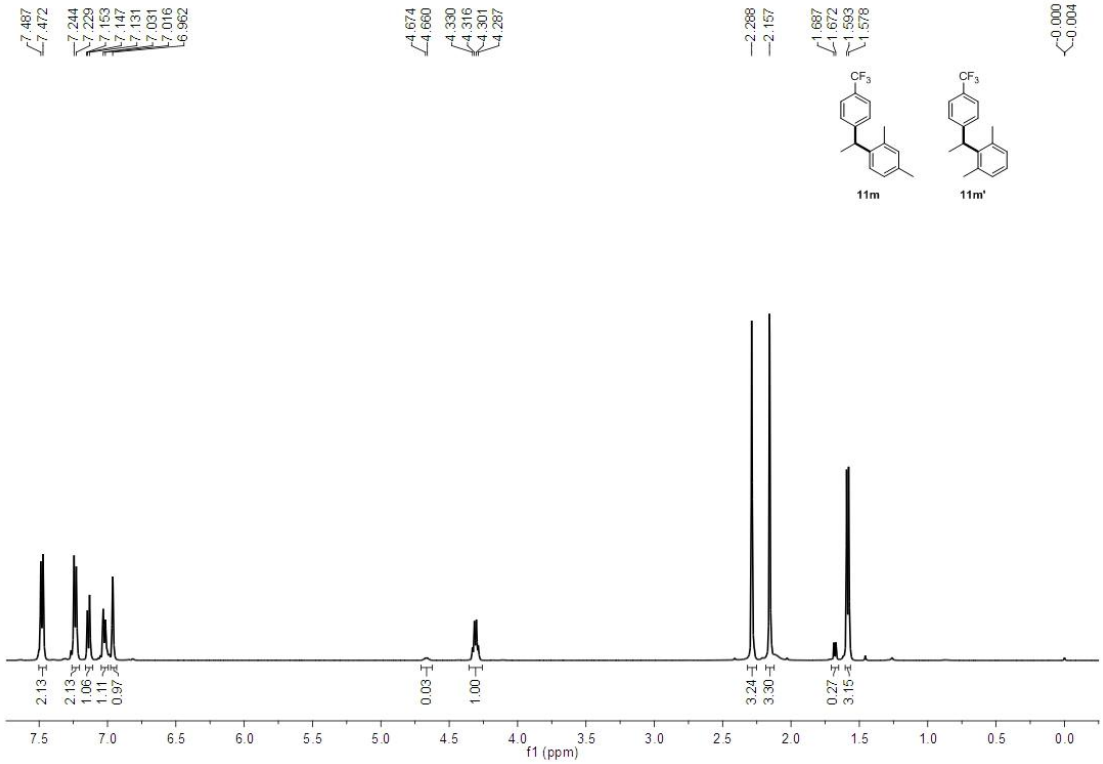
^{1}H NMR (500 MHz, $CDCl_3$) for **11l/11l'**



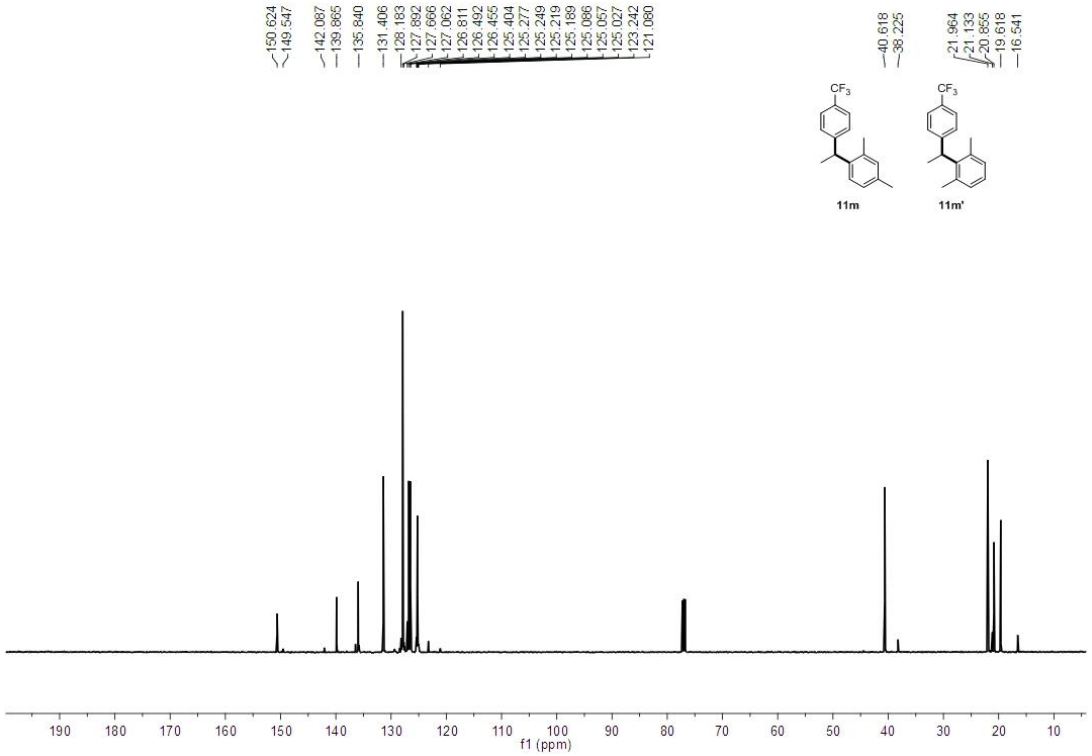
^{13}C NMR (125 MHz, $CDCl_3$) for **11l/11l'**



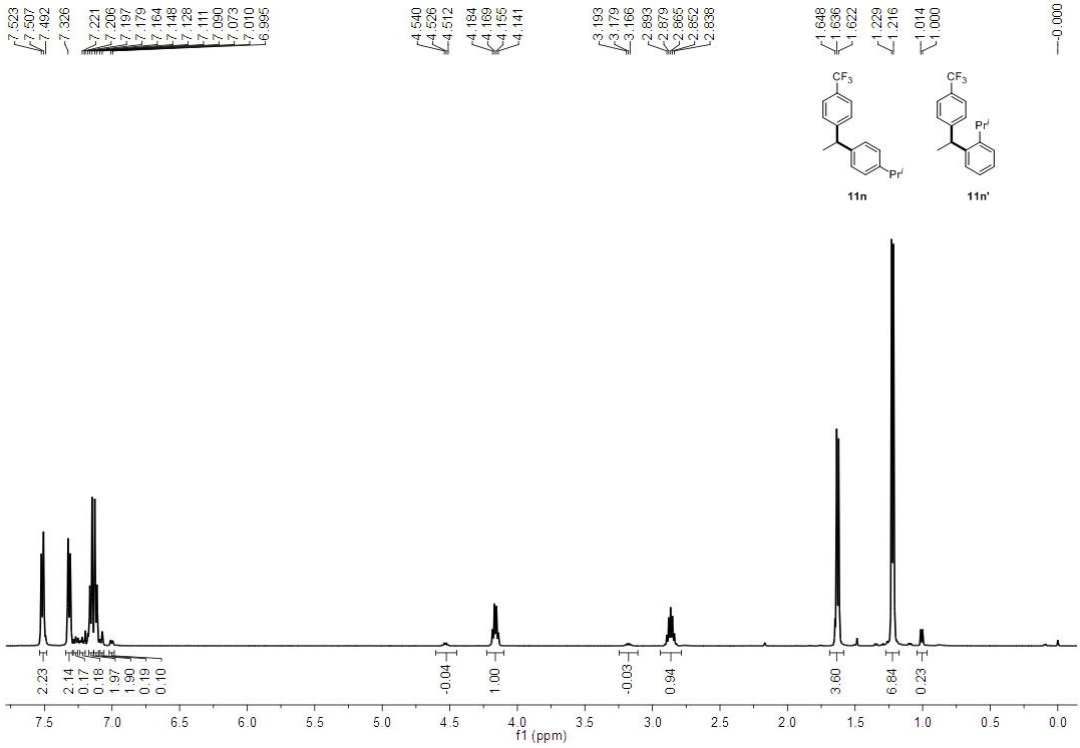
^{1}H NMR (500 MHz, $CDCl_3$) for **11m/11m'**



