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Supporting Information

Photocatalytic Hydroacylation of Trifluoromethyl Alkenes

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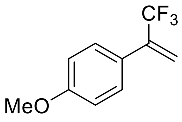
General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400M NMR spectrometers at ambient temperature in $CDCl_3$ or CD_3OD at 400 and 101 MHz. ^{19}F NMR were reported as ^{19}F exp. comp. pulse decoupling (F19CPD) unless otherwise noted. The chemical shifts are given in ppm relative to tetramethylsilane [^{1}H: δ ($SiMe_4$) = 0.00 ppm] as an internal standard or relative to the resonance of the solvent [^{1}H: δ ($CDCl_3$) = 7.26, ^{13}C: δ ($CDCl_3$) = 77.16 ppm]. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as *J* values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC was performed on Thermo UltiMate 3000. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

Unless otherwise noted, all reagents and starting materials were purchased from commercial vendors and used without further purification. TBADT (tetrabutyl ammonium decatungstate) was synthesized according to the reported methods[1].

Procedures for Synthesis of Starting Materials

Starting aldehydes were purchased from Aldrich, Energy, Alfa Aesar or Adamas-beta. Trifluoromethyl-substituted alkenes **1a-b**[2], **1c-f**[3], **1h**[4], **1i**[5], **1j**[2], **1k**[5], **1l-o**[3], **1p**[2], **1r-t**[4], **1u**[6] and **1v-x**[2] were synthesized according to the reported methods.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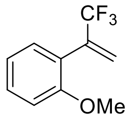
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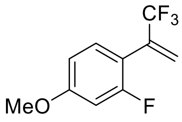
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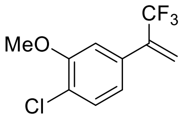
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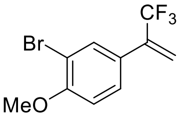
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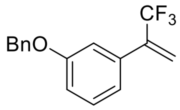
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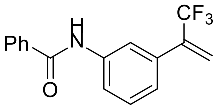
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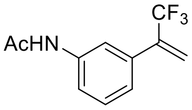
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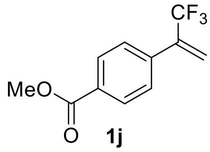
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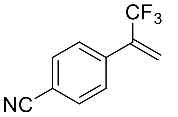
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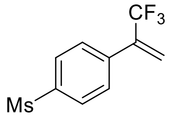
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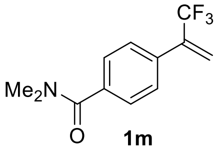
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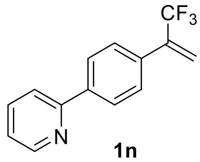
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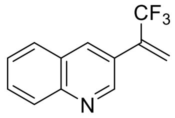
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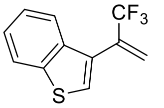
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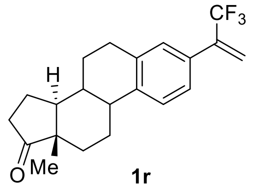
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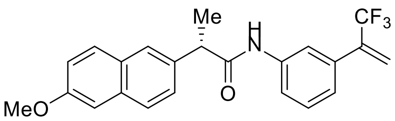
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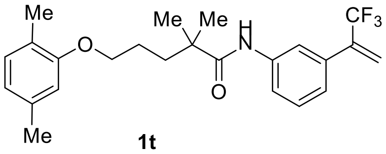
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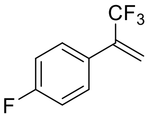
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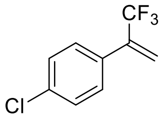
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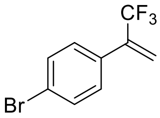
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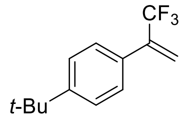
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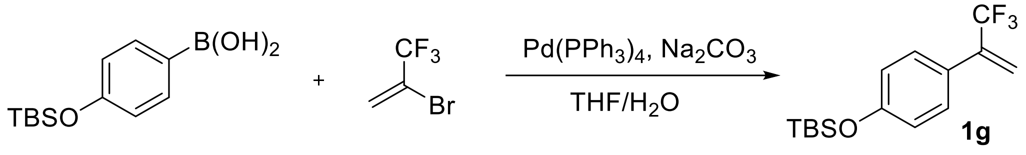
Procedure for the preparation of 1-(4-Methoxyphenyl)-3-(trifluoromethyl)decan-5-one (1g)



(4-((tert-Butyldimethylsilyl)oxy)phenyl)boronic acid (2.52 g, 10 mmol, 1 equiv), Na_2CO_3 (2.01 g, 20 mmol, 2 equiv) and $Pd(PPh_3)_4$ (0.57g , 0.5 mmol, 0.05 equiv) were mixed and degassed. To this mixture was added THF (40 mL), H_2O (40 mL) and 2-bromo-3,3,3-trifluoroprop-1-ene (3.50 g, 20 mmol, 2 equiv). The reaction tube was sealed and the reaction mixture was stirred at room temperature for one hour and then

60 °C overnight. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography over silica gel (5% EtOAc in petroleum ether) to give the desired styrene **1g** as a pale yellow oil in 62% yield (1.87 g).

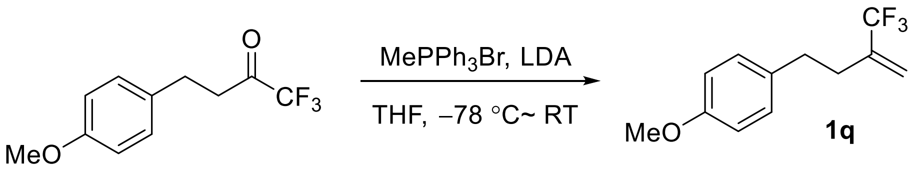
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.34 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.88-5.85 (m, 1H), 5.71-5.68 (m, 1H), 1.00 (s, 9H), 0.22 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.6, 138.5 (q, *J* = 29.7 Hz), 128.7 (2C), 126.7, 123.6 (d, *J* = 274.0 Hz), 120.2 (2C), 118.9 (q, *J* = 5.8 Hz), 25.8 (3C), 18.4, −4.3 (2C) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –64.78 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{15}H_{21}F_3OSiNa$ $[M+Na]^+$: 325.1206, found: 325.1210.

Procedure for the preparation of 1-(4-Methoxyphenyl)-3-(trifluoromethyl)decan-5-one (1q)



A flame dried flask was charged with methyl triphenylphosphonium bromide (4.46 g ,12.5 mmol, 1.25 equiv), and THF (15 mL) was added under N_2 atmosphere. The resulting suspension was cooled to 0 °C, and LDA (30 mL, 60 mmol, 1.2 equiv, 2.0 M solution in THF/n-heptane ethylbenzene) was added dropwise. After the resulting orange solution was stirred for 10 minutes and cooled to −78 °C, a solution of 1,1,1-trifluoro-4-(4-methoxyphenyl)butan-2-one[7] (2.32 g, 10 mmol, 1 equiv) in THF (10 mL) was added to the reaction mixture. The cooling bath was removed, and the solution was allowed to warm to room temperature. After stirring overnight the reaction was quenched with aq. NH_4Cl (sat.). The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography over silica gel (10% EtOAc in petroleum ether) to give the desired styrene **1q** as a pale yellow oil in 85% yield (1.97 g).

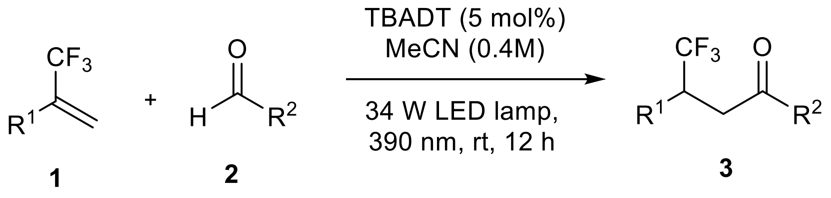
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.13 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.71-5.64 (m, 1H), 5.35-5.23 (m, 1H), 3.80 (s, 3H), 2.85-2.73 (m, 2H), 2.55-2.45 (m, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 158.2, 137.9 (q, *J* = 29.2 Hz), 132.8, 129.4 (2C), 123.9 (d, *J* = 273.7 Hz), 118.3 (q, *J* = 5.9 Hz), 114.0 (2C), 55.4, 33.0, 31.6 ppm.

^{19}**F NMR** (376 MHz, Chloroform-*d*) δ = –68.44 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{12}H_{13}F_3ONa$ $[M+Na]^+$: 253.0811, found: 253.0806.

General Procedure for Hydroacylation of Trifluoromethyl-Substituted Alkenes

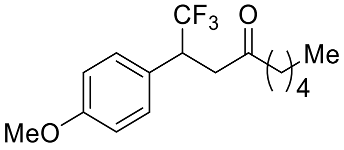


TBADT (5 mol%), aliphatic aldehydes (if solid, 0.4 mmol, 2.0 equiv)[a] or aromatic aldehydes (if solid, 0.6 mmol, 3.0 equiv), trifluoromethyl-substituted alkenes (if solid, 0.2 mmol, 1.0 equiv) were placed in a tube equipped with a stir bar. The tube was evacuated and filled with nitrogen (three cycles). To these solids, dry MeCN (0.5 mL, 0.4 M) were added under nitrogen atmosphere. Next, aliphatic aldehydes (if liquid, 0.4 mmol, 2.0 equiv) or aromatic aldehydes (if liquid, 0.6 mmol, 3.0 equiv) were added. Then trifluoromethyl-substituted alkenes (if liquid, 0.2 mmol, 1.0 equiv) was added. Subsequently, the reaction mixture was stirred and irradiated using a 34 W 390 nm LED lamp (Kessil PR160-390, 5 cm away, with adequate fans and a water bath to keep the reaction at room temperature) for 12 h.[a] After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate) to afford the desired products **3**.

[a] **3ra** was synthesized using 3 equiv of *n*-hexanal with the reaction time of 24h.

Characterization Data of the β-CF_3 Ketones 3

1,1,1-Trifluoro-2-(4-methoxyphenyl)nonan-4-one (3aa)



The title compound **3aa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a pale yellow solid (48.3 mg, 80%).

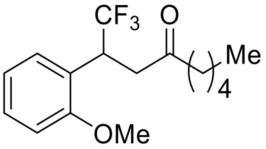
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.23 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 1H), 4.03-3.90 (m, 1H), 3.78 (s, 3H), 3.03-2.96 (m, 2H), 2.39 (dt, *J* = 16.9, 7.5 Hz, 1H), 2.28 (dt, *J* = 16.8, 7.3 Hz, 1H), 1.55-1.44 (m, 2H), 1.25-1.19 (m, 2H), 1.18-1.11 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.6, 159.6, 130.1 (2C), 126.9 (q, *J* = 279.3 Hz), 126.5 (q, *J* = 2.1 Hz), 114.2 (2C), 55.3, 43.9 (q, *J* = 27.7 Hz), 43.5, 42.2 (q, *J* = 1.8 Hz), 31.2, 23.3, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.21 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{21}F_3O_2Na$ $[M+Na]^+$: 325.1386, found: 325.1394.

1,1,1-Trifluoro-2-(2-methoxyphenyl)nonan-4-one (3ba)



The title compound **3ba** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as white solid (36.8 mg, 61%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.32-7.16 (m, 2H), 7.00-6.85 (m, 2H), 4.87-4.60 (m, 1H), 3.87 (s, 3H), 3.11-2.94 (m, 2H), 2.40 (dt, *J* = 16.9, 7.5 Hz, 1H), 2.31 (dt, *J* = 16.8, 7.3 Hz, 1H), 1.55-1.44 (m, 2H), 1.27-1.22 (m, 2H), 1.19-1.12 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm.

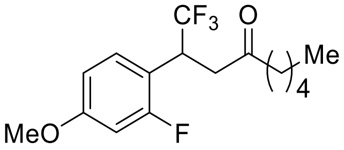
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.6, 157.9, 129.4, 128.3, 125.6 (q, q, *J* =

279.5 Hz), 123.1 (d, *J* = 2.0 Hz), 120.7, 111.3, 56.0, 43.1, 41.9 (q, *J* = 1.6 Hz), 36.4 (q, *J* = 28.0 Hz), 31.3, 23.3, 22.5, 13.9 ppm.

^{19}**F NMR** (376 MHz, Chloroform-*d*) δ = –70.01 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{21}F_3O_2Na$ $[M+Na]^+$: 325.1386, found: 325.1387.

1,1,1-Trifluoro-2-(2-fluoro-4-methoxyphenyl)nonan-4-one (3ca)



The title compound **3ca** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a white solid (54.9 mg, 86%).

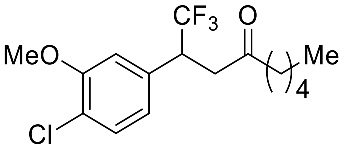
^{1}**H NMR** (400 MHz, Chloroform-*d*) δ = 7.22-7.14 (m, 1H), 6.72-6.54 (m, 2H), 4.39-4.24 (m, 1H), 3.77 (s, 3H), 3.13-2.96 (m, 2H), 2.41 (dt, *J* = 16.9, 7.6 Hz, 1H), 2.33 (dt, *J* = 16.7, 7.3 Hz, 1H), 1.58-1.45 (m, 2H), 1.31-1.21 (m, 2H), 1.21-1.12 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}**C NMR** (101 MHz, Chloroform-*d*) δ = 206.2, 162.0 (d, *J* = 222.8 Hz), 160.7 (d, *J* = 14.2 Hz), 129.8 (d, *J* = 5.2 Hz), 126.6 (q, *J* = 279.3 Hz), 113.3 (dq, *J* = 14.6, 1.8 Hz), 110.5 (d, *J* = 3.1 Hz), 101.8 (d, *J* = 26.5 Hz), 55.6, 43.1, 41.1 (q, *J* = 1.8 Hz), 37.1 (q, *J* = 28.9 Hz), 31.2, 23.3, 22.4, 13.9 ppm.

^{19}**F NMR** (376 MHz, Chloroform-*d*) δ = –69.99 (s, 3F), −113.96 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{20}F_4O_2Na$ $[M+Na]^+$: 343.1292, found: 343.1291.

2-(4-Chloro-3-methoxyphenyl)-1,1,1-trifluorononan-4-one (3da)



The title compound **3da** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a brown oil (54.4 mg, 81%).

^{1}**H NMR** (400 MHz, Chloroform-*d*) δ = 7.49 (d, *J* = 2.3 Hz, 1H), 7.23 (dd, *J* = 8.5, 2.3

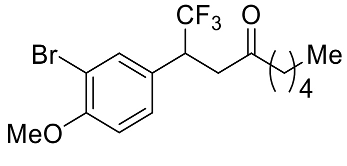
Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 3.98-3.90 (m, 1H), 3.87 (s, 3H), 3.07-2.91 (m, 2H), 2.40 (dt, *J* = 16.8, 7.5 Hz, 1H), 2.30 (dt, *J* = 16.7, 7.3 Hz, 1H), 1.55-1.43 (m, 2H), 1.28-1.20 (m, 2H), 1.19-1.11 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.2, 155.9, 133.4, 129.6, 128.0 (d, *J* = 2.1 Hz), 126.7 (d, *J* = 279.3 Hz), 111.9 (2C), 56.3, 43.6 (q, *J* = 27.8 Hz), 43.4, 42.1 (q, *J* = 1.8 Hz), 31.2, 23.3, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.15 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{20}ClF_3O_2Na$ $[M+Na]^+$: 359.0996, found: 359.1008.

2-(3-Bromo-4-methoxyphenyl)-1,1,1-trifluorononan-4-one (3ea)



The title compound **3ea** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as white solid (49.4 mg, 65%).

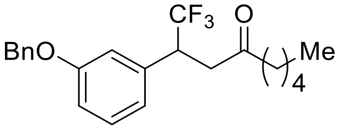
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.33-7.29 (m, 1H), 6.90-6.79 (m, 2H), 4.09-3.95 (m, 1H), 3.90 (s, 3H), 3.08-2.94 (m, 2H), 2.40 (dt, *J* = 16.8, 7.5 Hz, 1H), 2.29 (dt, *J* = 16.8, 7.3 Hz, 1H), 1.55-1.41 (m, 2H), 1.26-1.18 (m, 2H), 1.17-1.10 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.1, 155.0, 134.5 (q, *J* = 1.9 Hz), 130.4, 126.6 (q, *J* = 279.5 Hz), 122.6, 121.2, 113.3, 56.2, 44.5 (q, *J* = 27.7 Hz), 43.4, 42.1 (q, *J* = 1.6 Hz), 31.2, 23.3, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.82 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{20}BrF_3O_2Na$ $[M+Na]^+$: 403.0491, found: 403.0495.

2-(3-(Benzyloxy)phenyl)-1,1,1-trifluorononan-4-one (3fa)



The title compound **3fa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a white solid (53.7 mg, 71%).

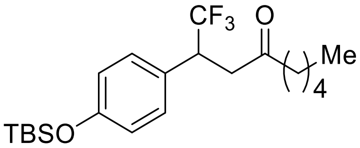
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.46-7.35 (m, 4H), 7.35-7.30 (m, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 6.97-6.85 (m, 3H), 5.03 (s, 2H), 4.13-3.86 (m, 1H), 3.06-2.93 (m, 2H), 2.37 (dt, *J* = 16.7, 7.5 Hz, 1H), 2.26 (dt, *J* = 16.7, 7.3 Hz, 1H), 1.54-1.42 (m, 2H), 1.30-1.20 (m, 2H), 1.20-1.10 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.3, 159.0, 136.8, 136.0 (q, *J* = 2.0 Hz), 129.8, 128.7 (2C), 128.1, 127.6 (2C), 126.8 (q, *J* = 279.2 Hz), 121.7, 115.9, 114.4, 70.1, 44.7 (q, *J* = 27.5 Hz), 43.4, 42.1 (q, *J* = 1.8 Hz), 31.2, 23.3, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.79 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{25}F_3O_2Na$ $[M+Na]^+$: 401.1699, found: 401.1710.

2-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)-1,1,1-trifluorononan-4-one (3ga)



The title compound **3ga** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a white solid (62.7 mg, 78%).

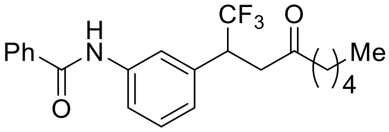
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.16 (d, *J* = 8.6 Hz, 2H), 6.85-6.73 (m, 2H), 4.03-3.84 (m, 1H), 3.04-2.91 (m, 2H), 2.38 (dt, *J* = 16.7, 7.5 Hz, 1H), 2.27 (dt, *J* = 16.7, 7.3 Hz, 1H), 1.54-1.41 (m, 2H), 1.27-1.20 (m, 2H), 1.18-1.11 (m, 2H), 0.97 (s, 9H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.19 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.5, 155.7, 130.1 (2C), 127.1 (q, *J* = 2.0 Hz), 126.9 (q, *J* = 279.4 Hz), 120.2 (2C), 44.0 (q, *J* = 27.7 Hz), 43.5, 42.3 (q, *J* = 1.8 Hz), 31.2, 25.7 (3C), 23.3, 22.4, 18.2, 13.9, −4.3 (2C) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.24 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{33}F_3O_2SiNa$ $[M+Na]^+$: 425.2094, found: 425.2092.

N-(3-(1,1,1-Trifluoro-4-oxononan-2-yl)phenyl)benzamide (3ha)



The title compound **3ha** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as white solid (56.3 mg, 72%).

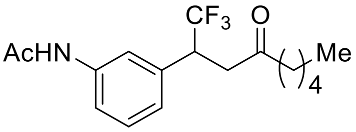
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.38-8.19 (m, 1H), 7.86-7.78 (m, 2H), 7.69-7.57 (m, 2H), 7.54-7.50 (m, 1H), 7.44-7.37 (m, 2H), 7.30-7.25 (m, 1H), 7.10-7.04 (m, 1H), 4.10-3.87 (m, 1H), 3.12-2.90 (m, 2H), 2.39 (dt, *J* = 15.5, 7.5 Hz, 1H), 2.29 (dt, *J* = 16.5, 7.4 Hz, 1H), 1.54-1.40 (m, 1H), 1.29-1.19 (m, 2H), 1.18-1.09 (m, 1H), 0.82 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.6, 166.1, 138.5, 135.4, 134.8, 131.9, 129.4, 128.8 (2C), 127.2 (2C), 126.7 (d, *J* = 279.5 Hz), 125.1, 120.7, 120.2, 44.5 (q, *J* = 27.6 Hz), 43.4, 41.9, 31.2, 23.2, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.74 (d, *J* = 9.5 Hz) ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{24}F_3NO_2Na$ $[M+Na]^+$: 414.1651, found: 414.1667.

N-(3-(1,1,1-Trifluoro-4-oxononan-2-yl)phenyl)acetamide (3ia)



The title compound **3ia** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a white solid (59.3 mg, 90%).

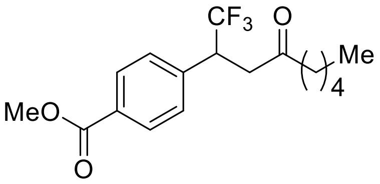
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.67 (s, 1H), 7.55-7.44 (m, 2H), 7.34-7.20 (m, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 4.11-3.83 (m, 1H), 3.10-2.96 (m, 2H), 2.40 (dt, *J* = 16.8, 7.5 Hz, 1H), 2.31 (dt, *J* = 16.8, 7.3 Hz, 1H), 2.15 (s, 3H), 1.55-1.42 (m, 2H), 1.26-1.21 (m, 2H), 1.19-1.12 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.6, 168.7, 138.5, 135.4, 129.4, 126.7 (d, *J* = 279.5 Hz), 124.8, 120.3, 119.8, 44.6 (q, *J* = 27.7 Hz), 43.4, 42.0, 31.2, 24.6, 23.2, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.81 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{22}F_3NO_2Na$ [M+Na]$^+$: 352.1495, found:352.1499

Methyl 4-(1,1,1-trifluoro-4-oxononan-2-yl)benzoate (3ja)



The title compound **3ja** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil, (54.7 mg, 83%).

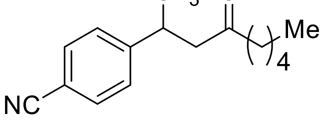
^{1}H NMR (400 MHz, Chloroform-*d*) δ = (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 4.18-4.00 (m, 1H), 3.89 (s, 3H), 3.14-2.98 (m, 2H), 2.39 (dt, *J* = 16.5, 7.5 Hz, 1H), 2.28 (dt, *J* = 16.7, 7.3 Hz, 1H), 1.51-1.42 (m, 2H), 1.25-1.19 (m, 2H), 1.17-1.09 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.0, 166.6, 139.5 (q, *J* = 1.9 Hz), 130.2, 130.0 (2C) , 129.1 (2C) , 126.5 (q, *J* = 279.6 Hz), 52.2 , 44.6 (q, *J* = 27.8 Hz), 43.3, 41.9 (q, *J* = 1.7 Hz), 31.2 , 23.2, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.62 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{21}F_3O_3Na$ [M+Na]$^+$: 353.1335, found: 353,1346.

4-(1,1,1-Trifluoro-4-oxononan-2-yl)benzonitrile (3ka)



The title compound **3ka** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow solid (35.0 mg, 59%).

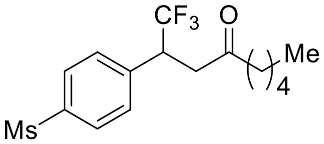
^{1}H NMR(400 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H)., 4.17-3.95 (m, 1H), 3.17-2.95 (m, 2H), 2.41 (dt, *J* = 16.8, 7.5 Hz, 1H), 2.30 (dt, *J* = 16.8, 7.3 Hz, 1H), 1.53-1.42 (m, 2H), 1.28-1.20 (m, 2H), 1.18-1.10 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 205.7, 139.9 (q, *J* = 1.8 Hz), 132.5, 130.0, 126.3 (q, *J* = 279.5 Hz), 118.3, 112.6, 44.7 (q, *J* = 28.1 Hz), 43.3, 41.9 (q, *J* = 1.3 Hz), 31.2, 23.3, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = –69.48 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{18}F_3NOH$ [M+H]$^+$: 298.1413, found: 298.1427.

1,1,1-Trifluoro-2-(4-(methylsulfonyl)phenyl)nonan-4-one (3la)



The title compound **3la** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a white solid (46.4 mg, 71%).

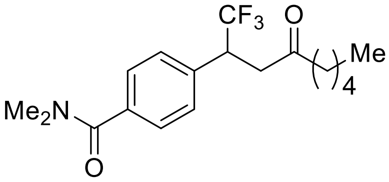
1H NMR (400 MHz, Chloroform-*d*) δ = 7.90 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 4.25-4.01 (m, 1H), 3.11-3.06 (m, 2H), 3.03 (s, 3H), 2.41 (dt, *J* = 16.9, 7.5 Hz, 1H), 2.29 (dt, *J* = 16.8, 7.3 Hz, 1H), 1.53-1.40 (m, 2H), 1.27-1.19 (m, 2H), 1.19-1.10 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H) ppm.

13C NMR (101 MHz, Chloroform-*d*) δ = 205.7, 140.8 (q, *J* = 1.9 Hz), 140.6, 130.1 (2C), 127.8 (2C), 126.3 (q, *J* = 279.2 Hz), 44.5 (q, *J* = 28.0 Hz), 44.4, 43.2, 41.8, 31.1, 23.2, 22.3, 13.9 ppm.

19F NMR (376 MHz, Chloroform-*d*) δ = –69.42 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{21}F_3O_3Na$ [M+Na]$^+$: 373.1056, found: 373.1062.

N,N-Dimethyl-4-(1,1,1-trifluoro-4-oxononan-2-yl)benzamide (3ma)



The title compound **3ma** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a white solid (34.9 mg, 51%).

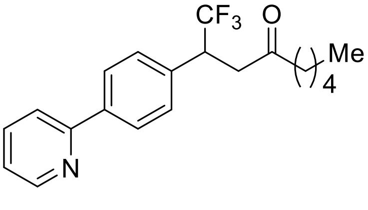
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.43-7.31 (m, 4H), 4.16-3.94 (m, 1H), 3.09 (s, 3H), 3.05-3.01 (m, 2H), 2.95 (s, 3H), 2.40 (dt, *J* = 16.9, 7.5 Hz, 1H), 2.28 (dt, *J* = 16.9, 7.3 Hz, 1H), 1.55-1.40 (m, 2H), 1.26-1.20 (m, 2H), 1.20-1.12 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.0, 171.0, 136.4, 136.0 (q, *J* = 1.8 Hz), 129.1 (2C) , 127.5 (2C) , 126.6 (d, *J* = 279.4 Hz), 44.4 (q, *J* = 27.8 Hz), 43.4, 42.1 (q, *J* = 1.7 Hz), 39.6, 35.4, 31.2, 23.2, 22.4, 13.9 ppm .

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.70 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{24}F_3NO_2$ $[M+Na]^+$: 366.1651, found: 366.1661.

1,1,1-Trifluoro-2-(4-(pyridin-2-yl)phenyl)nonan-4-one (3na)



The title compound **3na** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a pale yellow solid (61.4 mg, 88%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.74-8.58 (m, 1H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.76-7.60 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.23-7.15 (m, 1H), 4.22-3.96 (m, 1H), 3.17-2.94 (m, 2H), 2.47-2.33 (m, 1H), 2.33-2.21 (m, 1H), 1.58-1.39 (m, 2H), 1.27-1.18 (m, 2H), 1.18-1.07 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H) ppm.

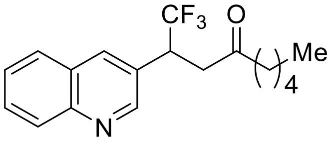
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.2, 156.7, 149.7, 139.4, 136.8, 135.2, 129.4

(2C), 127.2 (2C), 126.7 (q, *J* = 279.4 Hz), 122.3, 120.5, 44.4 (q, *J* = 27.5 Hz), 43.4, 42.0, 31.2, 23.2, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.74 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{22}F_3NONa$ $[M+Na]^+$: 372.1546, found: 372.1552.

1,1,1-Trifluoro-2-(quinolin-3-yl)nonan-4-one (3oa)



The title compound **3oa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a pale yellow solid (49.1 mg, 76%).

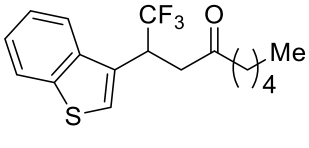
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.96-8.80 (m, 1H), 8.15 - 8.04 (m, 2H), 7.86-7.78 (m, 1H), 7.75-7.69 (m, 1H), 7.62-7.51 (m, 1H), 4.37-4.12 (m, 1H), 3.24-3.13 (m, 2H), 2.43 (dt, *J* = 16.8, 7.5 Hz, 1H), 2.31 (dt, *J* = 16.8, 7.3 Hz, 1H), 1.55-1.41 (m, 2H), 1.23-1.16 (m, 2H), 1.16-1.08 (m, 2H), 0.79 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR 13C NMR (101 MHz, Chloroform-*d*) δ = 205.8, 150.9, 147.9, 136.2, 130.1, 129.3, 127.9, 127.6, 127.6, 127.2, 126.6 (q, *J* = 279.5 Hz), 43.3, 42.7 (q, *J* = 28.1 Hz), 42.0, 31.2, 23.3, 22.4, 13.9 ppm.

