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Supporting Information

Aryltrifluoromethylative Cyclization of Unactivated Alkenes by the Use of PhIClCF_3 under Catalyst-Free Condition

Jia Guo,^a Cong Xu,^b Xiaowei Liu,^a and Mang Wang^{*,a,c}

^a Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis, College of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun (China)

^b National Engineering Laboratory for Druggable Gene and Protein Screening, School of Life Sciences, Northeast Normal University, 2555 Jingyue Street, Changchun (China)

^c State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Weijin Road 94, Tianjin (China).
E-mail: wangm452@nenu.edu.cn.

Table of Contents

I. General Information	2
II. Screen of Reaction Conditions	2
III. Procedures for the synthesis of substrates	4
IV. Synthetic Procedures and Analytical Data	9
V. Mechanistic Study	12
VI. References.....	13
VIII. NMR Spectra.....	14

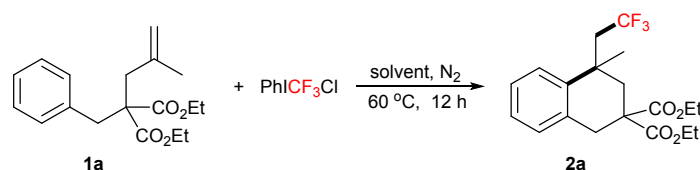
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I. General Information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. PIFA and TMSCF₃ were purchased from Energy Chemical Co. Ltd., Anhydrous MeCN, THF (Tetrahydrofuran), DMF (N, N-dimethylformamide), 1,4-dioxane were purchased from Innochem Co. Ltd., DCM (dichloromethane) was distilled over CaH₂ before use. The products were purified by column chromatography over silica gel (particle size 300-400 mesh ASTM, purchased from Taizhou, China). ¹H NMR, ¹³C NMR spectra were recorded at 25 °C on a Bruker 600 MHz or Varian 500 MHz, 400 MHz, and 151 MHz or 125 MHz spectrometer, respectively by using TMS as internal standard. ¹⁹F-NMR were recorded at 25 °C on a Bruker 565 MHz or Varian 470 MHz spectrometer by using (trifluoromethyl)benzene (δ -63.2 ppm) as external standard. Data for ¹H, ¹³C, ¹⁹F were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets). High-resolution mass spectra (HRMS) were obtained using a Bruker micro TOF II focus spectrometer (ESI). Melting points were uncorrected. PhICF₃Cl reagent was prepared according to literature procedures.^[1]

II. Screen of Reaction Conditions

Table S1. Screen of solvents.^[a]

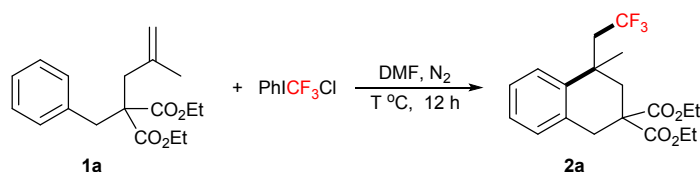


Entry	Solvent	Yield of 2a [%] ^[b]
1	MeCN	25
2	NMP	31
3	THF	44
4	1,4-dioxane	73
5	DCM	78
6	DMF	85

[a] Reaction conditions: **1a** (0.1 mmol), PhICF₃Cl (0.15 mmol), solvent (1 mL).

[b] ¹⁹F NMR yields using PhCF₃ as an internal standard.

Table S2. Screen of temperature.^[a]



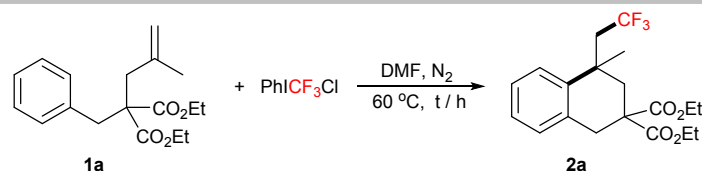
Entry	T [°C]	Yield of 2a [%] ^[b]
1	30	18
2	40	78
3	50	88
4	60	98

[a] Reaction conditions: **1a** (0.1 mmol), PhICF₃Cl (0.15 mmol), DMF (1 mL).

[b] ¹⁹F NMR yields using PhCF₃ as an internal standard.

Table S3. Screen of time.^[a]

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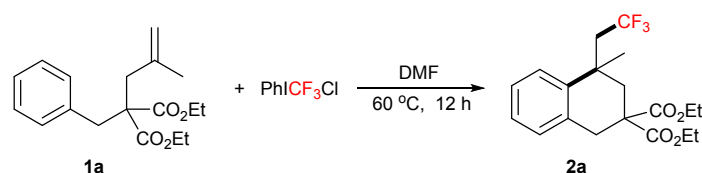


Entry	t	Yield of 2a [%] ^[b]
1	2h	32
2	4h	55
3	6h	68
4	8h	79
5	10h	87
6	12h	98

[a] Reaction conditions: **1a** (0.1 mmol), PhICF_3Cl (0.15 mmol), DMF (1 mL).

[b] ^{19}F NMR yields using PhCF_3 as an internal standard.

Table S4. Screen of reaction atmosphere.^[a]

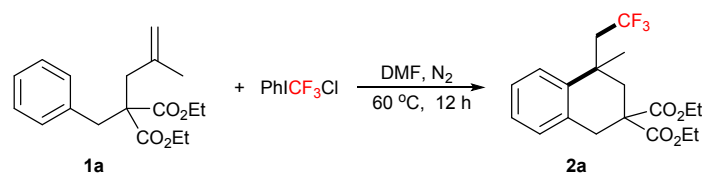


Entry	N_2 or Air	Yield of 2a [%] ^[b]
1	N_2	98
2	Air	51

[a] Reaction conditions: **1a** (0.1 mmol), PhICF_3Cl (0.15 mmol), DMF (1 mL).

[b] ^{19}F NMR yields using PhCF_3 as an internal standard.

Table S5. Screen of the ratio of **1a / PhICF_3Cl .**^[a]

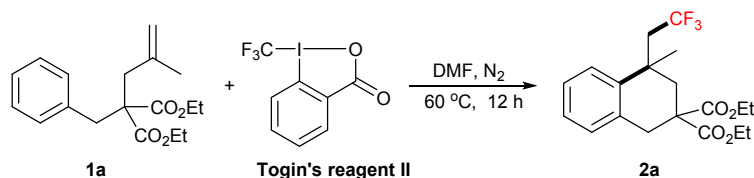


Entry	1a : PhICF_3Cl	Yield of 2a [%] ^[b]
1	1 : 1.2	87
2	1 : 1.5	98
3	1 : 2.0	98

[a] Reaction conditions: **1a** (0.1 mmol), PhICF_3Cl (x mmol), DMF (1 mL).

[b] ^{19}F NMR yields using PhCF_3 as an internal standard.

Table S6. Catalyst-free trifluoromethylation-carbocyclizations using Togni's reagent.^[a]



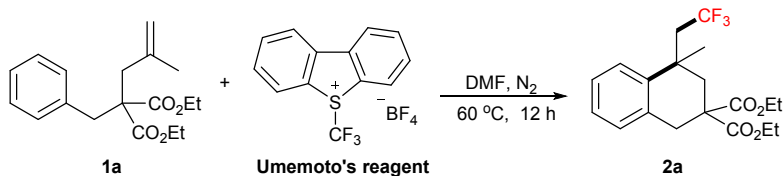
1a	Yield of 2a [%] ^[b]	Recovery of Togni's reagent II [%] ^[b]
	0	95

[a] Reaction conditions: **1a** (0.1 mmol), Togni's reagent II (0.15 mmol), DMF (1 mL).

[b] ^{19}F NMR yields using PhCF_3 as an internal standard.

Table S7. Catalyst-free trifluoromethylation-carbocyclizations using Umemoto's reagent.^[a]

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	Yield of 2a [%] ^[b]	Recovery of Umemoto's reagent [%] ^[b]
1a	0	99

[a] Reaction conditions: **1a** (0.1 mmol), **Umemoto's reagent II** (0.15 mmol), DMF (1 mL).

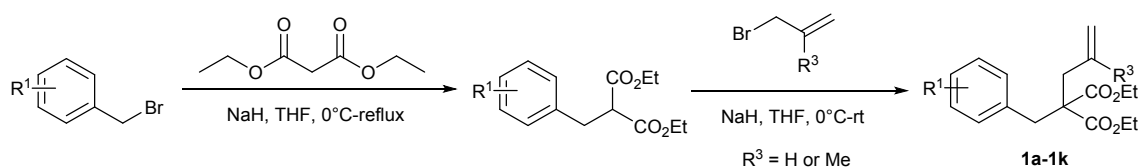
[b] ¹⁹F NMR yields using PhCF₃ as an internal standard.

III. Procedures for the synthesis of substrates

1. Synthesis of substrates 1.

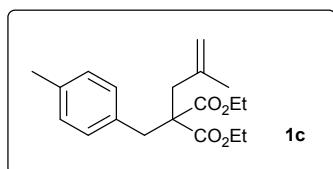
Substrates **1a-1q** were synthesized according to the literature, and the NMR spectroscopy were consistent with reported data.^[2,3] Substrates **1c**, **1e-1i**, **1l-1n** were new compounds synthesized according to the literature.^[2] The NMR spectroscopy were as follow:

Synthesis of substrates **1a-1k** (taking **1c** as an example):



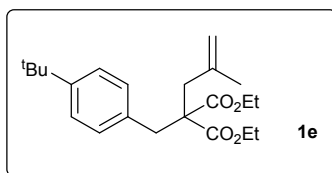
A 15 mL Schlenk tube was charged with a stir bar. The tube was evacuated and backfilled with N₂ (3 times). Diethyl malonate (0.92 mL, 6.0 mmol) was added drop-wise to a suspension of NaH (0.24 g, 60%, 6.0 mmol) in THF (5 mL) at 0 °C under N₂ and was stirred for 15 min. 1-(Bromomethyl)-4-methylbenzene (0.92 g, 5.0 mmol) was then added in one portion and the resulting milky mixture was stirred at reflux for 1 h. The reaction was then cooled and quenched by the addition of H₂O. THF was removed under reduced pressure and the resulting crude was dissolved in Et₂O and washed with water. The aqueous layer was extracted with Et₂O (3 x 10 mL), and the combined organics were washed with brine, dried over anhydrous MgSO₄ and concentrated under reduce pressure. Residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 15/1, v/v) to give 1.02 g (77%) of benzylated intermediate as a colourless oil. The NMR spectroscopy were consistent with reported data.^[2]

A 15 mL Schlenk tube was charged with a stir bar. The tube was evacuated and backfilled with N₂ (3 times). NaH (0.06 g, 60%, 1.5 mmol) was dissolved in dry THF (5 mL) under N₂ atmosphere. The benzylated intermediate (0.27g, 1.0 mmol) was added slowly. The suspension was stirred 0.5 h at room temperature and 3-bromo-2-methylprop-1-ene (0.13 mL 1.5 mmol) was added. Two hours later, the reaction was quenched with sat. NH₄Cl (10 mL). The reaction mixture was extracted with Et₂O (3x10 mL) and brine (3x10 mL), dried over anhydrous MgSO₄ and concentrated under reduce pressure. Residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 15/1, v/v) to give **1c** as a colourless oil.

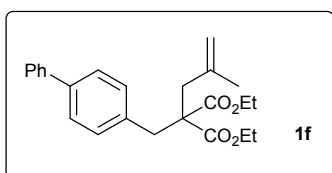


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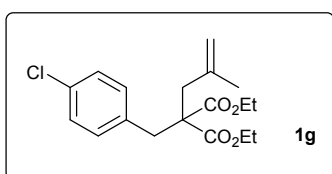
Diethyl-2-(2-methylallyl)-2-(4-methylbenzyl)malonate (1c). 254.6 mg, 80% yield. Colourless oil. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ = 7.03 (dd, J = 22.2 Hz, 7.8 Hz, 4H), 4.91 (s, 1H), 4.81 (s, 1H), 4.11 - 4.19 (m, 4H), 3.27 (s, 2H), 2.62 (s, 2H), 2.30 (s, 3H), 1.72 (s, 3H), 1.22 (t, J = 7.2 Hz, 6H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ = 171.2, 171.1, 141.2, 136.3, 133.3, 130.0, 130.0, 128.9, 128.8, 114.9, 61.2, 60.2, 58.5, 40.1, 38.4, 38.2, 23.8, 21.0, 13.9. HRMS (ESI): Calcd for $[\text{C}_{19}\text{H}_{26}\text{O}_4, \text{M}+\text{Na}]^+$: 341.1723, measured: 341.1730.



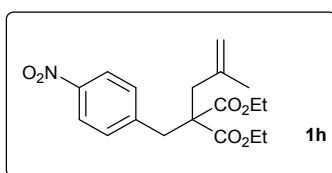
Diethyl-2-(4-(tert-butyl)benzyl)-2-(2-methylallyl)malonate (1e). 281.2 mg, 78% yield. Light yellow oil. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ = 7.25 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 4.91 (t, J = 1.2 Hz, 1H), 4.81 (s, 1H), 4.09 - 4.17 (m, 4H), 3.27 (s, 2H), 2.64 (s, 2H), 1.73 (s, 3H), 1.28 (s, 9H), 1.20 (t, J = 7.2 Hz, 6H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ = 171.3 (2C), 149.6, 141.1, 133.3, 129.8 (2C), 125.0 (2C), 115.0, 61.2 (2C), 58.5, 40.3, 38.2, 34.4, 31.3 (3C), 23.8, 13.9 (2C). HRMS (ESI): Calcd for $[\text{C}_{22}\text{H}_{32}\text{O}_4, \text{M}+\text{Na}]^+$: 383.2193, measured: 383.2191.



Diethyl-2-([1,1'-biphenyl]-4-ylmethyl)-2-(2-methylallyl)malonate (1f). 323.5 mg, 85% yield. Colourless oil. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ = 7.56 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H), 4.94 (s, 1H), 4.84 (s, 1H), 4.12 - 4.20 (m, 4H), 3.34 (s, 2H), 2.68 (s, 2H), 1.75 (s, 3H), 1.22 (t, J = 7.2 Hz, 6H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ = 171.2 (2C), 141.1, 140.9, 139.7, 135.6, 130.5 (2C), 128.7 (2C), 127.2, 127.0 (2C), 126.8 (2C), 115.0, 61.3 (2C), 58.5, 40.4, 38.4, 23.8, 14.0 (2C). HRMS (ESI): Calcd for $[\text{C}_{24}\text{H}_{28}\text{O}_4, \text{M}+\text{Na}]^+$: 403.1880, measured: 403.1868.



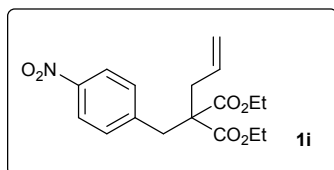
Diethyl-2-(4-chlorobenzyl)-2-(2-methylallyl)malonate (1g). 254.0 mg, 75% yield. White solid. mp: 46-47 °C. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ = 7.54 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.94 (s, 1H), 4.80 (s, 1H), 4.08 - 4.18 (m, 4H), 3.31 (s, 2H), 2.66 (s, 2H), 1.71 (s, 3H), 1.20 (t, J = 7.2 Hz, 6H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ = 170.7 (2C), 142.5, 140.5, 131.8 (2C), 131.0 (2C), 115.5, 110.8, 61.5 (2C), 58.2, 41.0, 38.8, 23.5, 13.9 (2C). HRMS (ESI): Calcd for $[\text{C}_{18}\text{H}_{23}\text{ClO}_4, \text{M}+\text{Na}]^+$: 361.1177, measured: 361.1180.



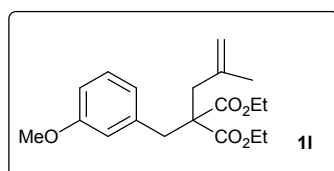
Diethyl-2-(2-methylallyl)-2-(4-nitrobenzyl)malonate (1h). 262.0 mg, 75% yield. White solid. mp: 38-39 °C. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ = 8.11 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 4.95 (s, 1H), 4.81 (s, 1H), 4.09 - 4.19 (m, 4H), 3.36 (s, 2H), 2.67 (s, 2H),

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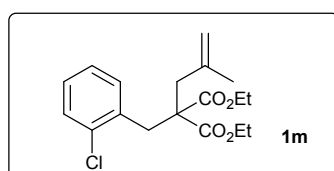
1.72 (s, 3H), 1.20 (t, $J = 7.2$ Hz, 6H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): $\delta = 170.7$ (2C), 147.0, 144.6, 140.5, 131.1 (2C), 123.2 (2C), 115.5, 61.6 (2C), 58.2, 41.0, 38.6, 23.5, 13.9 (2C). HRMS (ESI): Calcd for $[\text{C}_{18}\text{H}_{23}\text{NO}_6, \text{M}+\text{Na}]^+$: 372.1418, measured: 372.1423.



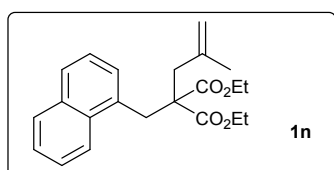
Diethyl-2-allyl-2-(4-nitrobenzyl) malonate (1i). 251.4 mg, 75 % yield. White solid. mp: 66-67 °C. $^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 8.13$ (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.69 - 5.76 (m, 1H), 5.16 - 5.21 (m, 2H), 4.13 - 4.23 (m, 4H), 3.32 (s, 2H), 2.58 (d, $J = 7.2$ Hz, 2H), 1.24 (t, $J = 7.2$ Hz, 6H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): $\delta = 170.2$ (2C), 147.1, 144.2, 132.0, 131.0 (2C), 123.4 (2C), 119.8, 61.6 (2C), 58.6, 38.1, 37.0, 14.0 (2C). HRMS (ESI): Calcd for $[\text{C}_{17}\text{H}_{21}\text{NO}_6, \text{M}+\text{Na}]^+$: 358.1261, measured: 358.1265.



Diethyl-2-(3-methoxybenzyl)-2-(2-methylallyl)malonate (1l). 260.6 mg, 78 % yield. Colourless oil. $^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 7.15$ (t, $J = 7.8$ Hz, 1H), 6.76 (d, $J = 8.4$ Hz, 1H), 6.71 (d, $J = 9.0$ Hz, 2H), 4.92 (s, 1H), 4.82 (s, 1H), 4.11 - 4.19 (m, 4H), 3.76 (s, 3H), 3.28 (s, 2H), 2.65 (s, 2H), 1.73 (s, 3H), 1.22 (t, $J = 7.2$ Hz, 6H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): $\delta = 171.2$ (2C), 159.3, 141.1, 137.9, 129.0, 122.5, 115.9, 114.9, 112.2, 61.3 (2C), 58.3, 55.1, 40.1, 38.6, 23.8, 14.0 (2C). HRMS (ESI): Calcd for $[\text{C}_{19}\text{H}_{26}\text{O}_5, \text{M}+\text{Na}]^+$: 357.1672, measured: 357.1679.



Diethyl-2-(2-chlorobenzyl)-2-(2-methylallyl)malonate (1m). **1m** can't be completely separated from the reaction mixture. 202.9 mg, 60 % yield. Colourless oil. $^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 7.34 - 7.35$ (m, 1H), 7.30 - 7.32 (m, 1H), 7.12 - 7.17 (m, 2H), 4.89 (s, 1H), 4.77 (s, 1H), 4.07 - 4.18 (m, 4H), 3.50 (s, 2H), 2.73 (s, 2H), 1.72 (s, 3H), 1.17 (t, $J = 7.2$ Hz, 6H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): $\delta = 171.1$ (2C), 141.1, 135.2, 134.9, 131.8, 129.4, 128.0, 126.4, 114.6, 61.4 (2C), 57.7, 41.4, 35.5, 23.9, 13.8 (2C). HRMS (ESI): Calcd for $[\text{C}_{18}\text{H}_{23}\text{ClO}_4, \text{M}+\text{Na}]^+$: 361.1177, measured: 361.1174.

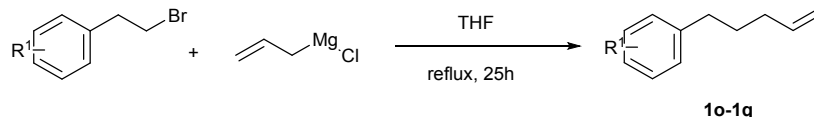


Diethyl-2-(2-methylallyl)-2-(naphthalen-1-ylmethyl)malonate (1n). 301.3 mg, 85% yield. Colourless oil. $^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 8.07$ (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 9.6$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.40 - 7.46 (m, 3H), 7.36 (t, $J = 8.4$ Hz, 1H), 4.94

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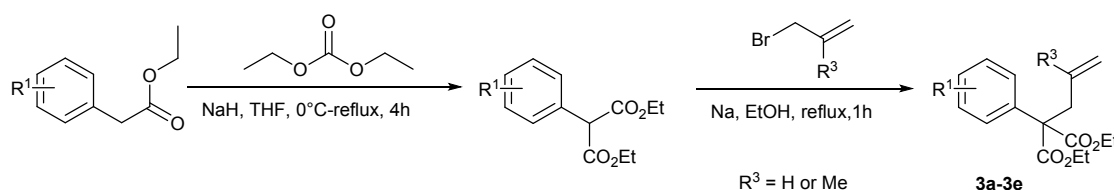
(s, 1H), 4.86 (s, 1H), 3.96 - 4.02 (m, 2H), 3.87 - 3.93 (m, 2H), 3.83 (s, 2H), 2.76 (s, 2H), 1.73 (s, 3H), 1.05 (t, $J = 7.2$ Hz, 6H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): $\delta = 171.4$ (2C), 141.4, 133.8, 133.2, 132.9, 128.7, 128.1, 127.5, 125.6, 125.4, 125.1, 124.0, 114.3, 61.3 (2C), 58.3, 41.1, 34.2, 24.0, 13.7 (2C). HRMS (ESI): Calcd for $[\text{C}_{22}\text{H}_{26}\text{O}_4, \text{M}+\text{Na}]^+$: 377.1723, measured: 377.1730.

Synthesis of substrates **1o-1q**:^[3]



2. Synthesis of substrates **3**.

Substrates **3a-3e** were synthesized according to the literature, and the NMR spectroscopy were consistent with reported data.^[2]

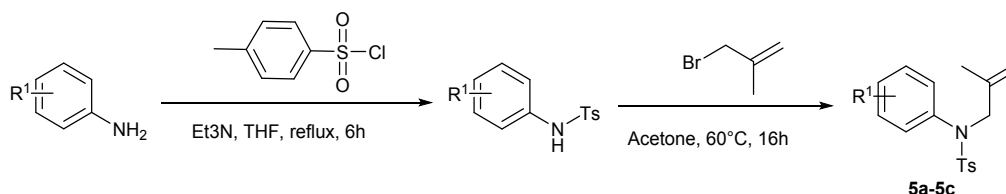


3. Synthesis of substrates **5**.

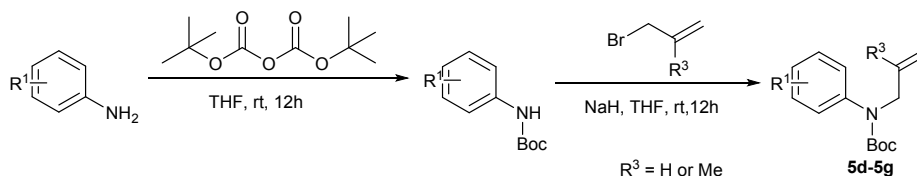
Substrates **5a-5i** were synthesized according to the literature, and the NMR spectroscopy were consistent with reported data.^[4,5,6,7]

Substrates **5d-5f** were new compounds synthesized according to the literature.^[5] The NMR spectroscopy were as follow:

Synthesis of substrates **5a-5c**:



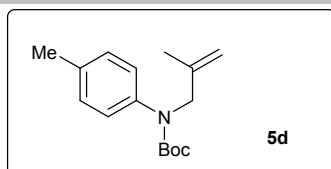
Synthesis of substrate **5d-5g** (taking **5d** as an example):



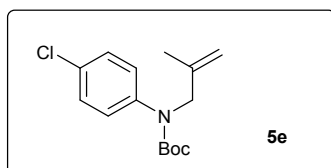
A solution of *p*-toluidine (0.54g, 5.0 mmol) and di-*tert*-butyl dicarbonate (1.28 mL, 6.0 mmol) in 20 mL of dry THF was stirred for 12 h at room temperature. The crude mixture was concentrated under reduced pressure, and purified by silica column chromatography (eluent: petroleum ether/EtOAc = 9/1, v/v) to give 0.88 g (85%) of *tert*-butyl *p*-tolylcarbamate as a white solid. The yield and NMR spectroscopy were consistent with reported data.^[5]

A solution of *tert*-butyl *p*-tolylcarbamate (0.83 g, 4.0 mmol) and NaH (0.19 g, 60%, 4.8 mmol) in 15 mL of dry THF was stirred at 0 °C under N_2 for 15 min. 3-Bromo-2-methylprop-1-ene (0.60 mL, 6.0 mmol) was added and the reaction was stirred at room temperature for 12 h. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were rinsed with brine, dried over anhydrous MgSO_4 and concentrated under reduced pressure. Residues were purified by silica column chromatography (eluent: petroleum ether/EtOAc = 15/1, v/v) to give **5d** as a colourless oil.

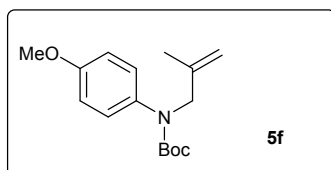
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Tert-butyl (2-methylallyl)(p-tolyl)carbamate (5d). 835.7 mg, 80 % yield. Colourless oil. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ = 7.10 - 7.13 (m, 4H), 4.83 (s, 1H), 4.80 (s, 1H), 4.14 (s, 2H), 2.31 (s, 3H), 1.74 (s, 3H), 1.44 (s, 9H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ = 154.8, 141.7, 140.3, 135.2, 129.1 (2C), 125.9 (2C), 111.3, 80.2, 55.9, 28.3 (3C), 20.9, 20.1. HRMS (ESI): Calcd for $[\text{C}_{16}\text{H}_{23}\text{NO}_2, \text{M}+\text{Na}]^+$: 284.1621, measured: 284.1630.

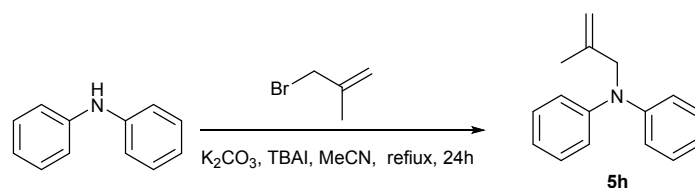


Tert-butyl (4-chlorophenyl)(2-methylallyl)carbamate (5e). 865.8 mg, 77 % yield. Colourless oil. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ = 7.25 - 7.26 (m, 2H), 7.17 (d, J = 7.8 Hz, 2H), 4.86 (s, 1H), 4.78 (s, 1H), 4.14 (s, 2H), 1.74 (s, 3H), 1.44 (s, 9H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ = 154.4, 141.4, 130.9, 128.6, (2C) 127.2, 111.6, 80.7, 55.7, 28.2 (3C), 20.1. HRMS (ESI): Calcd for $[\text{C}_{15}\text{H}_{20}\text{ClNO}_2, \text{M}+\text{Na}]^+$: 304.1075, measured: 304.1084

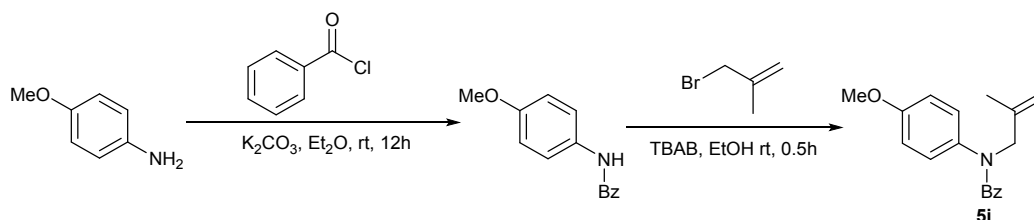


Tert-butyl (4-methoxyphenyl)(2-methylallyl)carbamate (5f). 909.1 mg, 82 % yield. Colourless oil. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ = 7.13 (s, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.83 (s, 1H), 4.79 (s, 1H), 4.12 (s, 2H), 3.78 (s, 3H), 1.75 (s, 3H), 1.43 (s, 9H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ = 157.3, 155.0, 141.7, 135.8, 127.5 (2C), 113.7 (2C), 111.6, 80.1, 56.2, 55.4, 28.3 (3C), 20.1. HRMS (ESI): Calcd for $[\text{C}_{16}\text{H}_{23}\text{NO}_3, \text{M}+\text{Na}]^+$: 300.1570, measured: 300.1578.

Synthesis of substrate **5h**:^[6]



Synthesis of substrate **5i**:^[7]



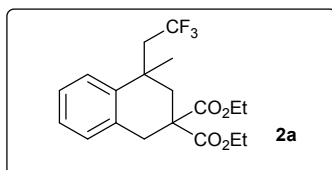
IV. Synthetic Procedures and Analytical Data

Typical procedures for catalyst-free intramolecular aryltrifluoromethylation of unactivated alkenes (taking **1a** as an example):

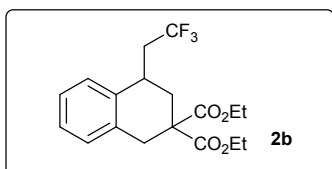
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To a dried polytetrafluoroethylene (PTFE) sealed pressure tube was added **1a** (91.3 mg, 0.3 mmol), PhICF_3Cl (138.6 mg, 4.5 mmol) and anhydrous DMF (3.0 mL) in sequence under N_2 . After the reaction mixture was stirred at 60 °C for 12 h, PhCF_3 (30 μL , 0.2436 mmol) was added as the internal standard and the NMR yield of **2a** was calculated from ^{19}F -NMR integrals. Then the mixture was washed with water and brine, extracted by CH_2Cl_2 . The combined organic phase was dried over anhydrous MgSO_4 and concentrated under reduce pressure. The residue was purified by silica column chromatography (eluent: petroleum ether/EtOAc = 20/1 to 15/1, v/v) to give **2a** as a yellow oil.^[8]

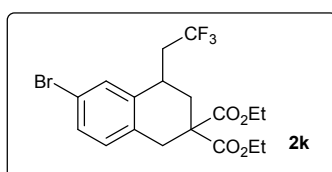
Analytical data for compounds 2a-2o:



Diethyl 4-methyl-4-(2,2,2-trifluoroethyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate (2a). 100.5 mg, 90% yield. Colourless oil.^[8] **$^1\text{H-NMR}$** (600 MHz, CDCl_3): δ = 7.24 (d, J = 7.8 Hz, 1H), 7.19 - 7.22 (m, 1H), 7.14 - 7.17 (m, 2H), 4.06 - 4.24 (m, 4H), 3.32 (d, J = 16.2 Hz, 1H), 3.32 (d, J = 16.2 Hz, 1H), 2.65 (d, J = 15.0 Hz, 1H), 2.47 - 2.56 (m, 1H), 2.34 - 2.44 (m, 2H), 1.42 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H). **$^{13}\text{C-NMR}$** (151 MHz, CDCl_3): δ = 171.7, 171.2, 140.8, 133.2, 129.1, 126.9, 126.8, 126.4 (q, J = 277.5 Hz), 126.0, 61.7, 61.5, 52.5, 45.9 (q, J = 25.7 Hz), 39.7, 35.2, 35.1, 29.6 (q, J = 0.9 Hz), 13.9, 13.9. **$^{19}\text{F-NMR}$** (565 MHz, CDCl_3): δ = -58.8 (t, J = 11.3 Hz). HRMS (ESI): Calcd for $[\text{C}_{19}\text{H}_{23}\text{F}_3\text{O}_4, \text{M}+\text{Na}]^+$: 395.1441, measured: 395.1421.



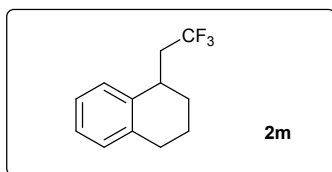
Diethyl 4-(2,2,2-trifluoroethyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate (2b). 91.3 mg, 85% yield. Yellow oil.^[8] **$^1\text{H-NMR}$** (600 MHz, CDCl_3): δ = 7.13 - 7.21 (m, 4H), 4.20 - 4.24 (m, 2H), 4.06 - 4.15 (m, 2H), 3.32 - 3.37 (m, 2H), 3.19 (d, J = 15.6 Hz, 1H), 2.84 (dd, J = 13.8 Hz, 6.0 Hz, 1H), 2.72 - 2.79 (m, 1H), 2.23 - 2.33 (m, 1H), 1.97 (dd, J = 13.8 Hz, 10.2 Hz, 1H), 1.27 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H). **$^{13}\text{C-NMR}$** (151 MHz, CDCl_3): δ = 171.5, 170.3, 136.2, 134.1, 129.3, 127.3 (q, J = 277.7 Hz), 126.9, 126.8, 126.7, 61.8, 61.4, 53.7, 40.9 (q, J = 27.3 Hz), 35.2, 34.8, 30.5 (q, J = 2.6 Hz), 14.0, 13.9. **$^{19}\text{F-NMR}$** (565 MHz, CDCl_3): δ = -63.5 (t, J = 10.7 Hz). HRMS (ESI): Calcd for $[\text{C}_{18}\text{H}_{21}\text{F}_3\text{O}_4, \text{M}+\text{Na}]^+$: 381.1284, measured: 381.1294.



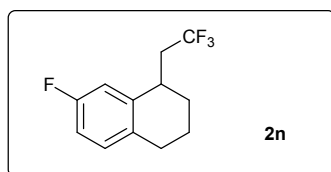
Diethyl 6-bromo-4-(2,2,2-trifluoroethyl)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate (2k). 65.6 mg, 50% yield. Yellow oil.^[8] **$^1\text{H-NMR}$** (600 MHz, CDCl_3): δ = 7.28 - 7.30 (m, 2H), 7.02 (d, J = 7.8 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 4.07 - 4.17 (m, 2H), 3.28 - 3.32

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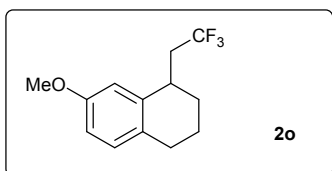
(m, 2H), 3.11 (d, $J = 16.2$ Hz, 1H), 2.82 (dd, $J = 13.8$ Hz, 7.2 Hz, 1H), 2.68 - 2.76 (m, 1H), 2.24 - 2.33 (m, 1H), 1.95 (dd, $J = 13.2$ Hz, 3.0 Hz, 1H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.15 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): $\delta = 171.2, 170.1, 138.5, 133.2, 130.9, 129.9, 129.8, 126.6$ (q, $J = 277.8$ Hz), 120.5, 61.9, 61.6, 53.4, 40.6 (q, $J = 27.6$ Hz), 34.7, 34.4, 30.5 (q, $J = 2.3$ Hz), 14.0, 13.9. $^{19}\text{F-NMR}$ (565 MHz, CDCl_3): $\delta = -63.4$ (t, $J = 10.7$ Hz). HRMS (ESI): Calcd for $[\text{C}_{18}\text{H}_{20}\text{BrF}_3\text{O}_4, \text{M}+\text{Na}]^+$: 459.0389, measured: 459.0381.



1-(2,2,2-Trifluoroethyl)-1,2,3,4-tetrahydronaphthalene (2m). **2m** was volatile and difficult to be isolated from the reaction mixture. $^{19}\text{F-NMR}$ yield: 80%. Colorless oil. Its NMR spectroscopy were consistent with the literature data.^[8] $^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 6.99 - 7.06$ (m, 4H), 3.12 - 3.14 (m, 1H), 2.64 - 2.74 (m, 2H), 2.24 - 2.43 (m, 2H), 1.84 - 1.90 (m, 1H), 1.77 - 1.83 (m, 1H), 1.70 - 1.76 (m, 2H). $^{19}\text{F-NMR}$ (565 MHz, CDCl_3): $\delta = -63.8$ (t, $J = 11.3$ Hz).



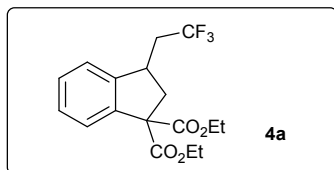
7-Fluoro-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydronaphthalene (2n). **2n** was volatile and difficult to be isolated from the reaction mixture. $^{19}\text{F-NMR}$ yield: 71%. Colorless oil. Its NMR spectroscopy were consistent with the literature data.^[8] $^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 7.02 - 7.04$ (m, 1H), 6.82 - 6.85 (m, 2H), 3.16 - 3.20 (m, 1H), 2.67 - 2.78 (m, 2H), 2.33 - 2.48 (m, 2H), 1.92 - 1.97 (m, 1H), 1.77 - 1.87 (m, 3H). $^{13}\text{C-NMR}$ (151 MHz, CDCl_3): $\delta = 161.1$ (d, $J = 343.7$ Hz), 140.4, 132.6, 130.7 (d, $J = 7.7$ Hz), 126.8 (q, $J = 277.7$ Hz), 114.7 (d, $J = 20.8$ Hz), 113.5 (d, $J = 21.1$ Hz), 40.7 (q, $J = 27.0$ Hz), 32.4, 28.6, 27.5, 19.1. $^{19}\text{F-NMR}$ (565 MHz, CDCl_3): $\delta = -63.9$ (t, $J = 10.8$ Hz, 3F), -117.0 (q, $J = 7.1$ Hz, 1F).



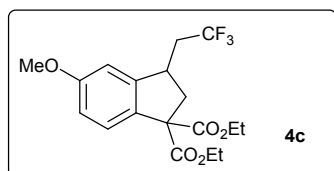
7-Methoxy-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydronaphthalene (2o). **2o** was volatile and difficult to be isolated from the reaction mixture. $^{19}\text{F-NMR}$ yield: 89%. Colorless oil. Its NMR spectroscopy were consistent with the literature data.^[8] $^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 6.82 - 6.86$ (m, 1H), 6.72 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 6.66 (d, $J = 2.4$ Hz, 1H), 3.78 (s, 3H), 3.15 - 3.19 (m, 1H), 2.65 - 2.75 (m, 2H), 2.32 - 2.50 (m, 2H), 1.90 - 1.96 (m, 1H), 1.83 - 1.87 (m, 1H), 1.73 - 1.80 (m, 2H). $^{19}\text{F-NMR}$ (565 MHz, CDCl_3): $\delta = -63.9$ (t, $J = 12.2$ Hz).

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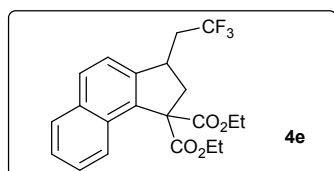
Analytical data for compounds 4a-4f:



Diethyl-3-(2,2,2-trifluoroethyl)-2,3-dihydro-1H-indene-1,1-dicarboxylate (4a). 69.2 mg, 67% yield. Colourless oil.^[8] **¹H-NMR** (600 MHz, CDCl₃): δ = 7.61 (d, J = 7.2 Hz, 1H), 7.30 - 7.37 (m, 2H), 7.20 (d, J = 7.2 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 4.14 - 4.24 (m, 2H), 3.60 - 3.65 (m, 1H), 3.09 (dd, J = 13.8 Hz, 7.8 Hz, 1H), 2.66 - 2.75 (m, 1H), 2.45 (dd, J = 13.2 Hz, 7.2 Hz, 1H), 2.23 - 2.33 (m, 1H), 1.30 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H). **¹³C-NMR** (151 MHz, CDCl₃): δ = 170.5, 170.1, 144.8, 139.0, 129.0, 127.7, 127.0, 126.7 (q, J = 275.6 Hz), 123.4, 64.8, 61.9, 61.8, 40.6, 39.2 (q, J = 27.8 Hz), 37.0 (q, J = 2.6 Hz), 14.1, 14.0. **¹⁹F-NMR** (565 MHz, CDCl₃): δ = -64.4 (t, J = 10.7 Hz). HRMS (ESI): Calcd for [C₁₇H₁₉F₃O₄, M+Na]⁺: 367.1128, measured: 367.1135.

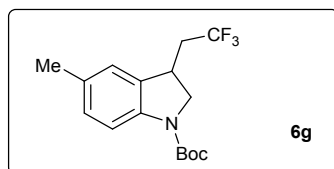


Diethyl-5-methoxy-3-(2,2,2-trifluoroethyl)-2,3-dihydro-1H-indene-1,1-dicarboxylate (4c). **4c** can't be completely separated from **3c**. **¹⁹F-NMR** yield: 72%. Colorless oil.^[8] **¹H-NMR** (600 MHz, CDCl₃): δ = 7.49 (d, J = 9.0 Hz, 1H), 6.85 - 6.87 (m, 1H), 6.70 (d, J = 2.4 Hz, 1H), 4.22 - 4.27 (m, 2H), 4.15 - 4.21 (m, 2H), 3.81 (s, 3H), 3.55 - 3.60 (m, 1H), 3.07 (dd, J = 13.8 Hz, 7.8 Hz, 1H), 2.62 - 2.71 (m, 1H), 2.45 (dd, J = 13.8 Hz, 7.8 Hz, 1H), 2.23 - 2.33 (m, 1H), 1.29 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H). **¹³C-NMR** (151 MHz, CDCl₃): δ = 170.7, 170.4, 160.7, 146.4, 131.0, 128.5 (q, J = 277.2 Hz), 127.7, 113.9, 108.6, 64.0, 61.8, 61.8, 55.5, 40.9, 39.1 (q, J = 28.7 Hz), 37.0 (q, J = 2.7 Hz), 14.1, 14.0. **¹⁹F-NMR** (565 MHz, CDCl₃): δ = -64.4 (t, J = 11.3 Hz). HRMS (ESI): Calcd for [C₁₈H₂₁F₃O₅, M+Na]⁺: 367.1128, measured: 367.1135.



Diethyl-3-(2,2,2-trifluoroethyl)-2,3-dihydro-1H-cyclopenta[a]naphthalene-1,1-dicarboxylate (4e). 76.9 mg, 65% yield. Yellow oil.^[8] **¹H-NMR** (600 MHz, CDCl₃): δ = 7.85 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.2 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.45 (t, J = 7.2 Hz, 1H), 7.37 (d, J = 7.2 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 4.26 - 4.30 (m, 1H), 4.15 - 4.20 (m, 1H), 3.46 - 3.50 (m, 1H), 3.10 (dd, J = 13.2 Hz, 3.6 Hz, 1H), 2.97 - 3.06 (m, 1H), 2.51 (t, J = 12.0 Hz, 1H), 2.37 - 2.46 (m, 1H), 1.33 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H). **¹³C-NMR** (151 MHz, CDCl₃): δ = 171.3, 170.2, 134.7, 134.0, 130.2, 128.8, 128.6, 127.6, 127.0 (q, J = 275.7 Hz), 126.3, 125.5, 125.3, 122.3, 62.1, 62.1, 59.7, 38.1 (q, J = 27.6 Hz), 34.9, 30.4 (q, J = 2.4 Hz), 14.0, 13.9. **¹⁹F-NMR** (565 MHz, CDCl₃): δ = -62.8 (t, J = 11.3 Hz). HRMS (ESI): Calcd for [C₂₁H₂₁F₃O₄, M+Na]⁺: 417.1284, measured: 417.1291.

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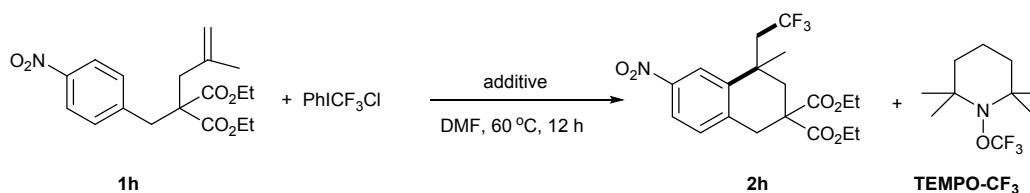


Tert-butyl-5-methyl-3-(2,2,2-trifluoroethyl)indoline-1-carboxylate (6g). 60.5 mg, 64% yield. Colorless oil.^[8] ¹H-NMR (600 MHz, CDCl₃): δ = 7.36 - 7.74 (br. 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.94 (s, 1H), 4.20 (s, 1H), 3.74 (s, 1H), 3.57 - 3.61 (m, 1H), 2.56 - 2.65 (m, 1H), 2.26 - 2.35 (m, 4H), 1.56 (s, 9H). ¹³C-NMR (151 MHz, CDCl₃): δ = 152.2, 132.1, 129.0, 127.1, 126.5 (q, *J* = 277.5 Hz), 124.3, 124.2, 114.7, 81.4, 65.9, 53.8, 39.2 (q, *J* = 27.6 Hz), 28.5 (3C), 20.9. ¹⁹F-NMR (470 MHz, CDCl₃): δ = -64.8 (t, *J* = 11.3 Hz). HRMS (ESI): Calcd for [C₁₆H₂₀F₃NO₂, M+Na]⁺: 338.1338, measured: 338.1346.