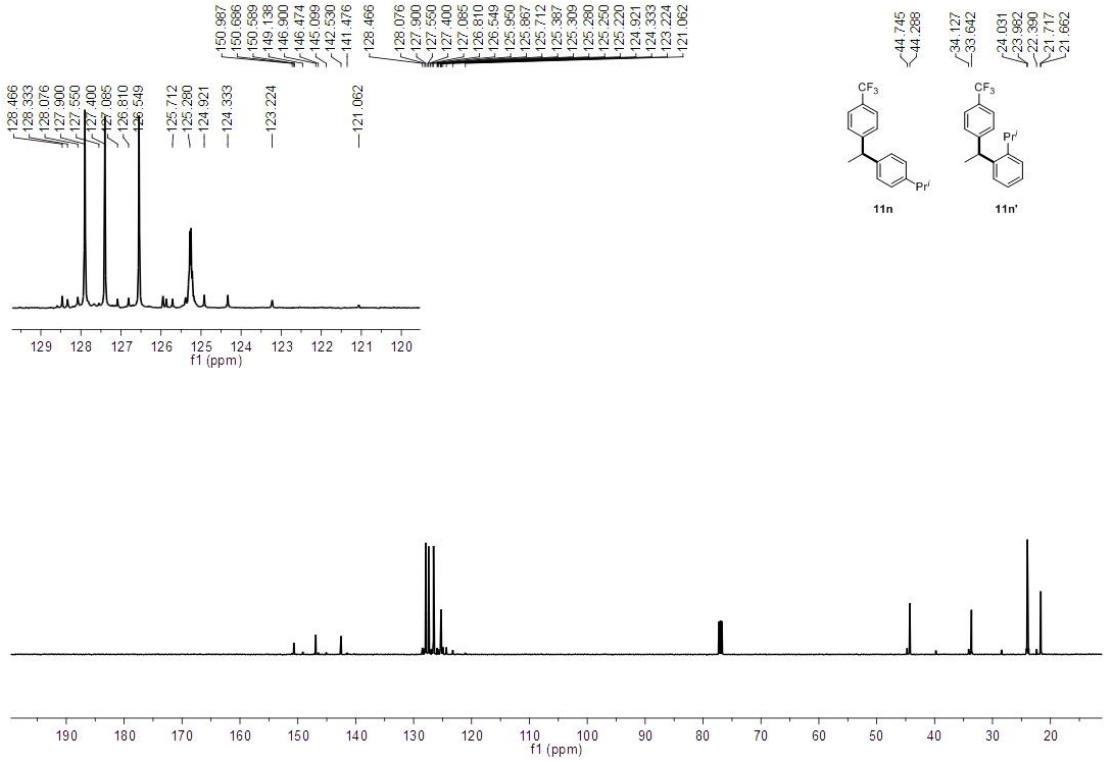
^{13}C NMR (125 MHz, $CDCl_3$) for **11m/11m'**



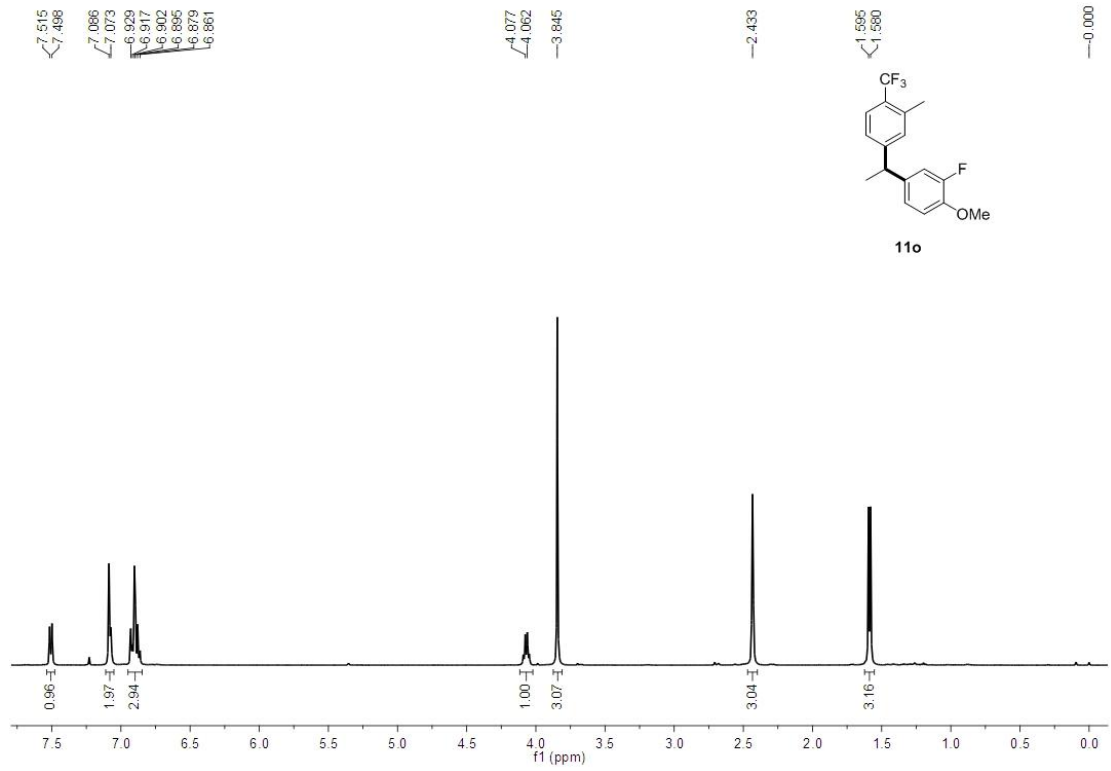
^{1}H NMR (500 MHz, $CDCl_3$) for **11n/11n'**



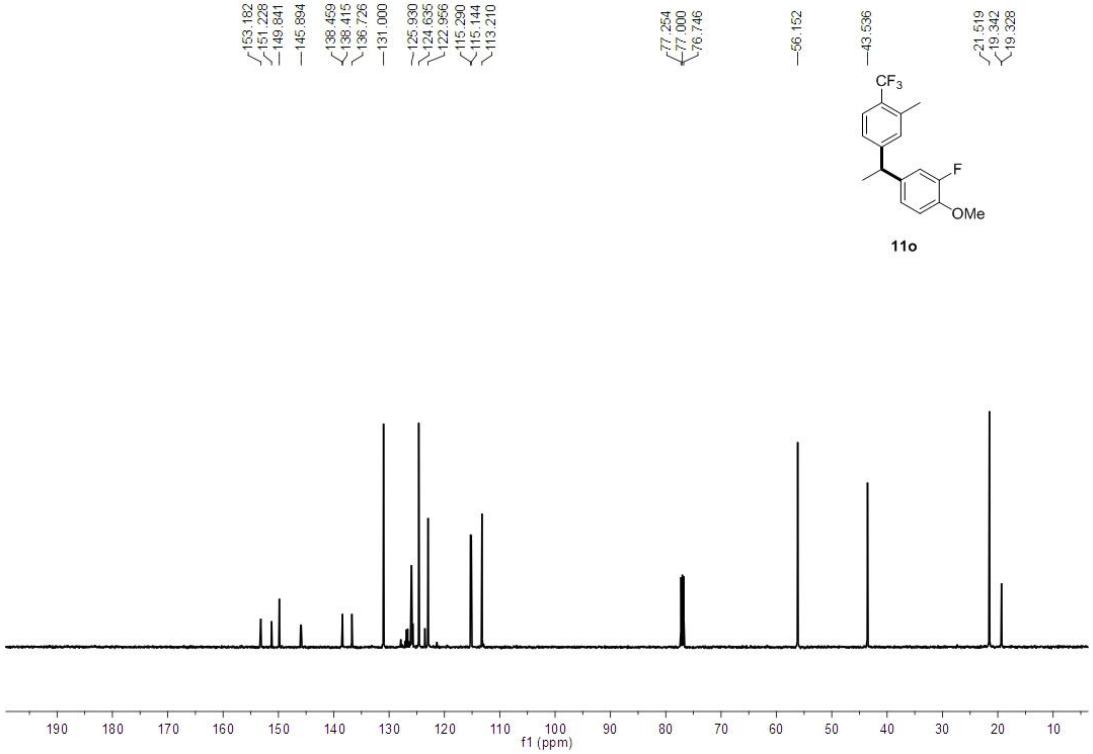
^{13}C NMR (125 MHz, $CDCl_3$) for **11n/11n'**



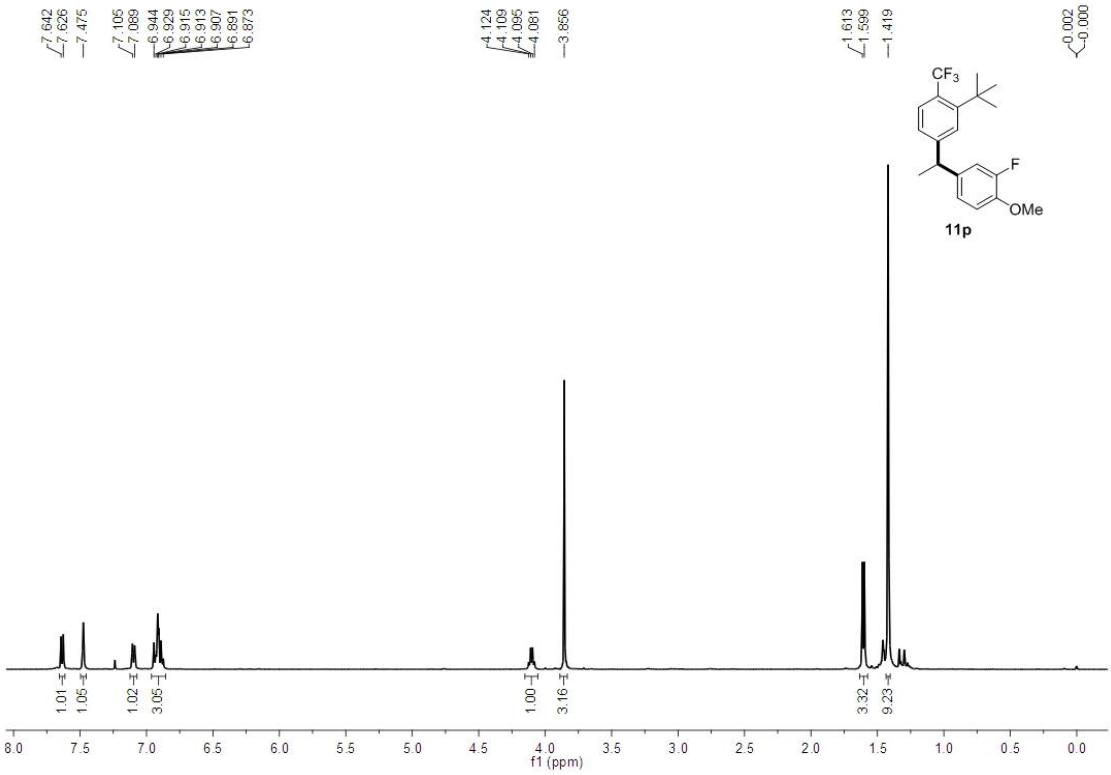
^{1}H NMR (500 MHz, $CDCl_3$) for **11o**



