Supporting Information to

Copper-catalyzed acyltrifluoromethylation of alkenes: rapid access to trifluoroethyl indanones and related compounds

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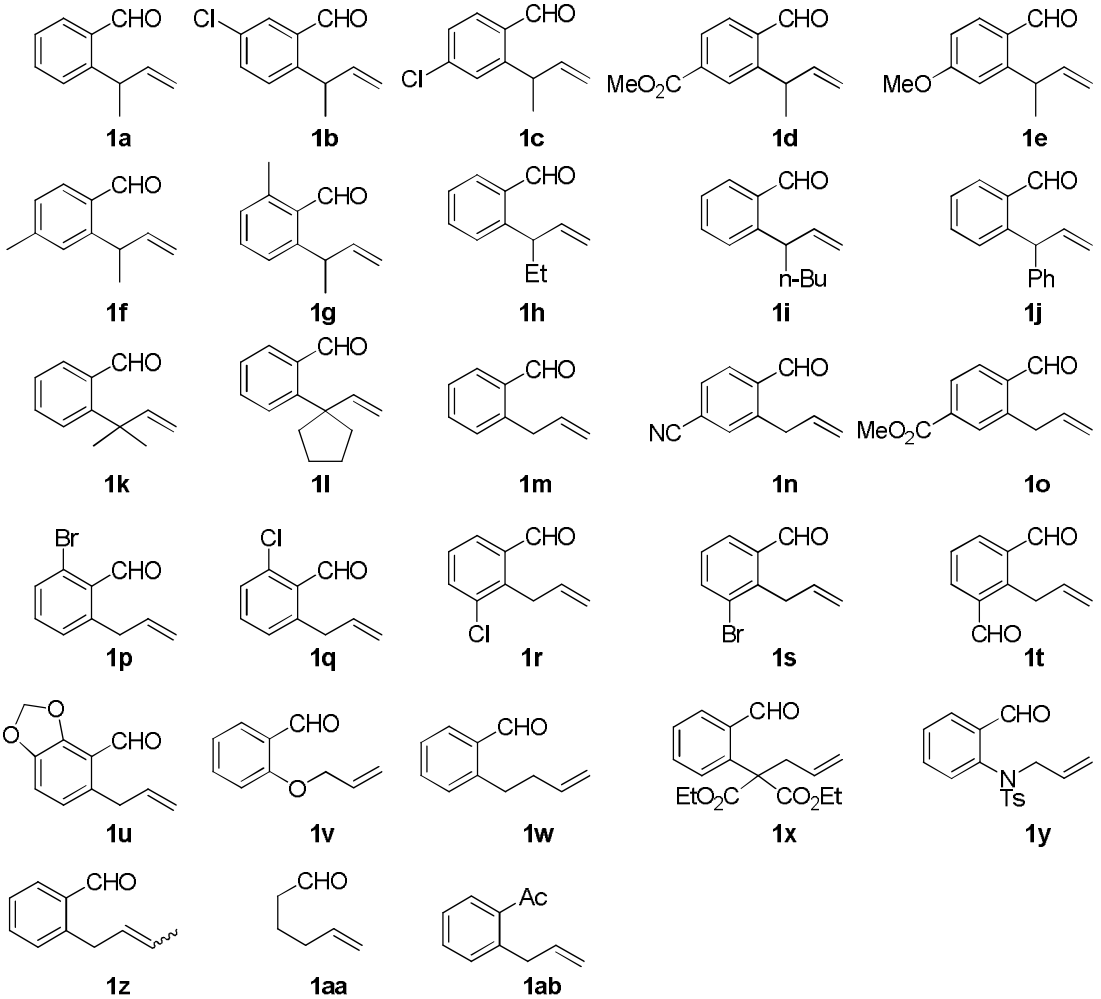
General information:

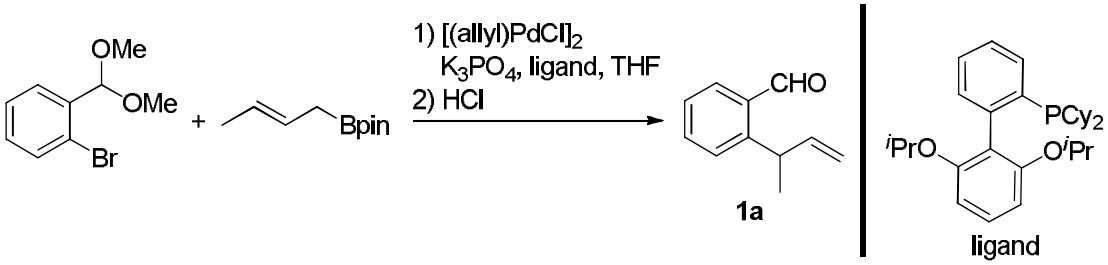
Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on a 600 or 400 MHz NMR spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are given in parts per million relative to TMS, and the coupling constants are given in hertz. High-resolution mass spectrometry (HRMS) analyses were carried out using a TOF MS instrument with ESI source. Column chromatography was performed using silica gel (300−400 mesh). The starting materials **1**[1] were prepared from aryl bromides via the Suzuki-Miyaura coupling,[1a] exemplified by the synthesis of **1a**.

compounds 1



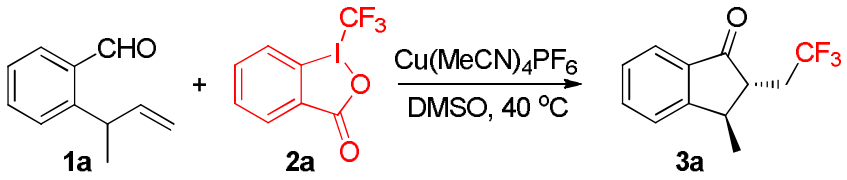
[1] (a) Y. Yang and S. L. Buchwald, *J. Am. Chem. Soc.,* 2013, **135**, 10642; (b) C. Cheng, S. Liu, D. Lu and G. Zhu, *Org. Lett.,* 2016, **18**, 2852; (c) X. Nie, C. Cheng and G. Zhu, *Angew. Chem., Int. Ed.,* 2017, **56**, 1898.

General procedure for the preparation of 1a:[1a]

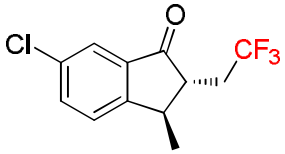


To a mixture of $[(allyl)PdCl]_2$ (18.2 mg, 0.05 mmol), ligand (93.3 mg, 0.2 mmol), *trans*-crotylboronic acid pinacol ester (1.37 g, 7.5 mmol), and 1-bromo-2-(dimethoxymethyl)benzene (1.15g, 5 mmol) in 5 mL of THF was added 2.5 M solution of aqueous K_3PO_4 (5 mL, 12.5 mmol). After stirring at 40 °C for 12 h, 1 M of aqueous HCl (10 mL, 10 mmol) was added to the reaction mixture, which was stirred at room temperature for another 2 h. Then, the organic layer was extracted with EtOAc, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:50) gave 696 mg of **1a** (yield: 87%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.34 (s, 1H), 7.85–7.81 (m, 1H), 7.56–7.52 (m, 1H), 7.41–7.34 (m, 2H), 6.11–6.03 (m, 1H), 5.13–5.01 (m, 2H), 4.59–4.52 (m, 1H), 1.41 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 192.4, 147.9, 142.3, 133.9, 133.2, 131.7, 127.9, 126.5, 114.1, 36.7, 20.5.

General procedure for the copper-catalyzed acyltrifluoromethylation of alkenes:

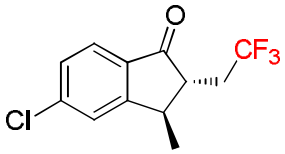


To a mixture of $Cu(MeCN)_4PF_6$ (9.3 mg, 0.025 mmol) in 2 mL of DMSO was added **1a** (40 mg, 0.25 mmol) under a nitrogen atmosphere. After stirring at 40 °C for 12 h, K_2CO_3 (69 mg, 0.5 mmol) was added, followed by being stirred for another 2 h. Then, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:50) gave 41 mg of **3a** (yield: 72%) as a colorless oil; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77–7.75 (m, 1H), 7.69–7.65 (m, 1H), 7.54–7.53 (m, 1H), 7.43–7.39 (t, J = 7.4 Hz, 1H), 3.28–3.23 (m, 1H), 3.00–2.89 (m, 1H), 2.50–2.45 (m, 1H), 2.22–2.12 (m, 1H), 1.52 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.6, 158.1, 135.6, 134.8, 127.9, 127.0 (q, J = 276.7 Hz), 125.1, 123.9, 50.1 (q, J = 1.9 Hz), 39.8, 34.8 (q, J = 29.5 Hz), 19.9; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.1; HRMS (ESI) calcd for $C_{12}H_{12}F_3O$ $(M + H)^+$ 229.0840, found 229.0831.



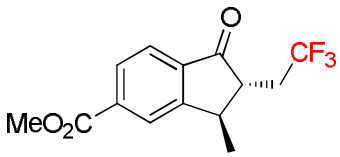
3b

Compound ***3b***. 42 mg, 64% yield; colorless oil; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72–7.70 (m, 1H), 7.63–7.60 (m, 1H), 7.48–7.45 (m, 1H), 3.26–3.19 (m, 1H), 2.97–2.89 (m, 1H), 2.53–2.47 (m, 1H), 2.22–2.14 (m, 1H), 1.50 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 203.2, 156.1, 136.3, 135.6, 134.3, 126.8 (q, J = 276.6), 126.5, 123.7, 50.5 (q, J = 2.0 Hz), 39.5, 34.6 (q, J = 29.7 Hz), 19.8; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.1; HRMS (ESI) calcd for $C_{12}H_{10}ClF_3NaO$ $(M + Na)^+$ 285.0270, found 285.0251.



3c

Compound ***3c***. 41 mg, 62% yield; colorless oil; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70–7.68 (m, 1H), 7.52–7.50 (m, 1H), 7.40–7.38 (m, 1H), 3.27–3.20 (m, 1H), 2.97–2.87 (m, 1H), 2.53–2.46 (m, 1H), 2.22–2.12 (m, 1H), 1.51 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 203.0, 159.5, 142.2, 133.2, 128.7, 126.8 (q, J = 276.6 Hz), 125.5, 125.1, 50.3 (q, J = 2.1 Hz), 39.6, 34.7 (q, J = 29.6 Hz), 19.7; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.1; HRMS (ESI) calcd for $C_{12}H_{10}ClF_3NaO$ $(M + Na)^+$ 285.0270, found 285.0252.

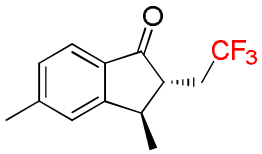


3d

Compound ***3d***. 37 mg, 52% yield; white solid, mp 104–107 °C; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22–8.19 (m, 1H), 8.08–8.05 (m, 1H), 7.82–7.79 (m, 1H), 3.98 (s, 3H), 3.33–3.25 (m, 1H), 2.99–2.89 (m, 1H), 2.57–2.49 (m, 1H), 2.25–2.15 (m, 1H), 1.56 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.0, 166.2, 157.7, 137.9, 136.3, 129.0, 126.8 (q, J = 276.7 Hz), 126.5, 123.8, 52.6, 50.6 (q, J = 1.9 Hz), 39.8, 34.6 (q, J = 29.7 Hz), 19.7; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.1; HRMS (ESI) calcd for $C_{14}H_{13}F_3NaO_3$ $(M + Na)^+$ 309.0714, found 309.0688.

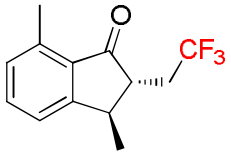
Crystal data for **3d** ($C_{14}H_{13}O_3F_3$, 286.24): Orthorhombic, space group *Pca2(1)*, a = 16.2998(10) Å, b = 10.3533(6) Å, c =7.8903(5) Å, U = 1331.54(14) Å^3, Z = 4, T = 296(2) K, absorption coefficient 0.127 mm^{-1}, reflections collected 20606, independent reflections 3066 [R(int) = 0.0647], refinement by full-matrix least-squares on F^2, data/restraints/parameters 3066/1/181, goodness-of-fit on F^2 = 0.922, final R indices [I>2s(I)] R_1 = 0.0475, wR_2 = 0.1244, R indices (all data) R_1 = 0.0781, wR_2 = 0.1512, largest diff peak and hole 0.128 and –0.184 e.Å^{-3}.

Crystallographic data for the structure **3d** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1540172.



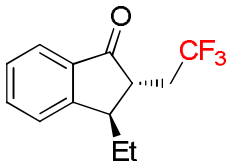
3f

*Compound **3f***. 38 mg, 62% yield; colorless oil; dr > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.63 (m, 1H), 7.32–7.30 (m, 1H), 7.23–7.20 (m, 1H), 3.24–3.14 (m, 1H), 3.00–2.85 (m, 1H), 2.49–2.43 (m, 4H), 2.22–2.06 (m, 1H), 1.49 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.1, 158.6, 146.9, 132.5, 129.1, 127.0 (q, J = 276.6 Hz), 125.5 123.8, 50.3 (q, J = 2.0 Hz), 39.7, 34.9 (q, J = 29.4 Hz), 22.2, 19.9; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.1; HRMS (ESI) calcd for $C_{13}H_{13}F_3NaO$ $(M + Na)^+$ 265.0816, found 265.0796.



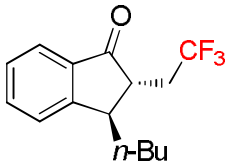
3g

*Compound **3g***. 47 mg, 77% yield; colorless oil; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52–7.49 (m, 1H), 7.35–7.32 (m, 1H), 7.16–7.13 (m, 1H), 3.23–3.13 (m, 1H), 2.96–2.87 (m, 1H), 2.64 (s, 3H), 2.46–2.41 (m, 1H), 2.20–2.09 (m, 1H), 1.49 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 205.3, 158.8, 139.0, 134.7, 132.3, 129.5, 127.1 (q, J = 276.4 Hz), 122.4, 50.3 (q, J = 1.7 Hz), 39.3, 34.8 (q, J = 29.4 Hz), 20.0, 18.4; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.0; HRMS (ESI) calcd for $C_{13}H_{13}F_3NaO$ $(M + Na)^+$ 265.0816, found 265.0788.



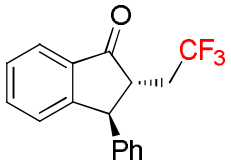
3h

*Compound **3h***. 43 mg, 71% yield; colorless oil; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78–7.75 (m, 1H), 7.68–7.64 (m, 1H), 7.54–7.51 (m, 1H), 7.44–7.40 (m, 1H), 3.34–3.30 (m, 1H), 2.87–2.78 (m, 1H), 2.65–2.61 (m, 1H), 2.29–2.15 (m, 1H), 1.98–1.86 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 205.3, 156.9, 135.5, 135.3, 127.9, 126.8 (q, J = 276.8 Hz), 125.6, 124.1, 46.3 (q, J = 1.7 Hz), 45.3, 35.4 (q, J = 29.2 Hz), 26.6, 9.9; ^{19}F NMR (565 MHz, $CDCl_3$): δ –63.7; HRMS (ESI) calcd for $C_{13}H_{13}F_3NaO$ $(M + Na)^+$ 265.0816, found 265.0794.



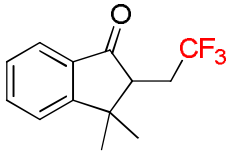
3i

Compound ***3i***. 50 mg, 74% yield; colorless oil; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78–7.73 (m, 1H), 7.68–7.63 (m, 1H), 7.55–7.49 (m, 1H), 7.43–7.38 (m, 1H), 3.38–3.30 (m, 1H), 2.85–2.75 (m, 1H), 2.65–2.60 (m, 1H), 2.28–2.16 (m, 1H), 1.91–1.79 (m, 2H), 1.38–1.31 (m, 3H), 1.22–1.14 (m, 1H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 205.4, 157.3, 135.4, 135.2, 127.8, 127.7 (q, J = 276.7 Hz), 125.7, 124.1, 47.2 (q, J = 2.0 Hz), 44.3, 35.4 (q, J = 29.1 Hz), 34.1, 28.1, 22.9, 13.9; ^{19}F NMR (565 MHz, $CDCl_3$): δ –63.6; HRMS (ESI) calcd for $C_{15}H_{17}F_3NaO$ $(M + Na)^+$ 293.1129, found 293.1104.



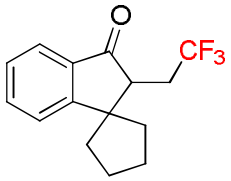
3j

Compound ***3j***. 44 mg, 61% yield; colorless oil; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85–7.82 (m, 1H), 7.61–7.57 (m, 1H), 7.46–7.43 (m, 1H), 7.35–7.32 (m, 2H), 7.31–7.27 (m, 1H), 7.19–7.13 (m, 3H), 4.37 (d, J = 4.6 Hz, 1H), 2.98–2.87 (m, 2H), 2.46–2.34 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.2, 156.8, 142.0, 135.8, 134.8, 128.9, 128.2, 128.0, 127.3, 126.7, 126.6 (q, J = 277.2 Hz), 123.8, 51.9, 51.0, 34.3 (q, J = 29.7 Hz); ^{19}F NMR (565 MHz, $CDCl_3$): δ –63.1; HRMS (ESI) calcd for $C_{17}H_{13}F_3NaO$ $(M + Na)^+$ 313.0816, found 313.0815.



3k

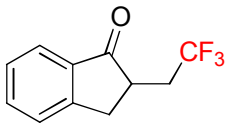
Compound ***3k***. 48 mg, 80% yield; white solid, mp 58–61 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78–7.71 (m, 1H), 7.69–7.64 (m, 1H), 7.58–7.54 (m, 1H), 7.43–7.36 (m, 1H), 3.07–2.95 (m, 1H), 2.72–2.69 (m, 1H), 2.33–2.20 (m, 1H), 1.58 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 203.3, 162.5, 135.4, 133.2, 127.8, 127.1 (q, J = 276.0 Hz), 123.8, 123.4, 54.3 (q, J = 2.3 Hz), 41.8, 29.9 (q, J = 30.1 Hz), 27.6, 26.9; ^{19}F NMR (375 MHz, $CDCl_3$): δ –64.0; HRMS (ESI) calcd for $C_{13}H_{13}F_3NaO$ $(M + Na)^+$ 265.0816, found 265.0800.



3l

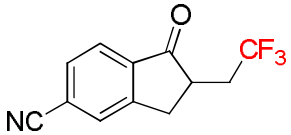
Compound ***3l***. 57 mg, 85% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72–7.68 (m, 1H), 7.66–7.60 (m, 1H), 7.51–7.46 (m, 1H), 7.40–7.35 (m, 1H), 3.00–2.93 (m, 1H), 2.91–2.87 (m, 1H), 2.33–2.25 (m, 1H), 2.23–2.17 (m, 1H), 2.12–2.06 (m, 1H), 2.01–1.92 (m, 3H), 1.86–1.78 (m, 2H), 1.51–1.39 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 203.5, 162.7, 135.4, 133.2, 127.5, 127.0 (q, J = 276.3 Hz), 123.8, 123.3, 53.2 (q, J = 2.0 Hz), 52.7, 38.7, 37.2, 30.0 (q, J = 29.8 Hz), 26.0, 25.9;

^{19}F NMR (375 MHz, $CDCl_3$): δ –64.1; HRMS (ESI) calcd for $C_{15}H_{15}F_3NaO$ $(M + Na)^+$ 291.0973, found 291.0970.



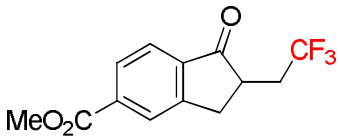
3m

Compound ***3m***. 35 mg, 66% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80–7.77 (m, 1H), 7.67–7.60 (m, 1H), 7.51–7.48 (m, 1H), 7.43–7.39 (m, 1H), 3.55–3.49 (m, 1H), 3.04–2.89 (m, 3H), 2.17–2.07 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.9, 153.0, 135.5, 135.4, 127.8, 127.0 (q, J = 276.6 Hz), 126.5, 124.2, 41.9 (q, J = 2.3 Hz), 34.9 (q, J = 29.2 Hz), 33.1; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.8; HRMS (ESI) calcd for $C_{11}H_9F_3NaO$ $(M + Na)^+$ 237.0503, found 237.0477.



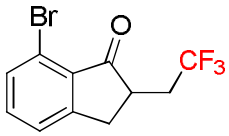
3n

Compound ***3n***. 36 mg, 60% yield; white solid, mp 143–145 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90–7.86 (m, 1H), 7.85–7.83 (m, 1H), 7.71–7.68 (m, 1H), 3.63–3.57 (m, 1H), 3.11–3.06 (m, 1H), 3.05–2.93 (m, 2H), 2.24–2.13 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 203.4, 152.7, 138.5, 131.4, 130.6, 126.7 (q, J = 276.6 Hz), 124.9, 118.3, 117.8, 42.1 (q, J = 2.3 Hz), 34.5 (q, J = 29.9 Hz), 32.7; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.7; HRMS (ESI) calcd for $C_{12}H_8F_3NNaO$ $(M + Na)^+$ 262.0456, found 262.0453.



3o

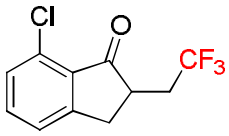
Compound ***3o***. 34 mg, 50% yield; white solid, mp 98–100 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17–8.16 (m, 1H), 8.08–8.05 (m, 1H), 8.45–8.20 (m, 1H), 3.97 (s, 3H), 3.59–3.54 (m, 1H), 3.07–2.96 (m, 3H), 2.20–2.11 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.3, 166.2, 152.7, 138.7, 136.1, 129.0, 127.8, 126.9 (q, J = 276.6 Hz), 124.1, 52.6, 42.4 (q, J = 2.2 Hz), 34.8 (q, J = 29.4 Hz), 33.0; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.8; HRMS (ESI) calcd for $C_{13}H_{11}F_3NaO_3$ $(M + Na)^+$ 295.0558, found 295.0532.



3p

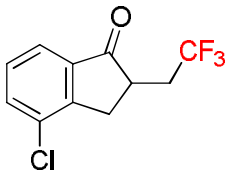
Compound ***3p***. 67 mg, 92% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60–7.52 (m, 1H), 7.51–7.38 (m, 2H), 3.51–3.42 (m, 1H), 3.03–2.93 (m, 3H), 2.18–2.07 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 201.9, 155.5, 135.7, 133.1, 132.8, 126.9 (q, J = 276.7 Hz), 125.5, 120.0, 42.6 (q,

J = 2.3 Hz), 34.8 (q, J = 29.3 Hz), 32.3; ^{19}F NMR (375 MHz, $CDCl_3$): δ –64.7; HRMS (ESI) calcd for $C_{11}H_8BrF_3NaO$ $(M + Na)^+$ 314.9608, found 314.9589.



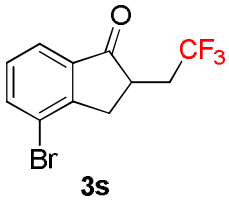
3q

Compound ***3q***. 54 mg, 87% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56–7.49 (m, 1H), 7.45–7.38 (m, 1H), 7.36–7.31 (m, 1H), 3.58–3.44 (m, 1H), 3.03–2.93 (m, 3H), 2.17–2.06 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 201.6, 155.1, 135.6, 132.4, 131.7, 129.4, 126.9 (q, J = 276.5 Hz), 124.9, 42.5 (q, J = 2.3 Hz), 34.8 (q, J = 29.3 Hz), 32.5; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.7; HRMS (ESI) calcd for $C_{11}H_8ClF_3NaO$ $(M + Na)^+$ 271.0113, found 271.0096.



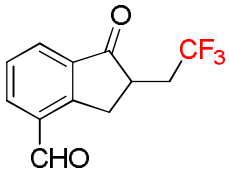
3r

Compound ***3r***. 51 mg, 82% yield; white solid, mp 58–60 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73–7.70 (m, 1H), 7.67–7.64 (m, 1H), 7.43–7.38 (m, 1H), 3.59–3.52 (m, 1H), 3.03–2.95 (m, 3H), 2.23–2.11 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.0, 150.6, 137.5, 134.2, 132.8, 129.4, 126.8 (q, J = 276.7 Hz), 122.4, 41.8 (q, J = 2.3 Hz), 34.8 (q, J = 29.5 Hz), 32.0; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.8; HRMS (ESI) calcd for $C_{11}H_8ClF_3NaO$ $(M + Na)^+$ 271.0113, found 271.0111.



3s

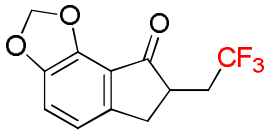
Compound ***3s***. 62 mg, 85% yield; white solid, mp 62–64 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83–7.79 (m, 1H), 7.77–7.70 (m, 1H), 7.35–7.29 (m, 1H), 3.51–3.45 (m, 1H), 3.00–2.90 (m, 3H), 2.19–2.11 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.1, 152.7, 138.1, 137.6, 129.6, 126.8 (q, J = 274.0 Hz), 123.1, 122.1, 41.9 (q, J = 2.4 Hz), 34.8 (q, J = 29.5 Hz), 34.1; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.8; HRMS (ESI) calcd for $C_{11}H_8BrF_3NaO$ $(M + Na)^+$ 314.9608, found 314.9581.



3t

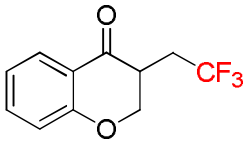
Compound ***3t***. 48 mg, 80% yield; white solid, mp 171–173 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.25 (s, 1H), 8.15–8.08 (m, 1H), 8.07–8.00 (m, 1H), 7.70–7.61 (m, 1H), 4.04–3.95 (m, 1H),

3.34–3.27 (m, 1H), 3.01–2.93 (m, 2H), 2.24–2.13 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.1, 191.3, 153.7, 138.8, 137.0, 133.4, 129.3, 128.5, 126.8 (q, J = 276.8 Hz), 41.8 (q, J = 2.2 Hz), 34.8 (q, J = 29.4 Hz), 32.9; ^{19}F NMR (375 MHz, $CDCl_3$): δ –64.7; HRMS (ESI) calcd for $C_{12}H_9F_3NaO_2$ $(M + Na)^+$ 265.0452, found 265.0443.



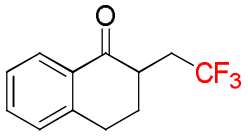
3u

Compound ***3u***. 38 mg, 59% yield; yellow solid, mp 107–109 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.05 (d, J = 7.9 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 6.14–6.12 (m, 2H), 3.49–3.40 (m, 1H), 2.98–2.90 (m, 3H), 2.17–2.06 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 201.8, 147.7, 144.6, 143.8, 126.9 (q, J = 276.6 Hz), 118.7, 118.2, 114.8, 103.0, 42.8 (q, J = 2.2 Hz), 34.8 (q, J = 29.2 Hz), 32.9; ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.8; HRMS (ESI) calcd for $C_{12}H_9F_3NaO_3$ $(M + Na)^+$ 281.0401, found 281.0385.



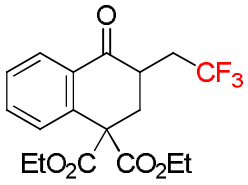
3v

Compound ***3v***. 35 mg, 60% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92–7.89 (m, 1H), 7.53–7.49 (m, 1H), 7.08–7.03 (m, 1H), 7.01–6.98 (m, 1H), 4.75–4.70 (m, 1H), 4.27–4.22 (m, 1H), 3.20–3.03 (m, 2H), 2.13–2.03 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 190.7, 161.5, 136.4, 127.6, 126.6 (q, J = 276.3 Hz), 121.8, 120.0, 117.9, 69.7 (q, J = 1.7 Hz), 40.5 (q, J = 2.0 Hz), 29.6 (q, J = 30.1 Hz); ^{19}F NMR (565 MHz, $CDCl_3$): δ –64.0; HRMS (ESI) calcd for $C_{11}H_9F_3NaO_2$ $(M + Na)^+$ 253.0452, found 252.0430.



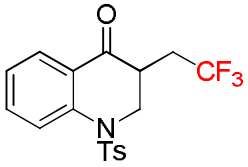
3w

Compound ***3w***. 32 mg, 57% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05–8.01 (m, 1H), 7.51–7.48 (m, 1H), 7.34–7.30 (m, 1H), 7.28–7.24 (m, 1H), 3.26–3.15 (m, 1H), 3.14–3.08 (m, 1H), 3.03–2.98 (m, 1H), 2.51–2.45 (m, 1H), 2.48 (m, 1H), 2.16–2.04 (m, 1H), 1.99–1.91 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.5, 143.7, 133.7, 131.7, 128.8, 127.7, 127.3 (q, J = 276.5 Hz), 126.8, 42.7 (q, J = 2.2 Hz), 33.3 (q, J = 28.7 Hz), 29.0, 28.9; ^{19}F NMR (565 MHz, $CDCl_3$): δ –63.6; HRMS (ESI) calcd for $C_{12}H_{11}F_3NaO$ $(M + Na)^+$ 251.0660, found 251.0657.



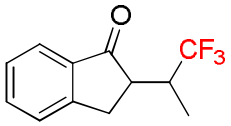
3x

Compound ***3x***. 69 mg, 74% yield; white solid, mp 51–53 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09–8.07 (m, 1H), 7.63–7.59 (m, 1H), 7.53–7.51 (m, 1H), 7.49–7.45 (m, 1H), 4.36–4.29 (m, 3H), 4.24–4.17 (m, 1H), 3.30–3.20 (m, 1H), 3.18–3.13 (m, 1H), 3.08–3.00 (m, 1H), 2.52 (t, J = 13.8 Hz, 1H), 2.17–2.05 (m, 1H), 1.34–1.26 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 194.4, 170.1, 168.9, 138.1, 133.8, 131.2, 129.7, 128.7, 127.8, 127.0 (q, J = 276.5 Hz), 62.5, 62.5, 58.8, 38.9 (q, J = 2.0 Hz), 35.2, 32.9 (q, J = 29.0 Hz), 13.9, 13.8; ^{19}F NMR (565 MHz, $CDCl_3$): δ –63.7; HRMS (ESI) calcd for $C_{18}H_{19}F_3NaO_5$ $(M + Na)^+$ 395.1082, found 395.1082.



3y

Compound ***3y***. 48 mg, 50% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00–7.90 (m, 2H), 7.64–7.55 (m, 3H), 7.30–7.23 (m, 3H), 4.78–4.74 (m, 1H), 3.72–3.64 (m, 1H), 3.04–2.93 (m, 2.6 Hz, 1H), 2.51–2.44 (m, 1H), 2.40 (s, 3H), 1.95–1.83 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 191.6, 144.9, 142.2, 136.5, 135.1, 130.2, 128.2, 126.8, 126.5 (q, J = 276.7 Hz), 125.6, 124.3, 124.0, 50.1, 39.5, 30.7 (q, J = 29.9 Hz), 21.6; ^{19}F NMR (565 MHz, $CDCl_3$): δ –63.8; HRMS (ESI) calcd for $C_{18}H_{16}F_3NNaO_3S$ $(M + Na)^+$ 406.0701, found 406.0686.

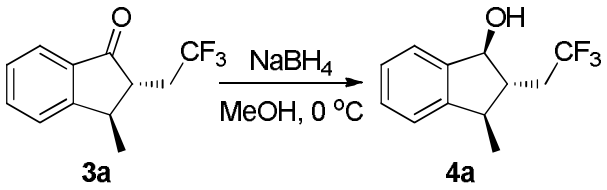


3z

Compound ***3z***. 23 mg, 40% yield; colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04–8.01 (m, 1H), 7.55–7.50 (m, 1H), 7.38–7.34 (m, 1H), 7.29–7.27 (m, 1H), 3.30–3.25 (m, 1H), 3.16–3.10 (m, 1H), 2.82–2.77 (m, 1H), 2.72–2.63 (m, 1H), 1.43–1.40 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.2, 139.6, 133.9, 131.1, 128.7, 127.6, 127.4, 126.8 (q, J = 280.9 Hz), 44.9 (q, J = 26.0 Hz), 42.1, 27.6, 13.9; ^{19}F NMR (565 MHz, $CDCl_3$): δ –69.0; HRMS (ESI) calcd for $C_{12}H_{11}F_3NaO$ $(M + Na)^+$ 251.0660, found 251.0656.

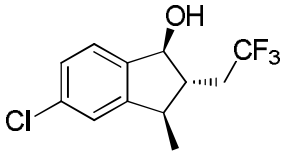
Experimental procedure for the preparation of compound 4a:[2]

[2] (a) X.-H. Li, B.-H. Zheng, C.-H. Ding and X.-L. Hou, *Org. Lett.*, 2013, **15**, 6086; (b) G. Yue, K. Kai, H. Hirao and J. Zhou, *Angew. Chem., Int. Ed.,* 2015, **54**, 6531.



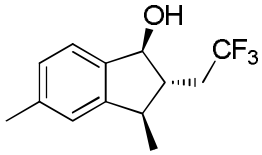
3a **4a**

To a solution of **3a** (57 mg, 0.25 mmol) in 2 mL of MeOH was added $NaBH_4$ (11.3 mg, 0.3 mmol) at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was quenched with 20 mL of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:5) gave 53 mg of **4a** (yield: 92%) as a white solid, mp 72–73 °C; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38–7.36 (m, 1H), 7.33–7.26 (m, 2H), 7.21–7.18 (m, 1H), 4.94 (t, J = 7.3 Hz, 1H), 2.86–2.77 (m, 1H), 2.52–2.44 (m, 2H), 2.24 (d, J = 7.3 Hz, 1H), 2.06–1.98 (m, 1H), 1.39 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.8, 142.9, 128.5, 127.3, 126.9 (q, J = 277.0 Hz), 123.7, 123.2, 79.9, 52.6 (q, J = 1.4 Hz), 42.0, 36.1 (q, J = 28.6 Hz), 18.3; ^{19}F NMR (565 MHz, $CDCl_3$): δ –63.1; HRMS (ESI) calcd for $C_{12}H_{13}F_3NaO$ $(M + Na)^+$ 253.0816, found 253.0811.



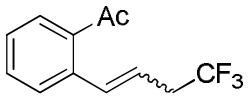
4b

*Compound **4b***. 58 mg, 88% yield; white solid, mp 88–89 °C; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36–7.35 (m, 1H), 7.28–7.26 (m, 1H), 7.12–7.10 (m, 1H), 4.93 (t, J = 7.3 Hz, 1H), 2.80–2.74 (m, 1H), 2.53–2.44 (m, 2H), 2.20 (d, J = 7.1 Hz, 1H), 2.10–2.02 (m, 1H), 1.38 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.8, 143.1, 133.1, 128.7, 126.1 (q, J = 276.9 Hz), 124.4, 124.1, 79.3, 52.8 (q, J = 1.6 Hz), 41.6, 36.0 (q, J = 28.8 Hz), 18.2; ^{19}F NMR (565 MHz, $CDCl_3$): δ –63.1; HRMS (ESI) calcd for $C_{12}H_{13}ClF_3O$ $(M + H)^+$ 265.0607, found 265.0593.



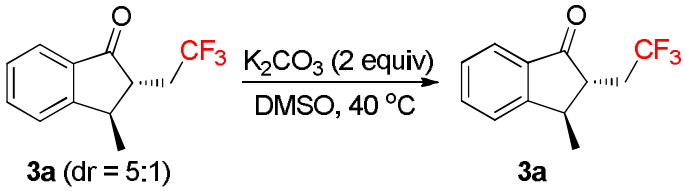
4c

*Compound **4c***. 52 mg, 86% yield; white solid, mp 75–76 °C; dr > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28–7.26 (m, 1H), 7.10 (m, 1H), 7.01 (m, 1H), 4.92 (t, J = 7.2 Hz, 1H), 2.82–2.74 (m, 1H), 2.51–2.43 (m, 2H), 2.37 (s, 3H), 2.06–1.99 (m, 2H), 1.38 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.1, 140.1, 138.5, 128.2,127.0 (q, J = 277.0 Hz), 123.9, 123.5, 79.8, 52.8 (q, J = 1.7 Hz), 42.0, 36.2 (q, J = 28.6 Hz), 21.5, 18.5; ^{19}F NMR (565 MHz, $CDCl_3$): δ –63.2; HRMS (ESI) calcd for $C_{13}H_{16}F_3O$ $(M + H)^+$ 245.1153, found 245.1150.