19F NMR (376 MHz, Chloroform-*d*) δ = –69.50 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{20}F_3NOH$ $[M+H]^+$: 324.1570, found: 324.1573.

2-(Benzo[b]thiophen-3-yl)-1,1,1-trifluorononan-4-one (3pa)



The title compound **3pa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a pale yellow solid (38.8 mg, 59%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.91 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.49-7.42 (m, 1H), 7.42-7.35 (m, 2H), 4.76-4.38 (m, 1H), 3.19 (dd, *J* = 17.5, 5.0

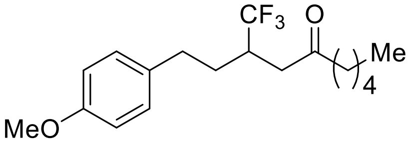
Hz, 1H), 3.09 (dd, *J* = 17.5, 8.2 Hz, 1H), 2.52-2.24 (m, 2H), 1.56-1.45 (m, 2H), 1.30-1.20 (m, 2H), 1.19-1.09 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.2, 140.1, 138.4, 129.9, 126.7 (q, *J* = 280.5 Hz), 124.9, 124.7, 124.6 122.8, 121.9, 43.3, 42.6, 37.7 (q, *J* = 28.7 Hz), 31.2, 23.3, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −69.81 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{19}F_3OSH$ $[M+H]^+$: 329.1181, found: 329.1196.

1-(4-Methoxyphenyl)-3-(trifluoromethyl)decan-5-one (3qa)



The title compound **3qa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a pale yellow liquid (27.7 mg, 42%).

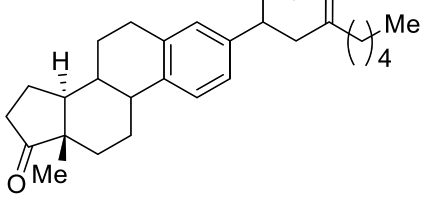
^{1}H NMR 1H NMR (400 MHz, Chloroform-*d*) δ = 7.08 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.99-2.83 (m, 1H), 2.74 (dd, *J* = 17.9, 4.9 Hz, 1H), 2.66-2.55 (m, 2H), 2.48 (dd, *J* = 17.9, 7.2 Hz, 1H), 2.43-2.35 (m, 2H), 1.96-1.85 (m, 1H), 1.69-1.62 (m, 1H), 1.60-1.54 (m, 2H), 1.36-1.20 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR 13C NMR (101 MHz, Chloroform-*d*) δ = 207.2, 157.9, 133.0, 129.2 (2C), 128.1 (q, *J* = 279.6 Hz), 113.8 (2C), 55.2, 43.1, 41.1 (q, *J* = 2.3 Hz), 37.6 (q, *J* = 26.1 Hz), 32.2, 31.3, 30.7 (q, *J* = 2.0 Hz), 23.4, 22.4, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.27 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{25}F_3O_2Na$ $[M+Na]^+$: 353.1699, found: 353.1705.

(13*S*,14*S*)-13-methyl-3-(1,1,1-trifluoro-4-oxononan-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (3ra)



The title compound **3ta** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a white solid (45.2 mg, 53%).

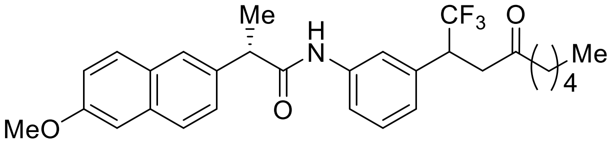
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.24 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 7.02 (s, 1H), 4.00-3.91 (m, 1H), 3.06-2.96 (m, 2H), 2.94-2.84 (m, 2H), 2.55-2.45 (m, 1H), 2.42-2.36 (m, 2H), 2.34-2.24 (m, 2H), 2.18-2.11 (m, 1H), 2.07-1.99 (m, 2H), 1.97-1.93 (m, 1H), 1.67-1.57 (m, 2H), 1.54-1.44 (m, 6H), 1.27-1.20 (m, 2H), 1.18-1.11 (m, 2H), 0.90 (s, 3H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 221.0, 206.5, 139.9, 136.9, 131.9, 129.8, 126.9 (q, *J* = 278.8 Hz), 126.0, 125.7, 50.6, 48.0, 44.4, 44.2 (q, *J* = 27.3 Hz), 43.4, 42.1 (q, *J* = 4.3 Hz), 38.0, 35.9, 31.6, 31.2, 29.4, 26.5, 25.6, 23.3, 22.4, 21.6, 14.0, 13.9 ppm .

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.90 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{27}H_{35}F_3O_2Na$ [M+Na]$^+$: 449.2662, found: 449.2683.

(2*S*)-2-(6-Methoxynaphthalen-2-yl)-*N*-(3-(1,1,1-trifluoro-4-oxononan-2-yl)phenyl)propanamide (3sa)



The title compound **3ra** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a white solid (61.9 mg, 62%).

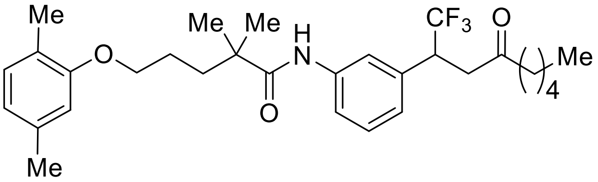
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.79-7.65 (m, 3H), 7.51-7.30 (m, 3H), 7.29-7.26 (m, 1H), 7.23-7.17 (m, 2H), 7.15-7.13 (m, 1H), 7.04-6.97 (m, 1H), 4.02-3.93 (m, 1H), 3.92 (s, 3H), 3.89-3.79 (m, 1H), 3.04-2.95 (m, 2H), 2.42-2.33 (m, 1H), 2.32-2.23 (m, 1H), 1.66 (d, *J* = 7.1 Hz, 3H), 1.50-1.38 (m, 2H), 1.24-1.17 (m, 2H), 1.17-1.08 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.4, 172.6, 158.0, 138.3, 135.9, 135.8, 135.4, 134.0, 129.3, 129.2, 129.1, 128.0, 126.7 (q, *J* = 279.6 Hz), 126.2, 124.9, 124.8, 120.1, 119.6, 105.8, 55.4, 48.2, 44.5 (q, *J* = 27.9 Hz), 43.4, 42.0 (q, *J* = 2.5 Hz), 31.2, 23.2, 22.4, 18.7, 13.9 ppm .

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.78 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{29}H_{32}F_3NO_3Na$ $[M+Na]^+$:522.2226, found: 522.2249.

5-(2,5-Dimethylphenoxy)-2,2-dimethyl-*N*-(3-(1,1,1-trifluoro-4-oxohexan-2-yl)phenyl)pentanamide (3ta)



The title compound **3sa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil, (74.7 mg, 72%).

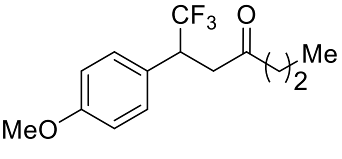
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.54-7.49 (m, 1H), 7.48-7.41 (m, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.60-6.57 (m, 1H), 4.02-3.94 (m, 1H), 3.94-3.88 (m, 2H), 3.03-2.98 (m, 2H), 2.43-2.33 (m, 1H), 2.33-2.27 (m, 1H), 2.26 (s, 3H), 2.15 (s, 3H), 1.84-1.76 (m, 4H), 1.54-1.40 (m, 2H), 1.31 (s, 6H), 1.23-1.18 (m, 2H), 1.16-1.08 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.4, 175.9, 156.9, 138.4, 136.6, 135.4 (q, *J* = 2.0 Hz), 130.4, 129.3, 126.7 (q, *J* = 279.7 Hz), 124.9, 123.5, 120.9, 120.5, 120.0, 112.2, 67.9, 44.5 (q, *J* = 27.7 Hz), 43.3, 42.9, 42.0, 37.7, 31.2, 25.6 (2C), 25.2, 23.3, 22.4, 21.4, 15.9, 13.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.72 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{30}H_{40}F_3NO_3Na$ $[M+Na]^+$: 542.2852, found: 542.2845.

1,1,1-Trifluoro-2-(4-methoxyphenyl)heptan-4-one (3ab)



The title compound **3ab** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a colorless oil (56.2 mg, 74%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.23 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz,

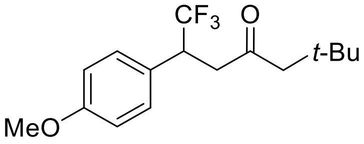
2H), 4.06-3.90 (m, 1H), 3.78 (s, 3H), 3.07-2.93 (m, 2H), 2.38 (dt, *J* = 16.8, 7.4 Hz, 1H), 2.27 (dt, *J* = 16.8, 7.2 Hz, 1H), 1.58-1.45 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.4, 159.5, 130.1 (2C), 126.9 (q, *J* = 279.3 Hz), 126.5 (q, *J* = 2.2 Hz), 114.2 (2C), 55.3, 45.4, 43.9 (q, *J* = 27.7 Hz), 42.3 (q, *J* = 1.9 Hz), 17.0, 13.6 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.30 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{17}F_3O_2Na$ [M+Na]$^+$: 297.1073, found: 403.2298.

1,1,1-Trifluoro-2-(4-methoxyphenyl)-6,6-dimethylheptan-4-one (3ac)



The title compound **3ac** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a colorless oil (51.3 mg, 85%).

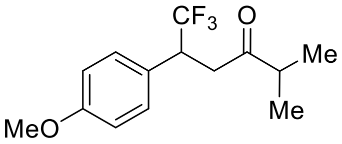
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.25-7.20 (m, 2H), 6.91-6.82 (m, 2H), 4.05-3.89 (m, 1H), 3.78 (s, 3H), 3.08-2.92 (m, 2H), 2.34-2.15 (m, 2H), 0.92 (s, 9H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 206.0, 159.5, 130.1 (2C), 127.0 (q, *J* = 279.3 Hz), 126.6 (q, *J* = 2.1 Hz), 114.1 (2C), 55.5, 55.3, 44.6 (q, *J* = 1.8 Hz), 43.8 (q, *J* = 27.6 Hz), 31.2, 29.6 (3C) ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = –70.15 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{21}F_3O_2Na$ [M+Na]$^+$: 325.1386, found: 325.1389.

6,6,6-Trifluoro-5-(4-methoxyphenyl)-2-methylhexan-3-one (3ad)



The title compound **3ad** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a colorless oil (36.8 mg, 67%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.23 (d, *J* = 8.5 Hz, 1H), 6.86 (d, *J* = 8.7 Hz,

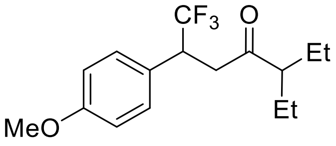
2H), 4.07-3.90 (m, 1H), 3.78 (s, 3H), 3.13-2.92 (m, 2H), 2.59-2.45 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.9, 159.5, 130.1 (2C), 127.0 (q, *J* = 279.3 Hz), 126.6 (q, *J* = 2.1 Hz), 114.1 (2C), 55.3, 44.0 (q, *J* = 27.6 Hz), 41.4, 40.2 (q, *J* = 1.8 Hz), 17.9, 17.8 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.16 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{14}H_{17}F_3O_2Na$ $[M+Na]^+$: 297.1073, found: 297.1088.

5-Ethyl-1,1,1-trifluoro-2-(4-methoxyphenyl)heptan-4-one (3ae)



The title compound **3ae** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a colorless oil (42.3 mg, 70%).

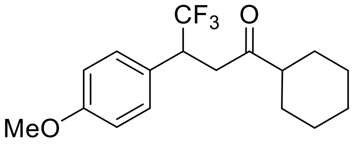
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.26-7.20 (m, 2H), 6.90-6.79 (m, 2H), 4.10-3.92 (m, 1H), 3.78 (s, 3H), 3.07 (dd, *J* = 17.7, 9.3 Hz, 1H), 2.96 (dd, *J* = 17.8, 4.3 Hz, 1H), 2.32-2.21 (m, 1H), 1.59-1.44 (m, 2H), 1.44-1.29 (m, 2H), 0.74 (t, *J* = 7.4 Hz, 3H), 0.63 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.9, 159.5, 130.2 (2C), 127.0 (q, *J* = 279.3 Hz), 126.7 (q, *J* = 2.2 Hz), 114.1 (2C) , 55.8, 55.3, 43.7 (q, *J* = 27.6 Hz), 42.0 (q, *J* = 1.9 Hz), 23.9, 23.8, 11.7, 11.4 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.10 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{21}F_3O_2Na$ $[M+Na]^+$: 325.1386, found: 325.1393.

1-Cyclohexyl-4,4,4-trifluoro-3-(4-methoxyphenyl)butan-1-one (3af)



The title compound **3af** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a white solid (54.0 mg, 86%).

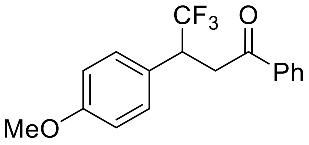
1H NMR (400 MHz, Chloroform-*d*) δ = 7.22 (d, *J* = 8.7 Hz, 2H), 6.89-6.82 (m, 2H), 4.10-3.88 (m, 1H), 3.78 (s, 3H), 3.13-2.92 (m, 2H), 2.33-2.16 (m, 1H), 1.79-1.63 (m, 4H), 1.39-1.09 (m, 6H) ppm.

13C NMR (101 MHz, Chloroform-*d*) δ = 209.2, 159.4, 130.1 (2C), 127.0 (q, *J* = 279.3 Hz), 126.6 (q, *J* = 2.1 Hz), 114.1 (2C), 55.2, 51.1, 43.8 (q, *J* = 27.5 Hz), 40.3 (q, *J* = 1.5 Hz), 28.1 (2C), 25.8, 25.5 (2C) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.15 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{21}F_3O_2Na$ $[M+Na]^+$: 337.1386, found: 337.1384.

4,4,4-Trifluoro-3-(4-methoxyphenyl)-1-phenylbutan-1-one (3ag)



The title compound **3ag** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (46.9 mg, 71%).

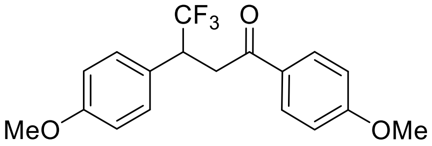
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.96-7.88 (m, 2H), 7.60-7.54 (m, 1H), 7.51-7.42 (m, 2H), 7.36-7.29 (m, 2H), 6.91-6.82 (m, 2H), 4.26-4.15 (m, 1H), 3.77 (s, 3H), 3.68 (dd, *J* = 17.7, 9.3 Hz, 1H), 3.57 (dd, *J* = 17.7, 4.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 195.5, 159.5, 136.4, 133.6, 130.1 (2C), 128.8 (2C) , 128.1 (2C) , 127.1 (q, *J* = 279.3 Hz), 126.6 (q, *J* = 2.0 Hz), 114.1 (2C) , 55.3, 44.1 (q, *J* = 27.6 Hz), 38.4 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.98 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{15}F_3O_2Na$ $[M+Na]^+$: 331.0916, found: 331.0928.

4,4,4-Trifluoro-1,3-bis(4-methoxyphenyl)butan-1-one (3ah)



The title compound **3ah** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a white solid (39.9 mg, 59%).

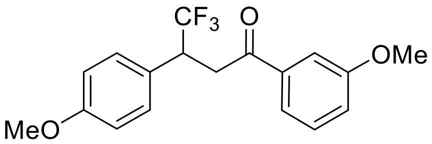
^{1}H NMR (400 MHz, Chloroform-d) δ= 7.90 (d, *J* = 8.9 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.26-4.11 (m, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.61 (dd, *J* = 17.4, 9.4 Hz, 1H), 3.50 (dd, *J* = 17.5, 4.0 Hz, 1H) ppm.

^{13}C NMR 1 (101 MHz, Chloroform-*d*) δ= 194.0, 163.9, 159.5, 130.5 (2C), 130.2 (2C), 129.6, 127.2 (q, J = 279.4 Hz), 126.8 (q, J = 1.9 Hz), 114.2 (2C), 113.9 (2C), 55.6, 55.3, 44.3 (q, J = 27.4 Hz), 38.0 (q, J = 1.8 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = –69.94 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{17}F_3O_3H$ [M+H]$^+$: 339.1203, found: 339.1193.

4,4,4-Trifluoro-1-(3-methoxyphenyl)-3-(4-methoxyphenyl)butan-1-one (3ai)



The title compound **3ai** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a white solid (45.3 mg, 67%).

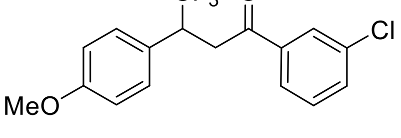
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.55-7.50 (m, 1H), 7.45-7.41 (m, 1H), 7.40-7.34 (m, 1H), 7.34-7.28 (m, 2H), 7.14-7.08 (m, 1H), 6.91-6.84 (m, 2H), 4.24-4.13 (m, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.66 (dd, *J* = 17.7, 9.4 Hz, 1H), 3.55 (dd, *J* = 17.7, 4.0 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 195.4, 160.0, 159.5, 137.8, 130.1 (2C), 129.8, 127.1 (d, *J* = 279.5 Hz), 126.6 (q, *J* = 2.0 Hz), 120.7, 120.1, 114.2 (2C), 112.3, 55.5, 55.3, 44.2 (q, *J* = 27.6 Hz), 38.5 (q, *J* = 2.0 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.98 (s, 3F) ppm

HRMS (ESI) m/z calculated for $C_{18}H_{17}F_3O_3Na$ [M+Na]$^+$: 361.1022, found: 361.1024.

1-(3-Chlorophenyl)-4,4,4-trifluoro-3-(4-methoxyphenyl)butan-1-one (3aj)



The title compound **3aj** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a colorless oil (38.9 mg, 57%).

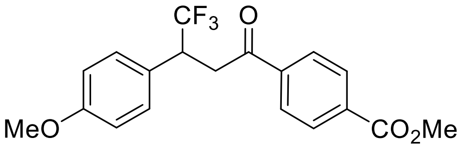
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.91-7.85 (m, 1H), 7.83-7.77 (m, 1H), 7.58-7.50 (m, 1H), 7.44-7.36 (m, 1H), 7.34-7.28 (m, 2H), 6.93-6.76 (m, 2H), 4.23-4.10 (m, 1H), 3.78 (s, 3H), 3.63 (dd, *J* = 17.8, 9.2 Hz, 1H), 3.54 (dd, *J* = 17.8, 4.2 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 194.3, 159.6, 137.9, 135.2, 133.5, 130.1 (3C), 128.2, 127.0 (q, *J* = 279.4 Hz), 126.3 (q, *J* = 2.0 Hz), 126.2, 114.2 (2C), 55.3, 44.14 (q, *J* = 27.6 Hz), 38.6 (q, *J* = 1.9 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.99 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{14}ClF_3O_2Na$ $[M+Na]^+$: 365.0527, found: 365.0537.

Methyl 4-(4,4,4-trifluoro-3-(4-methoxyphenyl)butanoyl)benzoate (3ak)



The title compound **3ak** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (39.5 mg, 54%).

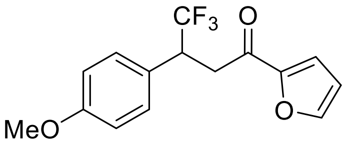
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.13-8.07 (m, 2H), 8.01-7.90 (m, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.90-6.82 (m, 2H), 4.24-4.12 (m, 1H), 3.94 (s, 3H), 3.77 (s, 3H), 3.68 (dd, *J* = 18.0, 9.1 Hz, 1H), 3.59 (dd, *J* = 17.9, 4.2 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 195.1, 166.1, 159.6, 139.5 (2C), 134.3 (2C), 130.1 (2C), 130.0 (2C), 127.0 (q, *J* = 279.4 Hz), 126.3 (q, *J* = 2.0 Hz), 114.2 (2C), 55.31, 52.6, 44.1 (q, *J* = 27.7 Hz), 38.8 (q, *J* = 1.9 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.00 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{17}F_3O_4Na$ $[M+Na]^+$: 389.0971, found: 389.0969.

4,4,4-Trifluoro-1-(furan-2-yl)-3-(4-methoxyphenyl)butan-1-one (3al)



The title compound **3al** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a white solid (22.1 mg, 37%).

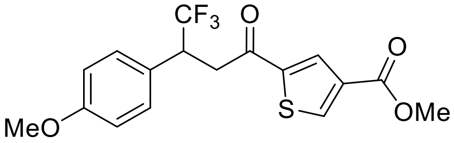
^{1}H NMR (400 MHz, Chloroform-d) δ= 7.59-7.56 (m, 1H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 3.7 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.52 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.23-4.06 (m, 1H), 3.77 (s, 3H), 3.52 (dd, J = 17.2, 9.4 Hz, 1H), 3.41 (dd, *J* = 17.2, 4.5 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ= 184.8, 159.6, 152.4, 146.8, 130.2 (2C), 126.9 (q, J = 279.3 Hz), 126.2 (q, J = 2.4 Hz), 117.6, 114.2 (2C), 112.6, 55.3, 43.9 (q, J = 27.9 Hz), 38.2 (q, J = 2.2 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = –70.18 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{15}H_{13}F_3O_3Na$ [M+Na]+: 321.0709, found: 321.0709.

Methyl 5-(4,4,4-trifluoro-3-(4-methoxyphenyl)butanoyl)thiophene-3-carboxylate (3am)



The title compound **3am** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (30.5 mg, 41%).

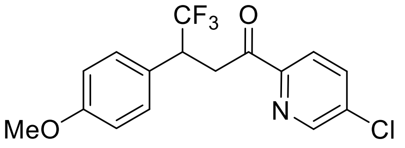
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.36-8.27 (m, 1H), 8.16-8.08 (m, 1H), 7.35-7.27 (m, 2H), 6.97-6.74 (m, 2H), 4.22-4.08 (m, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 3.60 (dd, *J* = 17.3, 9.2 Hz, 1H), 3.51 (dd, *J* = 17.4, 4.5 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 188.4, 162.3, 159.6, 144.2, 139.9, 134.3, 132.3, 130.1 (2C), 126.8 (q, *J* = 279.5 Hz), 126.0 (q, *J* = 1.9 Hz), 114.3 (2C), 55.3, 52.3, 44.1 (q, *J* = 27.9 Hz), 38.8 (q, *J* = 2.0 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.08 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{15}F_3NO_4SNa$ $[M+Na]^+$: 395.0535, found: 395.0538.

1-(5-Chloropyridin-2-yl)-4,4,4-trifluoro-3-(4-methoxyphenyl)butan-1-one (3an)



The title compound **3an** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (33.3 mg, 52%).

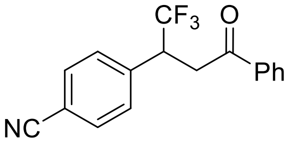
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.94-8.88 (m, 1H), 8.13 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.90-6.83 (m, 2H), 4.21-4.11 (m, 1H), 3.78 (s, 3H), 3.63 (dd, *J* = 17.7, 9.1 Hz, 1H), 3.54 (dd, *J* = 17.8, 4.3 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 193.4, 159.7, 156.2, 149.8, 138.1, 130.6, 130.1(2C) , 126.8 (q, *J* = 279.5 Hz), 126.0 (q, *J* = 1.9 Hz), 124.7, 114.3 (2C) , 55.3, 44.0 (q, *J* = 27.8 Hz), 38.8 (q, *J* = 2.0 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.03 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{16}H_{13}ClF_3NO_2Na$ $[M+Na]^+$: 344.0660, found: 344.0662

4-(1,1,1-Trifluoro-4-oxo-4-phenylbutan-2-yl)benzonitrile (3kg)



The title compound **3kg** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a white solid (41.2 mg, 68%).

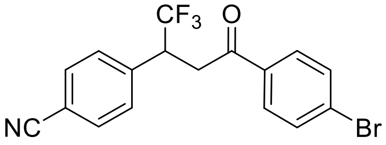
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.94-7.86 (m, 2H), 7.67-7.62 (m, 2H), 7.61-7.56 (m, 1H), 7.55-7.51 (m, 2H), 7.50-7.43 (m, 2H), 4.38-4.19 (m, 1H), 3.72 (dd, *J* = 18.1, 9.4 Hz, 1H), 3.65 (dd, *J* = 18.1, 4.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 194.7, 139.9 (q, *J* = 1.9 Hz), 135.8, 134.0, 132.5 (2C), 130.0 (2C) , 128.9 (2C) , 128.1 (2C) , 126.4 (q, *J* = 279.7 Hz), 118.4, 112.5, 45.0 (q, *J* = 27.9 Hz), 38.0 (q, *J* = 1.9 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.22 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{21}F_3NONa$ $[M+Na]^+$: 326.0763, found: 326.0767.

4-(4-(4-Bromophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)benzonitrile (3ko)



The title compound **3ko** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (44.8 mg, 59%).

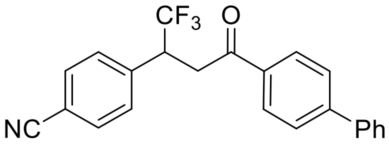
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.82-7.72 (m, 2H), 7.67-7.59 (m, 4H), 7.55-7.50 (m, 2H), 4.35-4.21 (m, 1H), 3.73-3.57 (m, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 193.7, 139.7 (q, *J* = 1.9 Hz), 134.5, 132.6 (2C), 132.3 (2C), 130.0 (2C), 129.6 (2C), 129.3, 126.4 (q, *J* = 279.8 Hz), 118.3, 112.6, 45.0 (q, *J* = 27.9 Hz), 38.0 (q, *J* = 1.9 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.22 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{11}BrF_3NO_2Na$ $[M+Na]^+$: 403.9868, found: 403.9857.

4-(4-([1,1'-Biphenyl]-4-yl)-1,1,1-trifluoro-4-oxobutan-2-yl)benzonitrile (3kp)



The title compound **3kp** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a colorless oil (58.4 mg, 77%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.02-7.96 (m, 2H), 7.72-7.59 (m, 6H), 7.56-7.52 (m, 2H), 7.50-7.45 (m, 2H), 7.44-7.40 (m, 1H), 4.40-4.26 (m, 1H), 3.75 (dd, *J* =

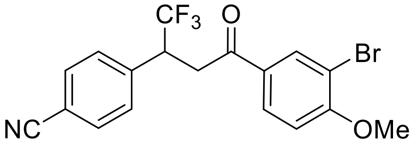
18.0, 9.5 Hz, 1H), 3.67 (dd, *J* = 18.0, 3.9 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 194.2, 146.6, 139.8 (q, *J* = 1.9 Hz), 139.4, 134.4, 132.5 (2C) , 130.0, 129.0 (2C) , 128.6 (2C) , 128.5 (2C) , 127.4 (2C), 127.2 (2C) , 126.4 (q, *J* = 279.6 Hz), 118.3, 112.4, 45.0 (q, *J* = 27.8 Hz), 38.0 (q, *J* = 1.9 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.16 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{16}F_3NONa$ [M+Na]$^+$: 402.1076, found: 402.1087.

4-(4-(3-Bromo-4-methoxyphenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)benzonitrile (3kq)



The title compound **3kq** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a colorless oil (37.1 mg, 45%).

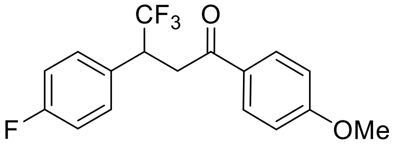
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.10 (d, *J* = 2.2 Hz, 1H), 7.87 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.66-7.61 (m, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 6.96-6.88 (m, 1H), 4.32-4.21 (m, 1H), 3.95 (s, 3H), 3.64 (dd, *J* = 18.0, 9.5 Hz, 1H), 3.56 (dd, *J* = 18.0, 4.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 192.1, 160.2, 139.8 (q, *J* = 2.1 Hz), 133.6, 132.5 (2C), 130.0 (2C) , 129.8, 129.39 , 126.4 (q, *J* = 279.6 Hz), 118.4, 112.5, 112.2, 111.3, 56.7 , 45.0 (q, *J* = 27.9 Hz), 37.7 (q, *J* = 1.7 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.17 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{13}BrF_3NO_2Na$ [M+Na]$^+$: 433.9974, found: 433.9975.

4,4,4-Trifluoro-3-(4-fluorophenyl)-1-(4-methoxyphenyl)butan-1-one (3uh)



The title compound **3ua** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a colorless oil (51.1 mg, 84%).

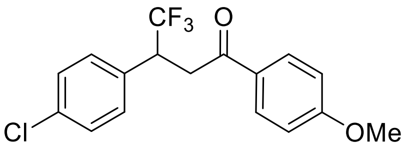
^{1}H NMR (400 MHz, Chloroform-d) δ= 7.91 (d, *J* = 8.9 Hz, 2H), 7.41-7.32 (m, 2H), 7.06-6.98 (m, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.27-4.16 (m, 1H), 3.86 (s, 3H), 3.63 (dd, *J* = 17.5, 9.5 Hz, 1H), 3.52 (dd, *J* = 17.6, 3.9 Hz, 1H) ppm.