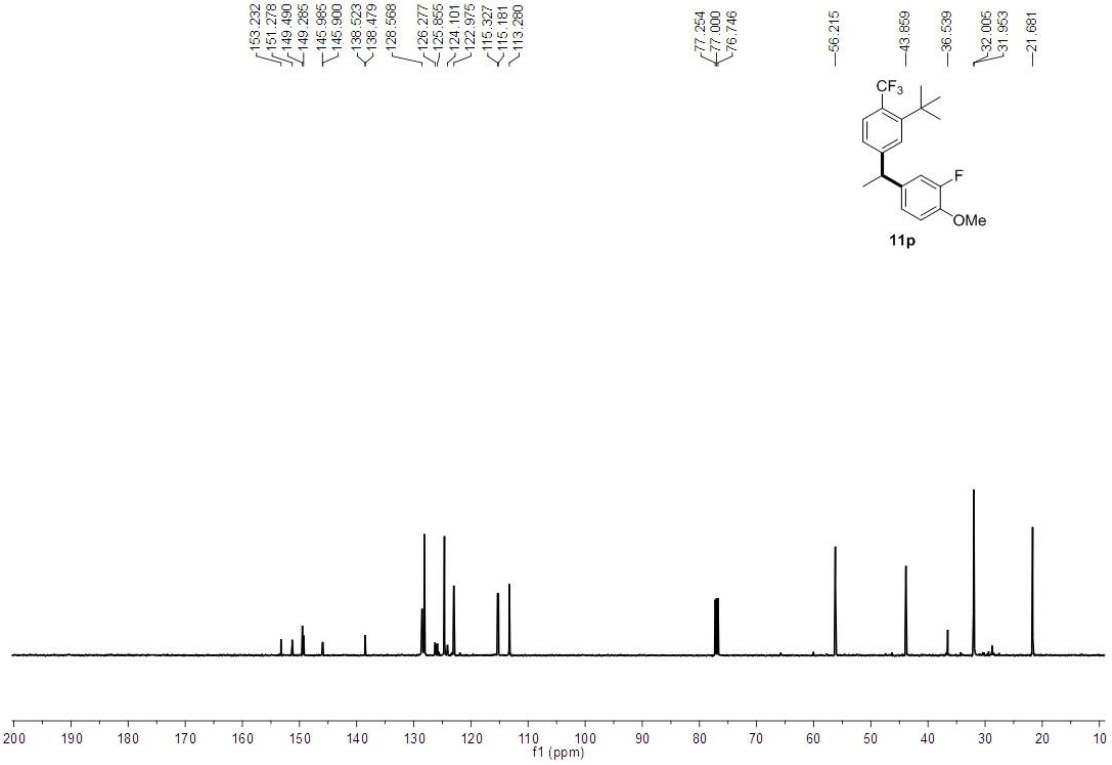
^{13}C NMR (125 MHz, $CDCl_3$) for **11o**



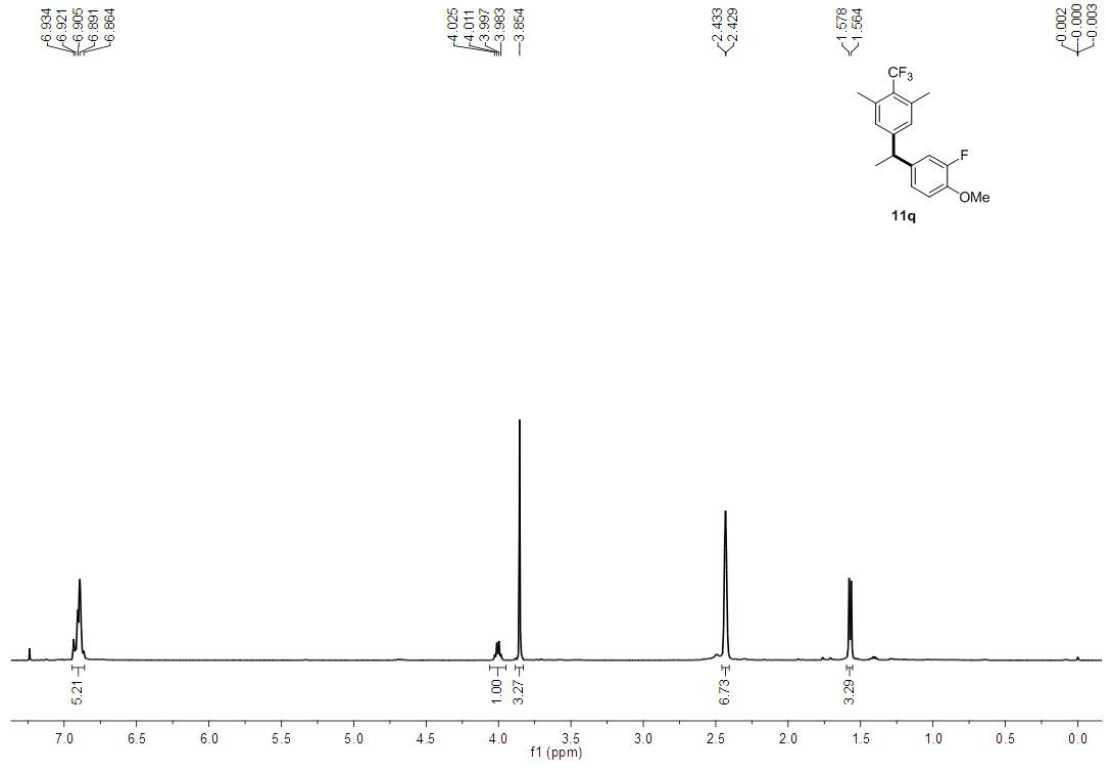
^{1}H NMR (500 MHz, $CDCl_3$) for **11p**



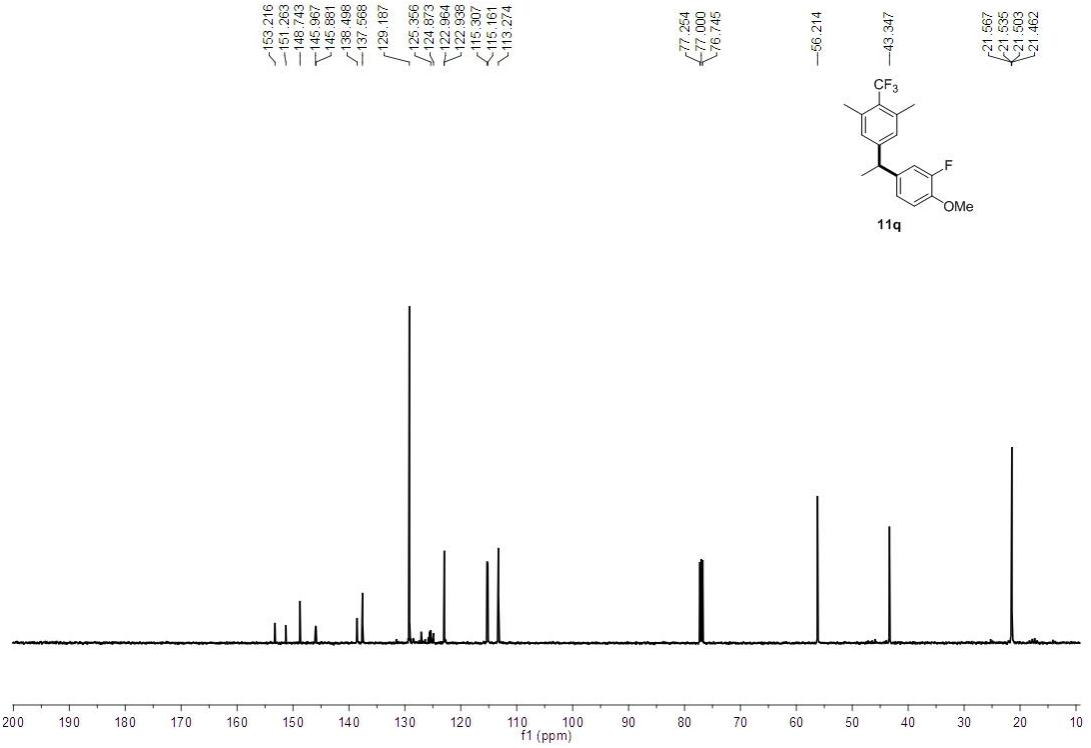
^{13}C NMR (125 MHz, $CDCl_3$) for **11p**