V. Mechanistic Study

Experimental Procedures: To a dried polytetrafluoroethene (PTFE) sealed pressure tube was added alkene **1h** (67.1 mg, 0.2 mmol), PhICF₃Cl (92.4 mg, 0.3 mmol), TEMPO/BHT and anhydrous DMF (2 mL) in sequence under N₂. The reaction mixture was stirred at 60 °C for 12 h, monitored by ¹⁹F NMR using PhCF₃ (20 μL, 0.1564 mmol) as the internal standard.

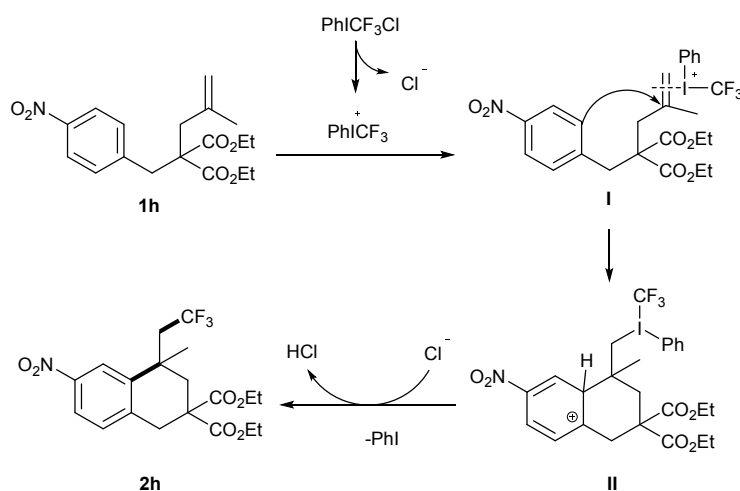
Table S8. Control experiments for trifluoromethylation of unactivated alkenes.^[a]



Entry	additive	eq	Yield of 2h [%] ^[b]	TEMPO-CF ₃ [%] ^[b]
1	--	--	91	--
2	TEMPO	1.5	59	0
3	BHT	1.5	90	--

[a] Reaction conditions: **1h** (0.2 mmol), PhICF₃Cl (0.30 mmol), DMF (2 mL)

[b] ¹⁹F NMR yields using PhCF₃ as an internal standard.



Plausible mechanistic:

Based on the above experimental results (**Table S7**), an ionic process is proposed as shown in **Scheme S1**. The unactivation of the alkene double bond of **1h** by [PhICF₃]⁺ affords iodonium complex I. Then exo-cyclization occurs via an attack of the aryl group affording

SUPPORTING INFORMATION

cyclic intermediate **II**. Finally, the deprotonation of **II** gives trifluoromethylated product **2h** along with the elimination of PhI.

VI. References

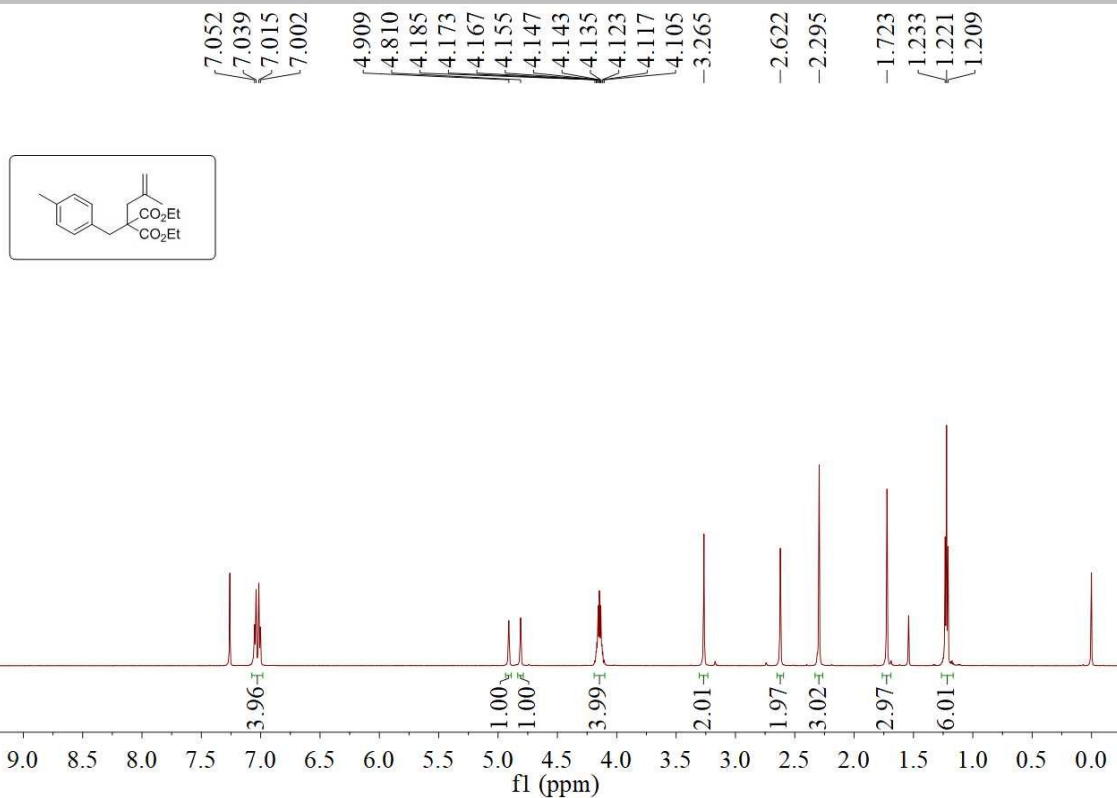
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VIII. NMR Spectra

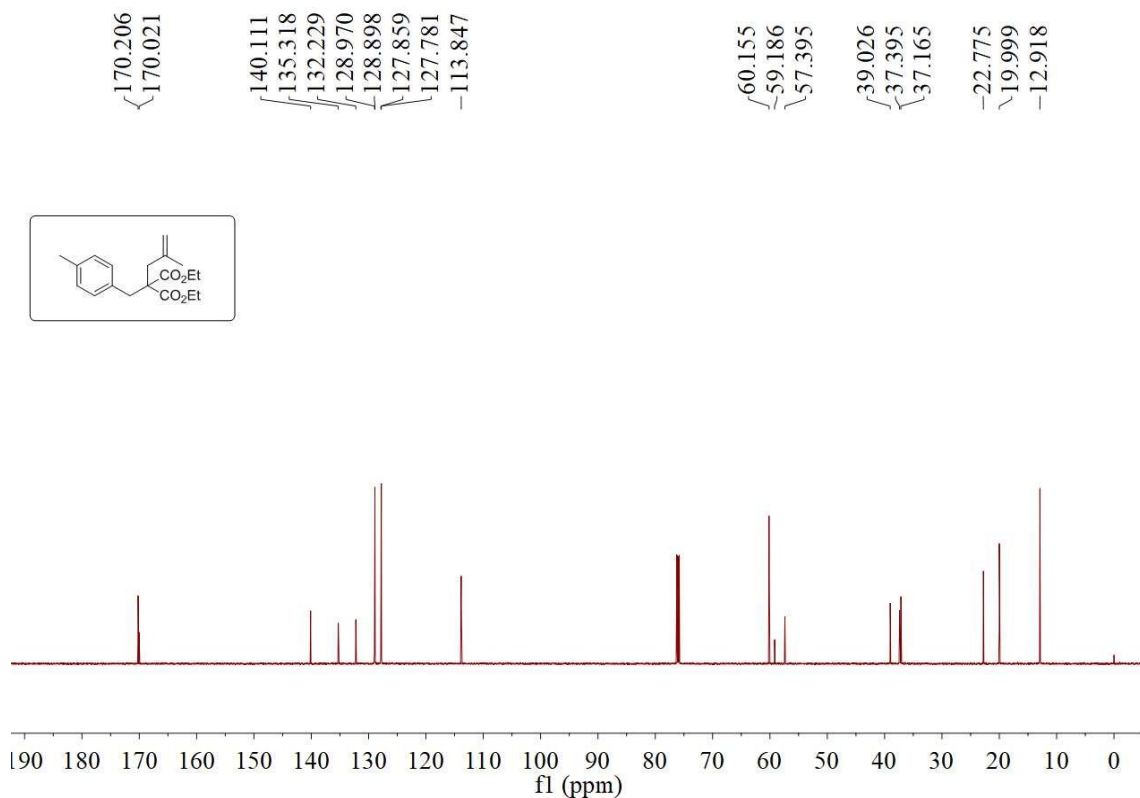
1. NMR Spectra of New Substrates

¹H-NMR Spectra of **1c**

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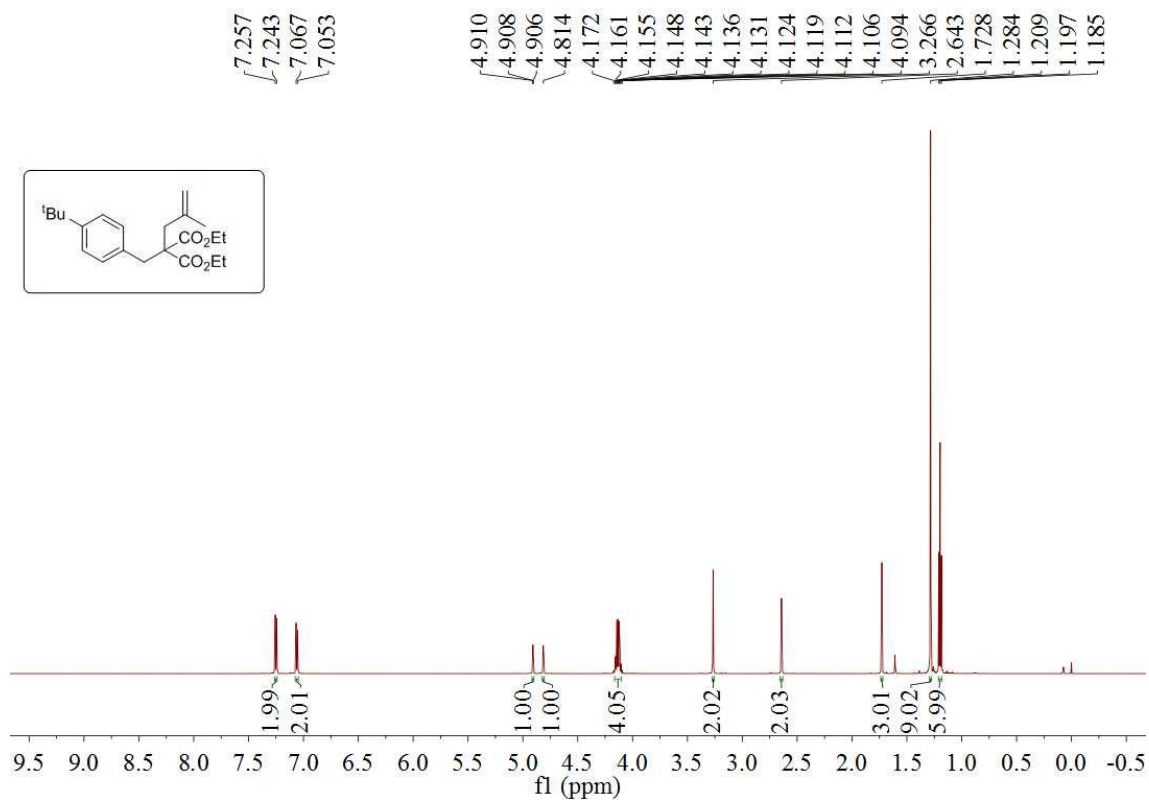


¹³C-NMR Spectra of 1c

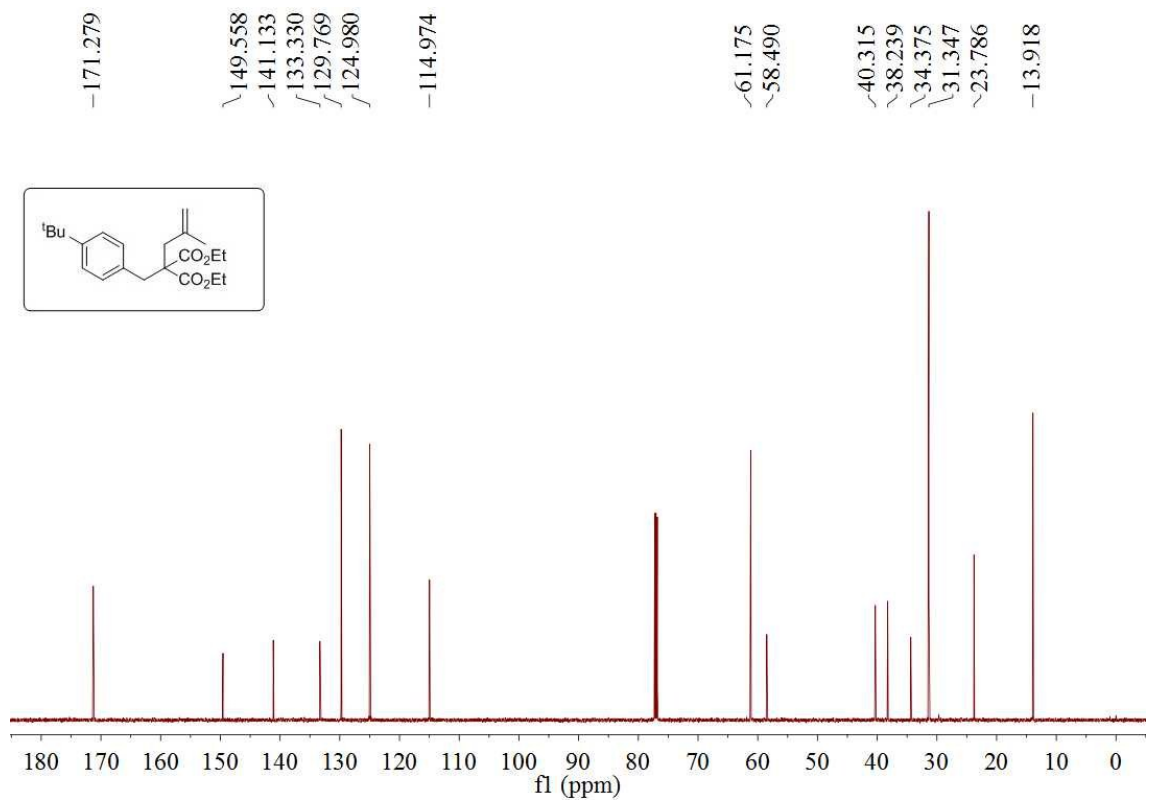


¹H-NMR Spectra of 1e

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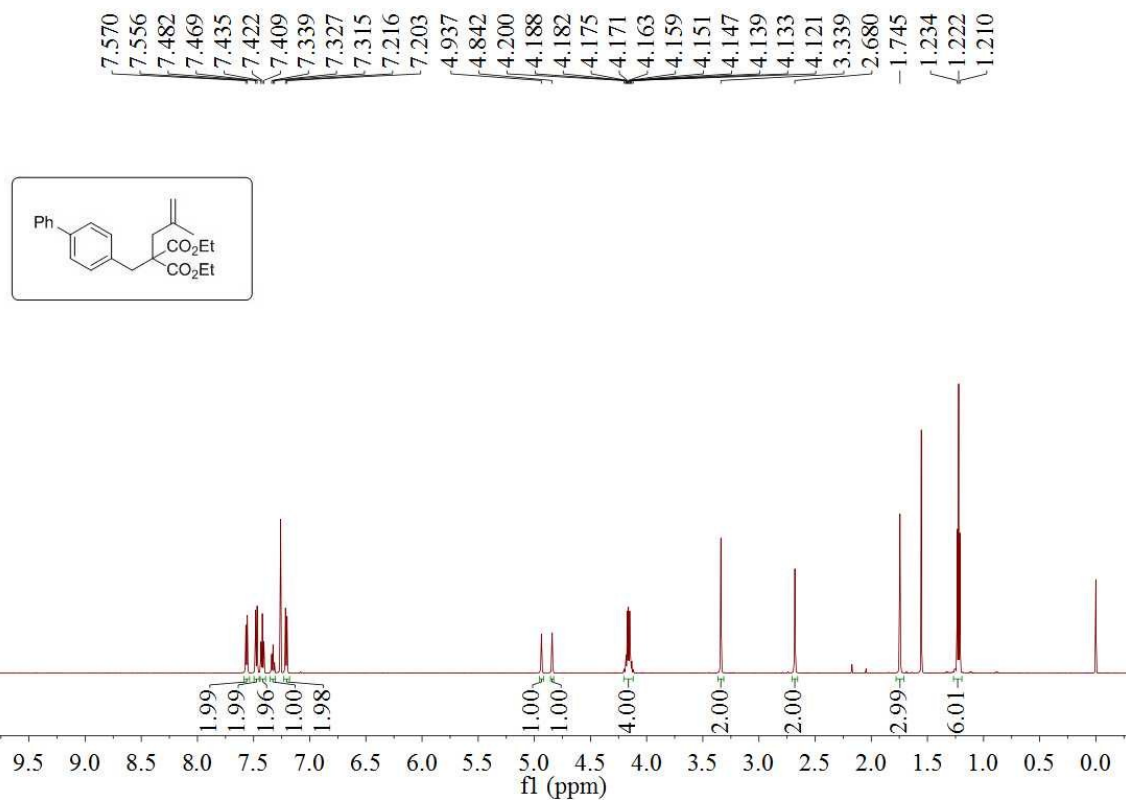


¹³C-NMR Spectra of 1e

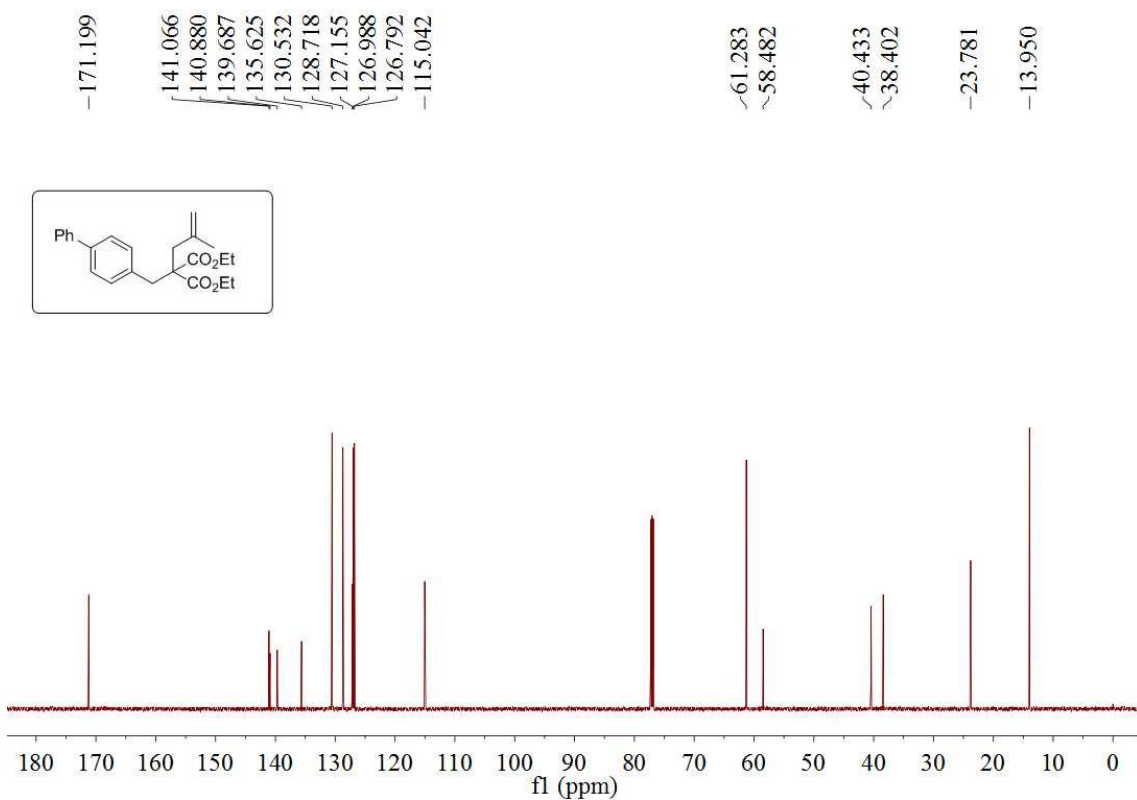


¹H-NMR Spectra of 1f

SUPPORTING INFORMATION

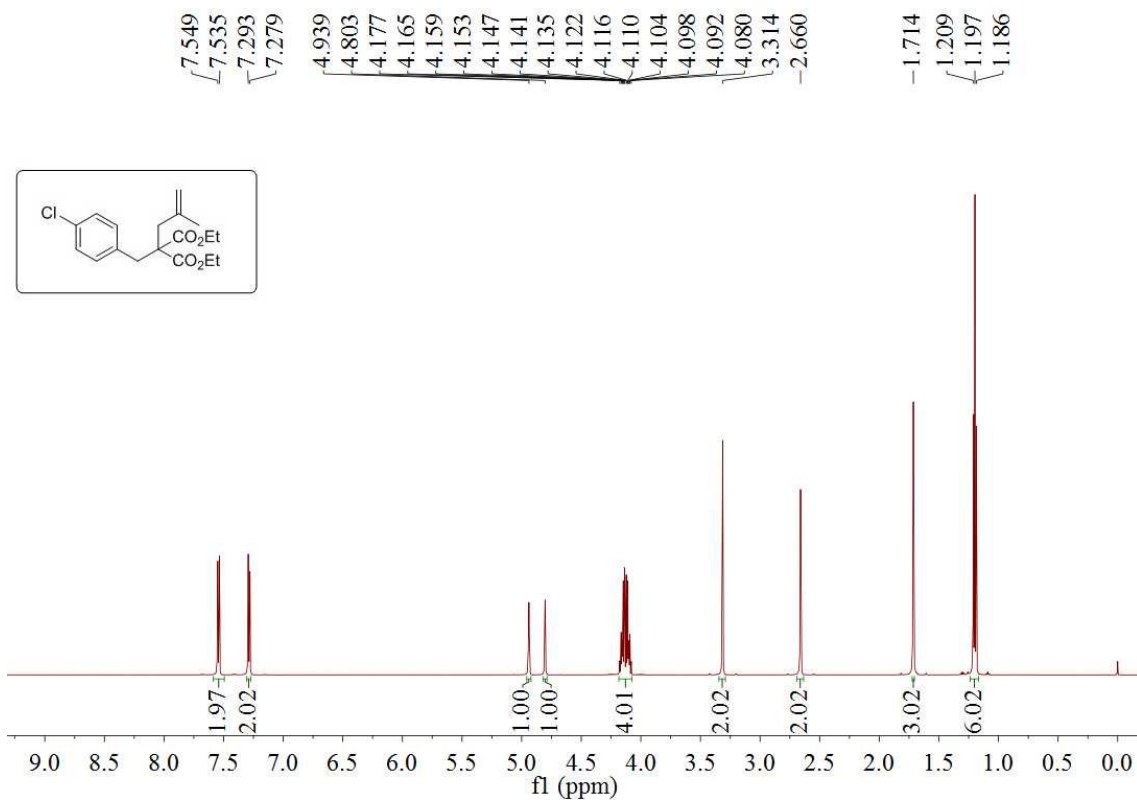


¹³C-NMR Spectra of 1f

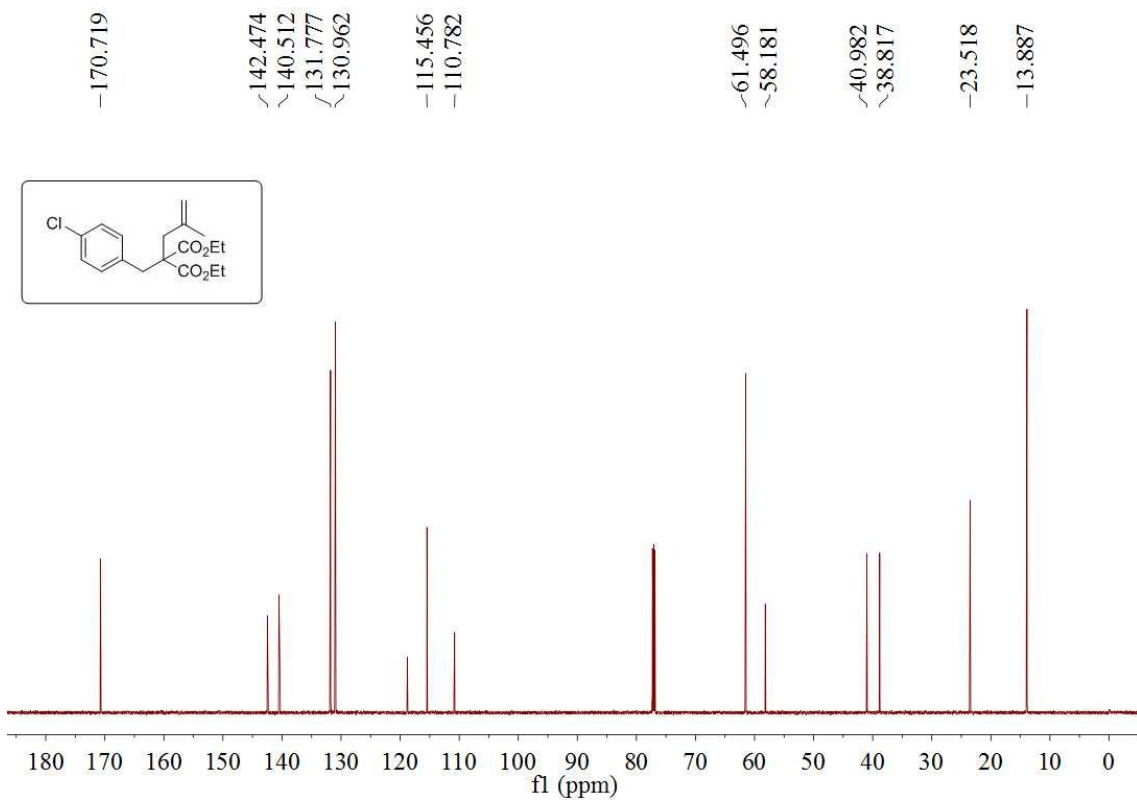


¹H-NMR Spectra of 1g

SUPPORTING INFORMATION

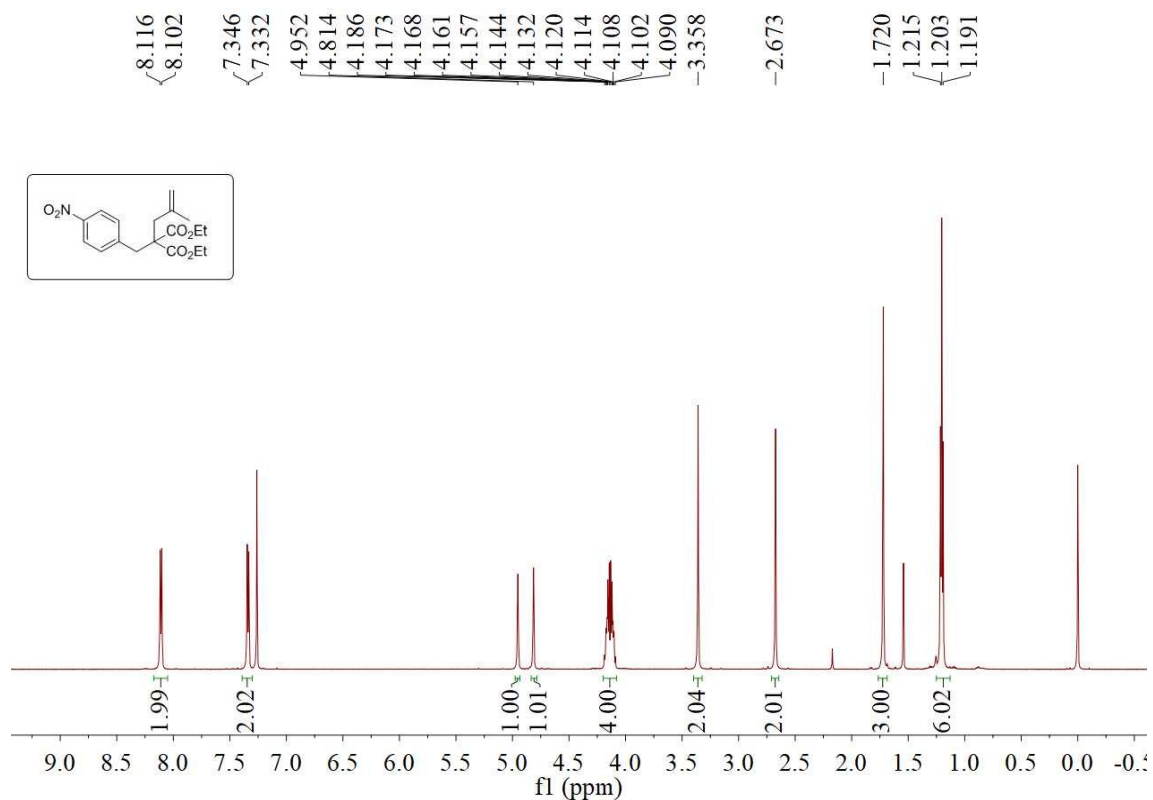


¹³C-NMR Spectra of 1g

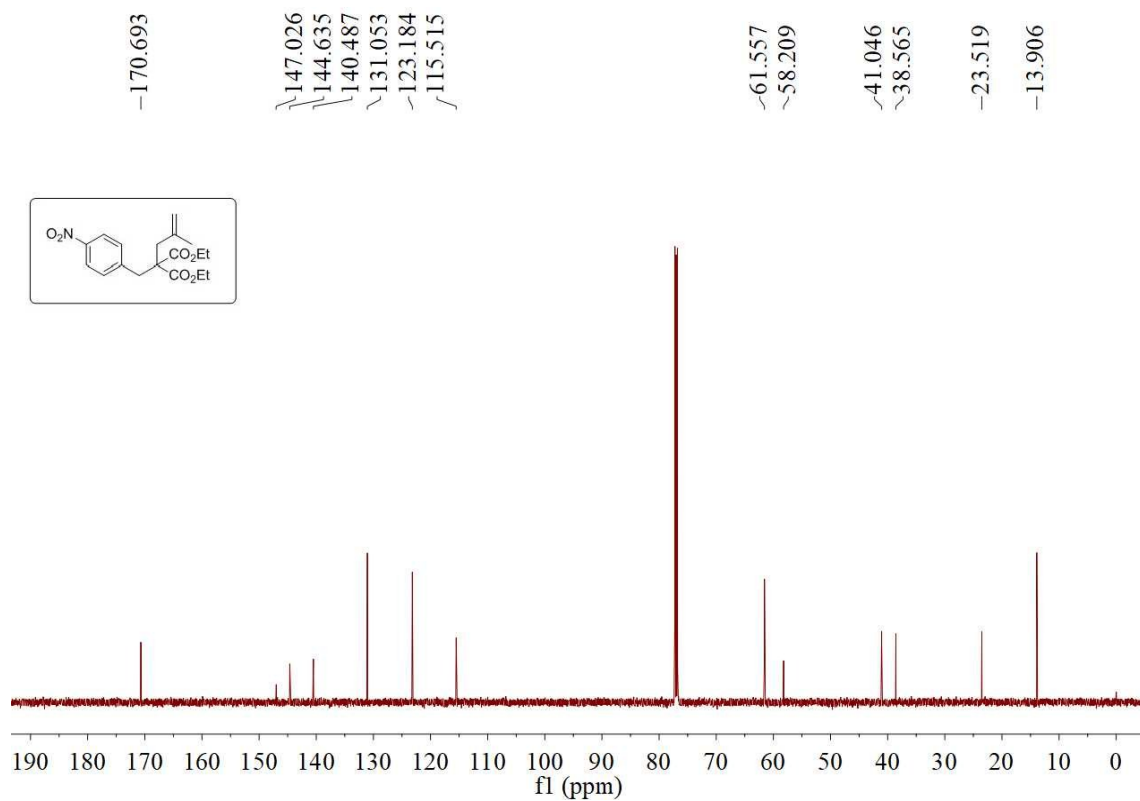


¹H-NMR Spectra of 1h

SUPPORTING INFORMATION



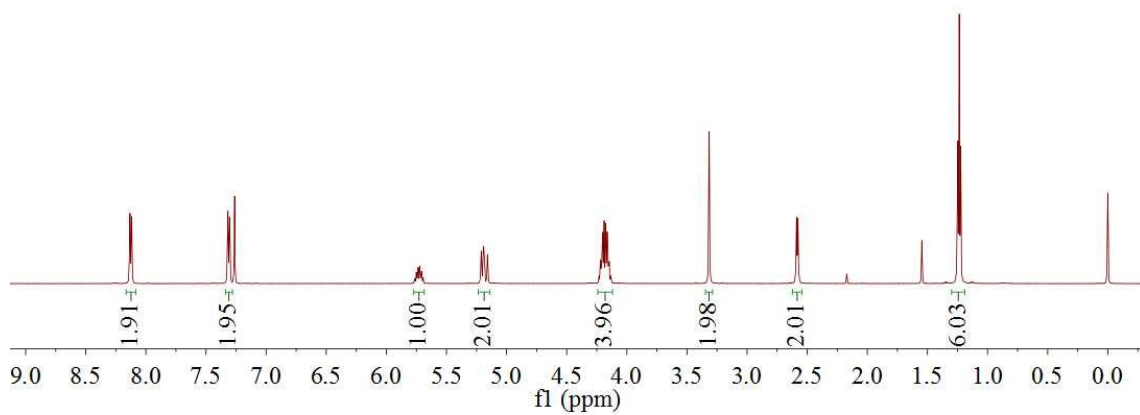
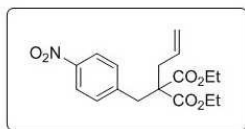
¹³C-NMR Spectra of 1h



¹H-NMR Spectra of 1i

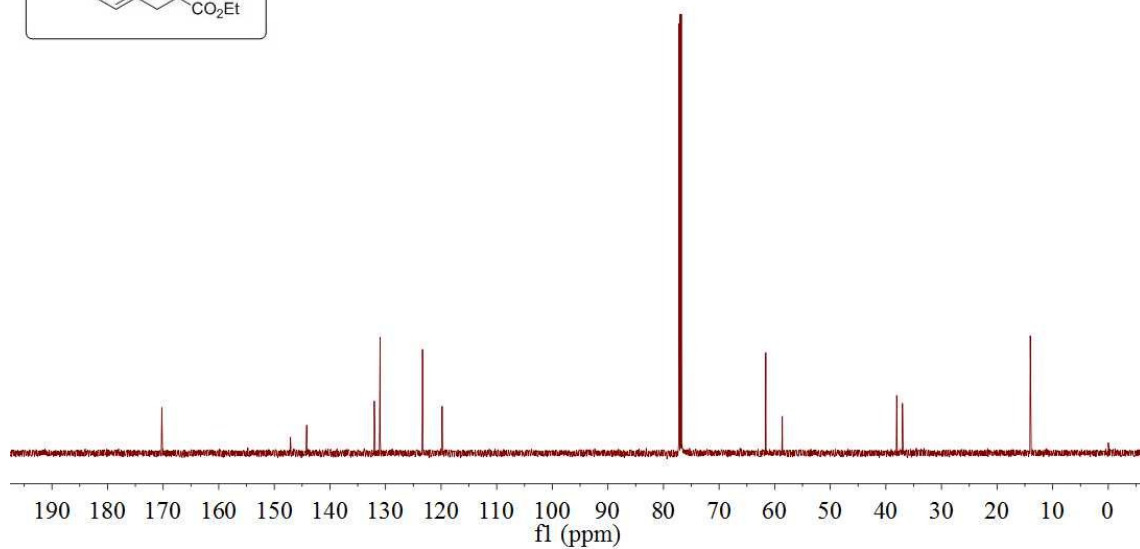
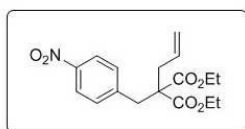
SUPPORTING INFORMATION

8.132
8.118
7.318
7.304
5.763
5.751
5.746
5.735
5.723
5.710
5.706
5.694
5.211
5.192
5.159
4.230
4.218
4.212
4.207
4.201
4.189
4.177
4.163
4.157
4.151
4.147
4.134
3.315
2.588
2.576
1.247
1.235
1.224



¹³C-NMR Spectra of 1i

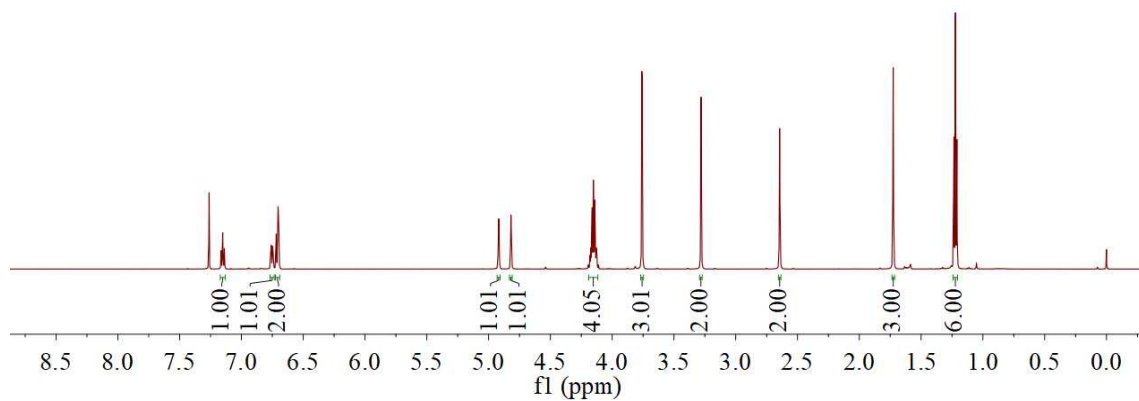
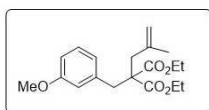
170.235
147.095
144.181
132.018
130.977
123.351
119.811
61.598
58.627
38.053
37.011
14.033



¹H-NMR Spectra of 1i

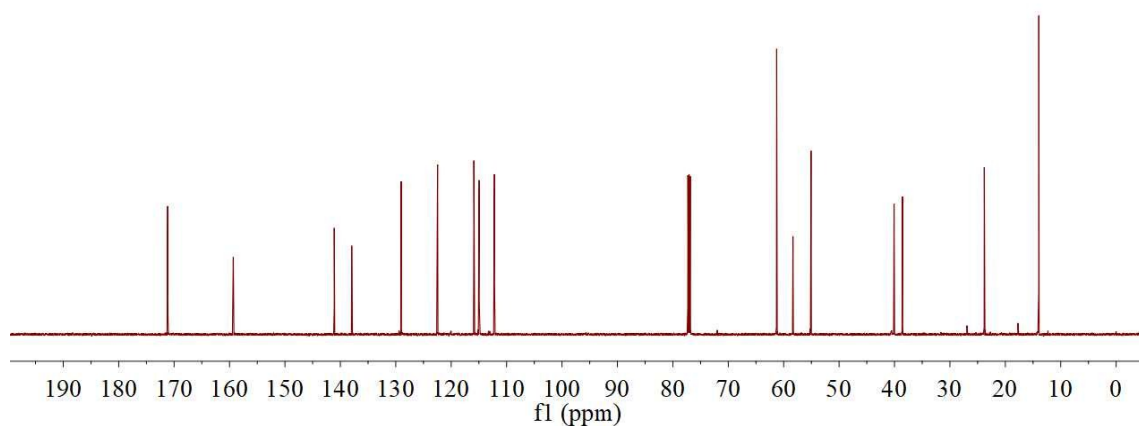
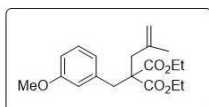
SUPPORTING INFORMATION

7.164
7.151
7.138
6.762
6.748
6.718
6.703
4.918
4.819
4.191
4.179
4.173
4.167
4.164
4.161
4.152
4.150
4.140
4.138
4.129
4.122
4.111
3.757
3.281
2.645
-1.726
-1.234
-1.222
-1.210



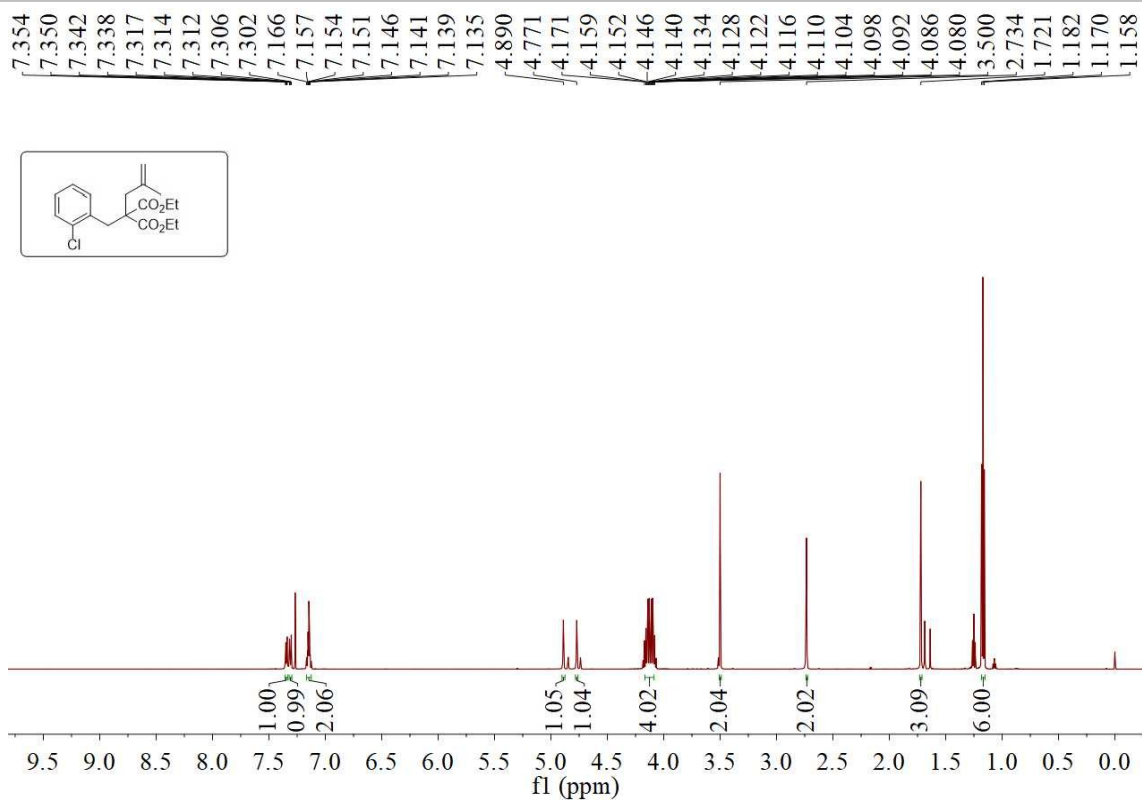
¹³C-NMR Spectra of 1l

-171.161
-159.319
-141.101
-137.947
-129.024
-122.453
-115.903
-114.948
-112.199
61.265
58.327
55.059
40.079
38.555
-23.797
-13.957