5b

Compound ***5b***. 25 mg, 43% yield; colorless oil; *E*/*Z* = 5:1; ^{1}H NMR (600 MHz, $CDCl_3$) data of major isomer: δ 7.70–7.67 (m, 1H), 7.55–7.52 (m, 1H), 7.49–7.45 (m, 1H), 7.38–7.35 (m, 1H), 7.17 (d, J = 15.8 Hz, 1H), 5.98 (dt, J = 15.8, 7.2 Hz, 1H), 3.06–2.99 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) data of major isomer: δ 201.7, 137.0, 136.4, 135.8, 131.8, 129.0, 128.0, 127.8, 125.9 (q, J = 276.9 Hz), 119.9 (q, J = 3.7 Hz), 37.7 (q, J = 29.9 Hz), 29.6; ^{19}F NMR (565 MHz, $CDCl_3$): δ –66.1; HRMS (ESI) calcd for $C_{12}H_{11}F_3NaO$ $(M + Na)^+$ 251.0660, found 251.0651.



3a (dr = 5:1) **3a**

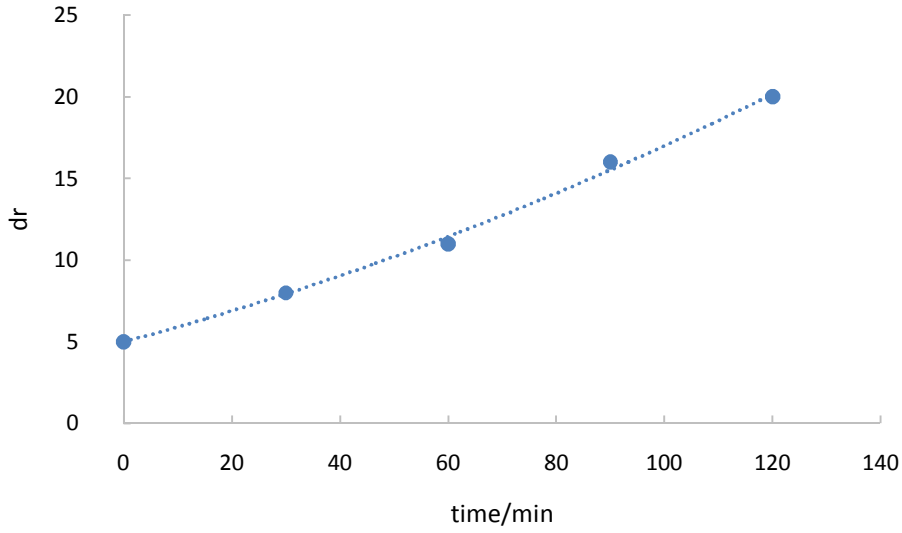
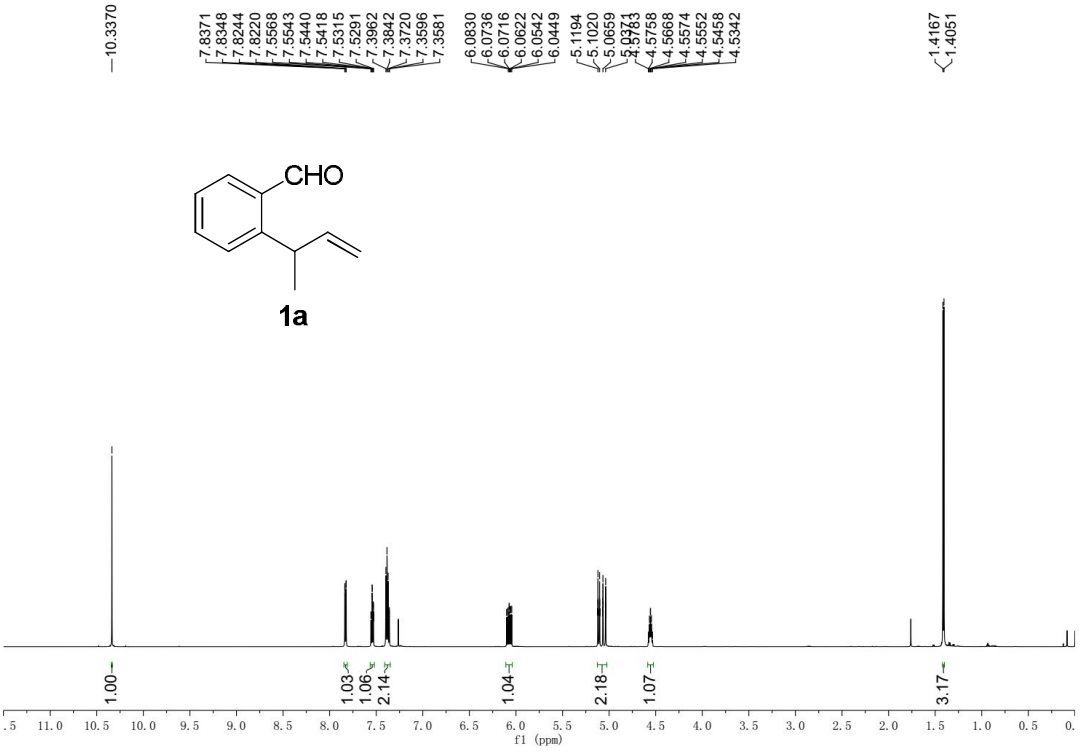


Figure S1. Kinetic profiles of K_2CO_3-promoted epimerization of **3a**, monitored by GC analysis. Reaction conditions: **3a** (0.25 mmol, dr = 5:1), K_2CO_3 (0.5 mmol), DMSO (2 mL), 40 °C.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1.06
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2.18
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3.17
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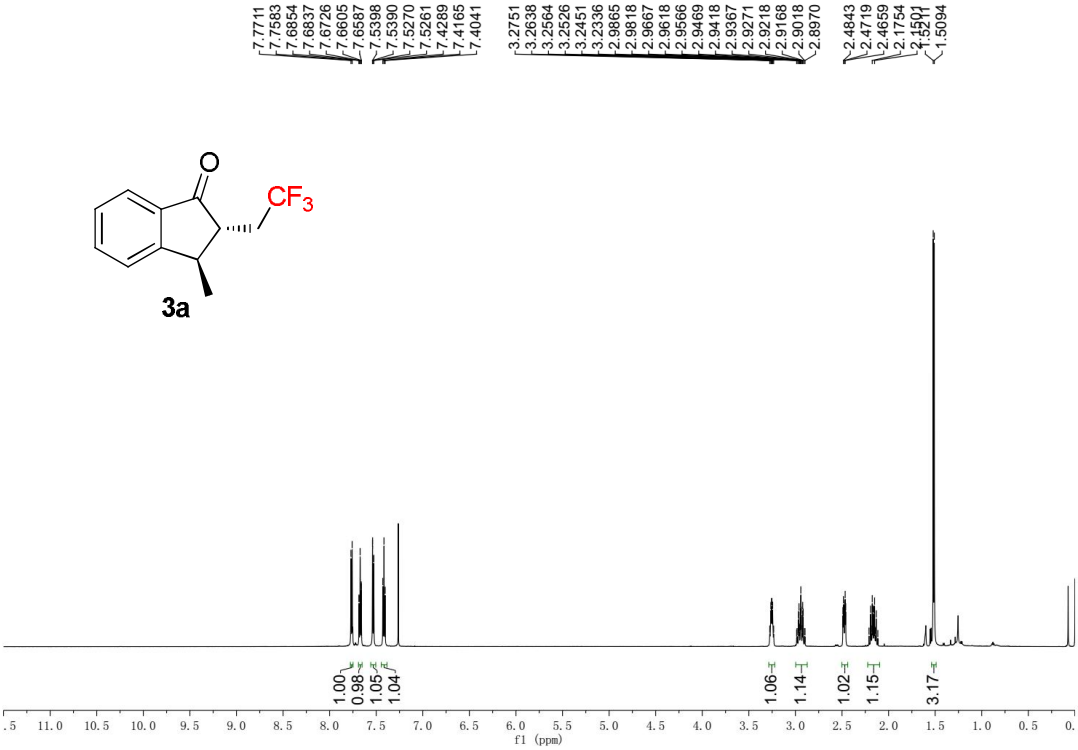
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3a
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1.04
1.06
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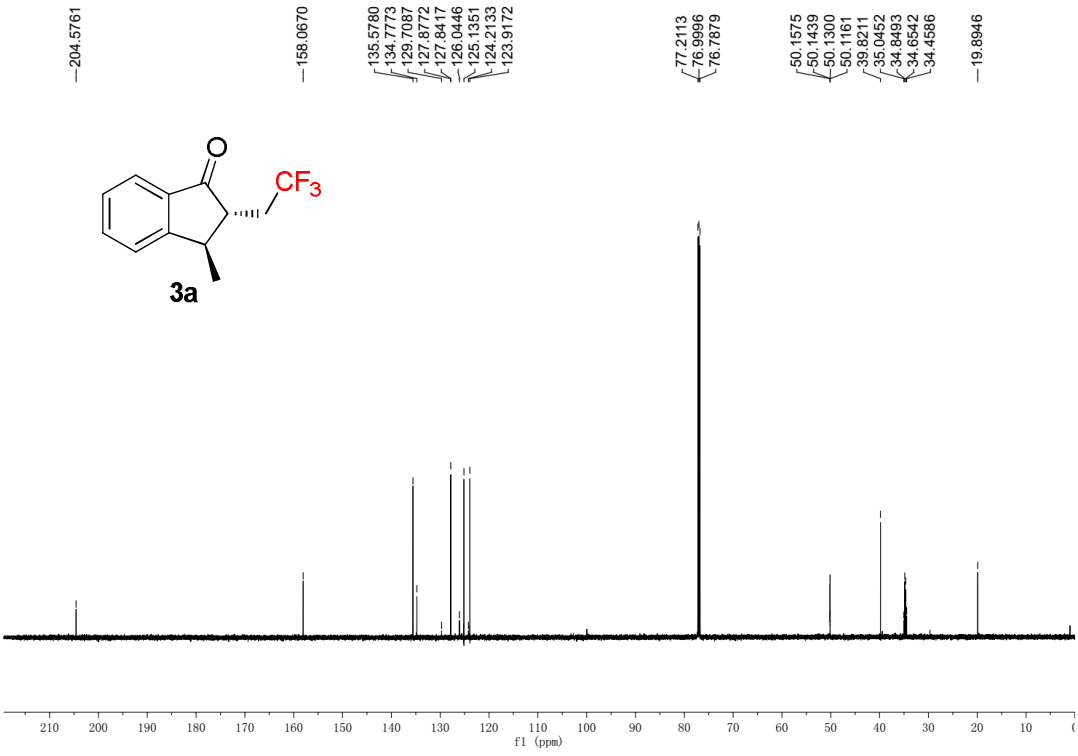
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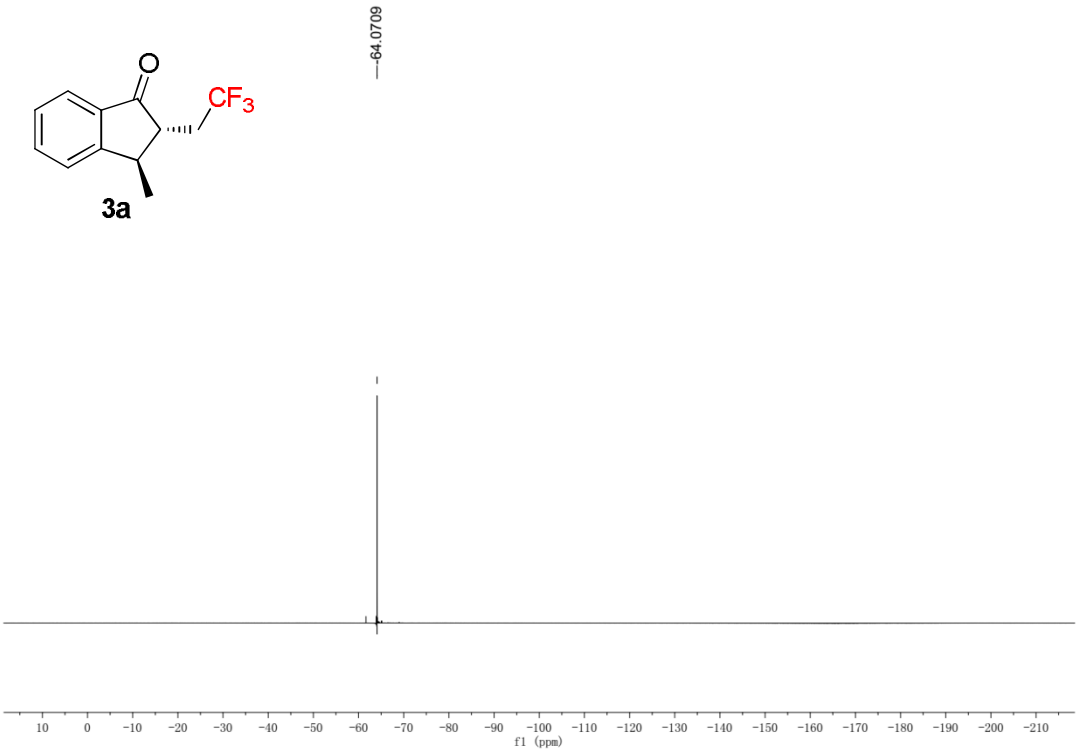
34.4586
19.8946
O
CF3
3a
f1 (ppm)

3a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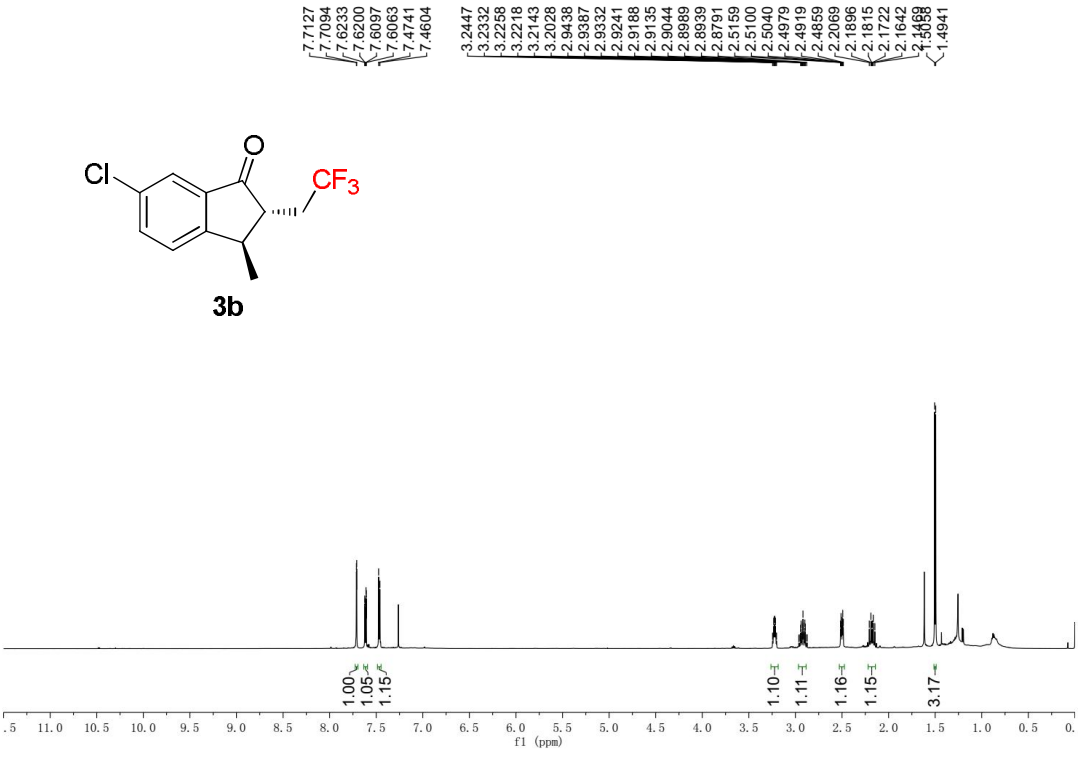
f1 (ppm)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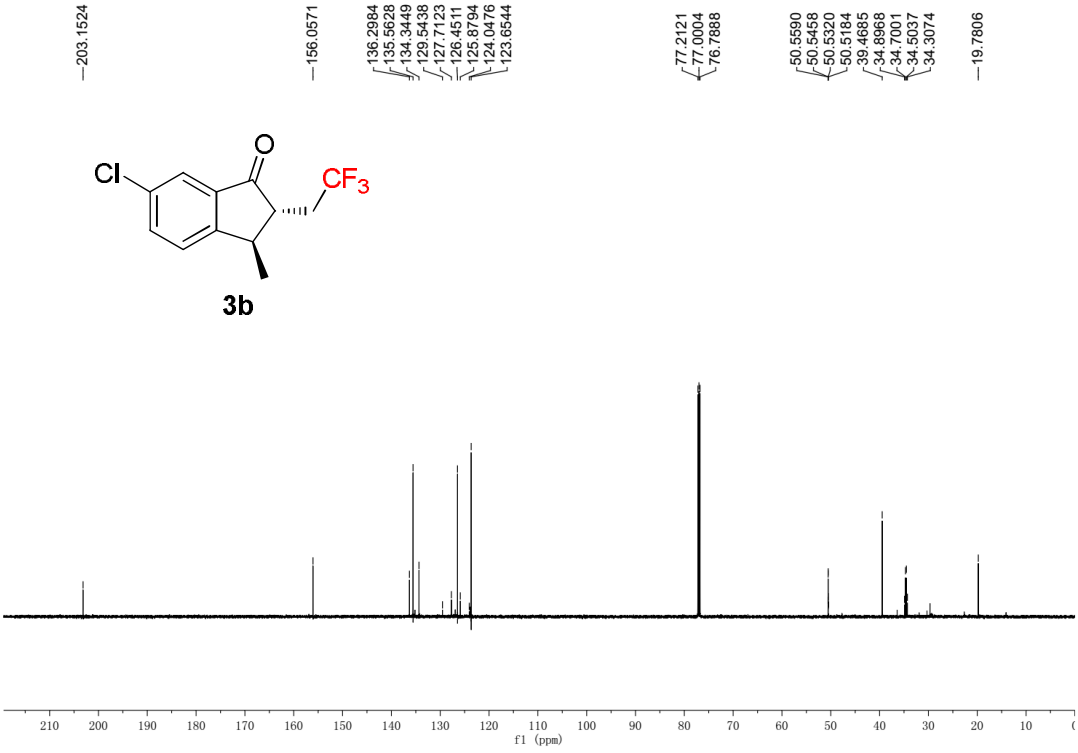
7.6097
7.6063
7.4741
7.4604
3.2447
3.2332
3.2258
3.2218
3.2143
3.2028
2.9438
2.9387
2.9332
2.9241
2.9188
2.9135
2.9044
2.8989
2.8939
2.8791
2.5159
2.5100
2.5040
2.4979
2.4919
2.4859
2.2069
2.1896
2.1815
2.1722
2.1642
2.1469
2.1058
1.4941
1.00
1.05
1.15
1.10
1.11
1.16
1.15
3.17
.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

3b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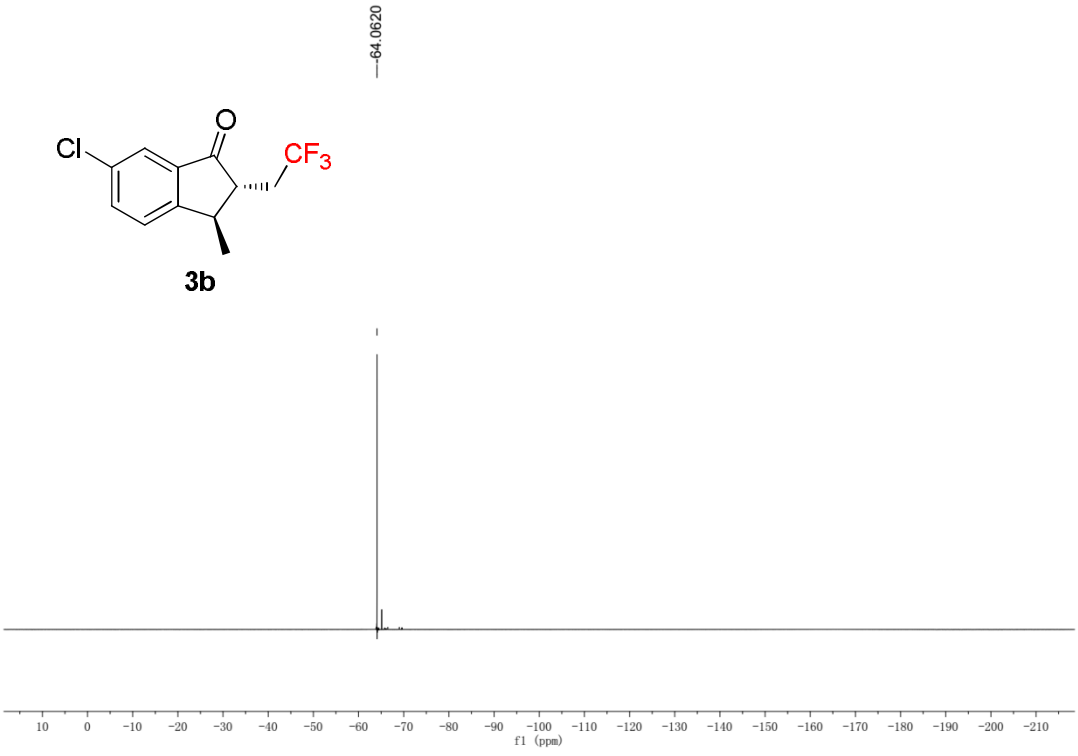
136.2984
135.5628
134.3449
129.5438
127.7123
126.4511
125.8794
124.0476
123.6544
77.2121
77.0004
76.7888
50.5590
50.5458
50.5320
50.5184
39.4685
34.8968
34.7001
34.5037
34.3074
19.7806
Cl
O
CF3
3b
f1 (ppm)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CF3
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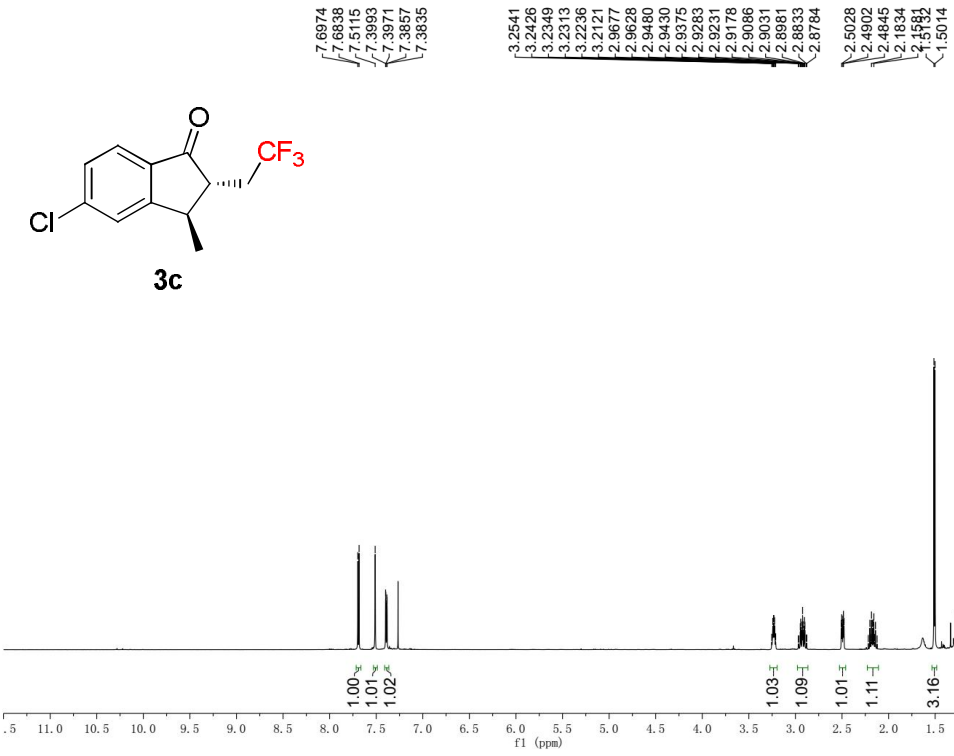
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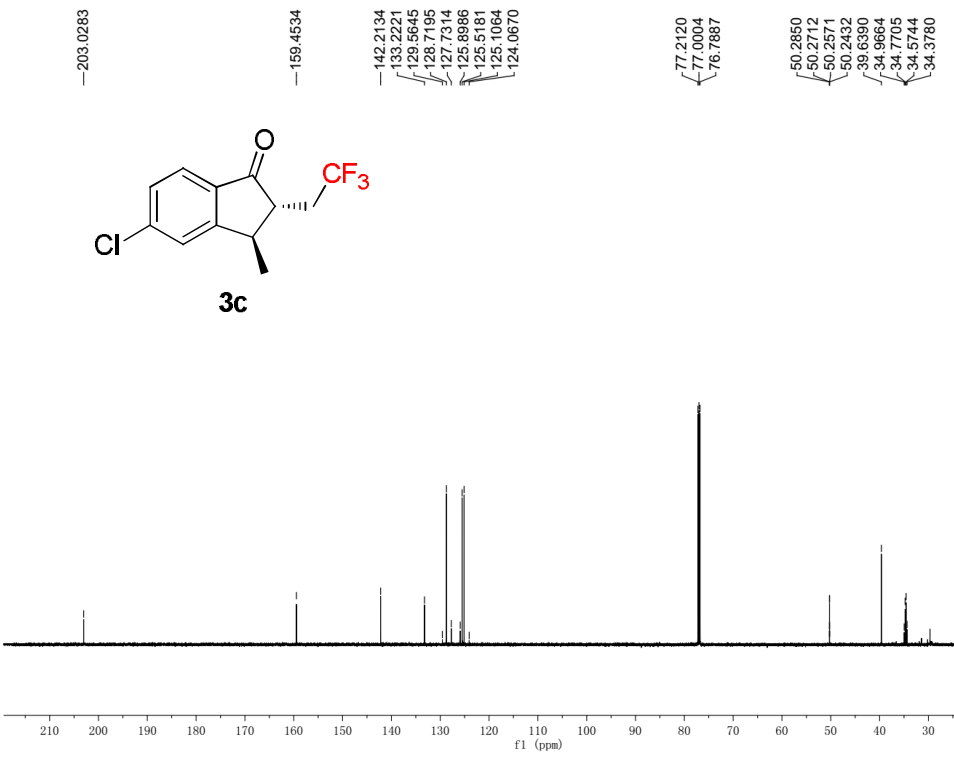
7.6838
7.5115
7.3993
7.3971
7.3857
7.3835
3.2541
3.2426
3.2349
3.2313
3.2236
3.2121
2.9677
2.9628
2.9480
2.9430
2.9375
2.9283
2.9231
2.9178
2.9086
2.9031
2.8981
2.8833
2.8784
2.5028
2.4902
2.4845
2.1834
2.1581
1.5132
1.5014
O
CF3
Cl
3c
1.00
1.01
1.02
1.03
1.09
1.01
1.11
3.16
f1 (ppm)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142.2134
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129.5645
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125.5181
125.1064
124.0670
77.2120
77.0004
76.7887
50.2850
50.2712
50.2571
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39.6390
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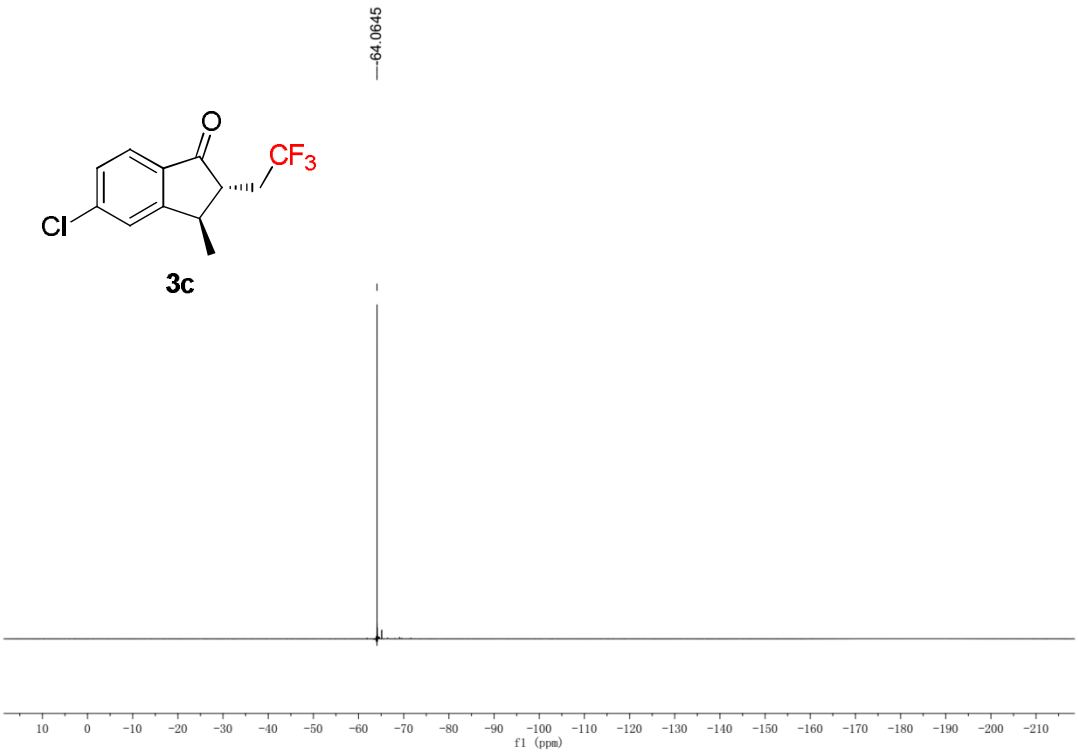
34.7705
34.5744
34.3780
19.7204
O
CF3
Cl
3c
f1 (ppm)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CF3
Cl
3c
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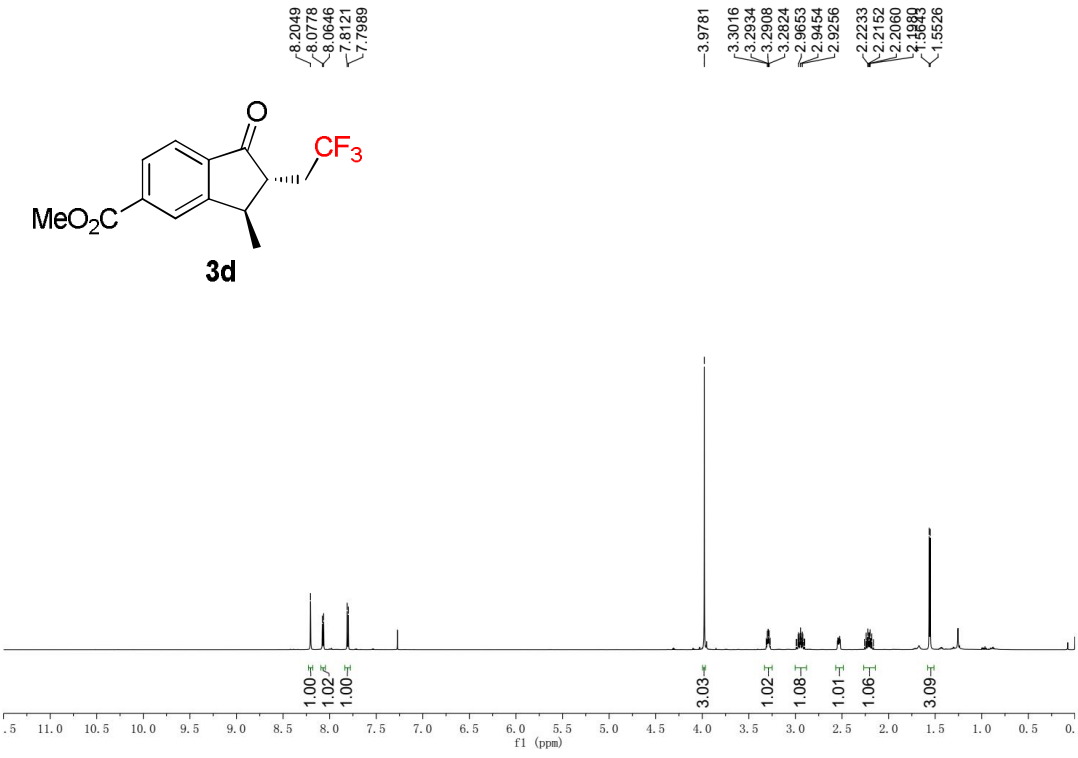
f1 (ppm)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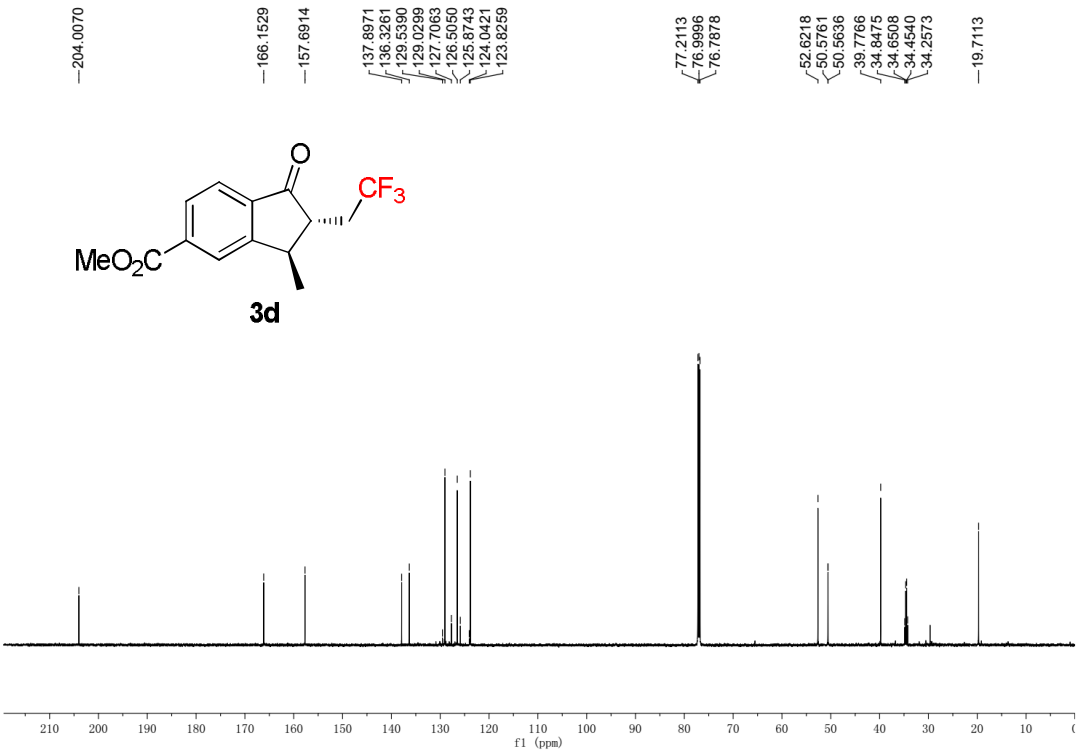
8.0646
7.8121
7.7989
3.9781
3.3016
3.2934
3.2908
3.2824
2.9653
2.9454
2.9256
2.2233
2.2152
2.2060
1.5526
O
CF3
MeO2C
3d
1.00
1.02
1.00
3.03
1.02
1.08
1.01
1.06
3.09
f1 (ppm)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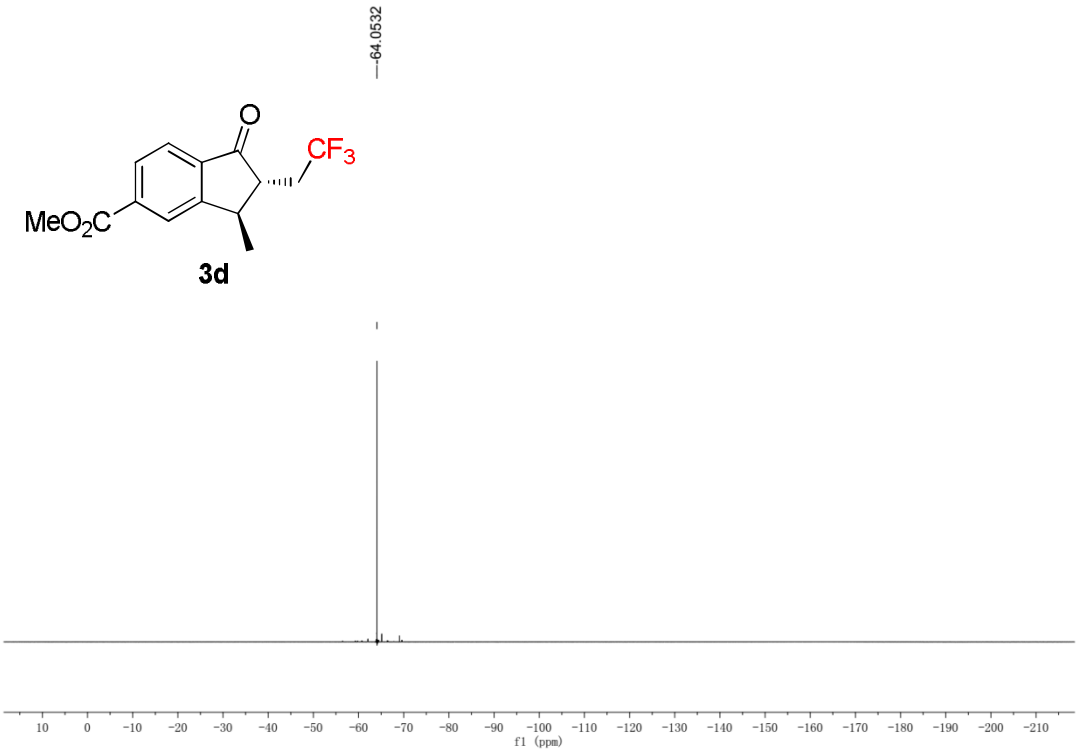
157.6914
137.8971
136.3261
129.5390
129.0299
127.7063
126.5050
125.8743
124.0421
123.8259
77.2113
76.9996
76.7878
52.6218
50.5761
50.5636
39.7766
34.8475
34.6508
34.4540
34.2573
19.7113
O
CF3
MeO2C
3d
f1 (ppm)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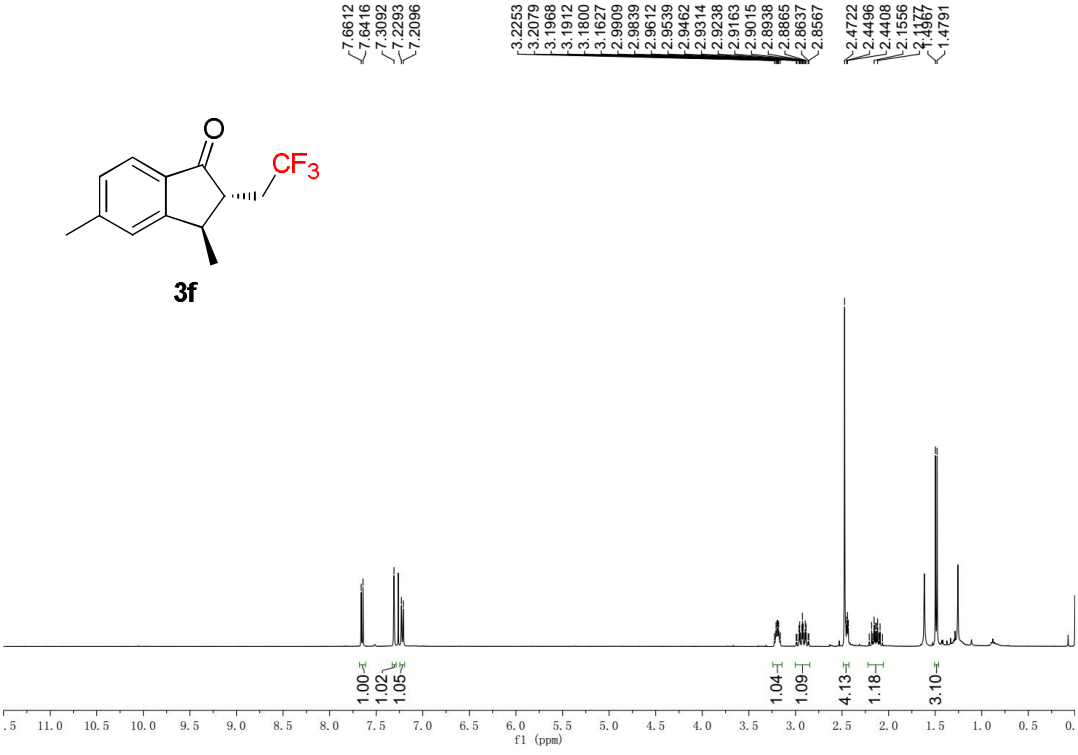
CF3
MeO2C
3d
f1 (ppm)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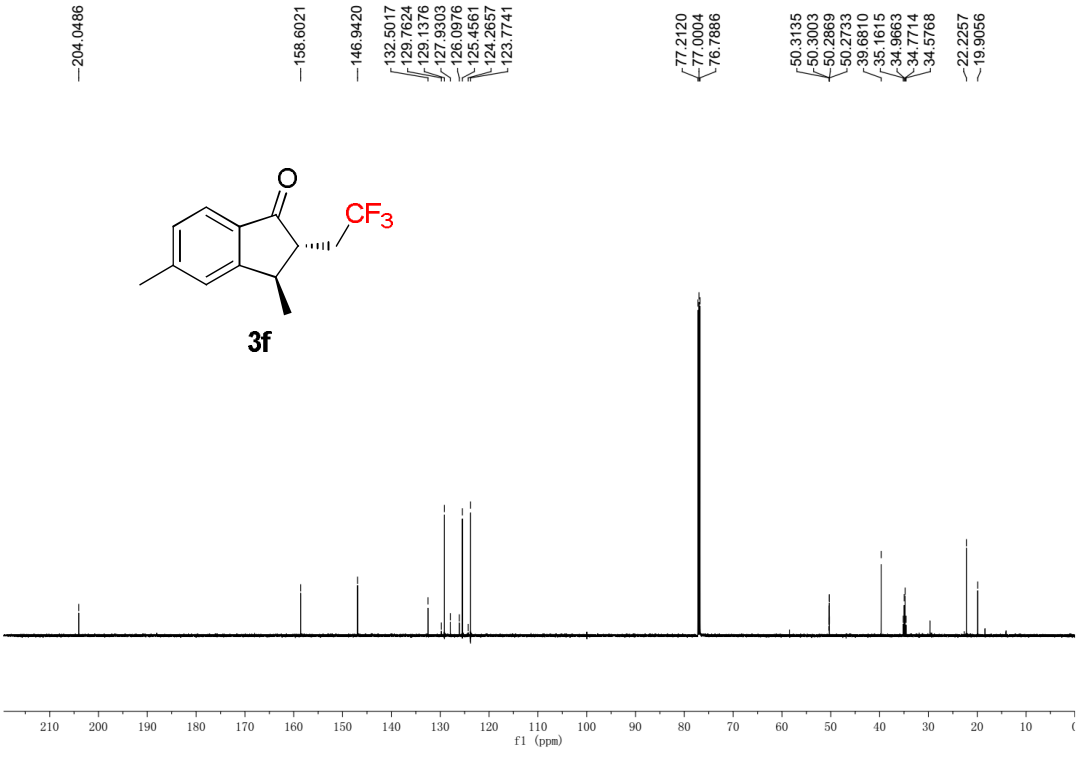
7.6416
7.3092
7.2293
7.2096
3.2253
3.2079
3.1968
3.1912
3.1800
3.1627
2.9909
2.9839
2.9612
2.9539
2.9462
2.9314
2.9238
2.9163
2.9015
2.8938
2.8865
2.8637
2.8567
2.4722
2.4496
2.4408
2.1556
2.1177
1.4967
1.4791
CF3
3f
1.00
1.02
1.05
1.04
1.09
4.13
1.18
3.10
f1 (ppm)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146.9420
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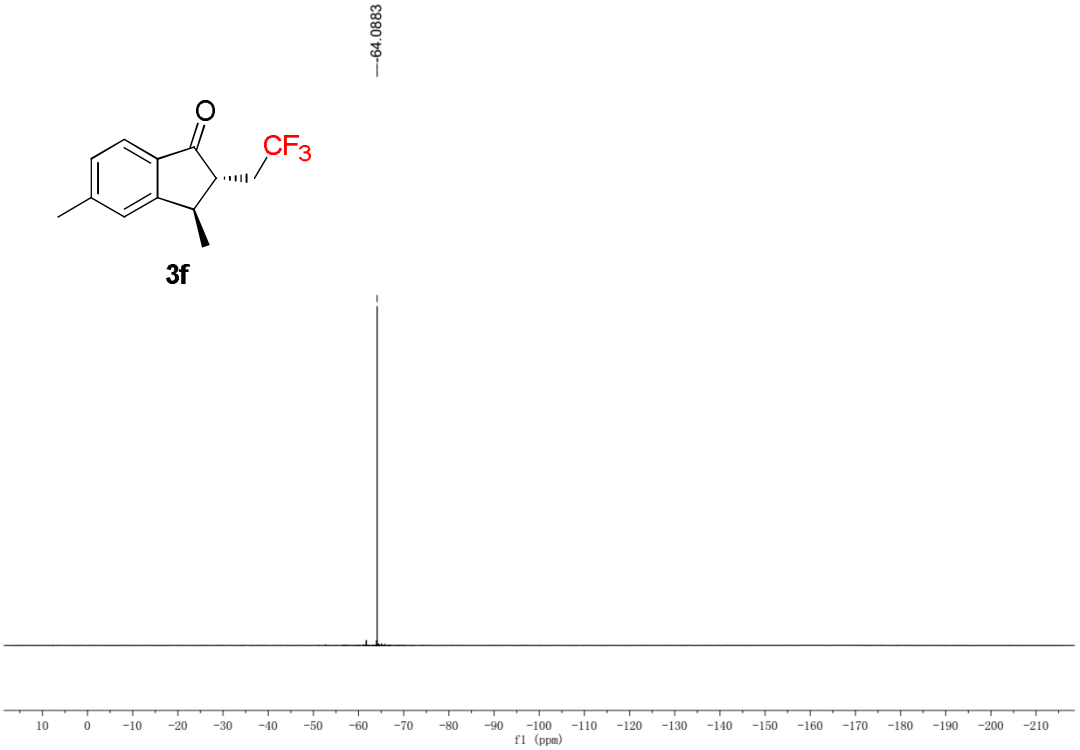
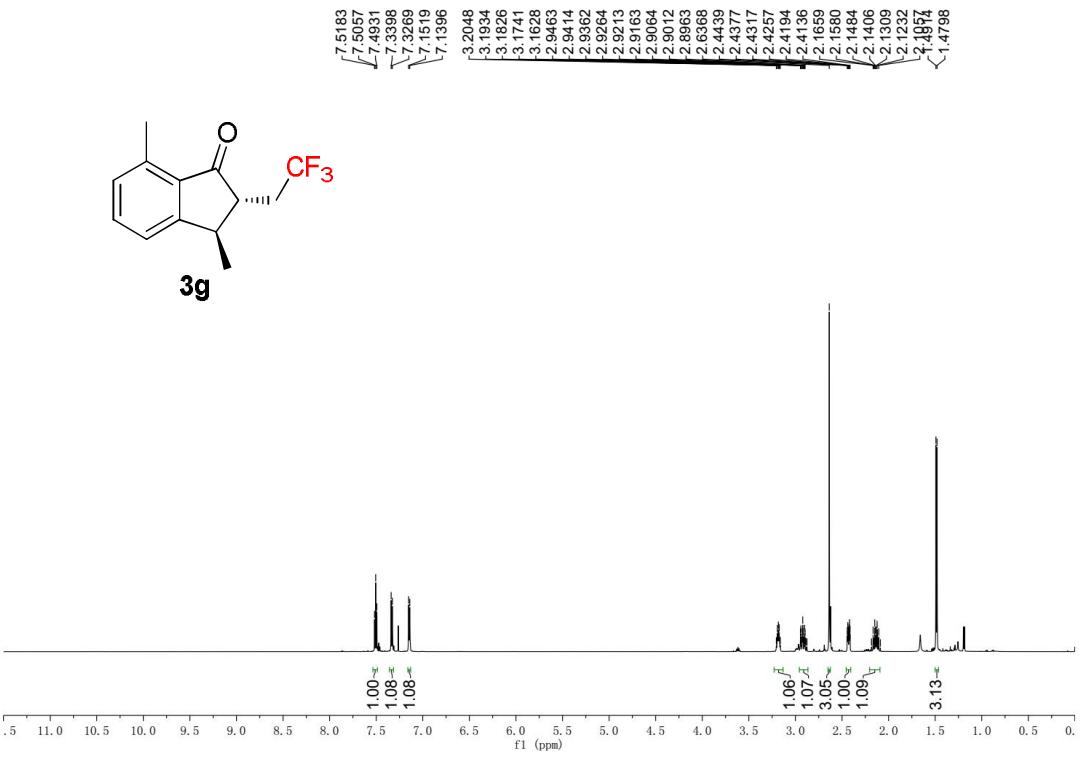
129.7624
129.1376
127.9303
126.0976
125.4561
124.2657
123.7741
77.2120
77.0004
76.7886
50.3135
50.3003
50.2869
50.2733
39.6810
35.1615
34.9663
34.7714
34.5768
22.2257
19.9056
CF3
3f
f1 (ppm)