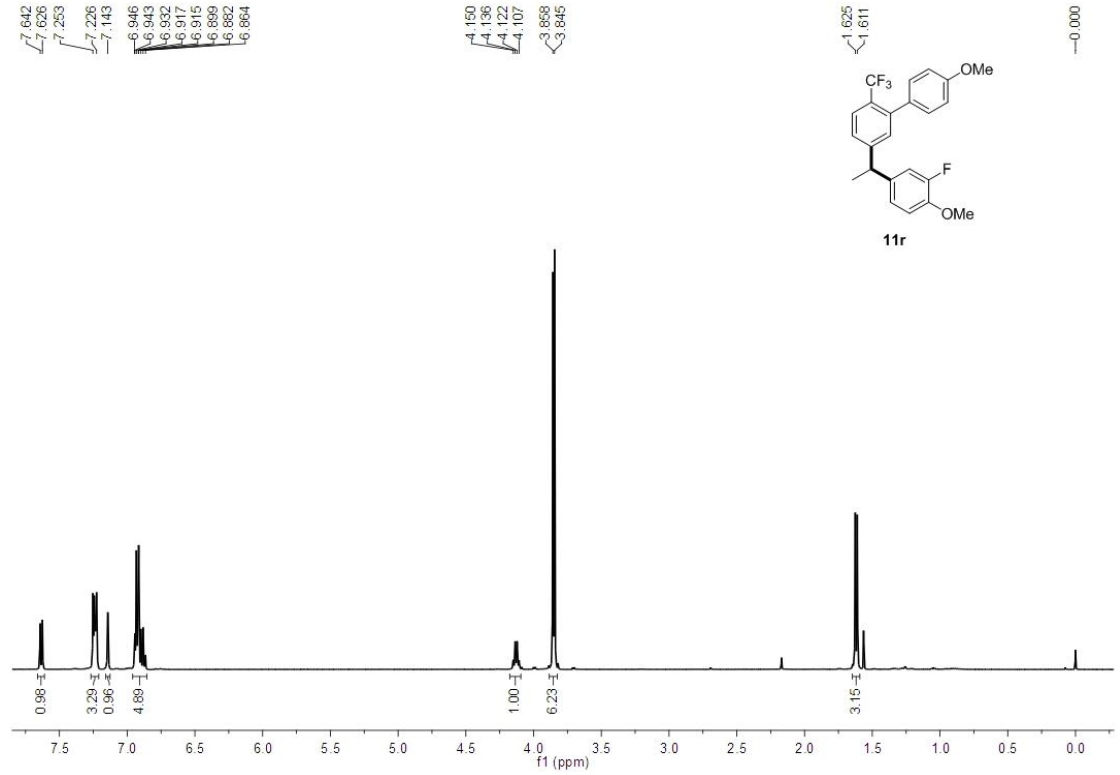
^{1}H NMR (500 MHz, $CDCl_3$) for **11q**



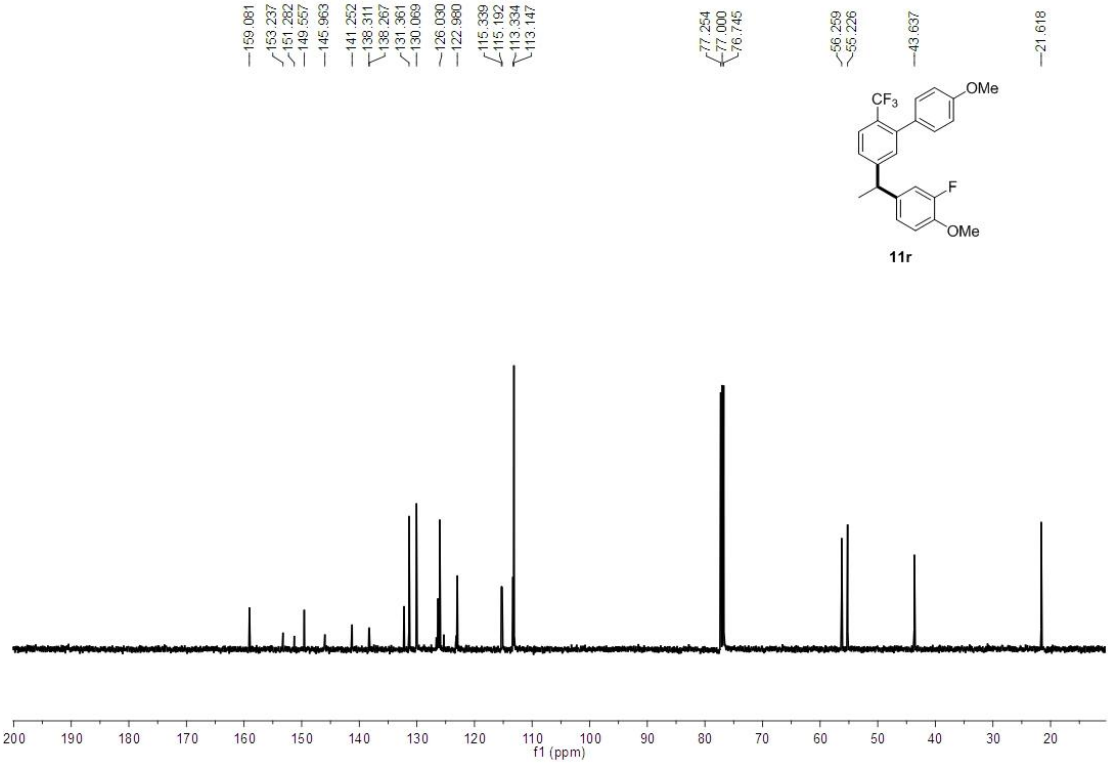
^{13}C NMR (125 MHz, $CDCl_3$) for **11q**



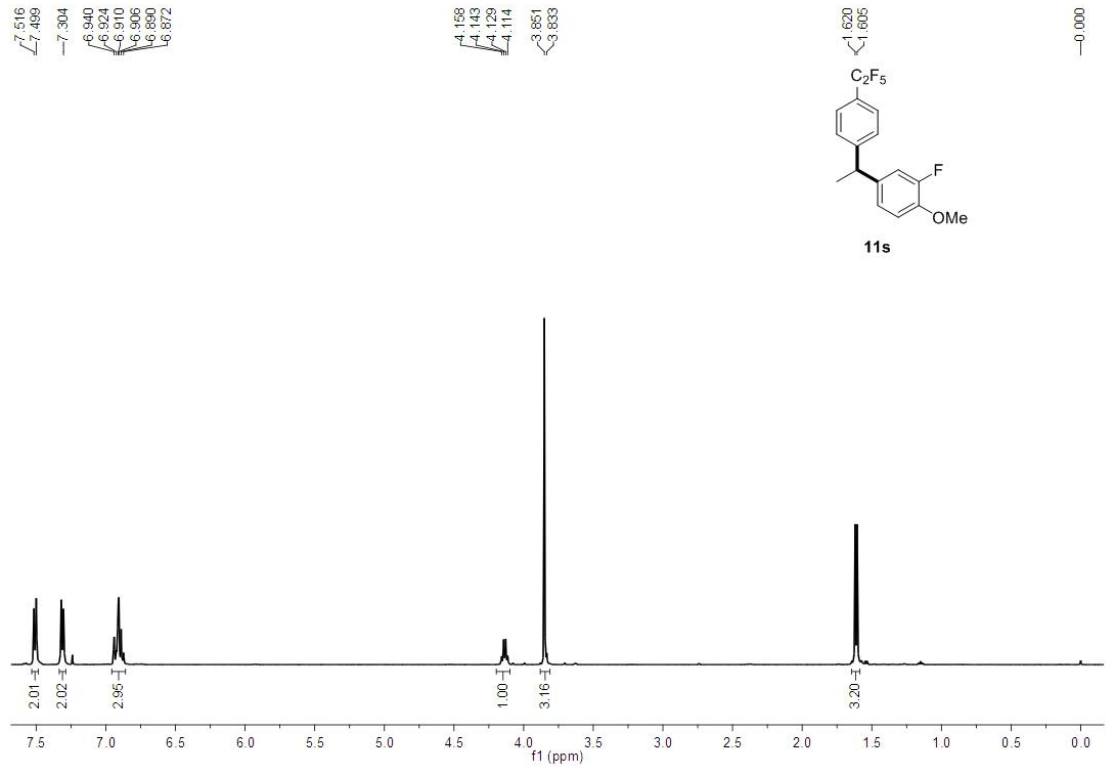
^{1}H NMR (500 MHz, $CDCl_3$) for **11r**



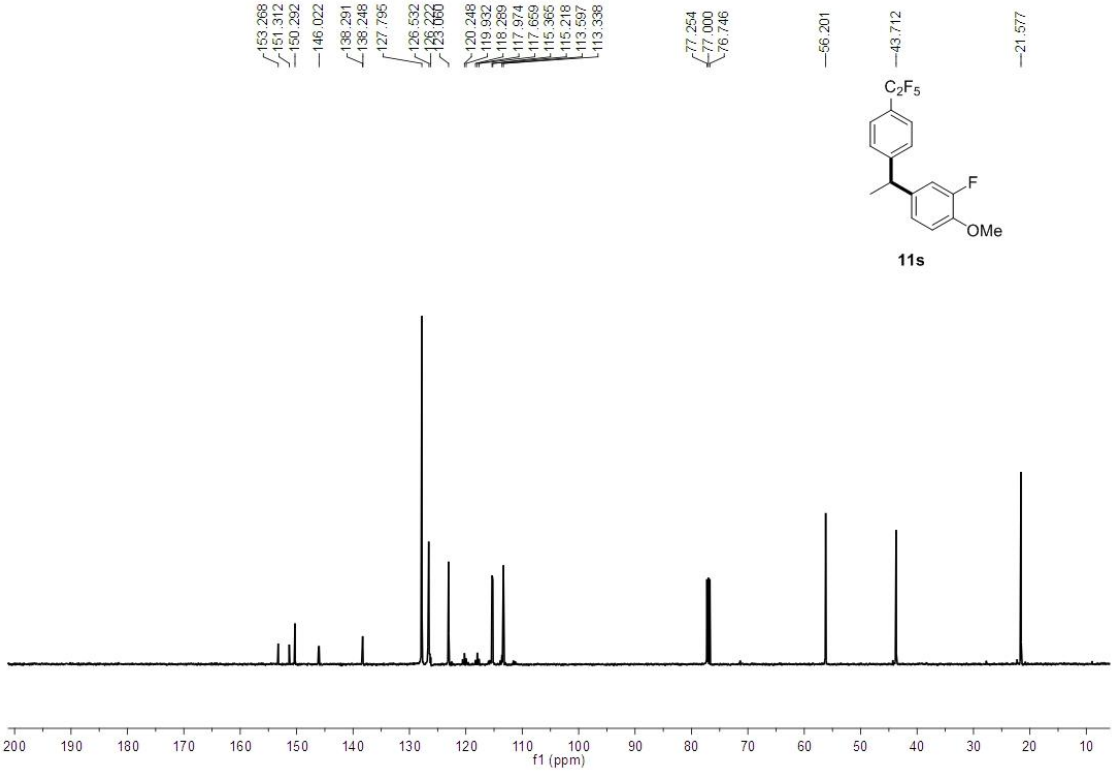
^{13}C NMR (125 MHz, $CDCl_3$) for **11r**