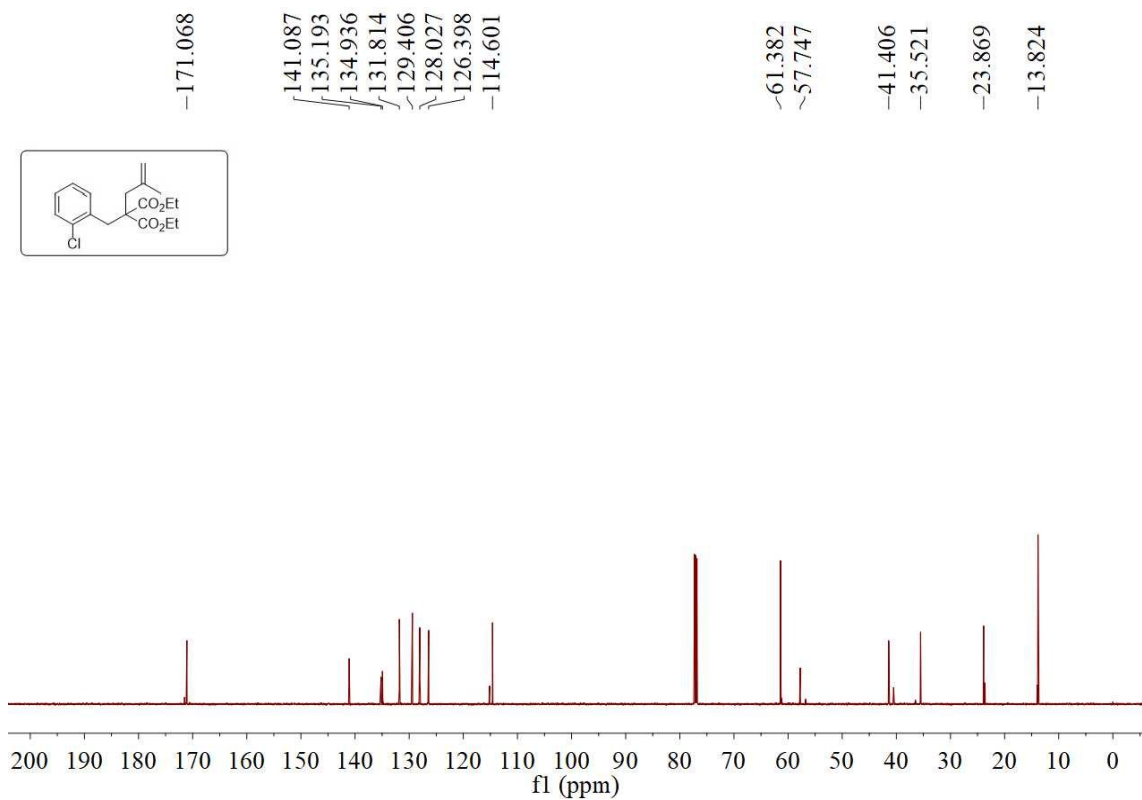


¹H-NMR Spectra of 1m

SUPPORTING INFORMATION



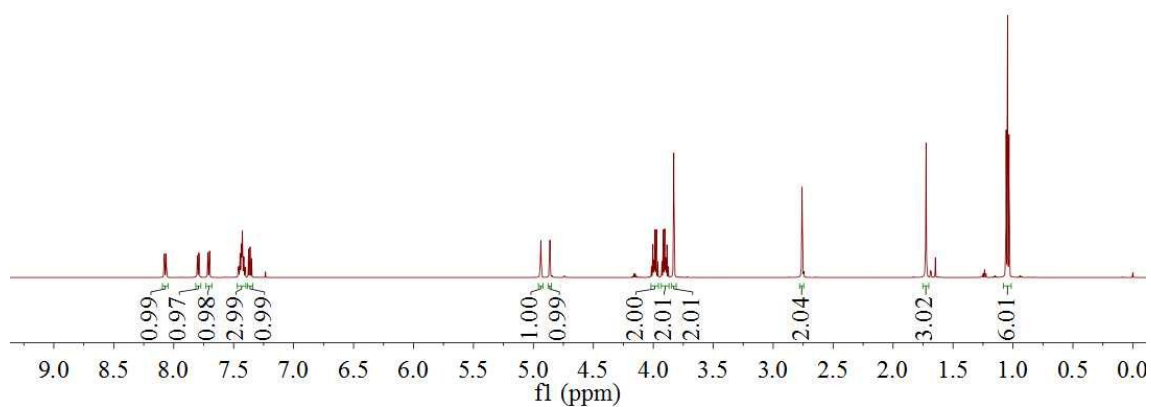
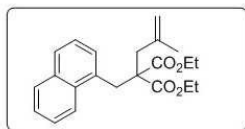
¹³C-NMR Spectra of 1m



¹H-NMR Spectra of 1n

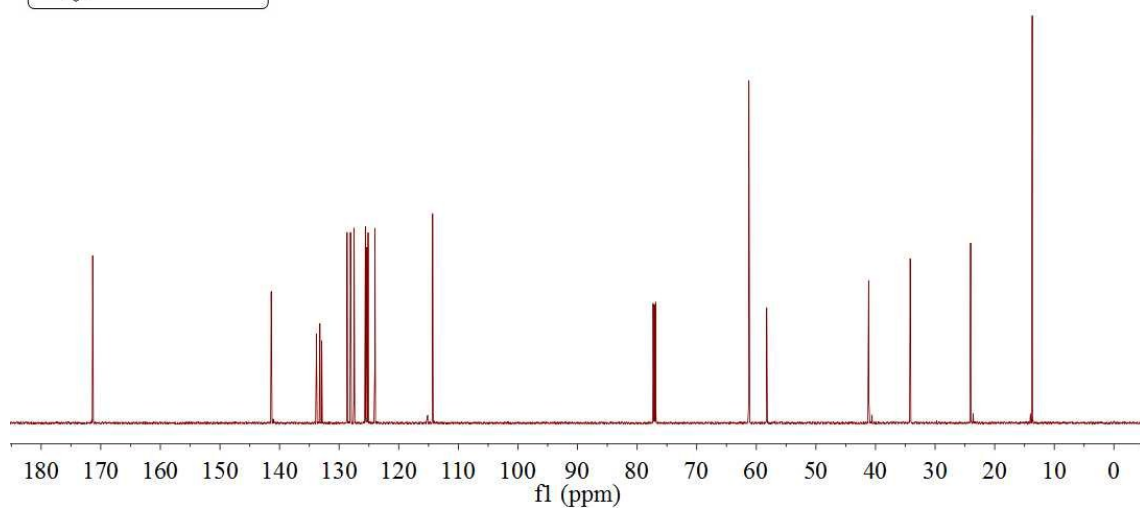
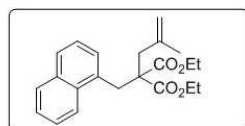
SUPPORTING INFORMATION

8.077
8.063
7.803
7.787
7.715
7.701
7.449
7.446
7.444
7.436
7.432
7.430
7.427
7.417
7.415
7.376
7.362
7.350
4.938
4.862
4.003
3.997
3.991
3.985
3.979
3.973
3.961
3.928
3.916
3.910
3.904
3.898
3.892
3.886
3.829
2.759
1.725
1.057
1.045
1.033



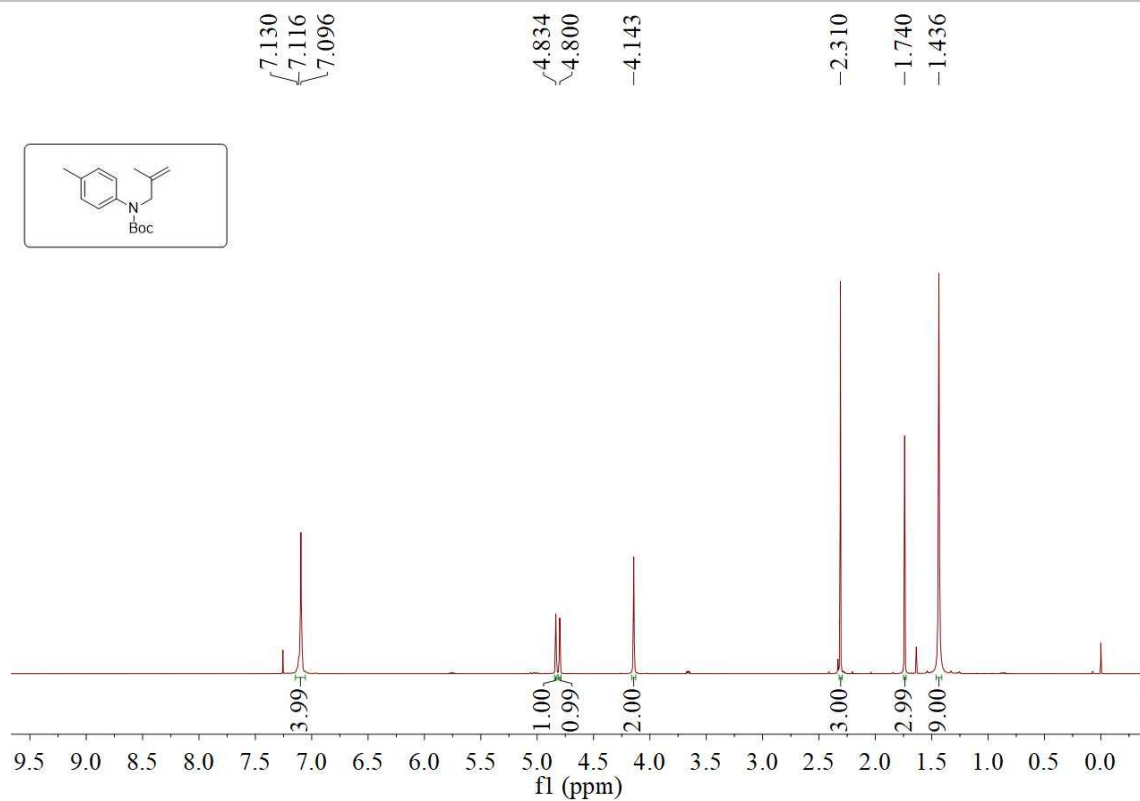
¹³C-NMR Spectra of 1n

-171.355
-141.396
-133.805
-133.230
-132.915
-128.668
-128.099
-127.484
-125.597
-125.350
-125.134
-123.988
-114.312
-61.250
-58.262
-41.146
-34.180
-24.044
-13.702

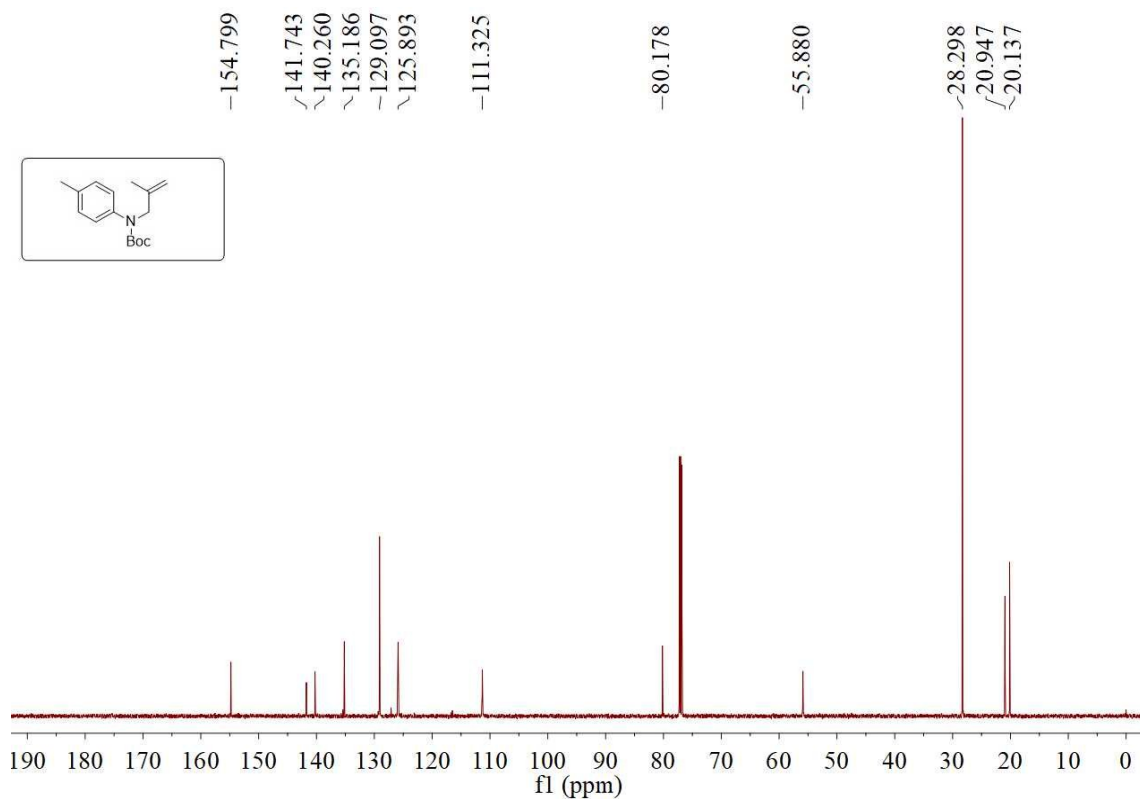


¹H-NMR Spectra of 5d

SUPPORTING INFORMATION

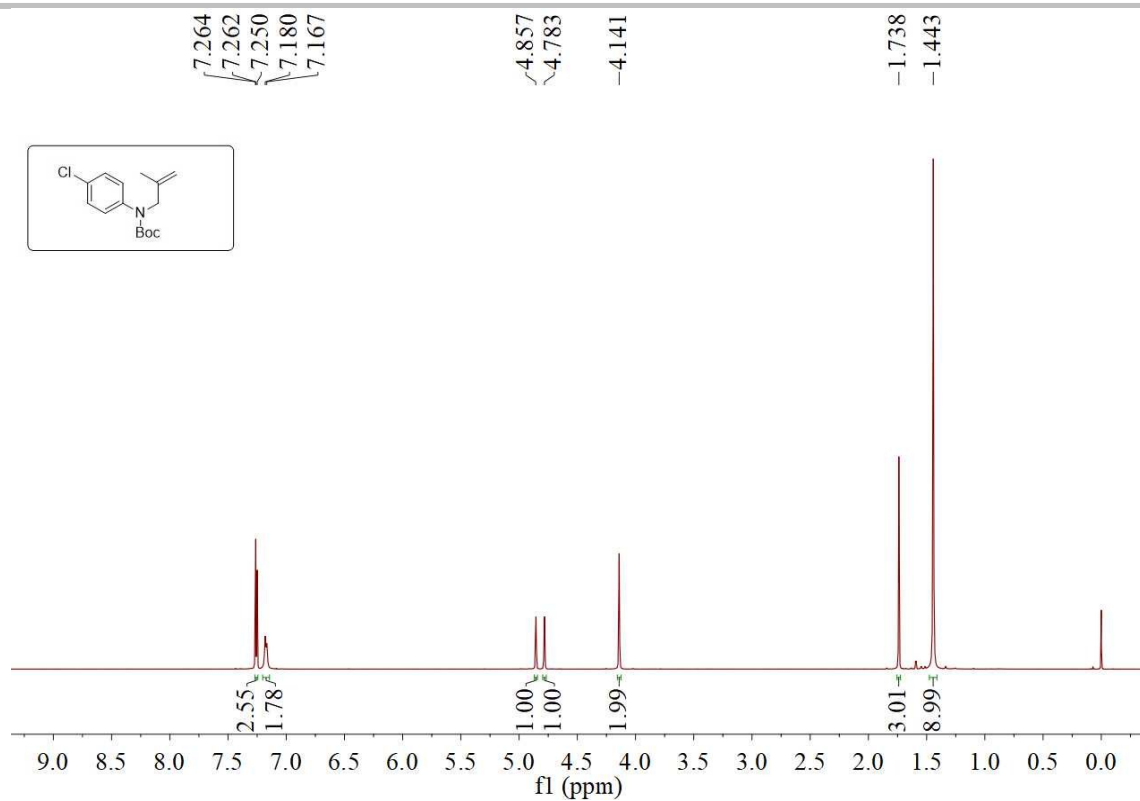


¹³C-NMR Spectra of 5d

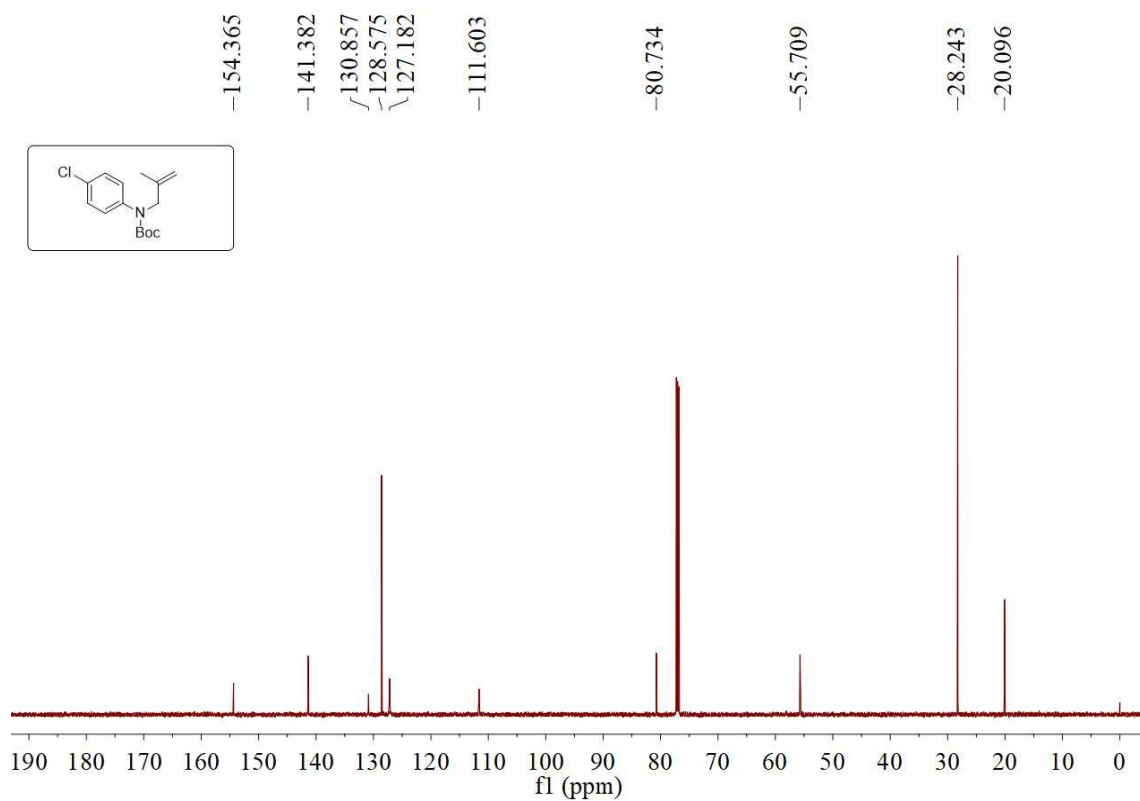


¹H-NMR Spectra of 5e

SUPPORTING INFORMATION

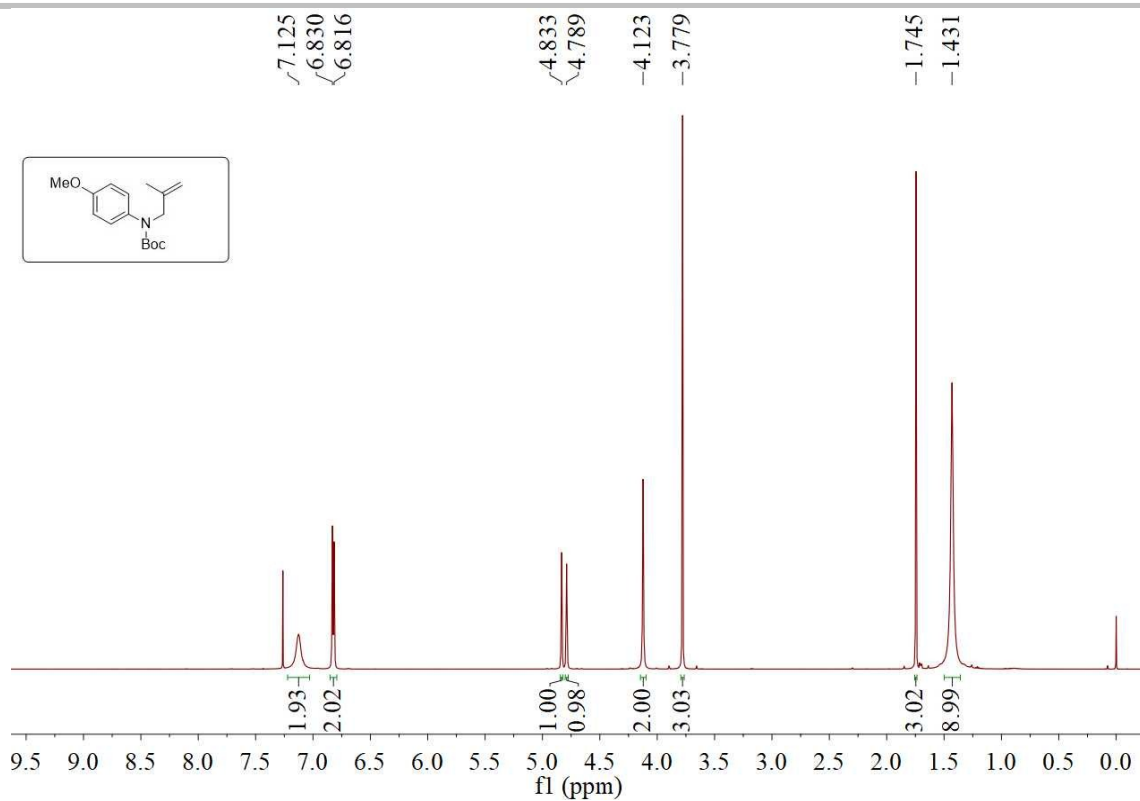


¹³C-NMR Spectra of 5e

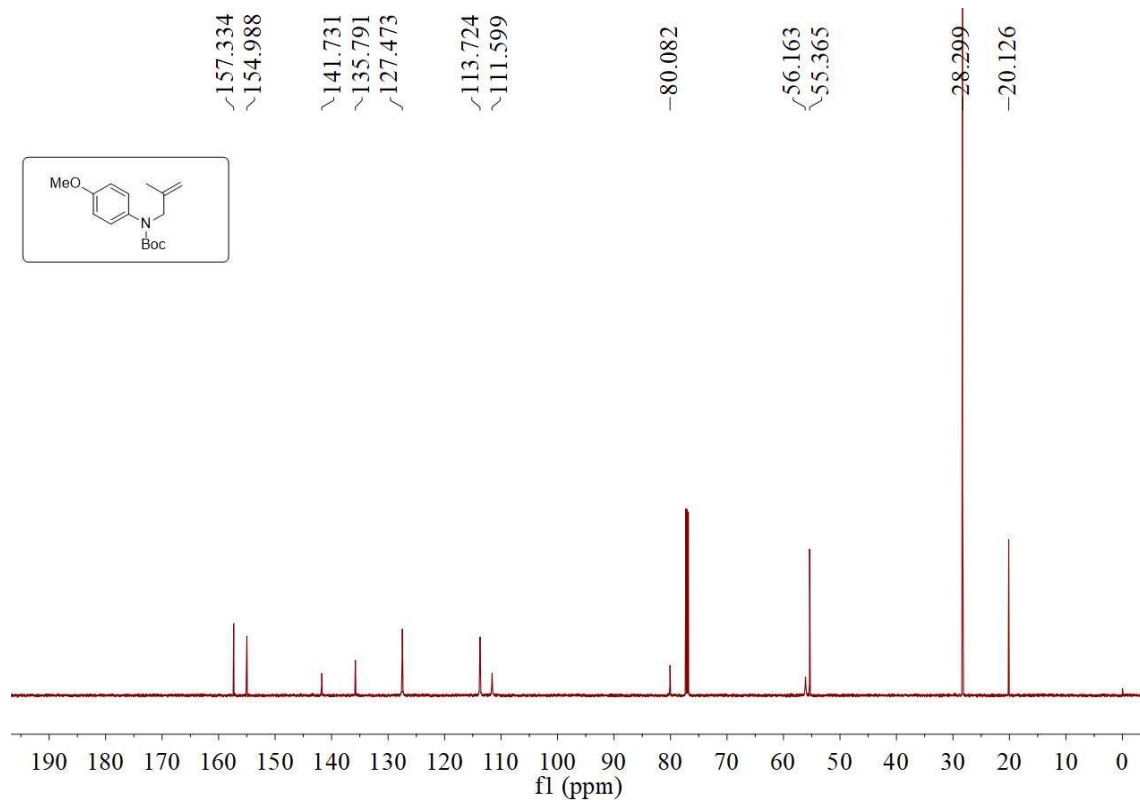


¹H-NMR Spectra of 5f

SUPPORTING INFORMATION



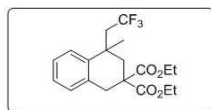
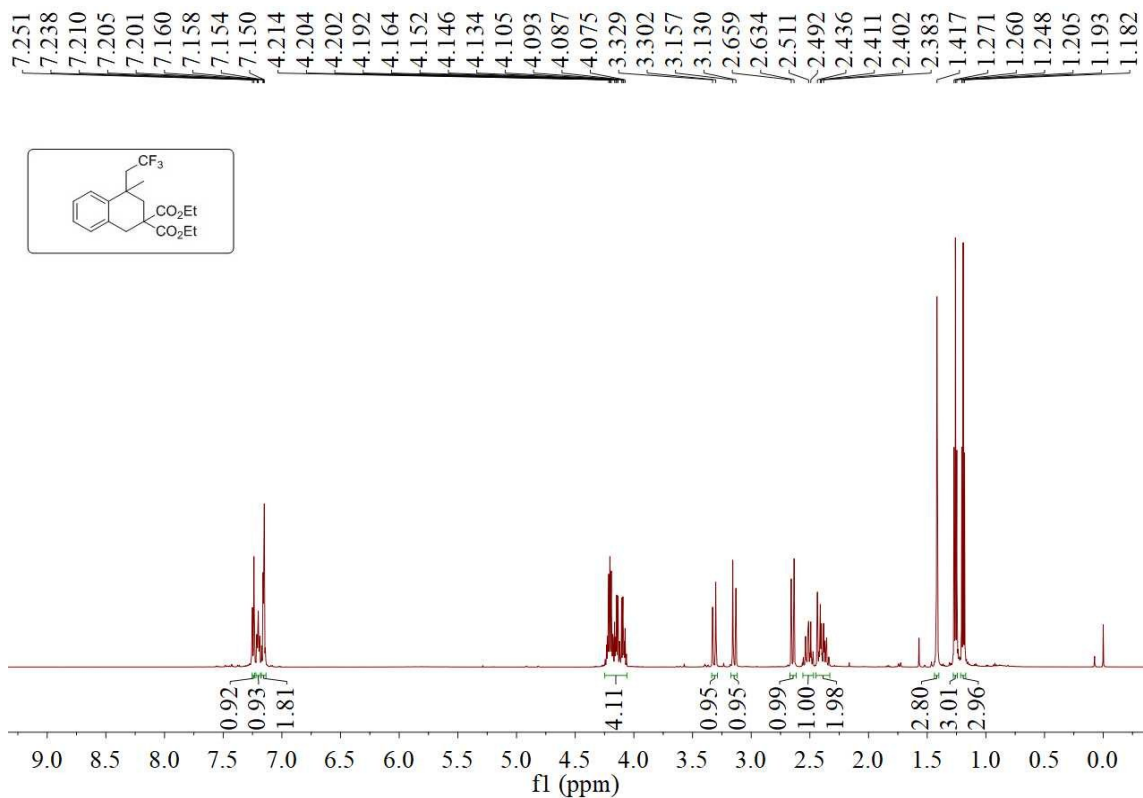
¹³C-NMR Spectra of 5f