-64.0883
CF3
3f
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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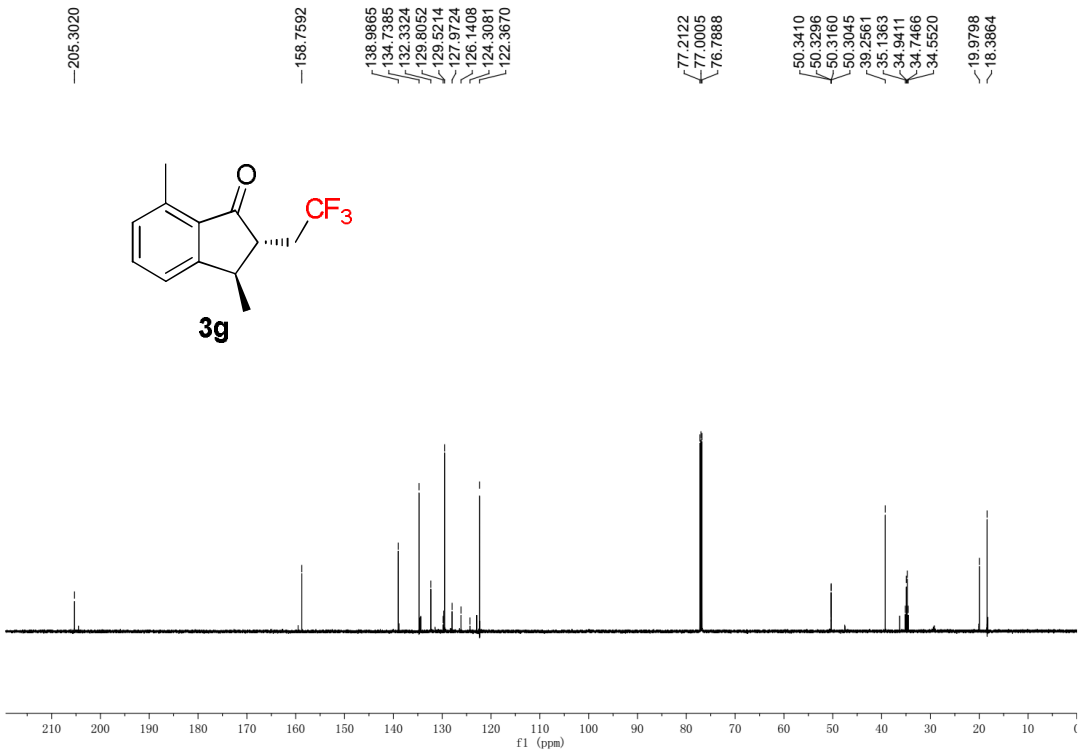
3.1934
3.1826
3.1741
3.1628
2.9463
2.9414
2.9362
2.9264
2.9213
2.9163
2.9064
2.9012
2.8963
2.6368
2.4439
2.4377
2.4317
2.4257
2.4194
2.4136
2.1659
2.1580
2.1484
2.1406
2.1309
2.1232
2.1057
1.4974
1.4798
CF3
3g
1.00
1.08
1.08
1.06
1.07
3.05
1.00
1.09
3.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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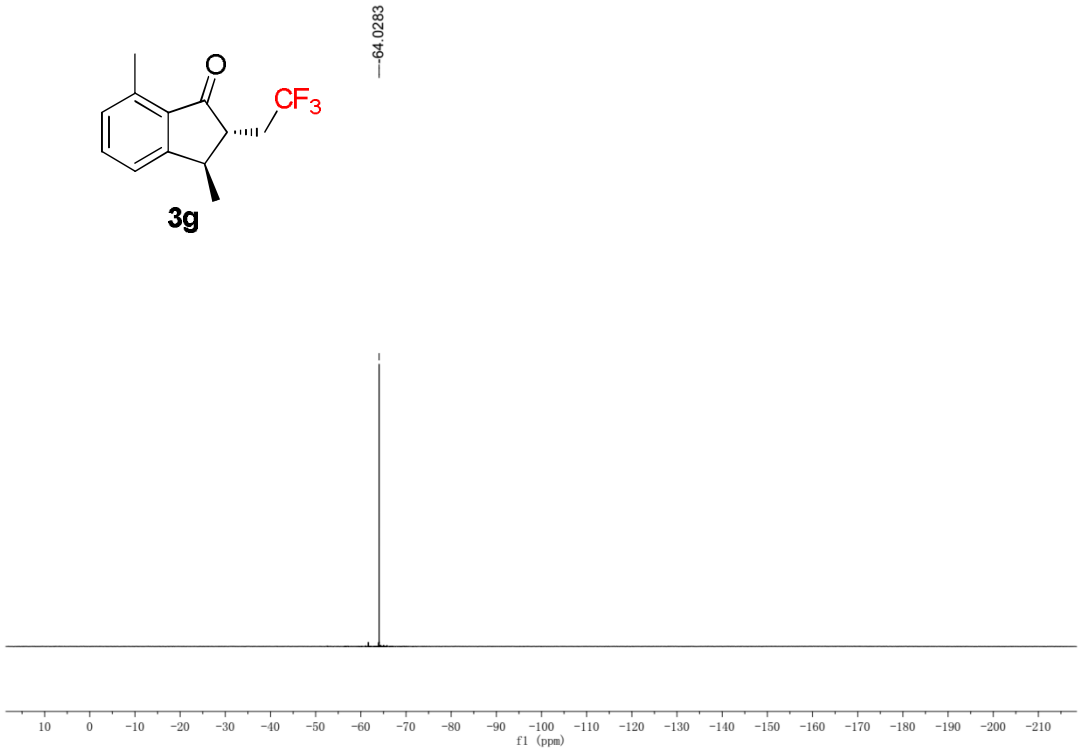
132.3324
129.8052
129.5214
127.9724
126.1408
124.3081
122.3670
77.2122
77.0005
76.7888
50.3410
50.3296
50.3160
50.3045
39.2561
35.1363
34.9411
34.7466
34.5520
19.9798
18.3864
O
CF3
3g
f1 (ppm)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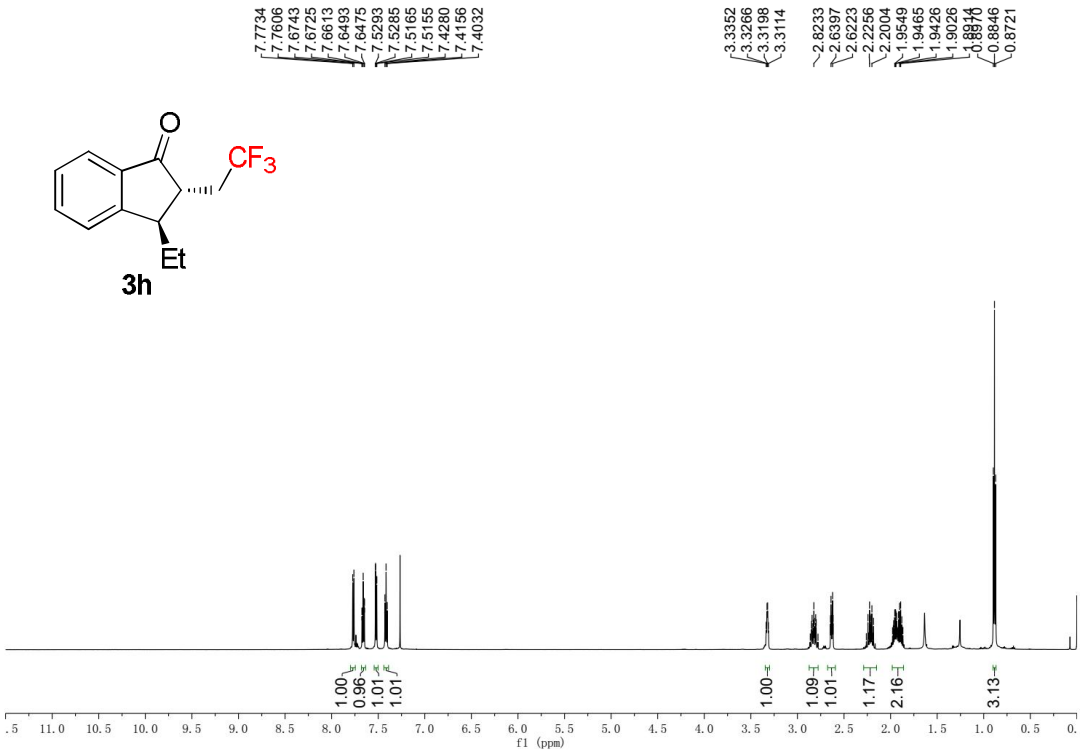
O
CF3
3g
f1 (ppm)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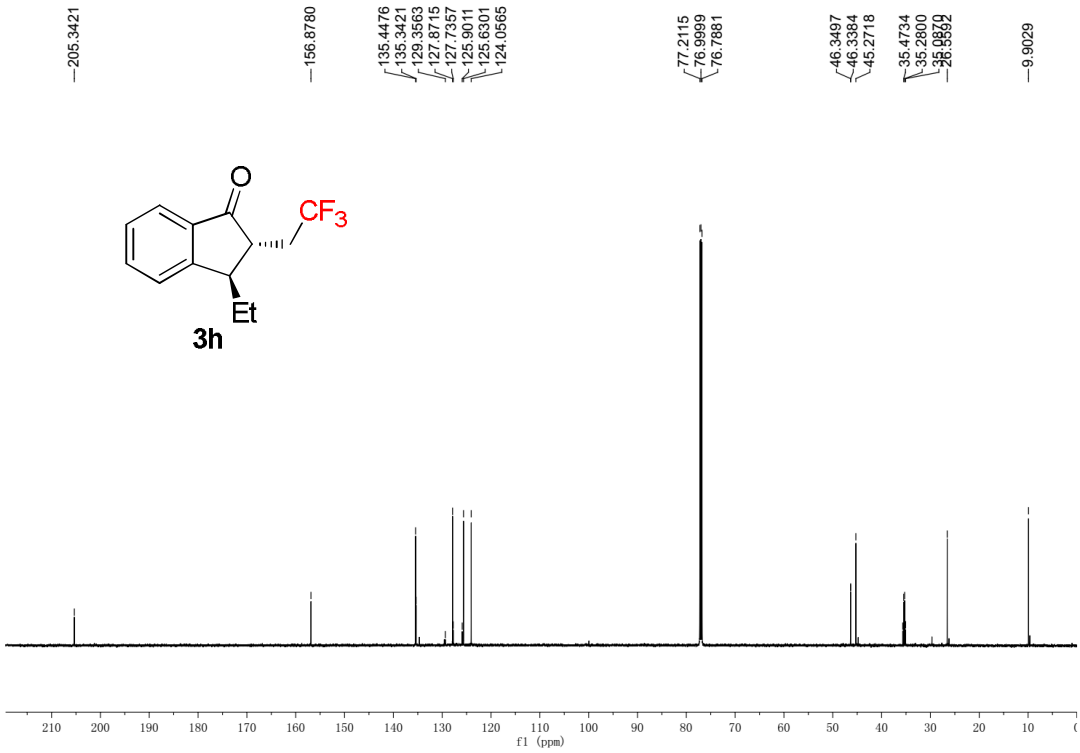
7.6743
7.6725
7.6613
7.6493
7.6475
7.5293
7.5285
7.5165
7.5155
7.4280
7.4156
7.4032
3.3352
3.3266
3.3198
3.3114
2.8233
2.6397
2.6223
2.2256
2.2004
1.9549
1.9465
1.9426
1.9026
0.8846
0.8721
O
CF3
Et
3h
1.00
0.96
1.01
1.01
1.00
1.09
1.01
1.17
2.16
3.13
f1 (ppm)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129.3563
127.8715
127.7357
125.9011
125.6301
124.0565
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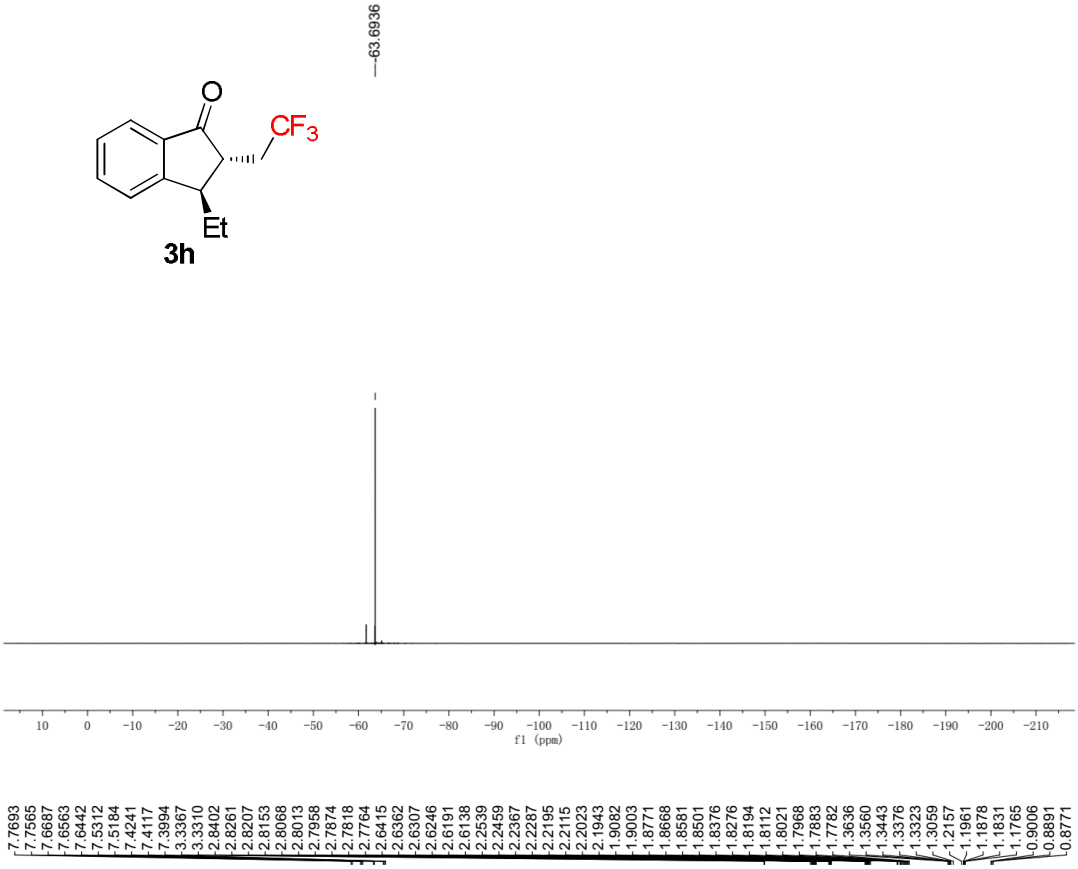
76.9999
76.7881
46.3497
46.3384
45.2718
35.4734
35.2800
9.9029
O
CF3
Et
3h
f1 (ppm)

O
CF3
Et

3h


-63.6936
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

7.7693
7.7565
7.6687
7.6563
7.6442
7.5312
7.5184
7.4241
7.4117
7.3994
3.3367
3.3310
2.8402
2.8261
2.8207
2.8153
2.8068
2.8013
2.7958
2.7874
2.7818
2.7764
2.6415
2.6362
2.6307
2.6246
2.6191
2.6138
2.2539
2.2459
2.2367
2.2287
2.2195
2.2115
2.2023
2.1943
1.9082
1.9003
1.8771
1.8668
1.8581
1.8501
1.8376
1.8276
1.8194
1.8112
1.8021
1.7968
1.7883
1.7782
1.3636
1.3560
1.3443
1.3376
1.3323
1.3059
1.2157
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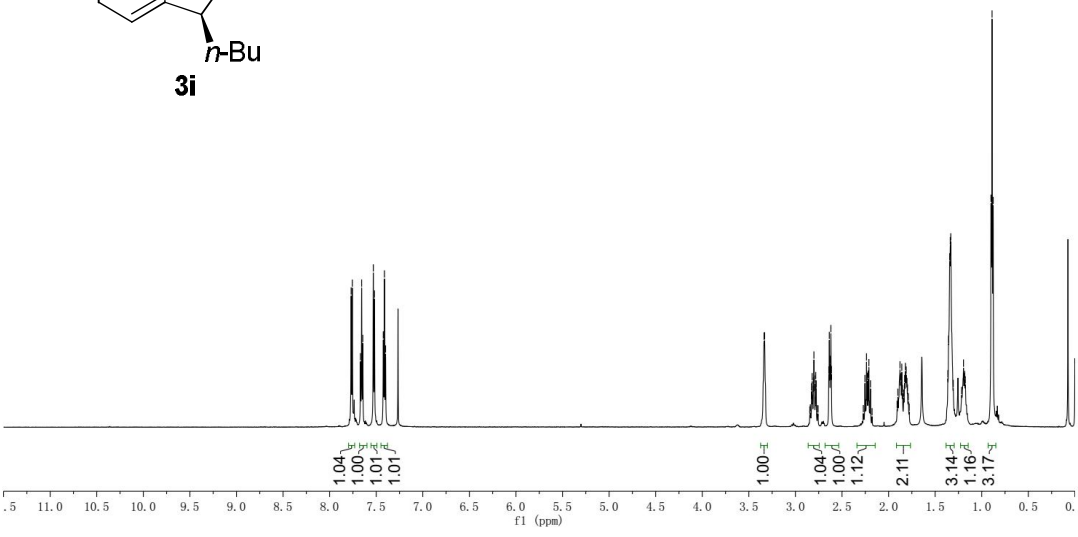
1.1831
1.1765
0.9006
0.8891
0.8771

O
CF3
n-Bu

3i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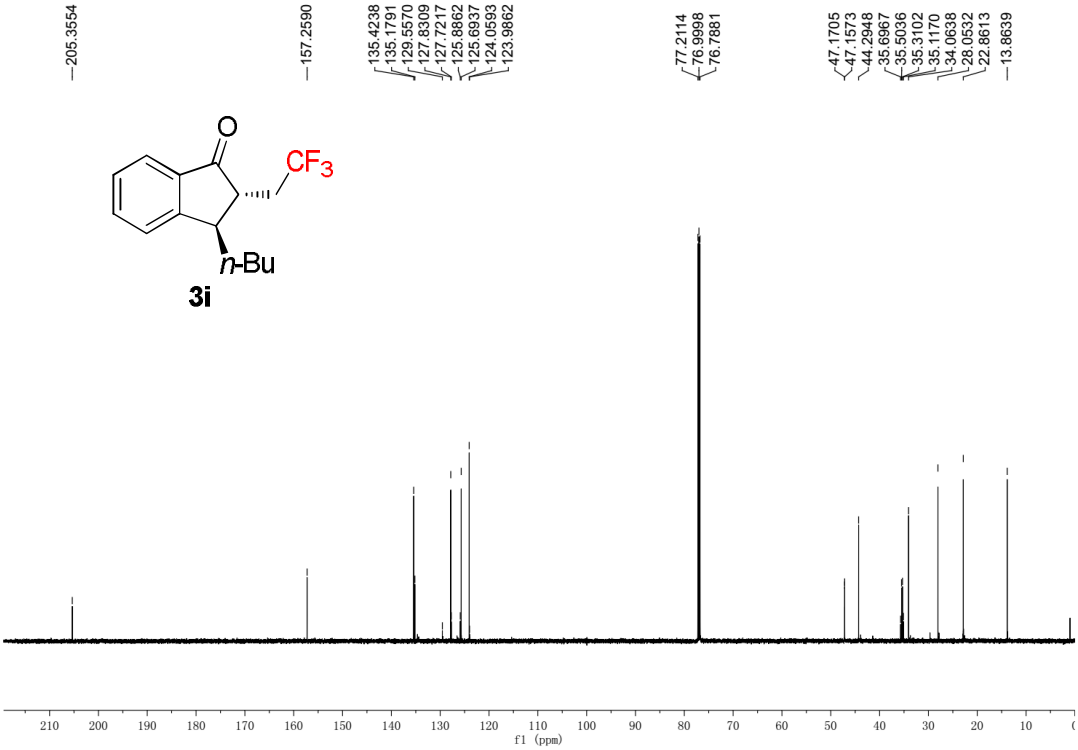
1.01
1.01
1.00
1.04
1.00
1.12
2.11
3.14
1.16
3.17
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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123.9862
77.2114
76.9998
76.7881
47.1705
47.1573
44.2948
35.6967
35.5036
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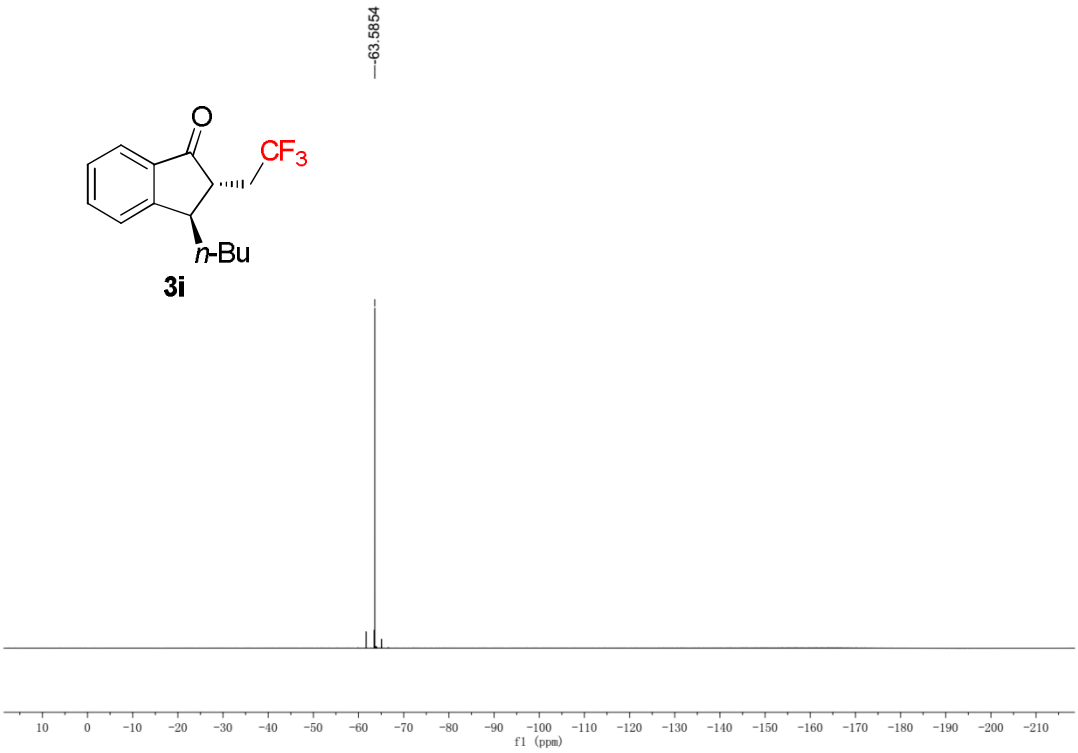
13.8639
O
CF3
n-Bu
3i
f1 (ppm)