^{13}C NMR 13C NMR (101 MHz, Chloroform-d) δ= 193.7, 164.1, 162.7 (d, *J* = 247.0 Hz), 130.8 (d, *J* = 8.3 Hz, 2C), 130.6 (q, *J* = 1.8 Hz), 130.5 (2C), 129.4, 127.0 (q, *J* = 279.3 Hz), 115.8 (d, *J* = 21.6 Hz, 2C), 114.0 (2C), 55.6, 44.4 (q, J = 27.6 Hz), 38.0 (q, *J* = 1.3 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ= −69.84 (s, 3F), −113.88 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{14}F_4O_2Na$ $[M+Na]^+$: 327.1003, found: 327.0993.

3-(4-Chlorophenyl)-4,4,4-trifluoro-1-(4-methoxyphenyl)butan-1-one (3vh)



The title compound **3va** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a white solid (51.3 mg, 75%).

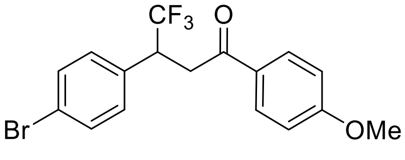
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.97-7.83 (m, 2H), 7.37-7.26 (m, 4H), 6.96-6.88 (m, 2H), 4.28-4.16 (m, 1H), 3.86 (s, 3H), 3.62 (dd, *J* = 17.6, 9.6 Hz, 1H), 3.52 (dd, *J* = 17.6, 3.9 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 193.5, 164.0, 134.3, 133.3 (q, *J* = 2.0 Hz), 130.4 (3C), 129.3 (2C) , 129.0 (2C), 126.9 (q, *J* = 279.4 Hz), 114.0 (2C), 55.6, 44.5 (q, *J* = 27.6 Hz), 37.8 (q, *J* = 1.9 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.66 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{14}ClF_3O_2Na$ $[M+Na]^+$: 365.0527, found: 365.0520.

3-(4-Bromophenyl)-4,4,4-trifluoro-1-(4-methoxyphenyl)butan-1-one (3wh)



The title compound **3wa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a white solid (60.2 mg, 78%).

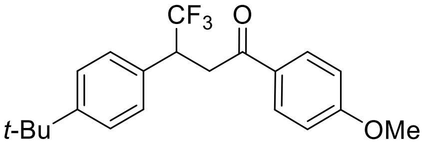
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.94-7.86 (m, 2H), 7.49-7.43 (m, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 6.95-6.89 (m, 2H), 4.24-4.14 (m, 1H), 3.86 (s, 3H), 3.62 (dd, *J* = 17.6, 9.6 Hz, 1H), 3.52 (dd, *J* = 17.6, 3.9 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 193.5, 164.0, 133.8 (q, *J* = 2.0 Hz), 131.9 (2C), 130.8 2C) , 130.4 (2C) , 129.3, 126.8 (q, *J* = 279.5 Hz), 122.5, 114.0 (2C), 55.6, 44.6 (q, *J* = 27.6 Hz), 37.7 (q, *J* = 1.9 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = –69.62 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{14}BrF_3O_2Na$ $[M+Na]^+$: 409.0021, found: 409.0027.

3-(4-(*tert*-Butyl)phenyl)-4,4,4-trifluoro-1-(4-methoxyphenyl)butan-1-one (3xh)



The title compound **3xa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) as a white solid (63.3 mg, 87%).

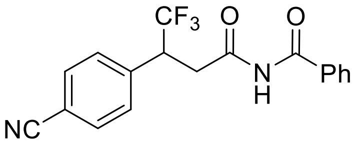
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.99-7.84 (m, 2H), 7.40-7.29 (m, 4H), 6.95-6.89 (m, 2H), 4.32-4.17 (m, 1H), 3.85 (s, 3H), 3.64 (dd, *J* = 17.6, 8.9 Hz, 1H), 3.54 (dd, *J* = 17.6, 4.2 Hz, 1H), 1.29 (s, 9H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 193.9, 163.8, 151.1, 131.7, 130.4 (q, *J* = 2.0 Hz), 129.5 (2C), 128.7 (2C), 127.2 (d, *J* = 279.5 Hz), 125.7 (2C), 113.9 (2C), 55.5, 44.3 (q, *J* = 27.2 Hz), 37.9 (q, *J* = 1.9 Hz), 34.5, 31.3 (3C) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.59 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{23}F_2O_2Na$ $[M+Na]^+$: 387.1542, found: 387.1545.

N-(3-(4-Cyanophenyl)-4,4,4-trifluorobutanoyl)benzamide (3ar)



The title compound **3ao** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) as a white solid (18.0 mg, 26%).

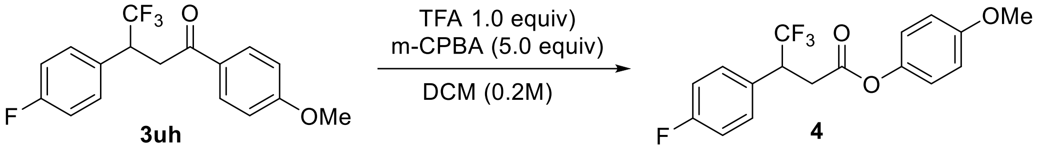
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.67-7.61 (m, 2H), 7.53 (s, 1H), 7.51-7.45 (m, 2H), 7.40-7.35 (m, 2H), 7.31-7.26 (m, 2H), 7.14-7.09 (m, 1H), 4.27-4.12 (m, 1H), 3.13 (dd, *J* = 15.7, 4.4 Hz, 1H), 2.87 (dd, *J* = 15.6, 9.9 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 166.4, 139.4 (q, *J* = 1.7 Hz), 137.1, 132.6 (2C), 129.9 (2C), 129.2 (2C), 126.2 (q, *J* = 279.9 Hz), 125.0 (2C), 120.1 (2C), 118.4, 112.6, 46.1 (q, *J* = 28.1 Hz), 36.7 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.34 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{13}F_3N_2O_2Na$ $[M+Na]^+$: 369.0821, found: 369.0830.

Procedures for Derivatizations



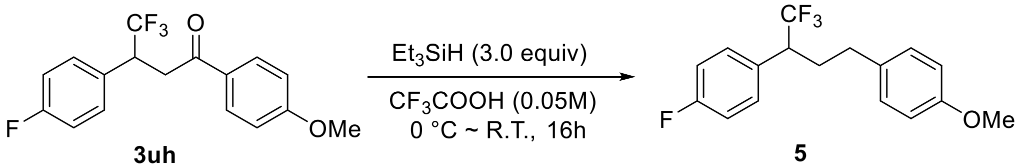
A mixture of **3uh** (65.1 mg, 0.2 mmol, 1.0 equiv), *m*-CPBA (202 mg, 1.0 mmol, 5.0 equiv, 85%) and TFA (23 mg, 0.2 mmol, 1.0 equiv) in DCM (1 mL) was stirred at room temperature for 12 h. The solvent was concentrated under reduced pressure. The residue was purified by column chromatography over silica gel (5% EtOAc in petroleum ether) to give the ester **4** as a pale yellow oil in 84% yield (57.4 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.43-7.33 (m, 2H), 7.12-7.05 (m, 2H), 6.86-6.79 (m, 2H), 6.79-6.72 (m, 2H), 4.05-3.96 (m, 1H), 3.77 (s, 3H), 3.26 (dd, *J* = 16.1, 5.1 Hz, 1H), 3.09 (dd, *J* = 16.1, 10.2 Hz, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d)* δ = 168.8, 162.9 (d, *J* = 248.0 Hz), 157.5, 143.7, 130.7 (d, *J* = 8.4 Hz, 2C), 129.2 (q, *J* = 2.1 Hz), 126.1 (d, *J* = 278.9 Hz, 2C), 121.9 (2C), 115.9 (d, *J* = 21.7 Hz), 114.5 (2C), 55.6, 45.7 (q, *J* = 28.2 Hz), 34.6 (d, *J* = 2.4 Hz). ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.53 (s, 3F), –112.95 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{14}F_4O_3Na$ $[M+Na]^+$: 365.0771, found: 365.0761.



A flame dried flask was charged with **3uh** (32.6 mg, 0.1 mmol, 1.0 equiv), and CF_3COOH (3.6 mL) was added under N_2 atmosphere. The resulting suspension was cooled to 0 °C and Et_3SiH (34.8 mg, 0.3 mmol, 3.0 equiv) was added dropwise. After the resulting orange solution was stirred for 10 minutes at 0 °C, the cooling bath was removed. The solution was allowed to warm to room temperature and stirred overnight.

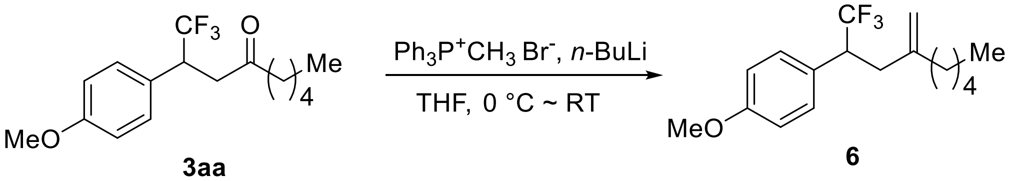
The solvent was concentrated under reduced pressure. The residue was purified through column chromatography over silica gel (5% EtOAc in petroleum ether) to give the desired product **5** as a pale yellow oil in 82% yield (25.6 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.31-7.24 (m, 2H), 7.13-7.06 (m, 2H), 7.02-6.97 (m, 2H), 6.87-6.80 (m, 2H), 3.80 (s, 3H), 3.30-3.10 (m, 1H), 2.60-2.48 (m, 1H), 2.41-2.24 (m, 2H), 2.23-2.07 (m, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d)* δ = 162.7 (d, *J* = 247.0 Hz), 158.3, 132.4, 130.9 (d, *J* = 8.1 Hz, 2C), 130.3 (q, *J* = 2.6 Hz), 129.4 (2C), 126.9 (q, *J* = 279.8 Hz), 115.9 (d, *J* = 21.5 Hz, 2C), 114.1 (2C), 55.4, 48.4 (q, *J* = 26.7 Hz), 31.57 , 30.40 (q, *J* = 2.2 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = –69.62 (s, 3F), –114.24 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{16}F_4ONa$ $[M+Na]^+$: 335.1029, found: 335.1035.



A flame dried flask was charged with methyl triphenylphosphonium bromide (214 mg, 0.6 mmol, 3 equiv), and THF (1 mL) was added under N_2 atmosphere. The resulting suspension was cooled to 0 °C, and *n*-BuLi (0.2 mL, 0.5 mmol, 2.5 equiv, 2.5 M solution in THF) was added dropwise. After the resulting orange solution was stirred for 30 minutes, a solution of **3aa** (60.4 mg, 0.2 mmol, 1 equiv) in THF (0.5 mL) was added to the reaction mixture. The cooling bath was removed, and the solution was allowed to warm to room temperature. After 24 h the reaction was quenched with aq. NH_4Cl (sat.). The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography over silica gel (3% EtOAc in petroleum ether) to give the desired styrene **6** as a pale yellow oil in 72% yield (43.2 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.19 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz,

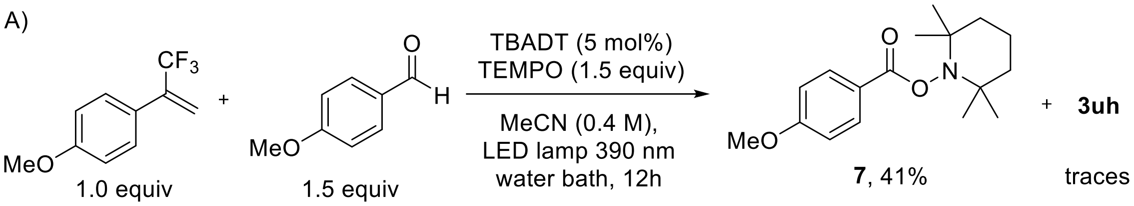
2H), 4.73-4.66 (m, 1H), 4.63-4.57 (m, 1H), 3.80 (s, 3H), 3.50-3.30 (m, 1H), 2.72 (dd, *J* = 14.7, 4.0 Hz, 1H), 2.55 (dd, *J* = 14.7, 11.3 Hz, 1H), 1.96-1.82 (m, 2H), 1.41-1.34 (m, 2H), 1.30-1.24 (m, 2H), 1.23-1.16 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 159.3, 144.8, 130.1 (2C), 126.9 (q, *J* = 279.9 Hz), 126.4, 113.9 (2C), 112.4, 55.2, 47.7 (q, *J* = 26.1 Hz), 35.6, 34.9, 31.4, 27.1, 22.5, 14.0 ppm.

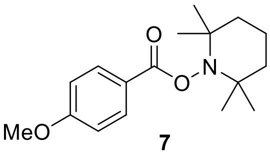
^{19}F NMR (376 MHz, Chloroform-*d*) δ = –70.15 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{23}F_3ONa$ $[M+Na]^+$: 323.1593, found: 323.1599.

Control Experiments.



2,2,6,6-Tetramethylpiperidin-1-yl 4-methoxybenzoate (7)



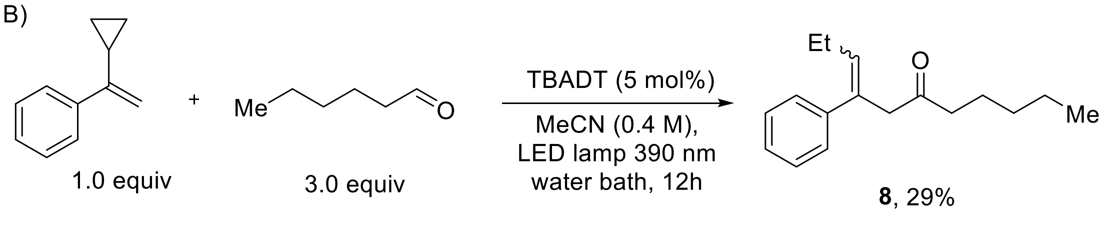
7

The title compound **7** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 10:1) as a yellow solid in 41% yield (23.9 mg)

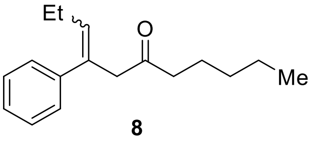
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.03 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 1.79-1.72 (m, 2H), 1.71-1.64 (m, 1H), 1.61-1.54 (m, 2H), 1.48-1.41 (m, 1H), 1.26 (s, 6H), 1.10 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 166.3, 163.4, 131.7 (2C), 122.1, 113.8 (2C), 60.5 (2C), 55.6, 39.2 (2C), 32.1 (2C), 21.0 (2C), 17.2 ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{15}NO_3Na$ [M+Na]$^+$: 314.1727, found: 314.1438.



4-Phenylundec-3-en-6-one (8)



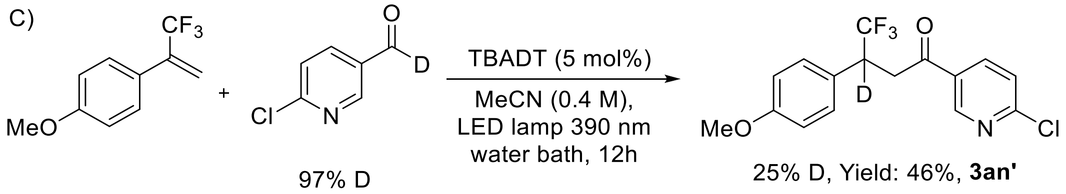
8

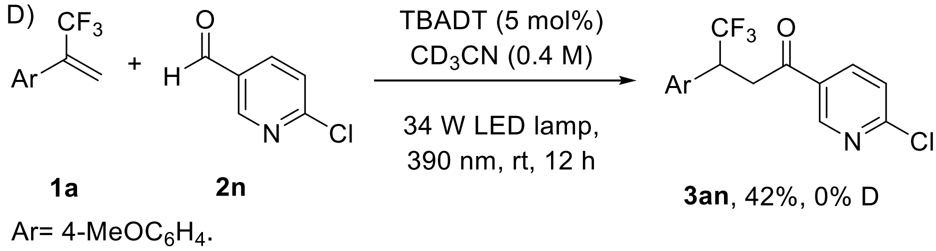
The title compound **8** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate 50:1) as a yellow oil in 29% yield (14.2 mg)

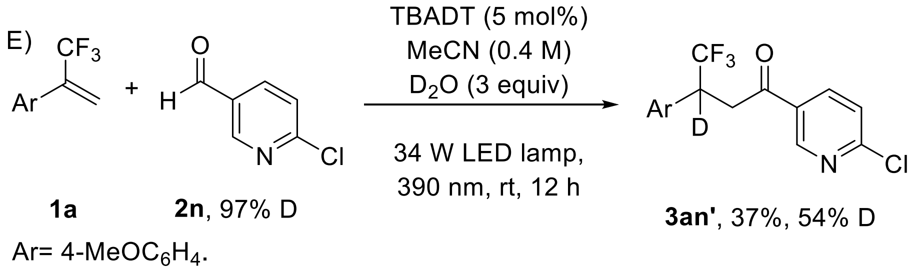
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.35-7.20 (m, 5H), 5.95 (t, *J* = 7.2 Hz, 1H), 3.57 (s, 2H), 2.37 (t, *J* = 7.4 Hz, 2H), 2.24-2.14 (m, 2H), 1.54-1.45 (m, 2H), 1.25-1.20 (m, 2H), 1.20-1.13 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 209.0, 142.5, 134.4, 132.5, 128.5 (2C), 127.0, 126.1 (2C), 45.2, 41.9, 31.4, 23.6, 22.6 (2C), 14.1 (2C) ppm.

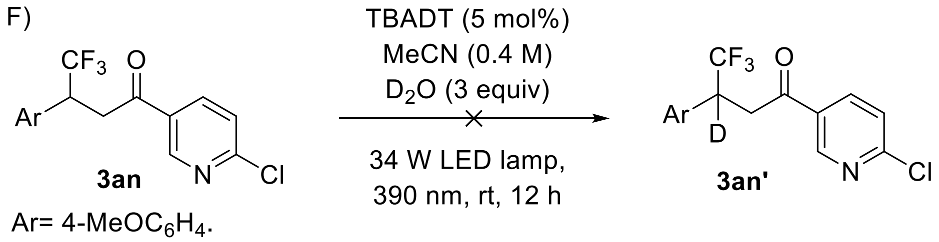
HRMS (ESI) m/z calculated for $C_{17}H_{24}ONa$ $[M+Na]^{+}$: 267.1719, found: 267.1725.







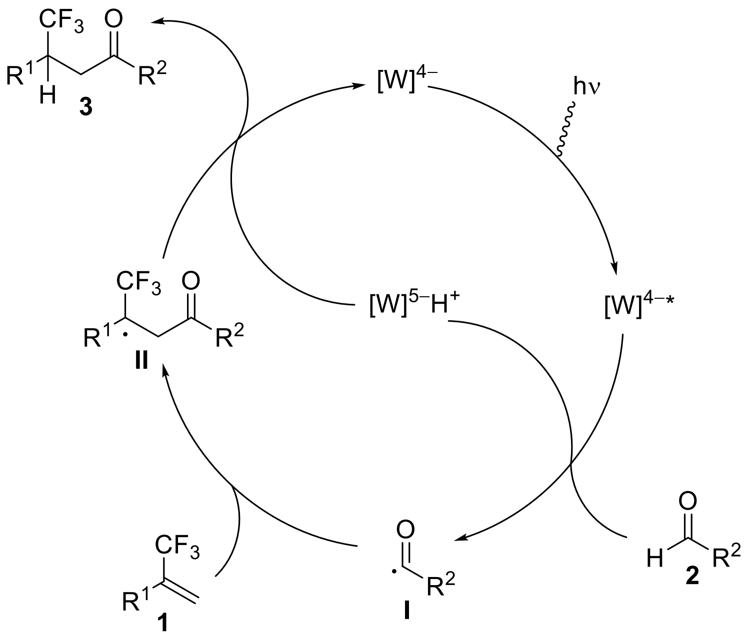
For 1H-spectra of **3an**’ used for determination of deuterium incorporation, see Page S136.



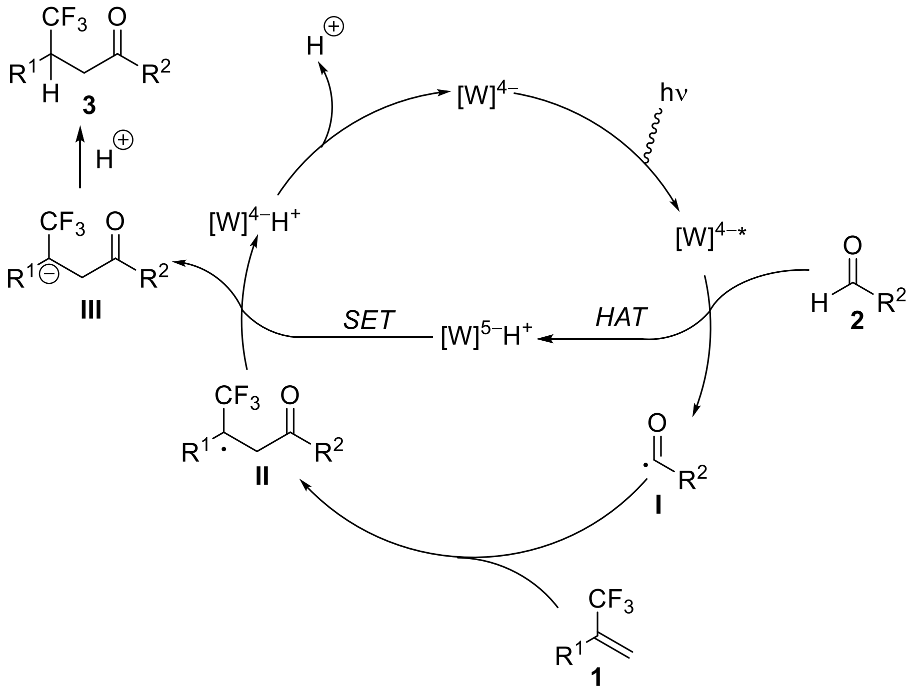
Discussion: It is known that TBADT is able to promote the hydroacylation of aldehydes to olefins via homolytic acyl C-H bond cleavage when irradiating with near-UV light.

We wonder if the same process occurs in our reaction. Therefore, a series of control experiments were carried out to gain some insight into the mechanism of this studied hydroacylation. In the presence of TEMPO as radical scavenger the hydroacylation was effectively inhibited, and the TEMPO adduct to the aldehyde was afforded in a moderate yield (Scheme A). Furthermore, a radical clock reaction involving α-cyclopropyl styrene was performed under the standard reaction conditions (Scheme B). In this case, the formation of the ring opening product **8** was observed. The results mentioned above indicate the formation of acyl radicals in this photocatalytic hydroacylation reaction. Moreover, the reaction between the trifluoromethyl alkene **1a** and deuterated 6-chloronicotinaldehyde (**2n'**) furnished the hydroacylation product **3an'** with 25% deuterium incorporation (Scheme C). This observation suggests that the upcoming hydrogen to the β-position of the carbonyl group in product likely originates from the aldehyde precursor. However, the low deuterium incorporation raised doubt whether another reaction pathway exists for the studied reaction. First, the reaction using the aldehyde **2n** with CD_3CN as solvent provided no deuterated product, ruling out the H/D-exchange between the solvent and the reaction intermediates or the final product (Scheme D). Next, we suspected that trace of water in the solvent gave rise to the low deuterium incorporation. Therefore, a reaction employing the aldehyde **2n** with 3 equiv D_2O as additive was performed in MeCN, yielding the product with 54% deuterium incorporation (Scheme E). In addition, treatment of compound **3an** with D_2O under the standard reaction conditions did not lead to the formation of its deuterium analogue **3an'** (Scheme F). These results confirm that water is probably engaged in the reaction pathway, but does not interact with the final product via H/D-exchange. The involvement of water in this reaction could be reasoned by the proton-exchange between water and the protonated decatungstate intermediate. However, the formation of α-CF_3-carbanion through SET followed by protonation by water cannot be excluded at this stage.

Possible Reaction Mechanism.



Mechanism A: Initially, under irradiation TBADT is activated to its excited state $[W]^{4-}*$, which is capable of abstracting the acyl hydrogen atom from the aldehydes **2**, affording $[W]^{5-}H^+$ and the acyl radical **I**. Next, the resultant radical **I** undergoes nucleophilic addition to the electron-deficient trifluoromethyl alkenes **1** on the less-substituted site, to generate the α-CF_3 carbon-centered radical **II**. Subsequently, the resultant radical **II** abstracts the hydrogen atom from $[W]^{5-}H^+$, to furnish the targeted product **3** with the simultaneous release of the catalyst $[W]^{4-}$ for the next catalytic cycle.



Mechanism B: Initially, under irradiation TBADT is activated to its excited state $[W]^{4-}*$, which is capable of abstracting the acyl hydrogen atom from the aldehydes **2**, affording $[W]^{5-}H^+$ and the acyl radical **I**. Next, the resultant radical **I** undergoes nucleophilic addition to the electron-deficient trifluoromethyl alkenes **1** on the less-substituted site, to generate the α-CF_3 carbon-centered radical **II**. Subsequently, the polar crossover of the radical **II** with $[W]^{5-}H^+$ furnishes the targeted product **3** and $[W]^{4-}H^+$. Deprotonation of the latter regenerates the catalyst $[W]^{4-}$ for the next catalytic cycle.

Reference

1. I. B. Perry, T. F. Brewer, P. J. Sarver, D. M. Schultz, D. A. Dirocco, D. W. C. MacMillan, Direct Arylation of Strong Aliphatic C–H Bonds. *Nature,* **2018**, *560*, 70−75.
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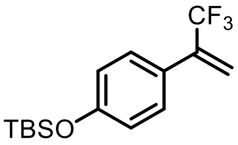
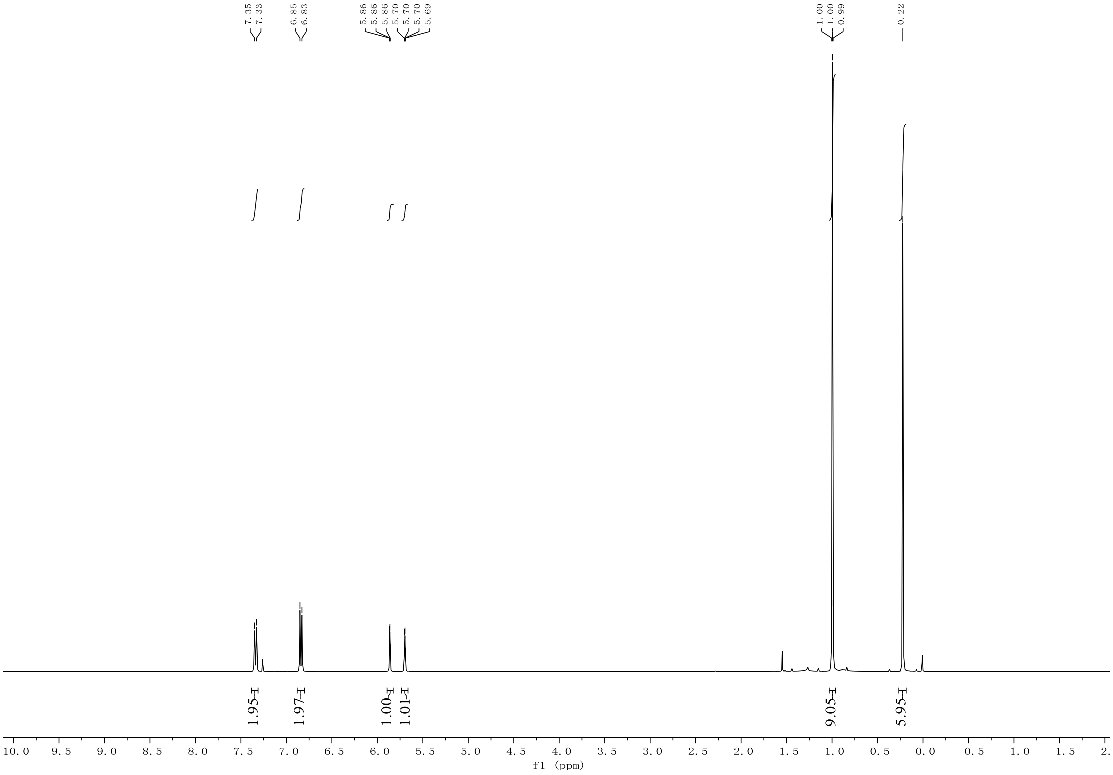
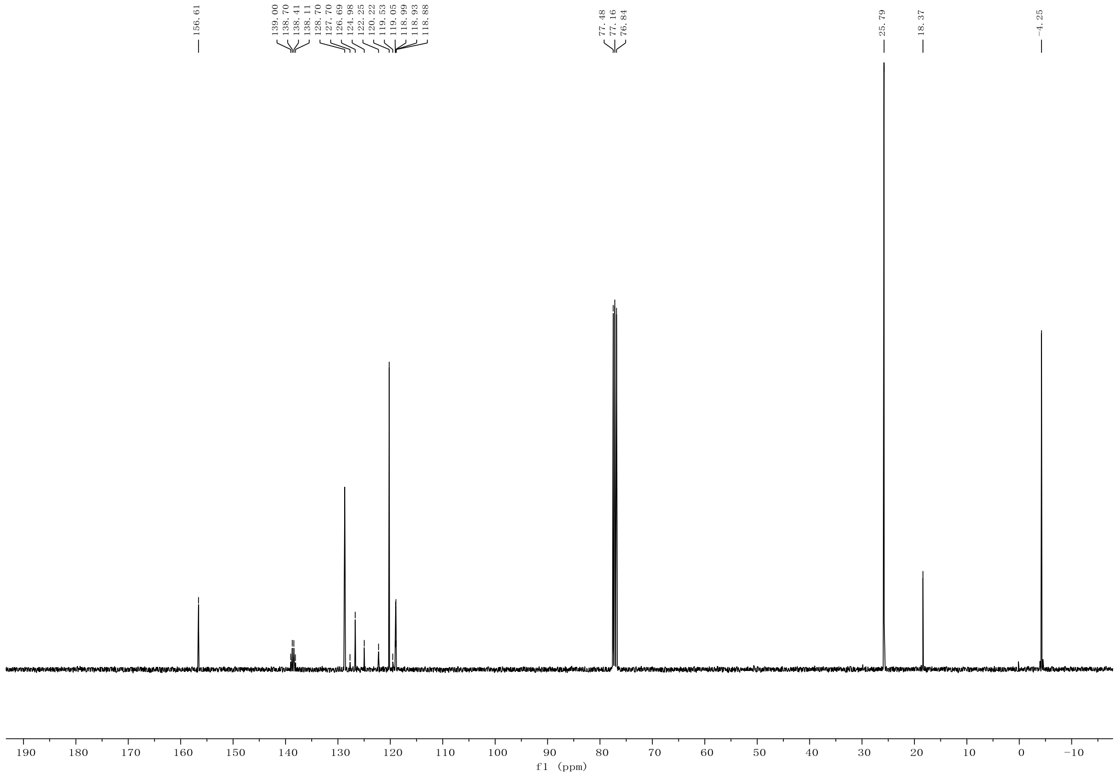
3. Y. Lan, F. Yang, C. Wang, Synthesis of *gem*-Difluoroalkenes via Nickel-Catalyzed Allylic Defluorinative Reductive Cross-Coupling. *ACS Catal*. **2018**, *8*, 9245−9251.
4. Z. Lin, Y. Lan, C. Wang, Synthesis of *gem*-Difluoroalkenes via Nickel-Catalyzed Reductive C–F and C–O Bond Cleavage. *ACS Catal*. **2019**, *9*, 775−780.
5. S. B. Lang, R. J. Wiles, C. B. Kelly, Molander, G. A. Photoredox Generation of Carbon-Centered Radicals Enables the Construction of 1,1-Difluoroalkene Carbonyl Mimics. *Angew. Chem. Int. Ed*. **2017**, *56*, 15073-15707.
6. M. Tomoya, I. Yoshiteru, M. Masahiro, Synthesis of *gem*-Difluoroalkenes via β-Fluoride Elimination of Organorhodium(I). *Chem. Lett*. **2008**, *37*, 1006−1007.
7. D. M. Rudzinski, C. B. Kellya, N. E. Leadbeater, A. Weinreb, Amide Approach to the Synthesis of Trifluoromethylketones. *Chem. Commun*. **2012**, *48*, 9610−9612.