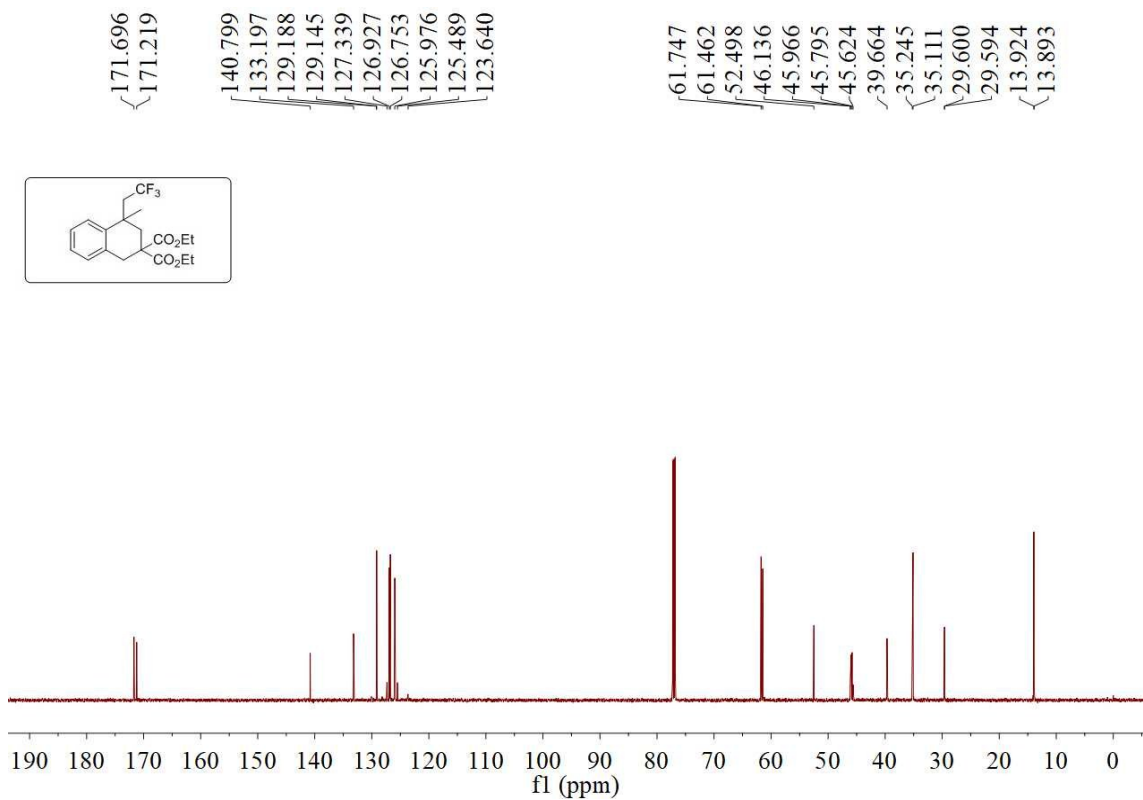
2. NMR Spectra of Products

¹H-NMR Spectra of 2a

SUPPORTING INFORMATION

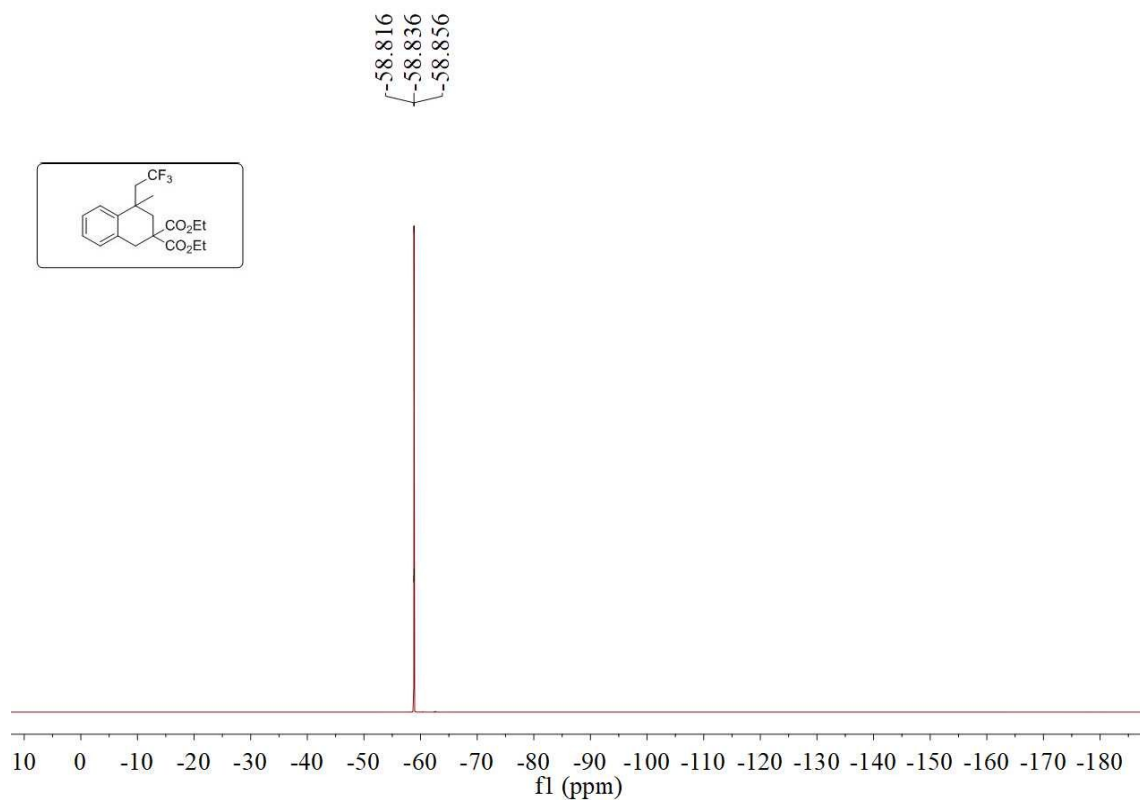


¹³C-NMR Spectra of 2a

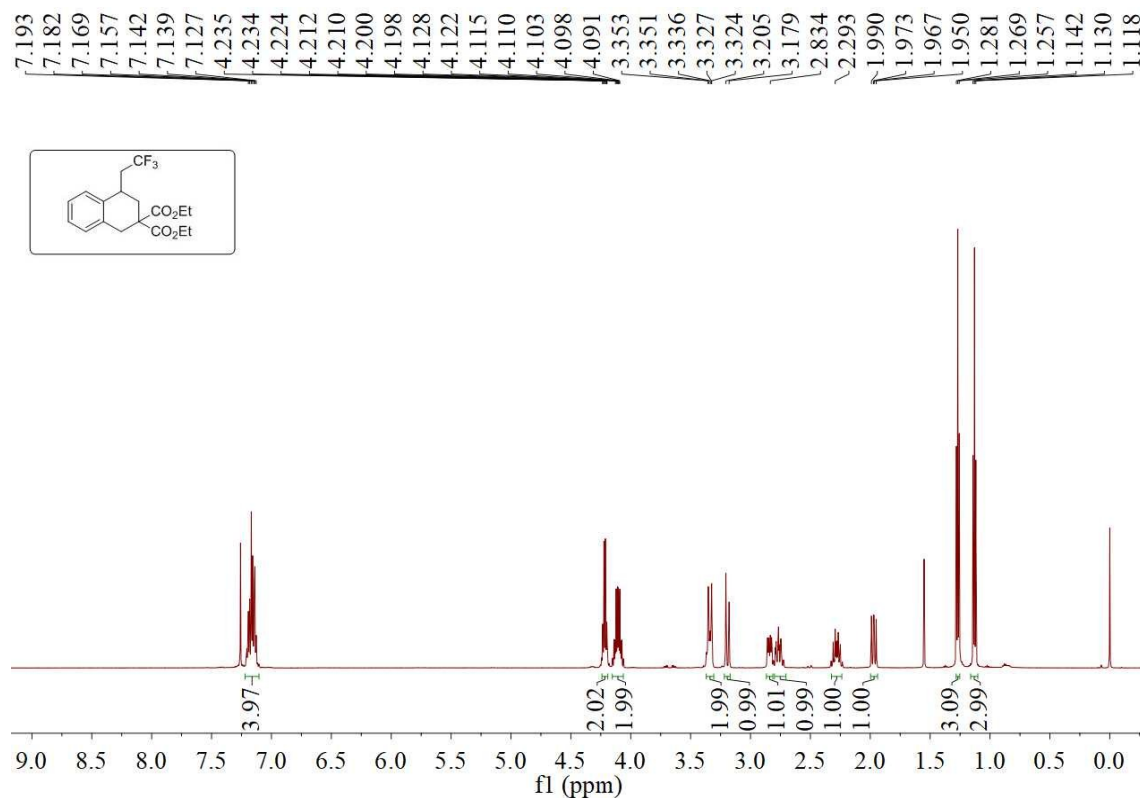


¹⁹F-NMR Spectra of 2a

SUPPORTING INFORMATION

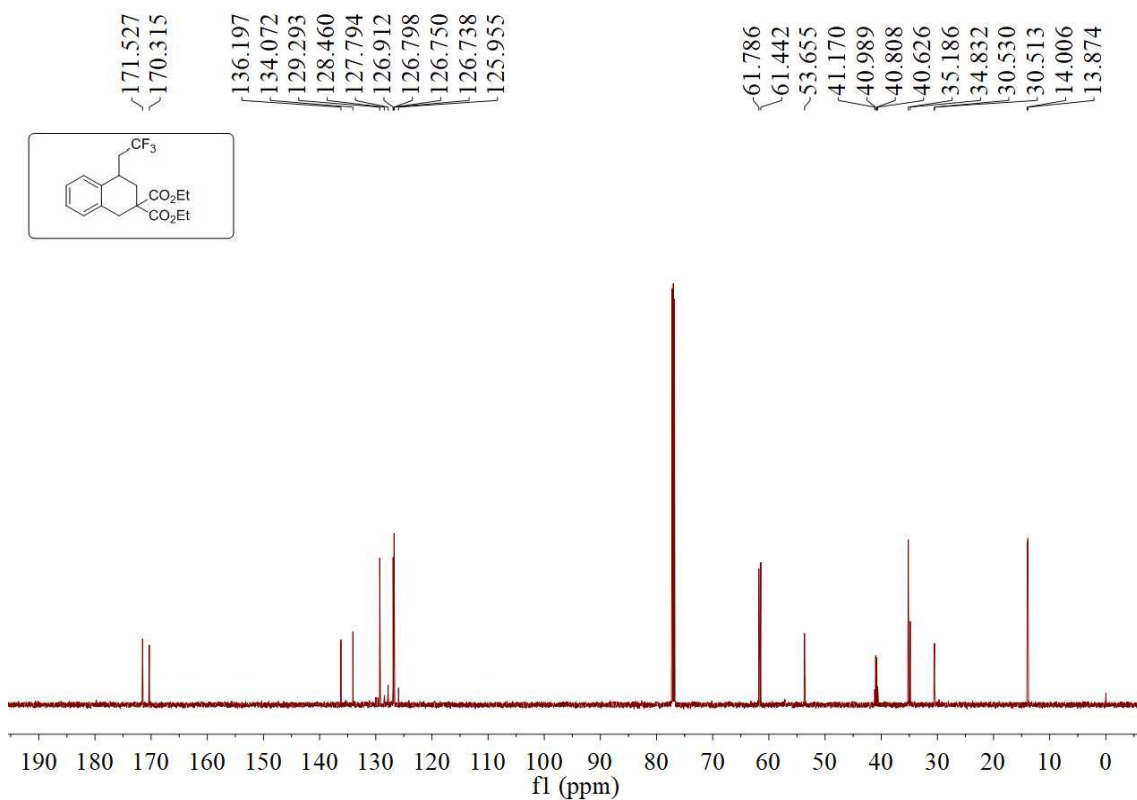


$^1\text{H-NMR}$ Spectra of 2b

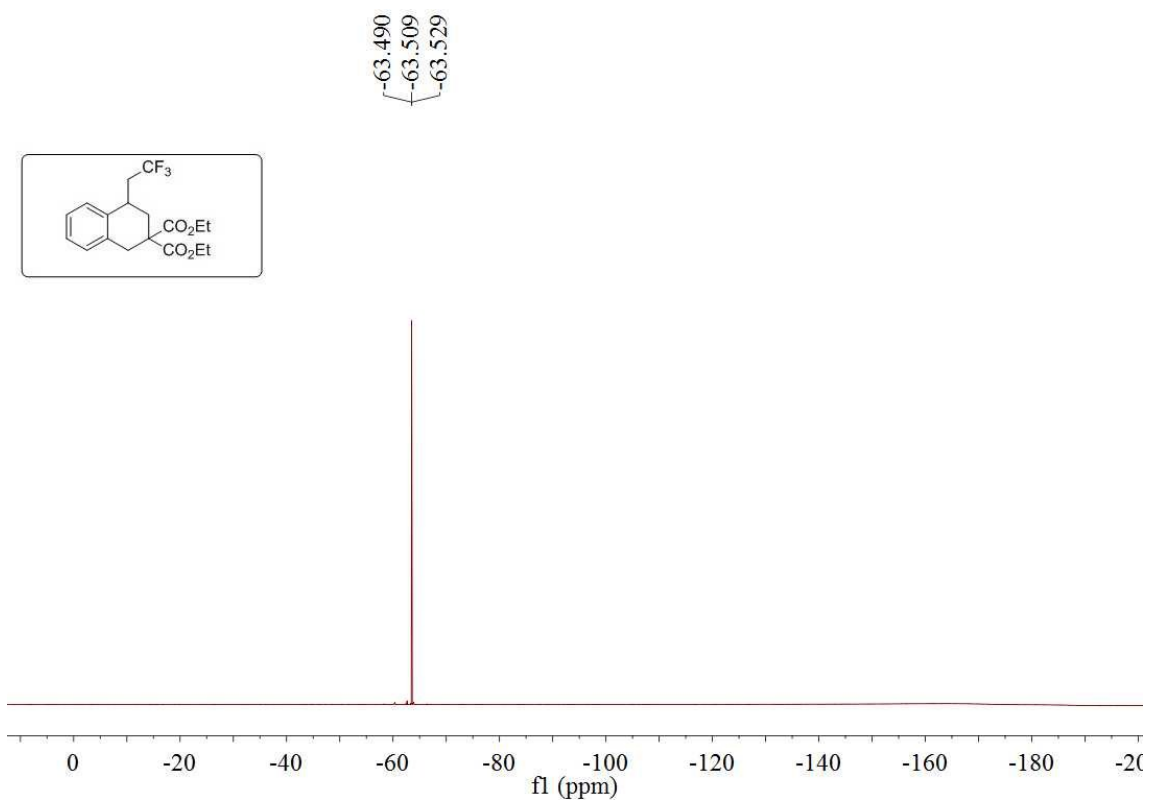


$^{13}\text{C-NMR}$ Spectra of 2b

SUPPORTING INFORMATION

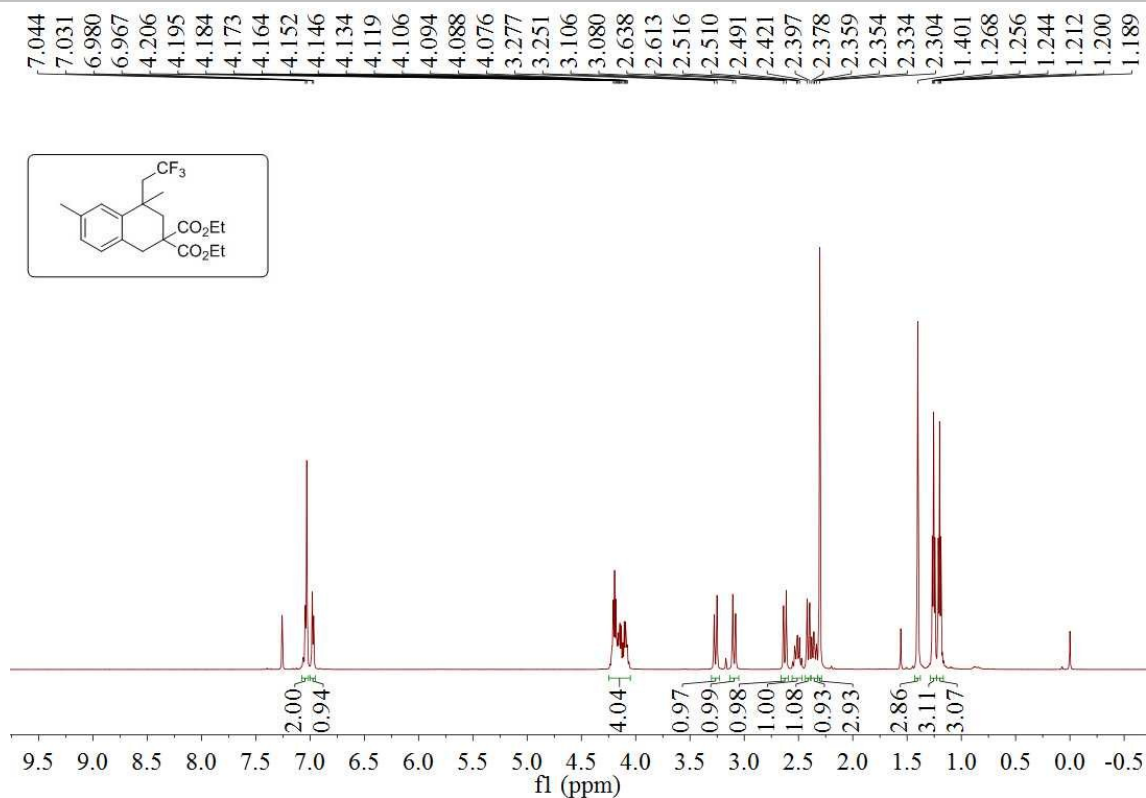


¹⁹F-NMR Spectra of 2b

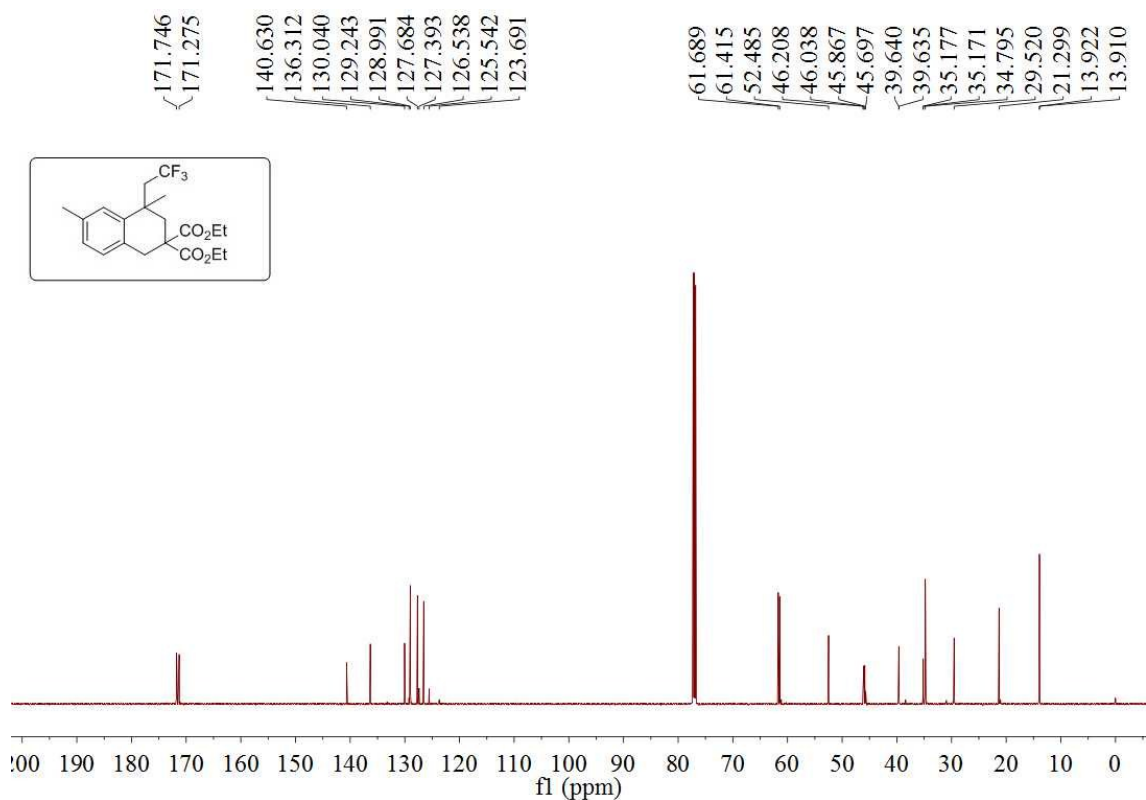


¹H-NMR Spectra of 2c

SUPPORTING INFORMATION

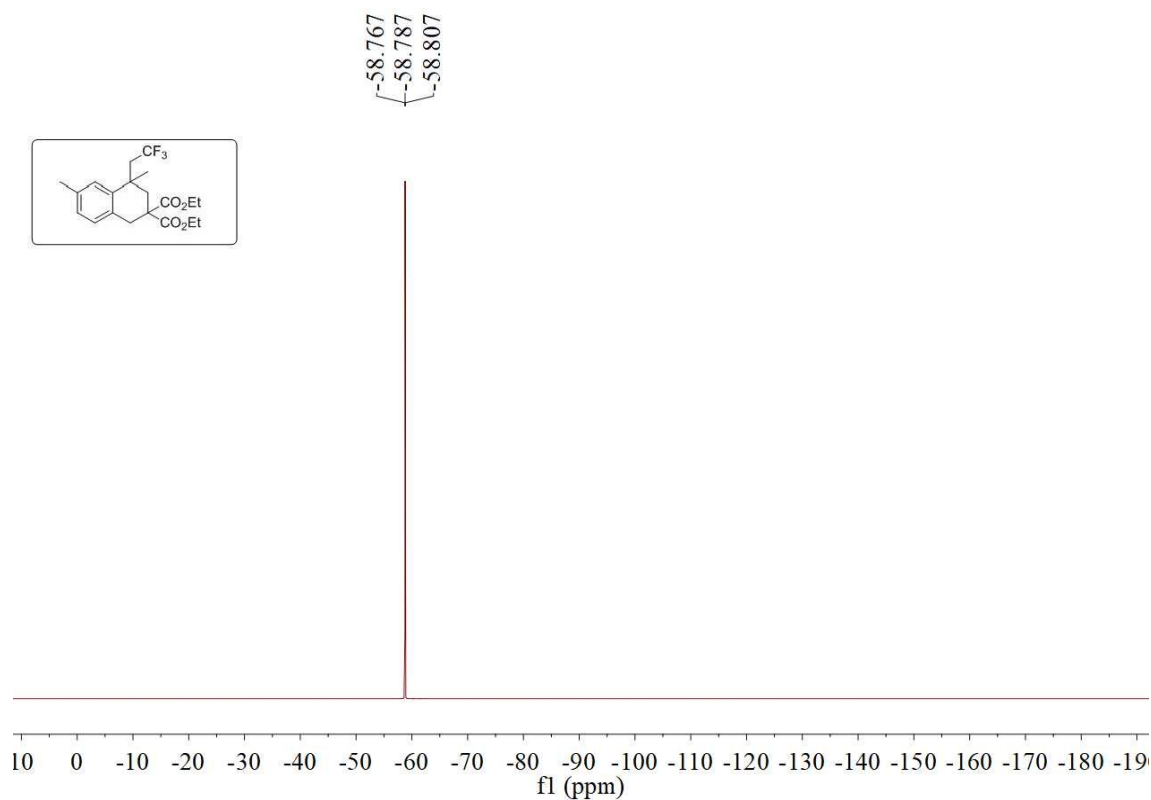


¹³C-NMR Spectra of 2c

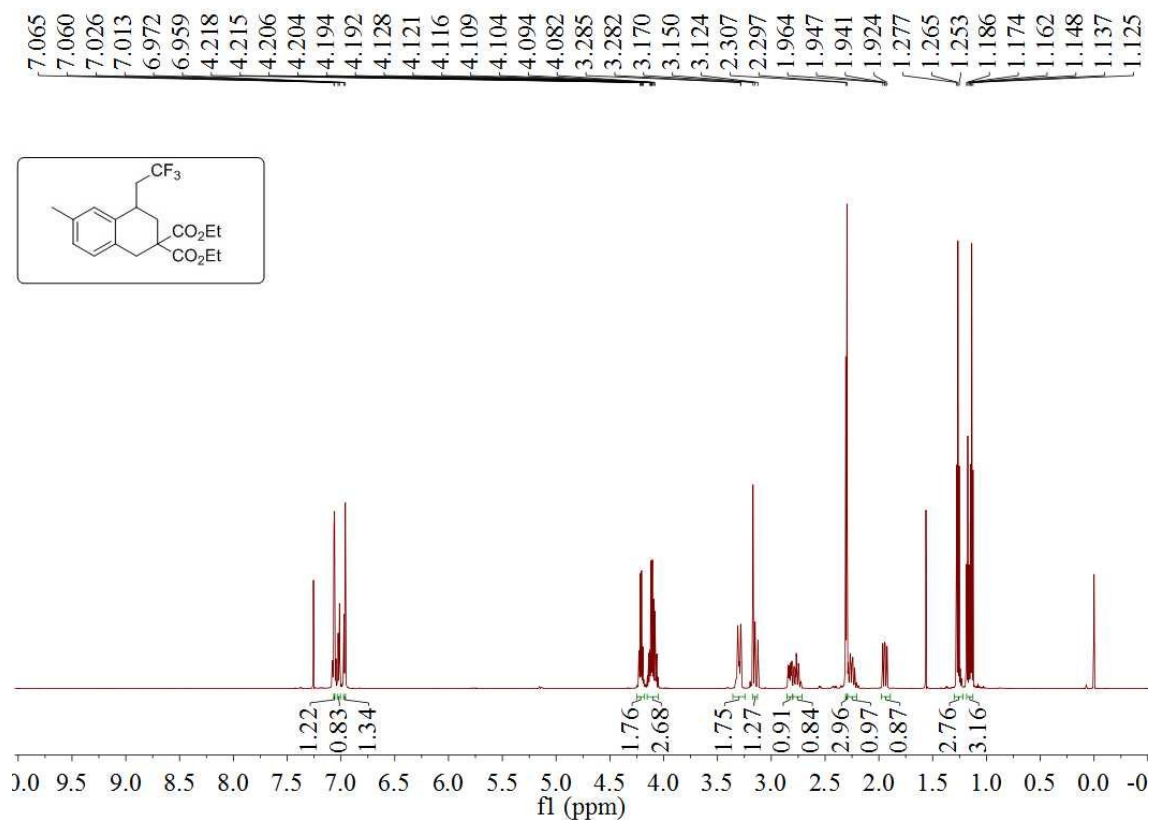


¹⁹F-NMR Spectra of 2c

SUPPORTING INFORMATION

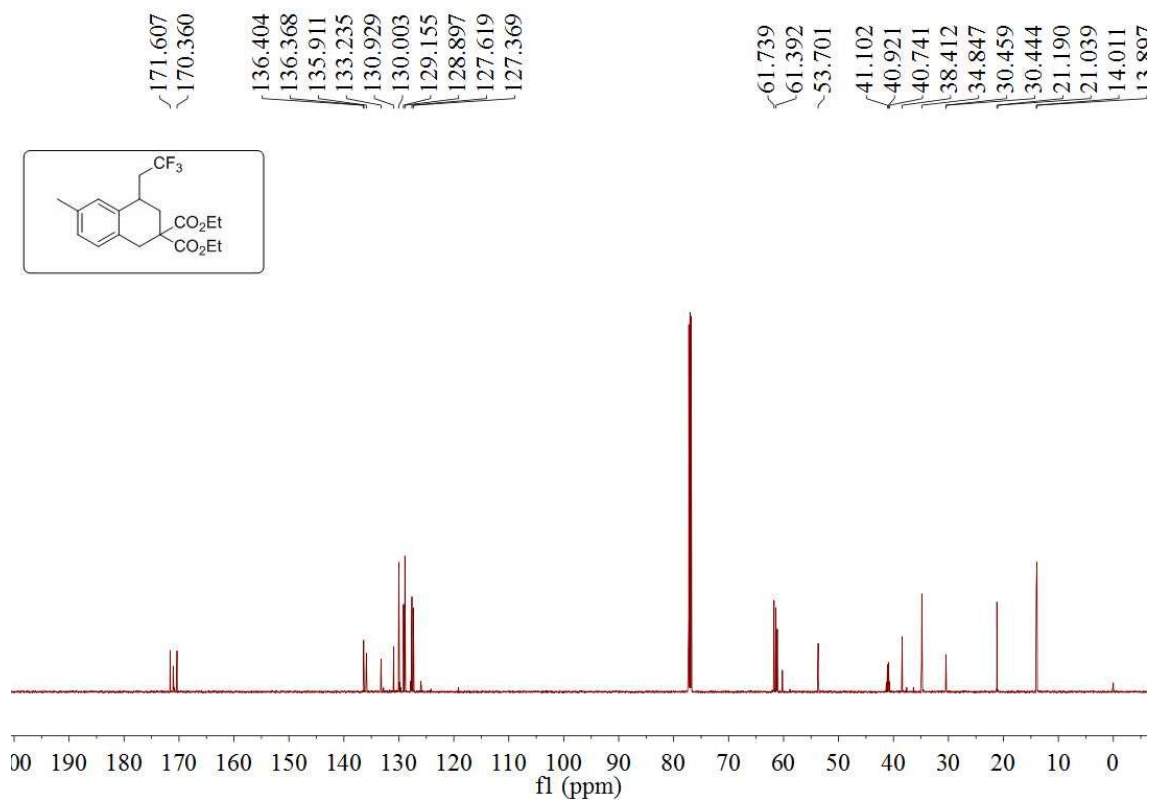


$^1\text{H-NMR}$ Spectra of 2d

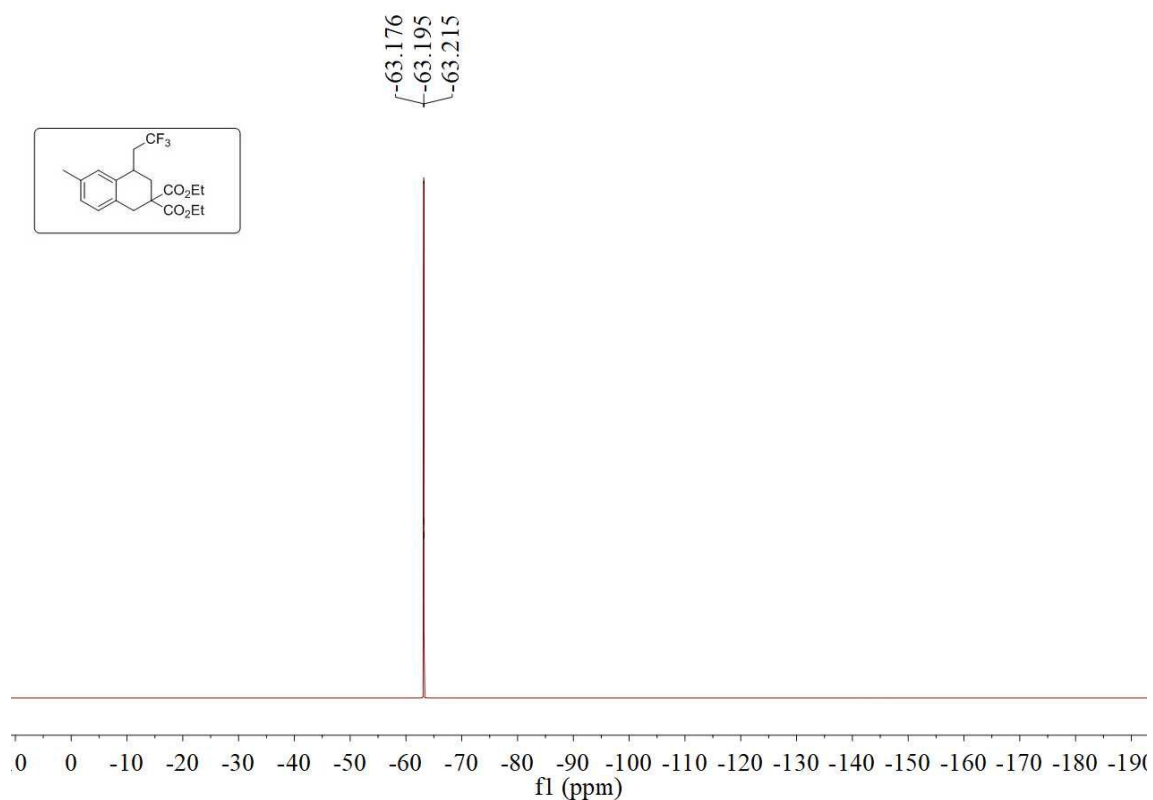


$^{13}\text{C-NMR}$ Spectra of 2d

SUPPORTING INFORMATION

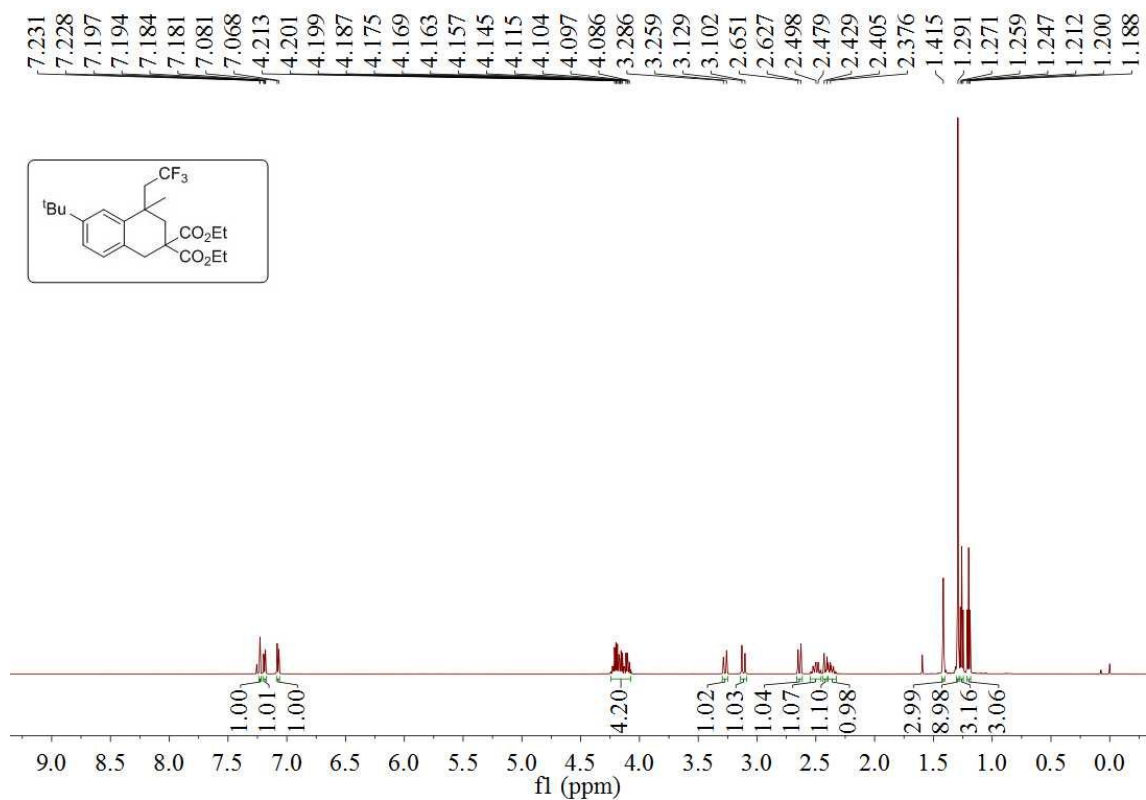


¹⁹F-NMR Spectra of 2d

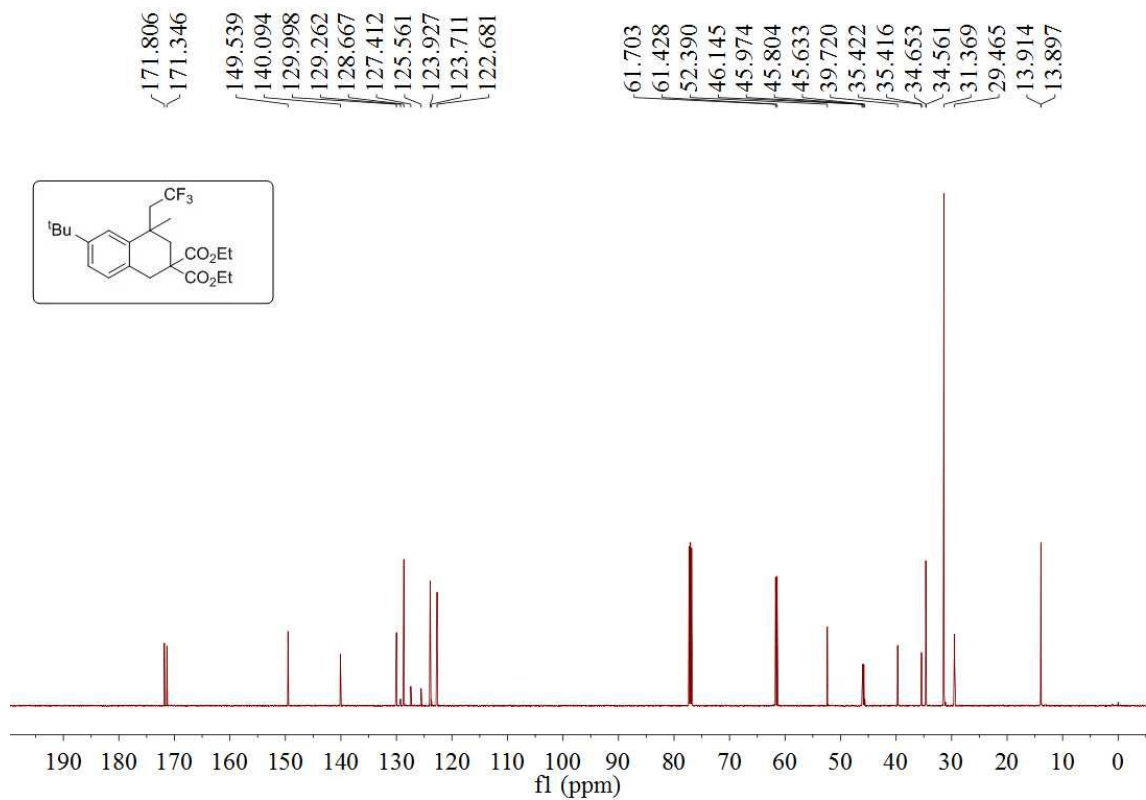


¹H-NMR Spectra of 2e

SUPPORTING INFORMATION

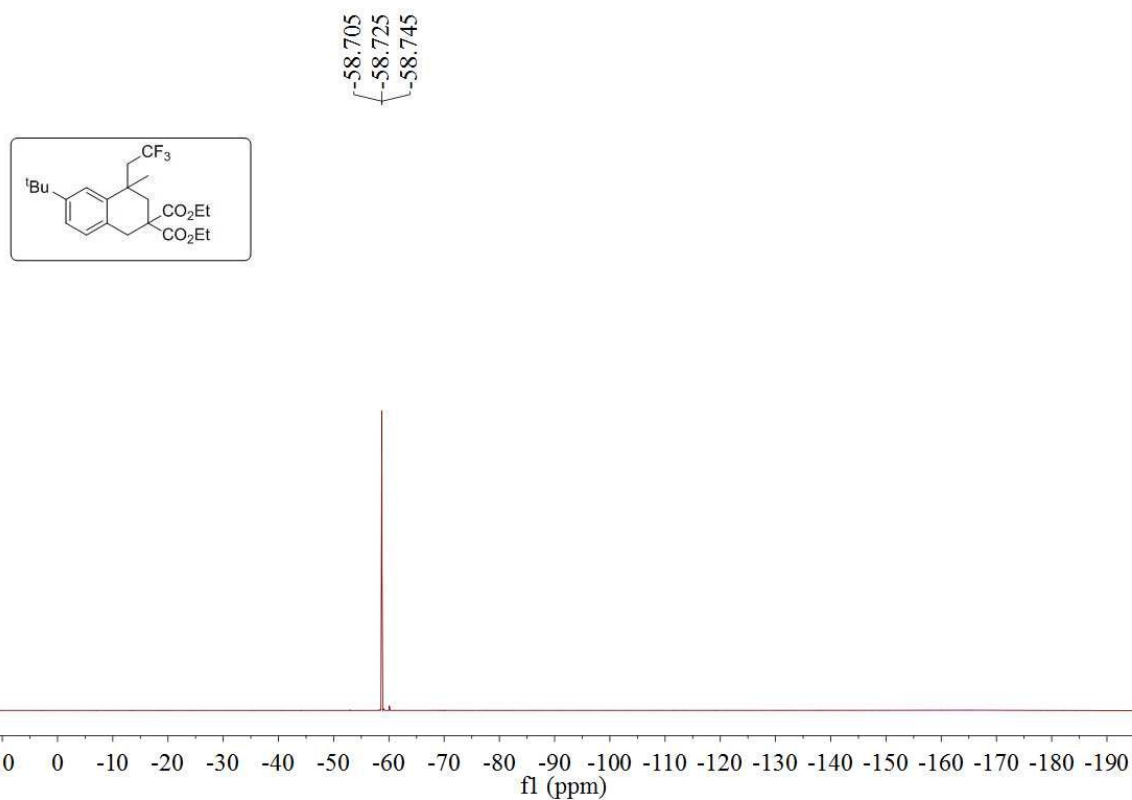


¹³C-NMR Spectra of 2e

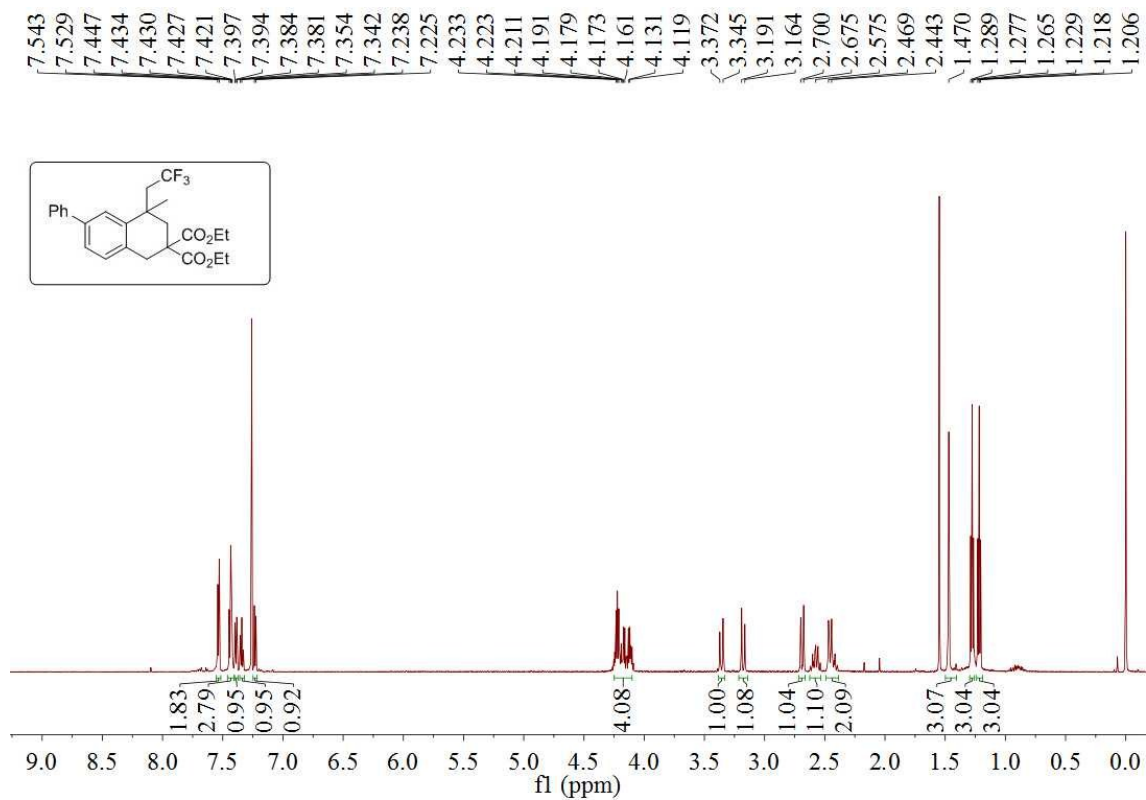


¹⁹F-NMR Spectra of 2e

SUPPORTING INFORMATION

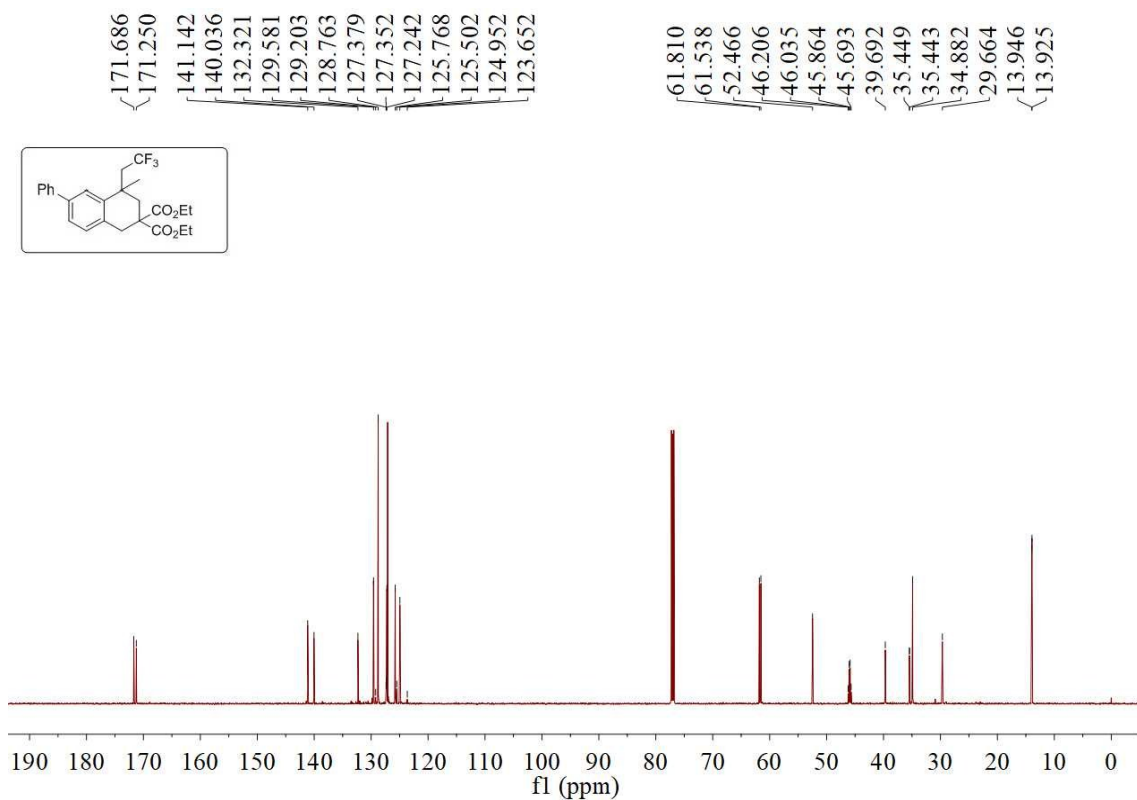


¹H-NMR Spectra of 2f

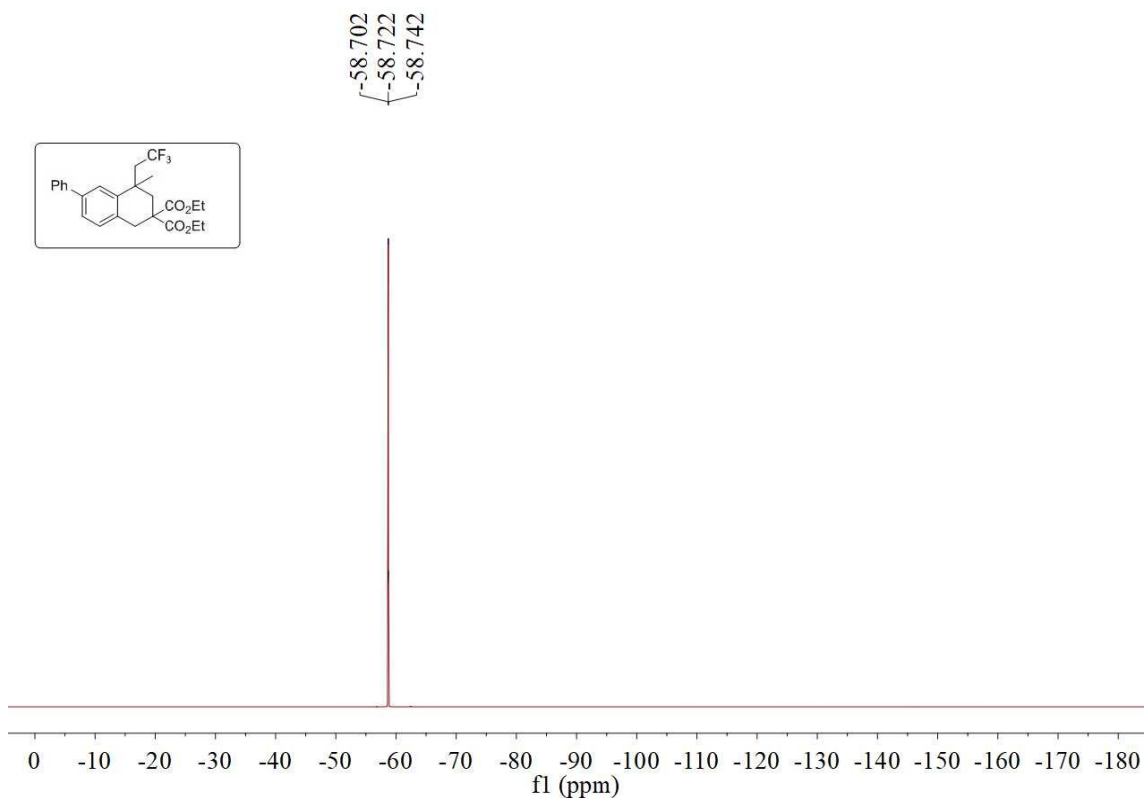


¹³C-NMR Spectra of 2f

SUPPORTING INFORMATION



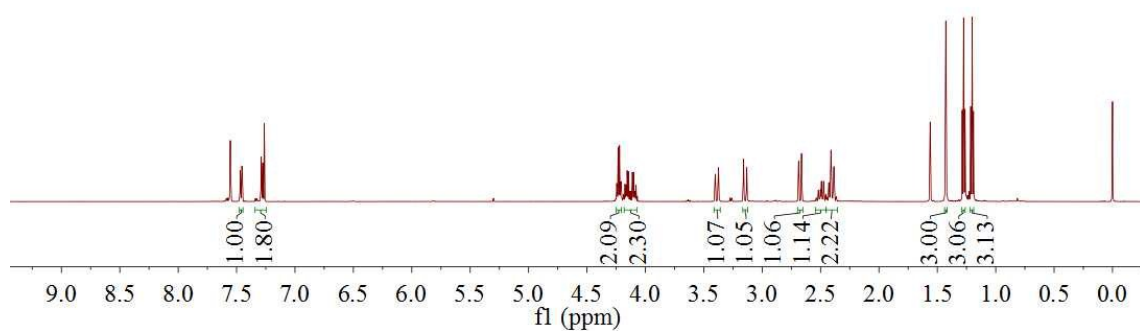
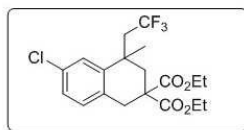
¹⁹F-NMR Spectra of 2f



¹H-NMR Spectra of 2g

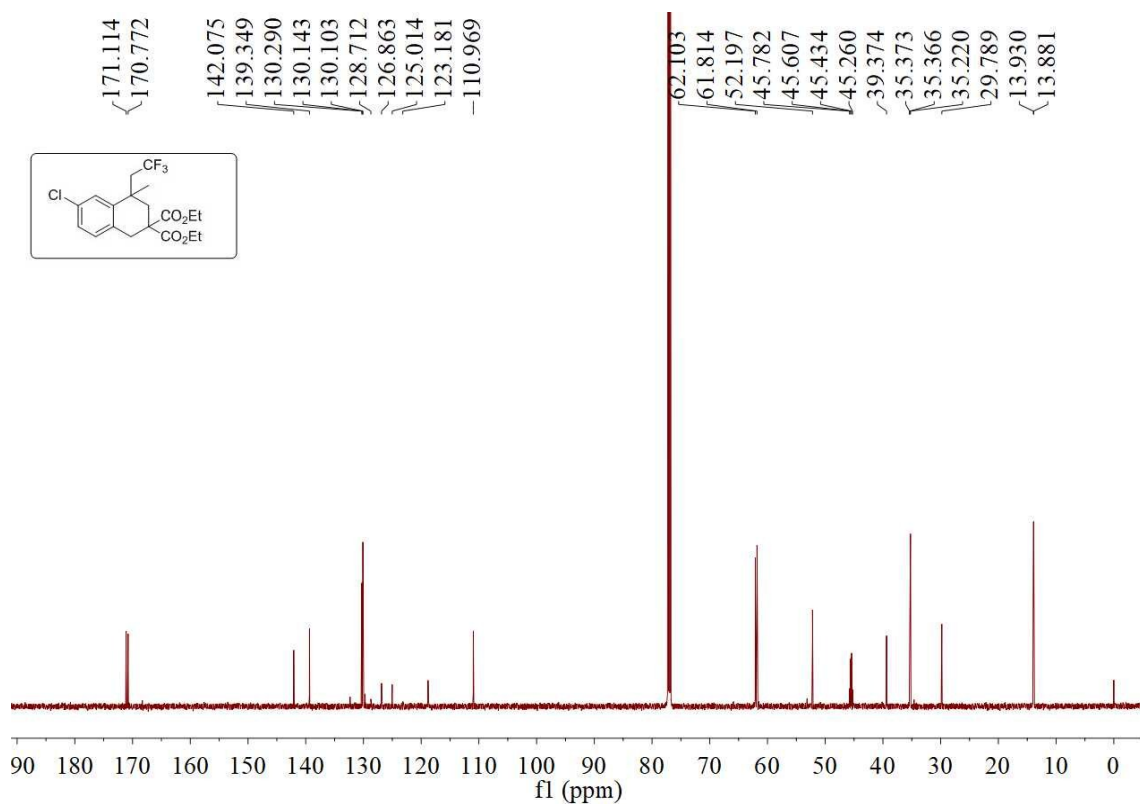
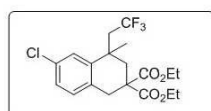
SUPPORTING INFORMATION

7.468
7.466
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7.289
7.276
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4.233
4.232
4.221
4.210
4.174
4.168
4.162
4.156
4.144
4.111
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4.093
4.081
3.401
3.374
3.159
3.132
2.687
2.663
2.492
2.474
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2.403
2.386
1.427
1.287
1.275
1.263
1.214
1.202
1.190



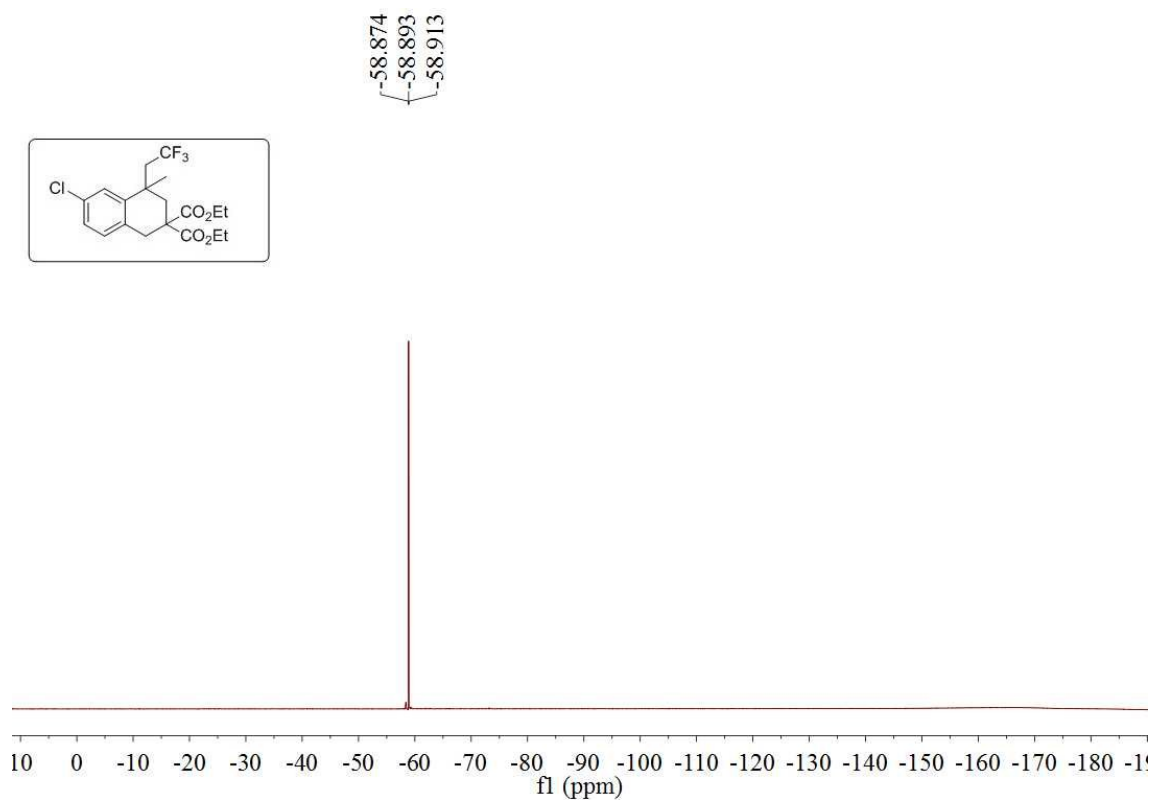
¹³C-NMR Spectra of 2g

171.114
170.772
142.075
139.349
130.290
130.143
130.103
128.712
126.863
125.014
123.181
110.969

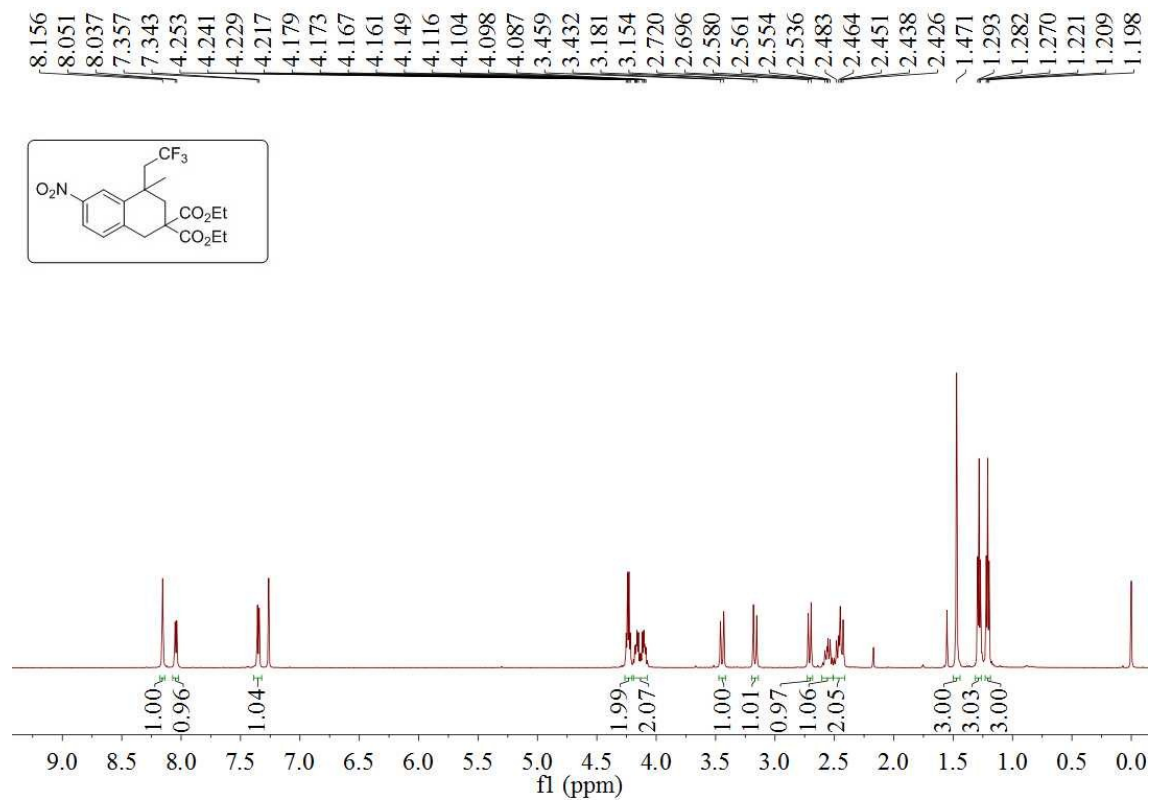


¹⁹F-NMR Spectra of 2g

SUPPORTING INFORMATION

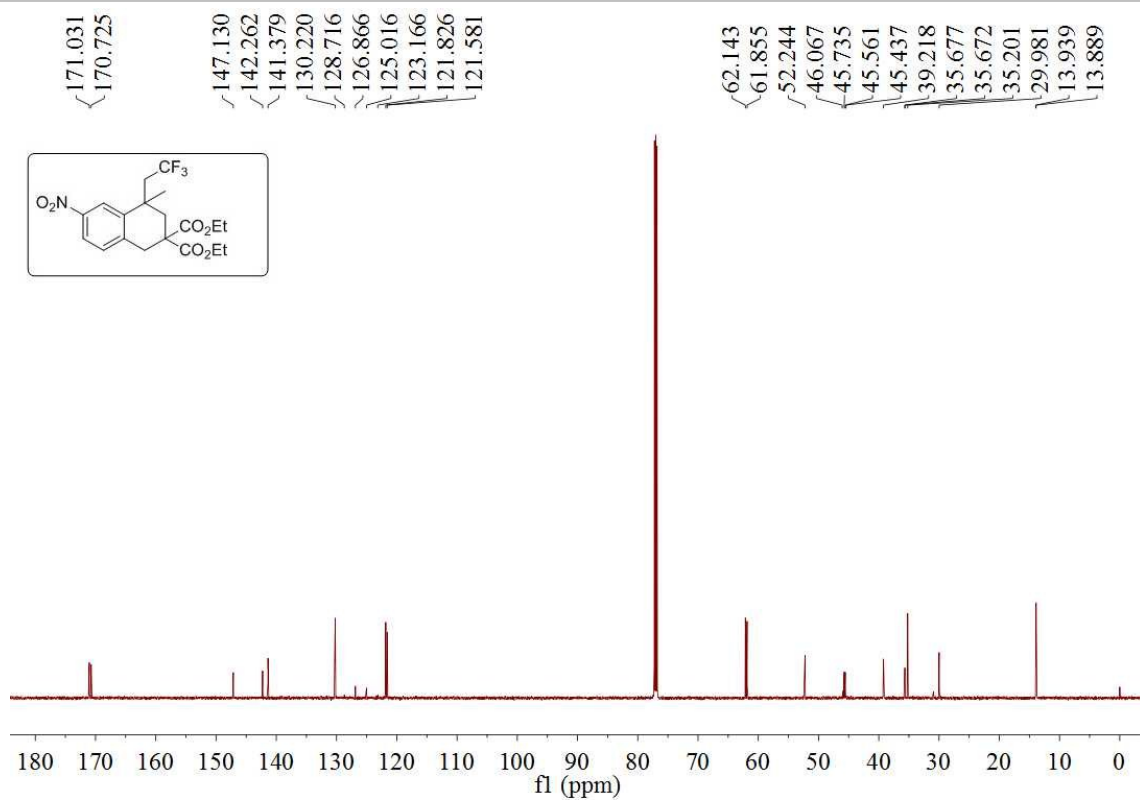


¹H-NMR Spectra of 2h

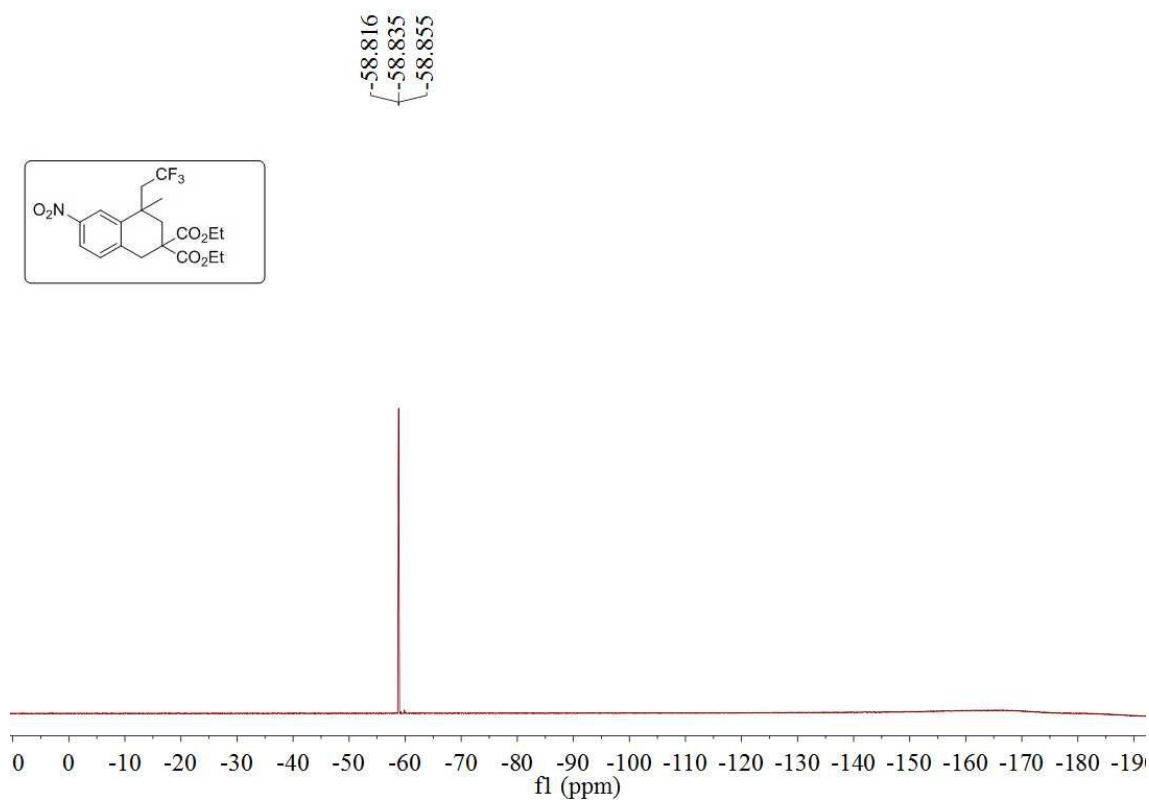


¹³C-NMR Spectra of 2h

SUPPORTING INFORMATION



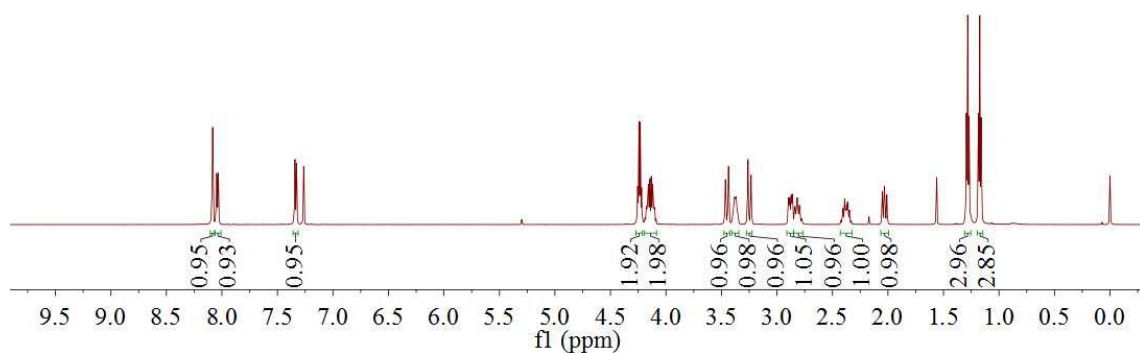
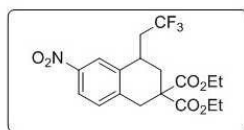
¹⁹F-NMR Spectra of 2h