63.5854
O
CF3
n-Bu
3i
f1 (ppm)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7.4451
7.4325
7.2969
7.2949
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7.2849
7.2809
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7.1728
7.1511
7.1392
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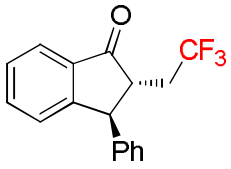
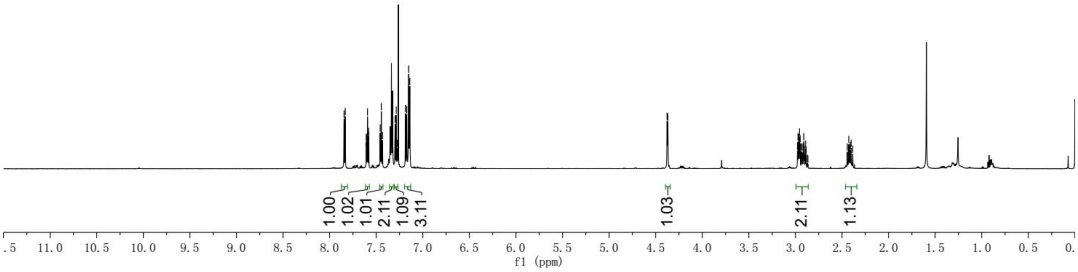
2.4017
2.3847


O
CF3
Ph

3j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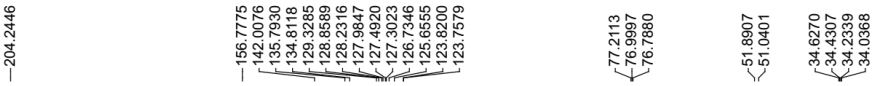
1.01
2.11
1.09
3.11
1.03
2.11
1.13
f1 (ppm)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126.7346
125.6555
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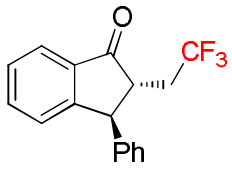
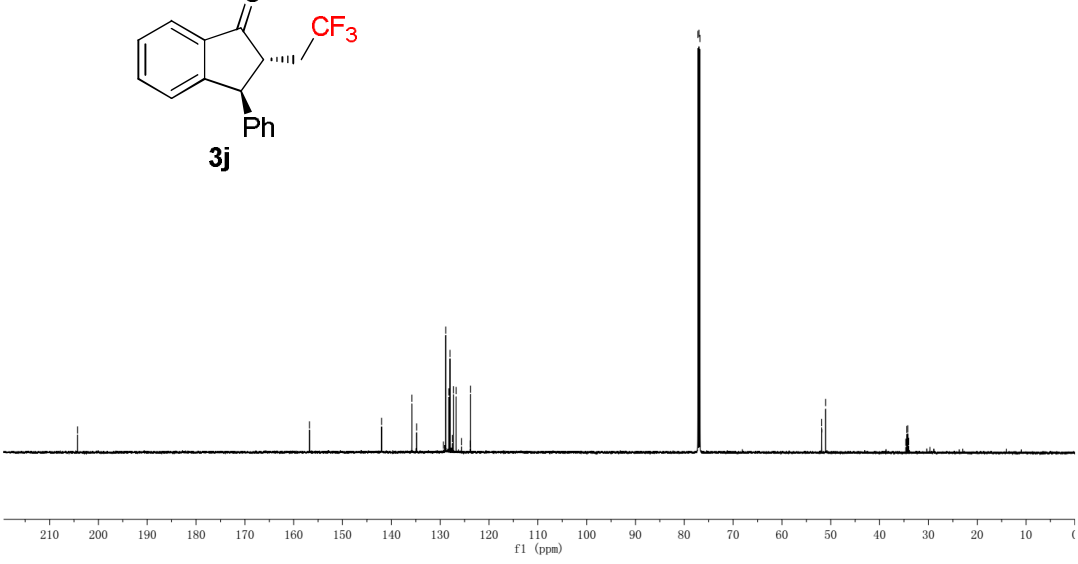
76.7880
51.8907
51.0401
34.6270
34.4307
34.2339
34.0368

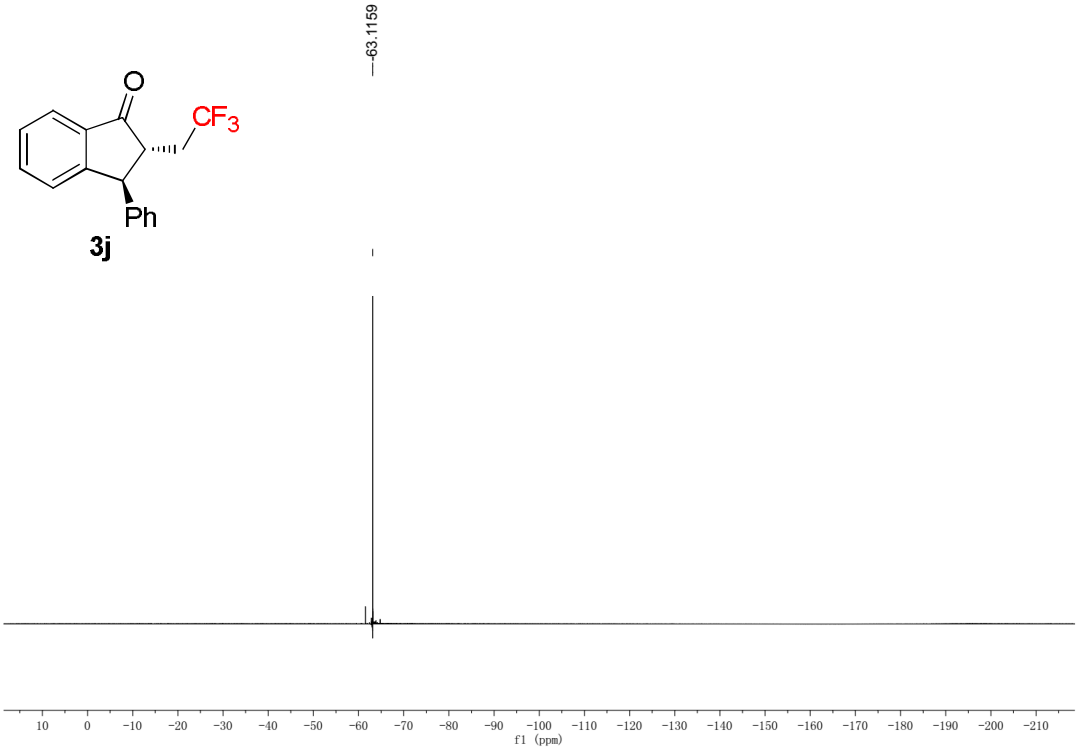

O
CF3
Ph

3j


f1 (ppm)

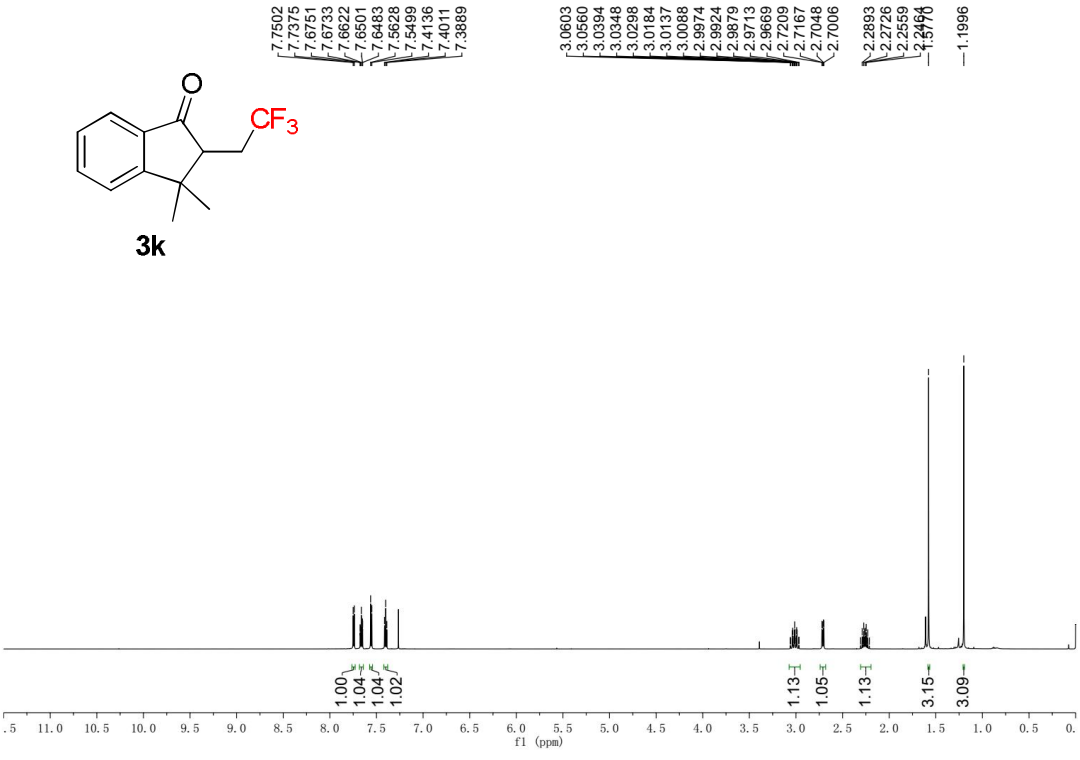
O
CF3
Ph

3j


-63.1159
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

O
CF3

3k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7.6751
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7.4136
7.4011
7.3889
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3.0560
3.0394
3.0348
3.0298
3.0184
3.0137
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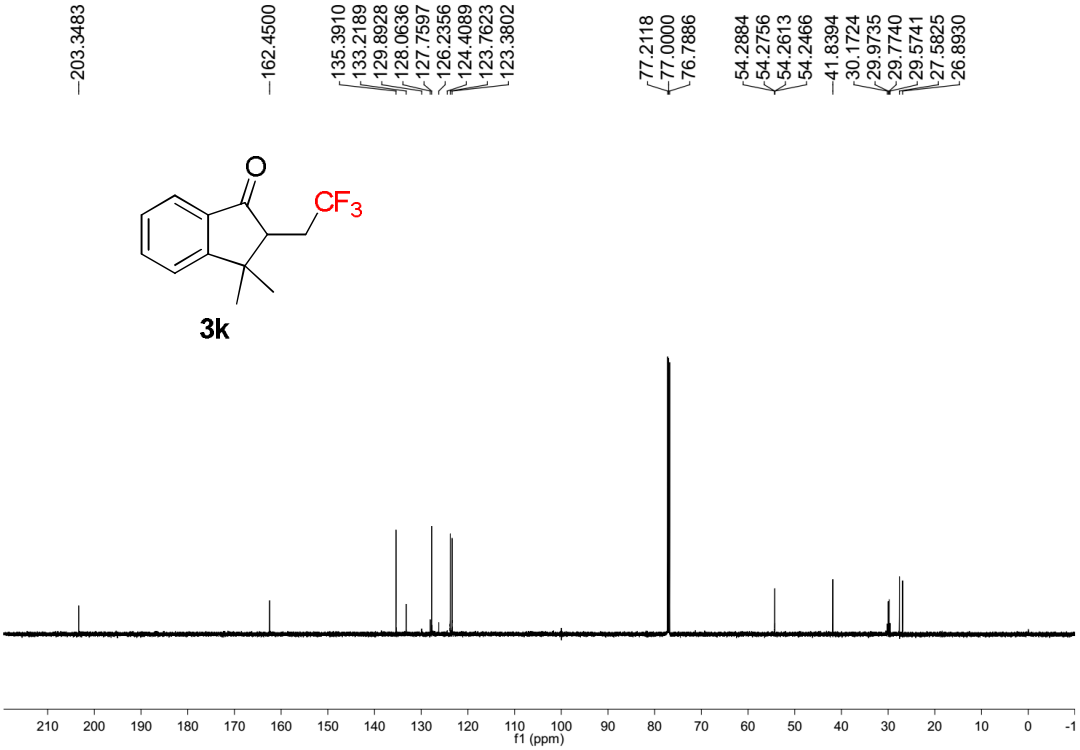
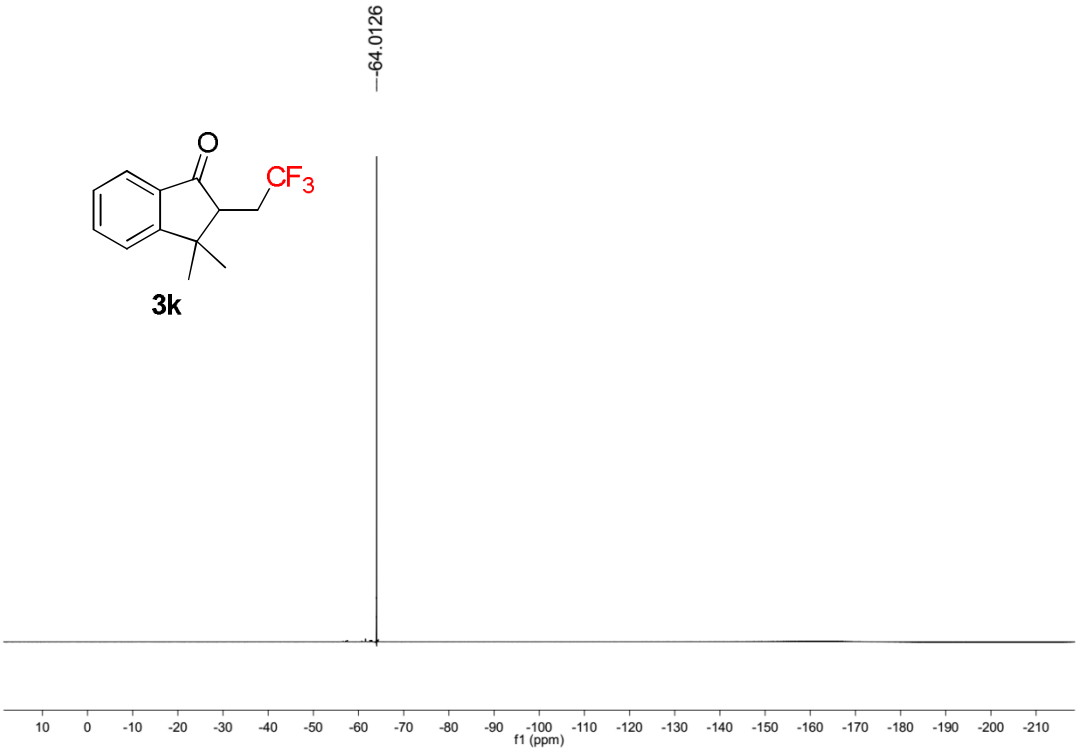
2.2464
1.5770
1.1996
1.00
1.04
1.04
1.02
1.13
1.05
1.13
3.15
3.09
f1 (ppm)


203.3483
162.4500
135.3910
133.2189
129.8928
128.0636
127.7597
126.2356
124.4089
123.7623
123.3802
77.2118
77.0000
76.7886
54.2884
54.2756
54.2613
54.2466
41.8394
30.1724
29.9735
29.7740
29.5741
27.5825
26.8930
O
CF3
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


64.0126
O
CF3
3k
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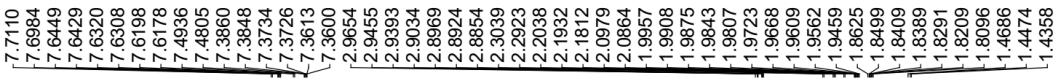
f1 (ppm)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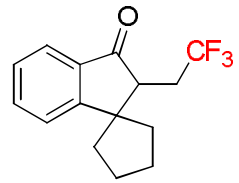
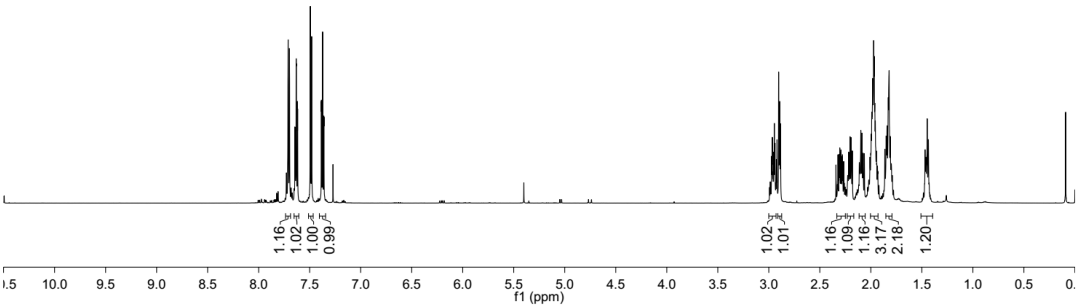
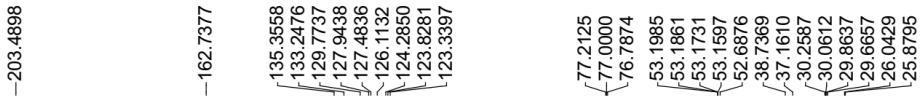
7.6984
7.6449
7.6429
7.6320
7.6308
7.6198
7.6178
7.4936
7.4805
7.3860
7.3848
7.3734
7.3726
7.3613
7.3600
2.9654
2.9455
2.9393
2.9034
2.8969
2.8924
2.8854
2.3039
2.2923
2.2038
2.1932
2.1812
2.0979
2.0864
1.9957
1.9908
1.9875
1.9843
1.9807
1.9723
1.9668
1.9609
1.9562
1.9459
1.8625
1.8499
1.8409
1.8389
1.8291
1.8209
1.8096
1.4686
1.4474
1.4358


O
CF3

3l


1.16
1.02
1.00
0.99
1.02
1.01
1.16
1.09
1.16
3.17
2.18
1.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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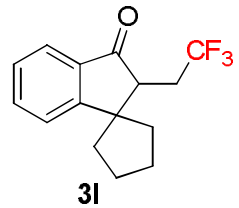
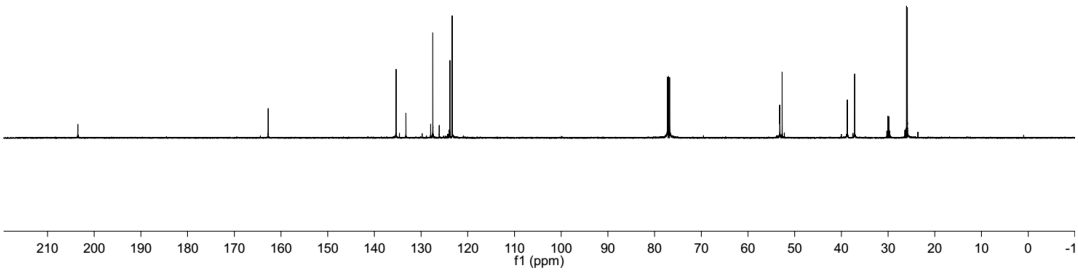
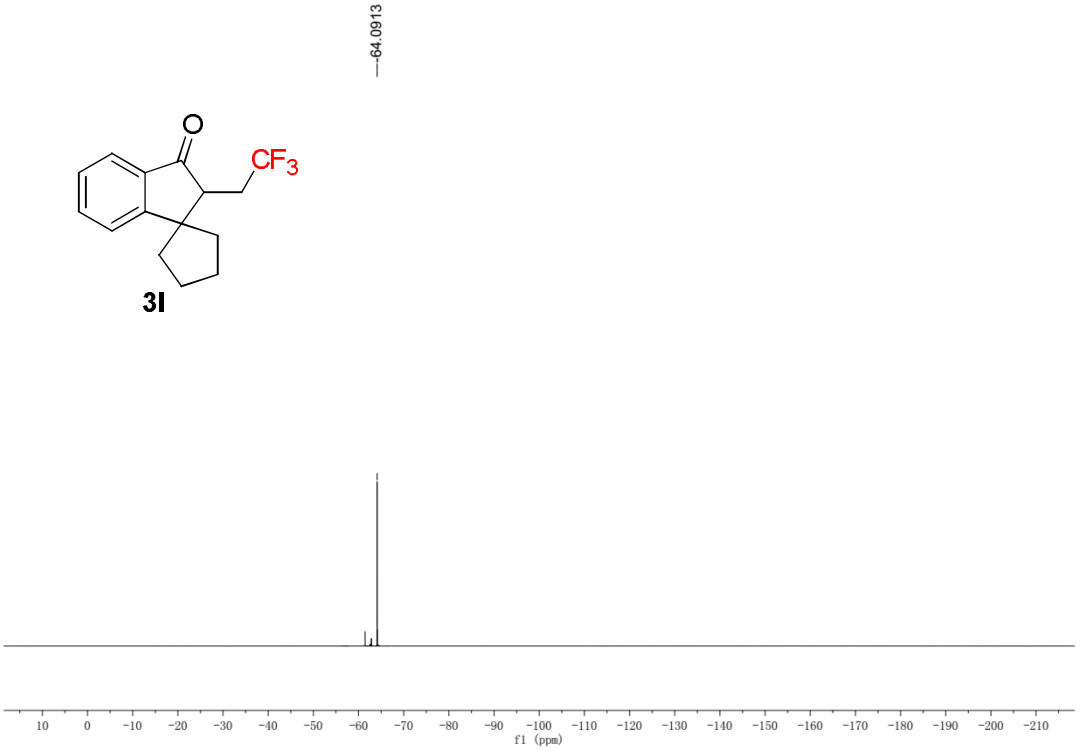
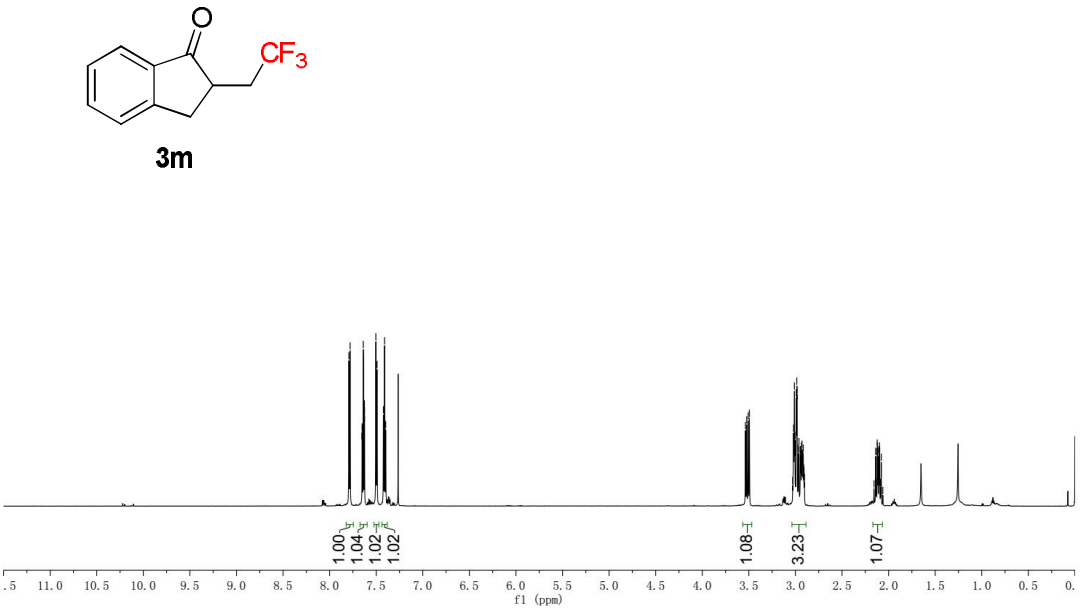
162.7377
135.3558
133.2476
129.7737
127.9438
127.4836
126.1132
124.2850
123.8281
123.3397
77.2125
77.0000
76.7874
53.1985
53.1861
53.1731
53.1597
52.6876
38.7369
37.1610
30.2587
30.0612
29.8637
29.6657
26.0429
25.8795

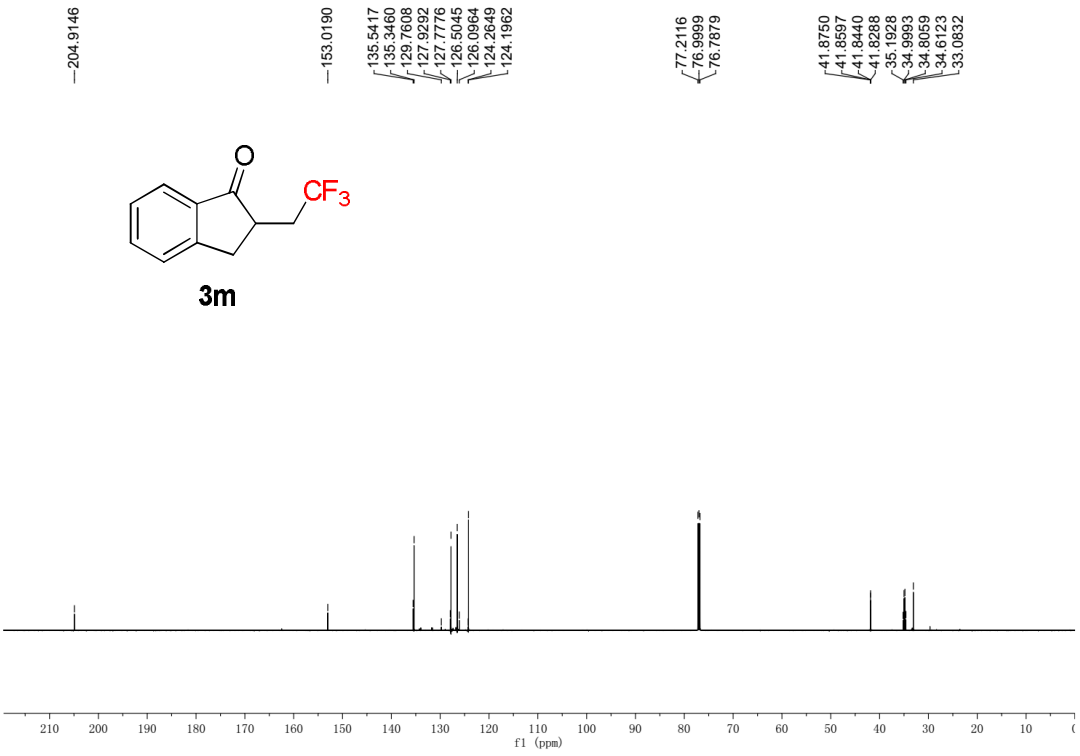

O
CF3

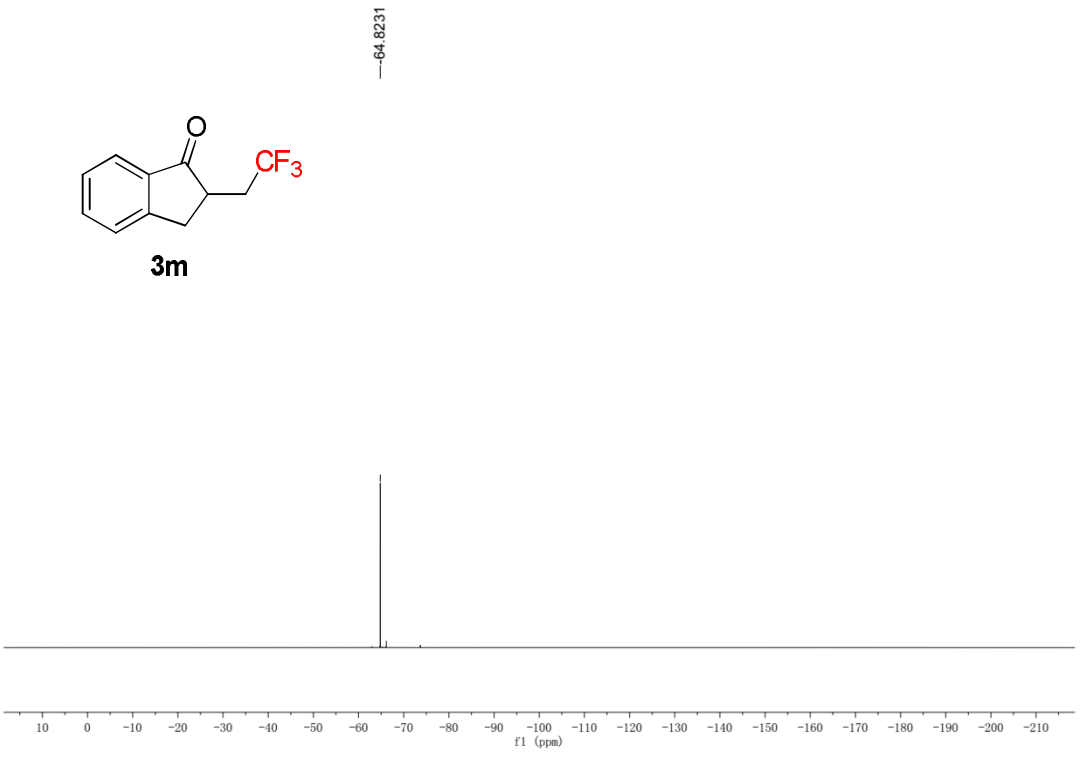
3l

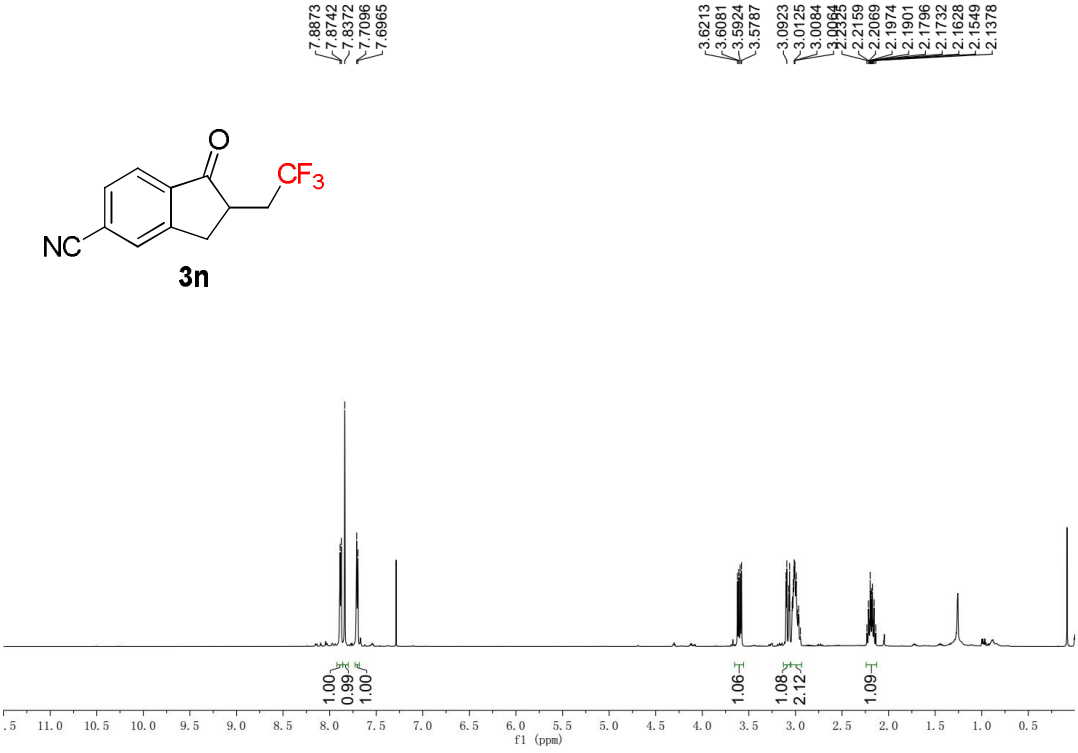

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

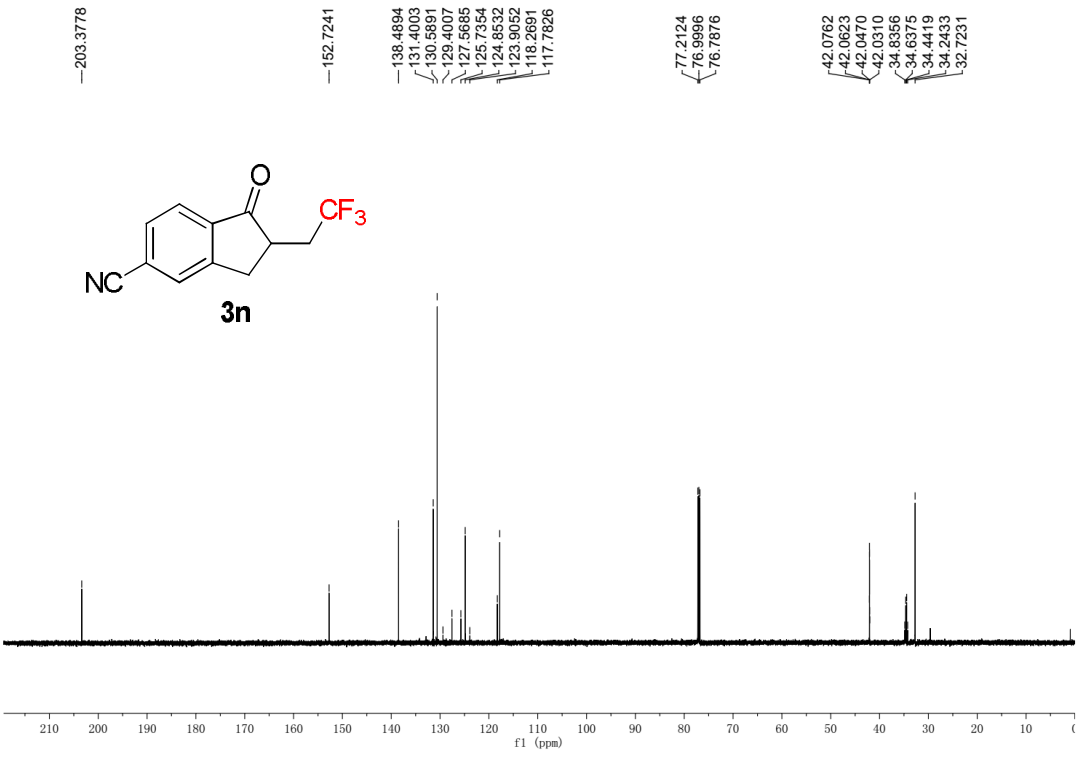

-64.0913
CF3
3l
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
7.7930
7.7802
7.6515
7.6498
7.6388
7.6266
7.6249
7.5037
7.4909
7.4228
7.4102
7.3980
3.5361
3.5227
3.5074
3.4940
3.0106
2.9911
2.9852
2.1393
2.1313
2.1222
2.1201
2.1143
2.1031
2.0973
2.0952
2.0861
2.0782
2.0617