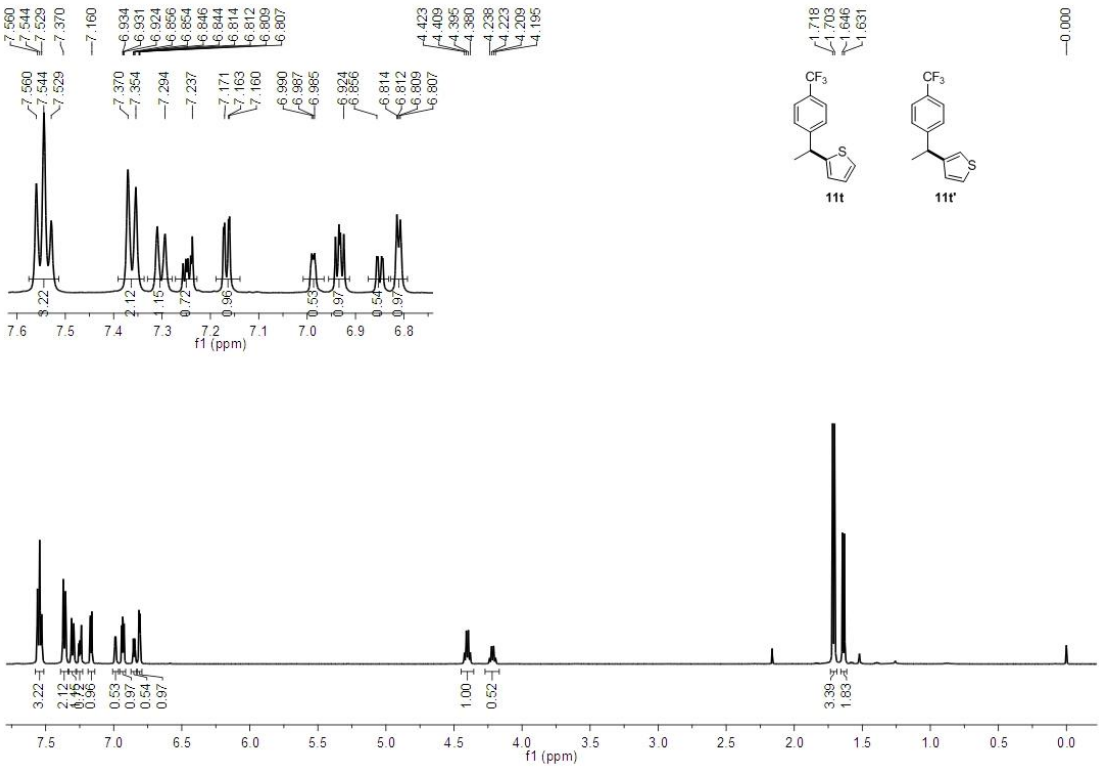
^{1}H NMR (500 MHz, $CDCl_3$) for **11s**



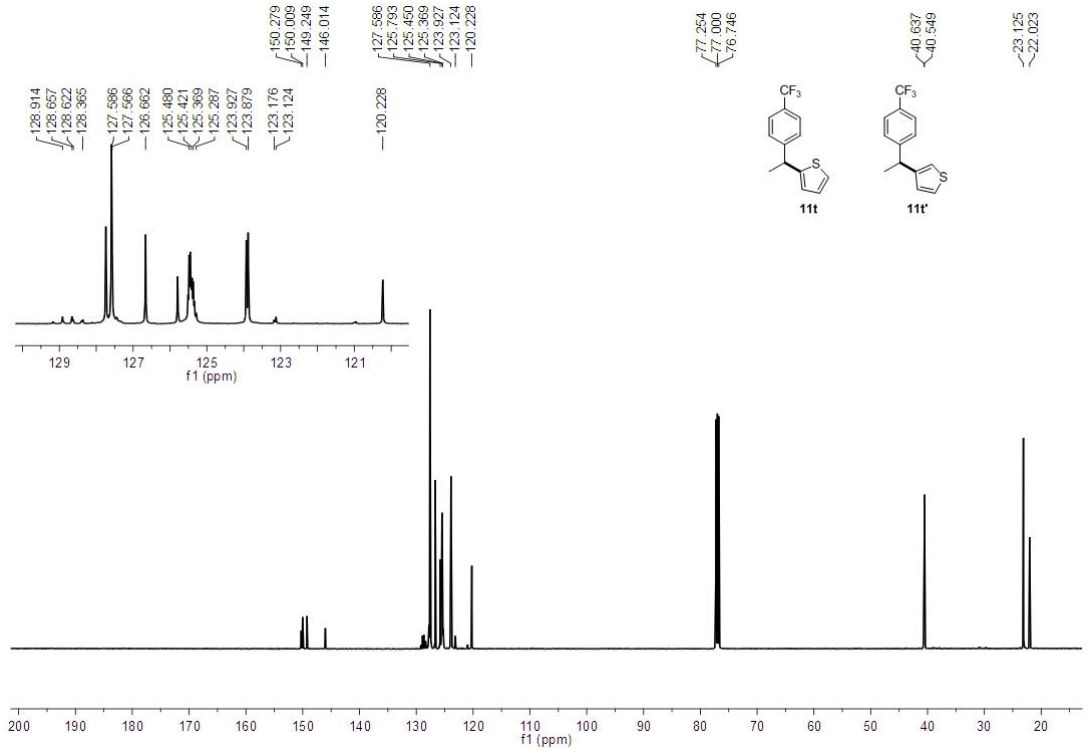
^{13}C NMR (125 MHz, $CDCl_3$) for **11s**



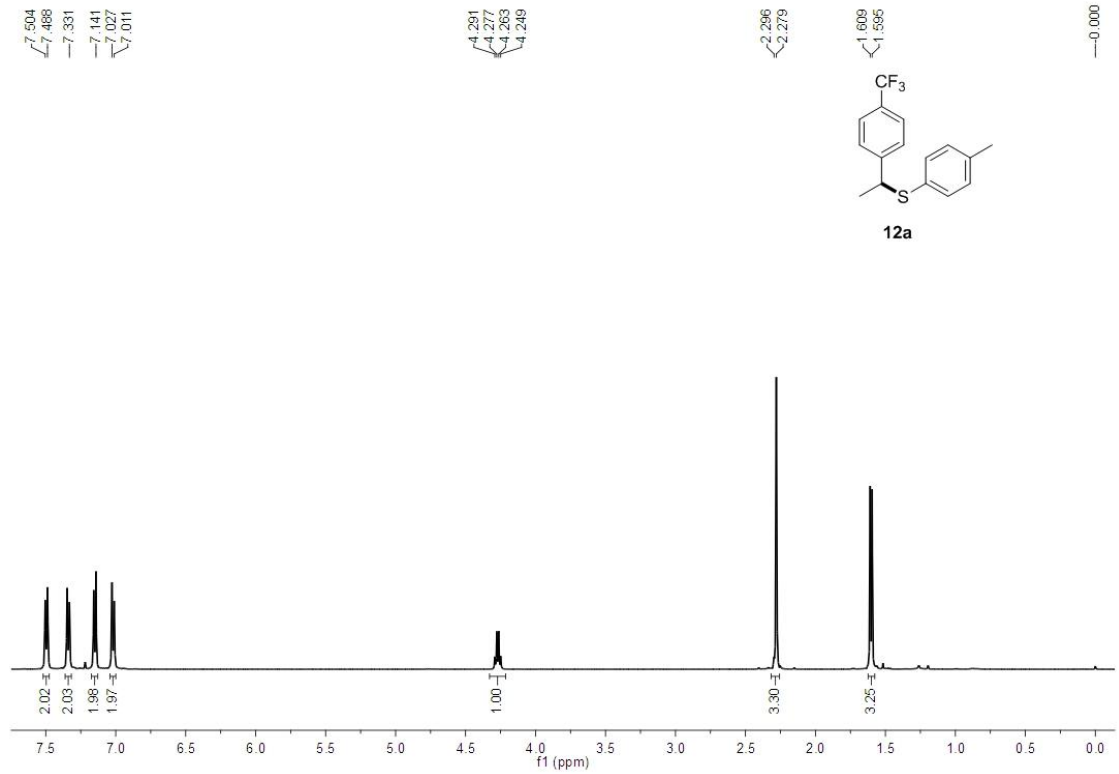
^{1}H NMR (500 MHz, $CDCl_3$) for **11t/11t'**