¹H-NMR Spectra of 2i

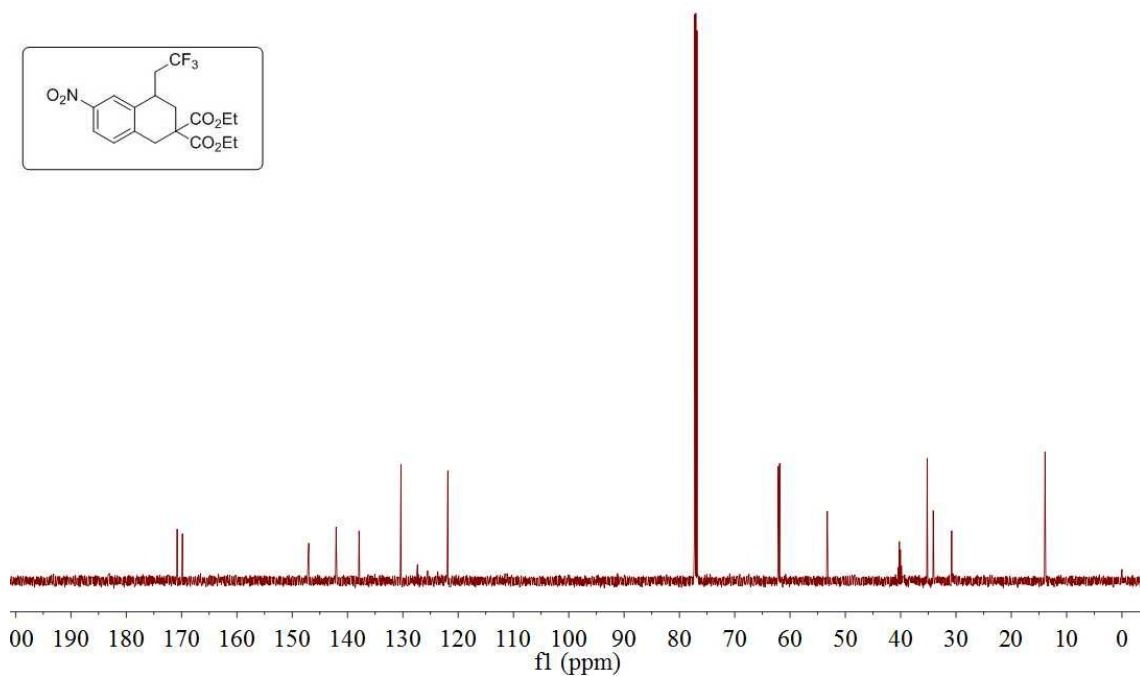
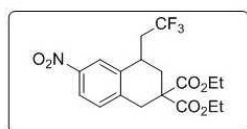
SUPPORTING INFORMATION

8.084
8.047
8.033
7.342
7.328
4.255
4.243
4.231
4.220
4.176
4.145
4.132
4.120
4.115
3.464
3.436
3.382
3.368
3.261
3.233
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2.885
2.872
2.862
2.817
2.798
2.389
2.381
2.372
2.364
2.050
2.032
2.028
2.010
1.294
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1.270
1.184
1.173
1.161



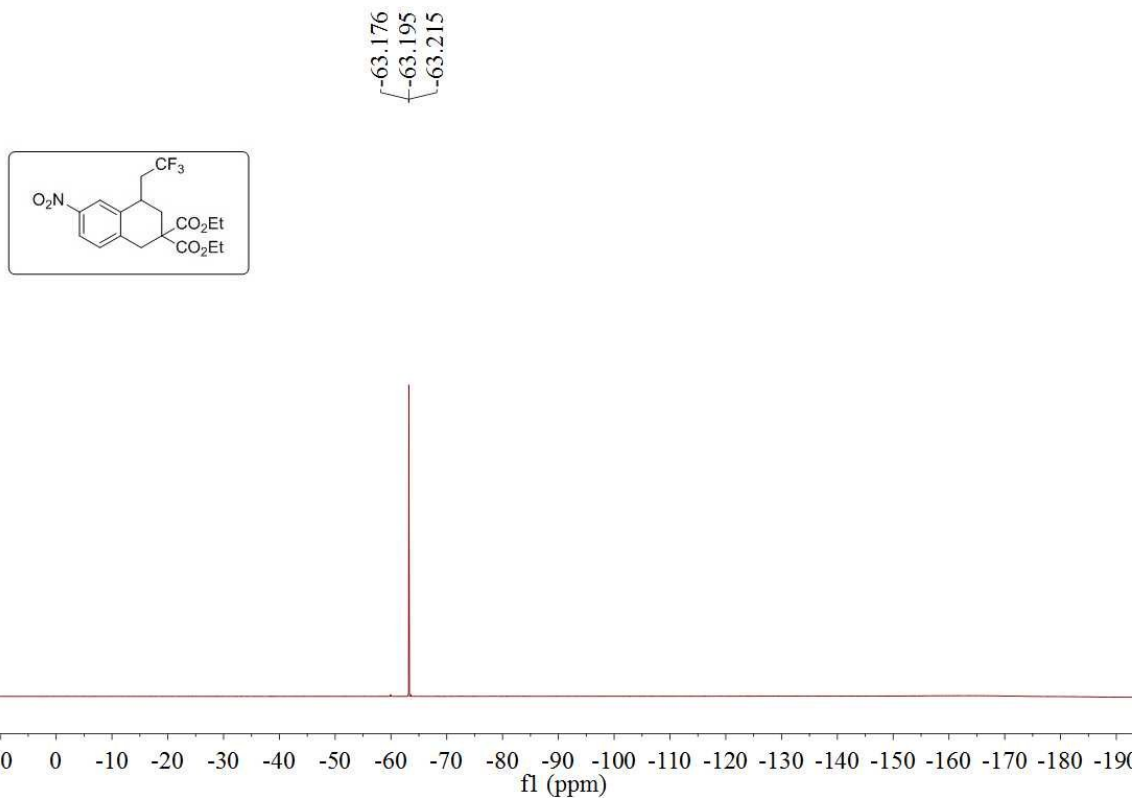
¹³C-NMR Spectra of 2i

170.800
169.847
147.003
142.070
137.923
130.333
127.356
125.516
123.676
121.941
121.866
62.144
61.880
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40.224
40.039
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34.123
30.782
30.768
13.991
13.906

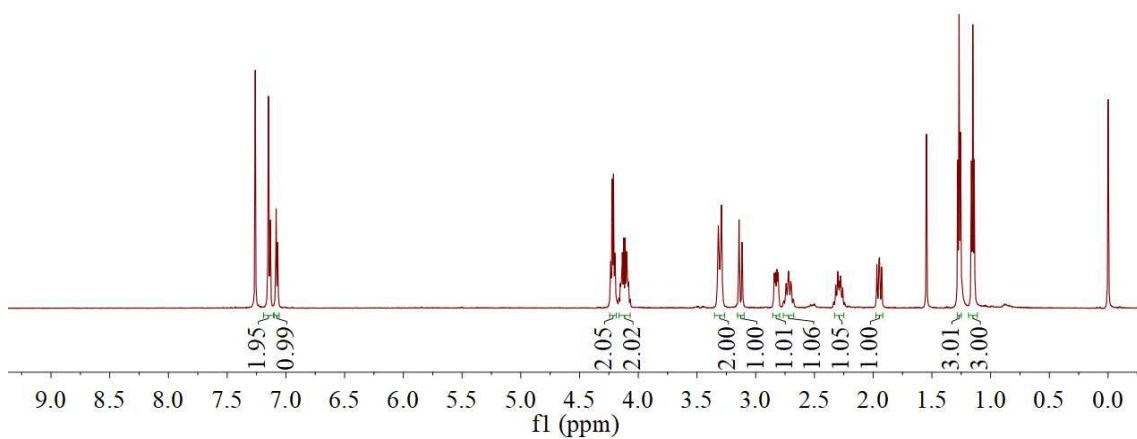
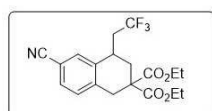
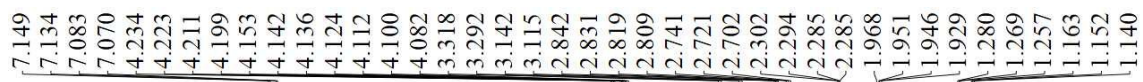


¹⁹F-NMR Spectra of 2i

SUPPORTING INFORMATION

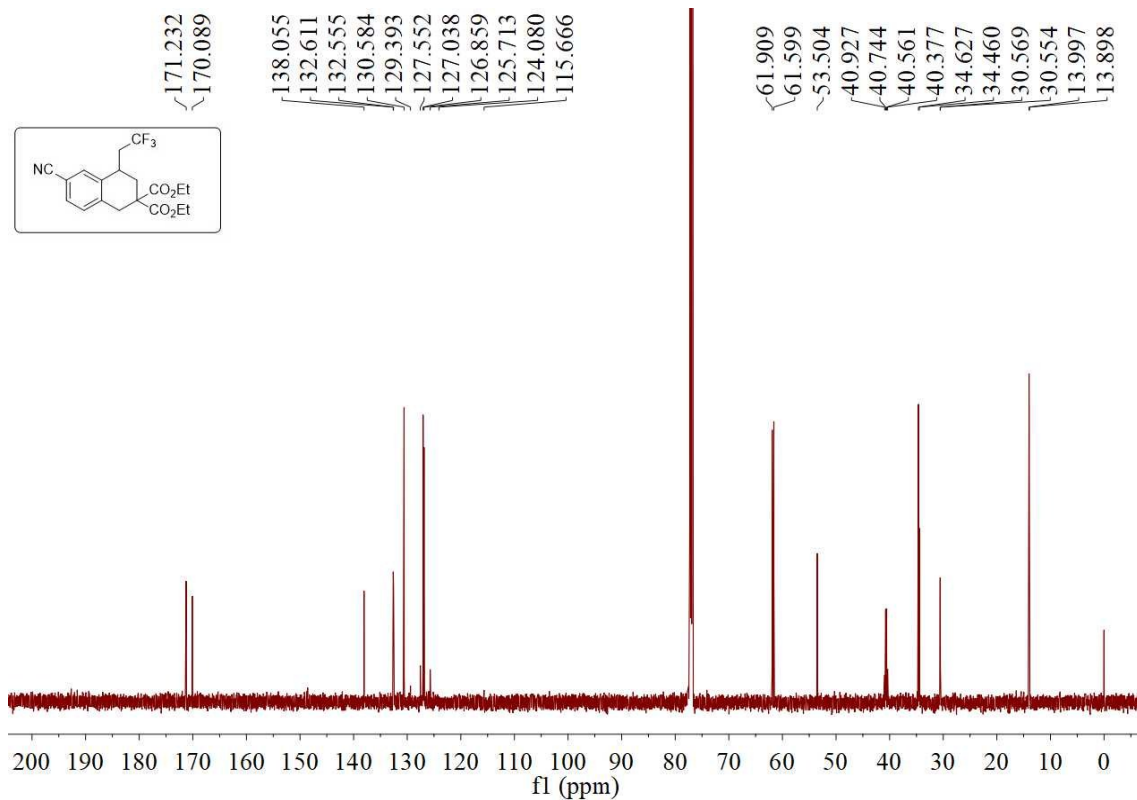


¹H-NMR Spectra of 2j

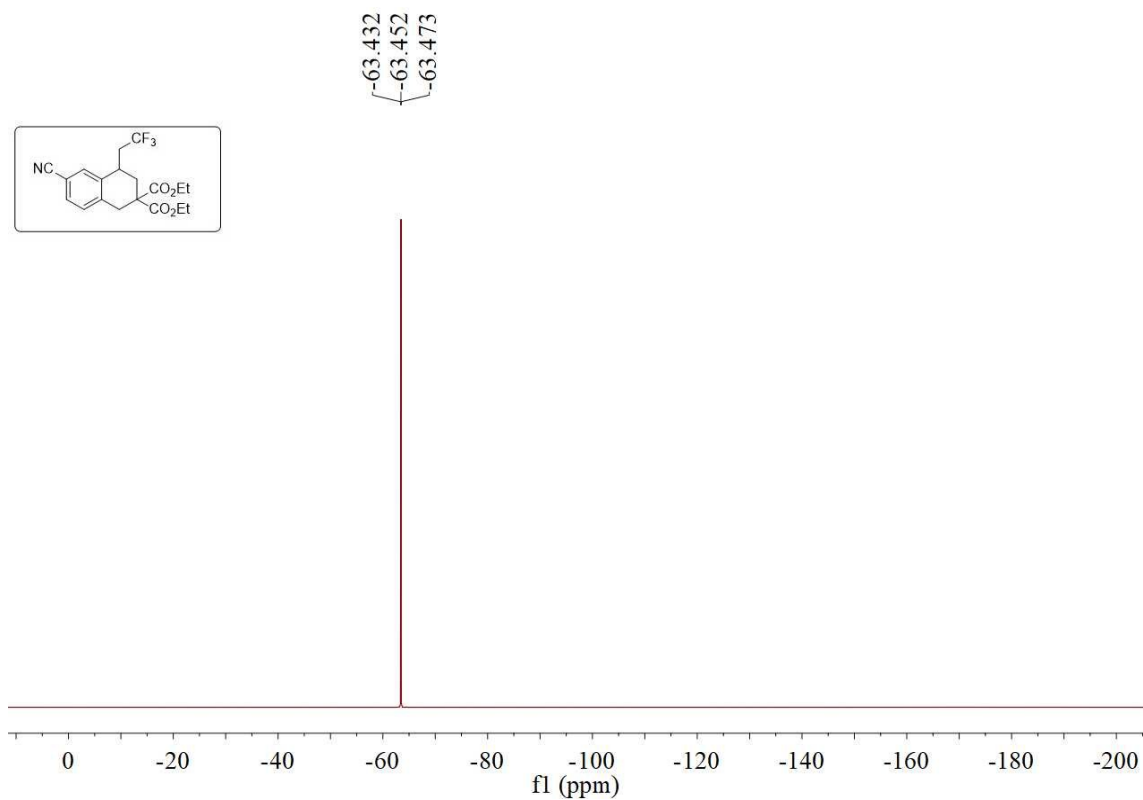


¹³C-NMR Spectra of 2j

SUPPORTING INFORMATION

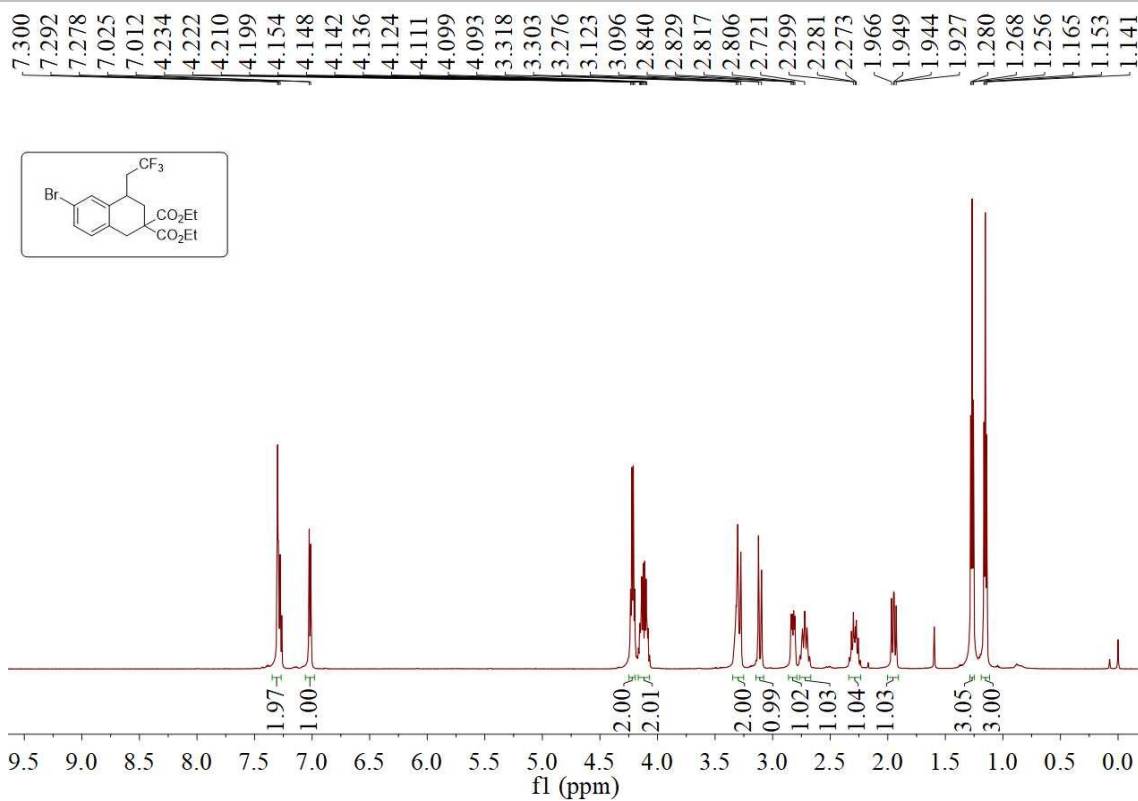


¹⁹F-NMR Spectra of 2j

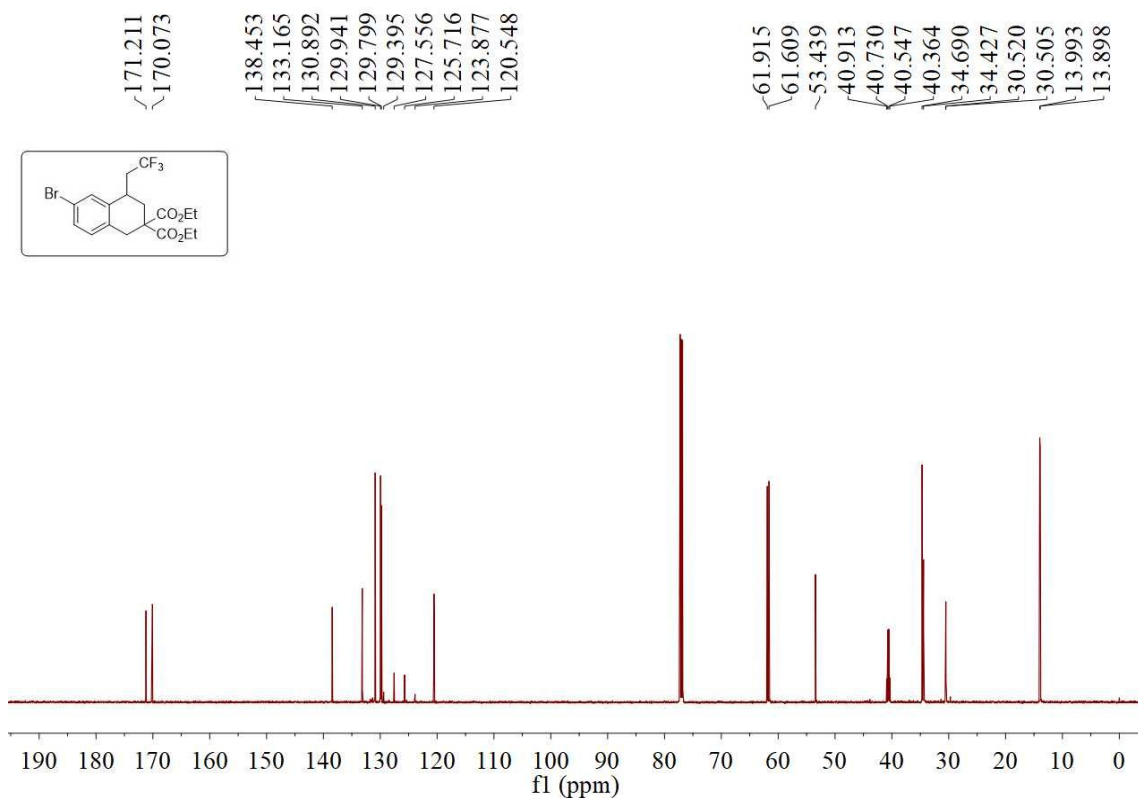


¹H-NMR Spectra of 2k

SUPPORTING INFORMATION

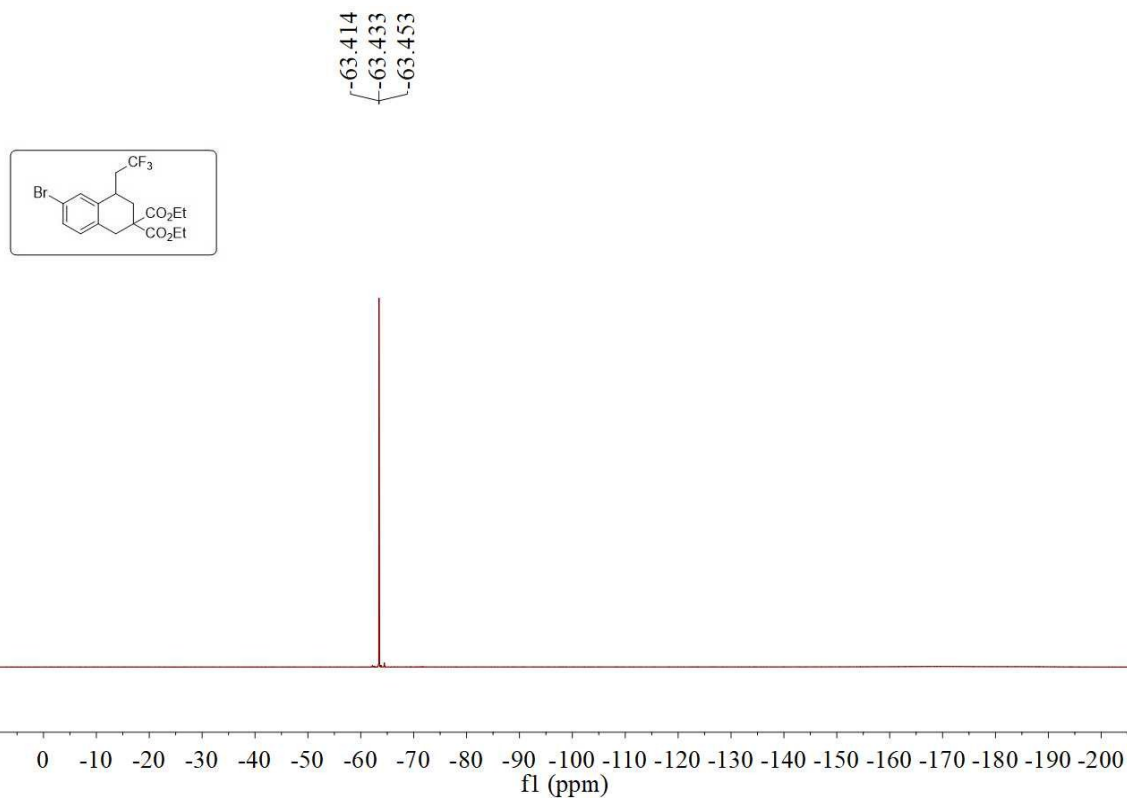


¹³C-NMR Spectra of 2k

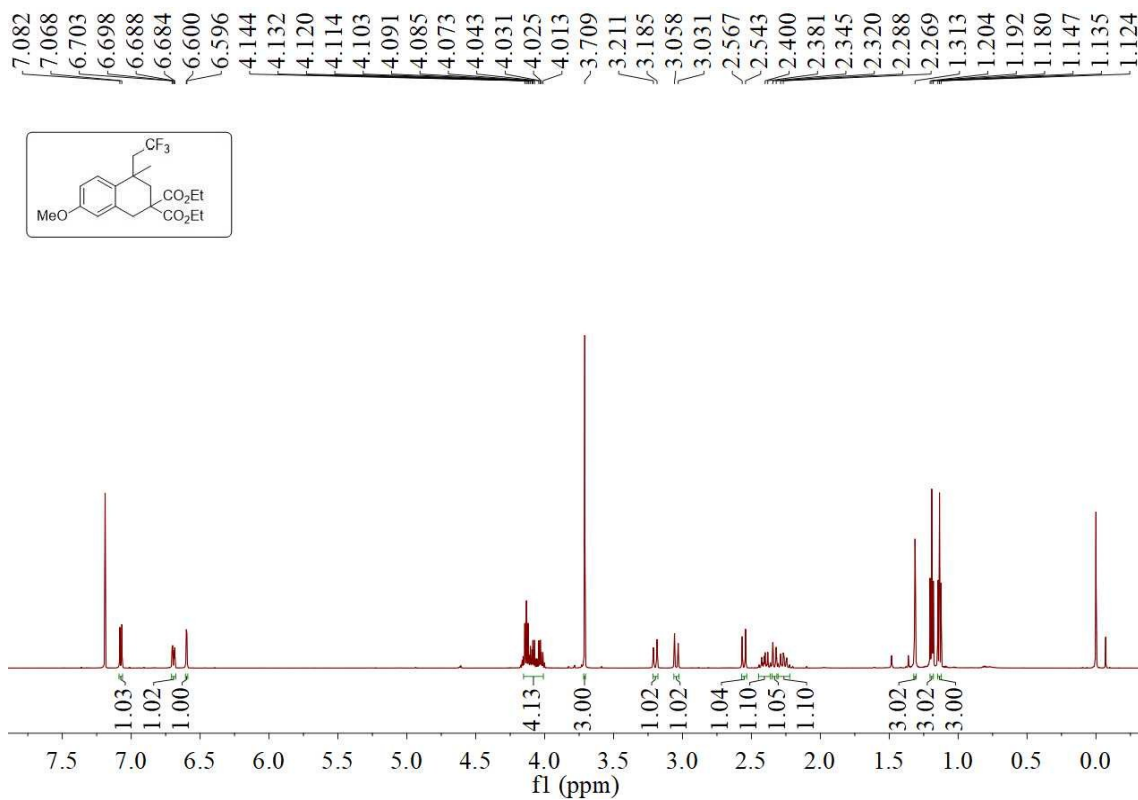


¹⁹F-NMR Spectra of 2k

SUPPORTING INFORMATION

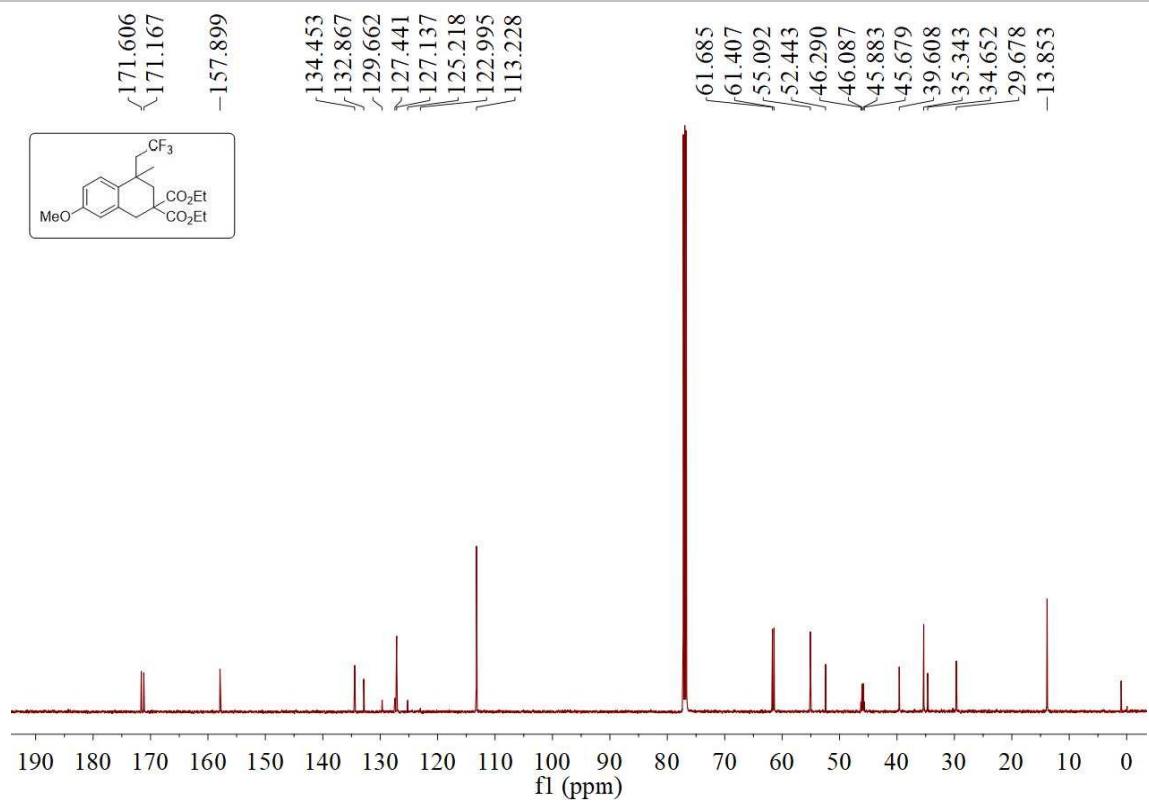


¹H-NMR Spectra of 2l

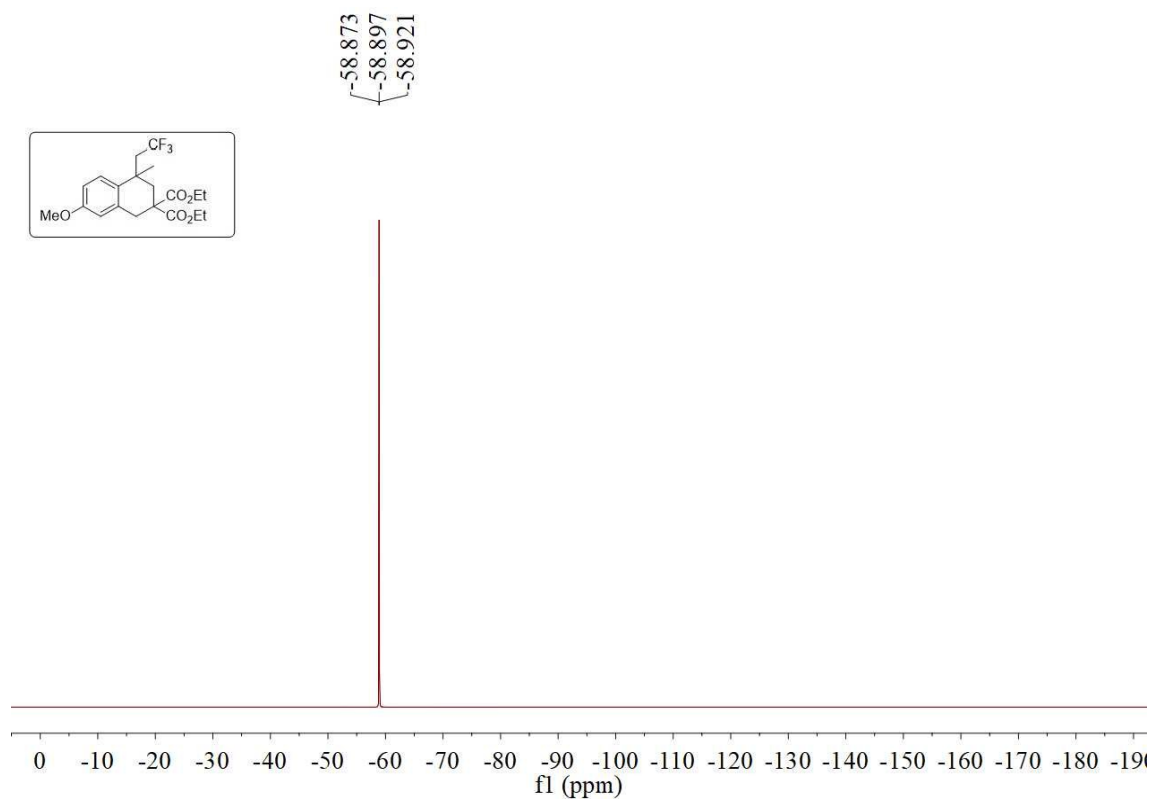


¹³C-NMR Spectra of 2l

SUPPORTING INFORMATION



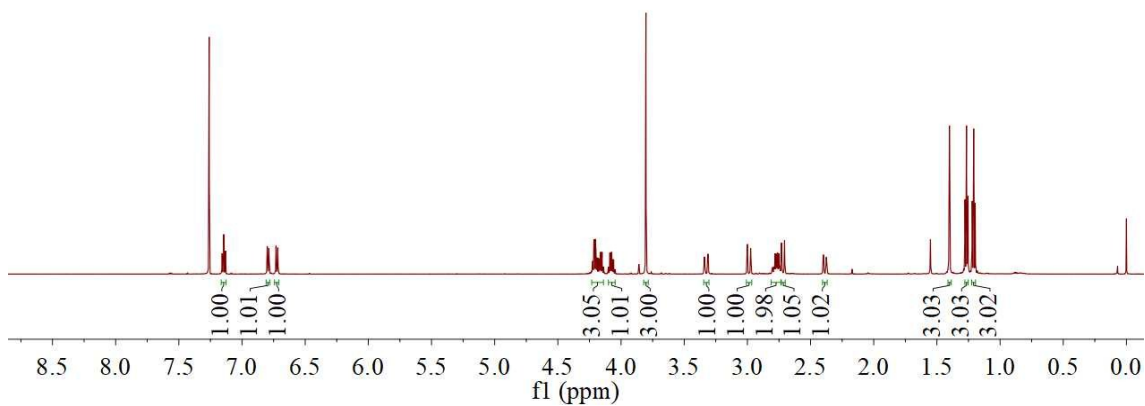
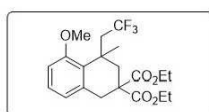
¹⁹F-NMR Spectra of 2l



¹H-NMR Spectra of 2l

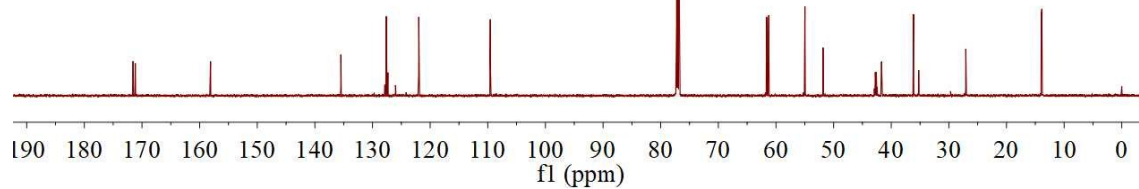
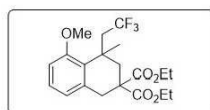
SUPPORTING INFORMATION

7.157
7.144
7.131
6.800
6.787
6.731
6.717
4.215
4.211
4.203
4.199
4.191
4.162
4.150
4.088
4.077
3.803
3.340
3.336
3.314
3.310
3.000
2.974
2.781
2.771
2.761
2.752
2.730
2.706
2.400
2.396
2.376
2.372
1.401
1.277
1.266
1.254
1.220
1.209
1.197



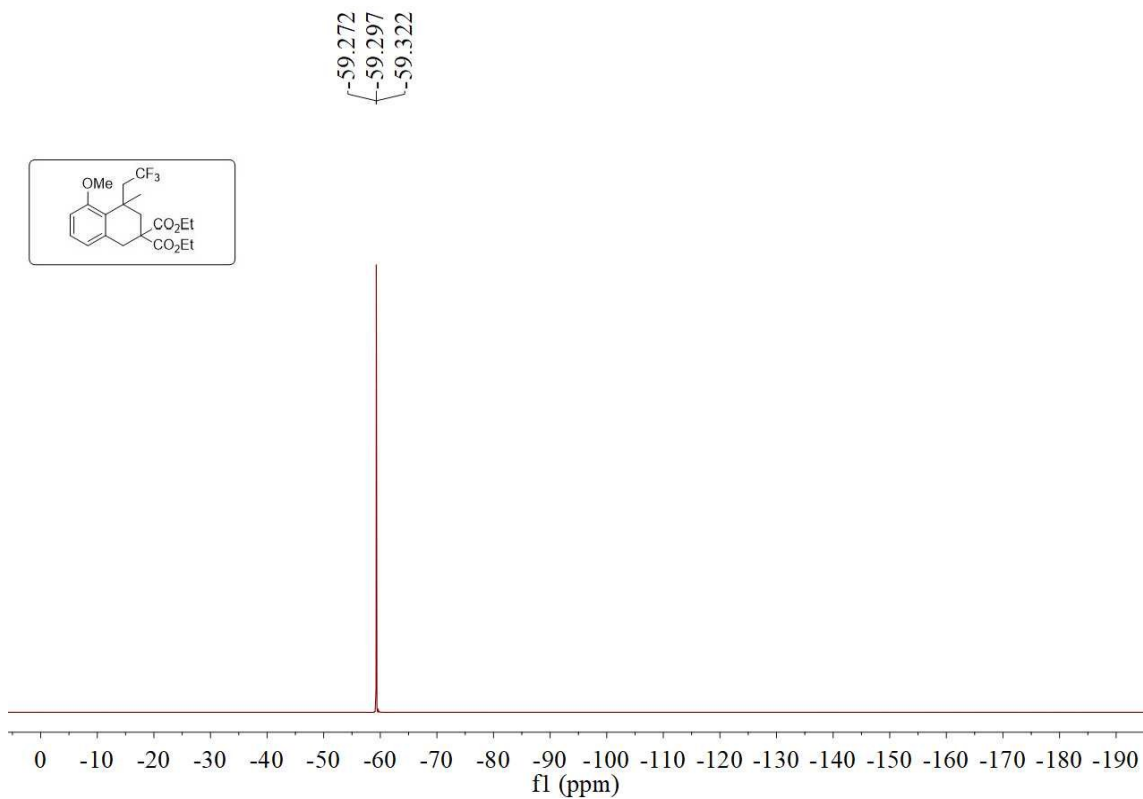
¹³C-NMR Spectra of 2l

171.551
171.157
-158.097
135.487
129.712
127.863
127.614
127.324
126.013
124.165
121.976
-109.562
61.615
61.252
54.977
51.830
42.933
42.766
42.599
42.432
41.689
41.677
36.130
35.233
27.056
13.956
13.864