CF3
3m
1.00
1.04
1.02
1.02
1.08
3.23
1.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


204.9146
153.0190
135.5417
135.3460
129.7608
127.9292
127.7776
126.5045
126.0964
124.2649
124.1962
77.2116
76.9999
76.7879
41.8750
41.8597
41.8440
41.8288
35.1928
34.9993
34.8059
34.6123
33.0832
O
CF3
3m
f1 (ppm)


64.8231
O
CF3
3m
f1 (ppm)


7.8873
7.8742
7.8372
7.7096
7.6965
3.6213
3.6081
3.5924
3.5787
3.0923
3.0125
3.0084
2.2159
2.2069
2.1974
2.1901
2.1796
2.1732
2.1628
2.1549
2.1378
O
CF3
NC
3n
1.00
0.99
1.00
1.06
1.08
2.12
1.09
f1 (ppm)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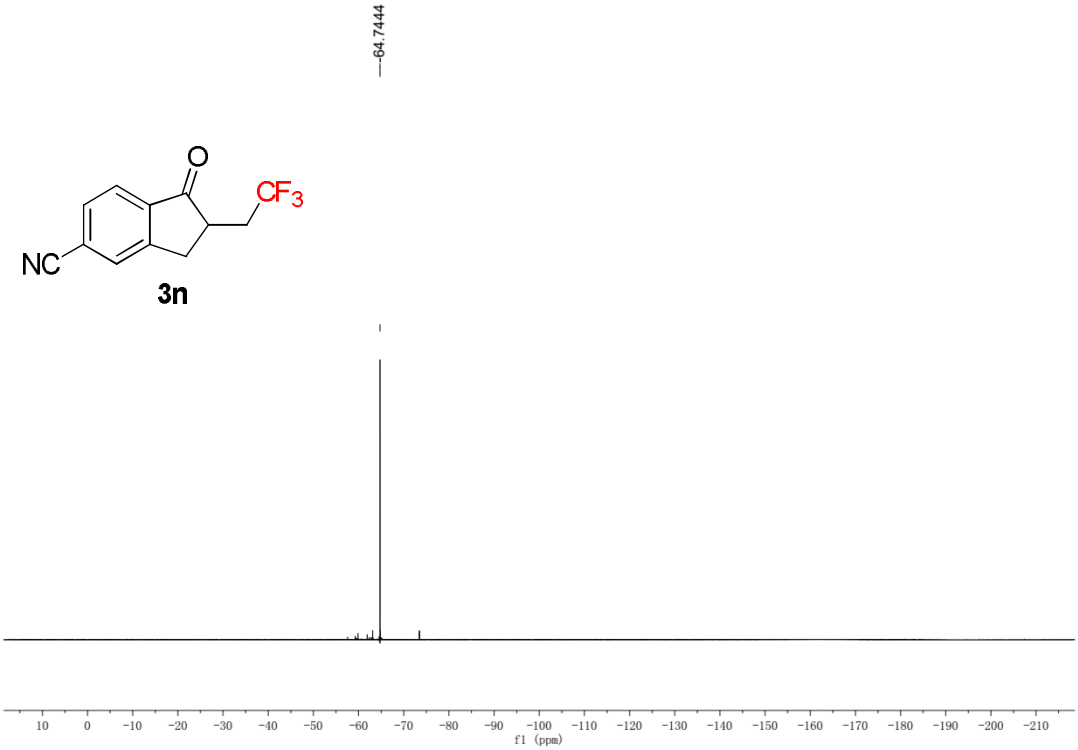
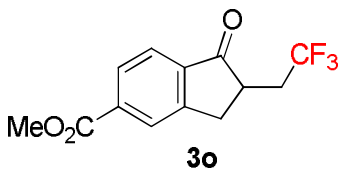
152.7241
138.4894
131.4003
130.5891
129.4007
127.5685
125.7354
124.8532
123.9052
118.2691
117.7826
77.2124
76.9996
76.7876
42.0762
42.0623
42.0470
42.0310
34.8356
34.6375
34.4419
34.2433
32.7231
O
CF3
NC
3n
f1 (ppm)

O
CF3
NC

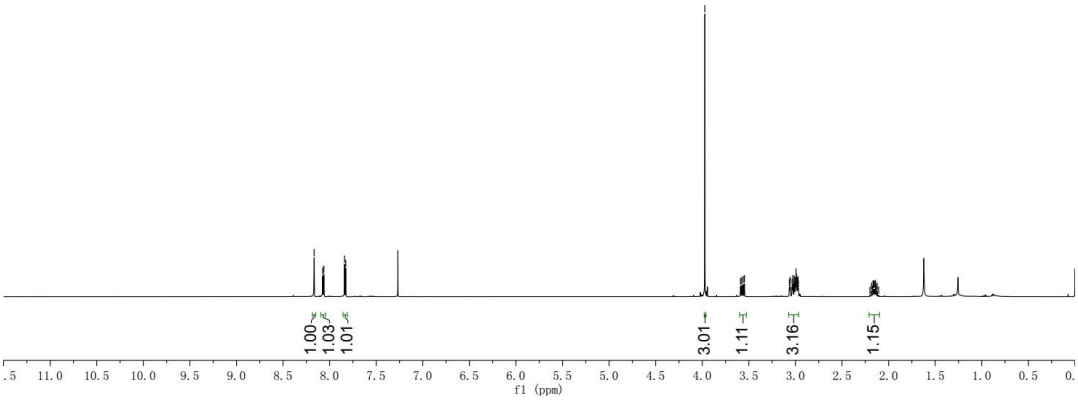
3n

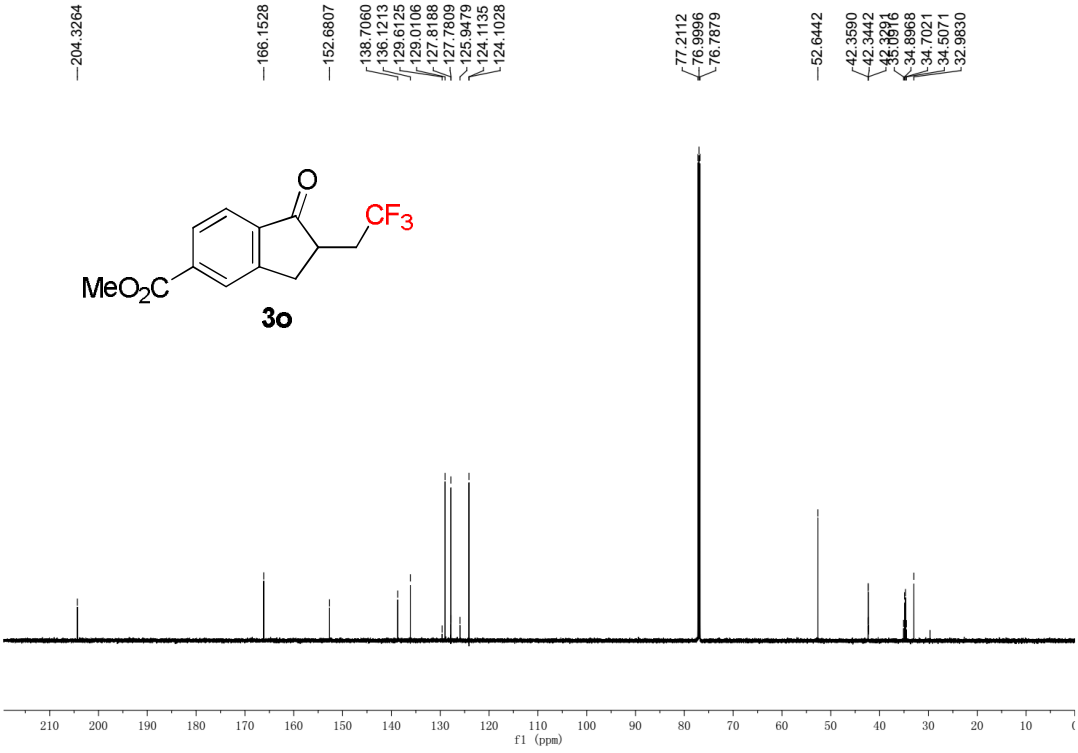

-64.7444
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

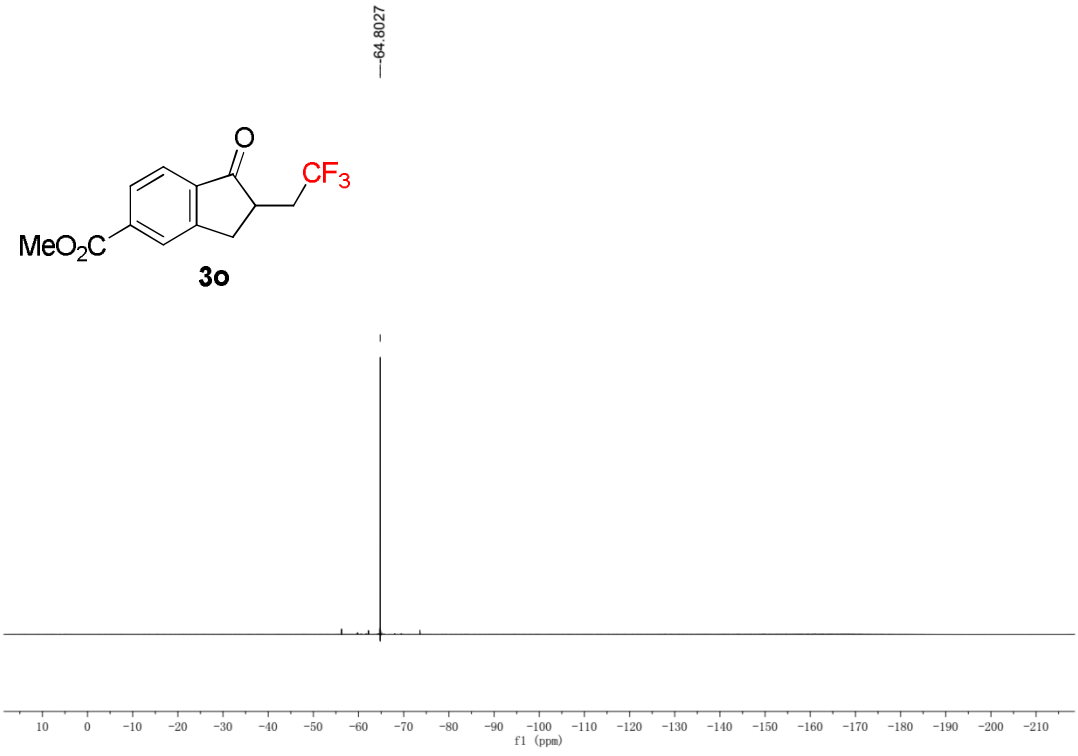

8.1663
8.0751
8.0619
7.8399
7.8266
3.9722
3.5758
3.5603
3.5472
3.0276
3.0124
2.9936
2.1838
2.1754
2.1672
2.1646
2.1585
2.1478
2.1416
2.1390
2.1309
2.1222
2.1062


O
CF3
MeO2C

3o


1.00
1.03
1.01
3.01
1.11
3.16
1.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


204.3264
166.1528
152.6807
138.7060
136.1213
129.6125
129.0106
127.8188
127.7809
125.9479
124.1135
124.1028
77.2112
76.9996
76.7879
52.6442
42.3590
42.3442
34.8968
34.7021
34.5071
32.9830
O
CF3
MeO2C
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


64.8027
O
CF3
MeO2C
3o
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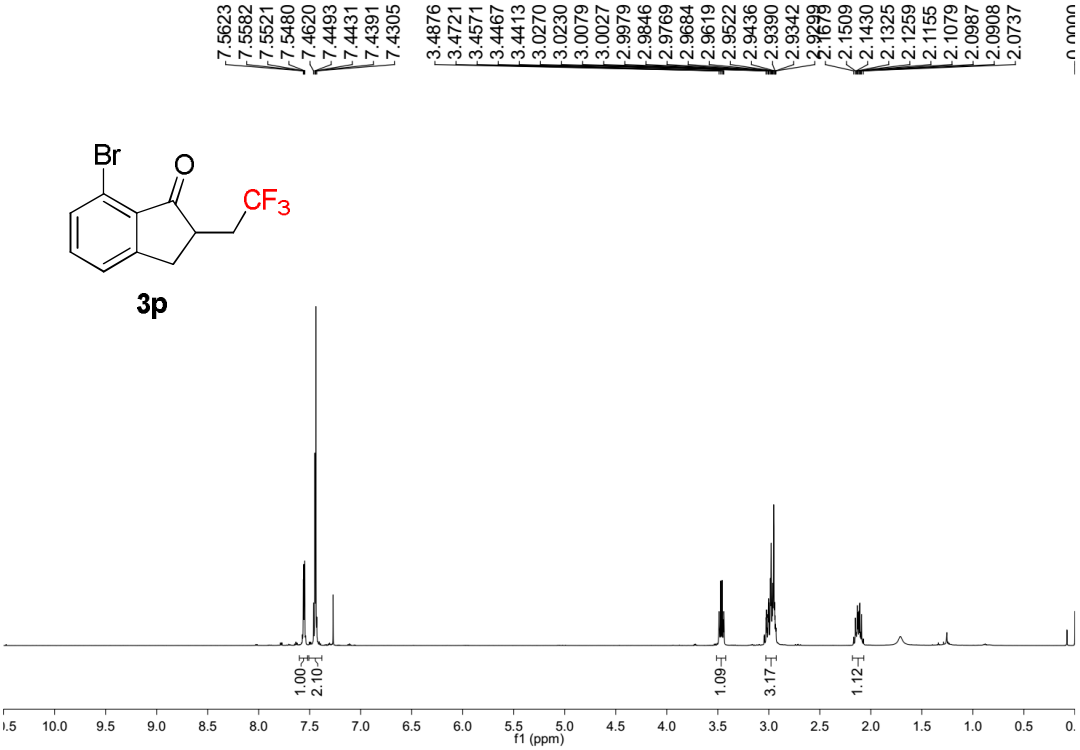
f1 (ppm)


7.5623
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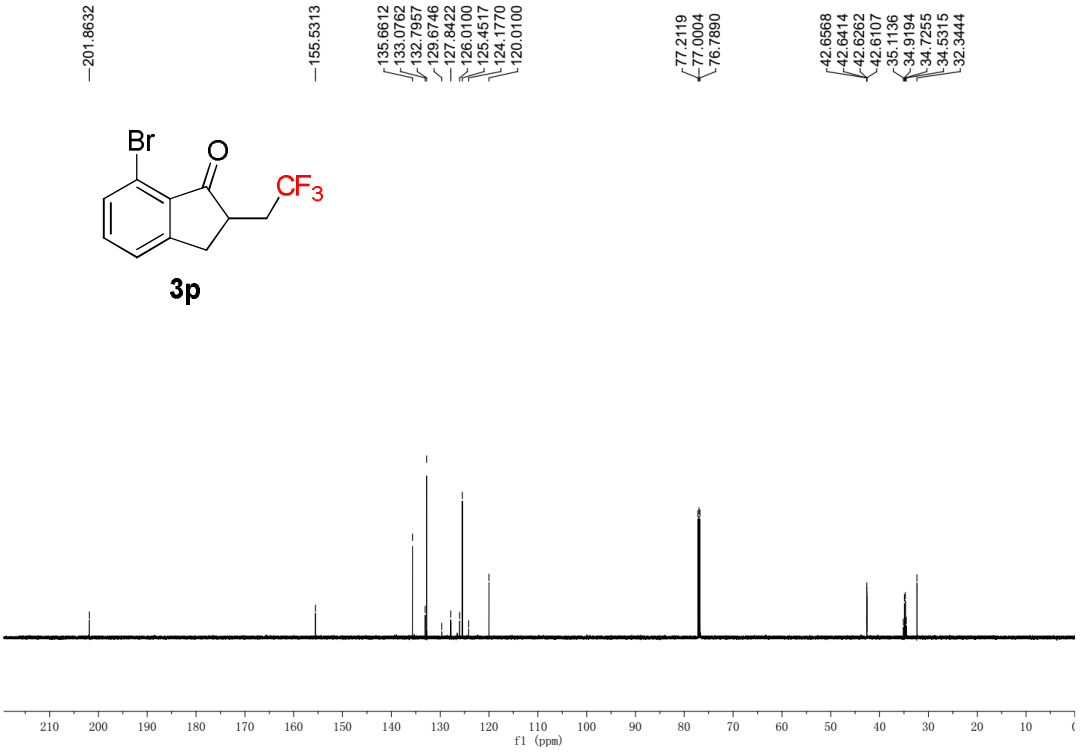
7.5521
7.5480
7.4620
7.4493
7.4431
7.4391
7.4305
3.4876
3.4721
3.4571
3.4467
3.4413
3.0270
3.0230
3.0079
3.0027
2.9979
2.9846
2.9769
2.9684
2.9619
2.9522
2.9436
2.9390
2.9342
2.1509
2.1430
2.1325
2.1259
2.1155
2.1079
2.0987
2.0908
2.0737
Br
O
CF3
3p
1.00
2.10
1.09
3.17
1.12
f1 (ppm)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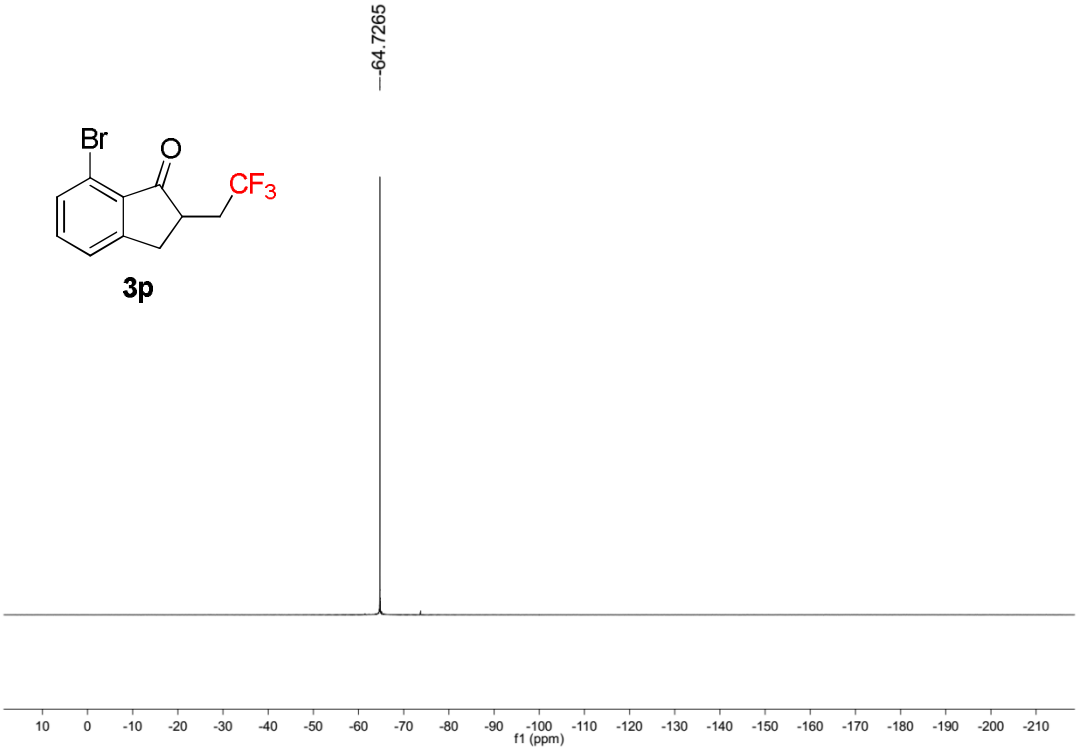
135.6612
133.0762
132.7957
129.6746
127.8422
126.0100
125.4517
124.1770
120.0100
77.2119
77.0004
76.7890
42.6568
42.6414
42.6262
42.6107
35.1136
34.9194
34.7255
34.5315
32.3444
Br
O
CF3
3p
f1 (ppm)


-64.7265
Br
O
CF3
3p
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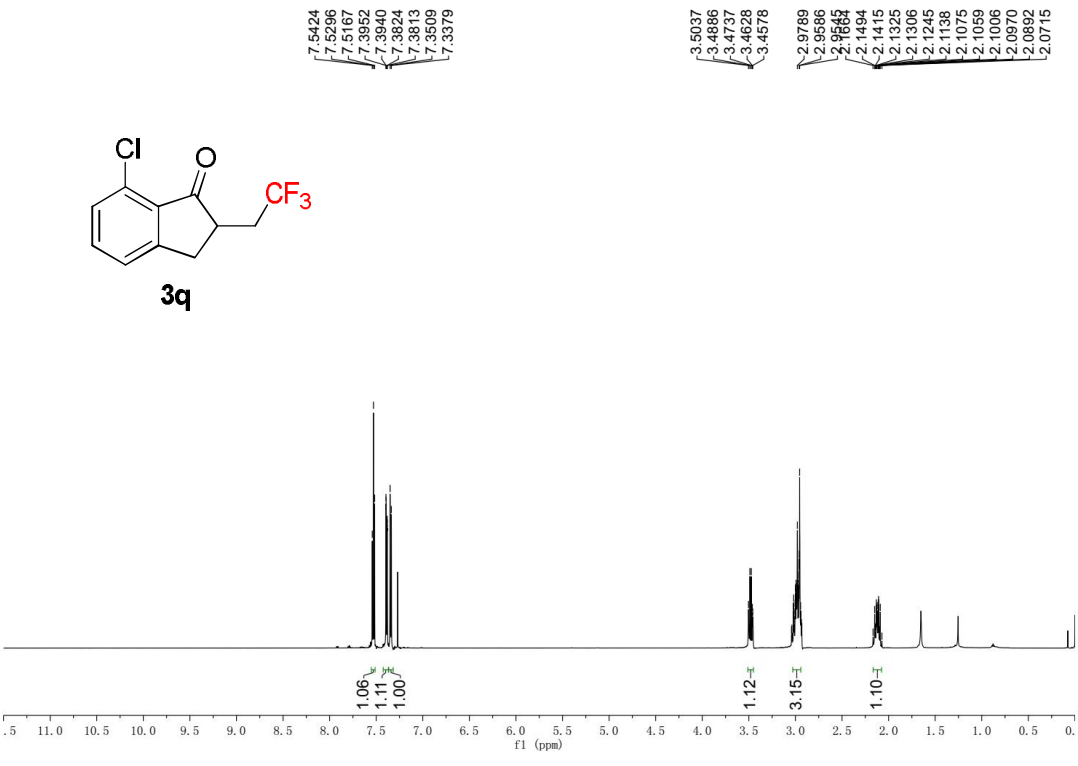
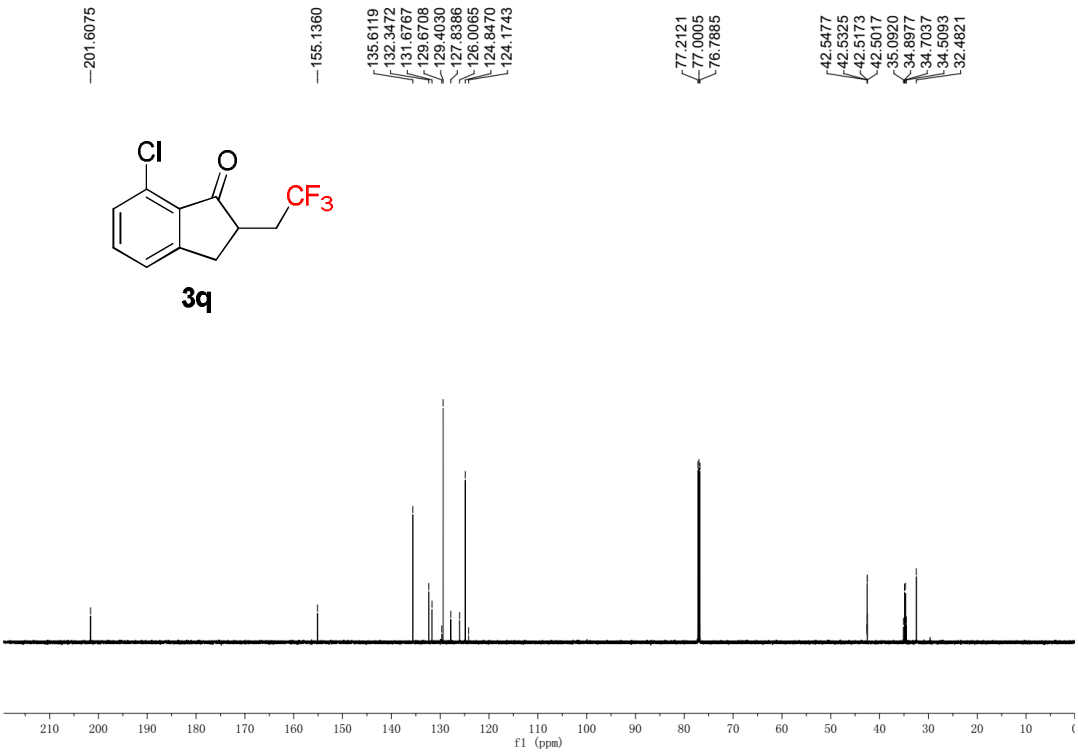
f1 (ppm)


7.5424
7.5296
7.5167
7.3952
7.3940
7.3824
7.3813
7.3509
7.3379
3.5037
3.4886
3.4737
3.4628
3.4578
2.9789
2.9586
2.1494
2.1415
2.1325
2.1306
2.1245
2.1138
2.1075
2.1059
2.1006
2.0970
2.0892
2.0715
Cl
O
CF3
3q
1.06
1.11
1.00
1.12
3.15
1.10
f1 (ppm)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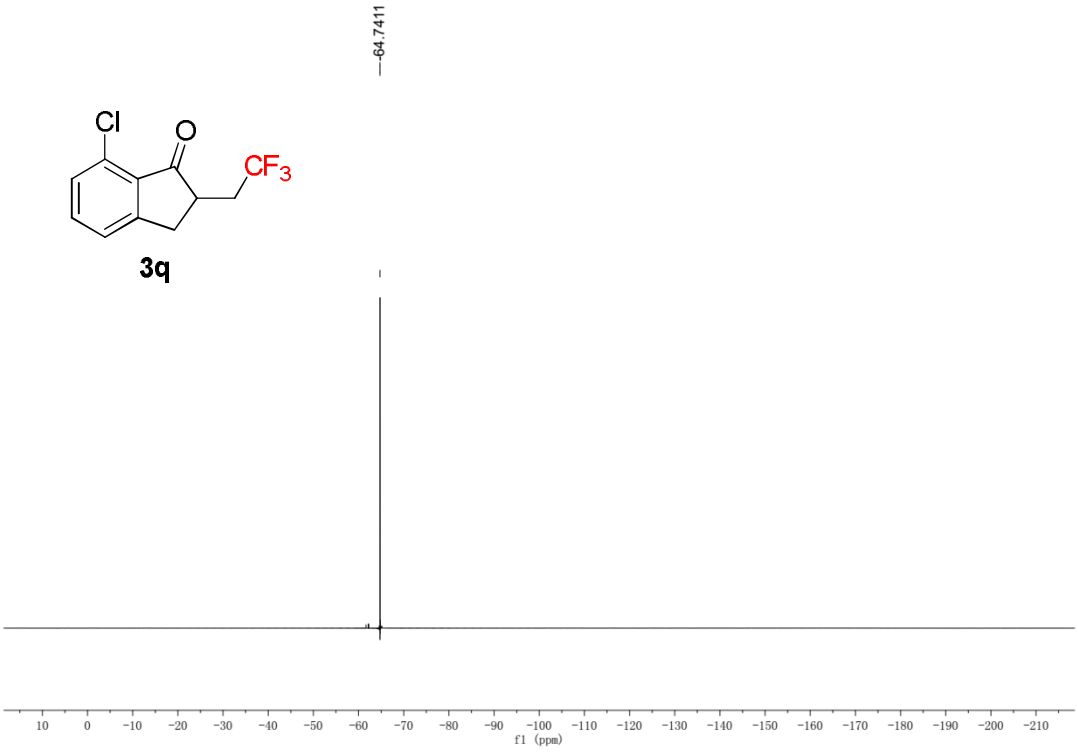
132.3472
131.6767
129.6708
129.4030
127.8386
126.0065
124.8470
124.1743
77.2121
77.0005
76.7885
42.5477
42.5325
42.5173
42.5017
35.0920
34.8977
34.7037
34.5093
32.4821
Cl
O
CF3
3q
f1 (ppm)


64.7411
Cl
O
CF3
3q
f1 (ppm)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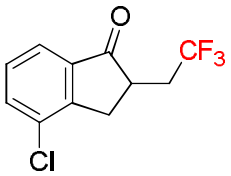
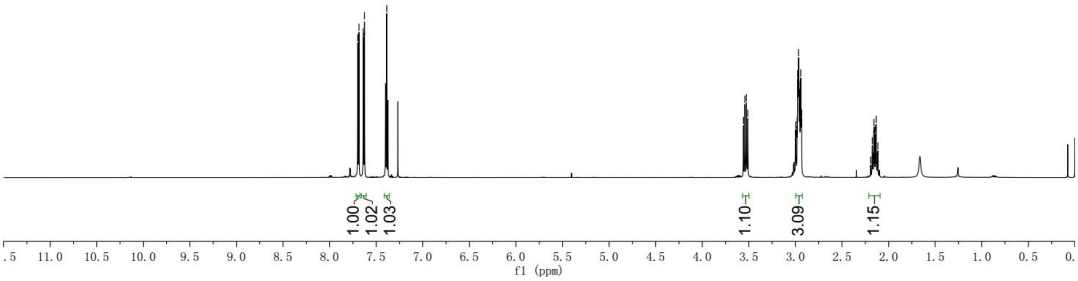
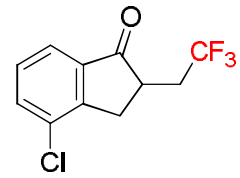
7.6380
7.6263
7.6250
7.3871
3.5579
3.5428
3.5264
3.5112
2.9759
2.9671
2.1746
2.1673
2.1591
2.1571
2.1505
2.1403
2.1333
2.1236
2.1147


O
CF3
Cl

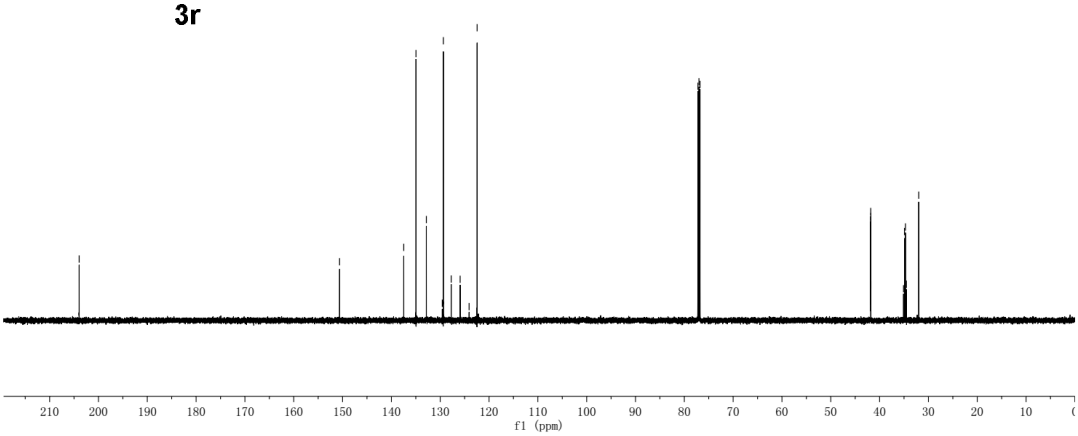
3r


1.00
1.02
1.03
1.10
3.09
1.15
f1 (ppm)


203.9505
150.6116
137.4675
134.9608
132.8421
129.5812
129.3542
127.7488
125.9160
124.0829
122.4415
77.2119
77.0003
76.7885
41.8308
41.8159
41.8009
41.7848
35.0994
34.9038
34.7092
34.5135
31.9853

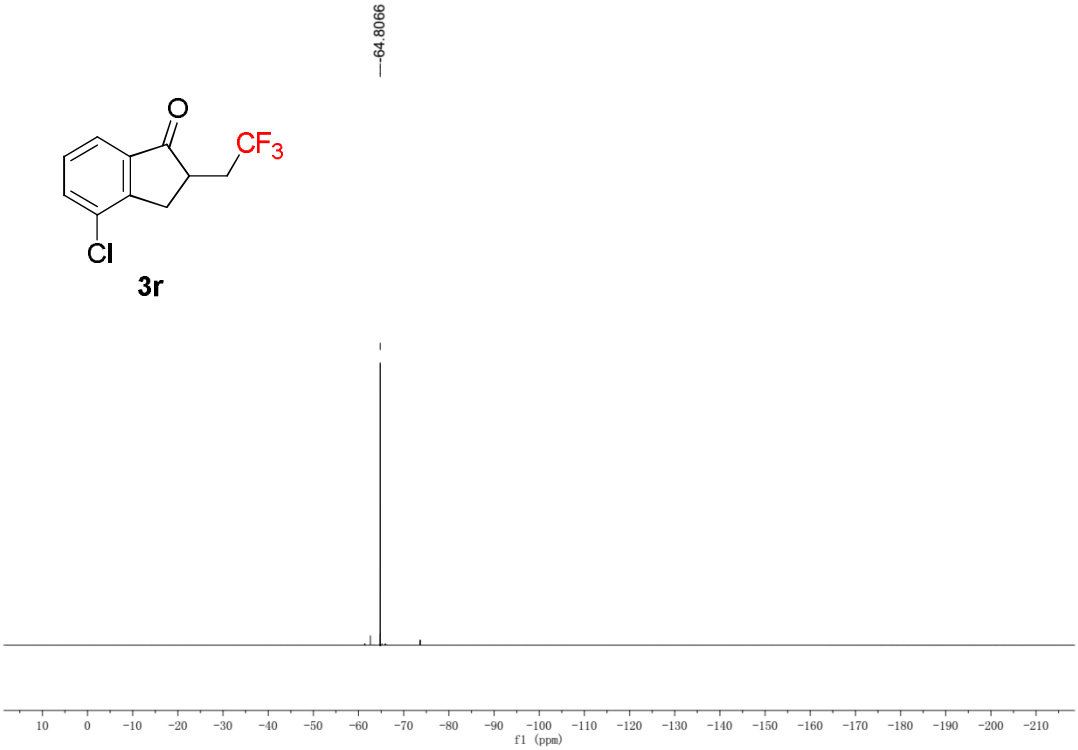

O
CF3
Cl

3r

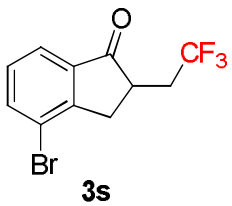

f1 (ppm)