^{1}H, ^{13}C and ^{19}F-spectra

1-(4-Methoxyphenyl)-3-(trifluoromethyl)decan-5-one (1g)



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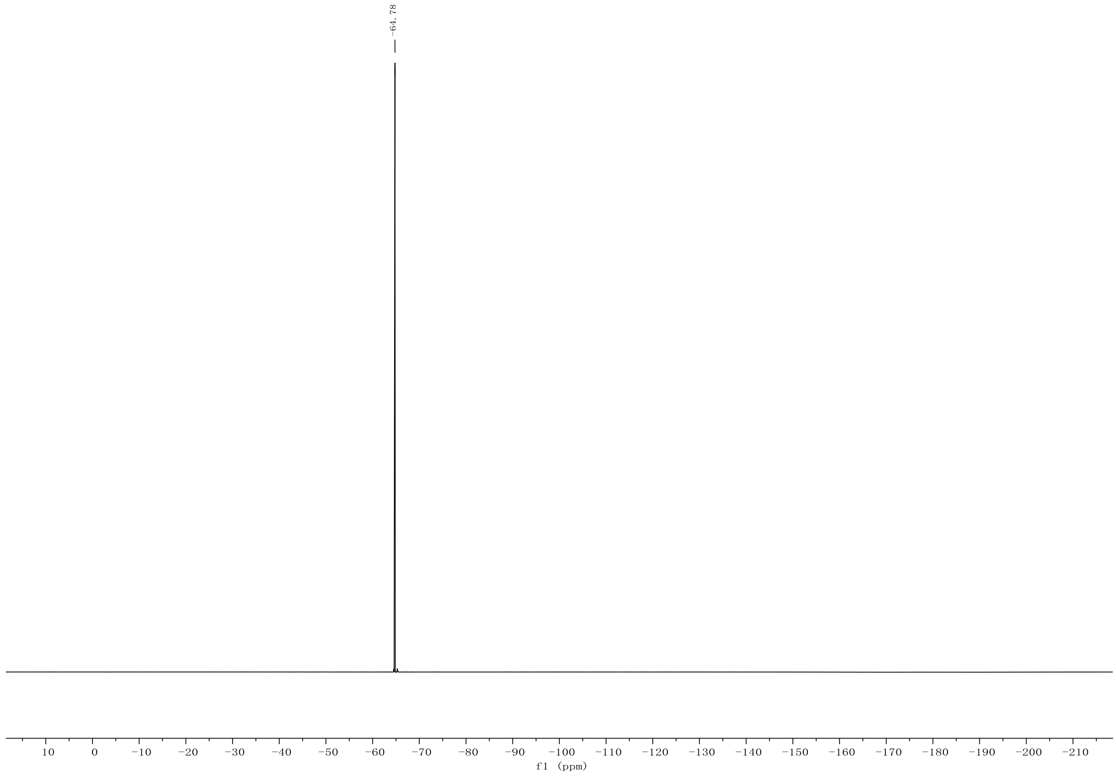
138.70
138.41
138.11
128.70
127.70
126.69
124.98
122.25
120.22
119.53
119.05
118.99
118.93
118.88
77.48
77.16
76.84
25.79
18.37
−4.25
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


−64.78
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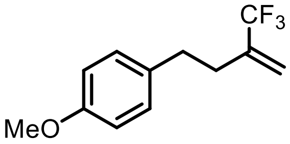
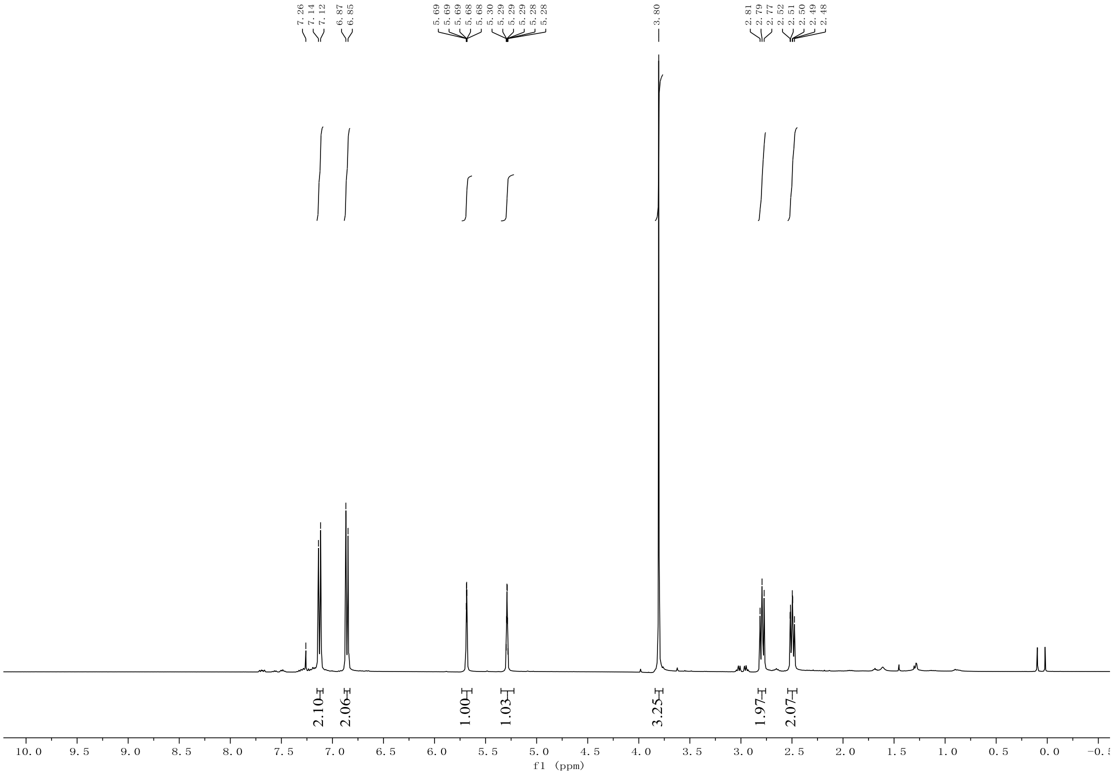
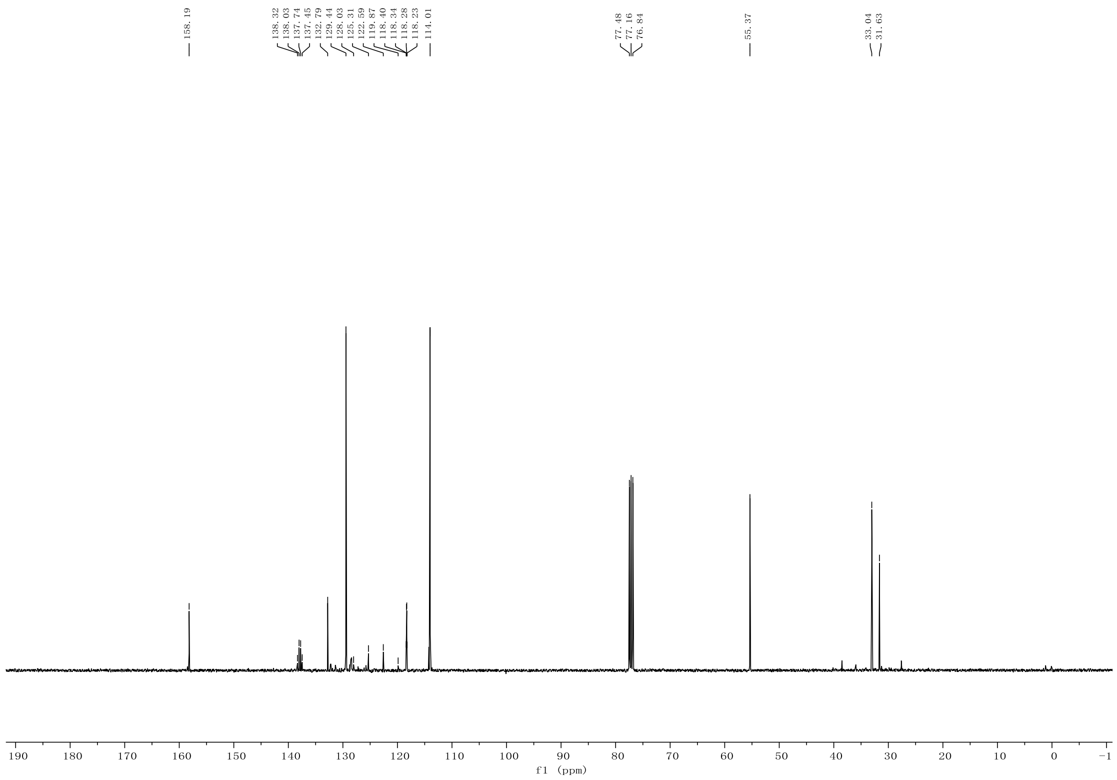
f1 (ppm)

1-(4-Methoxyphenyl)-3-(trifluoromethyl)decan-5-one (1q)



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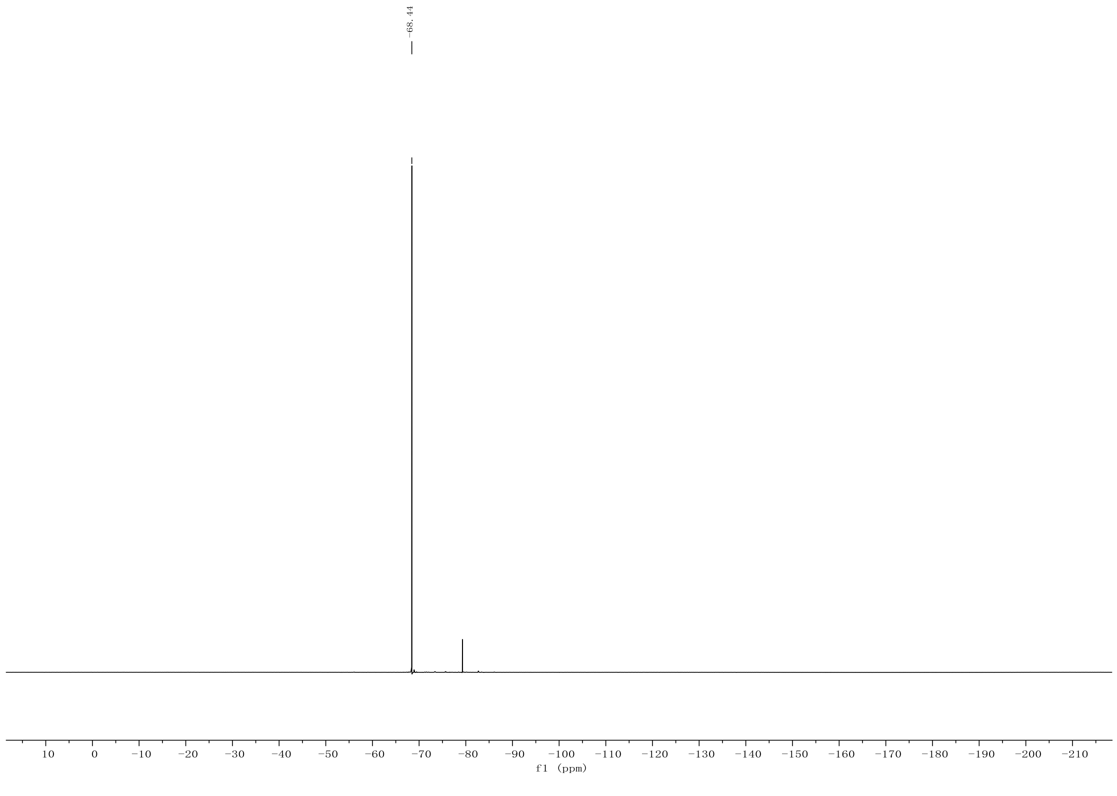
129.44
128.03
125.31
122.59
119.87
118.40
118.34
118.28
118.23
114.01
77.48
77.16
76.84
55.37
33.04
31.63
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


-68.44
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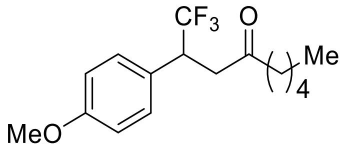
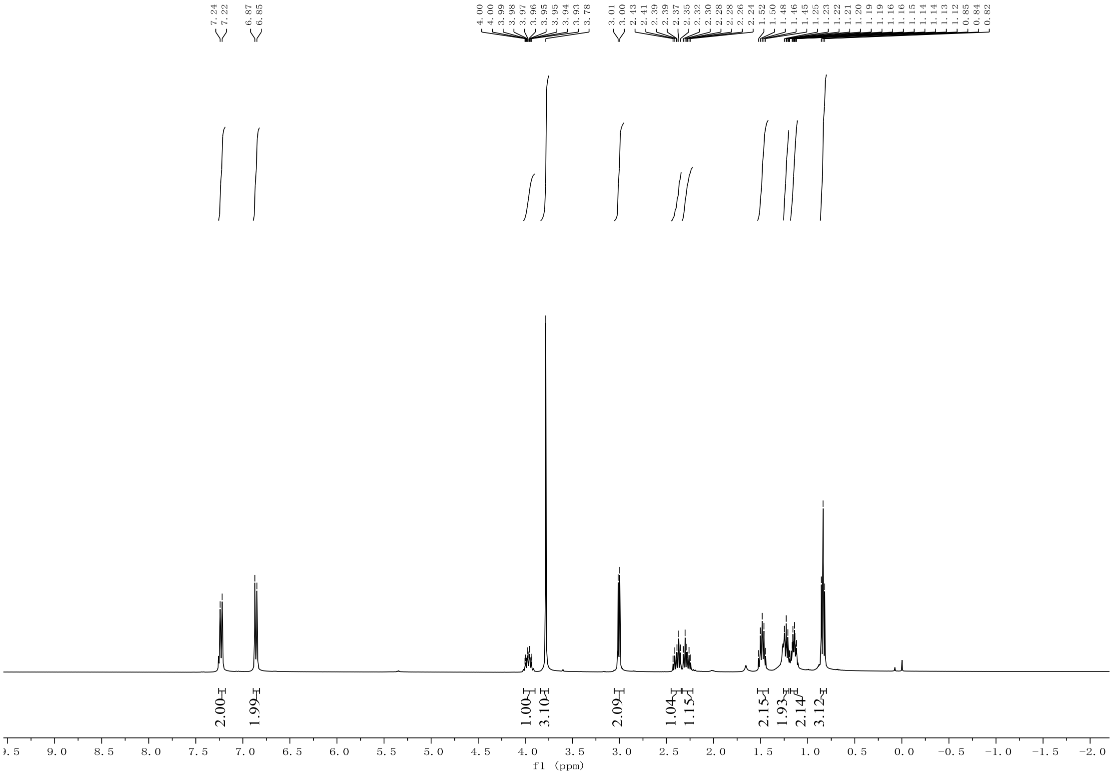
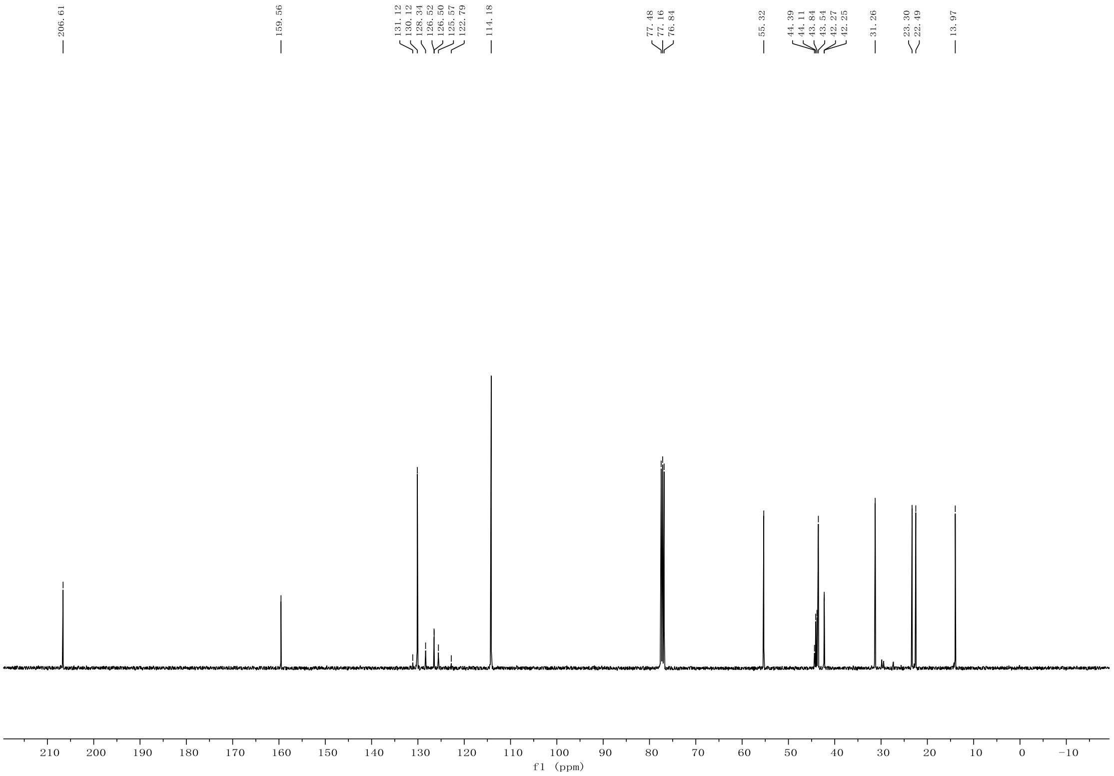
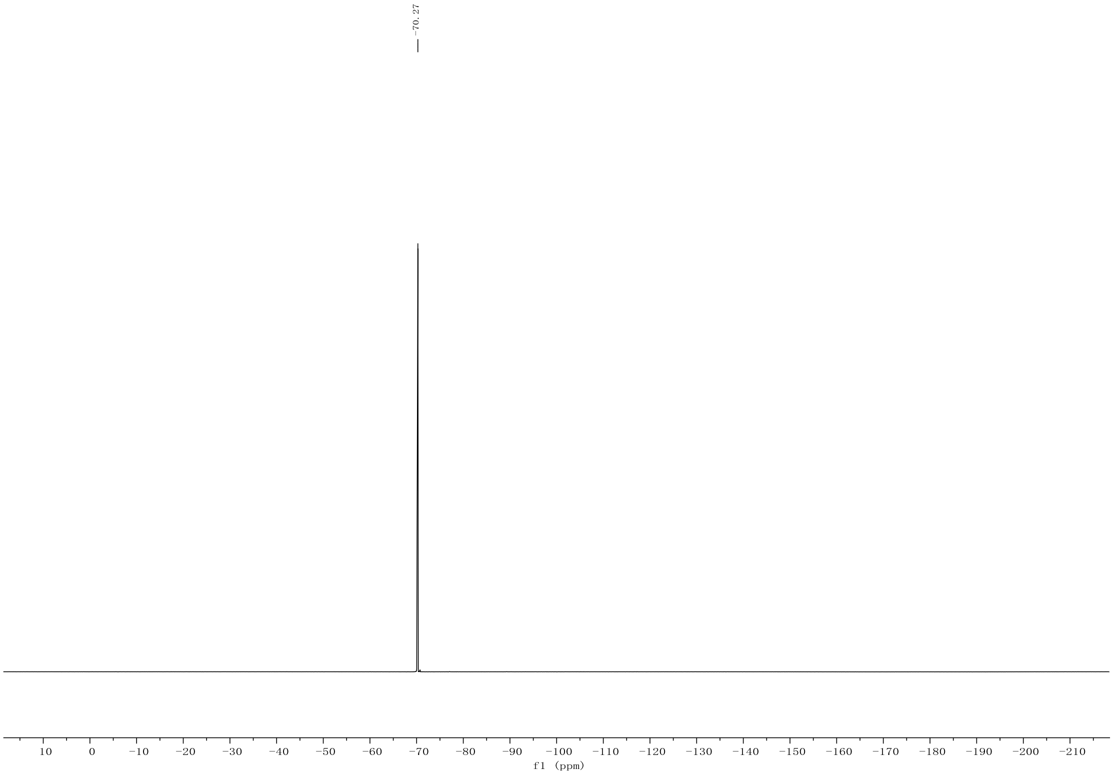
f1 (ppm)

1,1,1-Trifluoro-2-(4-methoxyphenyl)nonan-4-one (3aa)





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-110
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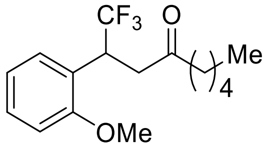
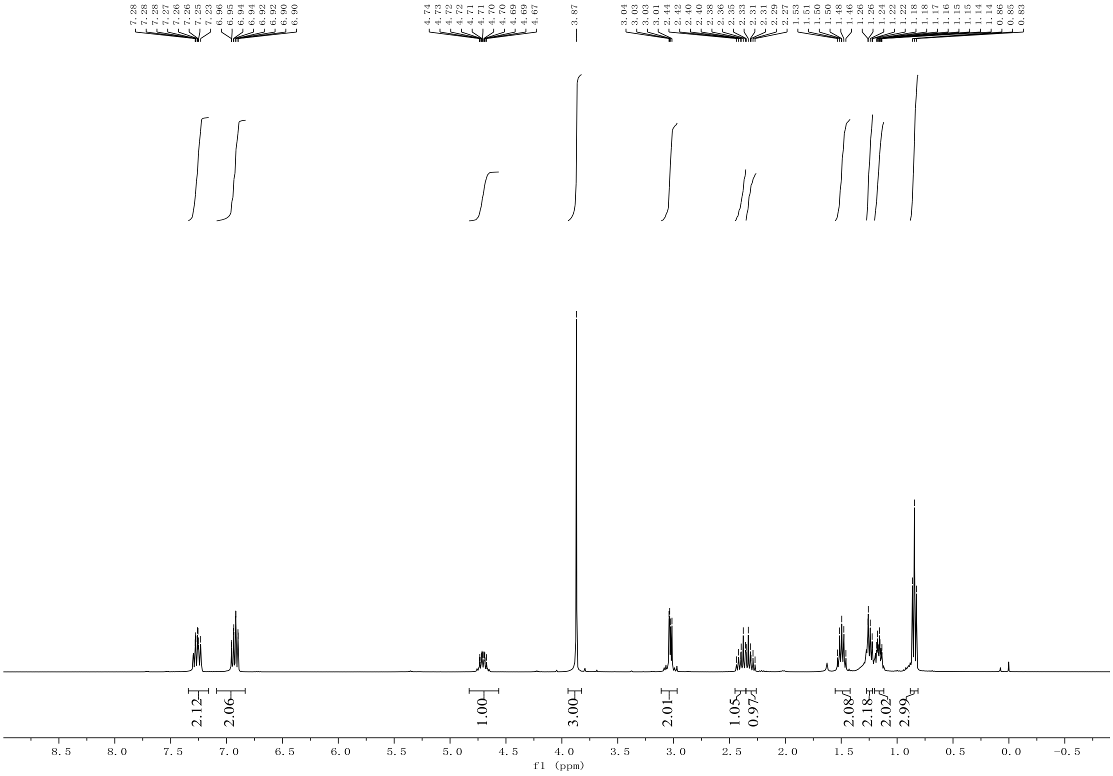
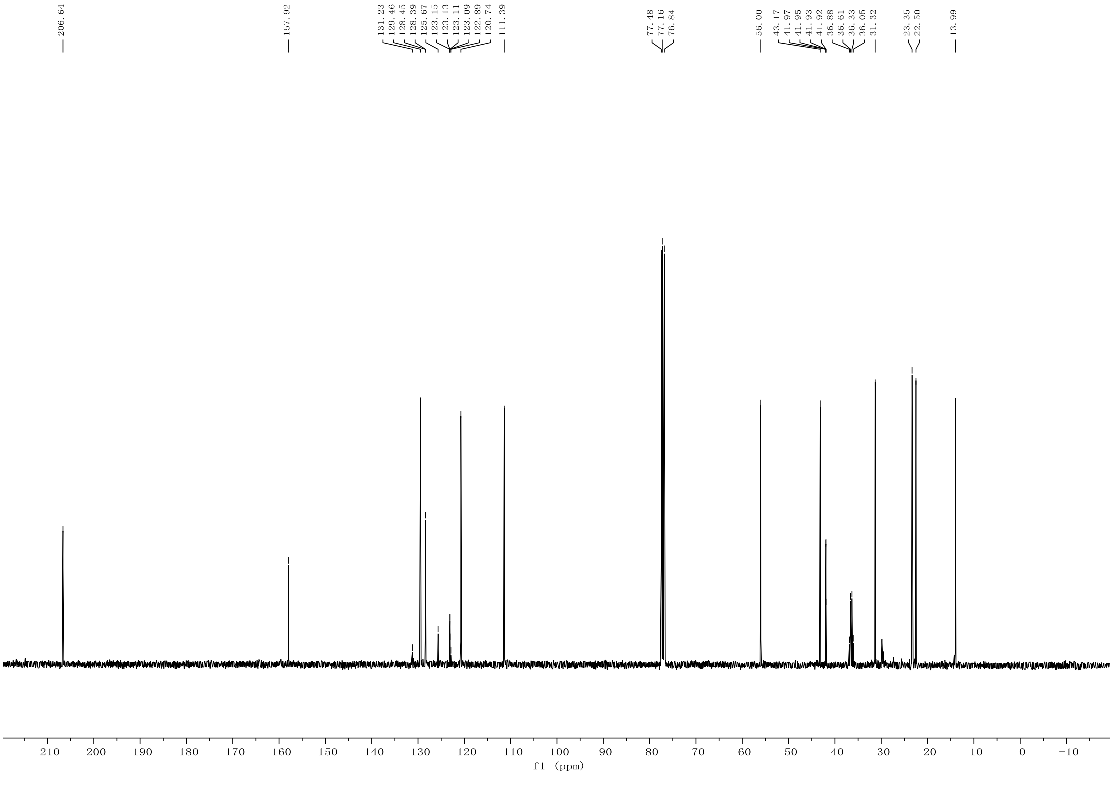
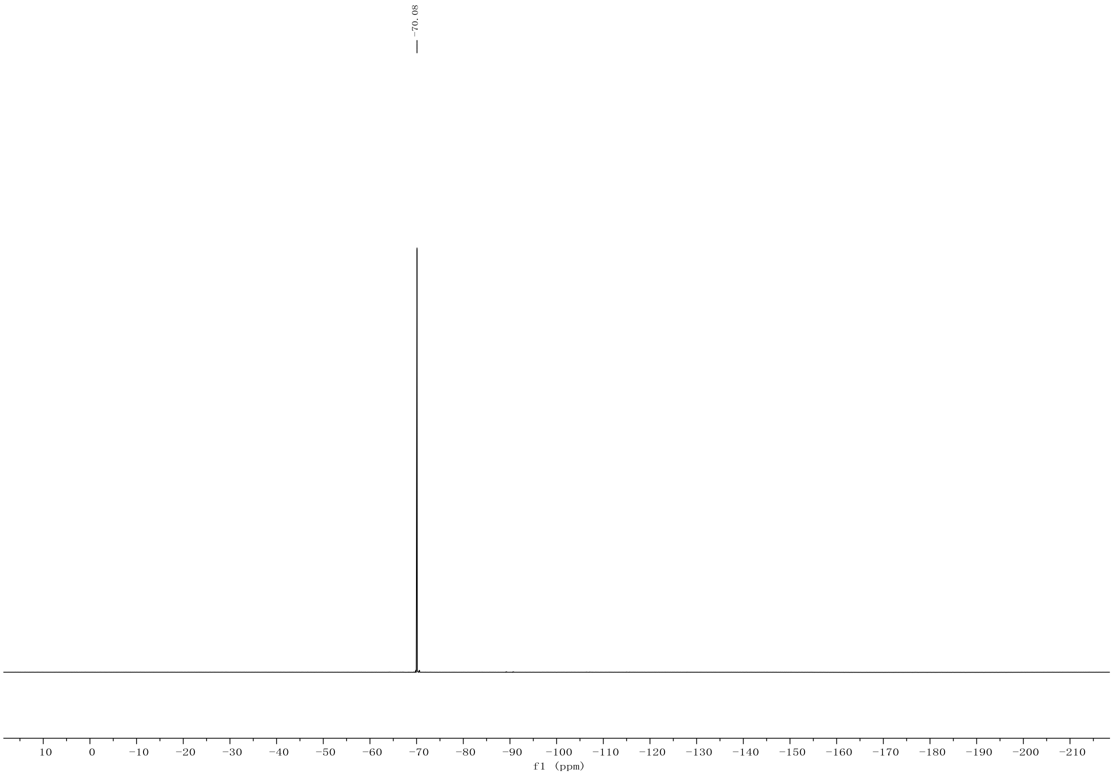
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