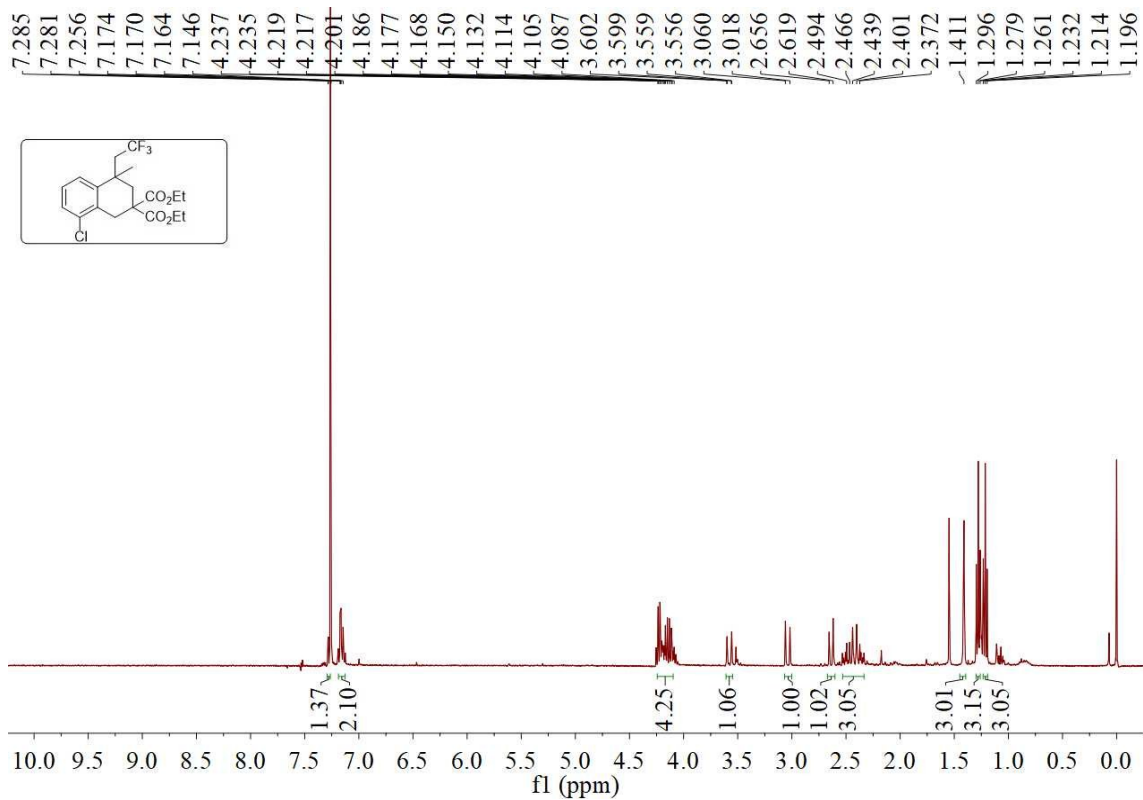


¹⁹F-NMR Spectra of 2l

SUPPORTING INFORMATION

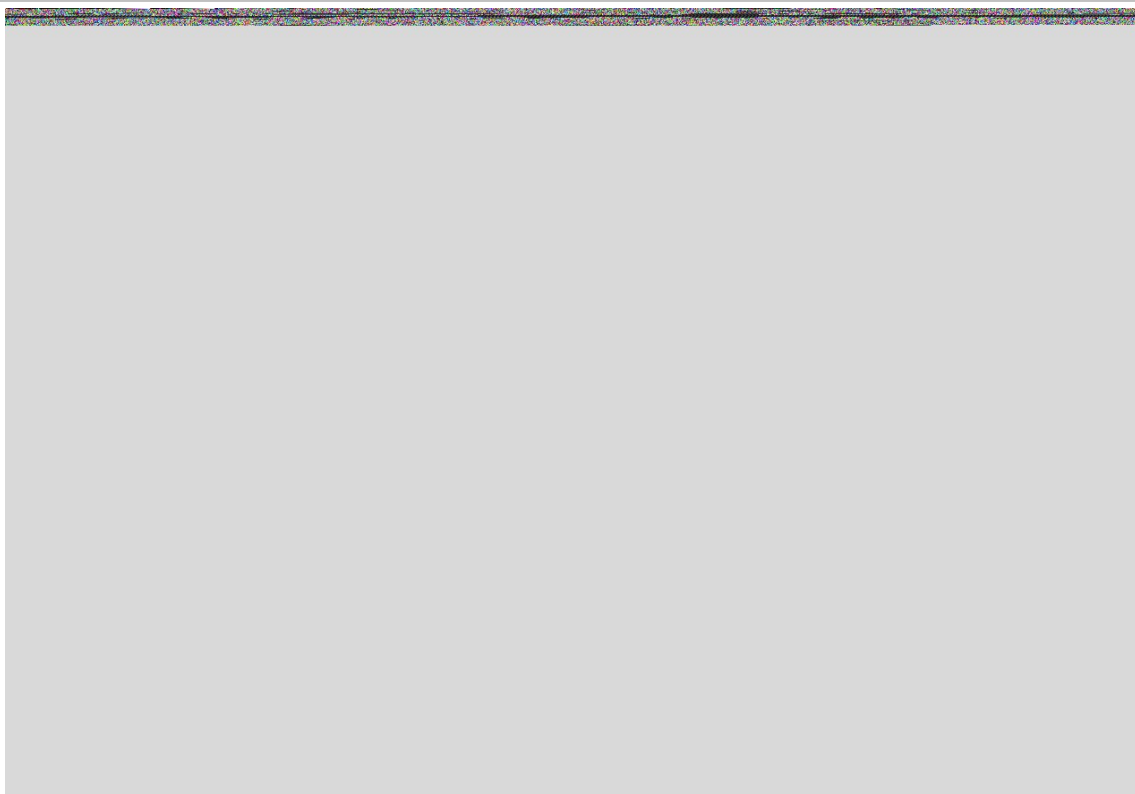


$^1\text{H-NMR}$ Spectra of 2m

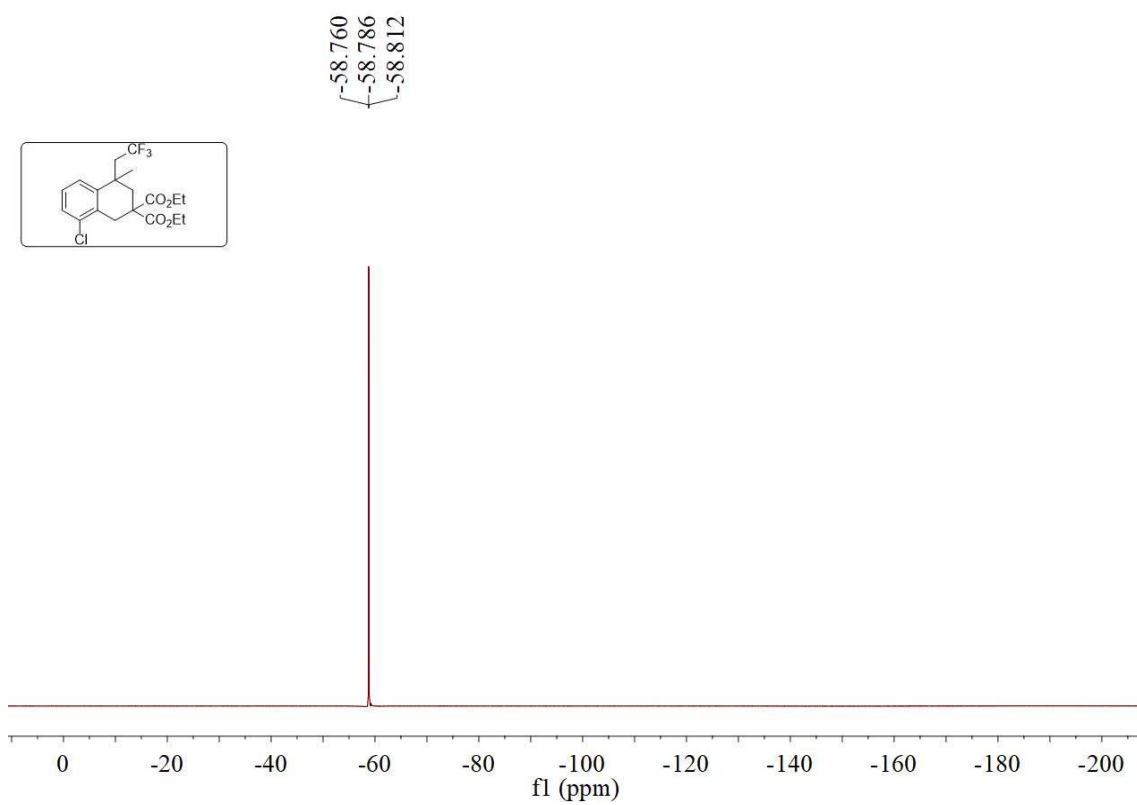


$^{13}\text{C-NMR}$ Spectra of 2m

SUPPORTING INFORMATION



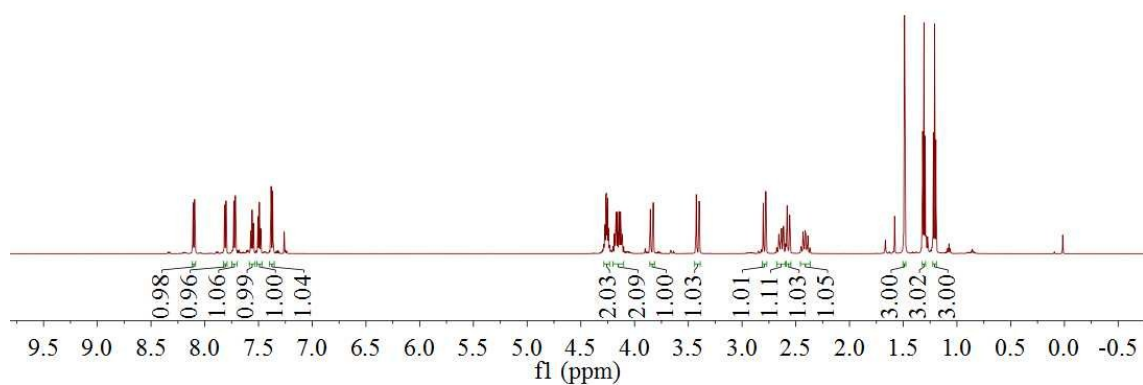
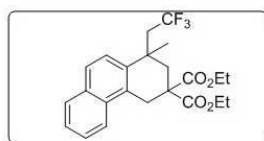
¹⁹F-NMR Spectra of 2m



¹H-NMR Spectra of 2n

SUPPORTING INFORMATION

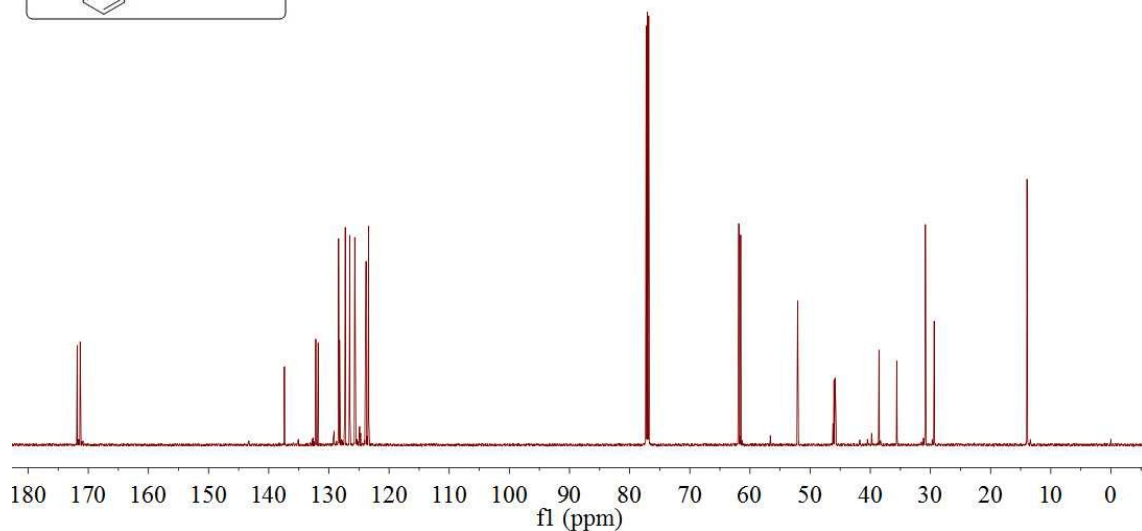
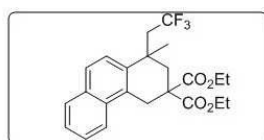
8.108
8.094
7.816
7.802
7.730
7.715
7.559
7.547
7.504
7.492
7.480
7.382
7.368
4.275
4.268
4.263
4.256
4.251
4.244
4.171
4.159
4.143
4.131
3.854
3.826
3.426
3.399
2.803
2.779
2.633
2.614
2.581
2.557
1.488
1.319
1.307
1.295
1.220
1.208
1.196



¹³C-NMR Spectra of 2n

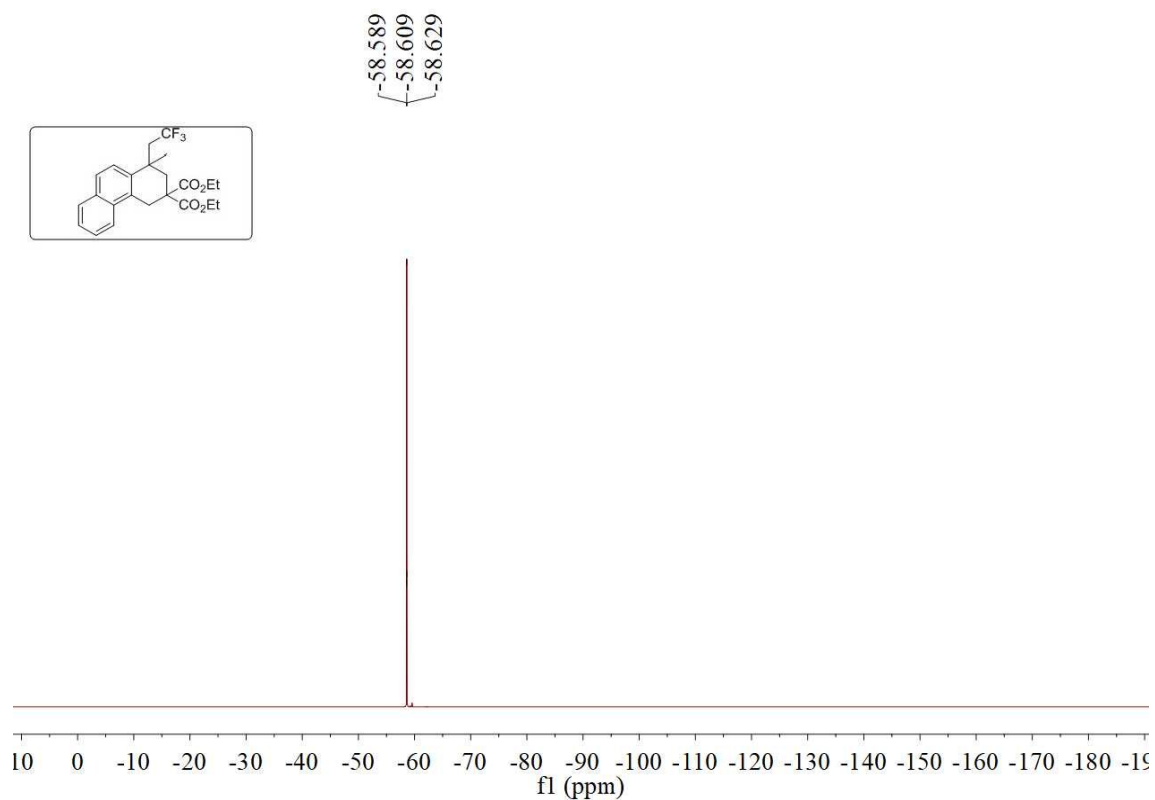
171.850
171.351
137.396
132.176
131.779
129.144
128.386
128.224
127.379
127.279
126.509
125.701
125.528
123.826
123.678
123.388

61.861
61.542
52.080
46.207
46.035
45.864
45.692
38.556
35.599
35.593
30.840
29.382
13.947
13.897