O
CF3
Cl

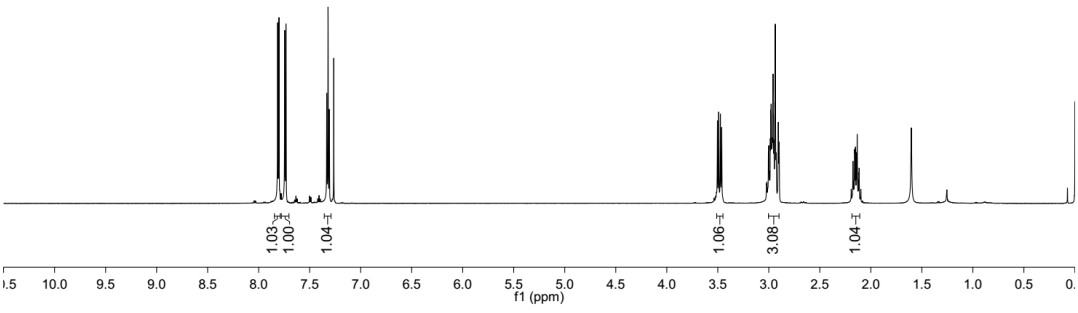
3r

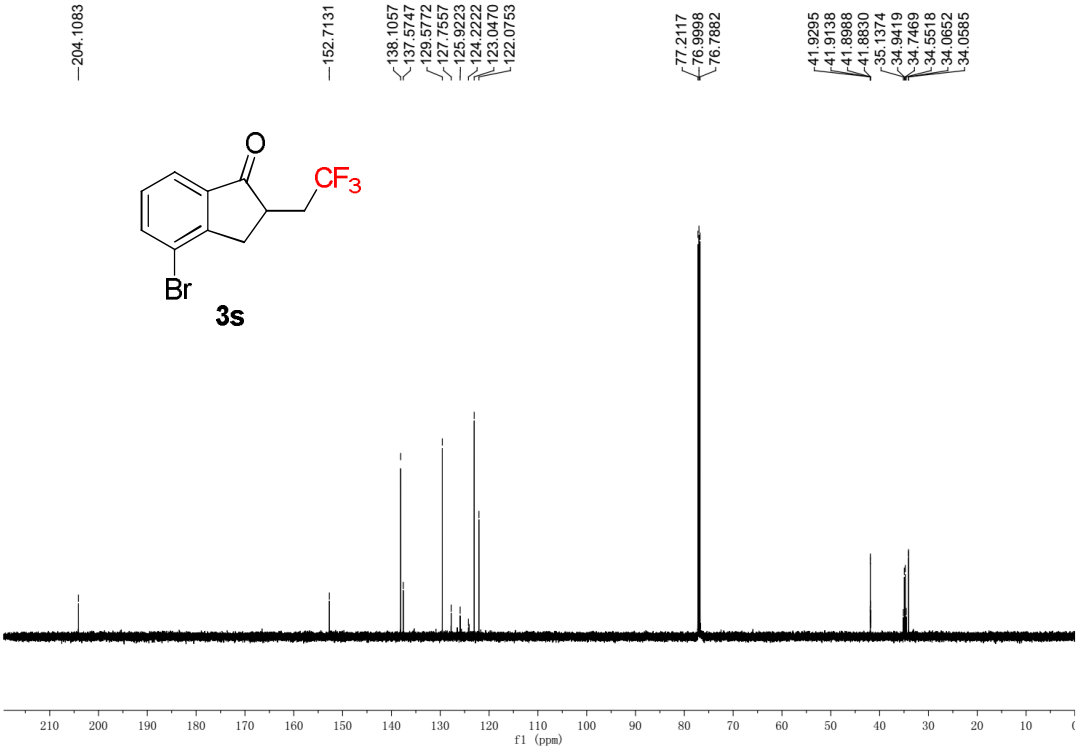

-64.8066
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

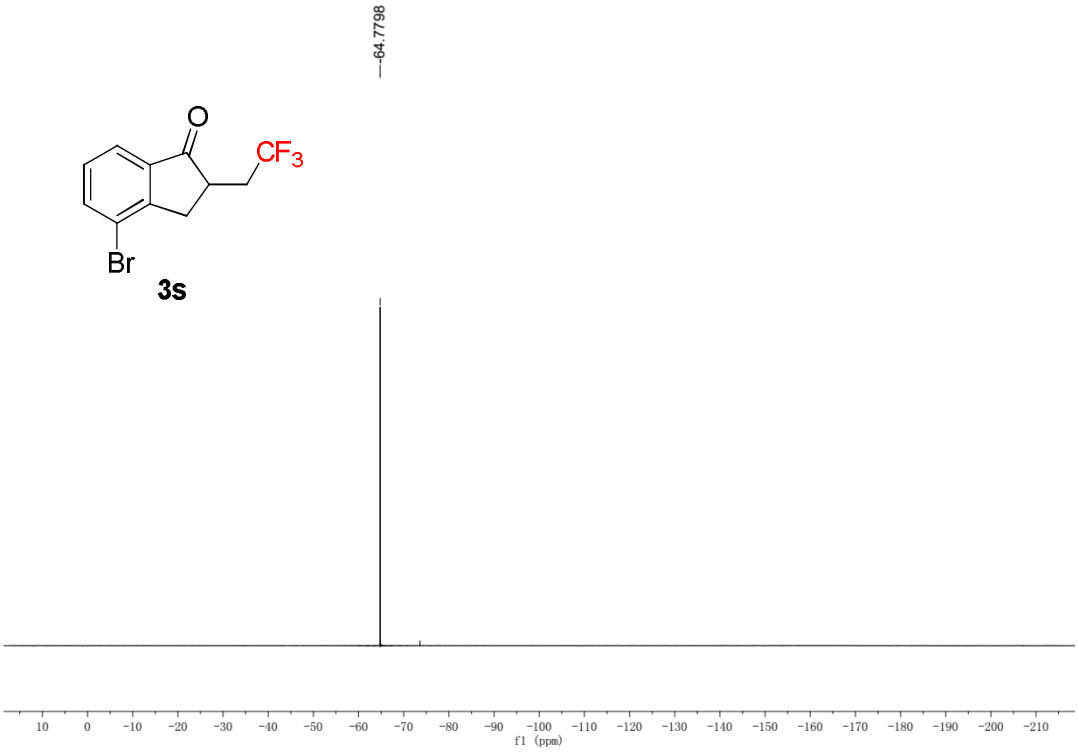

7.8136
7.8008
7.7447
7.7322
7.3327
7.3199
7.3071
3.5033
3.4911
3.4747
3.4621
2.9581
2.9407
2.9366
2.1922
2.1750
2.1673
2.1592
2.1569
2.1505
2.1403
2.1336
2.1235
2.1170
2.1145

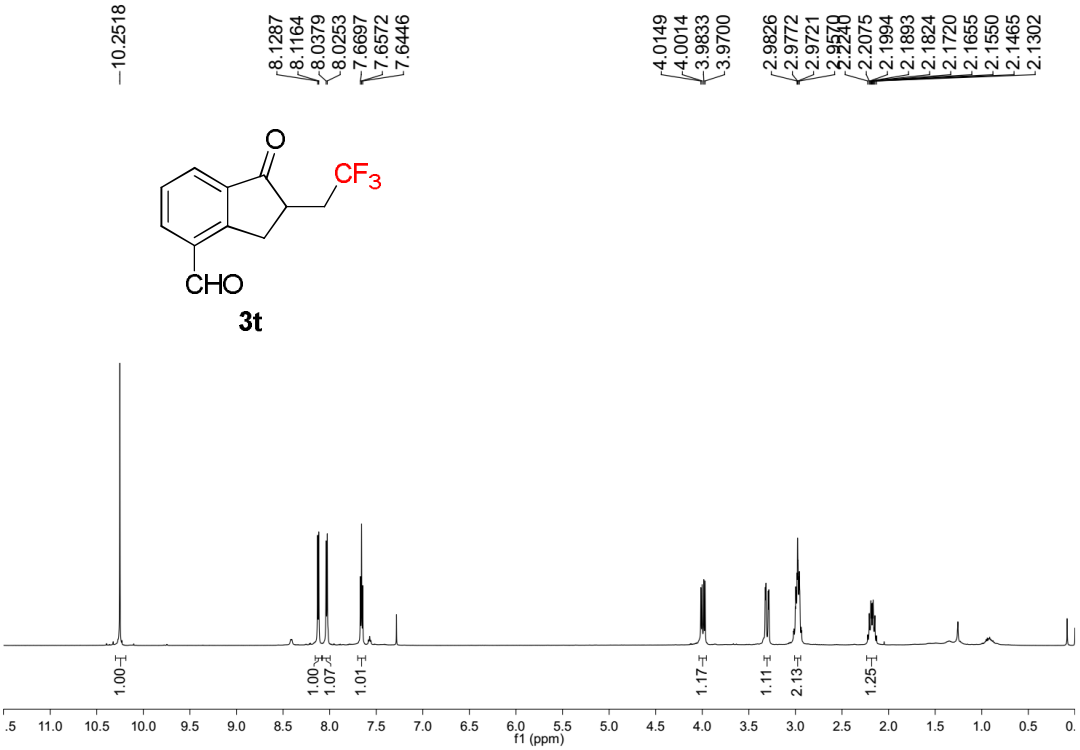

O
CF3
Br

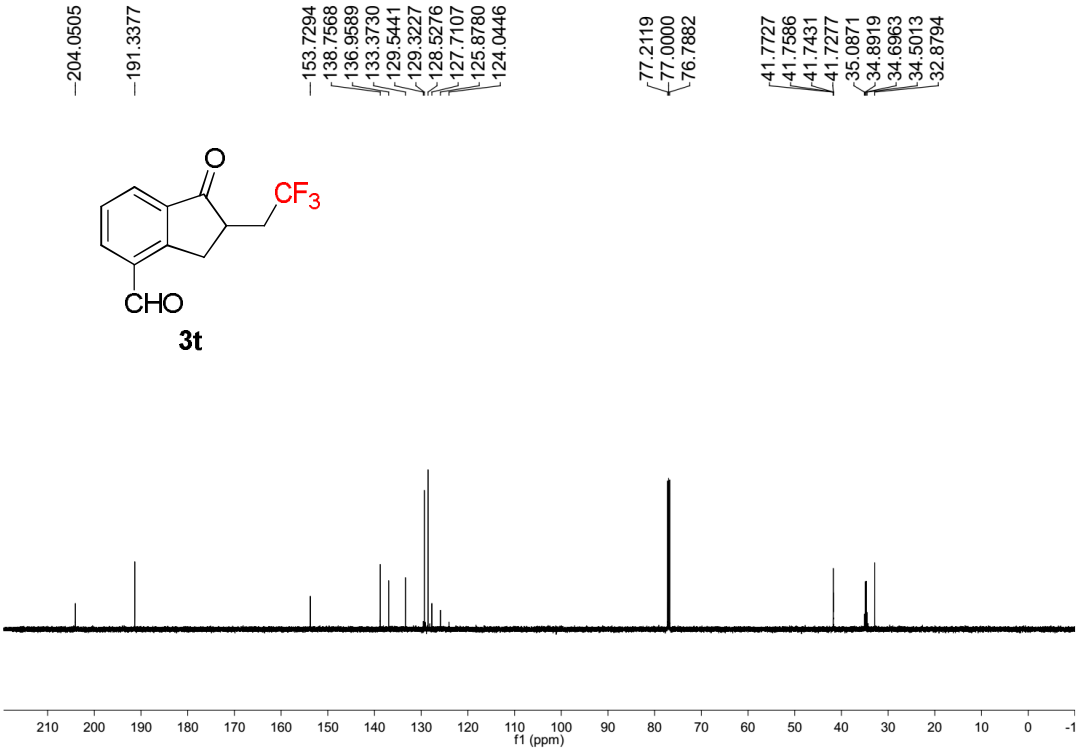
3s


1.03
1.00
1.04
1.06
3.08
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


204.1083
152.7131
138.1057
137.5747
129.5772
127.7557
125.9223
124.2222
123.0470
122.0753
77.2117
76.9998
76.7882
41.9295
41.9138
41.8988
41.8830
35.1374
34.9419
34.7469
34.5518
34.0652
34.0585
O
CF3
Br
3s
f1 (ppm)


64.7798
O
CF3
Br
3s
f1 (ppm)


10.2518
8.1287
8.1164
8.0379
8.0253
7.6697
7.6572
7.6446
4.0149
4.0014
3.9833
3.9700
2.9826
2.9772
2.9721
2.2075
2.1994
2.1893
2.1824
2.1720
2.1655
2.1550
2.1465
2.1302
O
CF3
CHO
3t
1.00
1.07
1.01
1.17
1.11
2.13
1.25
f1 (ppm)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153.7294
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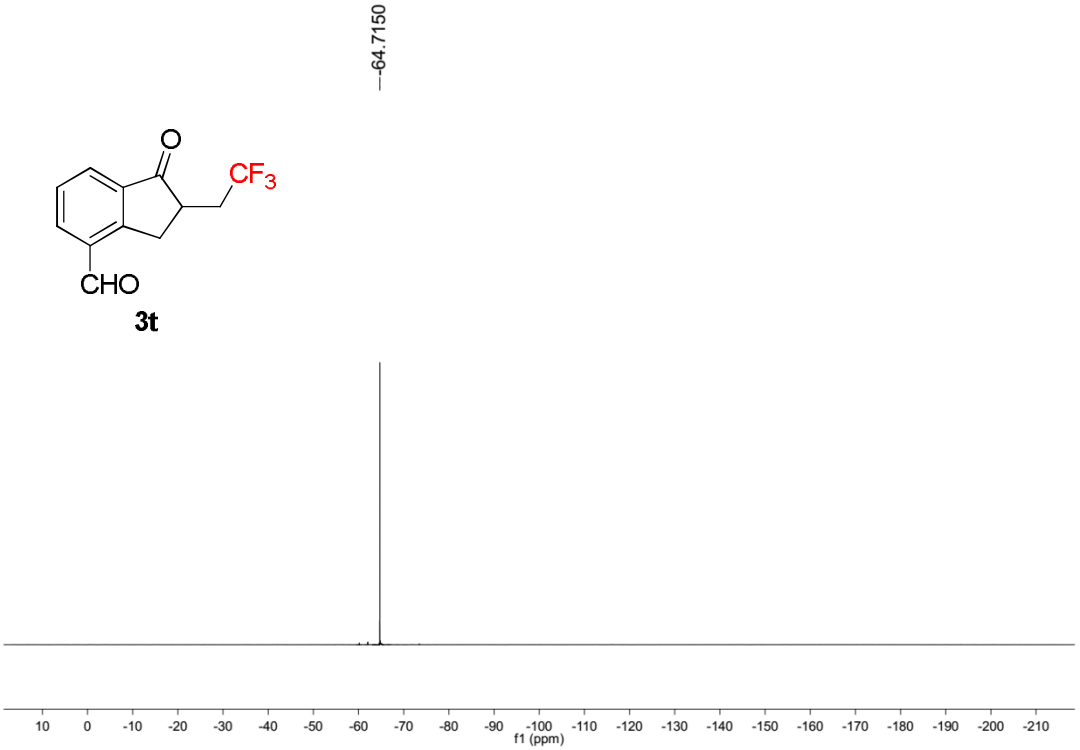
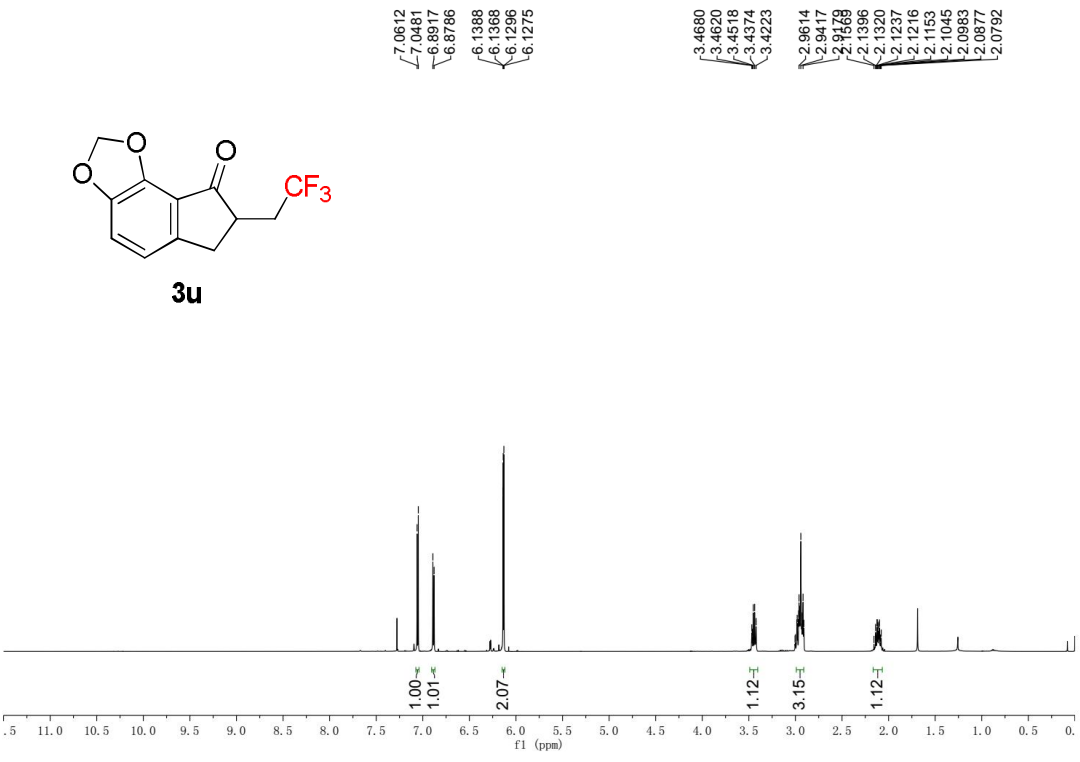
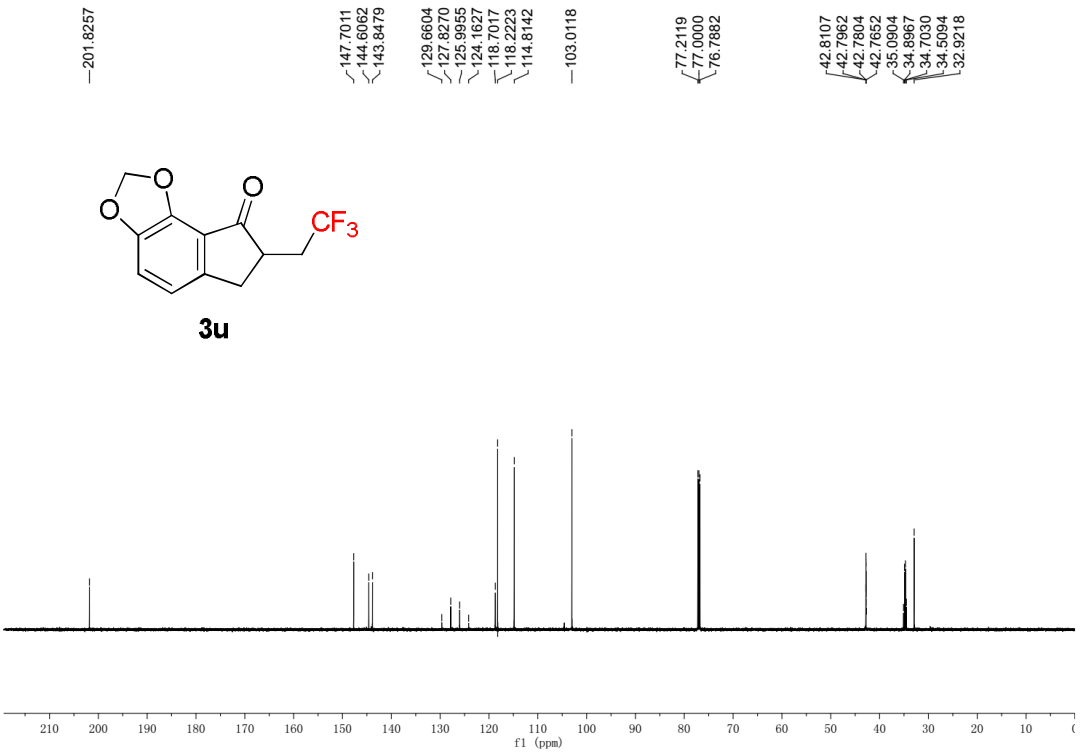
133.3730
129.5441
129.3227
128.5276
127.7107
125.8780
124.0446
77.2119
77.0000
76.7882
41.7727
41.7586
41.7431
41.7277
35.0871
34.8919
34.6963
34.5013
32.8794
O
CF3
CHO
3t
f1 (ppm)


-64.7150
O
CF3
CHO
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3t


7.0612
7.0481
6.8917
6.8786
6.1388
6.1368
6.1296
6.1275
3.4680
3.4620
3.4518
3.4374
3.4223
2.9614
2.9417
2.1396
2.1320
2.1237
2.1216
2.1153
2.1045
2.0983
2.0877
2.0792
O
O
O
CF3
1.00
1.01
2.07
1.12
3.15
1.12
f1 (ppm)

3u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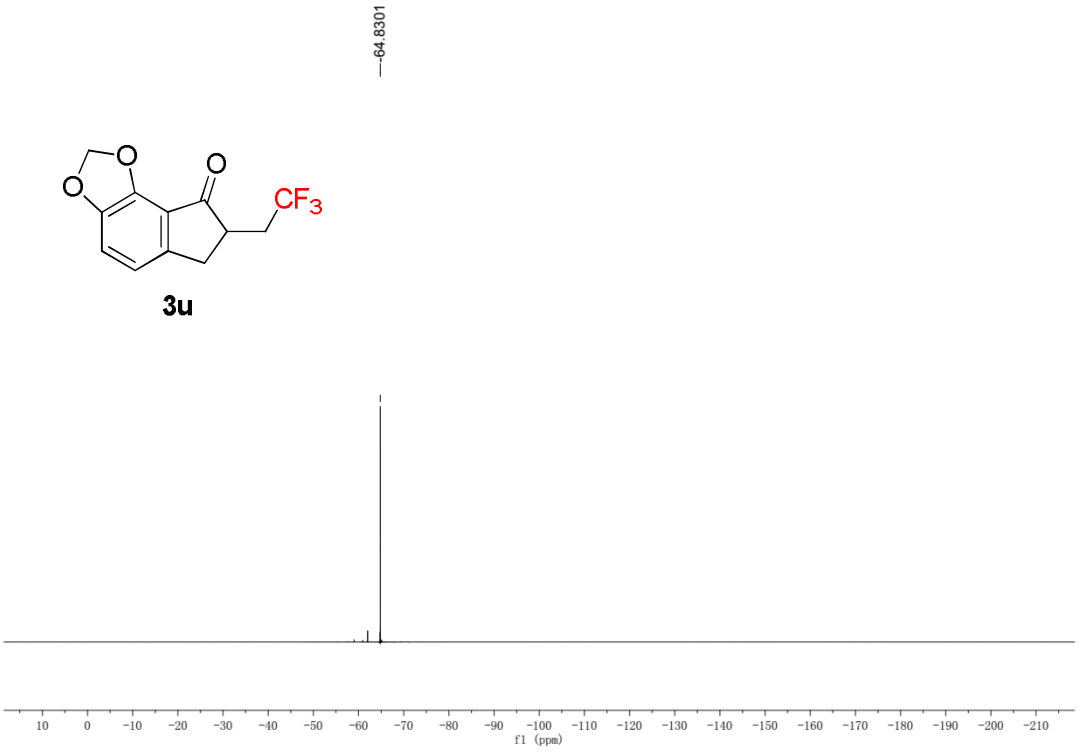
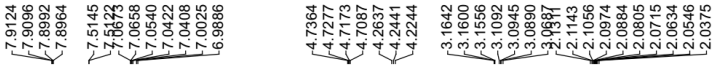
147.7011
144.6062
143.8479
129.6604
127.8270
125.9955
124.1627
118.7017
118.2223
114.8142
103.0118
77.2119
77.0000
76.7882
42.8107
42.7962
42.7804
42.7652
35.0904
34.8967
34.7030
34.5094
32.9218
O
O
O
CF3
3u
f1 (ppm)


64.8301
O
O
O
CF3
3u
f1 (ppm)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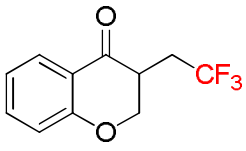
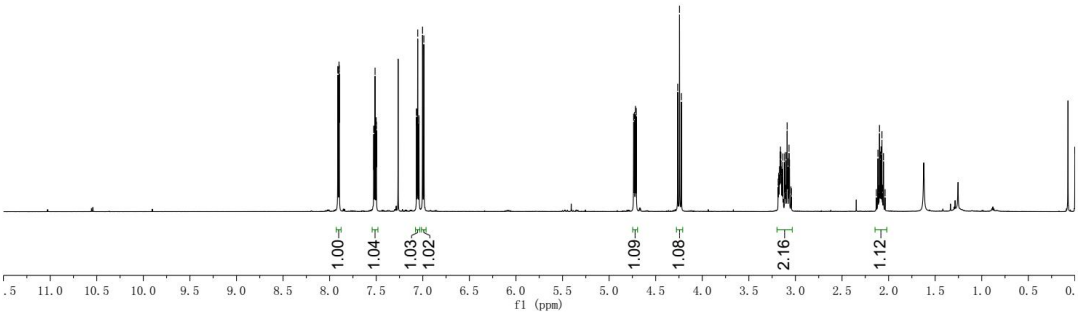
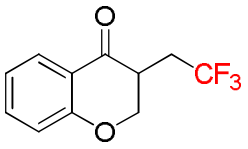
7.9096
7.8992
7.8964
7.5145
7.0658
7.0540
7.0422
7.0408
7.0025
6.9886
4.7364
4.7277
4.7173
4.7087
4.2637
4.2441
4.2244
3.1642
3.1600
3.1556
3.1092
3.0945
3.0890
2.1143
2.1056
2.0974
2.0884
2.0805
2.0715
2.0634
2.0546
2.0375


O
CF3
O

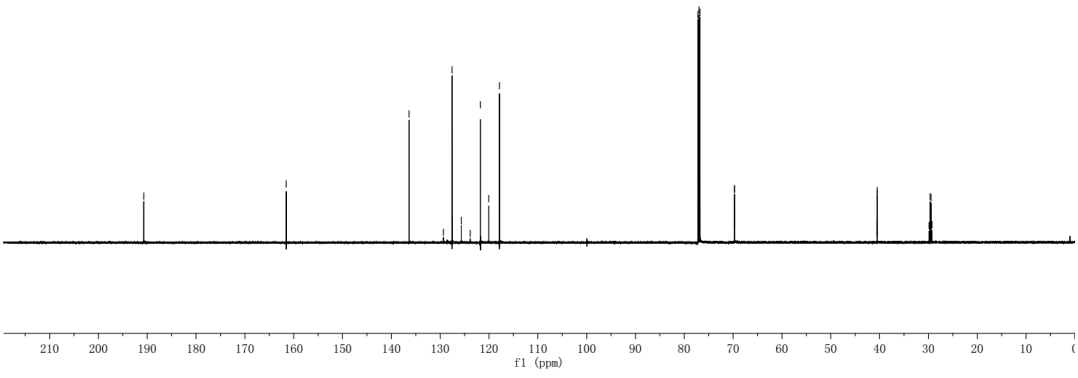
3v


1.00
1.04
1.03
1.02
1.09
1.08
2.16
1.12
f1 (ppm)

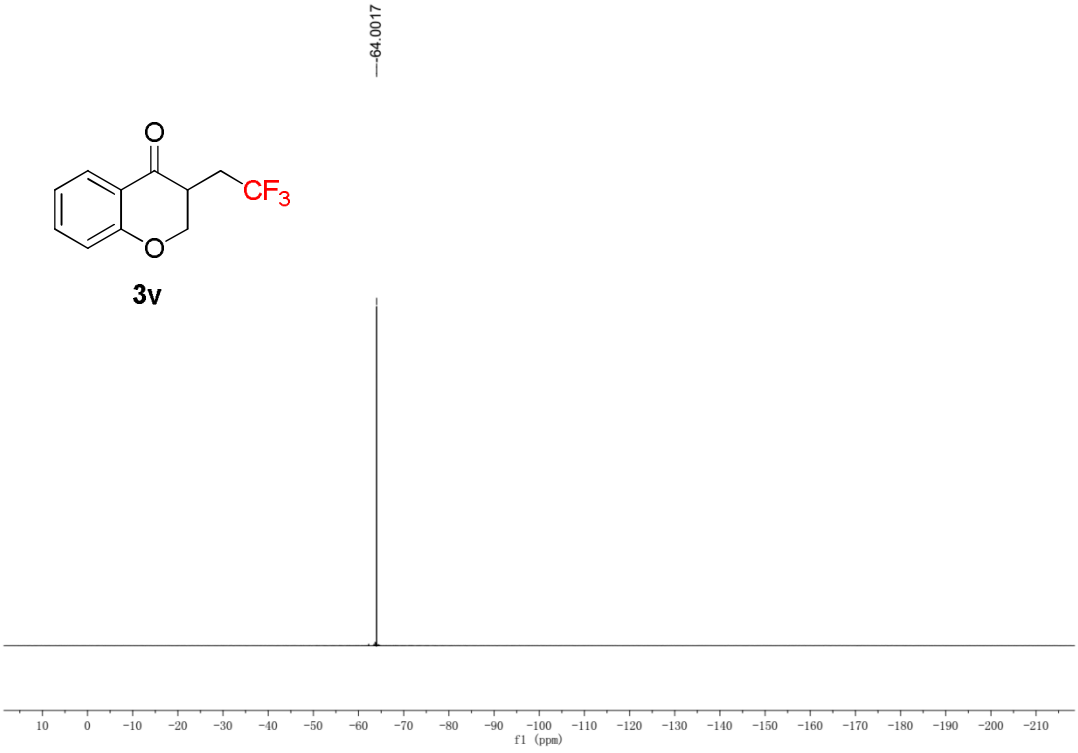

190.7050
161.5300
136.3719
129.3448
127.5628
127.5122
125.6812
123.8498
121.7750
120.0359
117.8647
77.2112
76.9996
76.7879
69.7473
69.7362
69.7248
69.7132
40.4964
40.4836
40.4699
40.4563
29.8627
29.6628
29.4629
29.2636

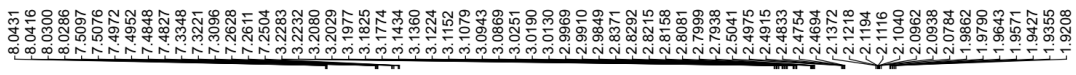

O
CF3
O

3v


f1 (ppm)

3v


-64.0017
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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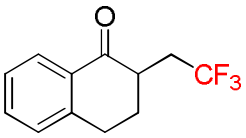
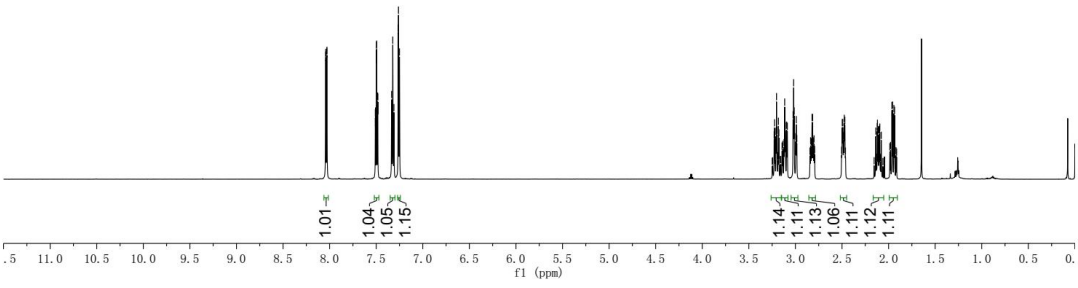
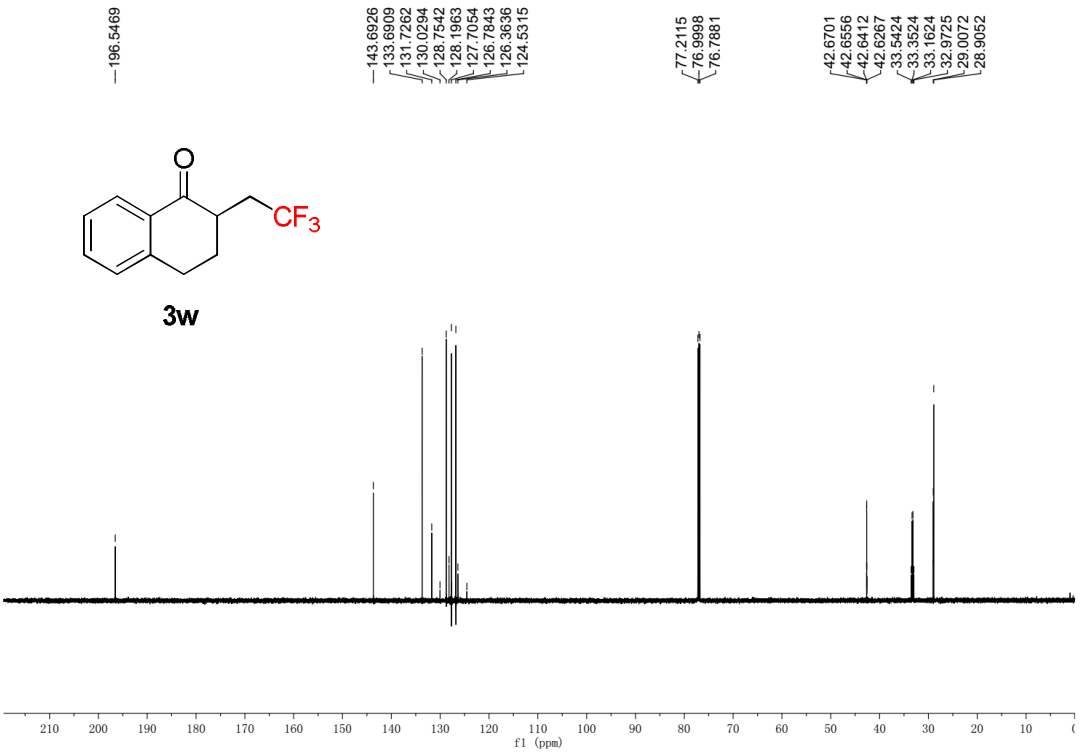
8.0416
8.0300
8.0286
7.5097
7.5076
7.4972
7.4952
7.4848
7.4827
7.3348
7.3221
7.3096
7.2628
7.2611
7.2504
3.2283
3.2232
3.2080
3.2029
3.1977
3.1825
3.1774
3.1434
3.1360
3.1224
3.1152
3.1079
3.0943
3.0869
3.0251
3.0190
3.0130
2.9969
2.9910
2.9849
2.8371
2.8292
2.8215
2.8158
2.8081
2.7999
2.7938
2.5041
2.4975
2.4915
2.4833
2.4754
2.4694
2.1372
2.1218
2.1194
2.1116
2.1040
2.0962
2.0938
2.0784
1.9862
1.9790
1.9643
1.9571
1.9427
1.9355
1.9208