1,1,1-Trifluoro-2-(2-methoxyphenyl)nonan-4-one (3ba)





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-140
-150
-160
-170
-180
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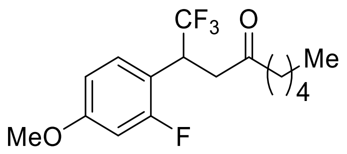
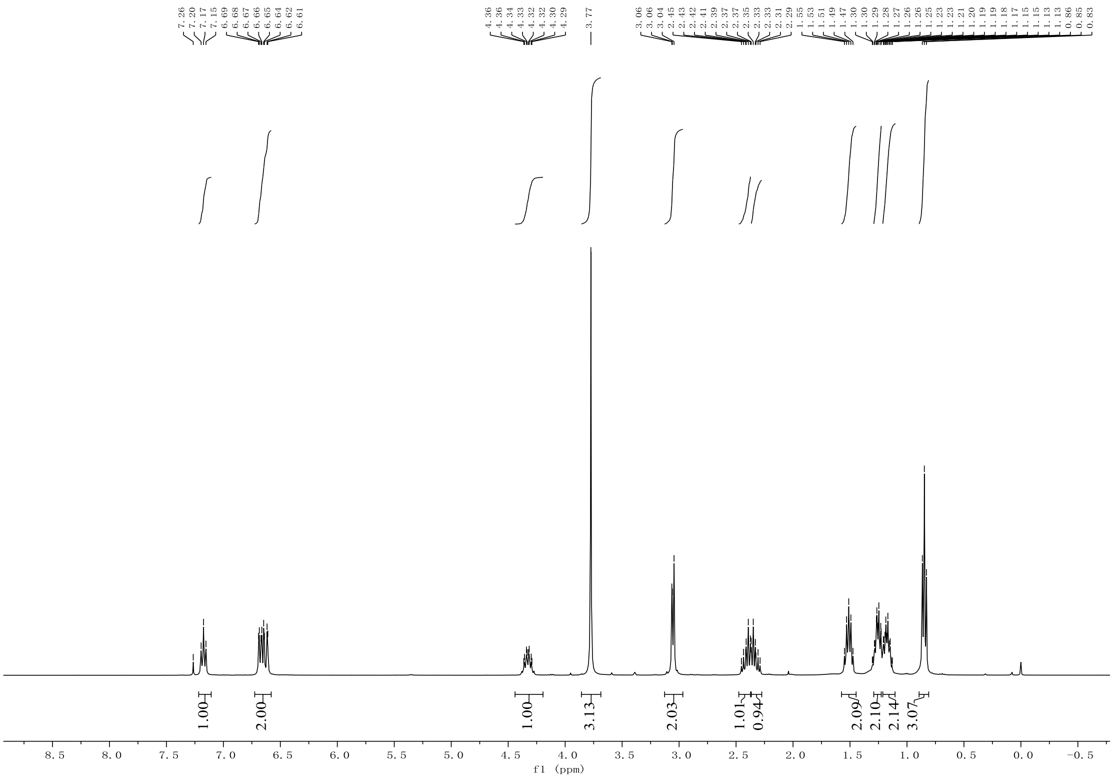
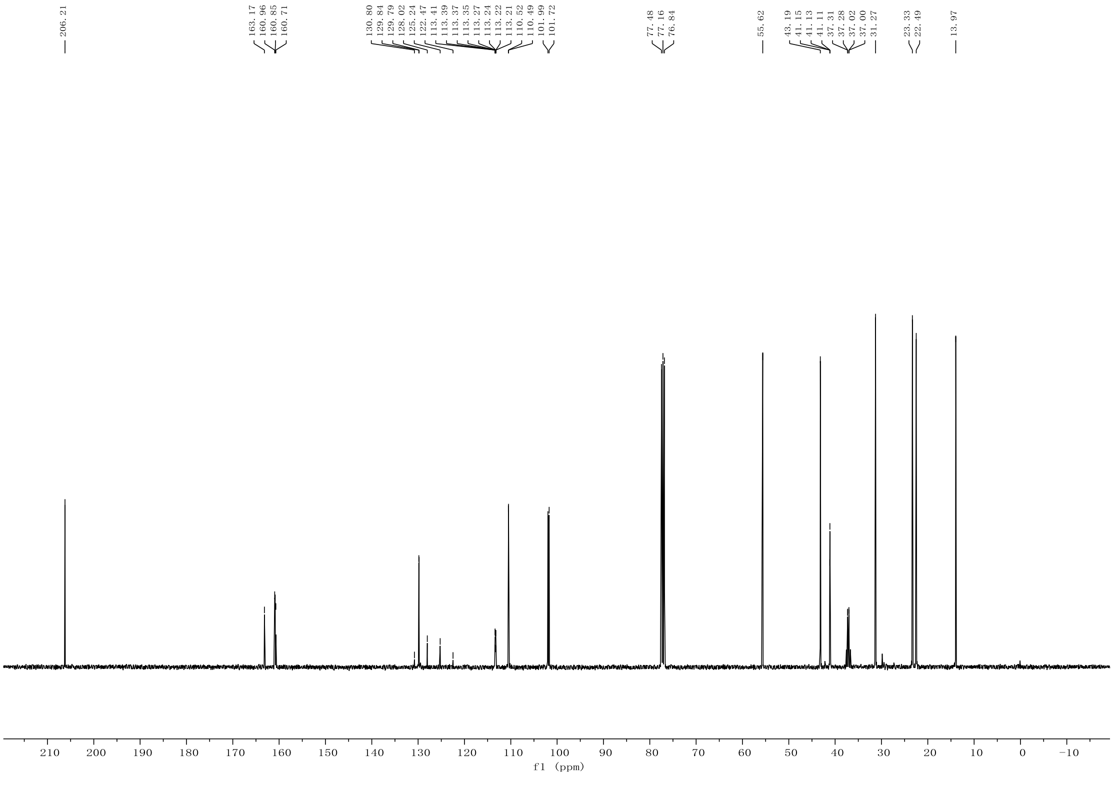
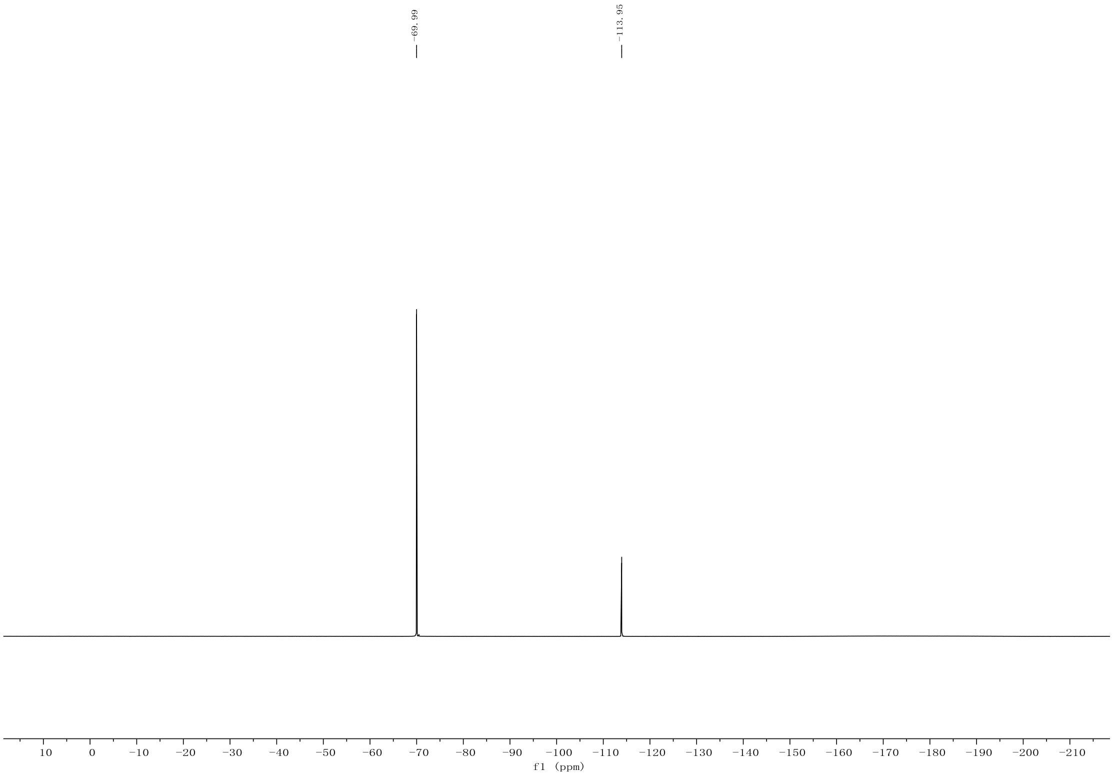
-200
-210
f1 (ppm)

1,1,1-Trifluoro-2-(2-fluoro-4-methoxyphenyl)nonan-4-one (3ca)





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0
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−50
−60
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−80
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−110
−120
−130
−140
−150
−160
−170
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−190
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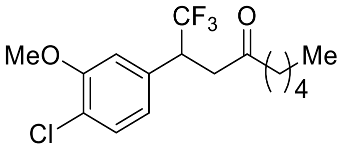
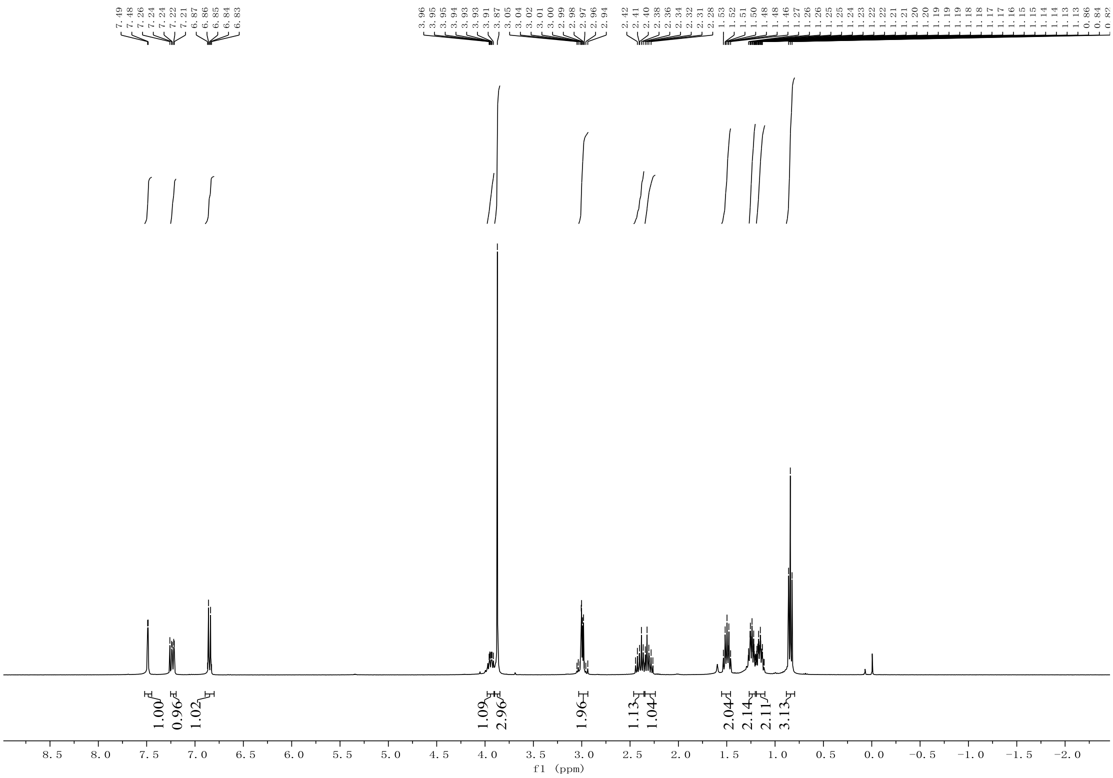
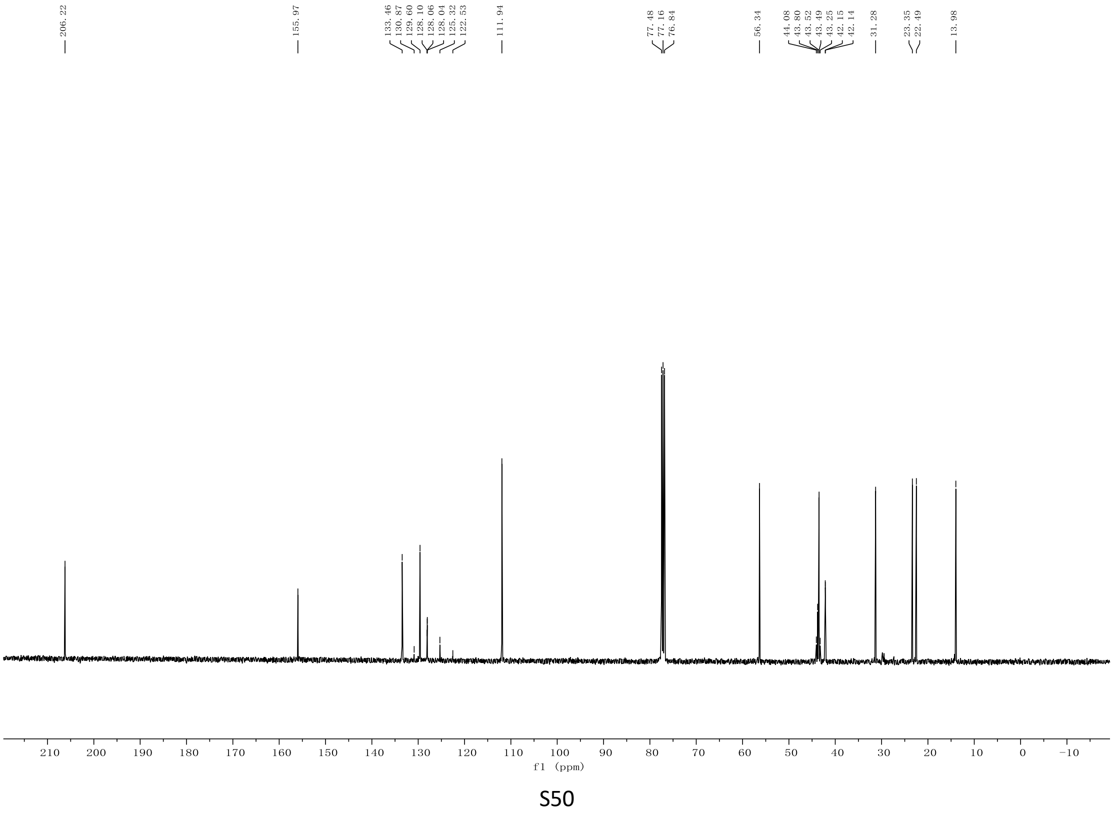
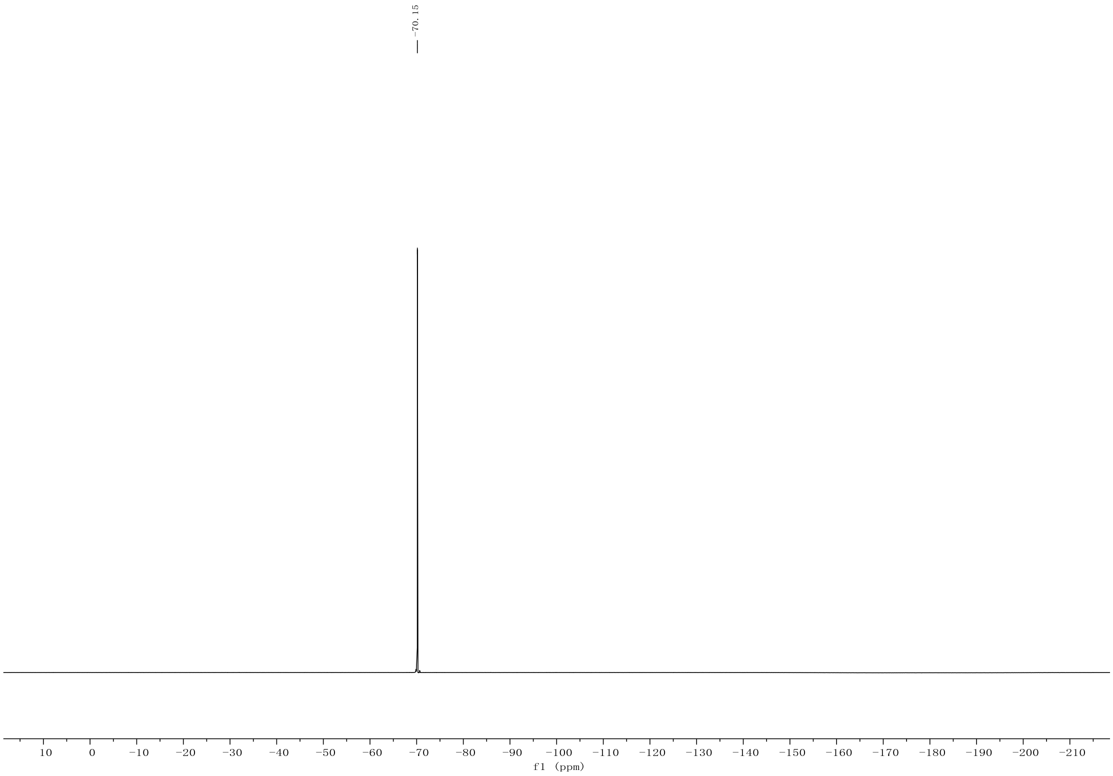
−210
f1 (ppm)

2-(4-Chloro-3-methoxyphenyl)-1,1,1-trifluorononan-4-one (3da)





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-70
-80
-90
-100
-110
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-130
-140
-150
-160
-170
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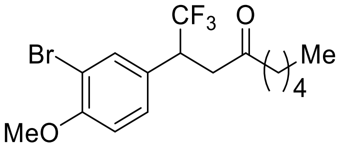
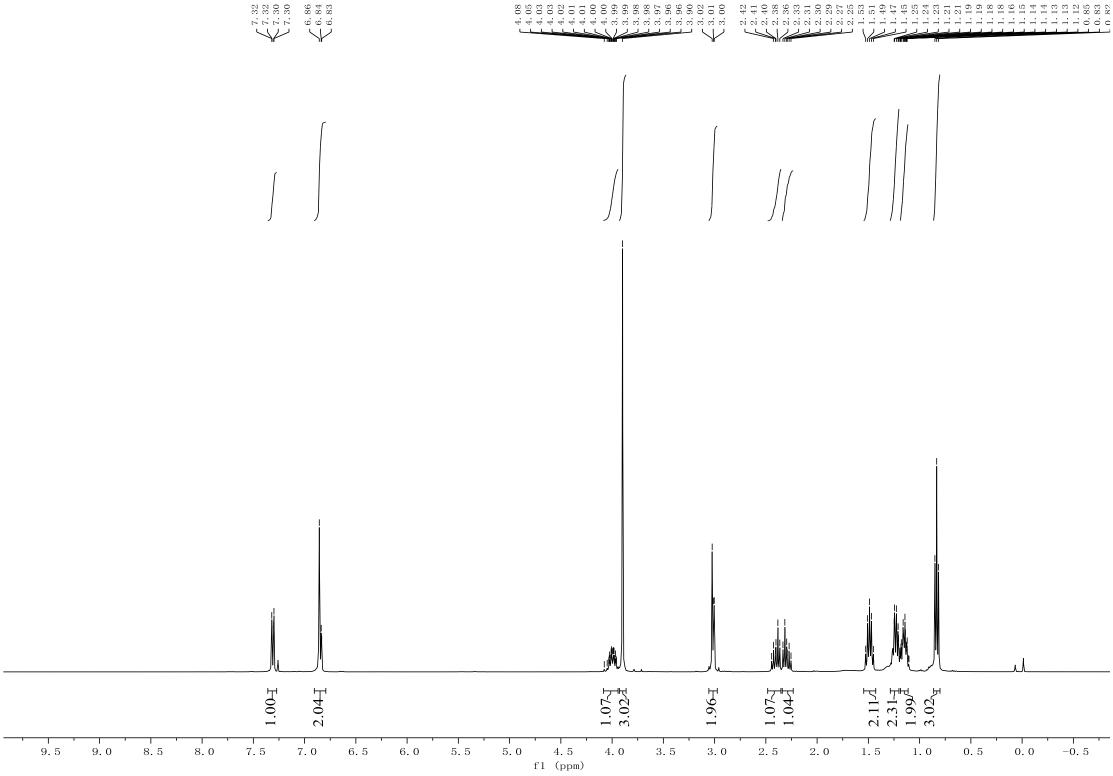
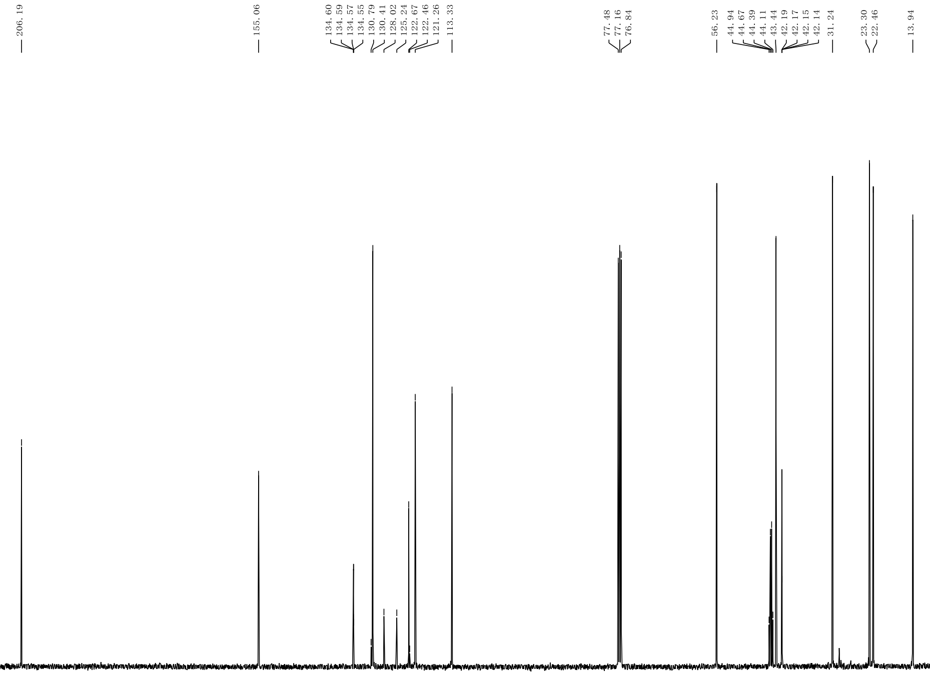
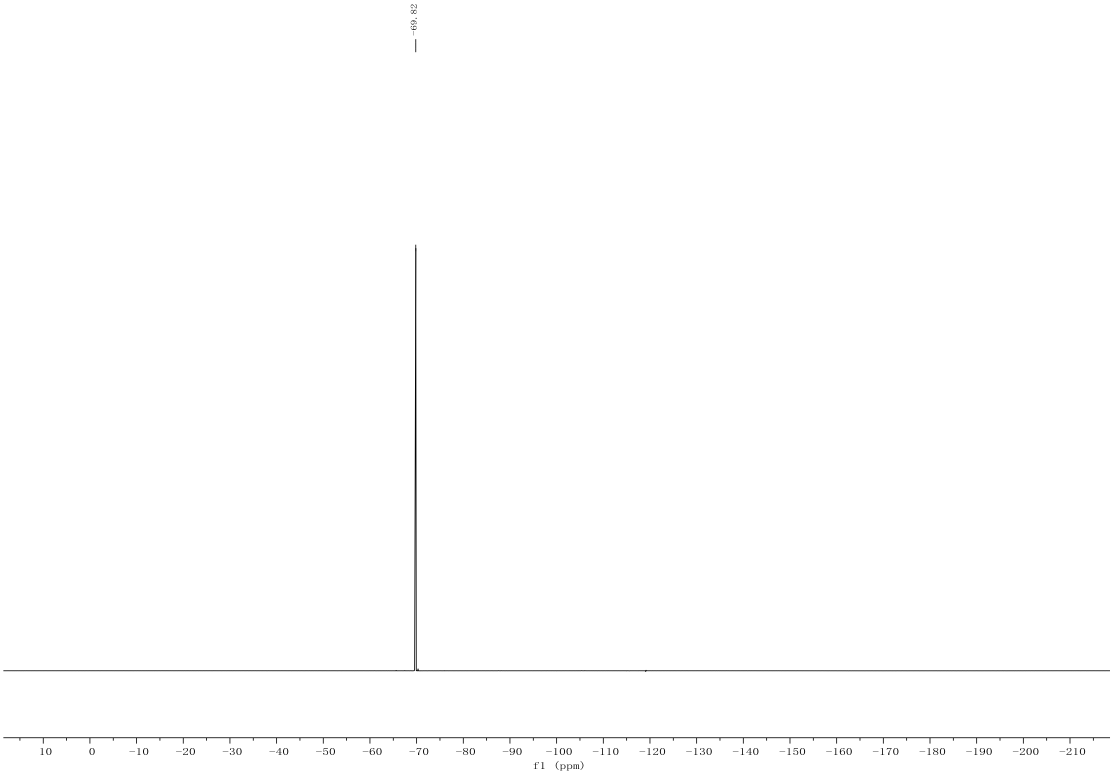
-210
f1 (ppm)

2-(3-Bromo-4-methoxyphenyl)-1,1,1-trifluorononan-4-one (3ea)