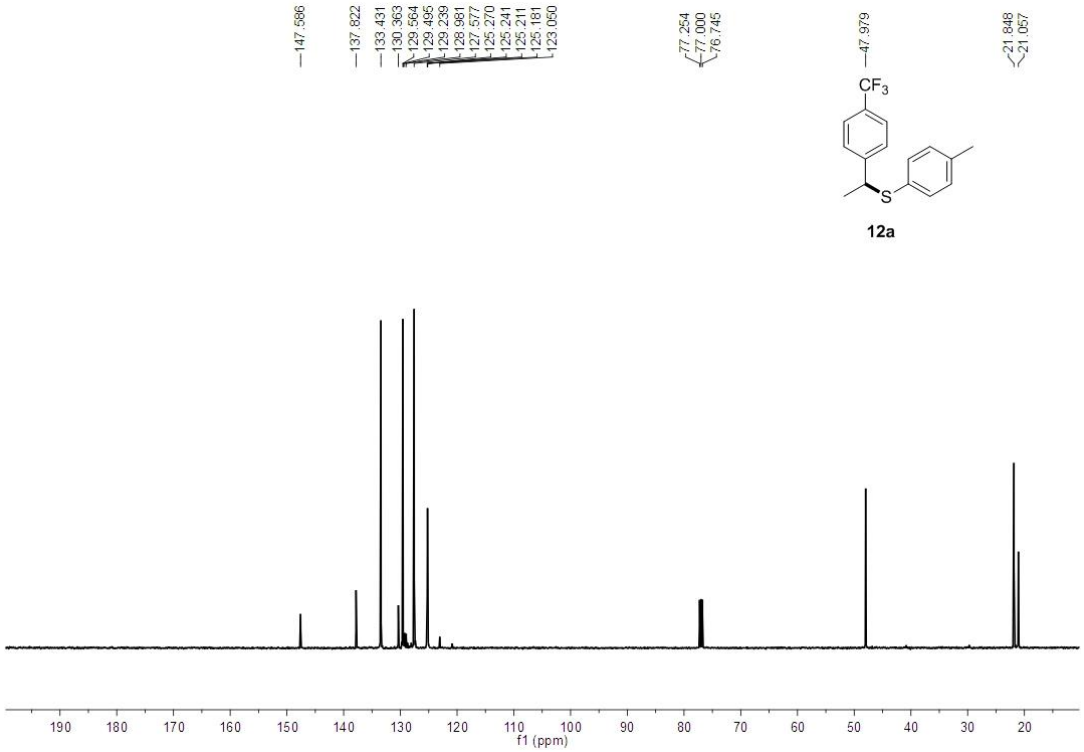
^{13}C NMR (125 MHz, $CDCl_3$) for **11t/11t'**



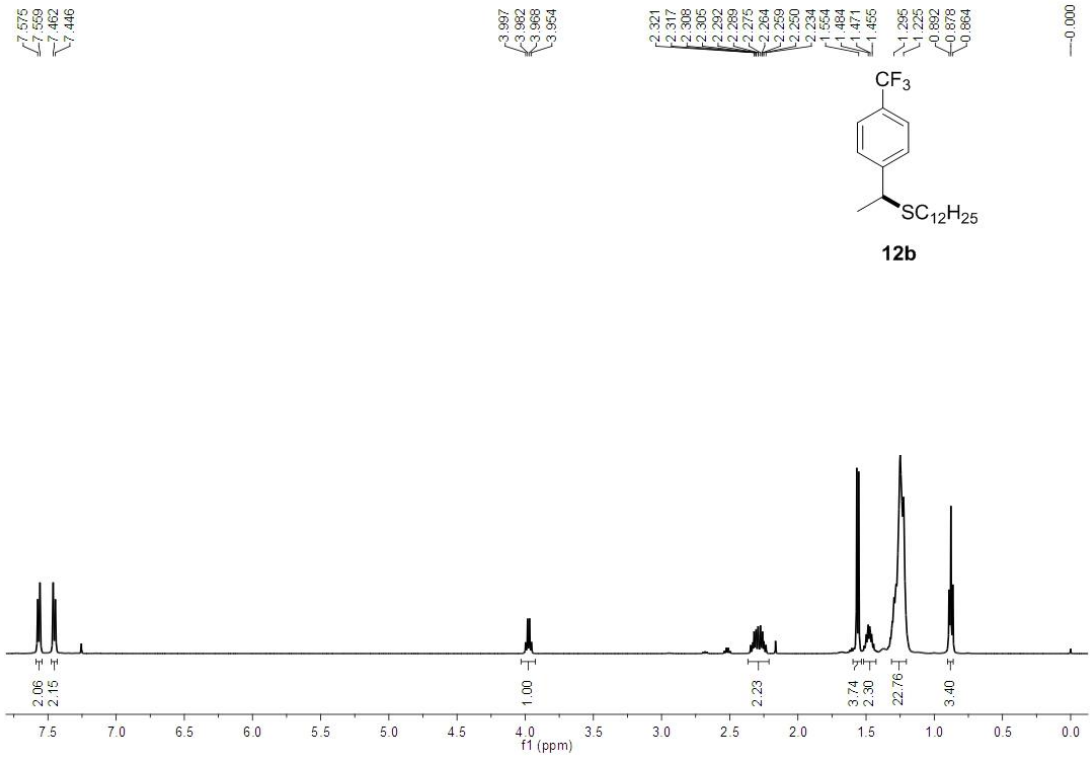
^{1}H NMR (500 MHz, $CDCl_3$) for **12a**



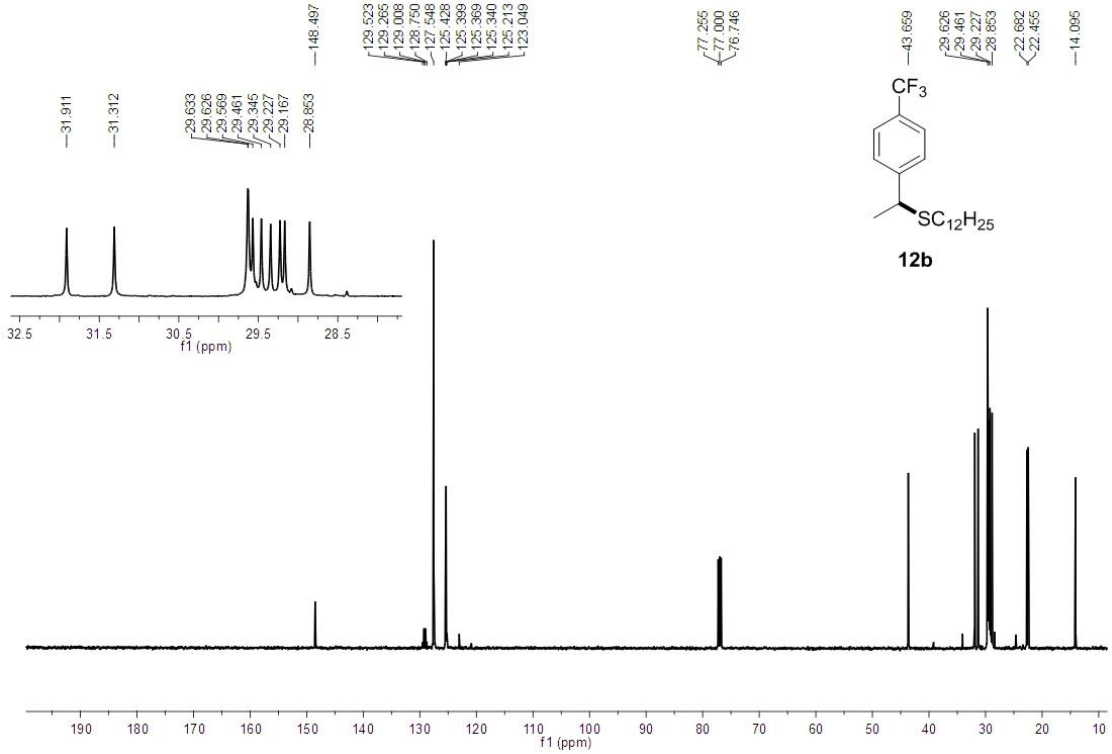
^{13}C NMR (125 MHz, $CDCl_3$) for **12a**