3w


1.01
1.04
1.05
1.15
1.14
1.11
1.13
1.06
1.11
1.12
1.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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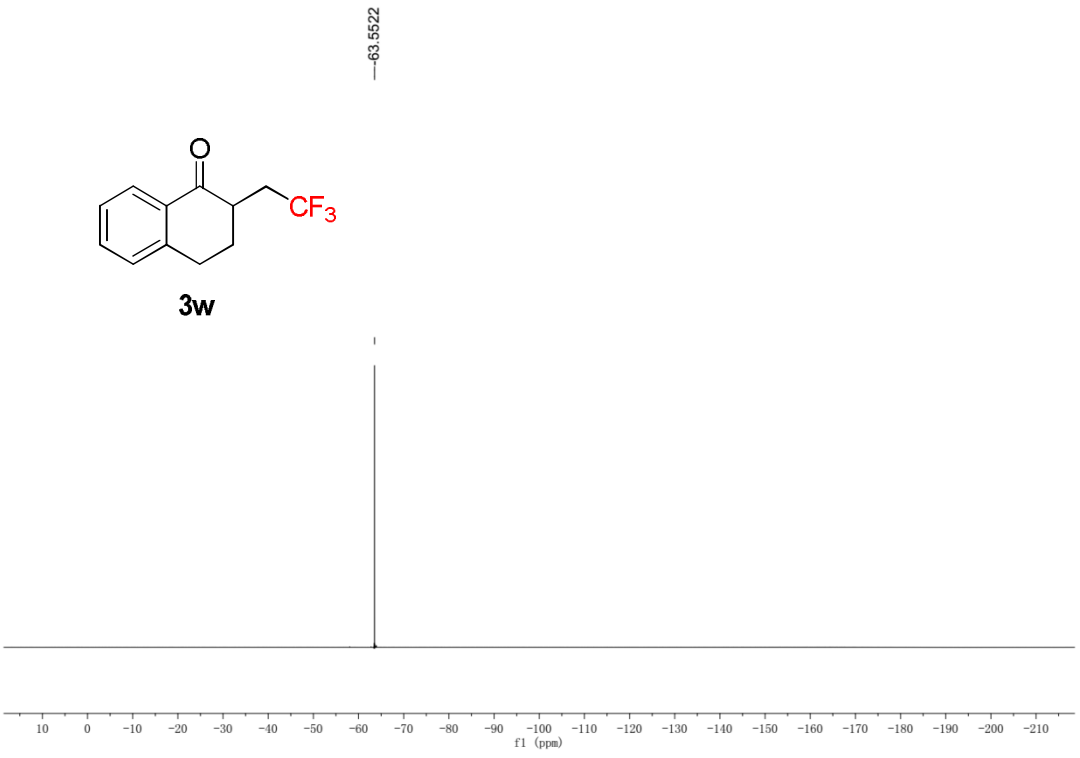
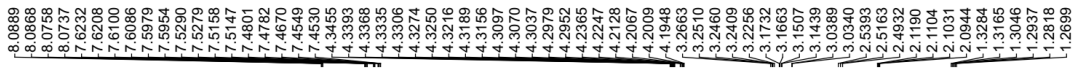
143.6926
133.6909
131.7262
130.0294
128.7542
128.1963
127.7054
126.7843
126.3636
124.5315
77.2115
76.9998
76.7881
42.6701
42.6556
42.6412
42.6267
33.5424
33.3524
33.1624
32.9725
29.0072
28.9052
O
CF3
3w
f1 (ppm)


63.5522
O
CF3
3w
f1 (ppm)


8.0889
8.0868
8.0758
8.0737
7.6232
7.6208
7.6100
7.6086
7.5979
7.5954
7.5290
7.5279
7.5158
7.5147
7.4801
7.4782
7.4670
7.4549
7.4530
4.3455
4.3393
4.3368
4.3335
4.3306
4.3274
4.3250
4.3216
4.3189
4.3156
4.3097
4.3070
4.3037
4.2979
4.2952
4.2365
4.2247
4.2128
4.2067
4.2009
4.1948
3.2663
3.2510
3.2460
3.2409
3.2256
3.1732
3.1663
3.1507
3.1439
3.0389
3.0340
2.5393
2.5163
2.4932
2.1190
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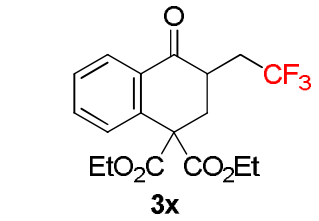
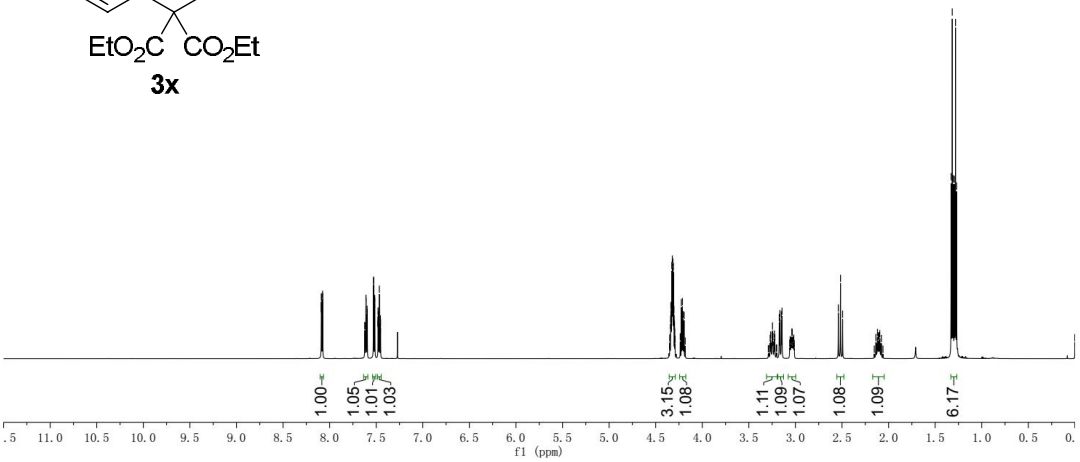
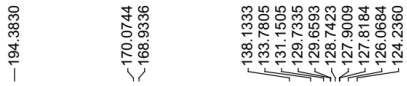
2.1031
2.0944
1.3284
1.3165
1.3046
1.2937
1.2818
1.2699


O
CF3
EtO2C
CO2Et

3x


1.00
1.05
1.01
1.03
3.15
1.08
1.11
1.09
1.07
1.08
1.09
6.17
f1 (ppm)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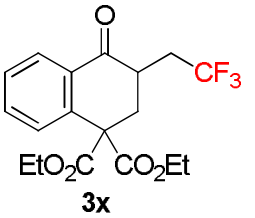
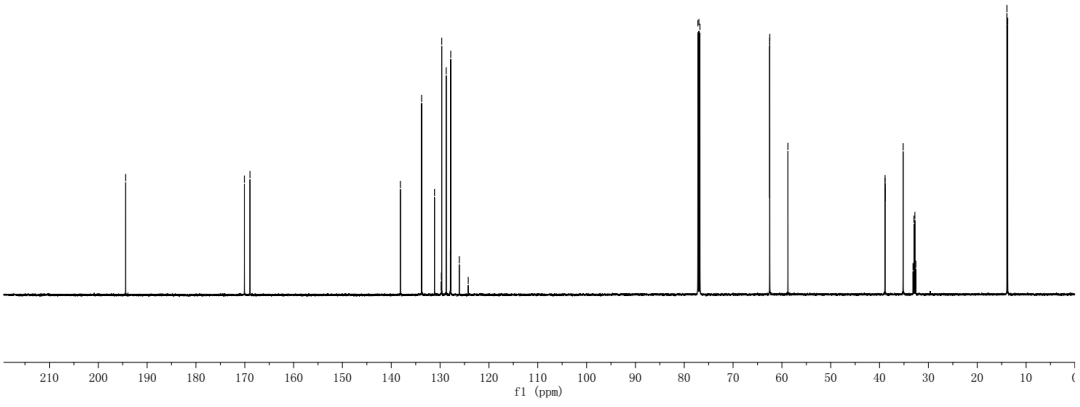
170.0744
168.9336
138.1333
133.7805
131.1505
129.7335
129.6593
128.7423
127.9009
127.8184
126.0684
124.2360
77.2120
77.0001
76.7880
62.5054
62.4805
58.7651
38.8844
38.8713
35.1748
33.1489
32.9566
32.7641
32.5716
13.9144
13.7574

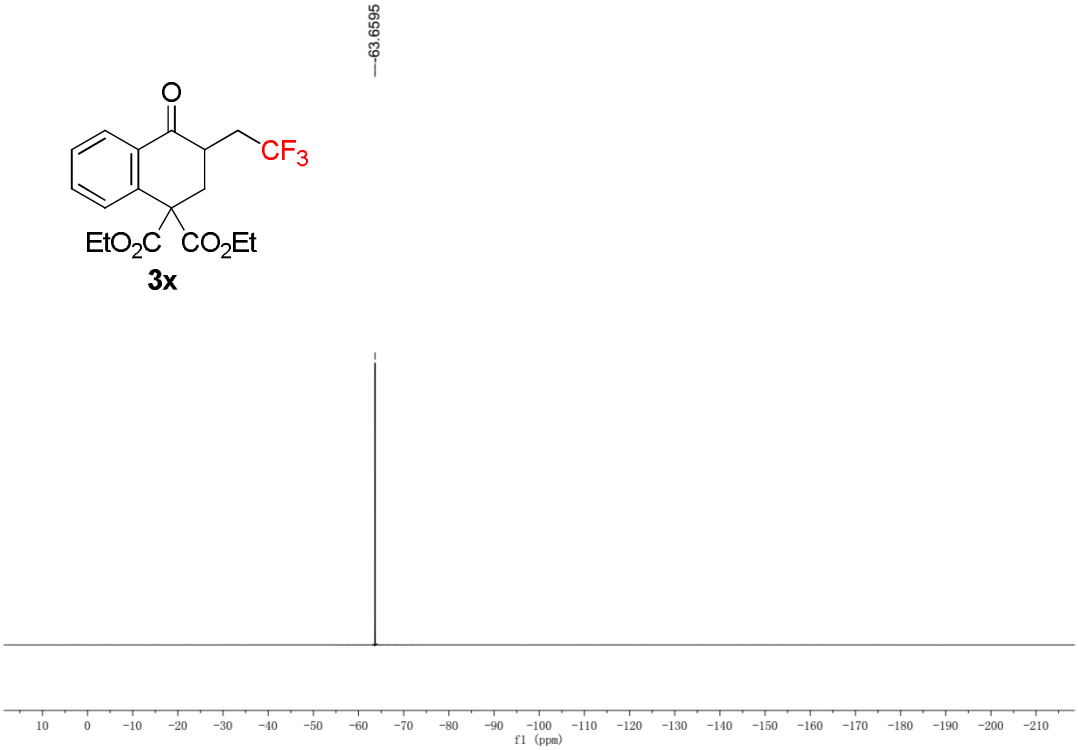

O
CF3
EtO2C
CO2Et

3x


f1 (ppm)

O
CF3
EtO2C
CO2Et

3x


-63.6595
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.9677
7.9649
7.9549
7.9518
7.9423
7.9417
7.6225
7.6197
7.6103
7.6082
7.6058
7.5935
7.5835
7.5696
7.2952
7.2939
7.2816
7.2700
7.2683
7.2659
7.2579
7.2444
4.7761
4.7678
4.7521
4.7437
3.7104
3.6872
3.6638
3.0059
2.9854
2.9648
2.4658
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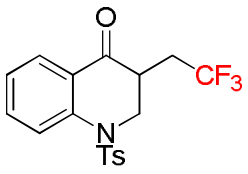
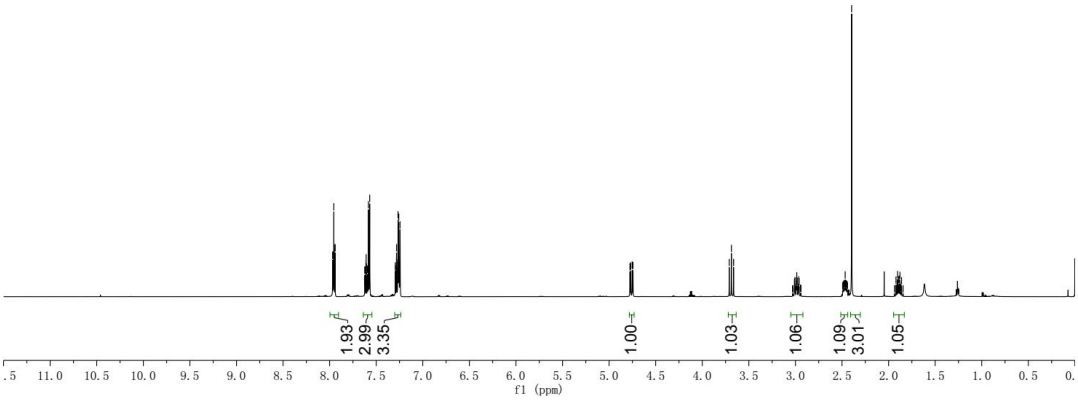
1.8868
1.8776
1.8699
1.8608
1.8439


O
CF3
N
Ts

3y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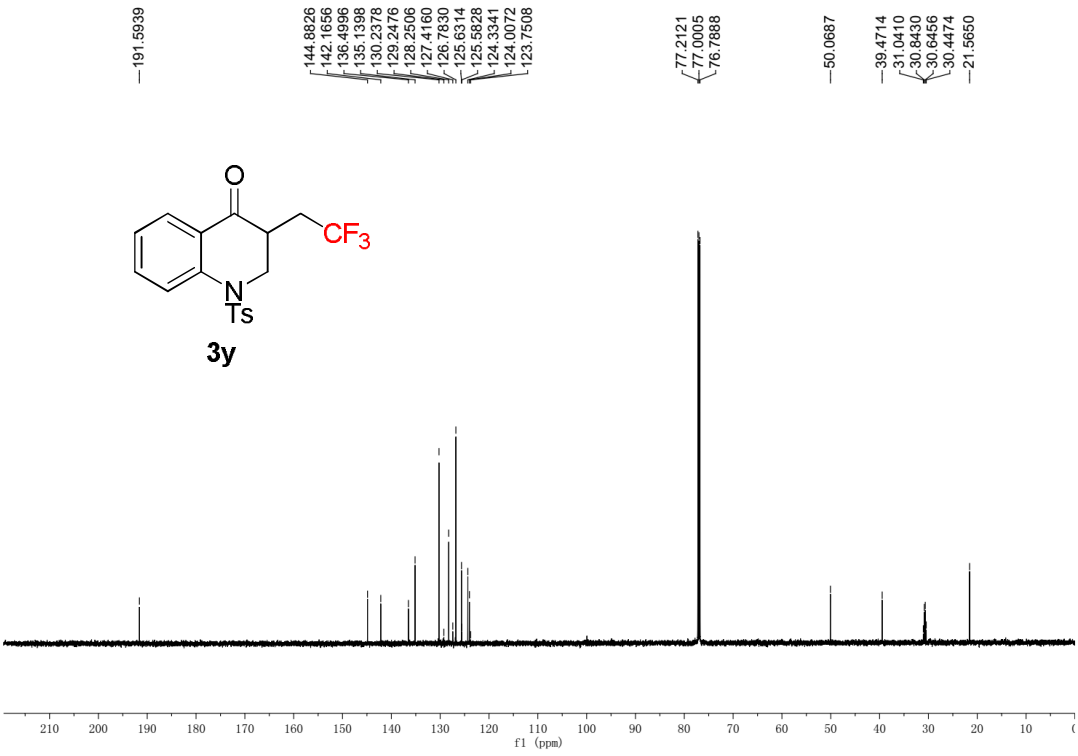
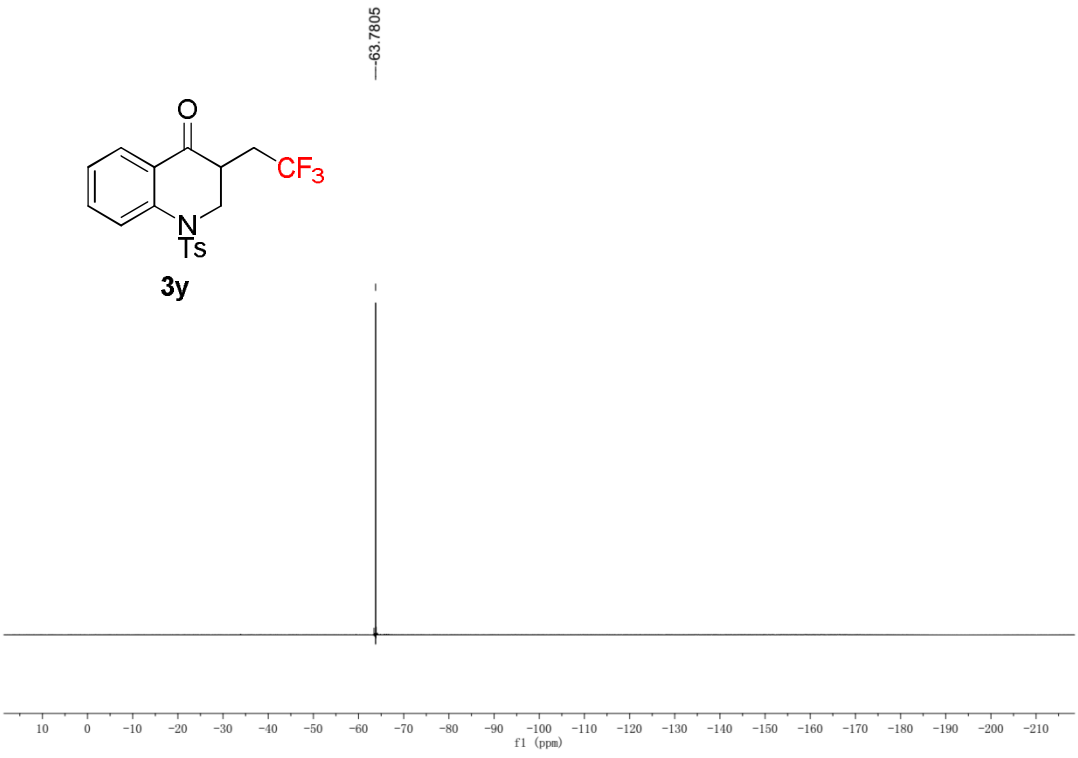
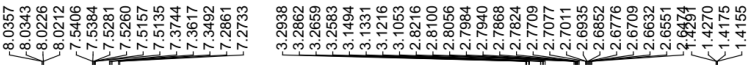
2.99
3.35
1.00
1.03
1.06
1.09
3.01
1.05
f1 (ppm)


191.5939
144.8826
142.1656
136.4996
135.1398
130.2378
129.2476
128.2506
127.4160
126.7830
125.6314
125.5828
124.3341
124.0072
123.7508
77.2121
77.0005
76.7888
50.0687
39.4714
31.0410
30.8430
30.6456
30.4474
21.5650
O
CF3
N
Ts
3y
f1 (ppm)


63.7805
O
CF3
N
Ts
3y
f1 (ppm)


8.0357
8.0343
8.0226
8.0212
7.5406
7.5384
7.5281
7.5260
7.5157
7.5135
7.3744
7.3617
7.3492
7.2861
7.2733
3.2938
3.2862
3.2659
3.2583
3.1494
3.1331
3.1216
3.1053
2.8216
2.8100
2.8056
2.7984
2.7940
2.7868
2.7824
2.7709
2.7077
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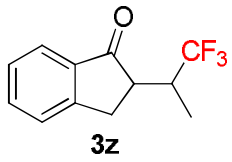
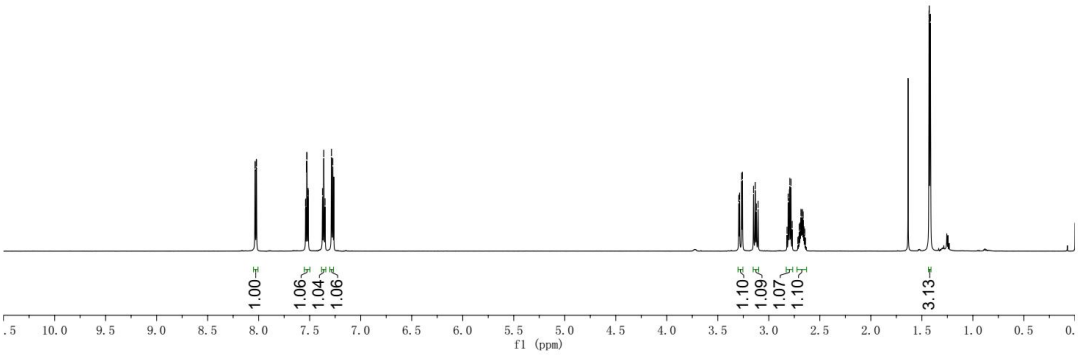
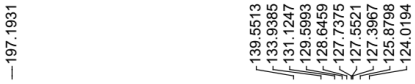
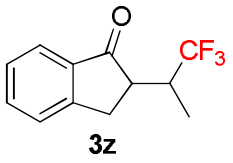
2.6632
2.6551
1.4270
1.4175
1.4155


O
CF3

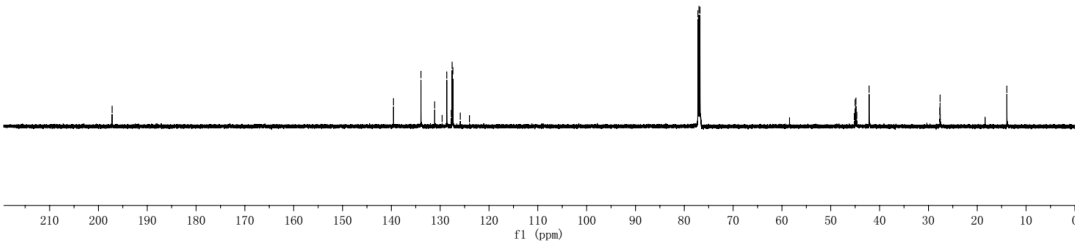
3z


1.00
1.06
1.04
1.06
1.10
1.09
1.07
1.10
3.13
f1 (ppm)


197.1931
139.5513
133.9385
131.1247
129.5993
128.6459
127.7375
127.5521
127.3967
125.8798
124.0194
77.2118
77.0003
76.7882
45.1872
45.0150
44.8412
44.6682
42.1446
27.6067
13.9306

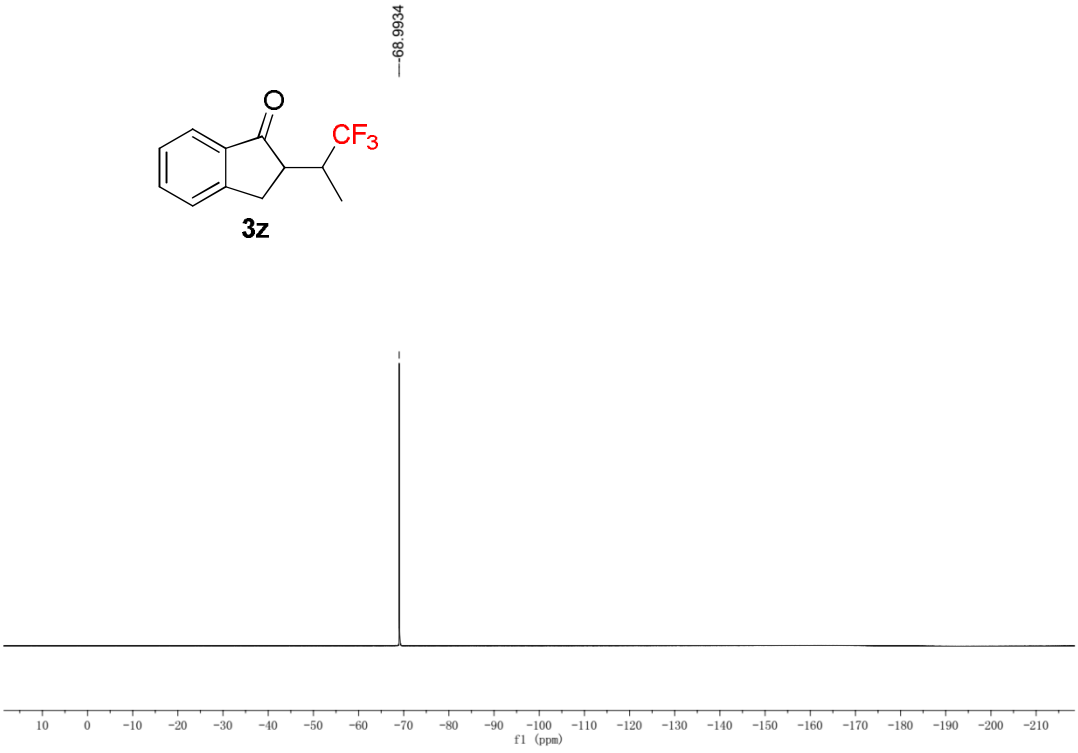

O
CF3

3z


f1 (ppm)

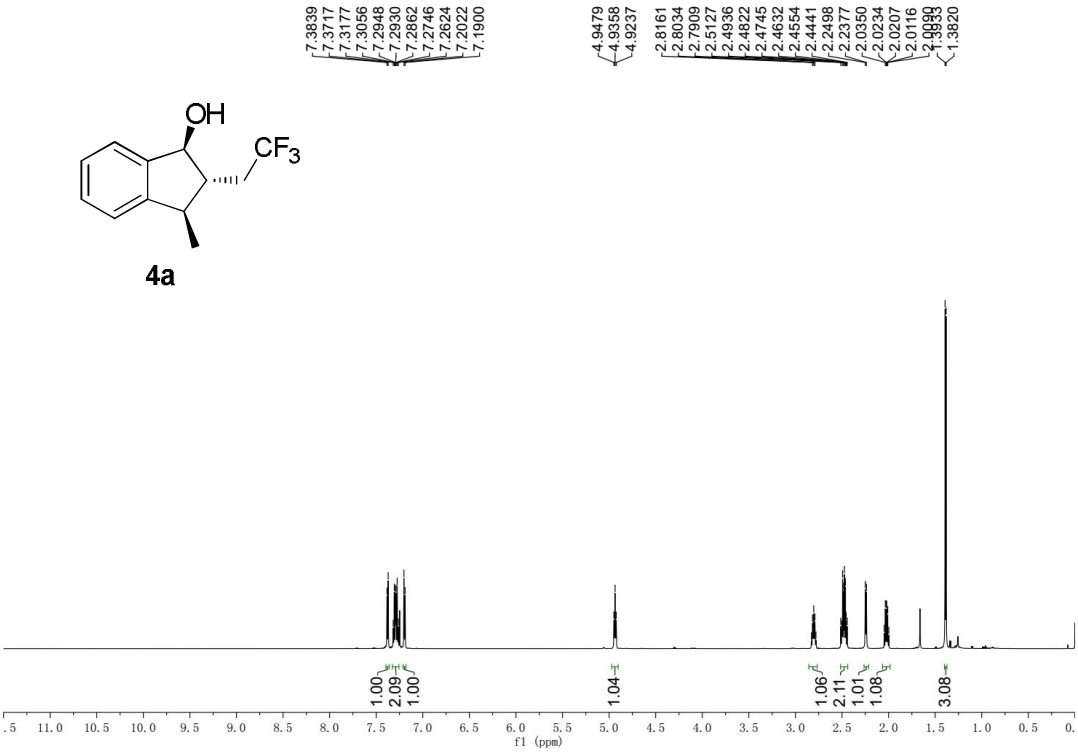
O
CF3

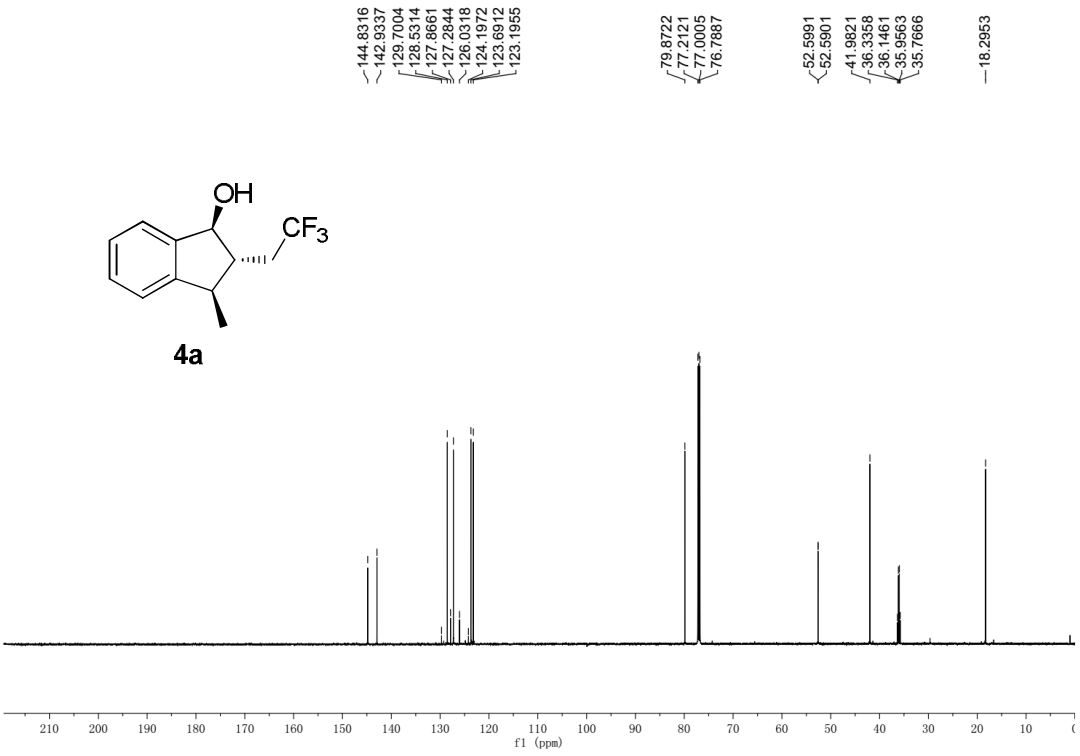
3z

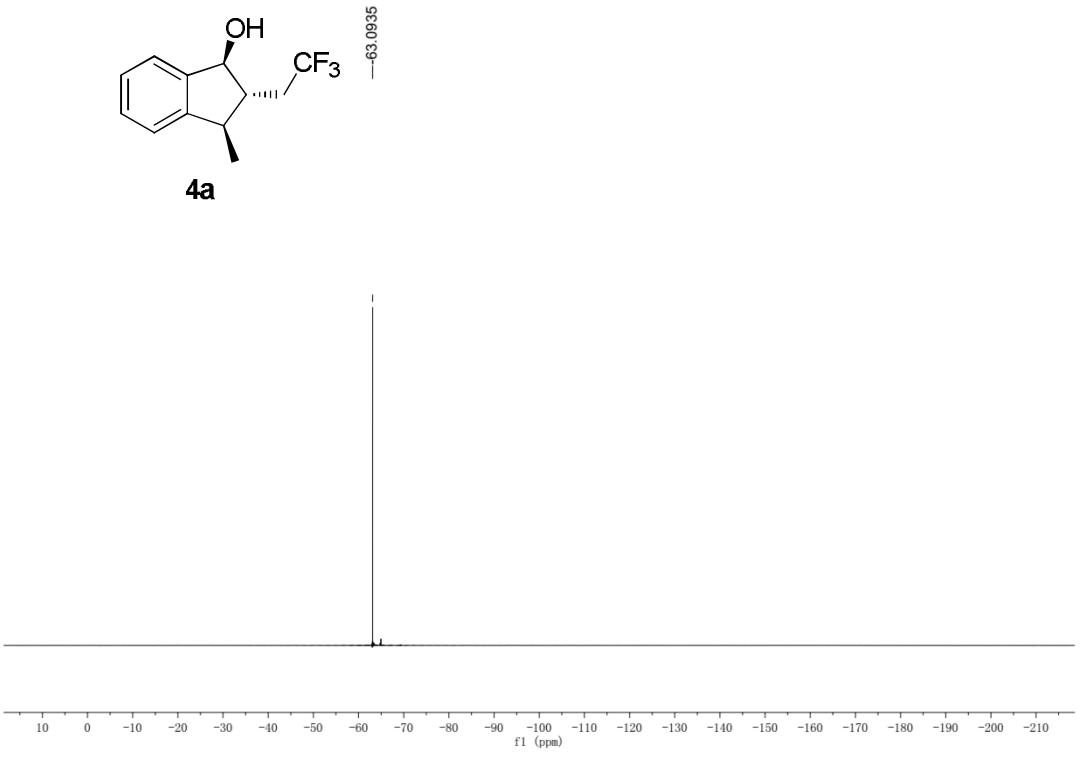

-68.9934
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

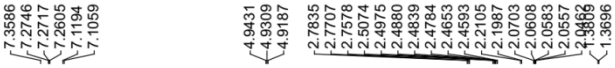
OH
CF3

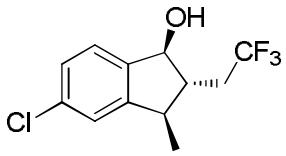
4a


7.3839
7.3717
7.3177
7.3056
7.2948
7.2930
7.2862
7.2746
7.2624
7.2022
7.1900
4.9479
4.9358
4.9237
2.8161
2.8034
2.7909
2.5127
2.4936
2.4822
2.4745
2.4632
2.4554
2.4441
2.2498
2.2377
2.0350
2.0234
2.0207
2.0116
1.3933
1.3820
1.00
2.09
1.00
1.04
1.06
2.11
1.01
1.08
3.08
f1 (ppm)

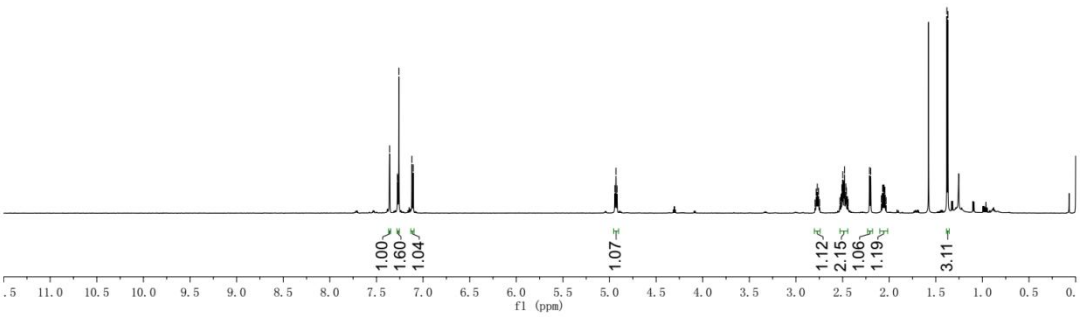

144.8316
142.9337
129.7004
128.5314
127.8661
127.2844
126.0318
124.1972
123.6912
123.1955
79.8722
77.2121
77.0005
76.7887
52.5991
52.5901
41.9821
36.3358
36.1461
35.9563
35.7666
18.2953
OH
CF3
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

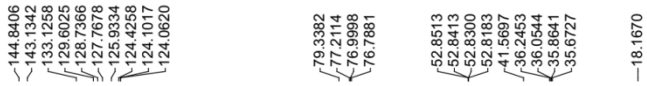

63.0935
OH
CF3
4a
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

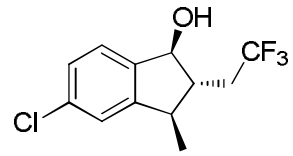

7.3586
7.2746
7.2717
7.2605
7.1194
7.1059
4.9431
4.9309
4.9187
2.7835
2.7707
2.7578
2.5074
2.4975
2.4880
2.4839
2.4784
2.4653
2.4593
2.2105
2.1987
2.0703
2.0608
2.0583
2.0557
1.3809
1.3696


OH
CF3
Cl

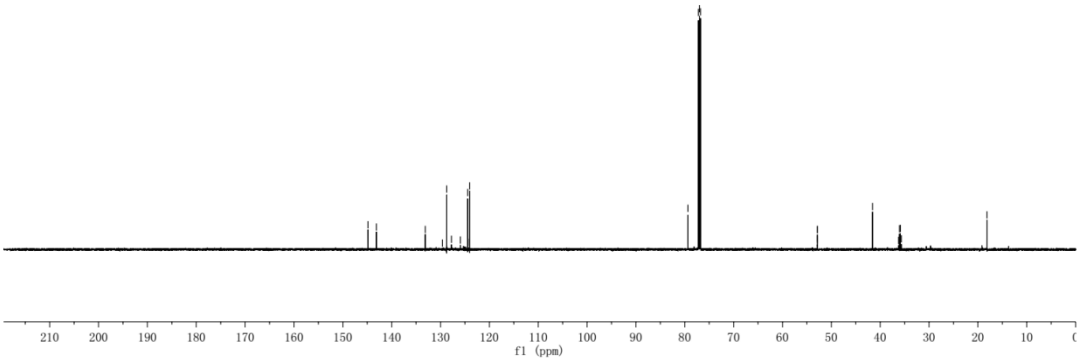
4b


1.00
1.60
1.04
1.07
1.12
2.15
1.06
1.19
3.11
f1 (ppm)