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-150
-160
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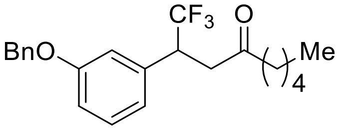
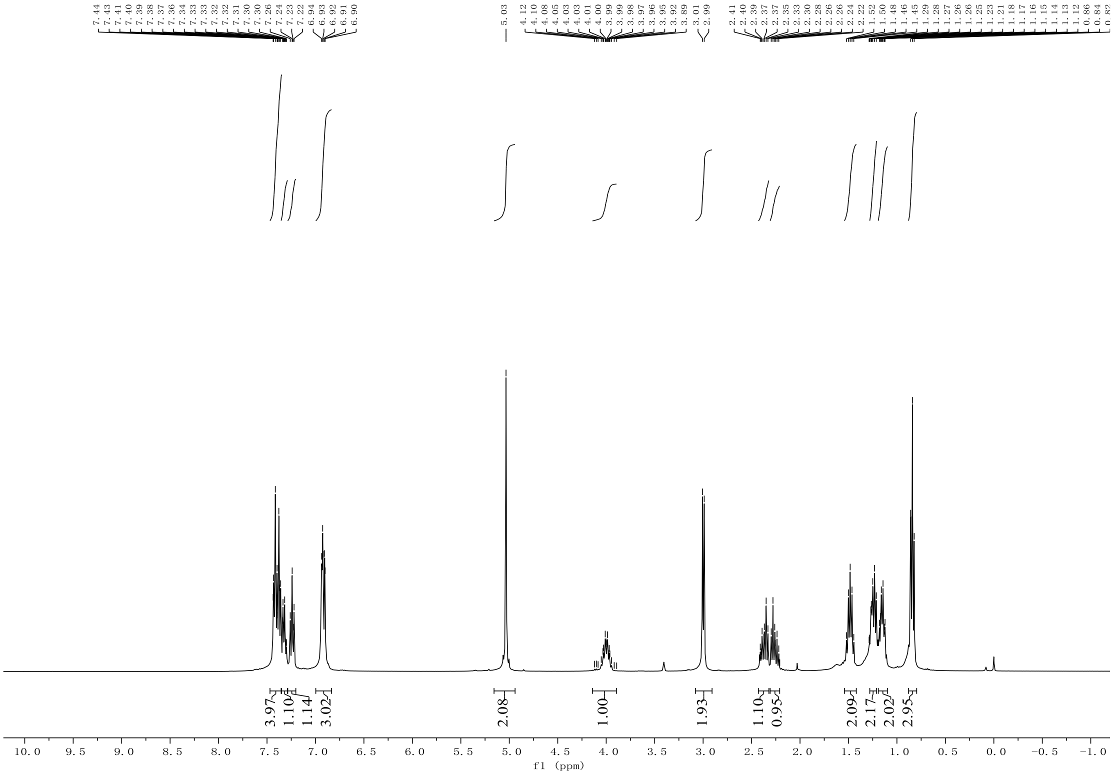
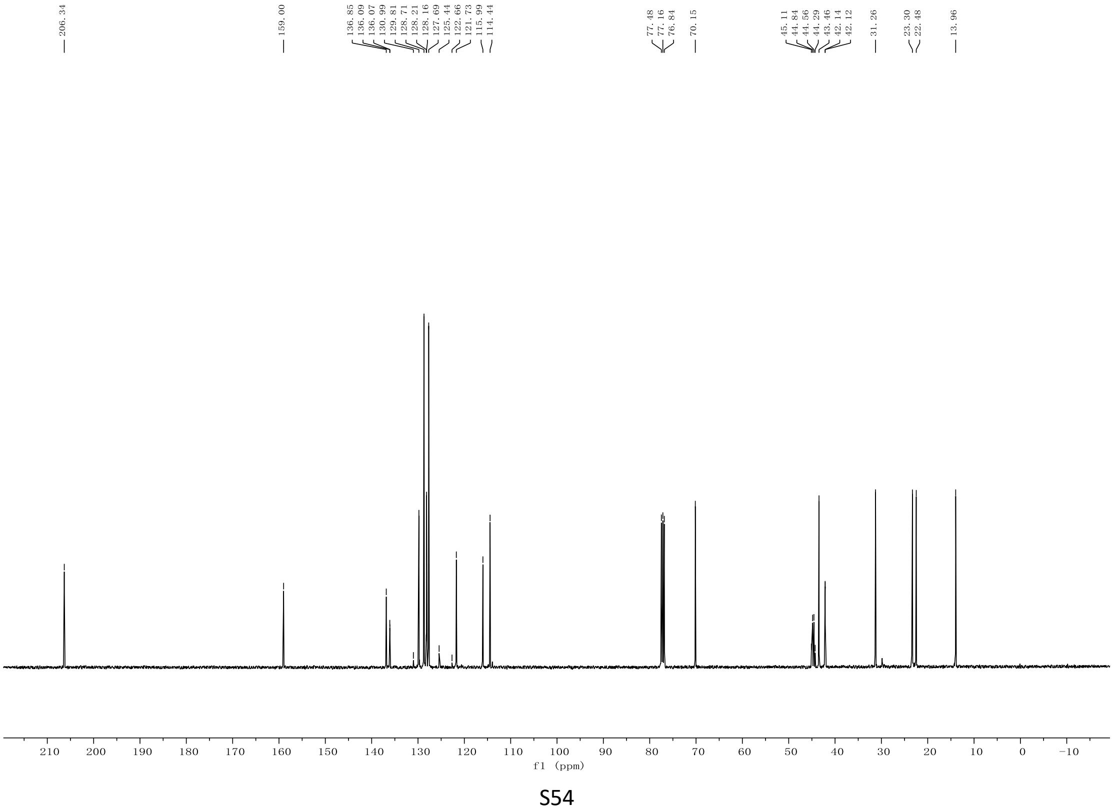
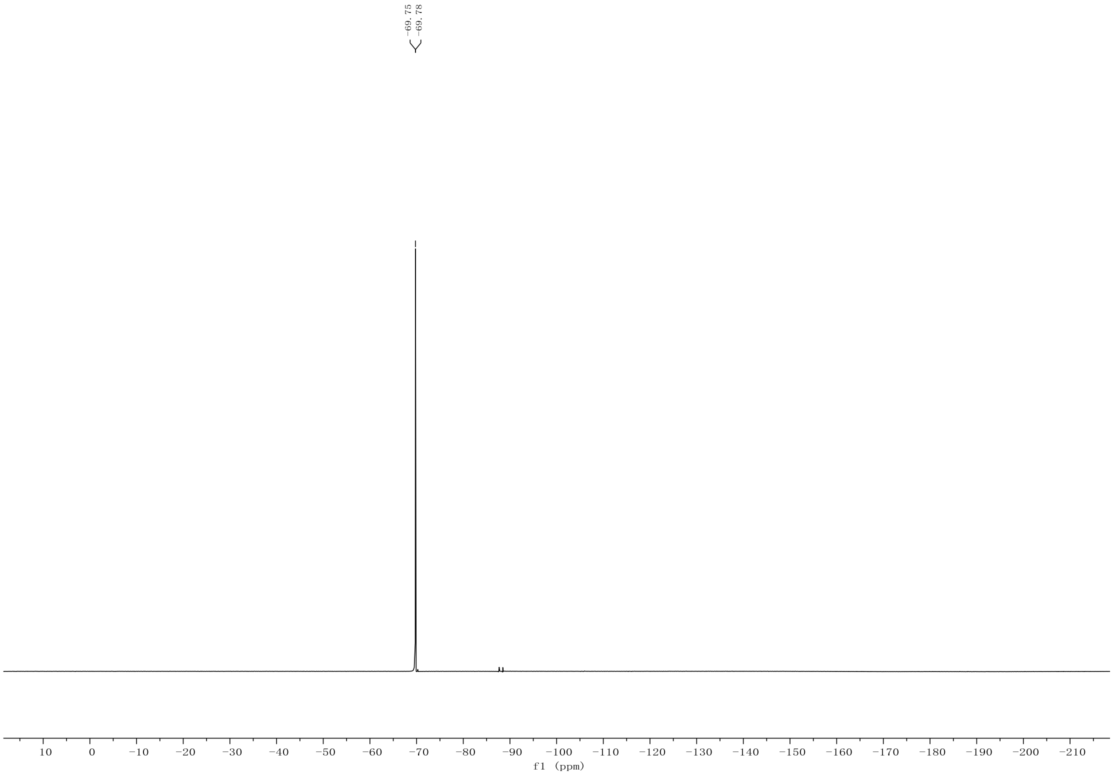
-200
-210
f1 (ppm)

2-(3-(Benzyloxy)phenyl)-1,1,1-trifluorononan-4-one (3fa)





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-60
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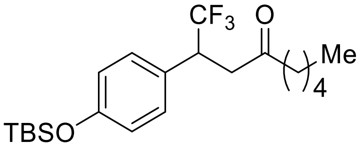
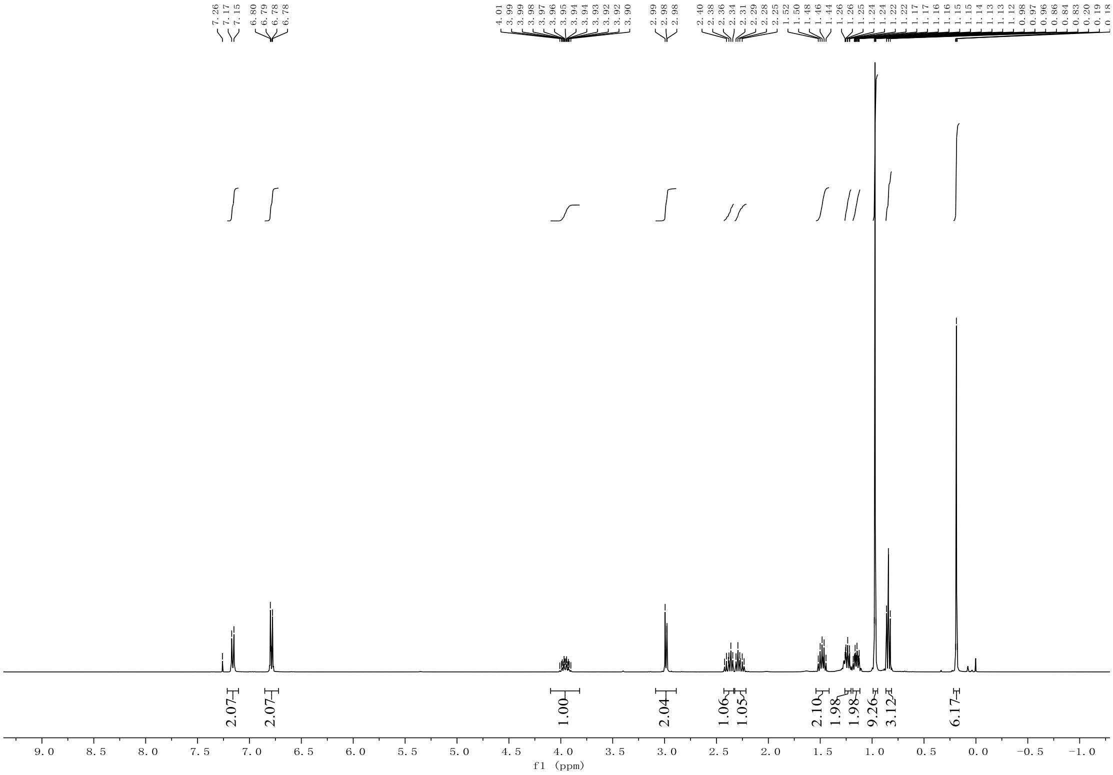
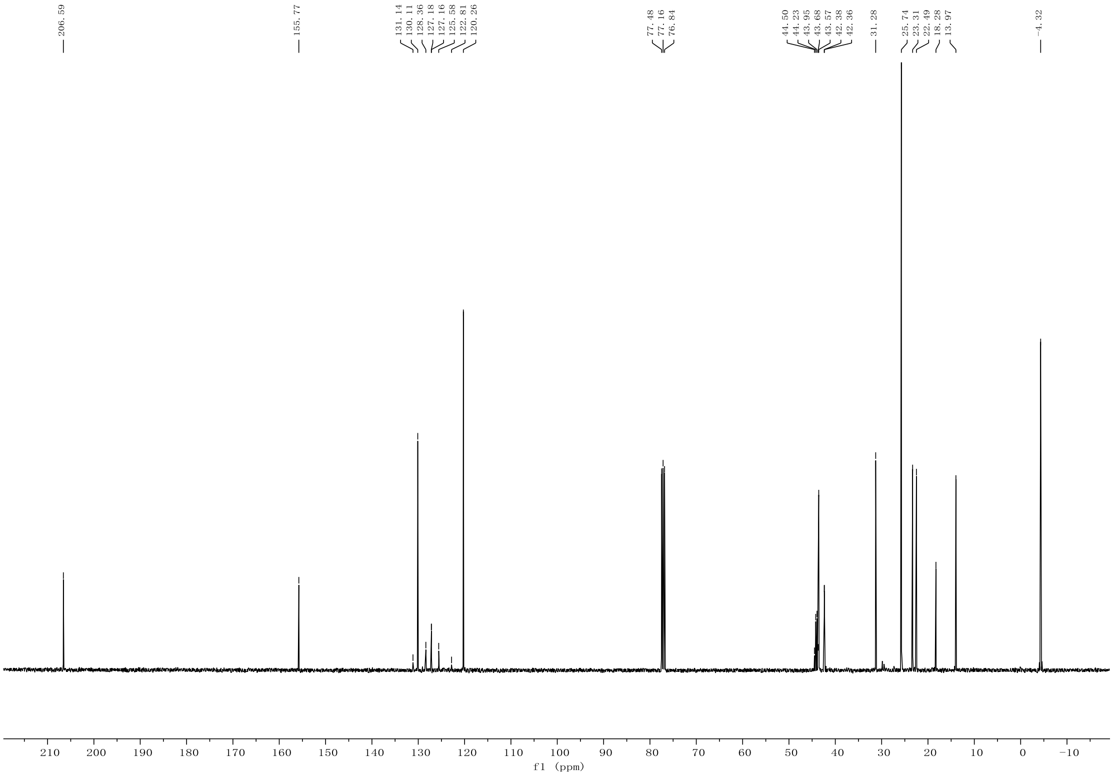
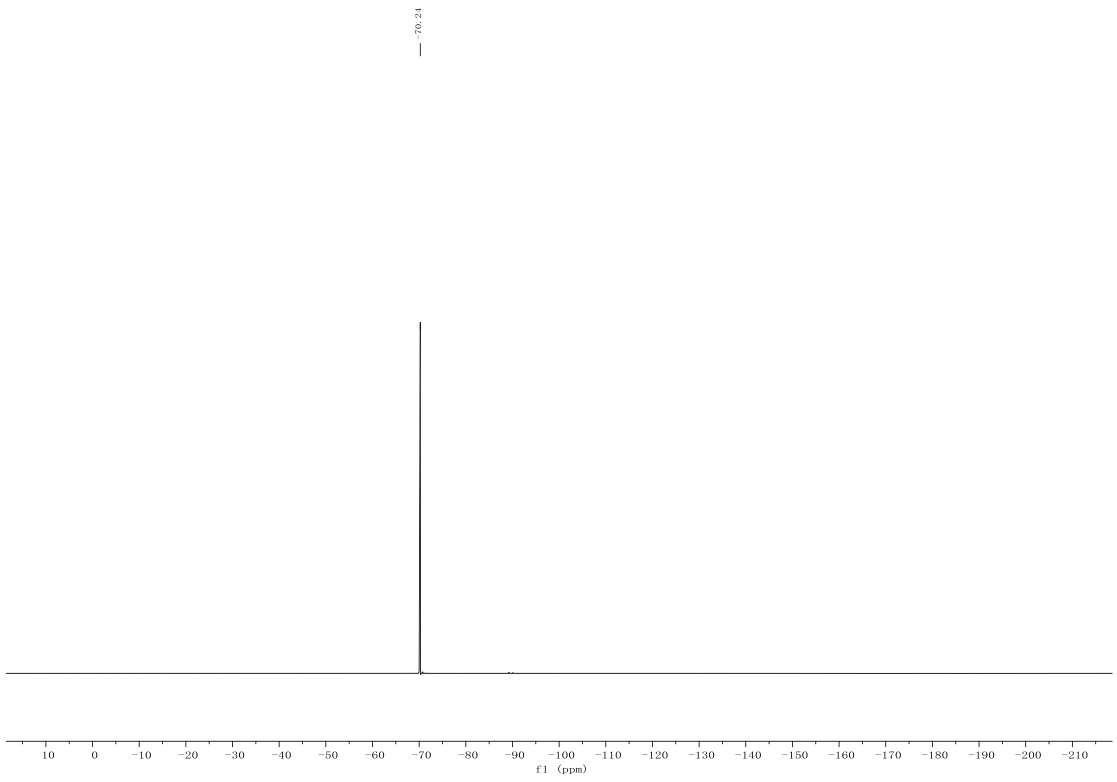
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

2-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)-1,1,1-trifluorononan-4-one (3ga)





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-80
-90
-100
-110
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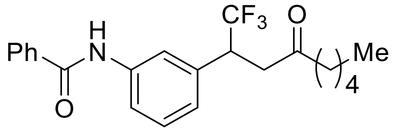
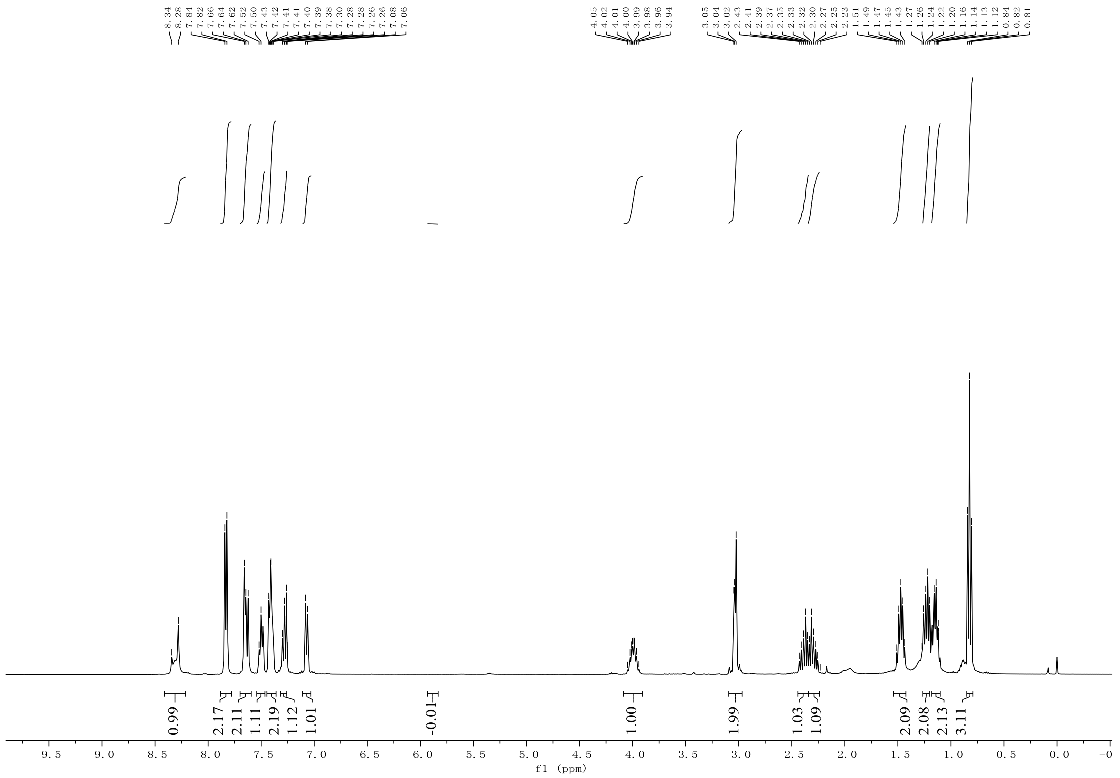
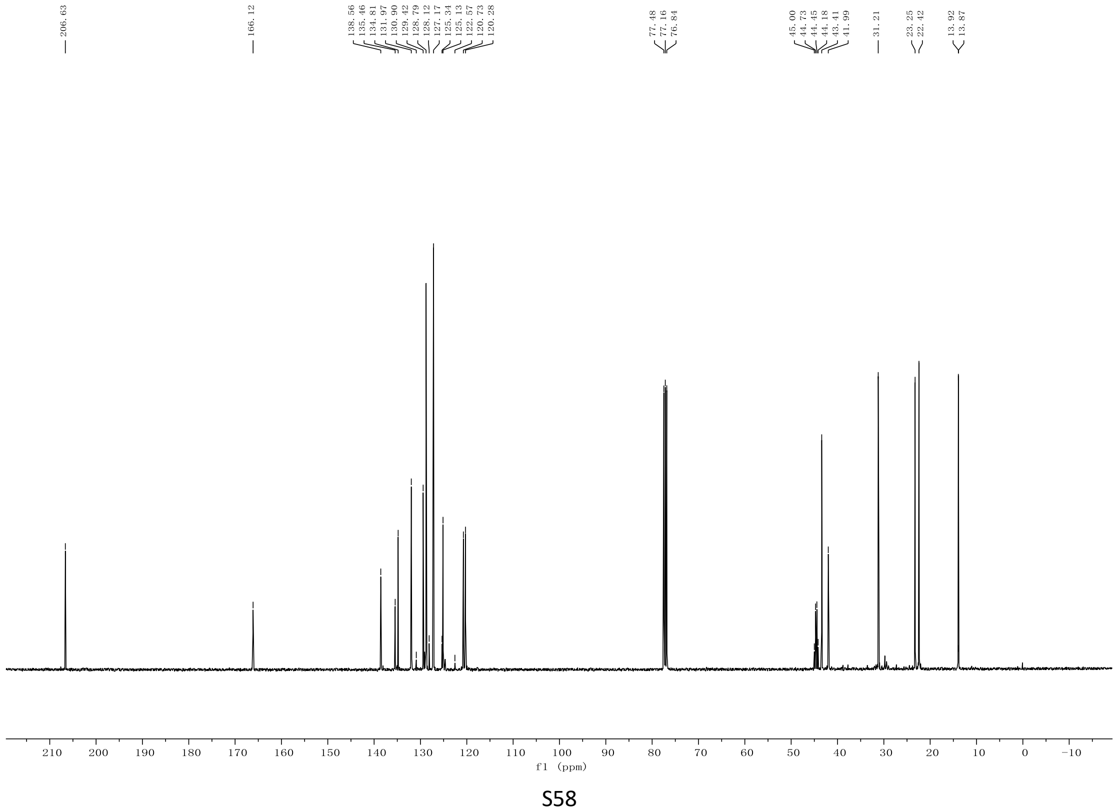
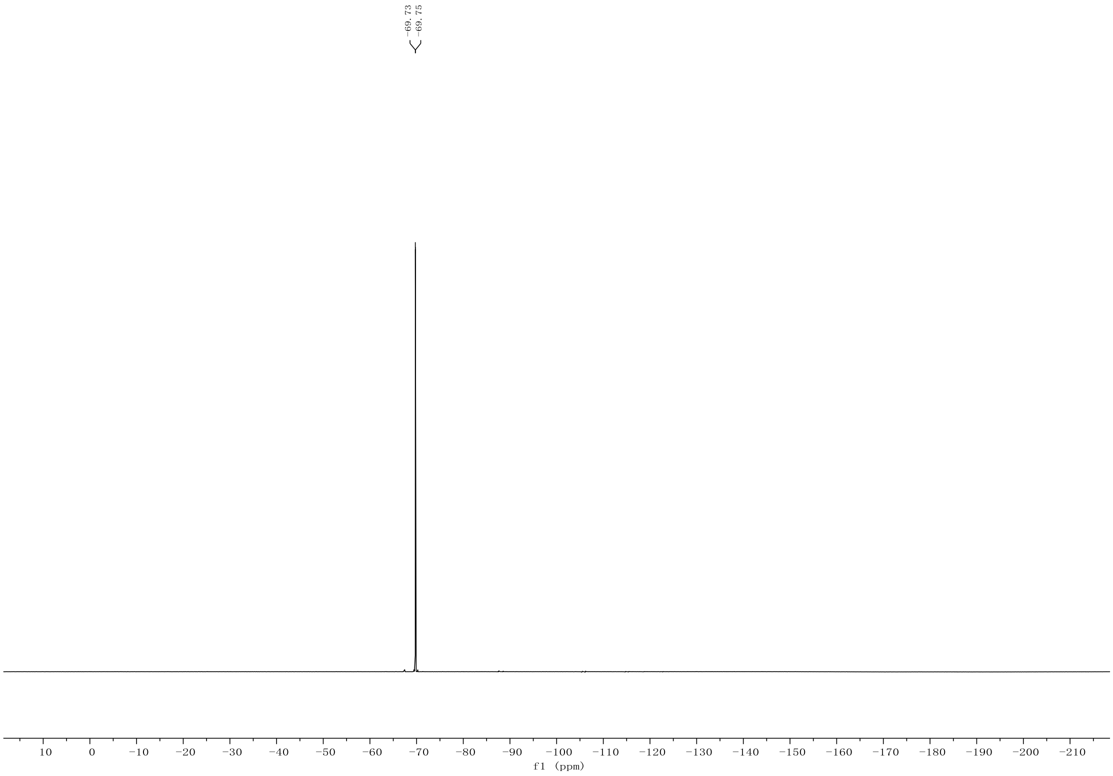
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

N-(3-(1,1,1-Trifluoro-4-oxononan-2-yl)phenyl)benzamide (3ha)

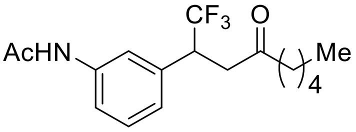


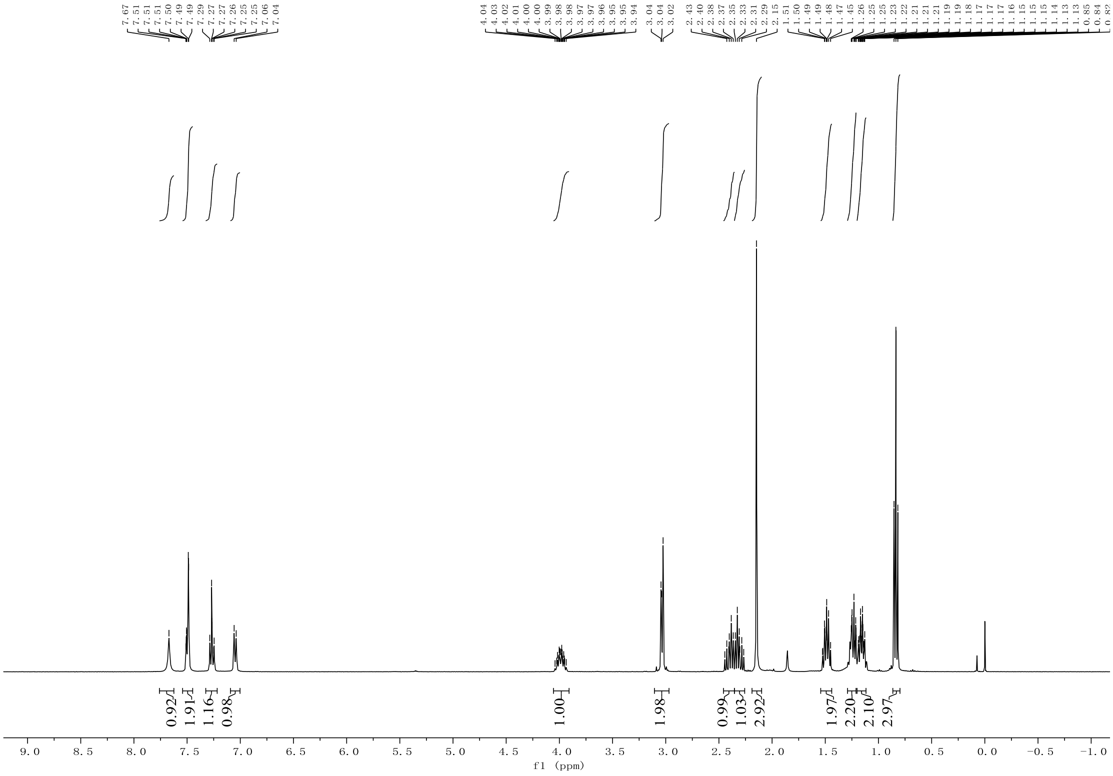


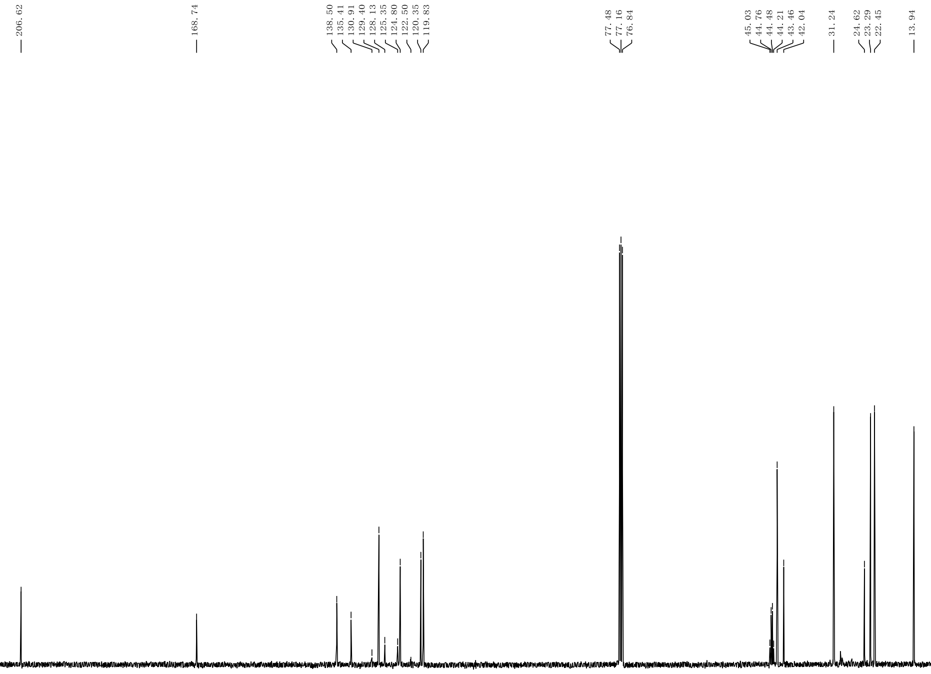


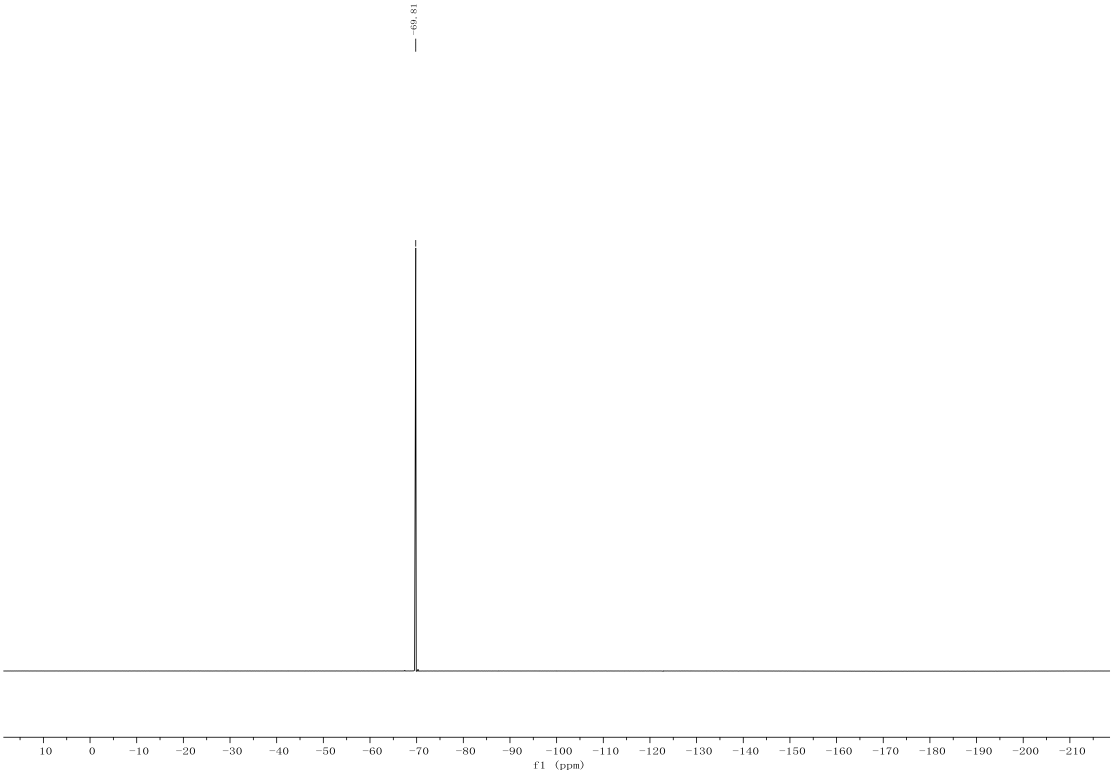

-69.73
-69.75
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

N-(3-(1,1,1-Trifluoro-4-oxononan-2-yl)phenyl)acetamide (3ia)