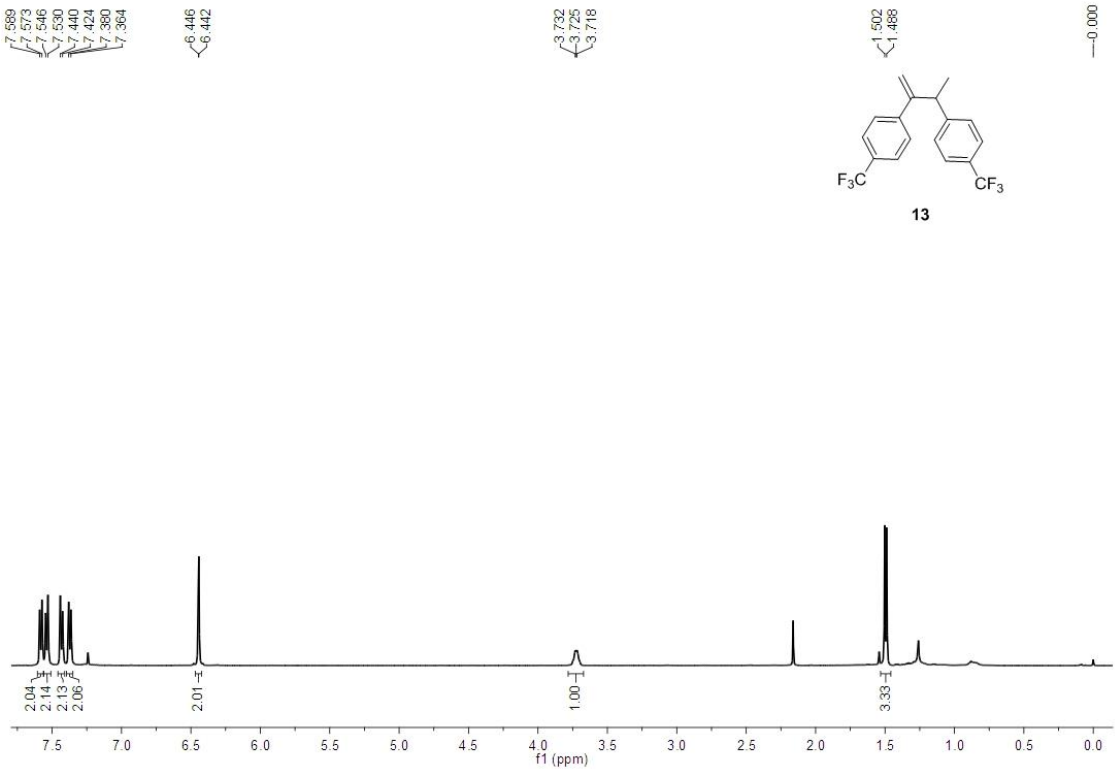
^{1}H NMR (500 MHz, $CDCl_3$) for **12b**



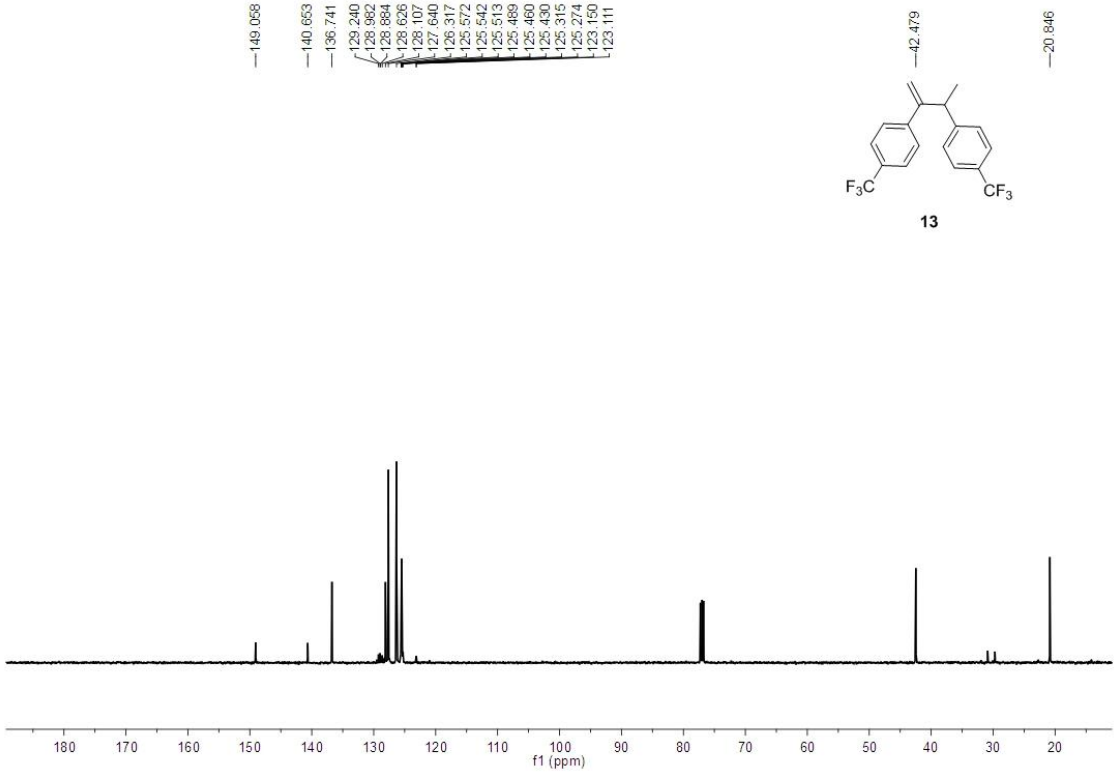
^{13}C NMR (125 MHz, $CDCl_3$) for **12b**



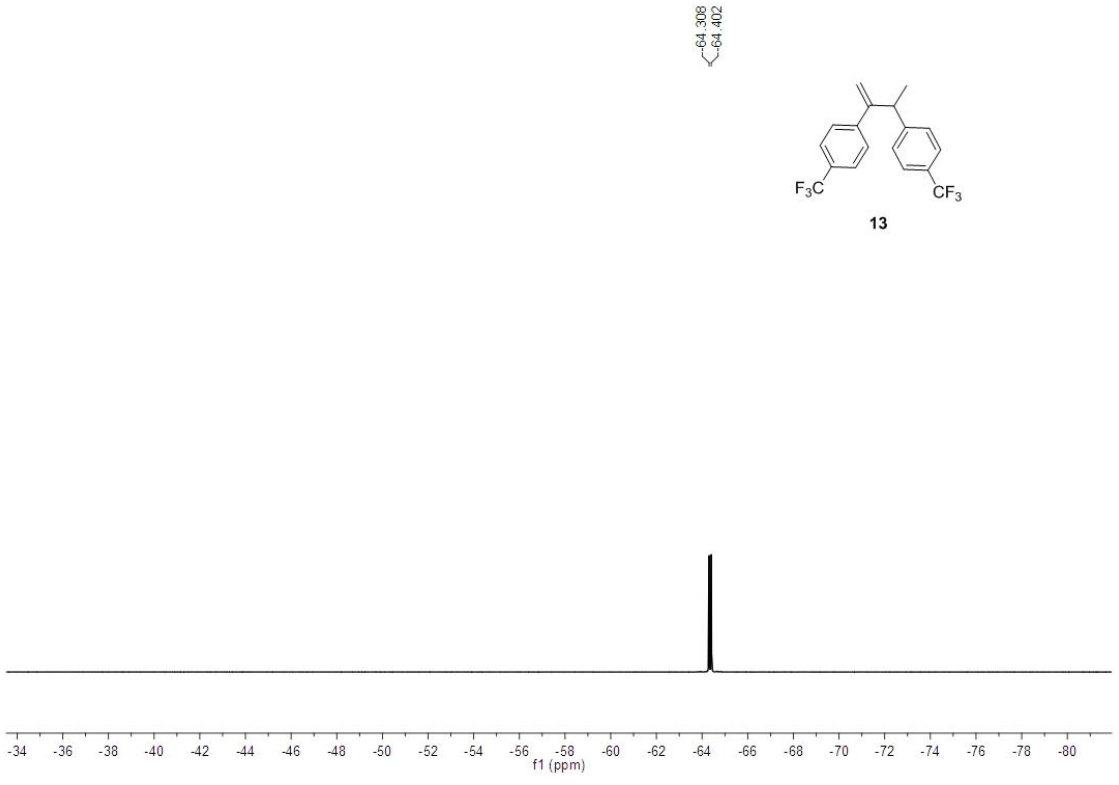
^{1}H NMR (500 MHz, $CDCl_3$) for **13**



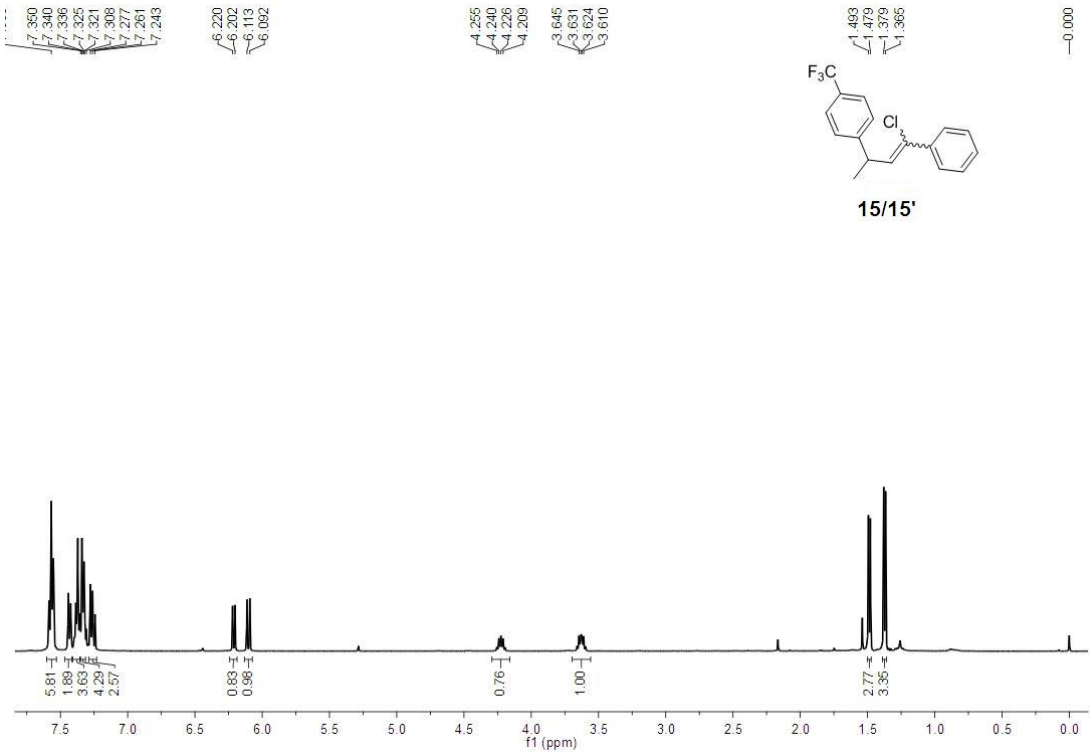
^{13}C NMR (125 MHz, $CDCl_3$) for **13**