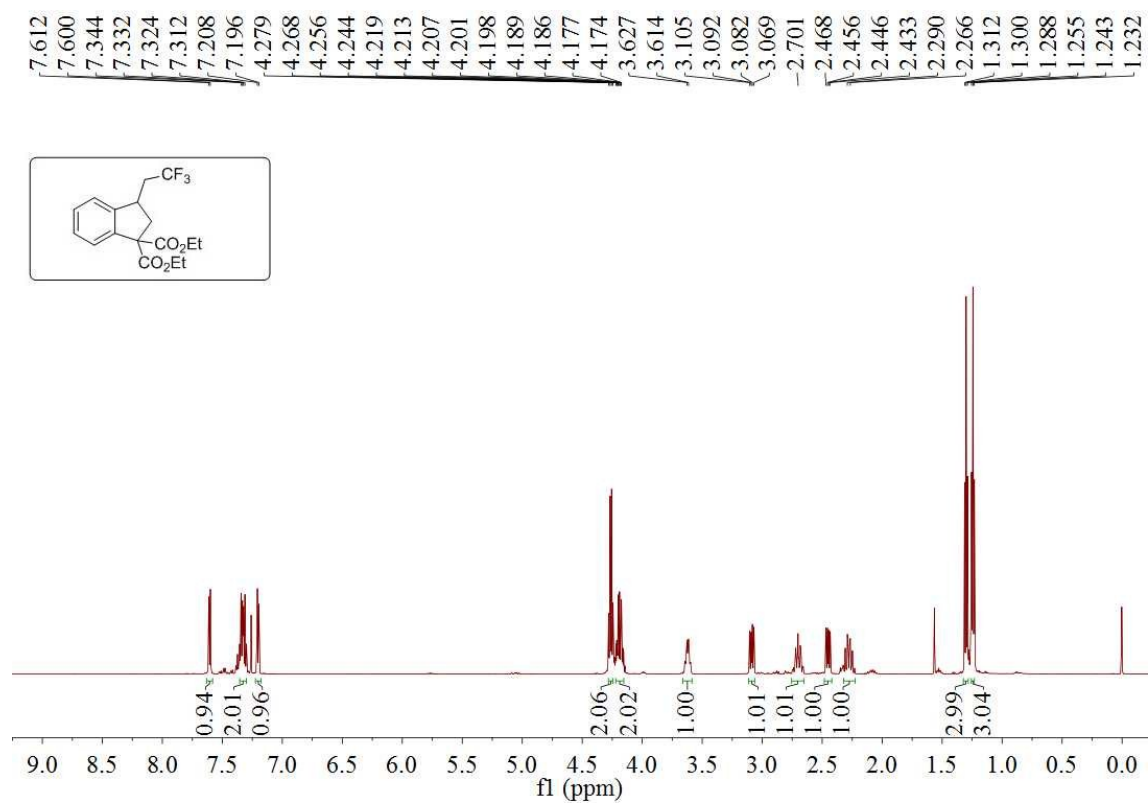


¹⁹F-NMR Spectra of 2n

SUPPORTING INFORMATION

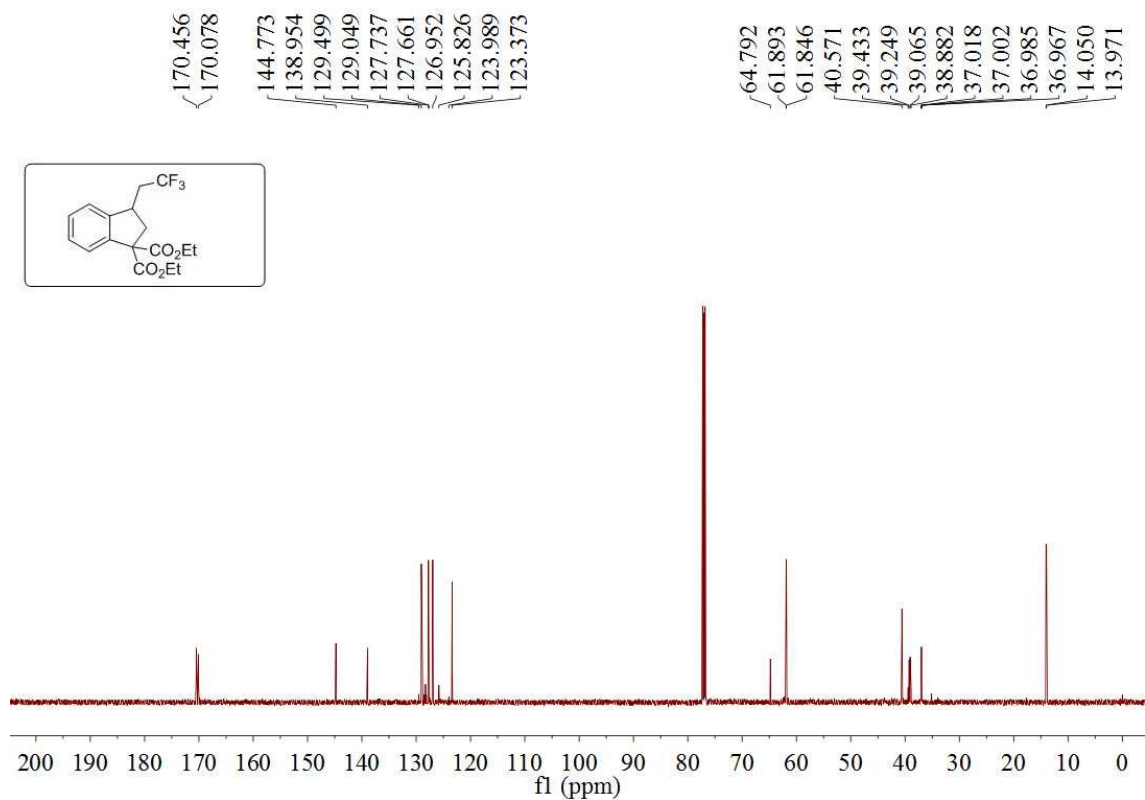


$^1\text{H-NMR}$ Spectra of 4a

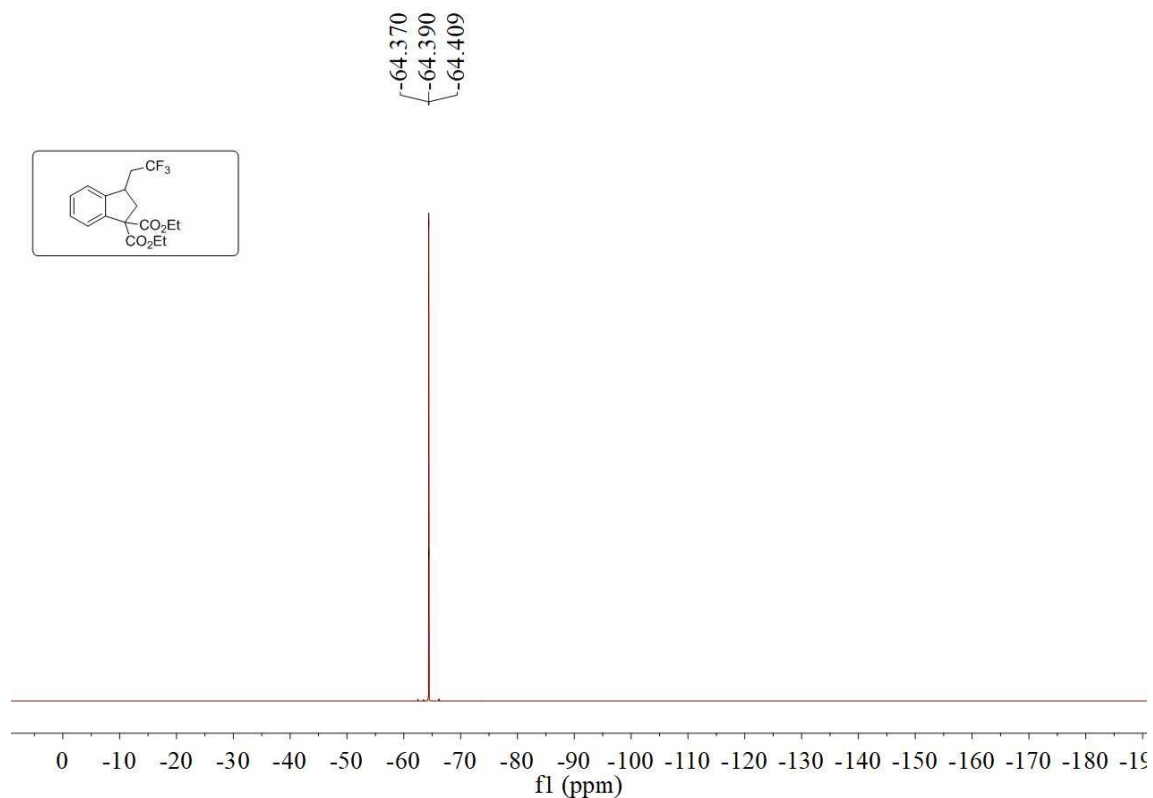


$^{13}\text{C-NMR}$ Spectra of 4a

SUPPORTING INFORMATION

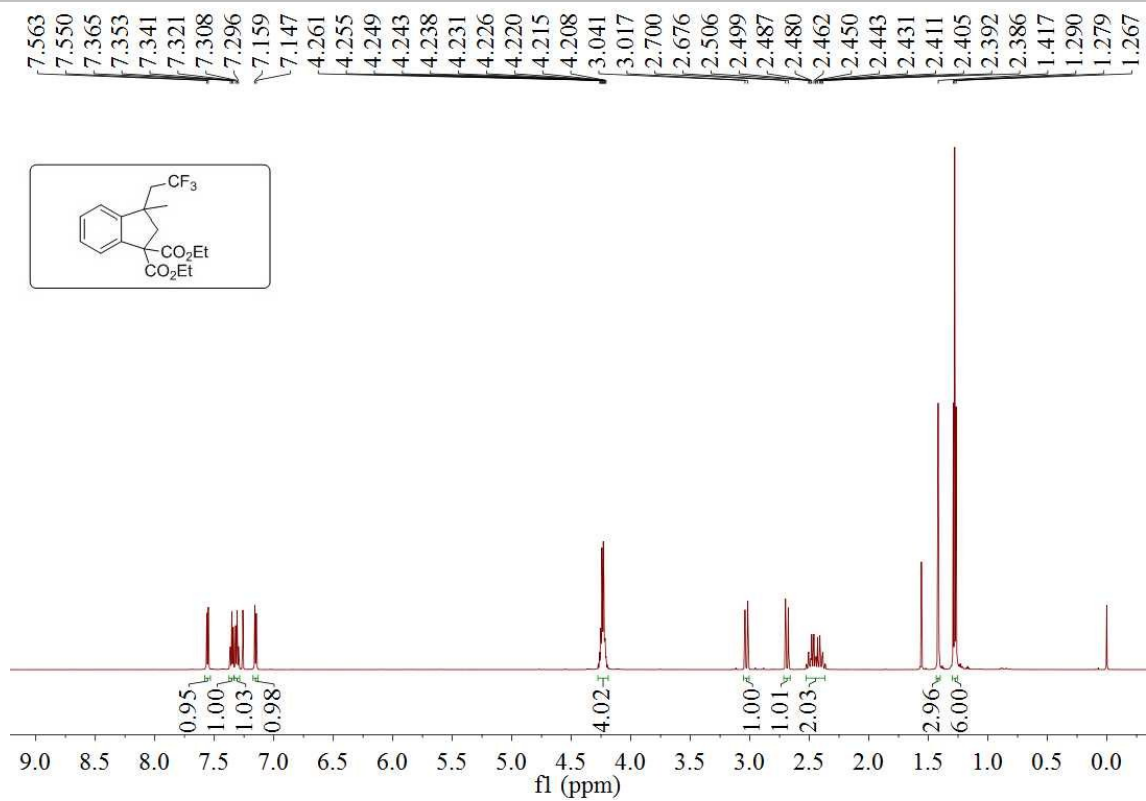


¹⁹F-NMR Spectra of 4a

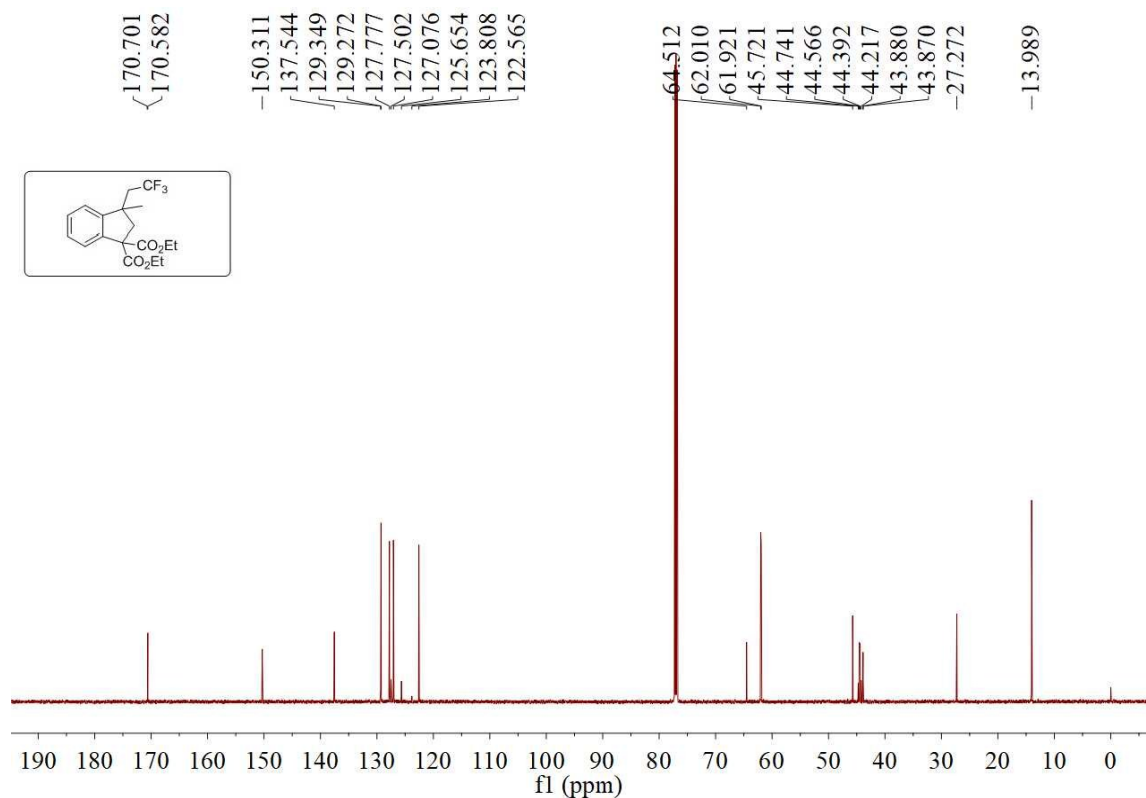


¹H-NMR Spectra of 4b

SUPPORTING INFORMATION

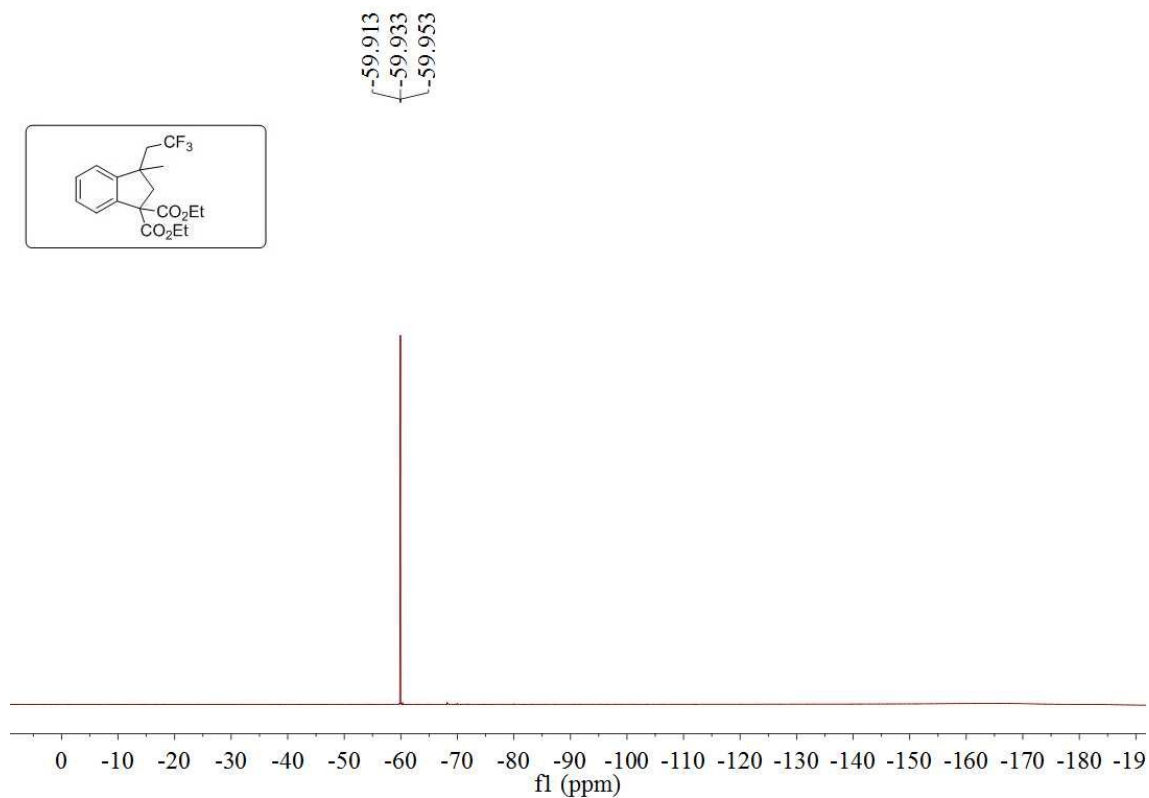


¹³C-NMR Spectra of 4b

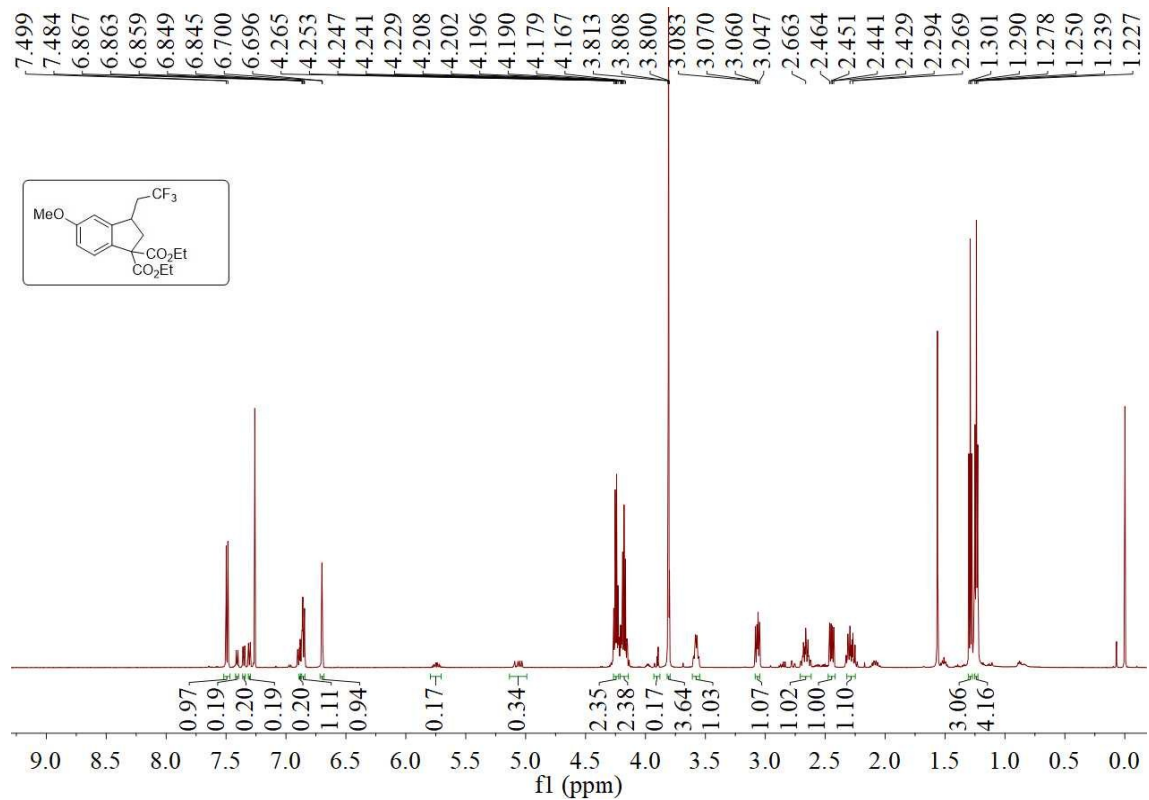


¹⁹F-NMR Spectra of 4b

SUPPORTING INFORMATION

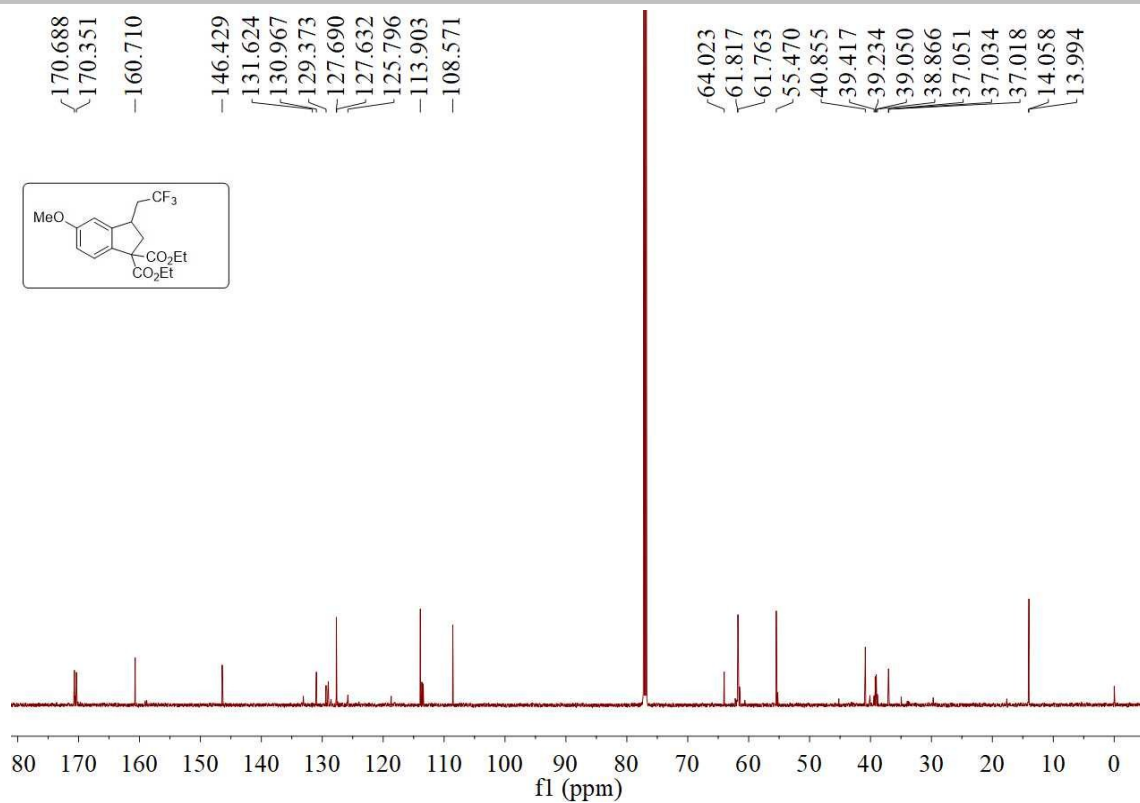


¹H-NMR Spectra of 4c

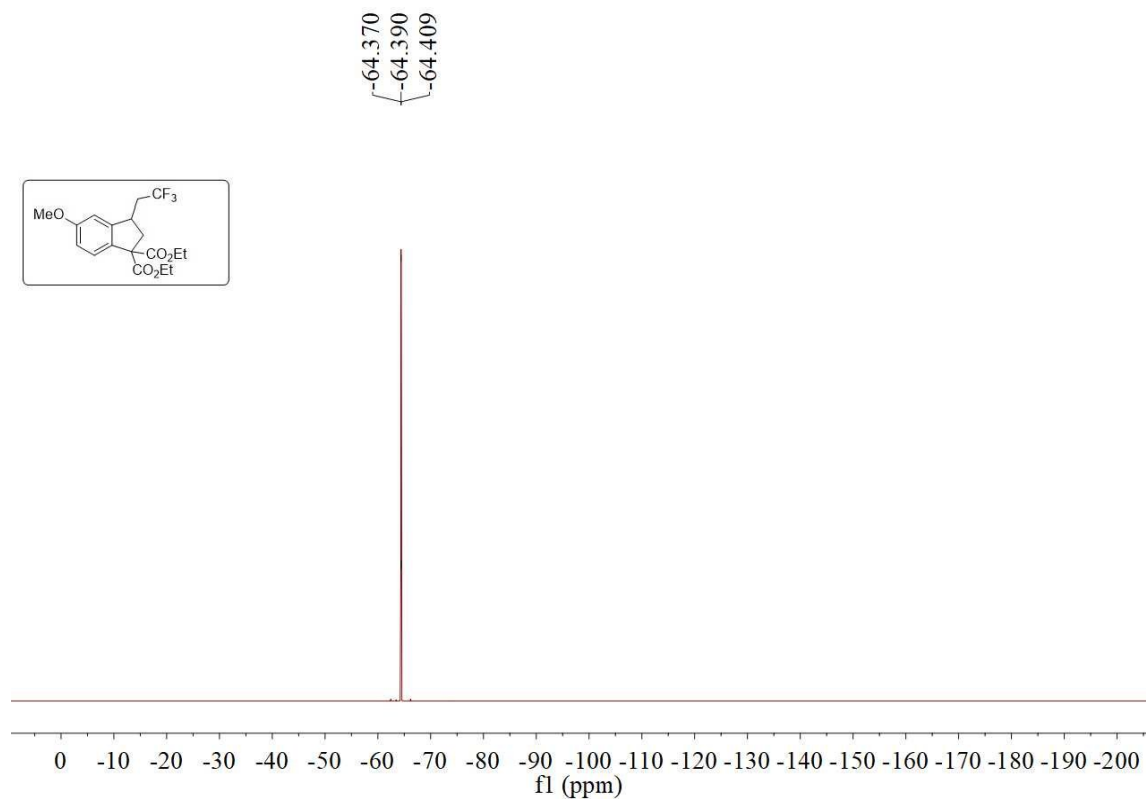


¹³C-NMR Spectra of 4c

SUPPORTING INFORMATION

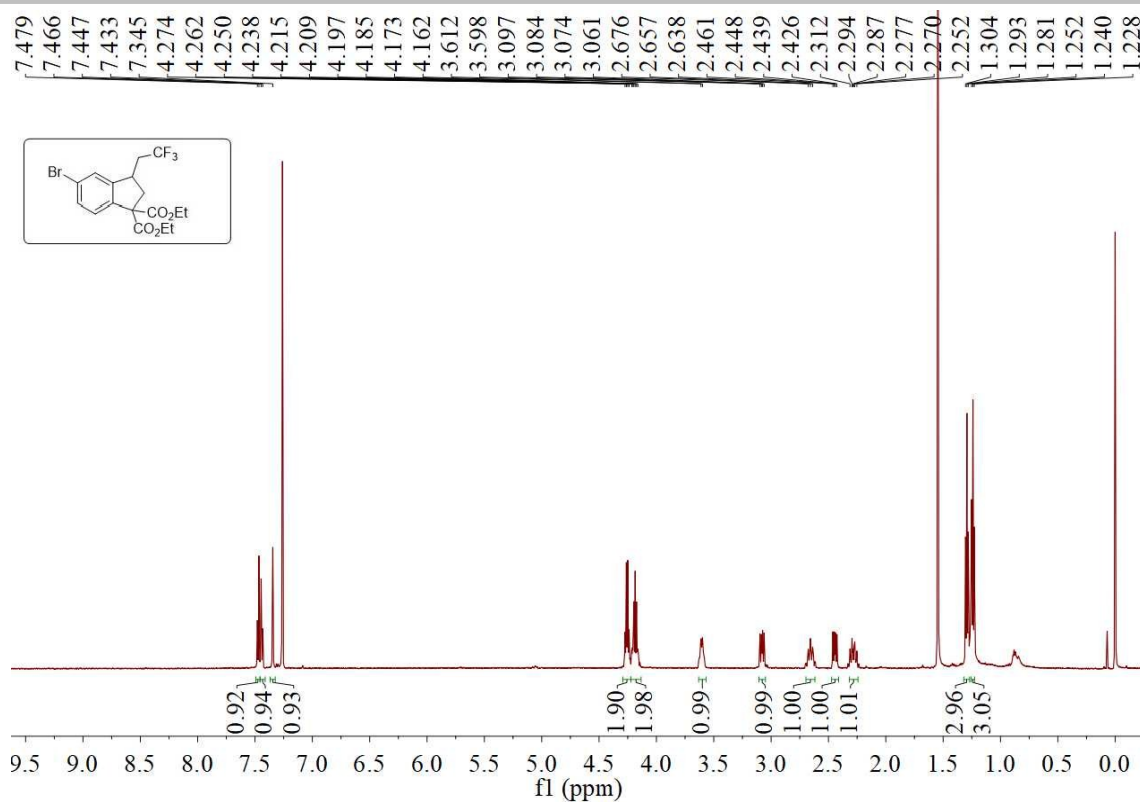


¹⁹F-NMR Spectra of 4c

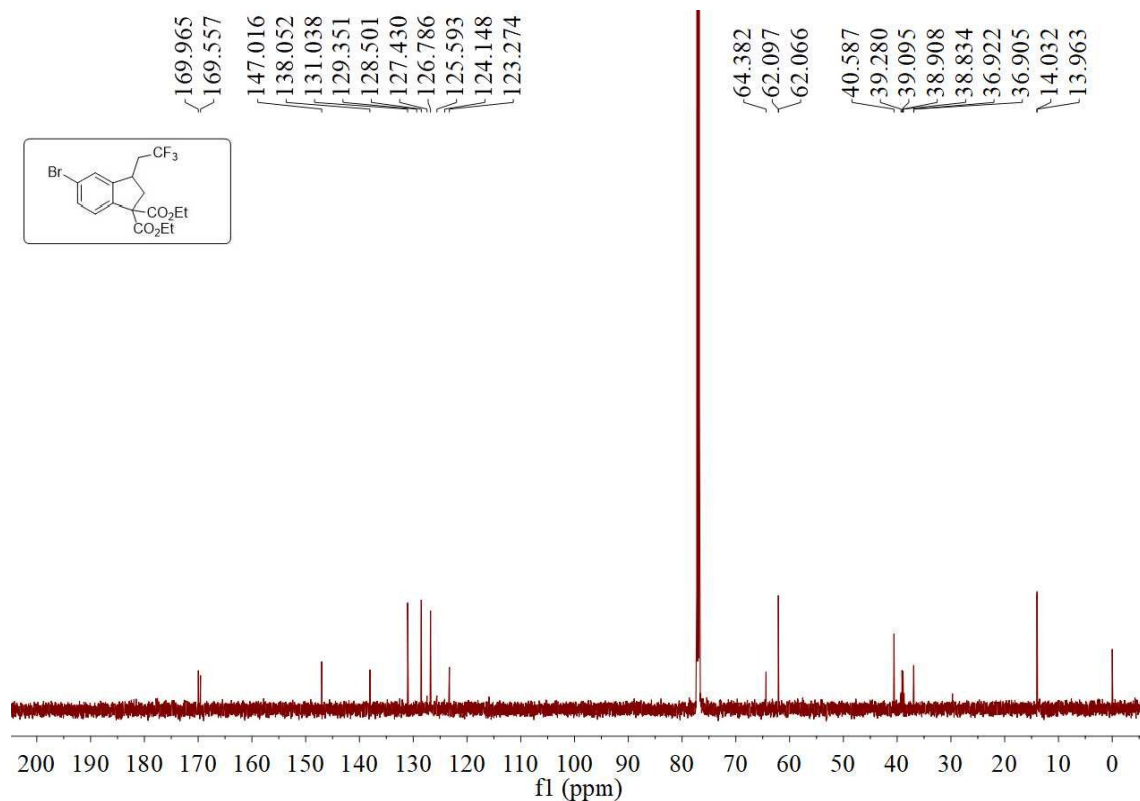


¹H-NMR Spectra of 4d

SUPPORTING INFORMATION

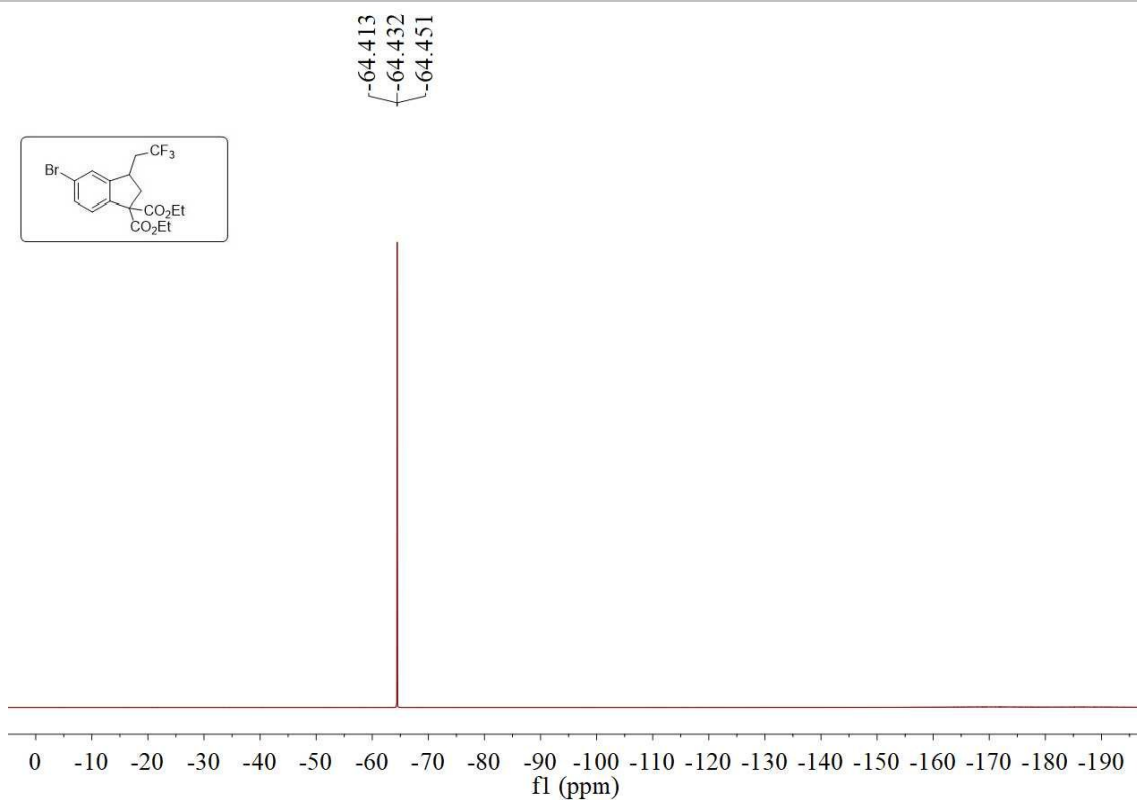


¹³C-NMR Spectra of 4d

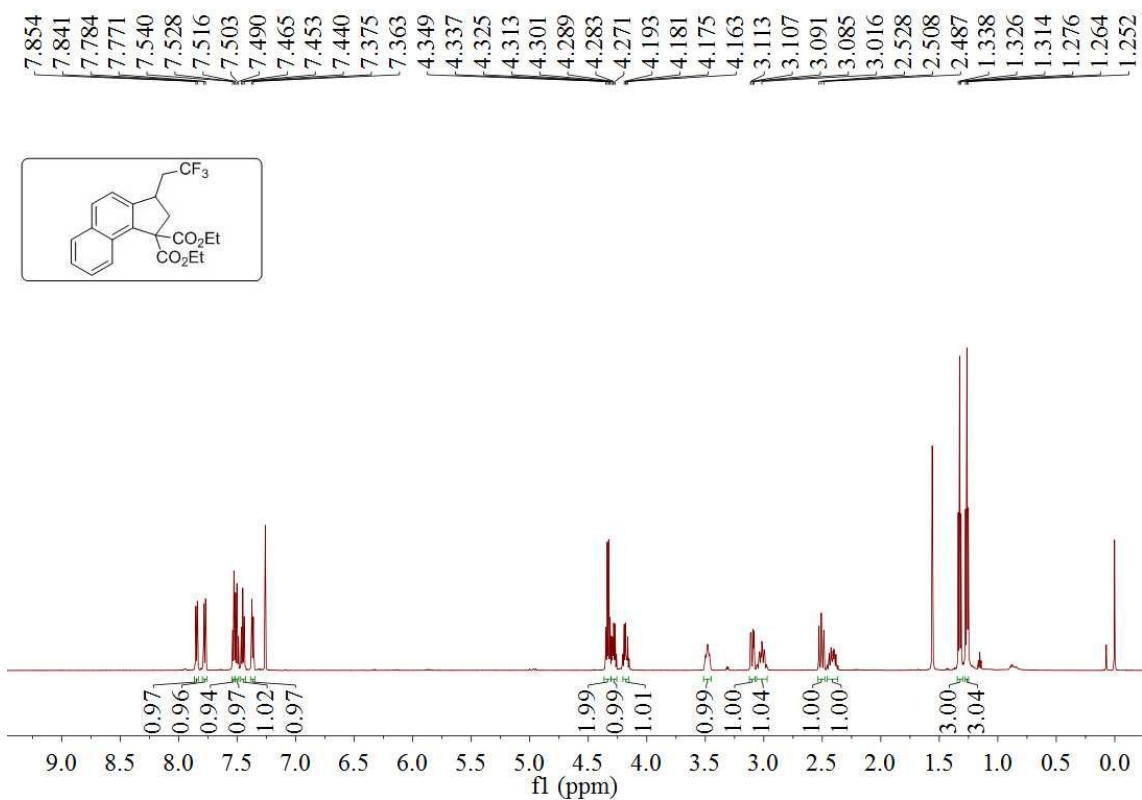


¹⁹F-NMR Spectra of 4d

SUPPORTING INFORMATION

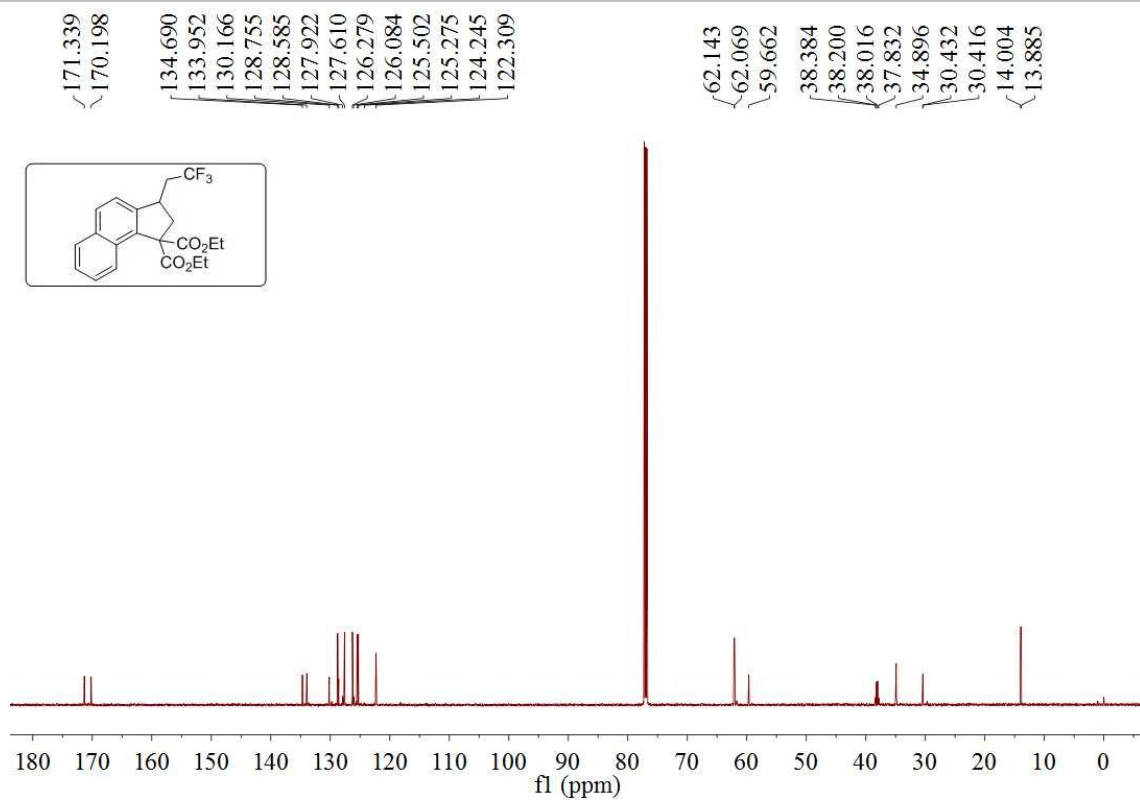


$^1\text{H-NMR}$ Spectra of 4e

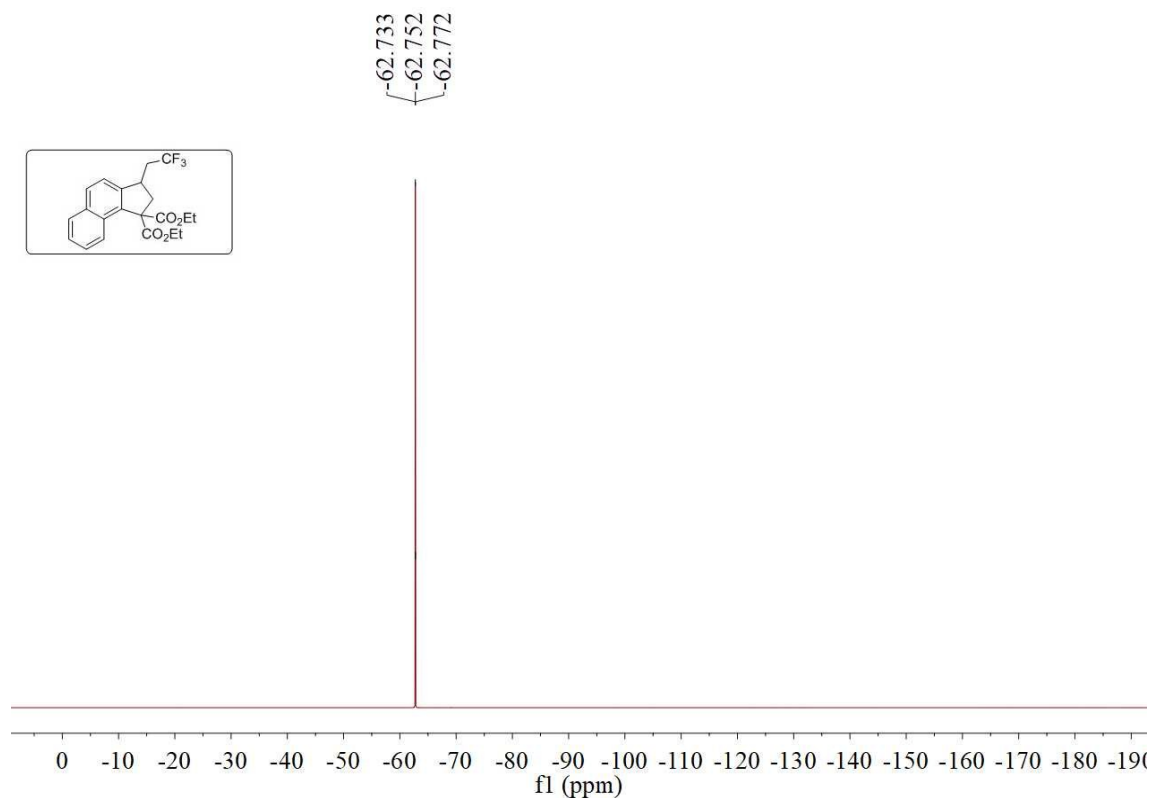


$^{13}\text{C-NMR}$ Spectra of 4e

SUPPORTING INFORMATION

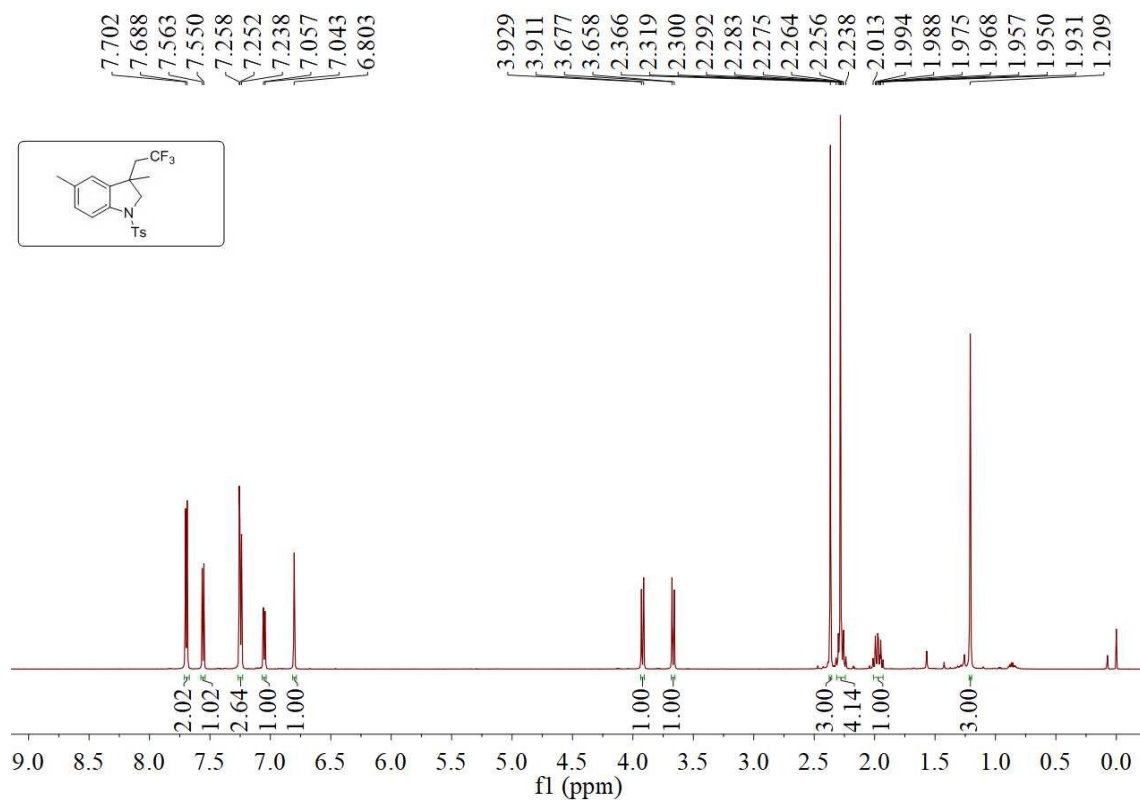


¹⁹F-NMR Spectra of 4e

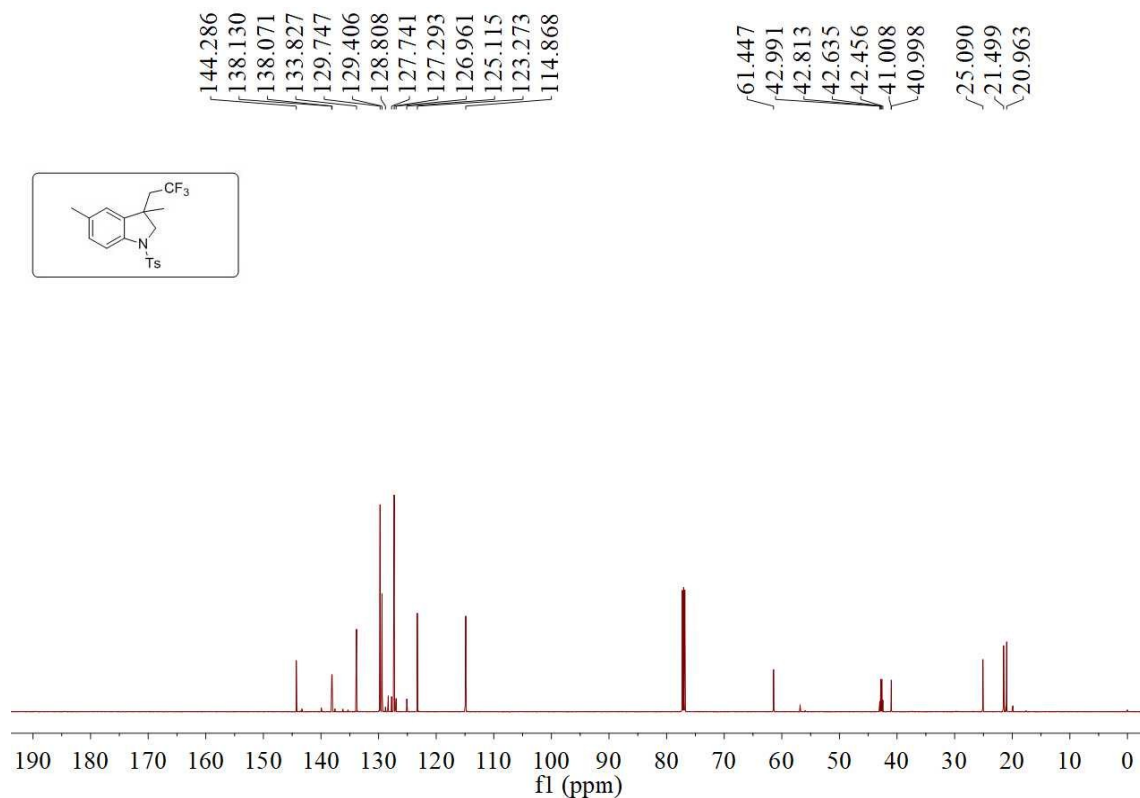


¹H-NMR Spectra of 6a

SUPPORTING INFORMATION

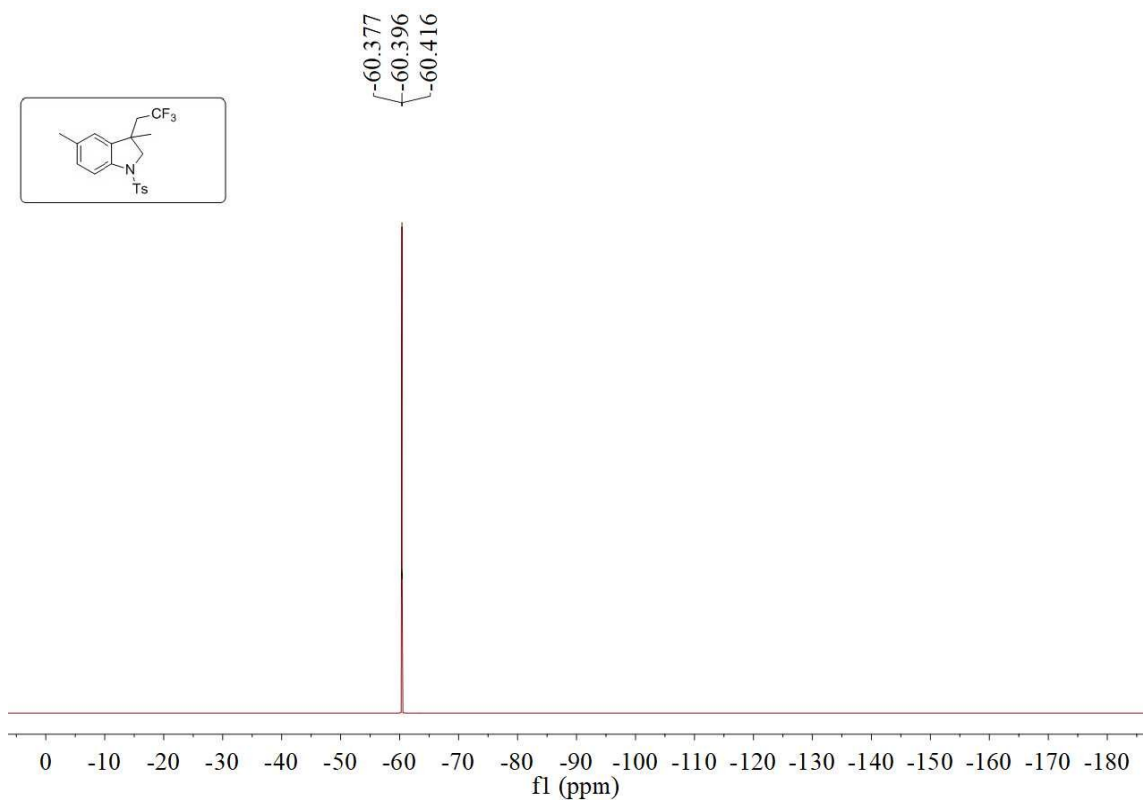


¹³C-NMR Spectra of 6a

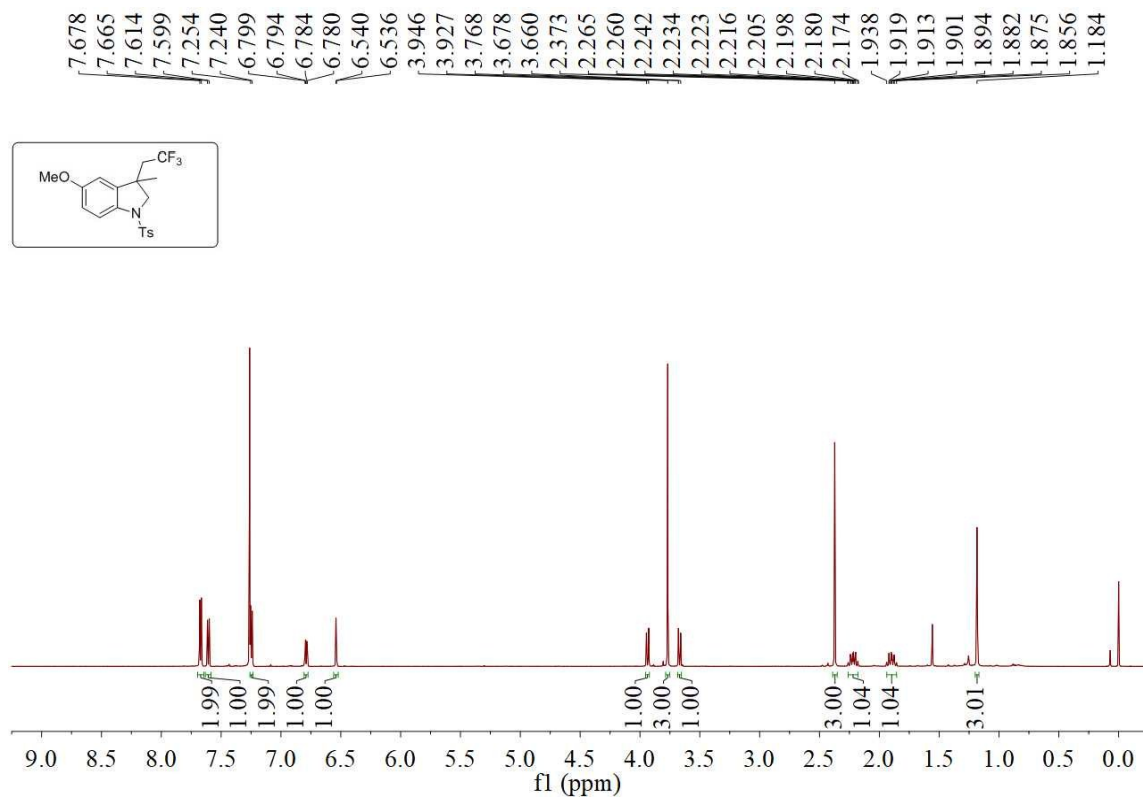


¹⁹F-NMR Spectra of 6a

SUPPORTING INFORMATION

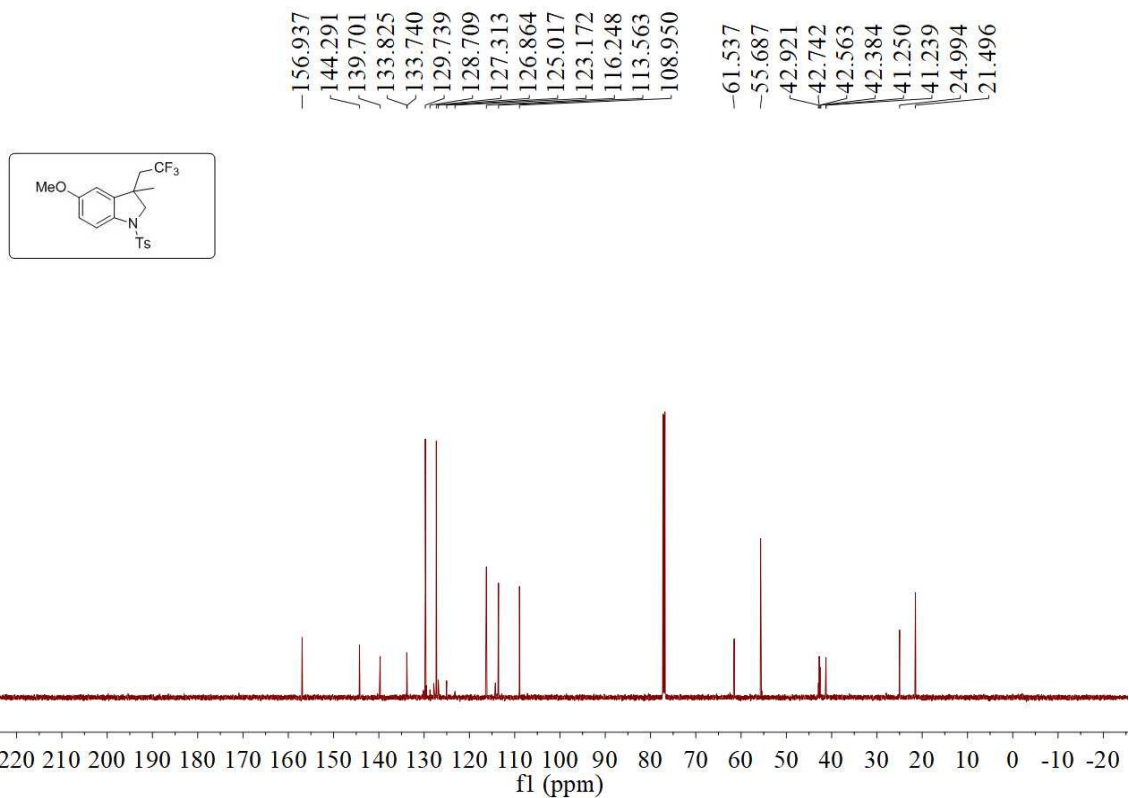


1H-NMR Spectra of 6b

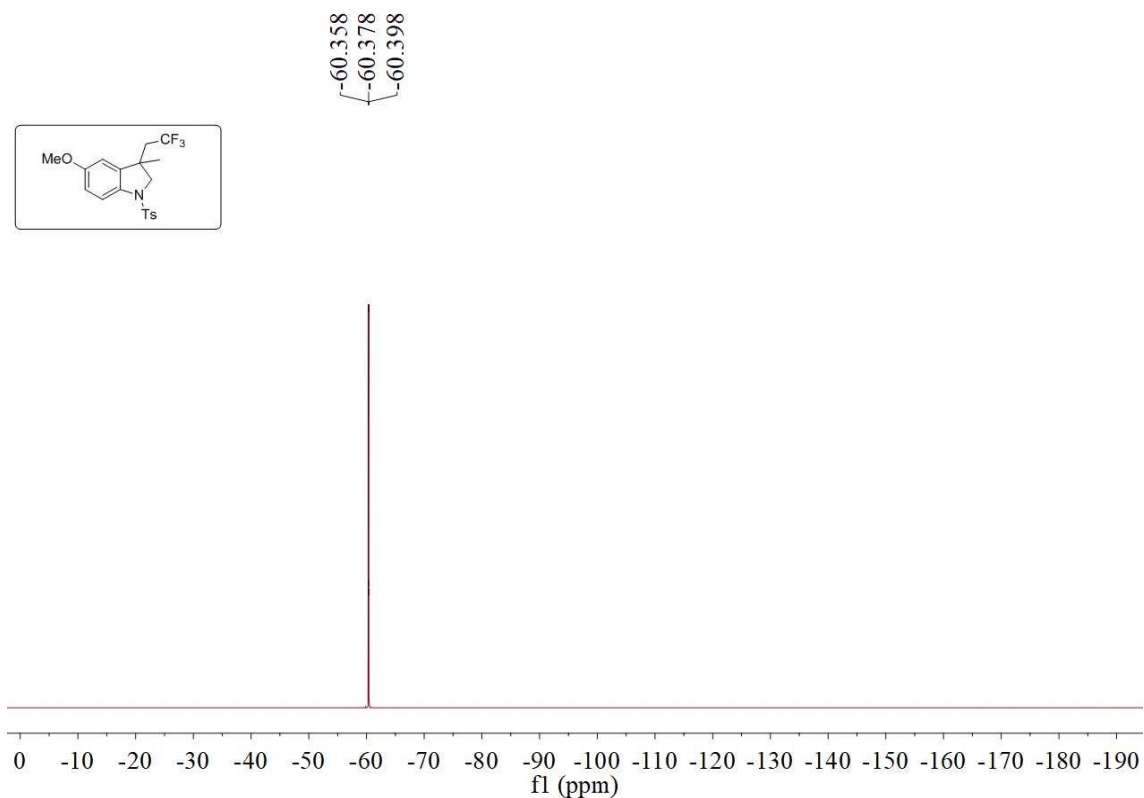


13C-NMR Spectra of 6b

SUPPORTING INFORMATION