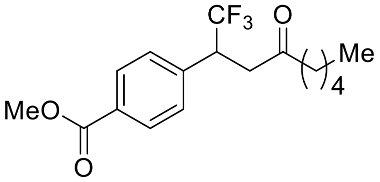


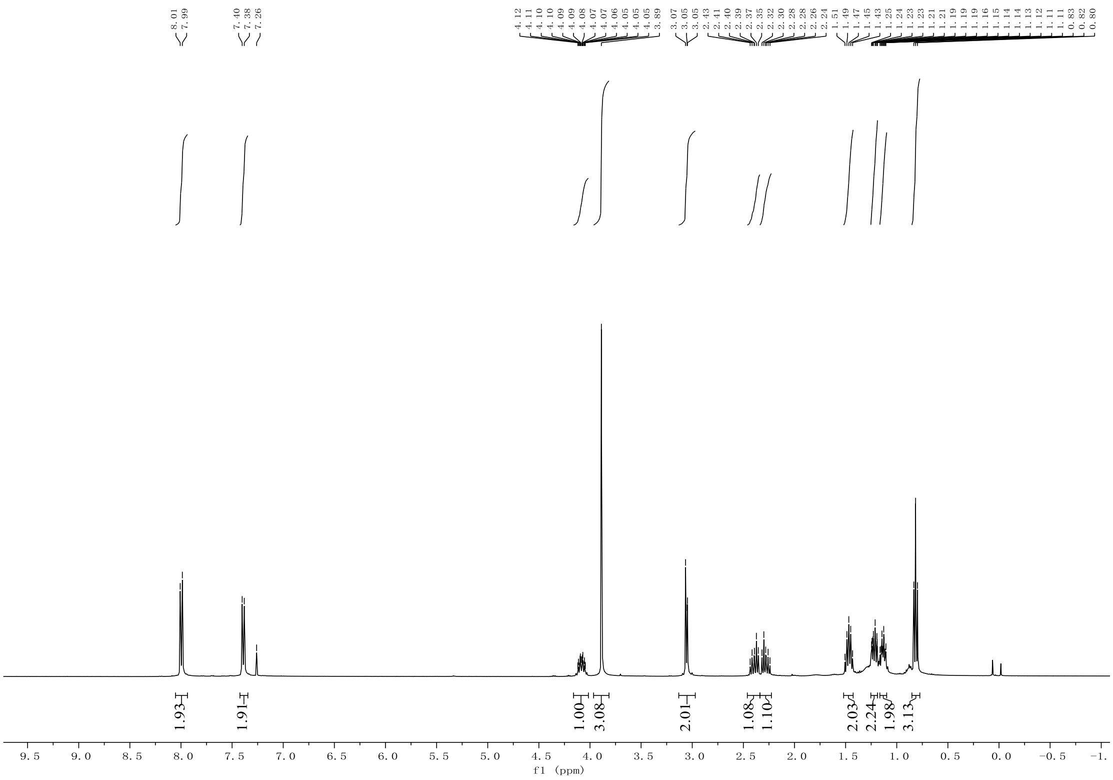


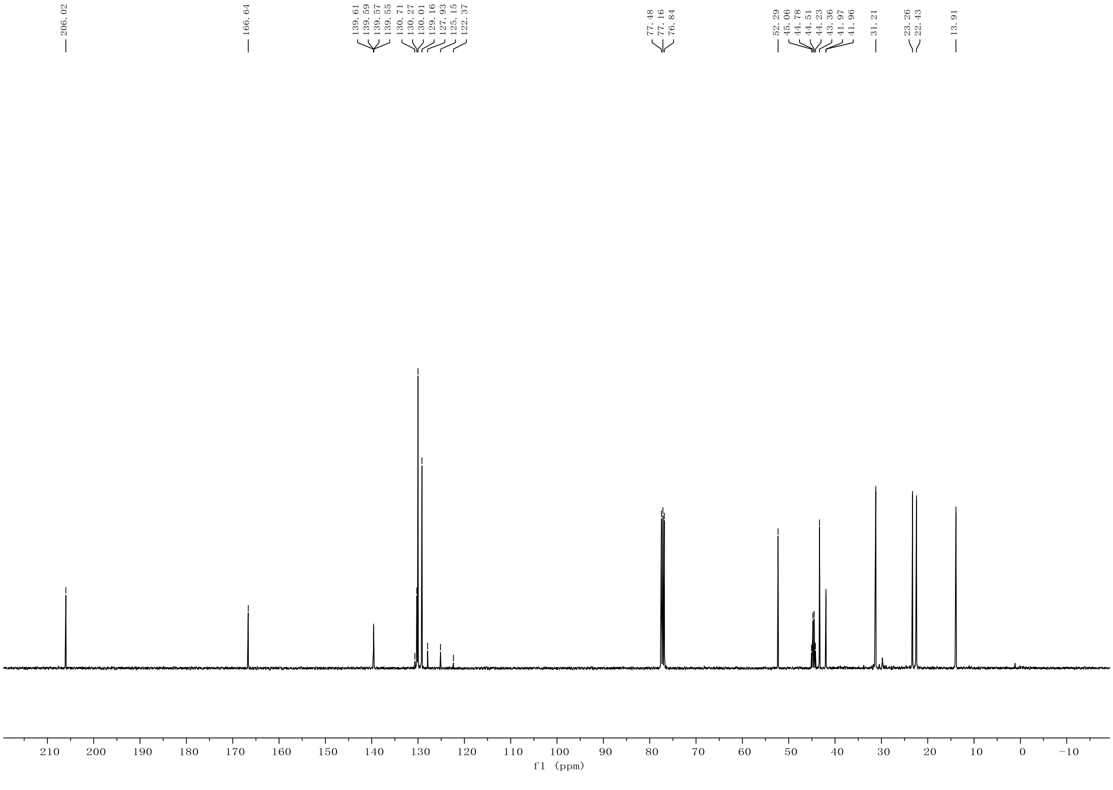


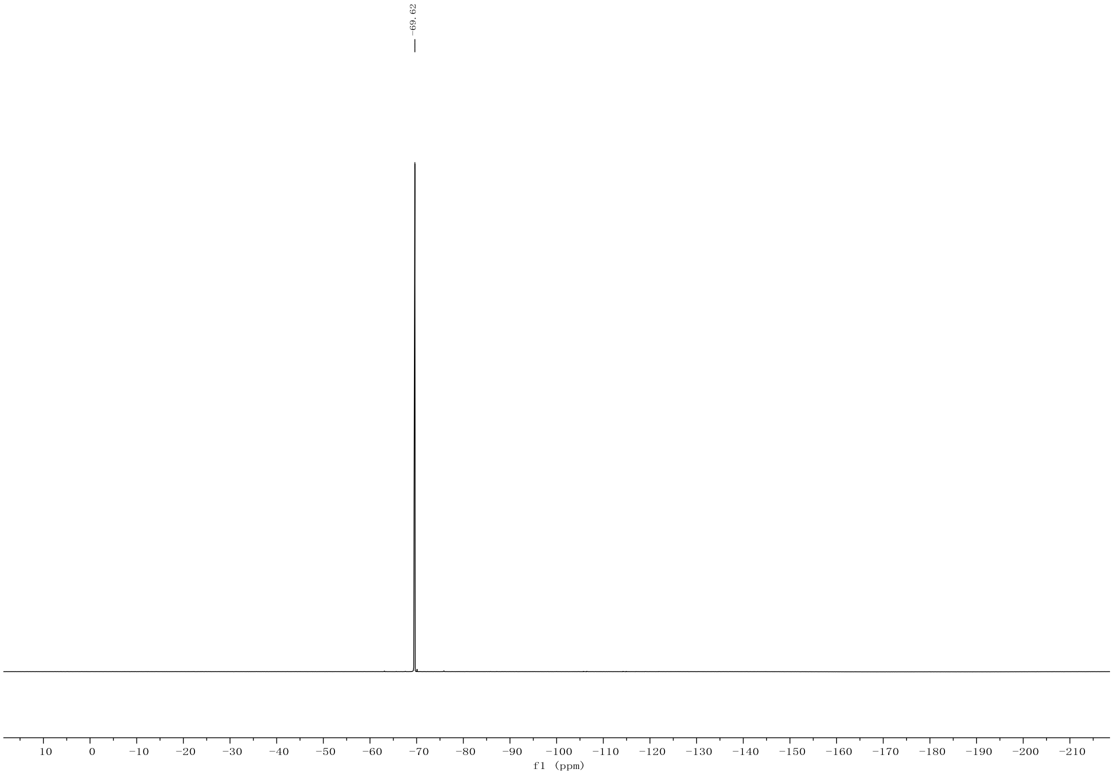

-69.81
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

Methyl 4-(1,1,1-trifluoro-4-oxononan-2-yl)benzoate (3ja)

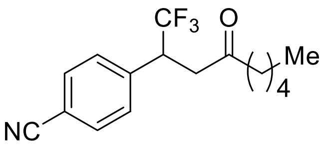


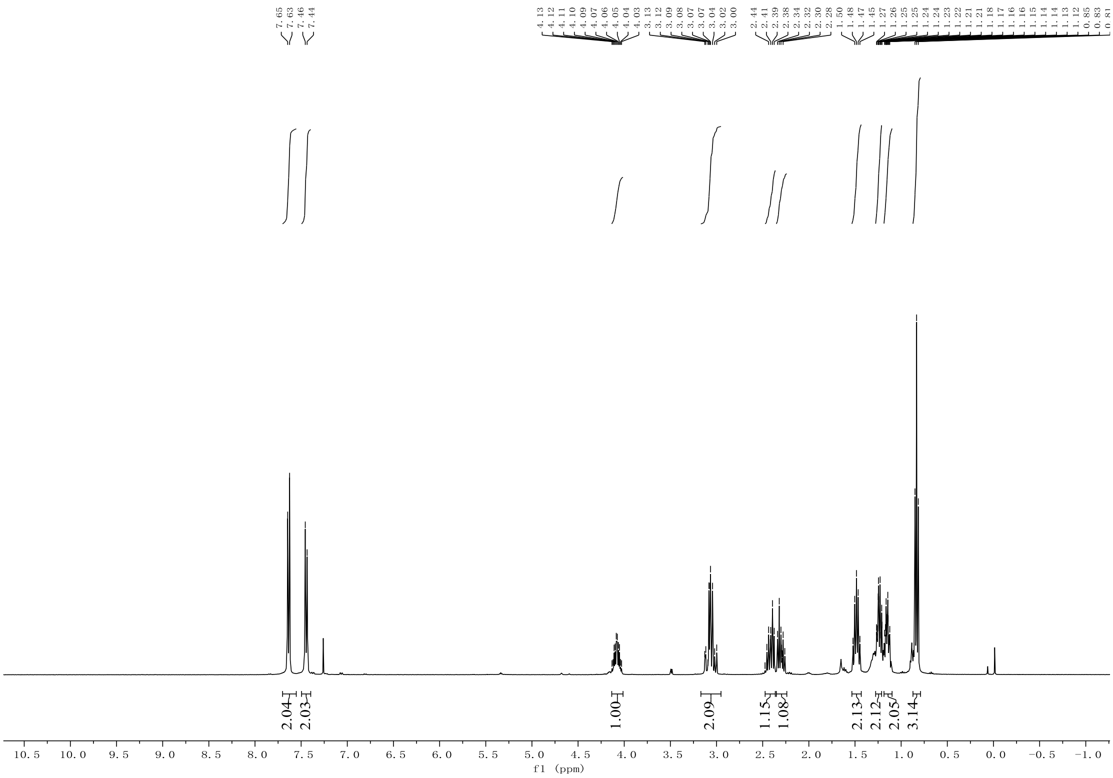


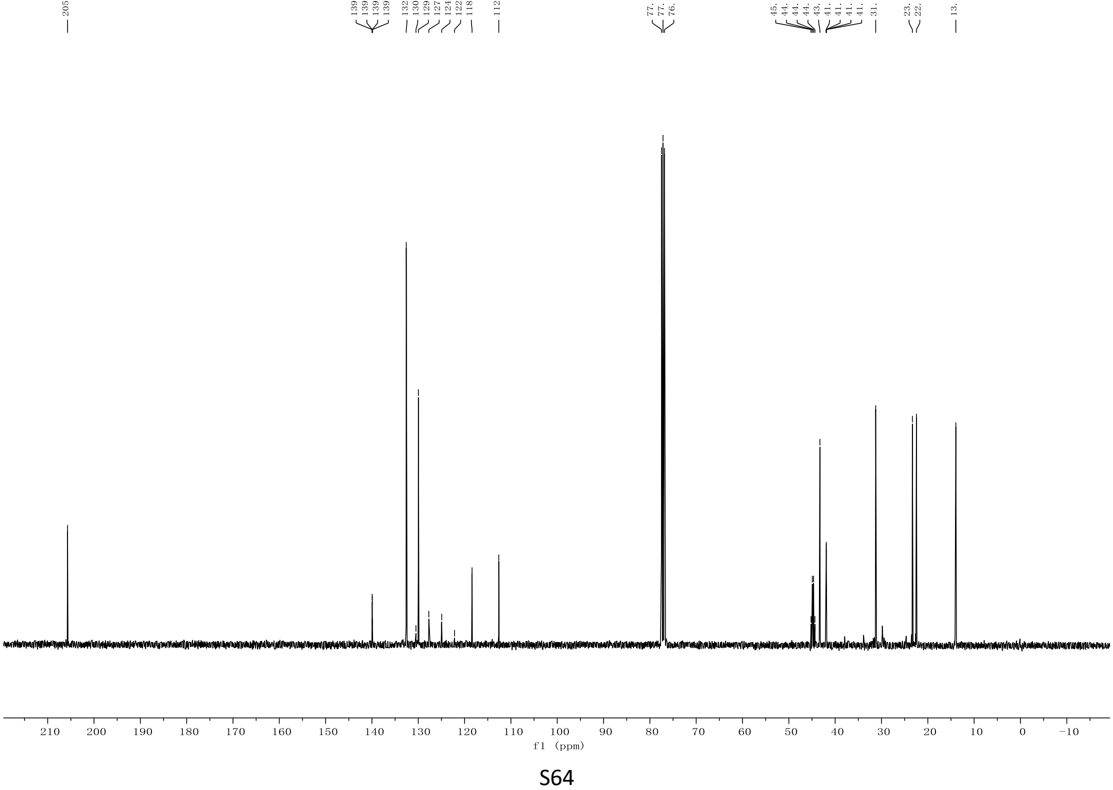


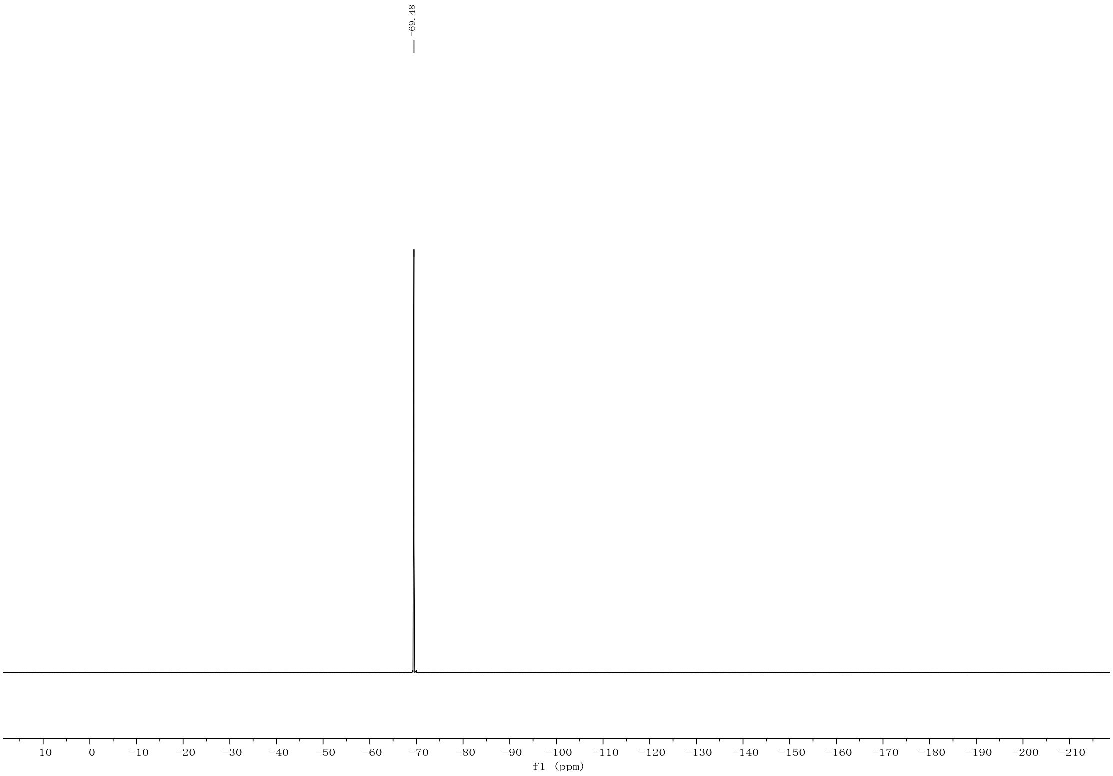

-69.62
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

4-(1,1,1-Trifluoro-4-oxononan-2-yl)benzonitrile (3ka)

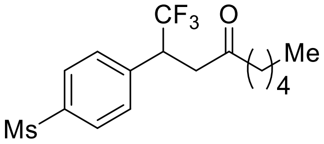


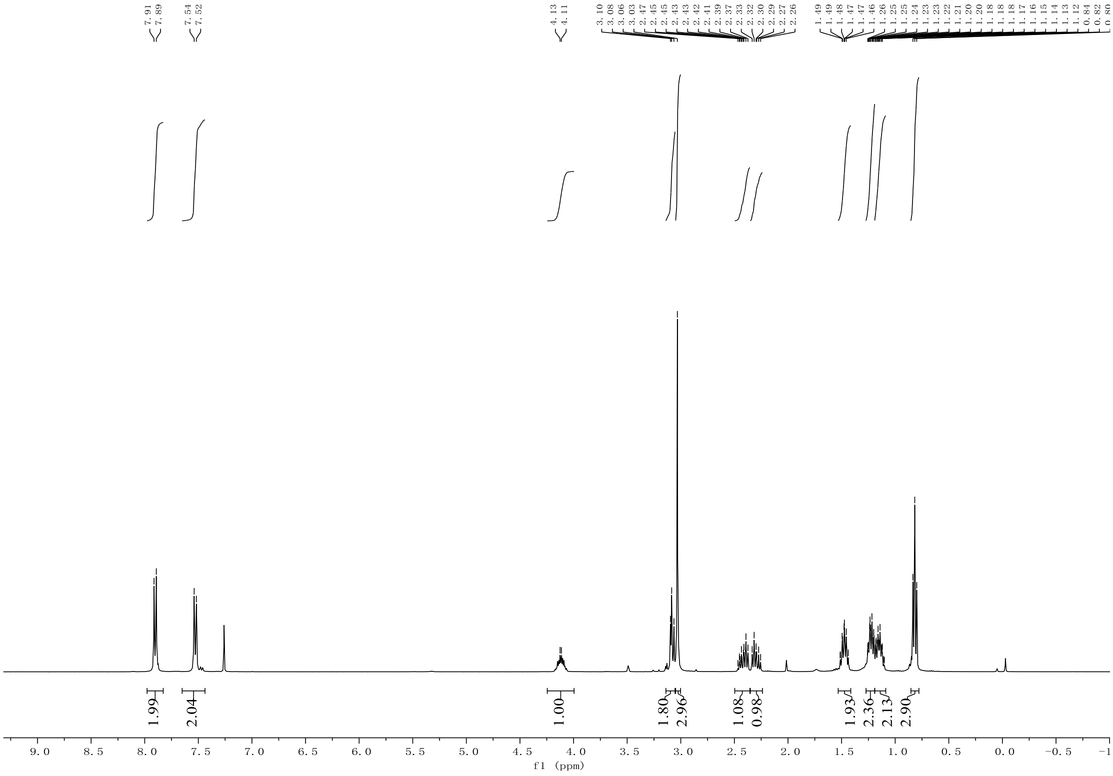


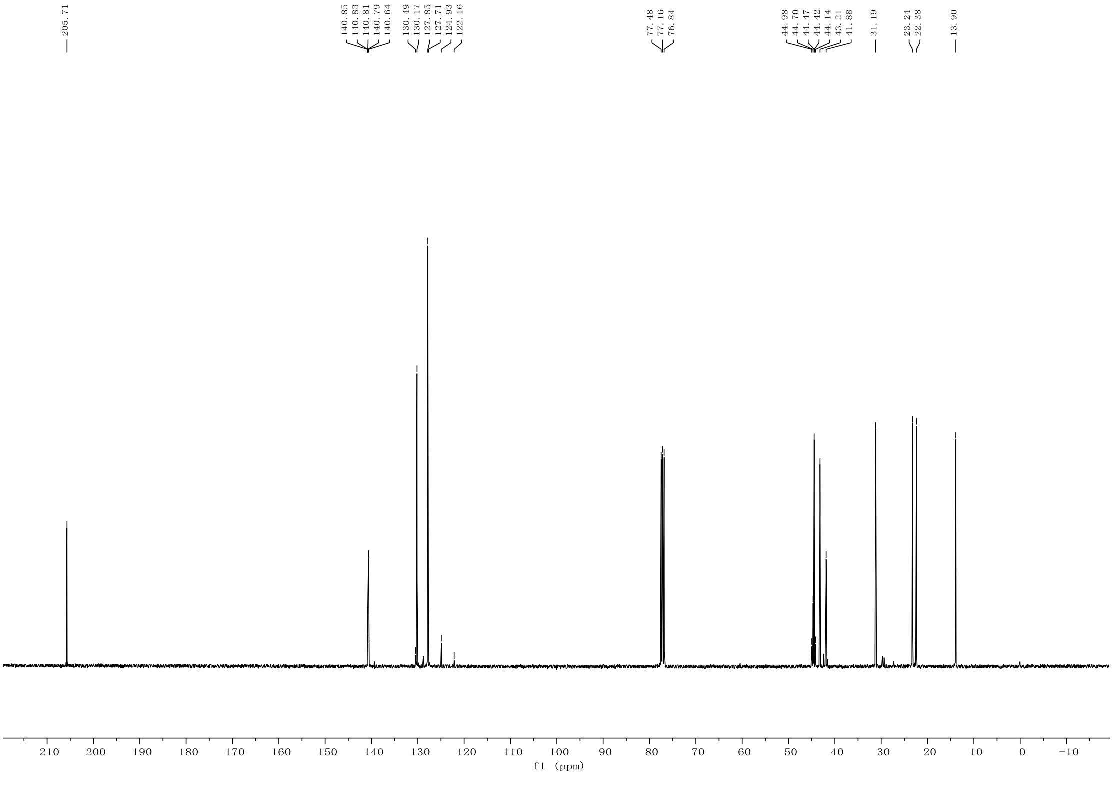


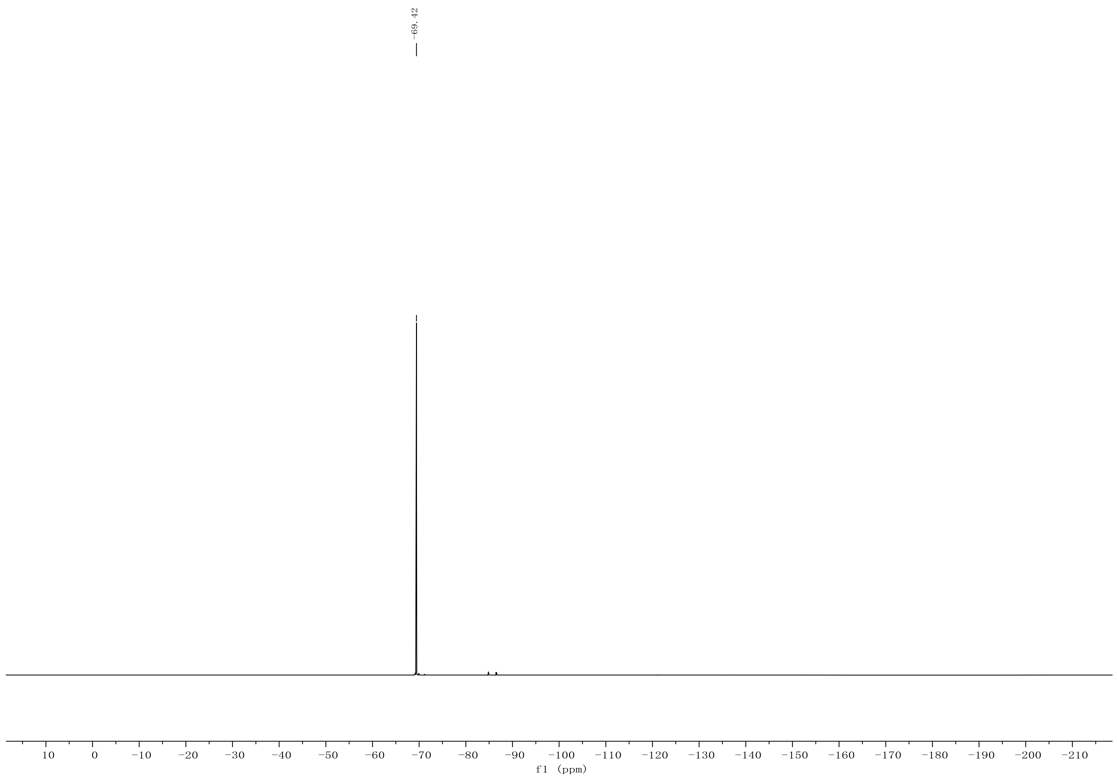

-69.48
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

1,1,1-Trifluoro-2-(4-(methylsulfonyl)phenyl)nonan-4-one (3la)