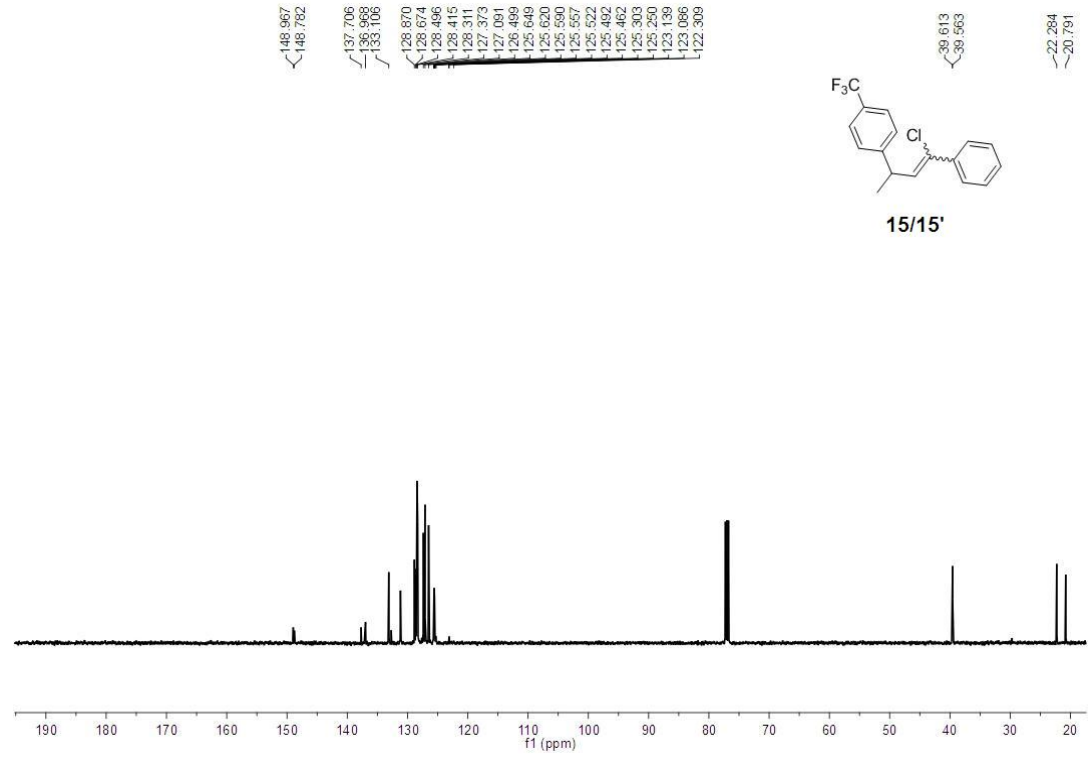
^{19}F NMR (470 MHz, $CDCl_3$) for **13**



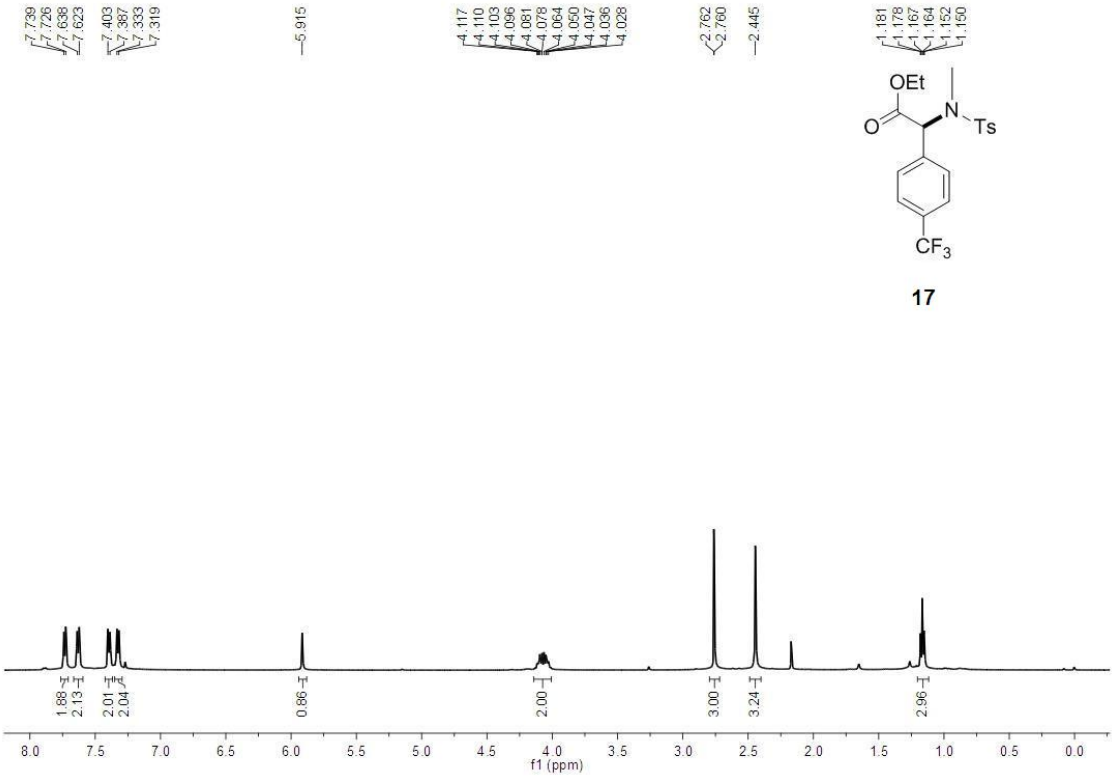
^{1}H NMR (500 MHz, $CDCl_3$) for **15/15'**



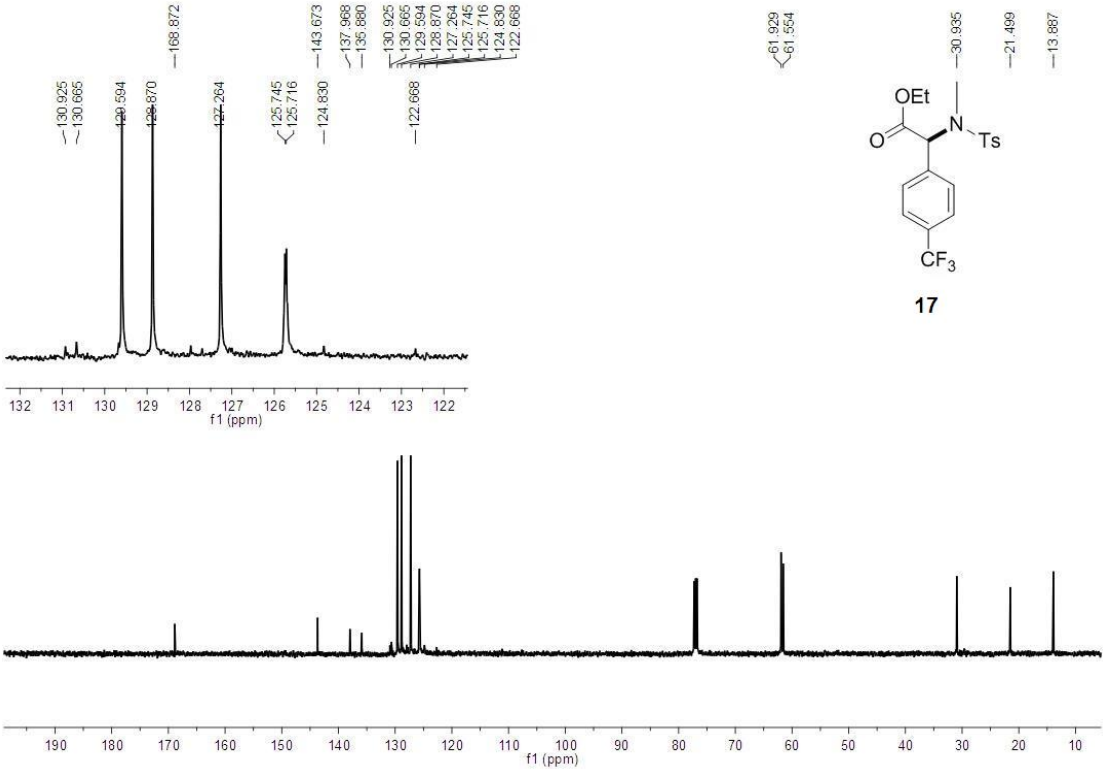
^{13}C NMR (125 MHz, $CDCl_3$) for **15/15'**



^{1}H NMR (500 MHz, $CDCl_3$) for **17**



^{13}C NMR (125 MHz, $CDCl_3$) for **17**



^{19}F NMR (470 MHz, $CDCl_3$) for **17**