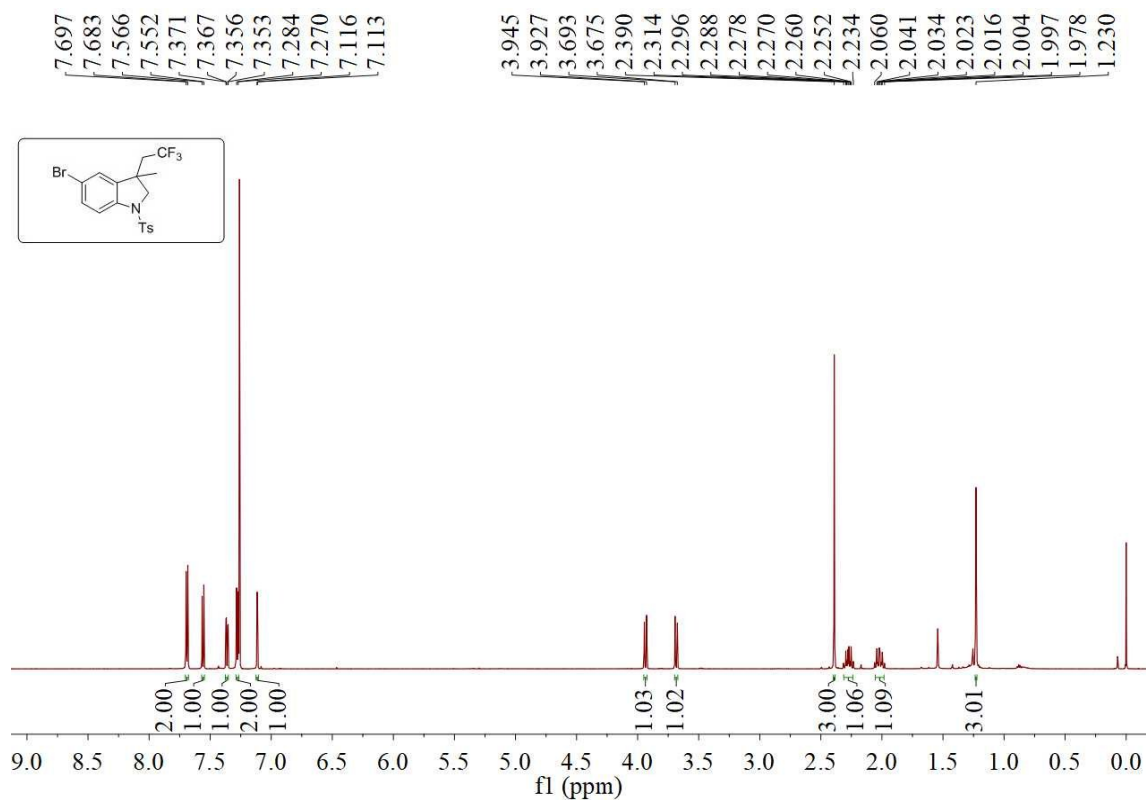


¹⁹F-NMR Spectra of 6b

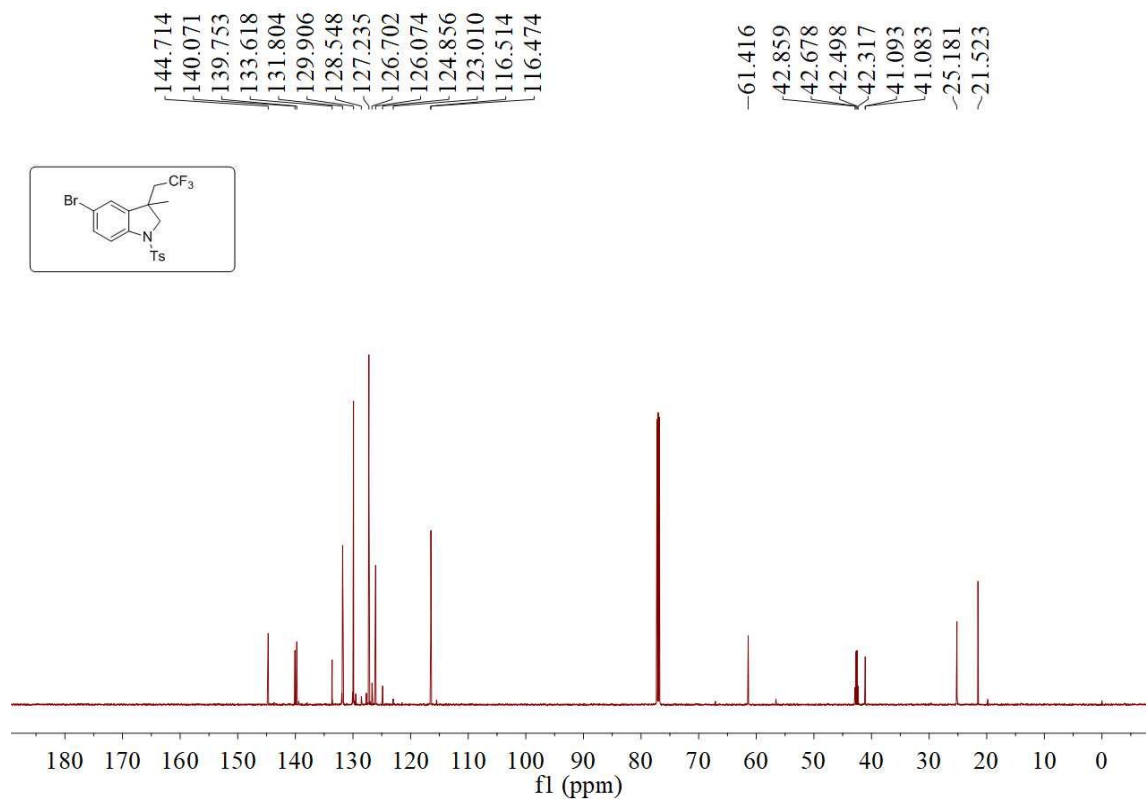


¹H-NMR Spectra of 6c

SUPPORTING INFORMATION

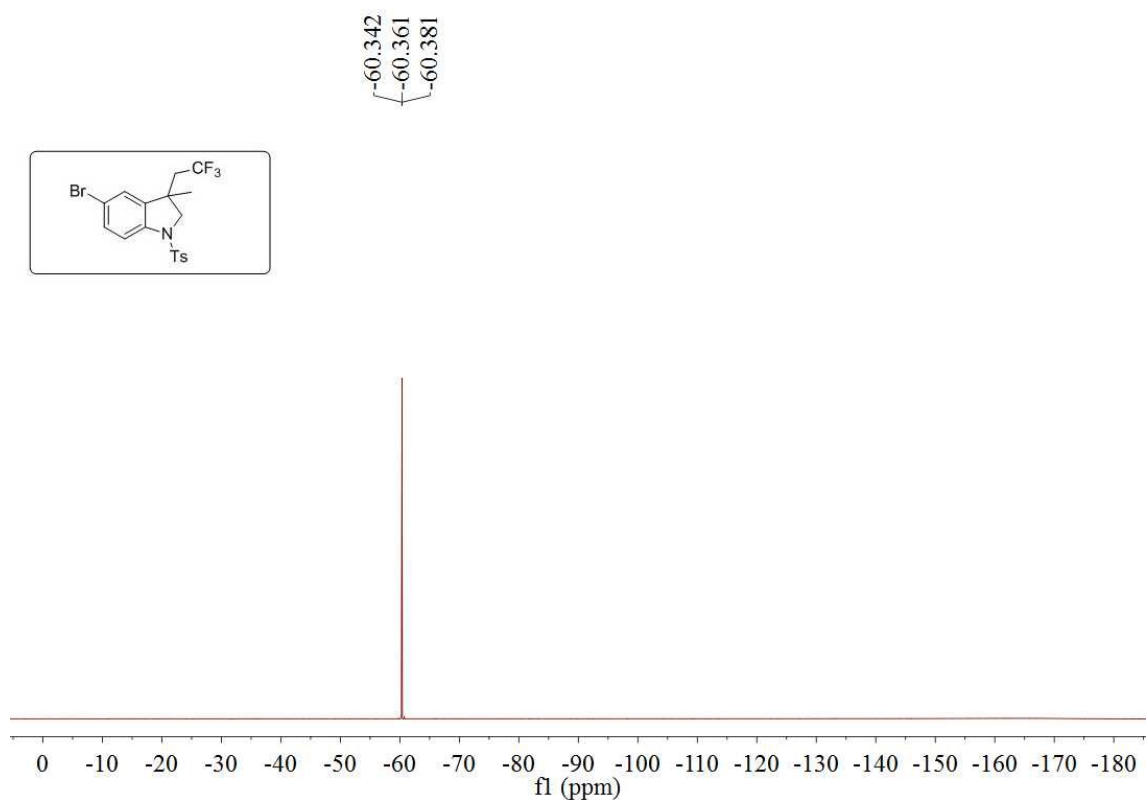


¹³C-NMR Spectra of 6c

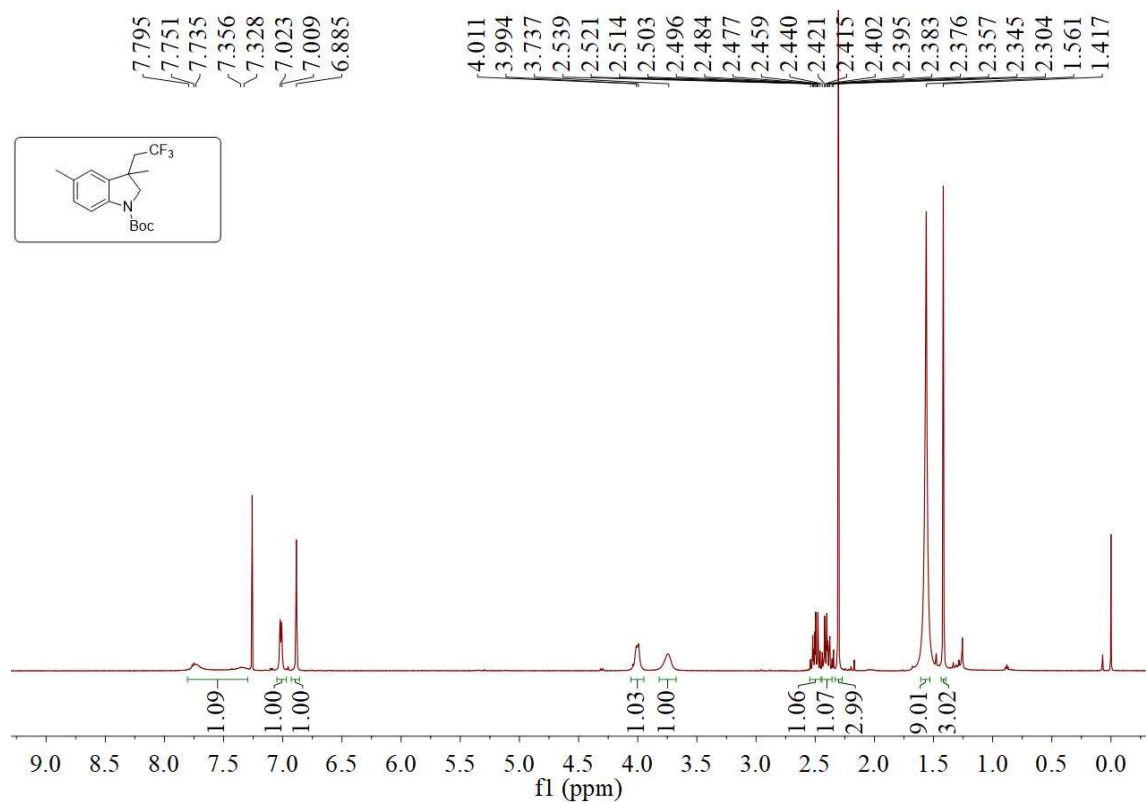


¹⁹F-NMR Spectra of 6c

SUPPORTING INFORMATION

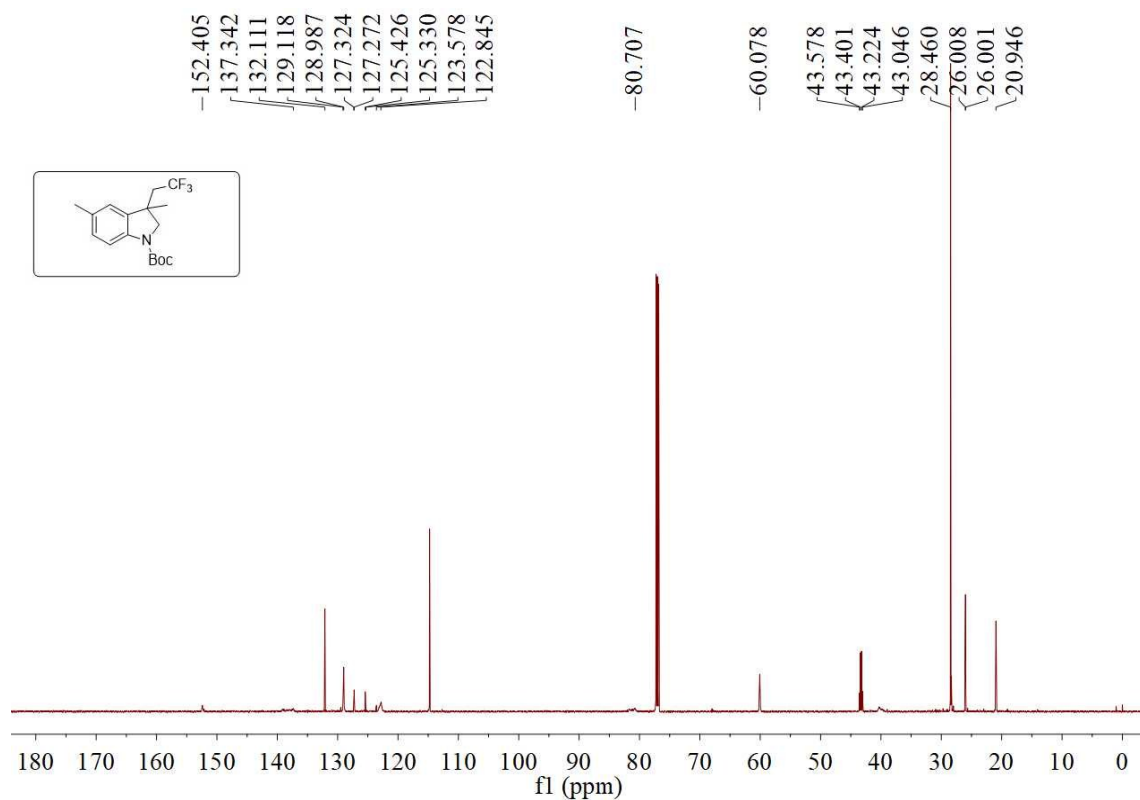


¹H-NMR Spectra of 6d

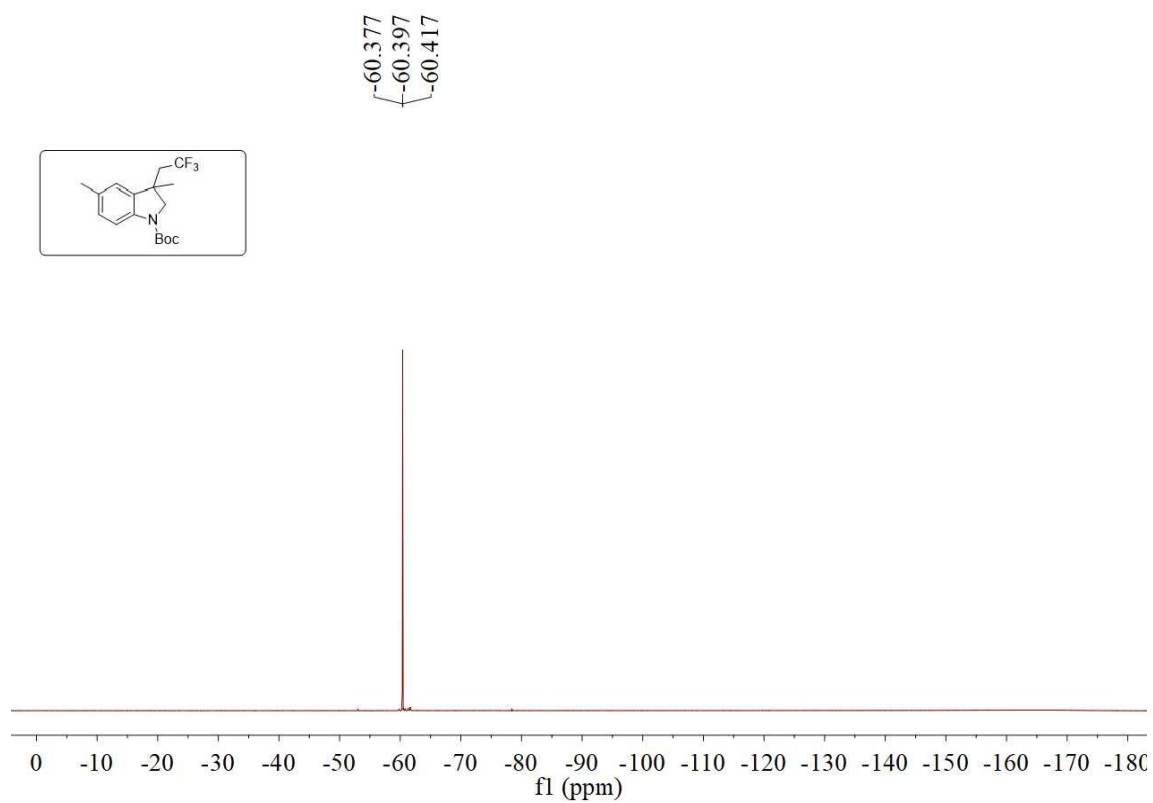


¹³C-NMR Spectra of 6d

SUPPORTING INFORMATION

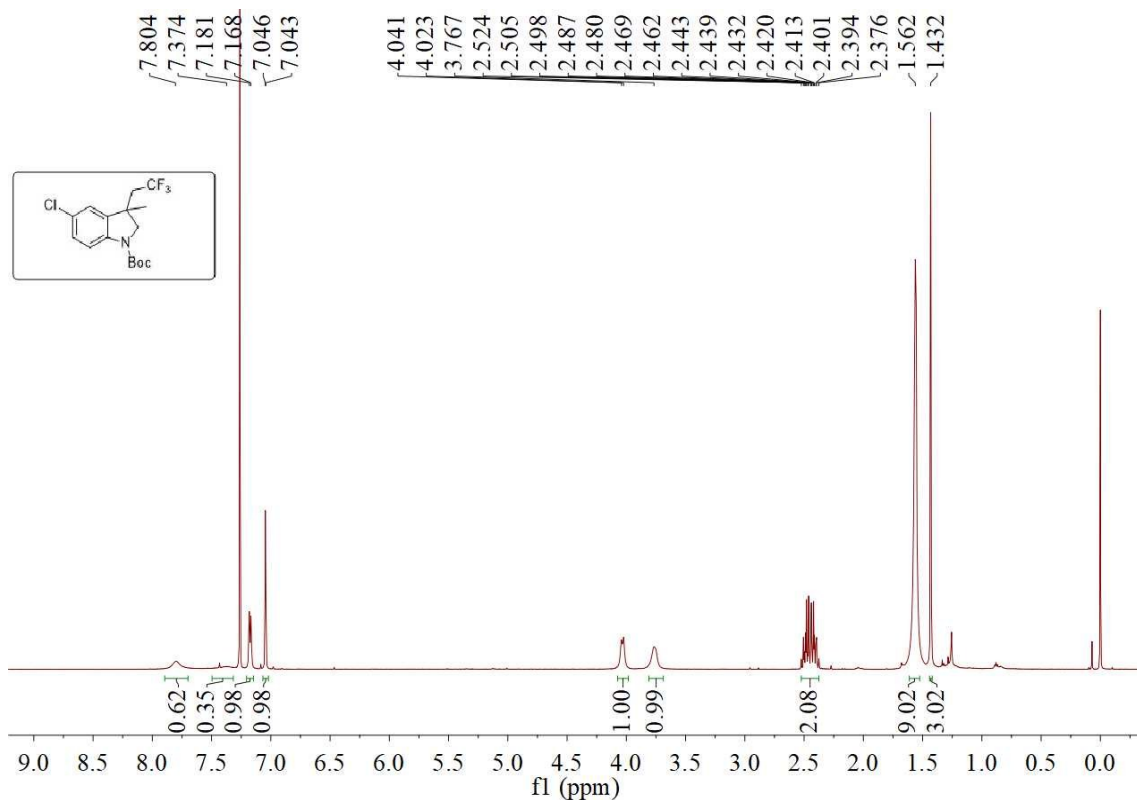


¹⁹F-NMR Spectra of 6d

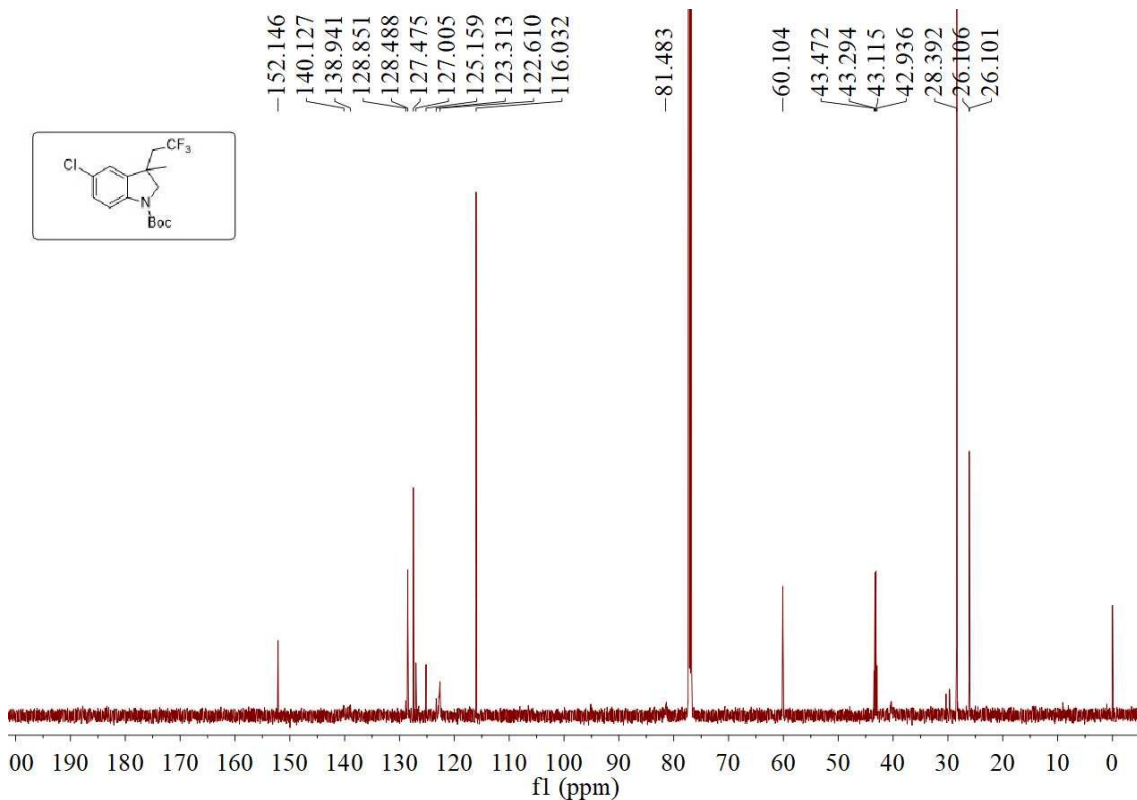


¹H-NMR Spectra of 6e

SUPPORTING INFORMATION

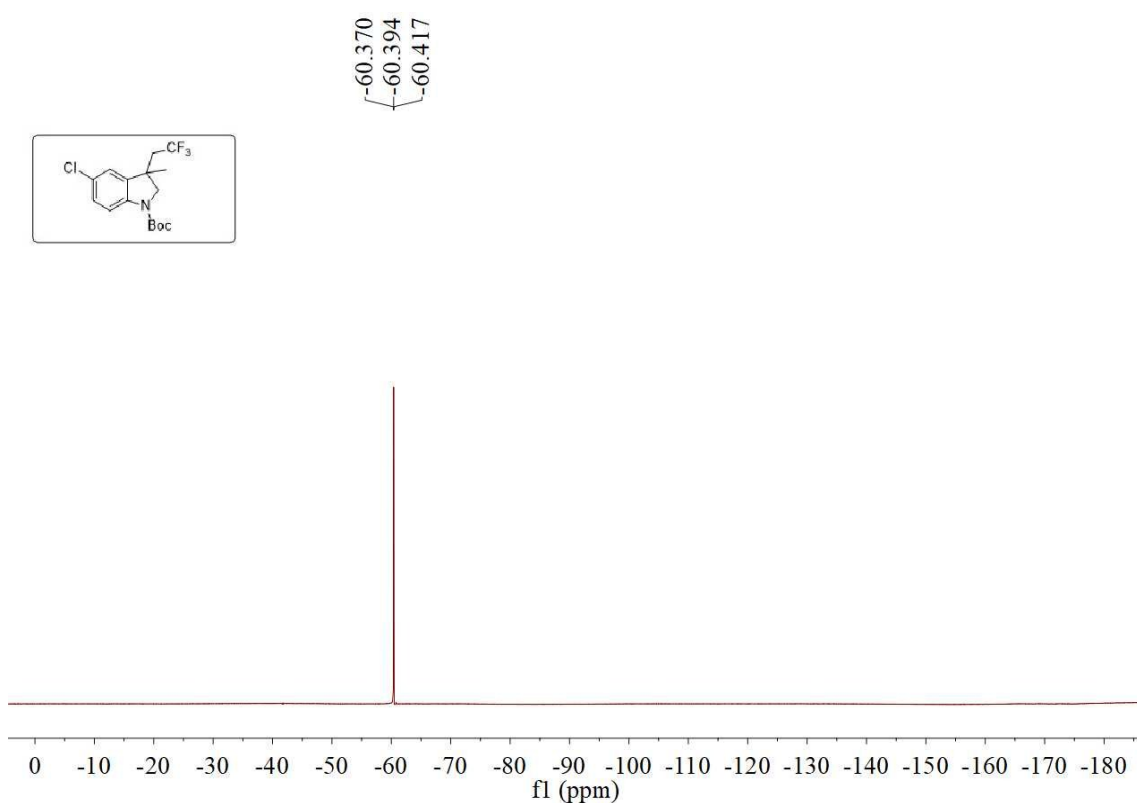


¹³C-NMR Spectra of 6e

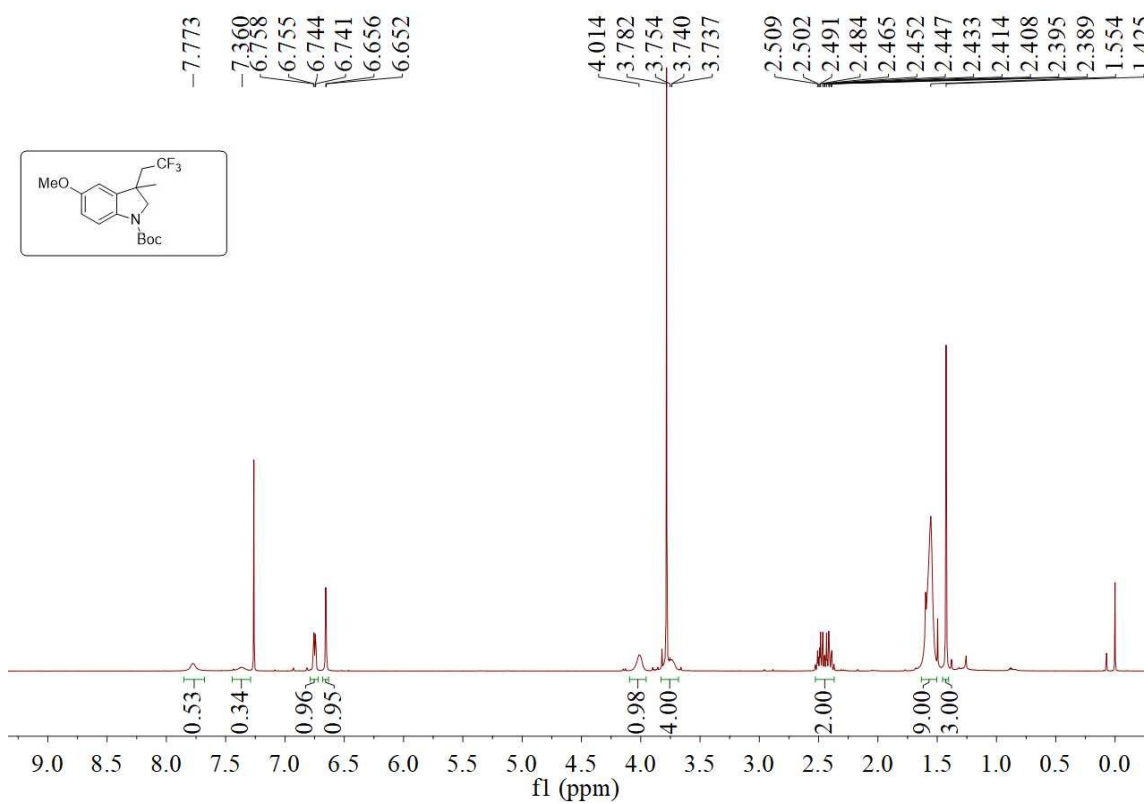


¹⁹F-NMR Spectra of 6e

SUPPORTING INFORMATION

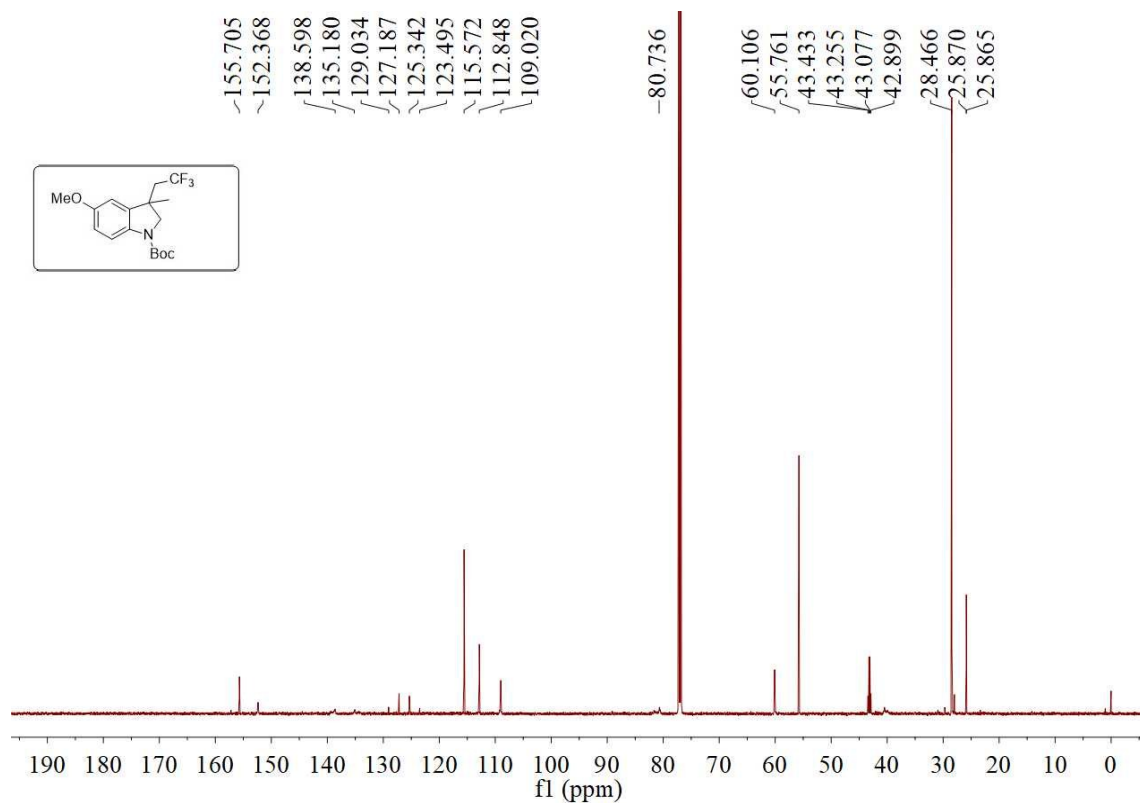


$^1\text{H-NMR}$ Spectra of 6f

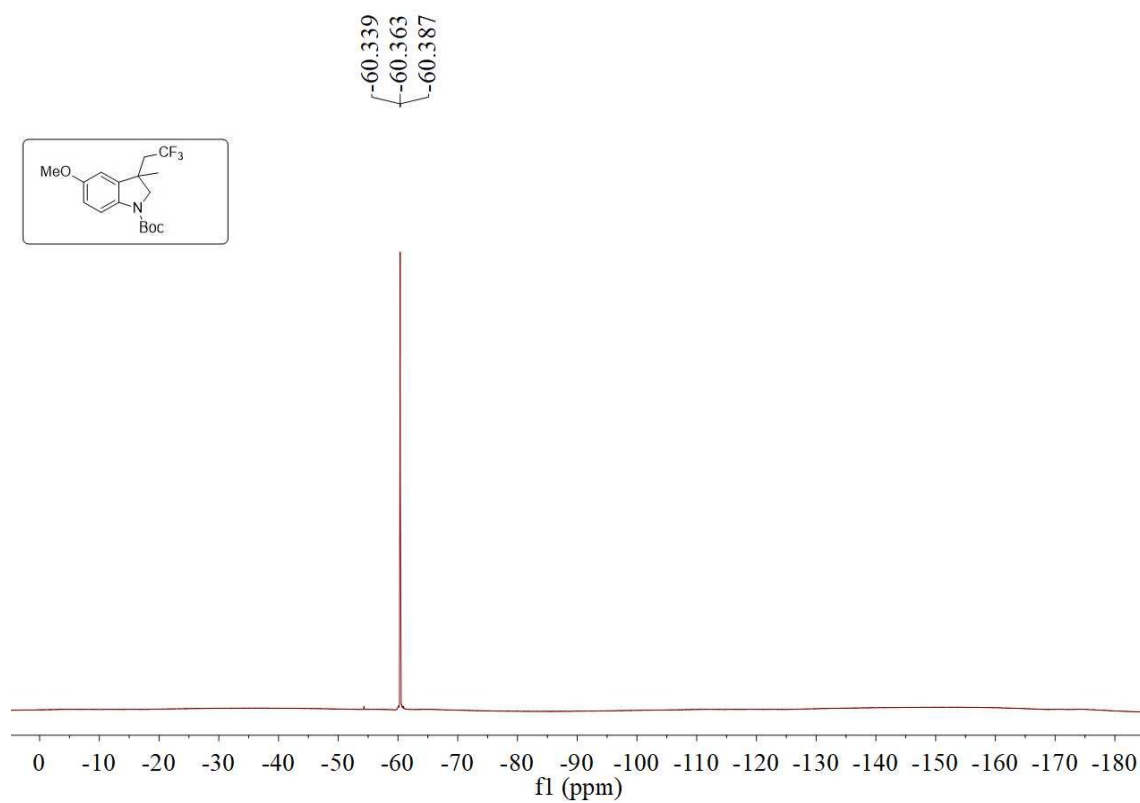


$^{13}\text{C-NMR}$ Spectra of 6f

SUPPORTING INFORMATION

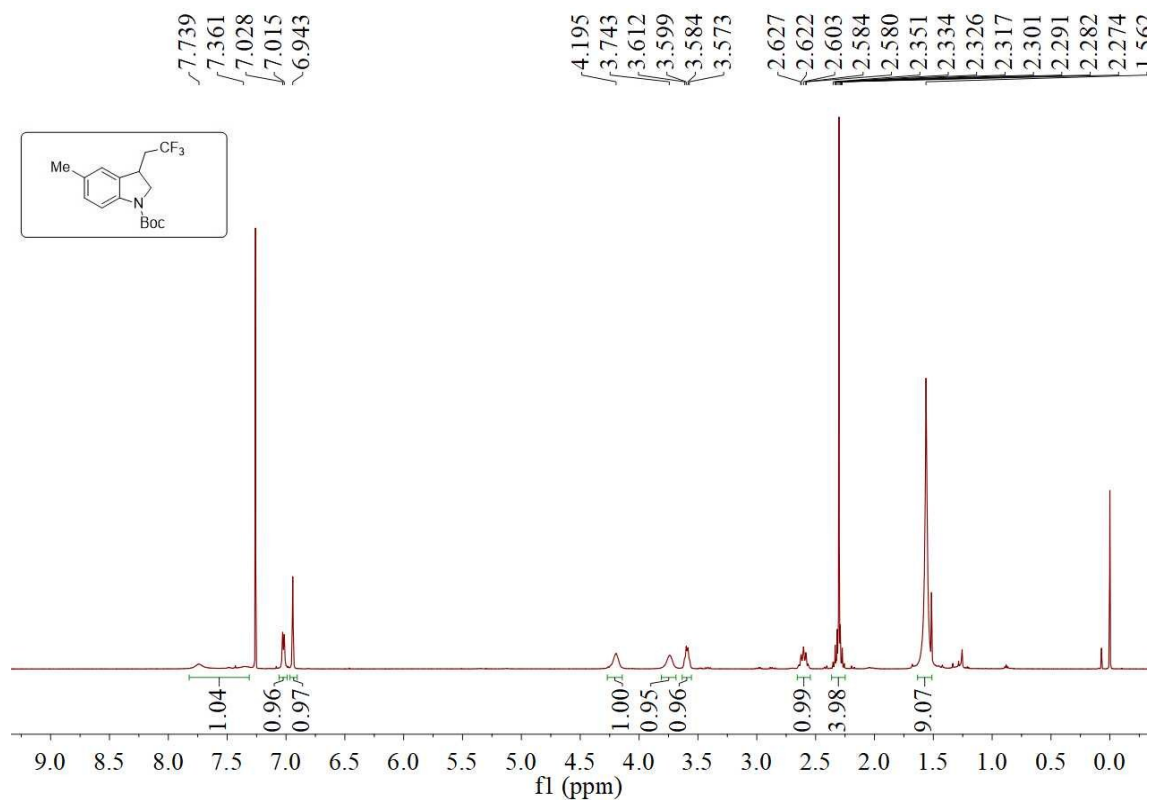


¹⁹F-NMR Spectra of 6f

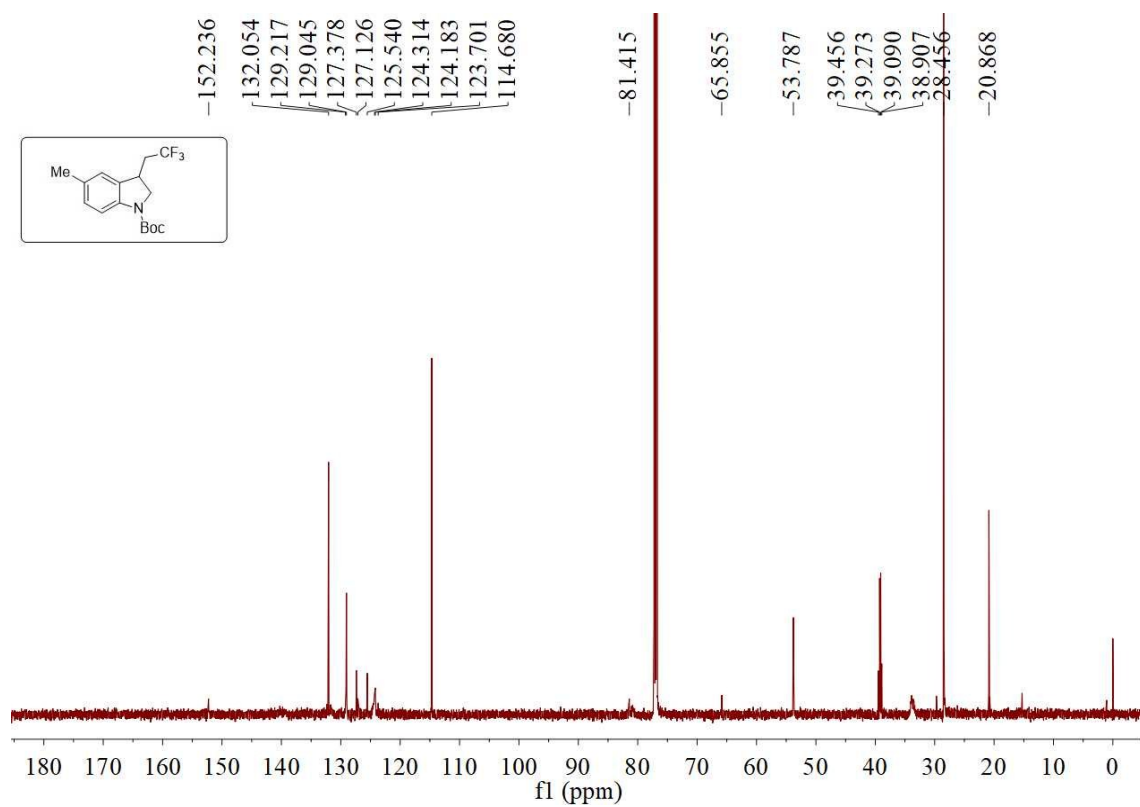


¹H-NMR Spectra of 6g

SUPPORTING INFORMATION

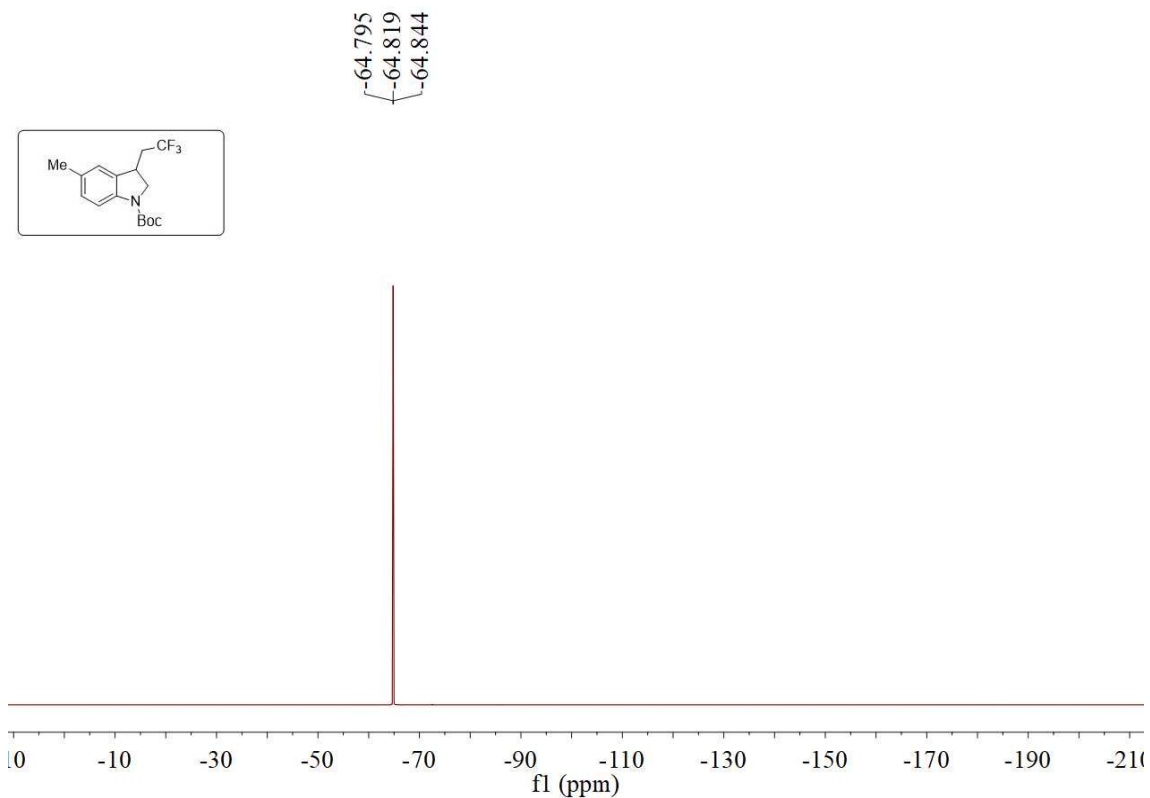


¹³C-NMR Spectra of 6g

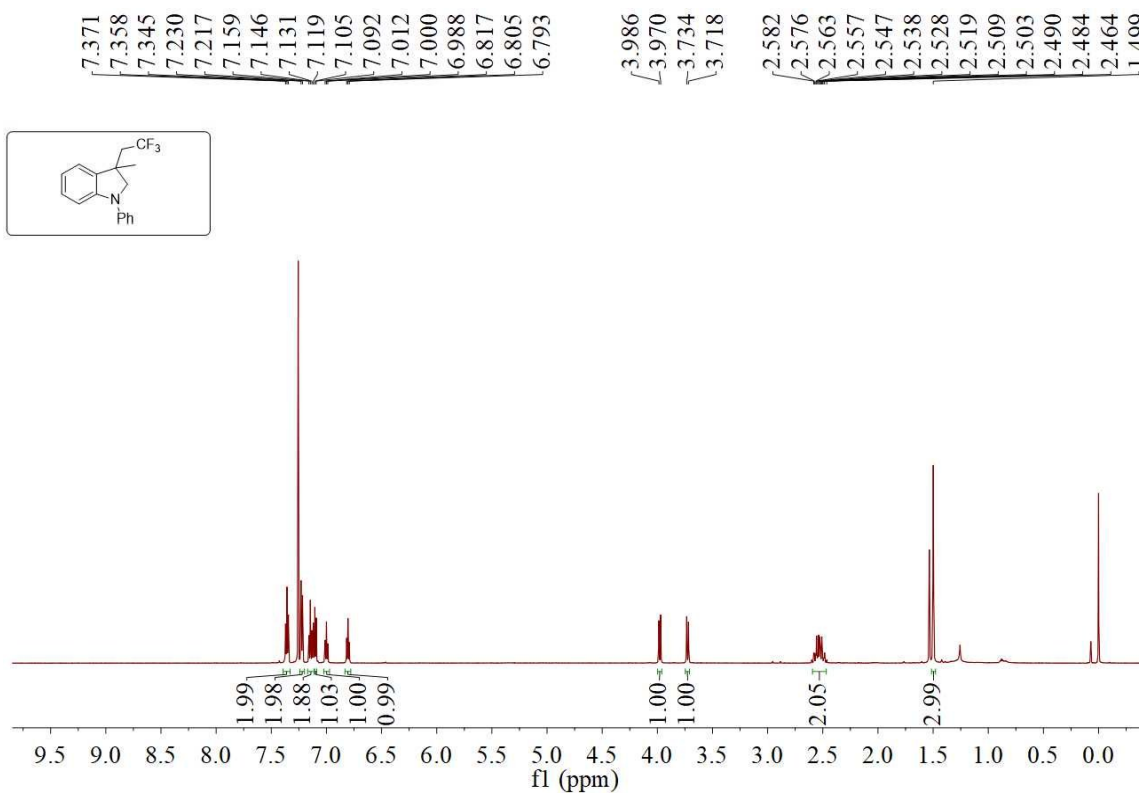


¹⁹F-NMR Spectra of 6g

SUPPORTING INFORMATION

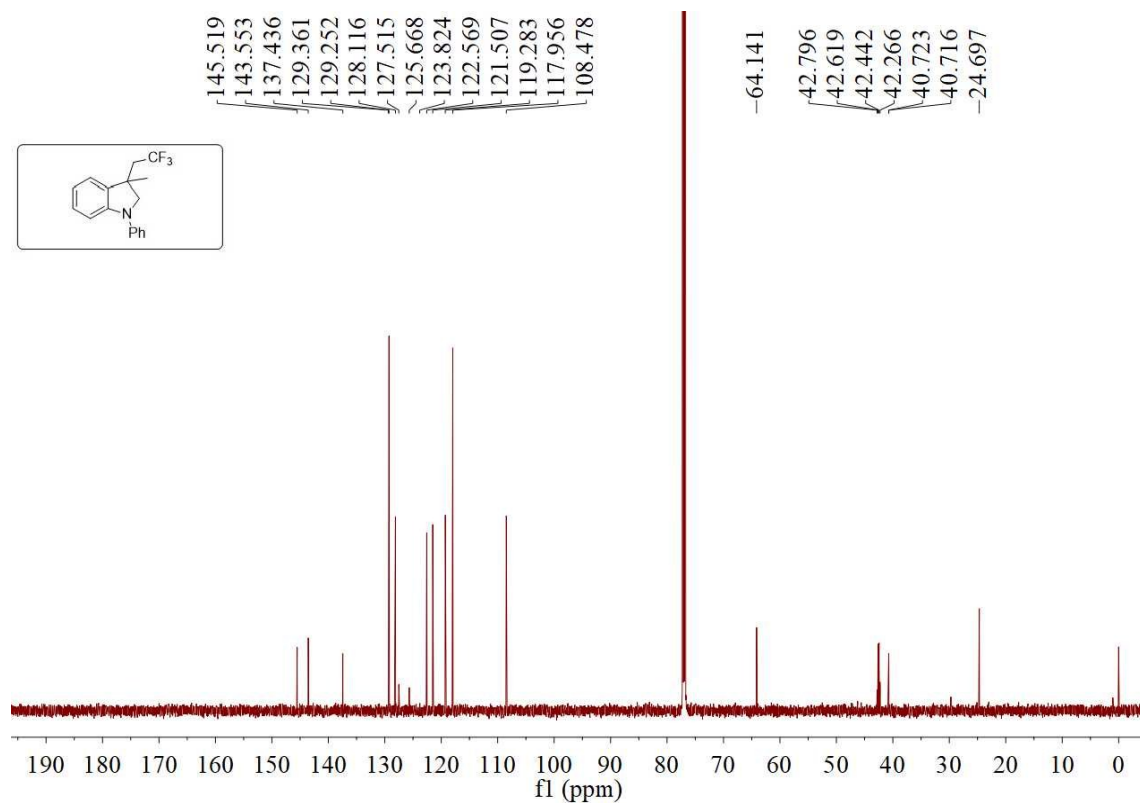


$^1\text{H-NMR}$ Spectra of 6h

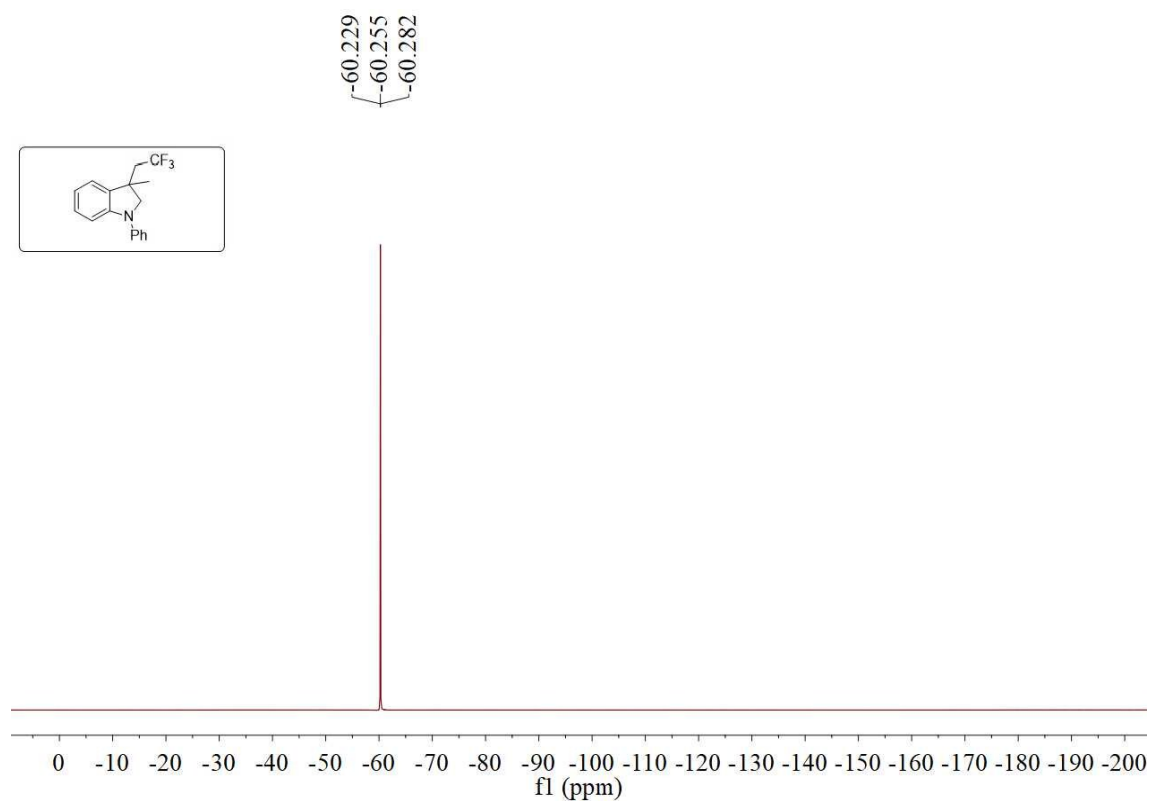


$^{13}\text{C-NMR}$ Spectra of 6h

SUPPORTING INFORMATION

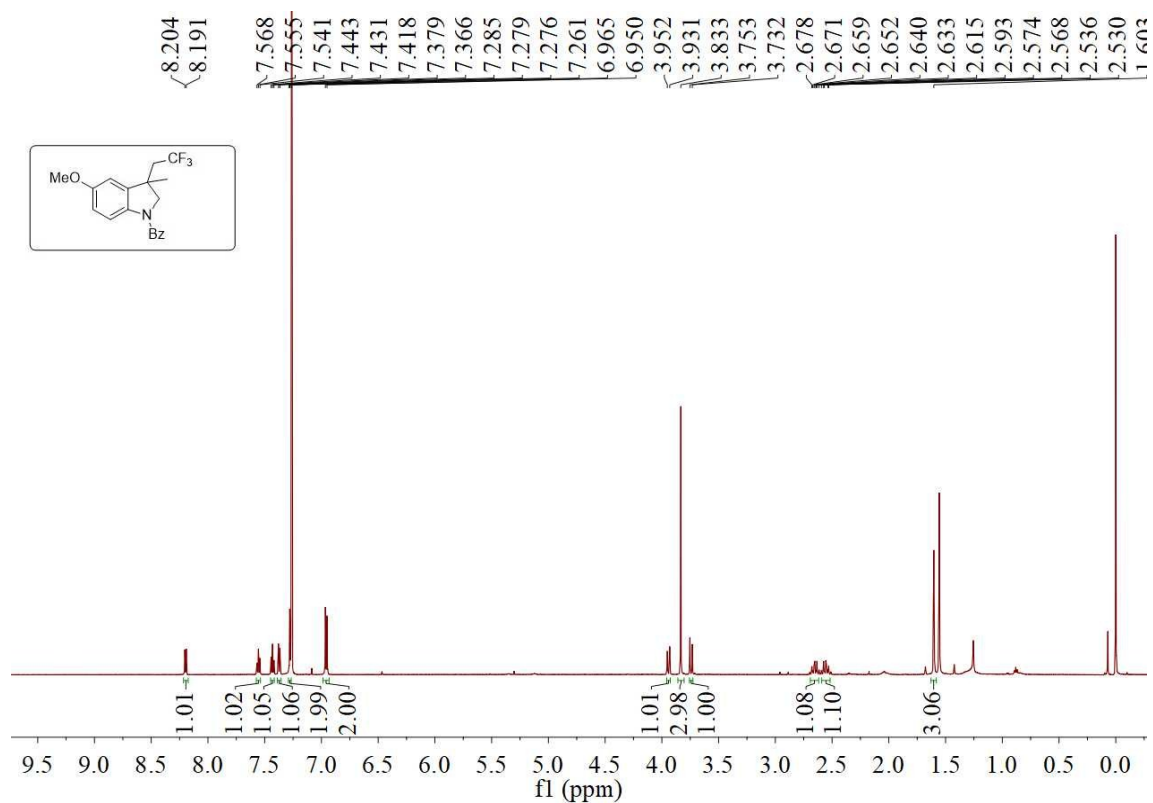


¹⁹F-NMR Spectra of 6h

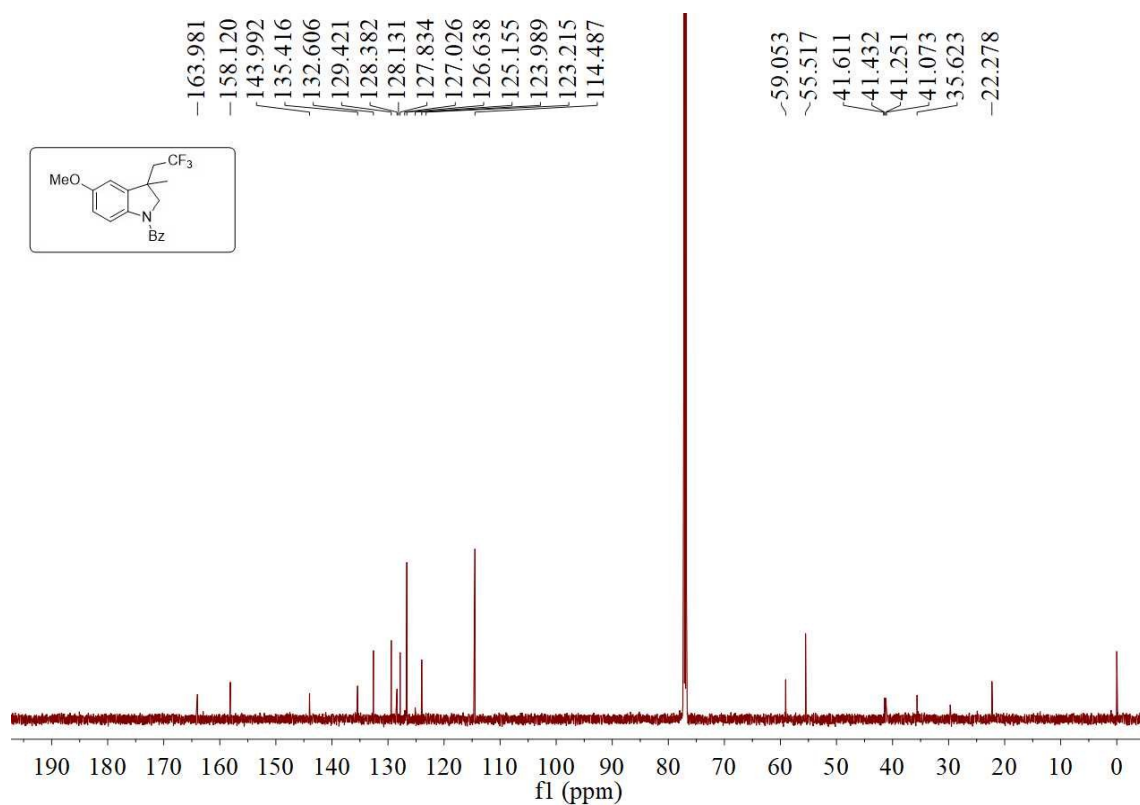


¹H-NMR Spectra of 6i

SUPPORTING INFORMATION



¹³C-NMR Spectra of 6i



¹⁹F-NMR Spectra of 6i

SUPPORTING INFORMATION