144.8406
143.1342
133.1258
129.6025
128.7366
127.7678
125.9334
124.4258
124.1017
124.0620
79.3382
77.2114
76.9998
76.7881
52.8513
52.8413
52.8300
52.8183
41.5697
36.2453
36.0544
35.8641
35.6727
18.1670

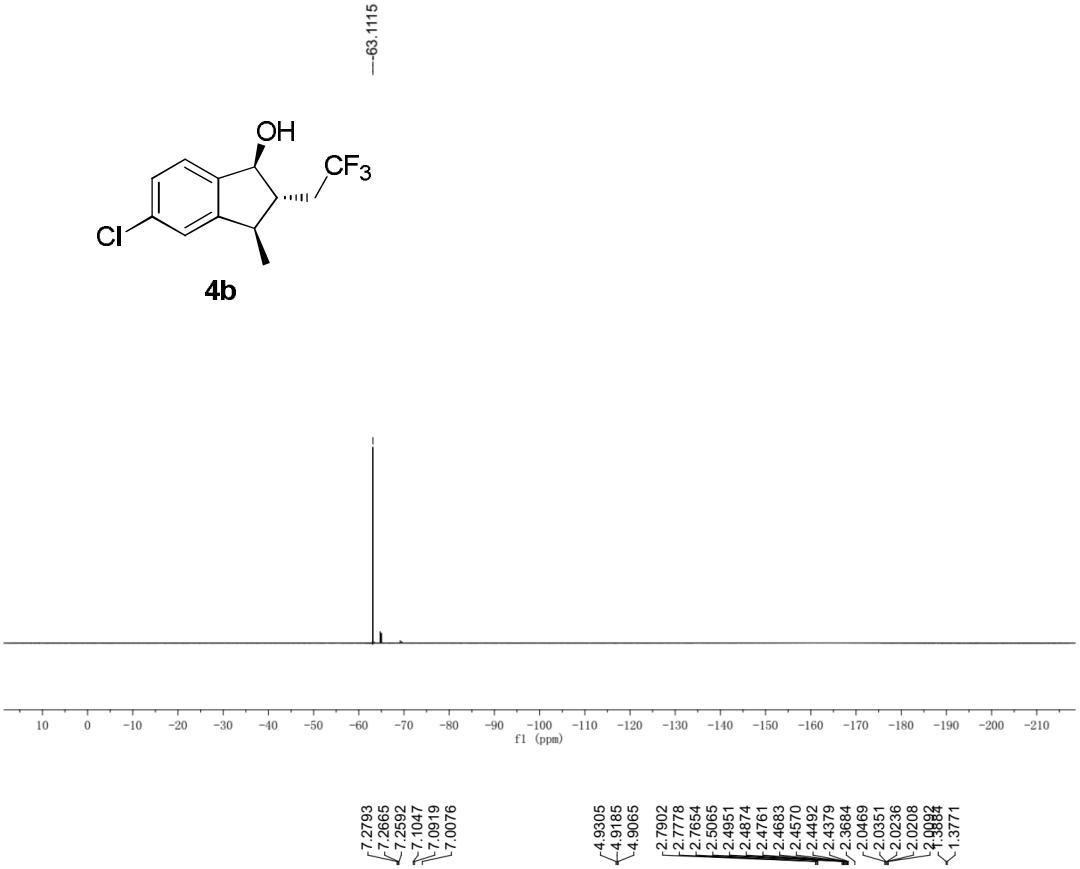

OH
CF3
Cl

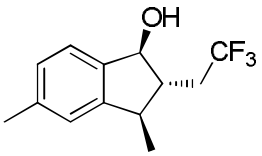
4b


f1 (ppm)

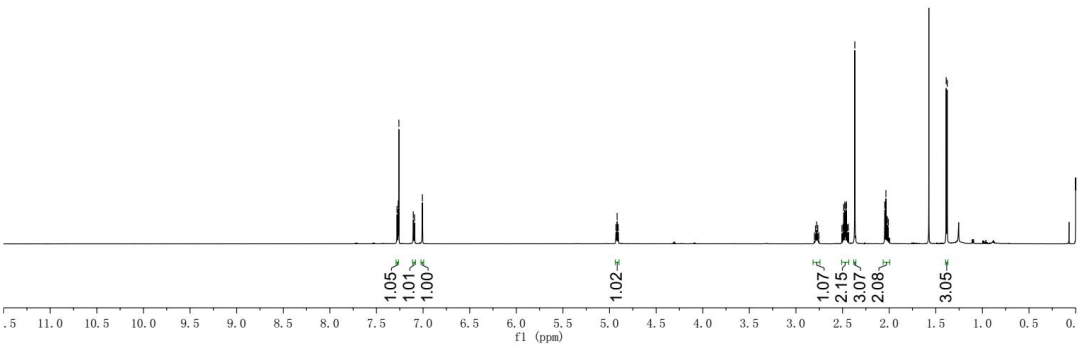
OH
CF3
Cl

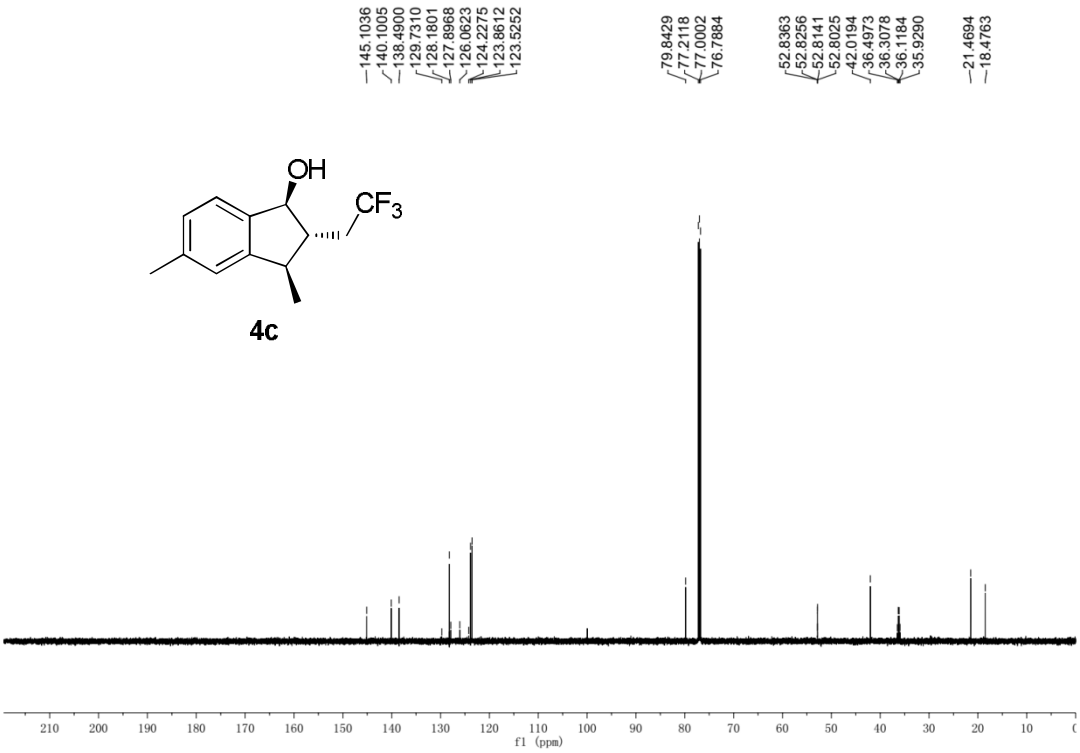
4b

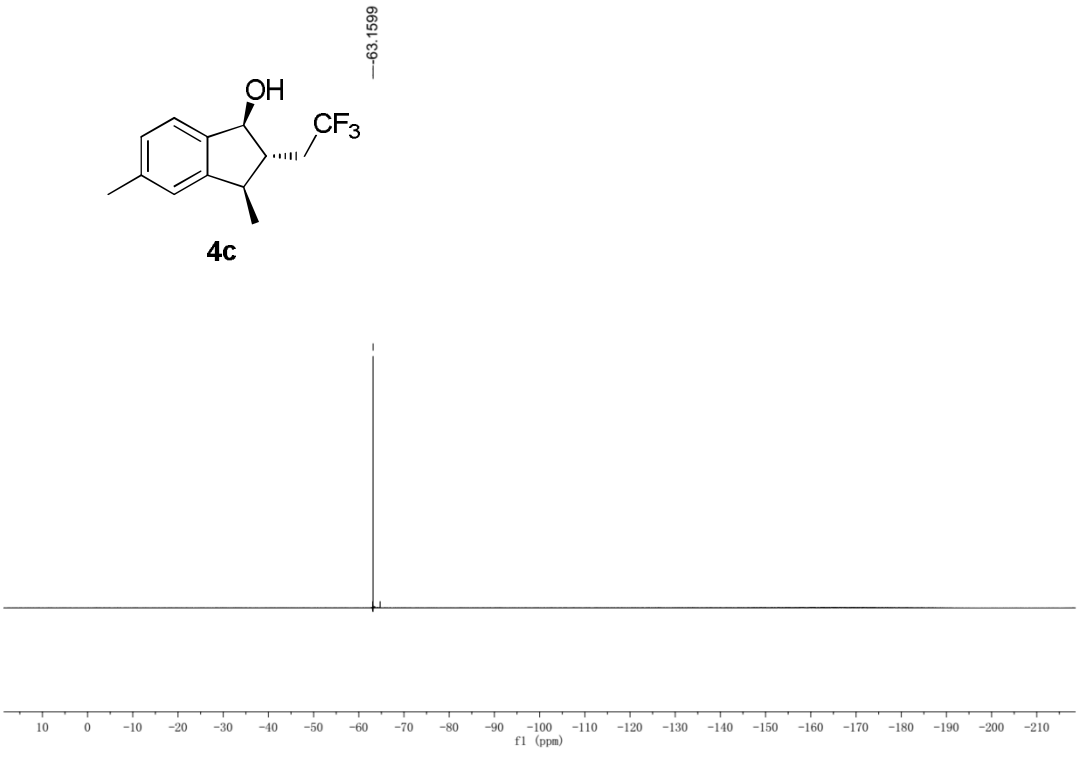

-63.1115
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
7.2793
7.2665
7.2592
7.1047
7.0919
7.0076
4.9305
4.9185
4.9065
2.7902
2.7778
2.7654
2.5065
2.4951
2.4874
2.4761
2.4683
2.4570
2.4492
2.4379
2.3684
2.0469
2.0351
2.0236
2.0208
1.3884
1.3771

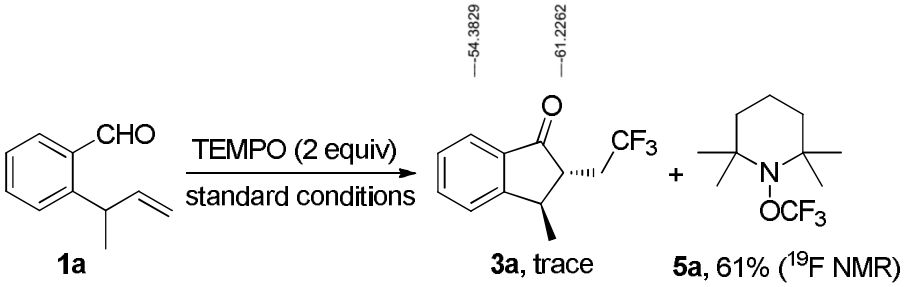

OH
CF3

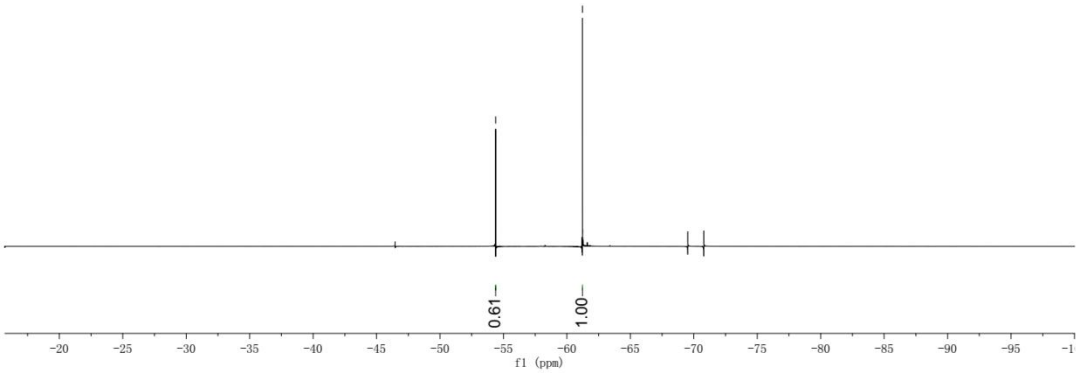
4c

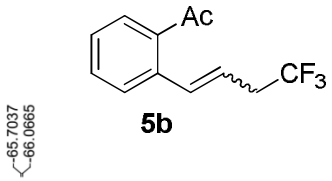

1.05
1.01
1.00
1.02
1.07
2.15
3.07
2.08
3.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

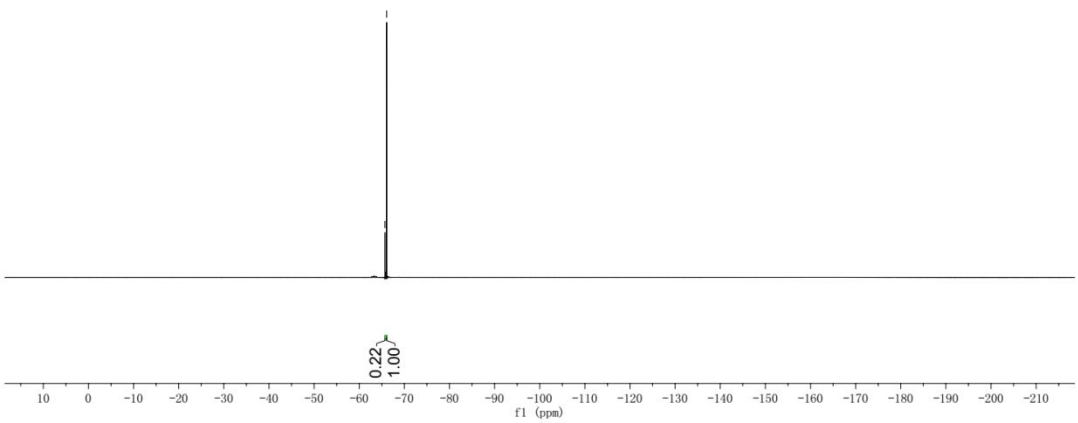

145.1036
140.1005
138.4900
129.7310
128.1801
127.8968
126.0623
124.2275
123.8612
123.5252
79.8429
77.2118
77.0002
76.7884
52.8363
52.8256
52.8141
52.8025
42.0194
36.4973
36.3078
36.1184
35.9290
21.4694
18.4763
OH
CF3
4c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

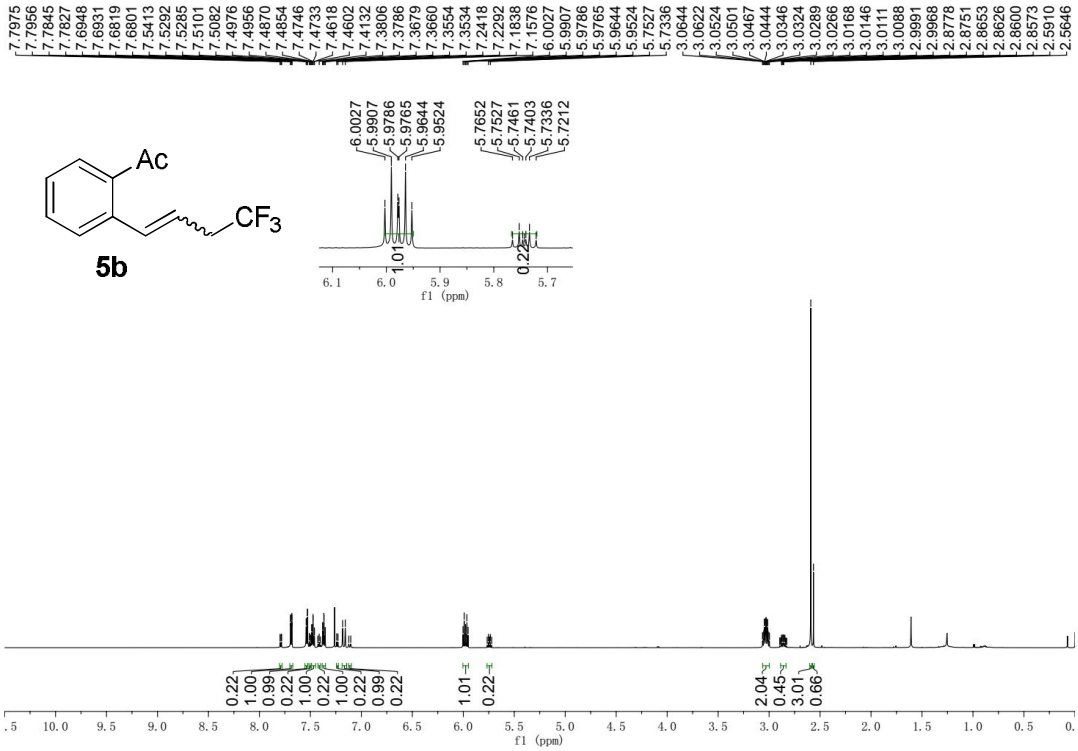

63.1599
OH
CF3
4c
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

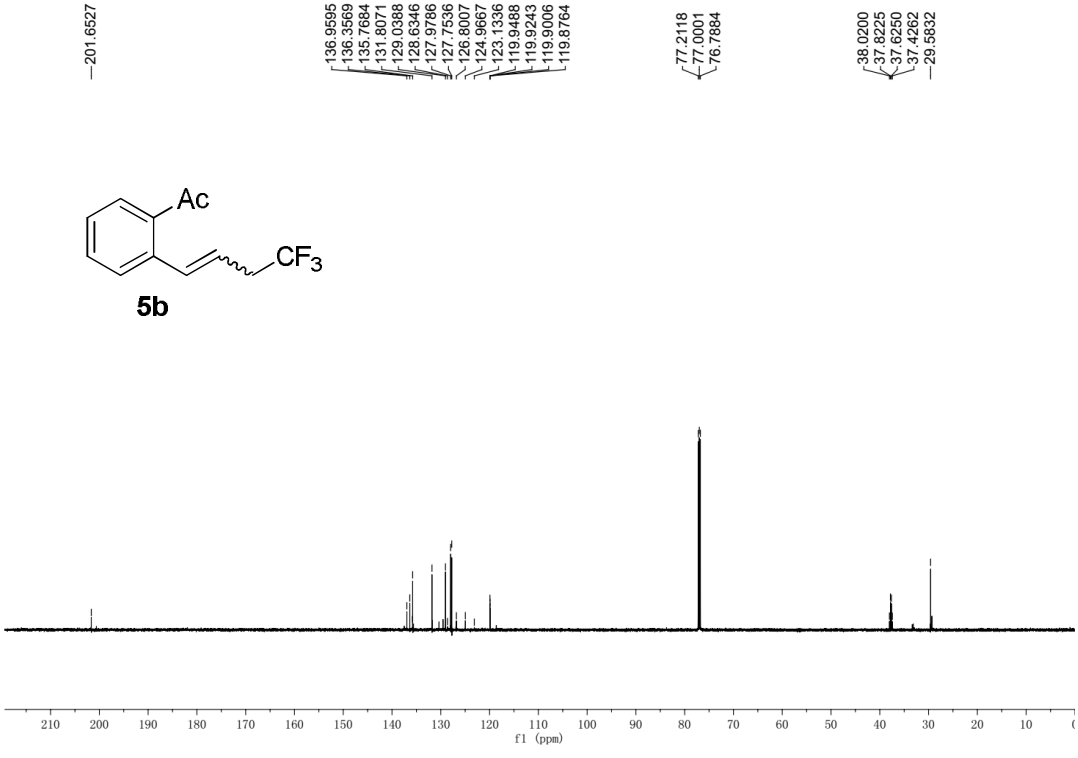

CHO
TEMPO (2 equiv)
standard conditions
O
CF3
N
OCF3
1a
3a, trace
5a, 61% (19F NMR)


-54.3829
-61.2262
0.61
1.00
f1 (ppm)

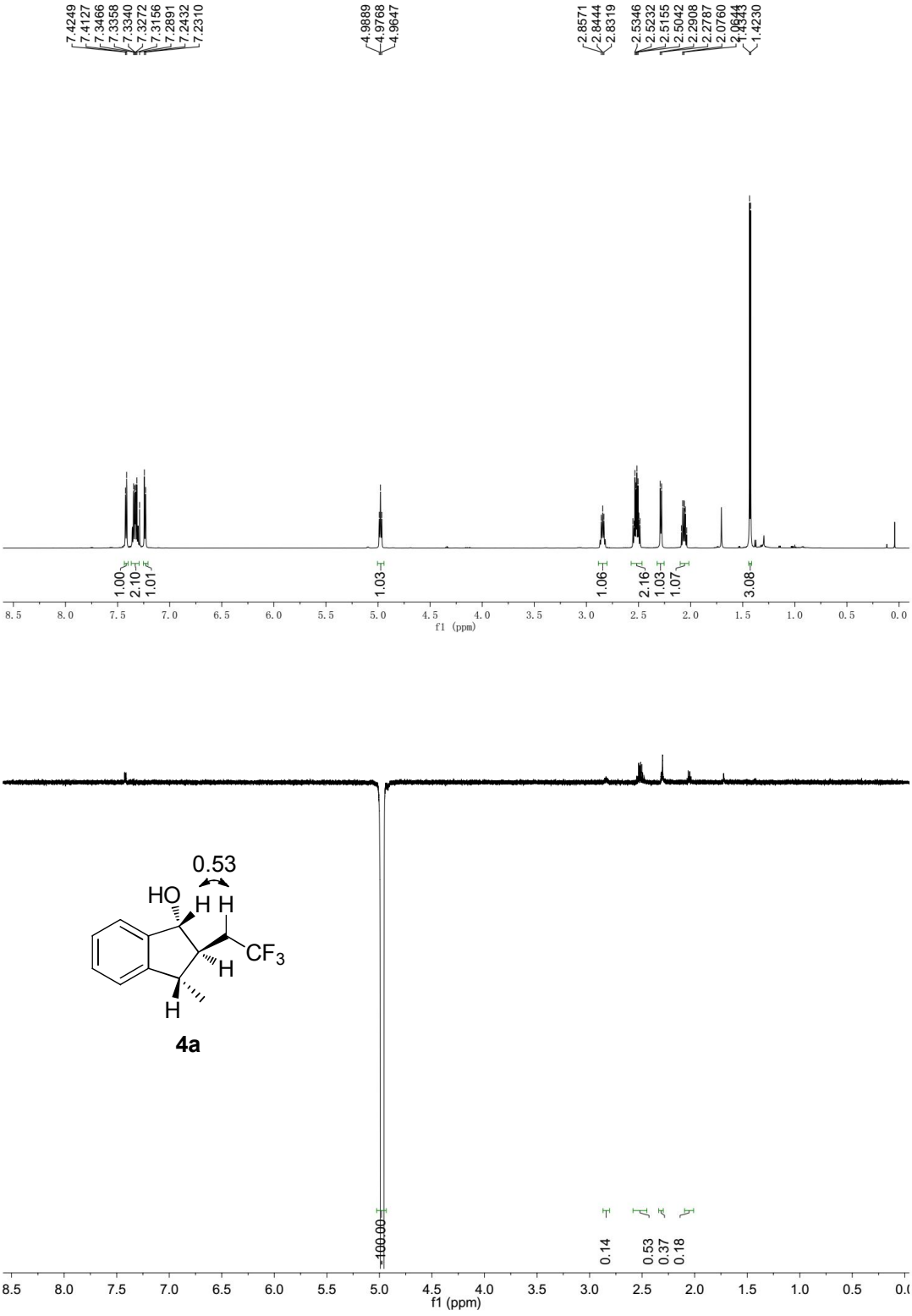

Ac
CF3
5b

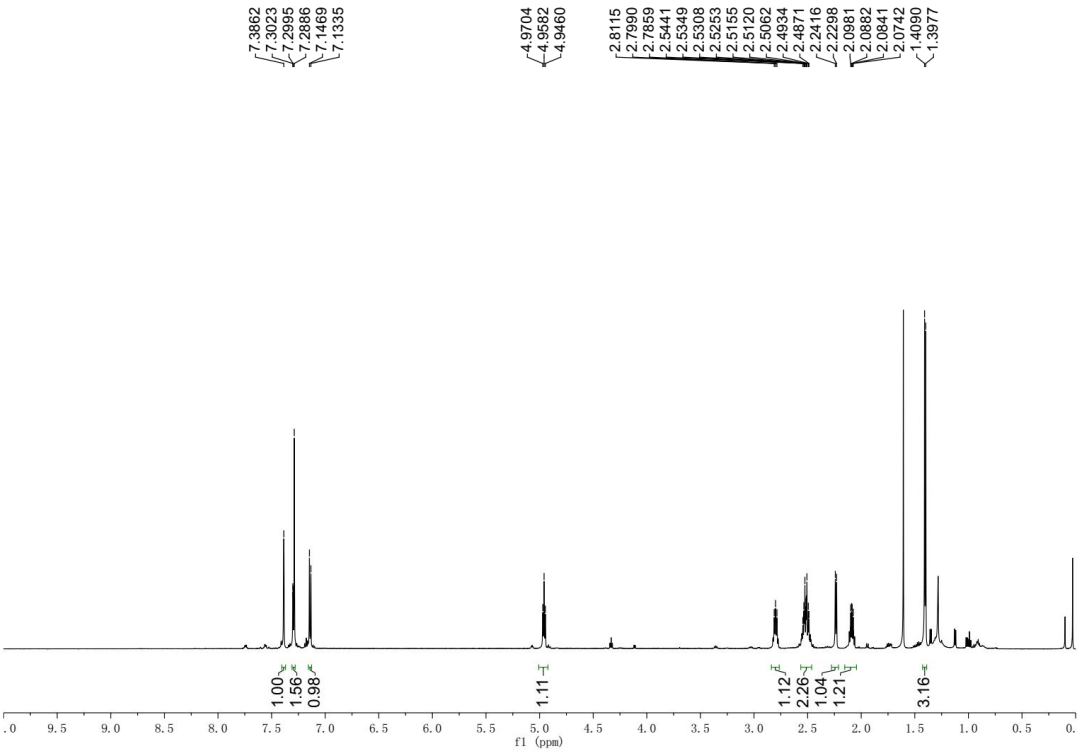

-65.7037
-66.0665
0.22
1.00
f1 (ppm)

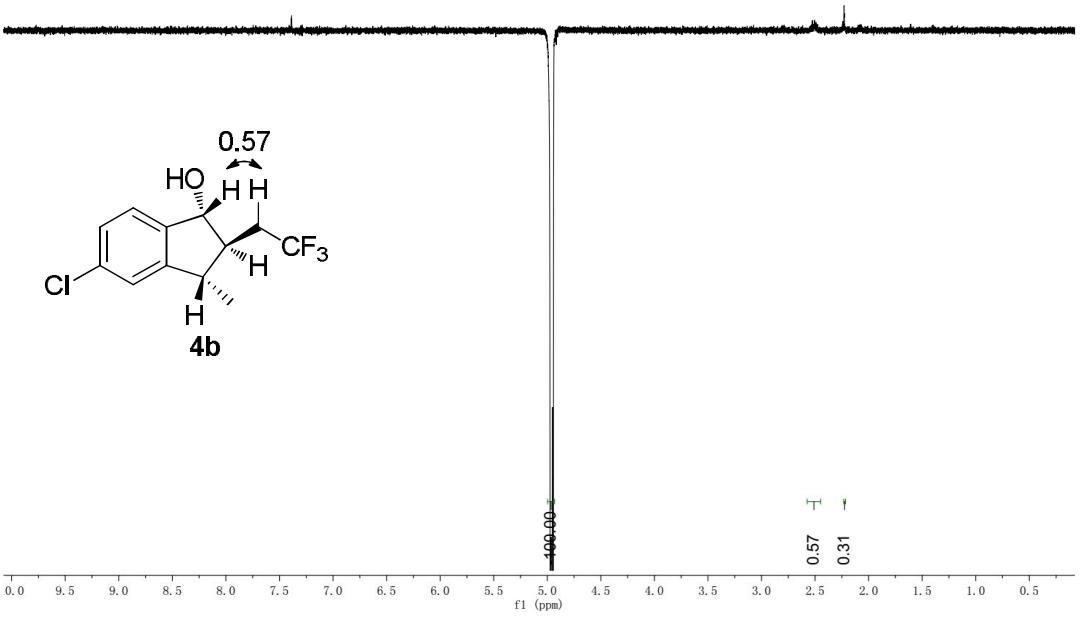

Ac
CF3
5b
f1 (ppm)

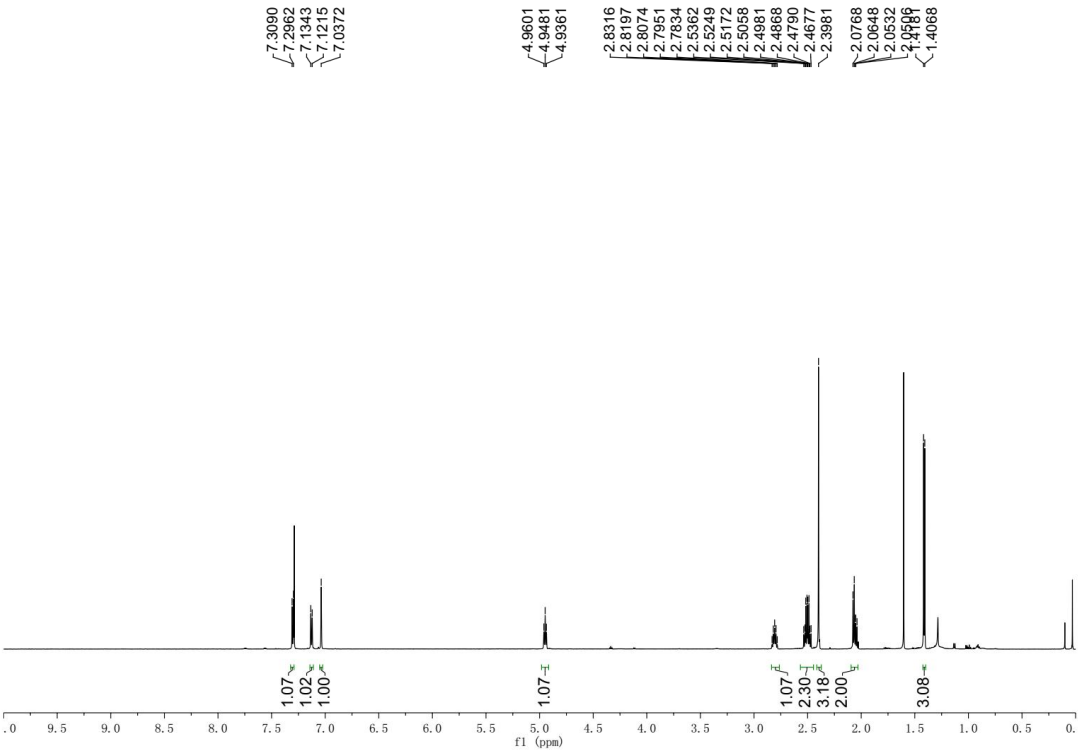

Ac
CF3
5b
f1 (ppm)

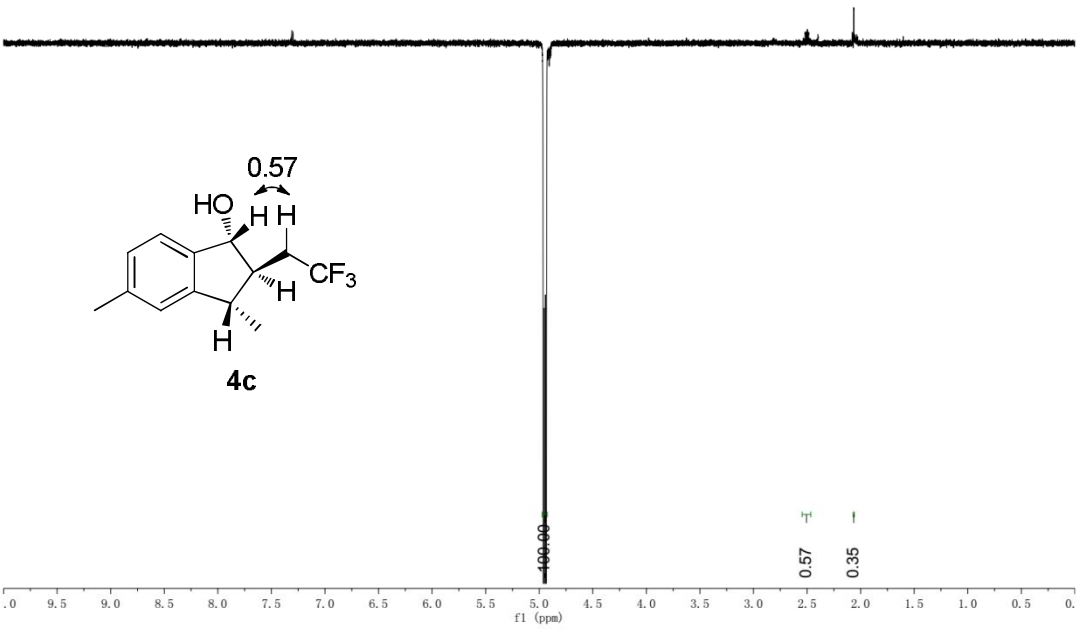
NOE spectra


7.4249
7.4127
7.3466
7.3358
7.3340
7.3272
7.3156
7.2891
7.2432
7.2310
4.9889
4.9768
4.9647
2.8571
2.8444
2.8319
2.5346
2.5232
2.5155
2.5042
2.2908
2.2787
2.0760
1.4230
1.00
2.10
1.01
1.03
1.06
2.16
1.03
1.07
3.08
f1 (ppm)
0.53
HO
H H
CF3
H
H
4a
100.00
0.14
0.53
0.37
0.18
f1 (ppm)


7.3862
7.3023
7.2995
7.2886
7.1469
7.1335
4.9704
4.9582
4.9460
2.8115
2.7990
2.7859
2.5441
2.5349
2.5308
2.5253
2.5155
2.5120
2.5062
2.4934
2.4871
2.2416
2.2298
2.0981
2.0882
2.0841
2.0742
1.4090
1.3977
1.00
1.56
0.98
1.11
1.12
2.26
1.04
1.21
3.16
f1 (ppm)


0.57
HO
H H
CF3
H
Cl
H
4b
100.00
0.57
0.31
f1 (ppm)


7.3090
7.2962
7.1343
7.1215
7.0372
4.9601
4.9481
4.9361
2.8316
2.8197
2.8074
2.7951
2.7834
2.5362
2.5249
2.5172
2.5058
2.4981
2.4868
2.4790
2.4677
2.3981
2.0768
2.0648
2.0532
2.0506
1.4181
1.4068
1.07
1.02
1.00
1.07
1.07
2.30
3.18
2.00
3.08
f1 (ppm)


0.57
HO
H H
CF3
H
H
100.00
0.57
0.35
f1 (ppm)

4c