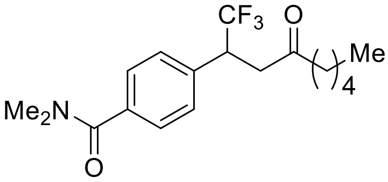


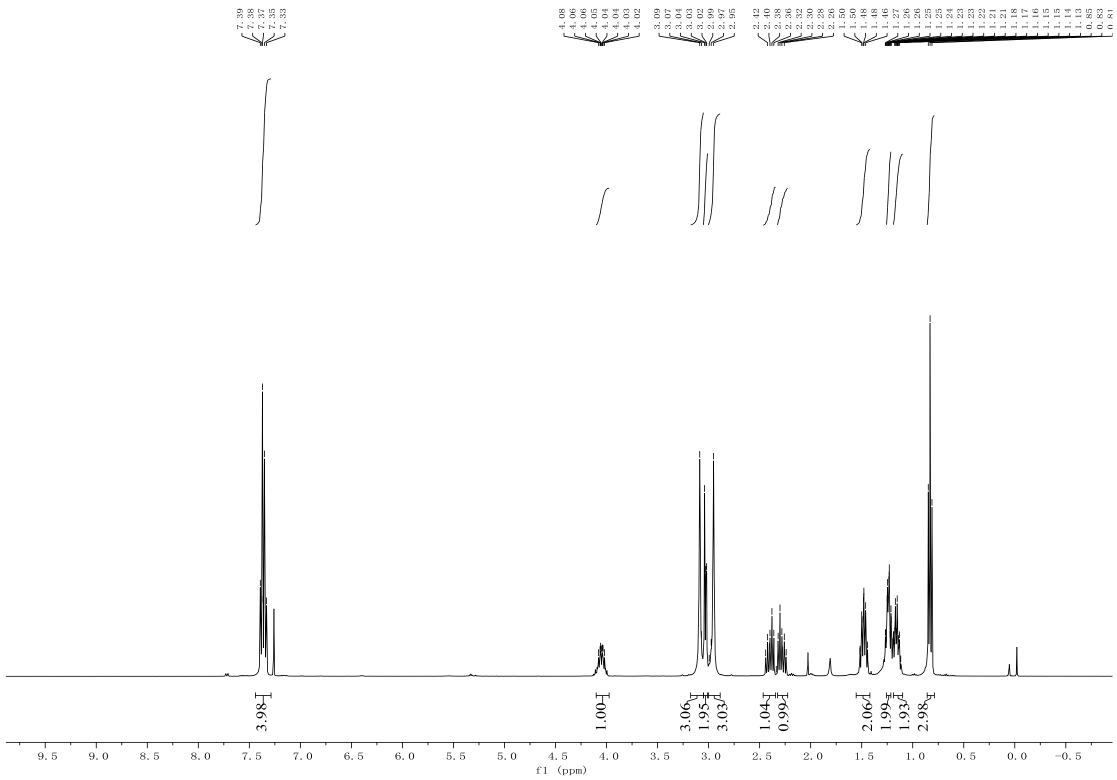


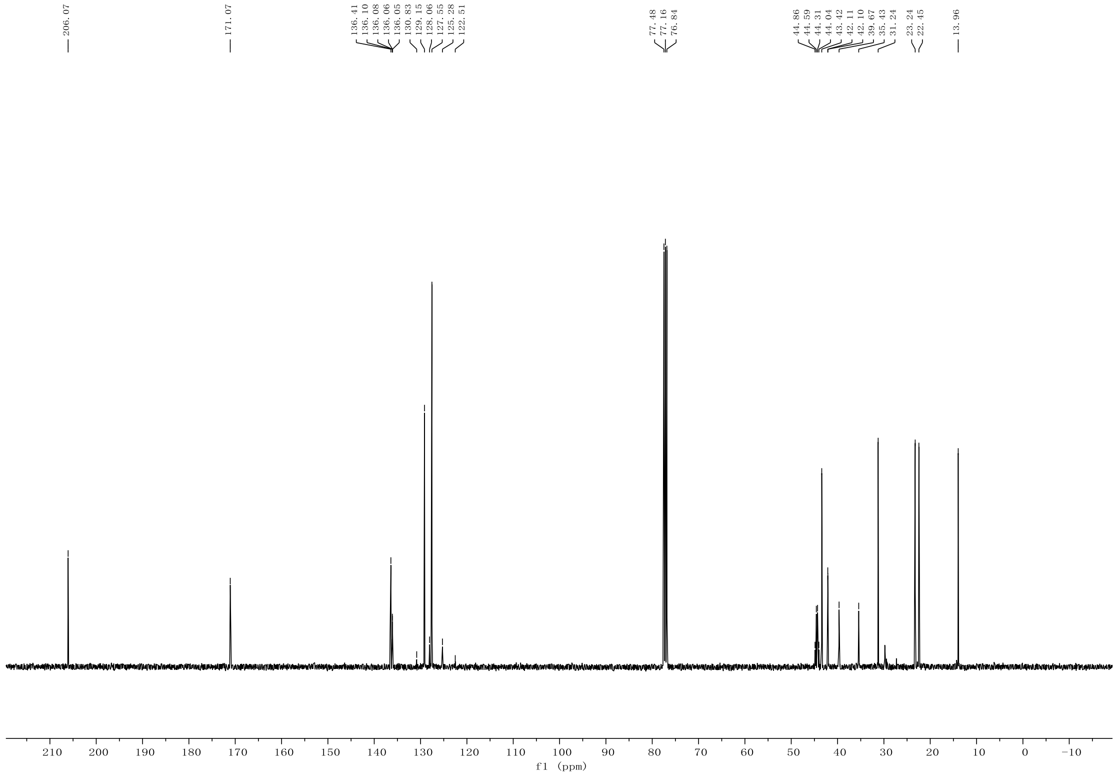


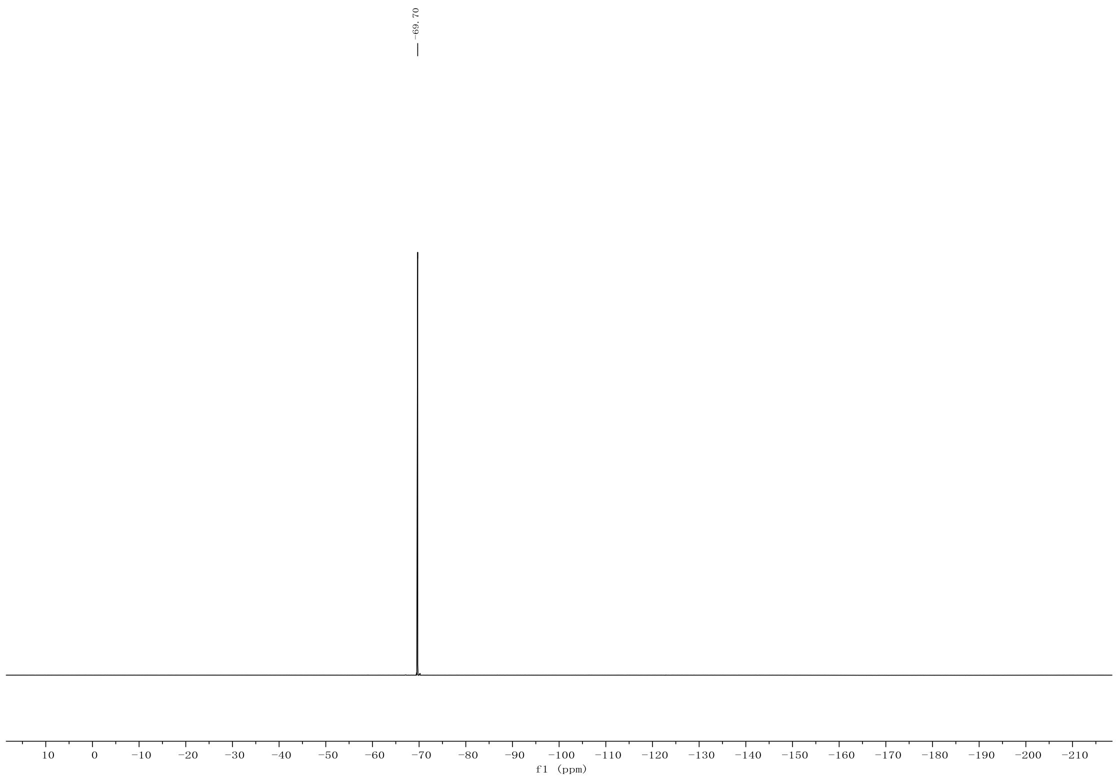

-69.42
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

N,*N*-Dimethyl-4-(1,1,1-trifluoro-4-oxononan-2-yl)benzamide (3ma)

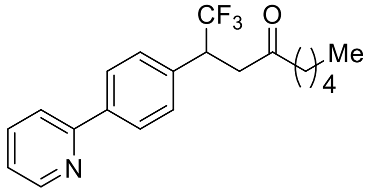


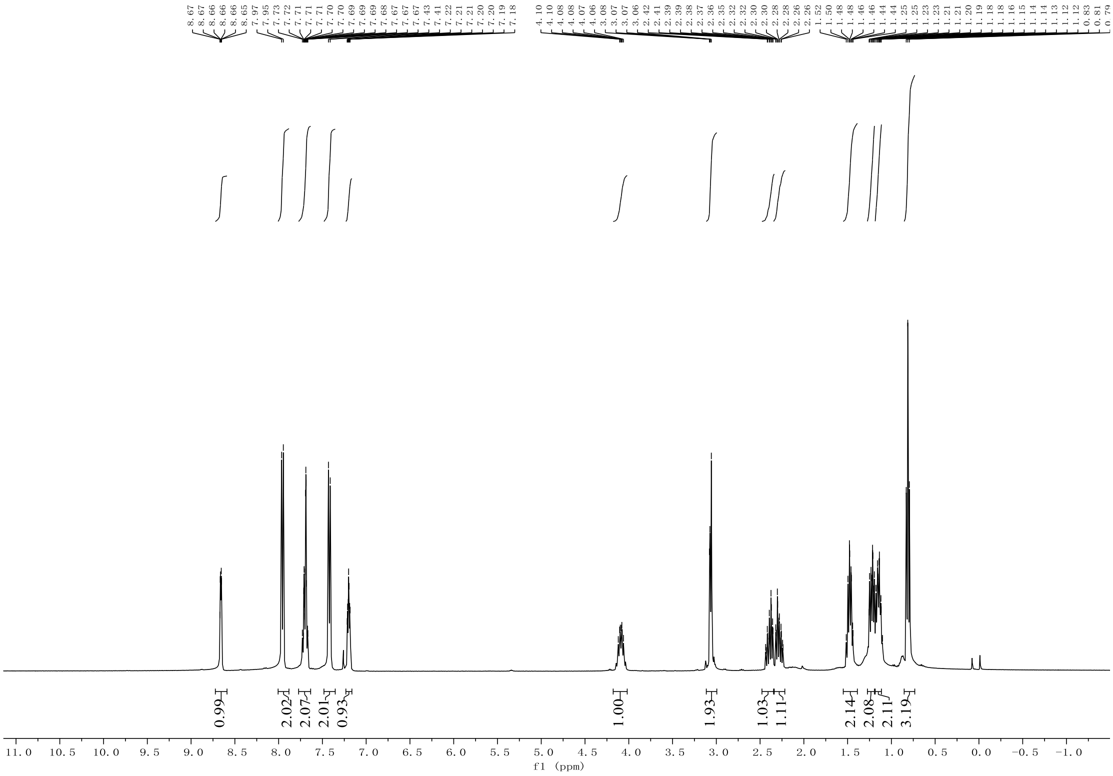


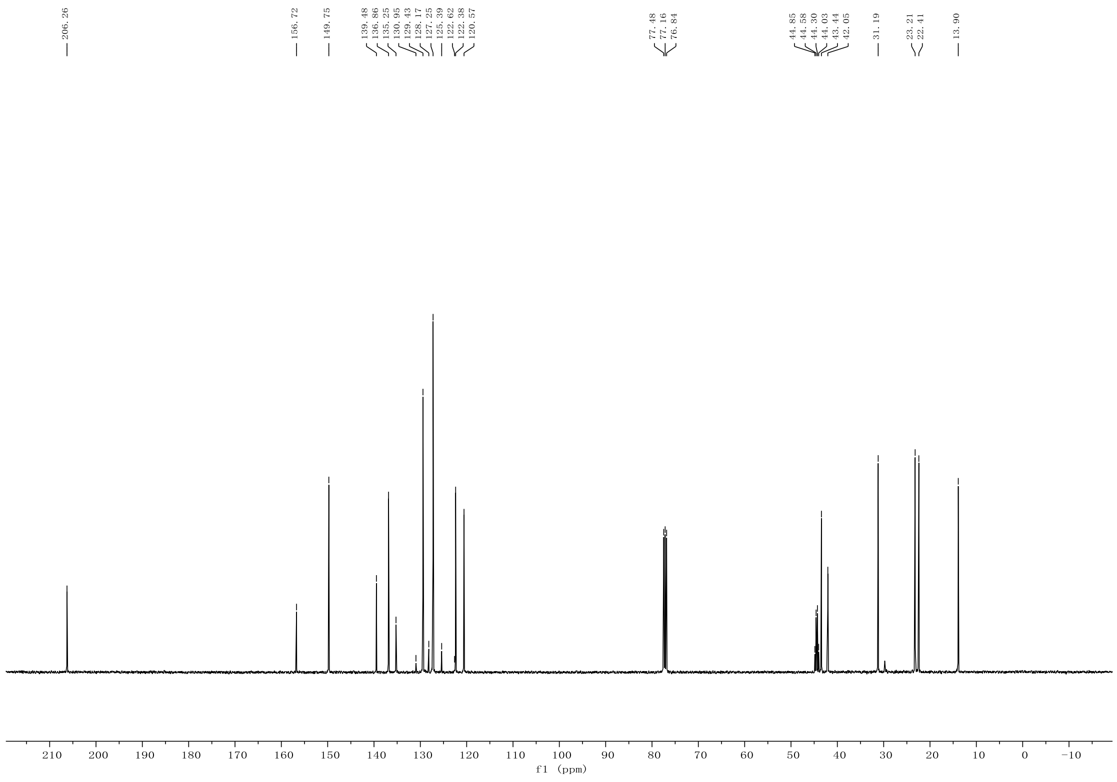


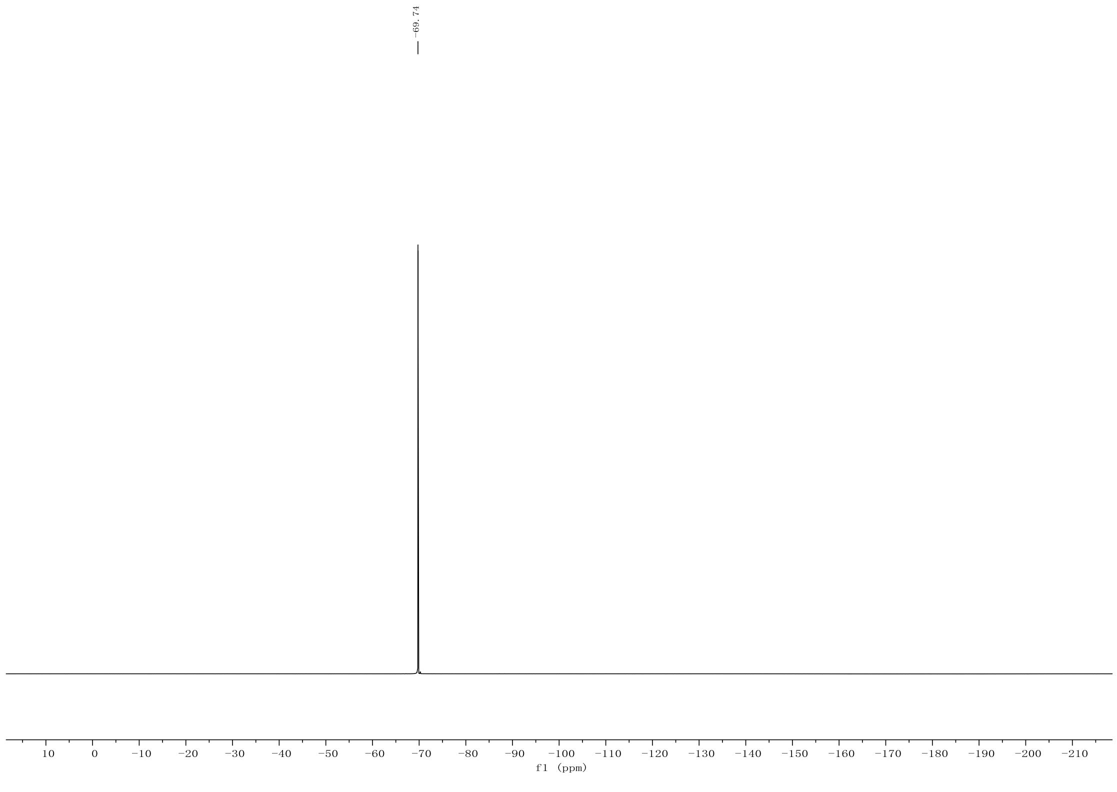

-69.70
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

1,1,1-Trifluoro-2-(4-(pyridin-2-yl)phenyl)nonan-4-one (3na)

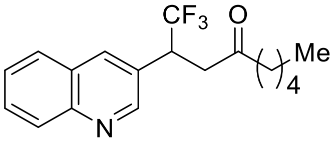


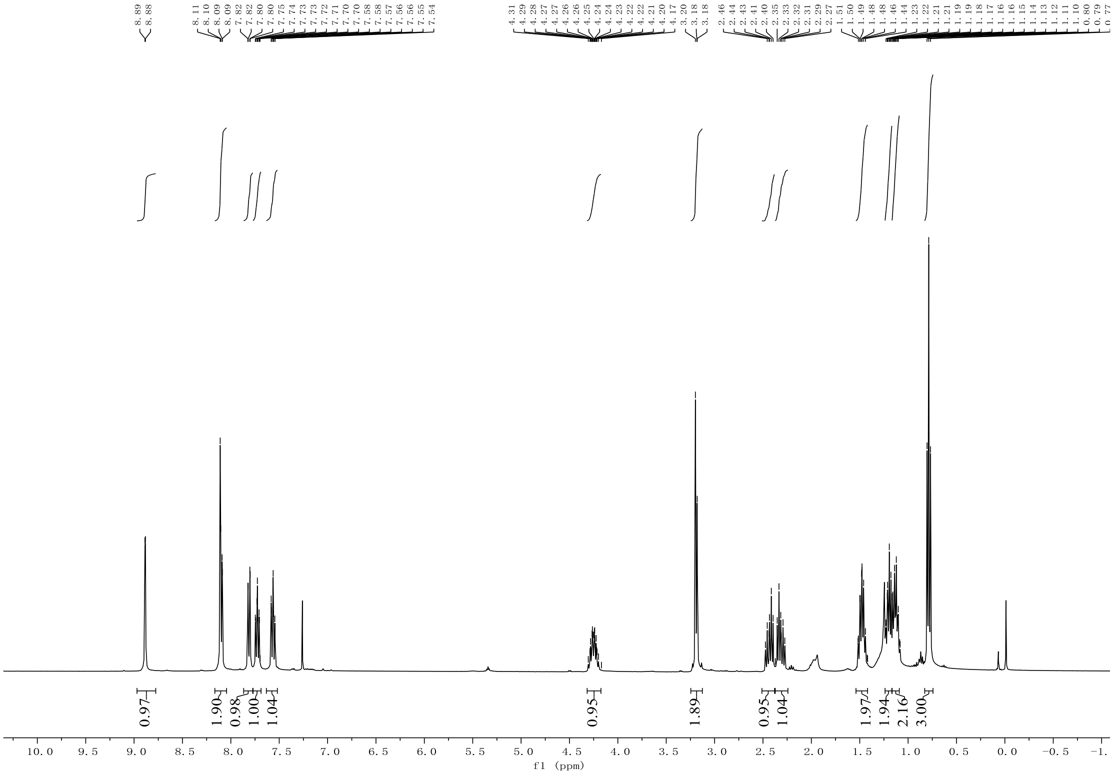


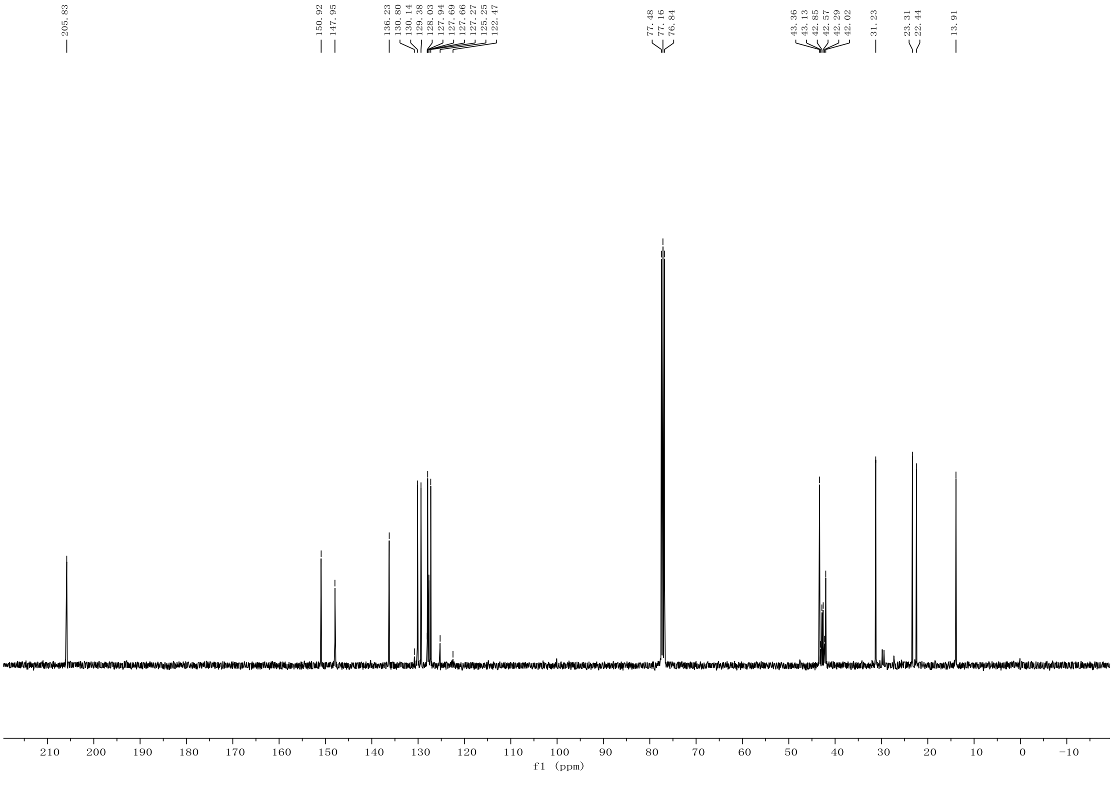

206.26
156.72
149.75
139.48
136.86
135.25
130.95
129.43
128.17
127.25
125.39
122.62
122.38
120.57
77.48
77.16
76.84
44.85
44.58
44.30
44.03
43.44
42.65
31.19
23.21
22.41
13.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

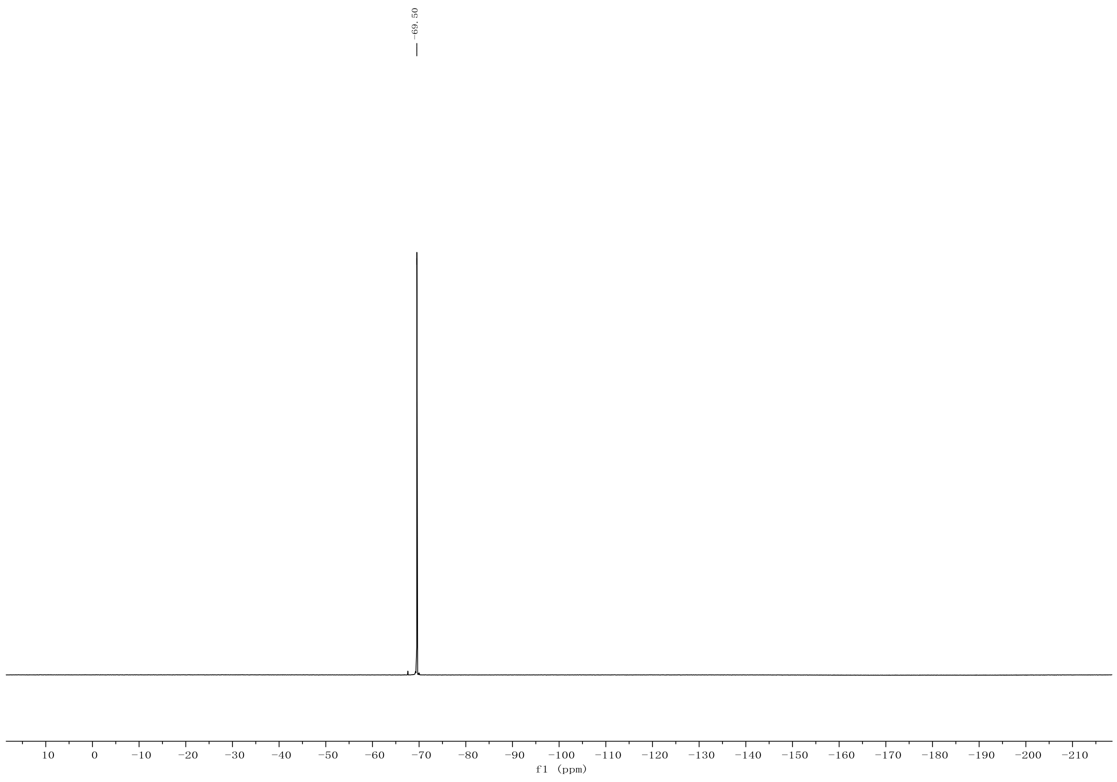

−69.74
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

1,1,1-Trifluoro-2-(quinolin-3-yl)nonan-4-one (3oa)

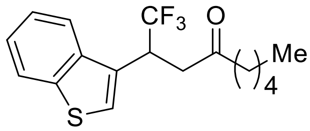


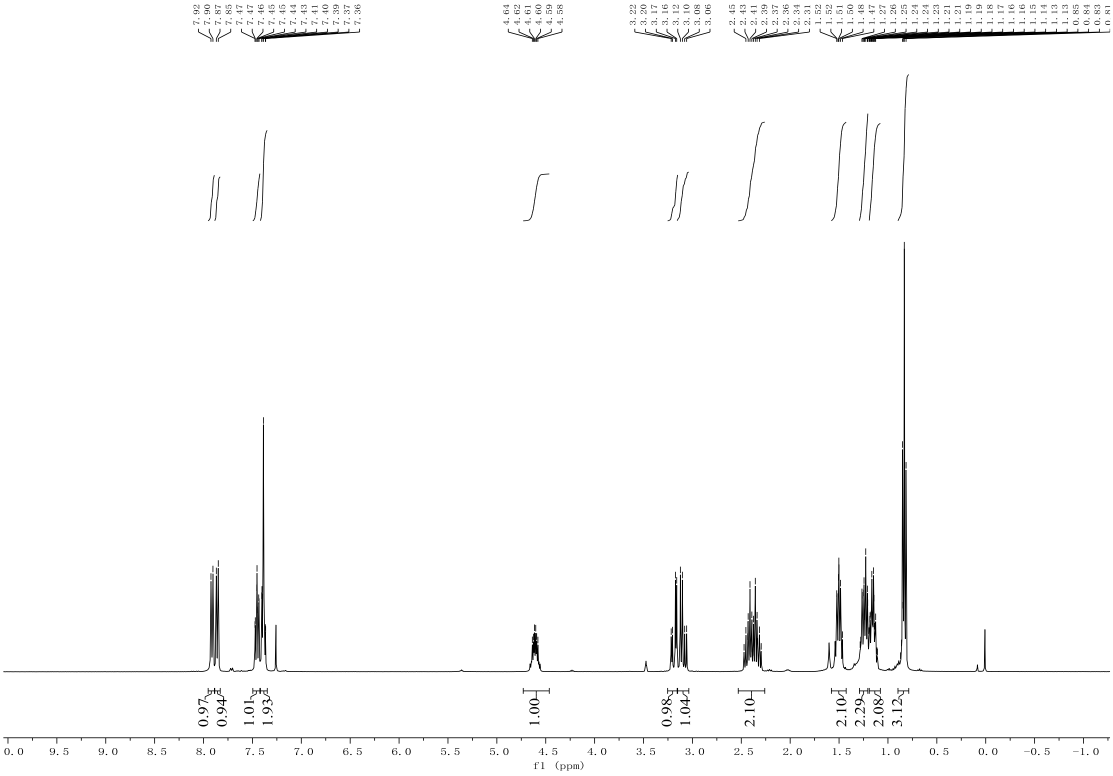


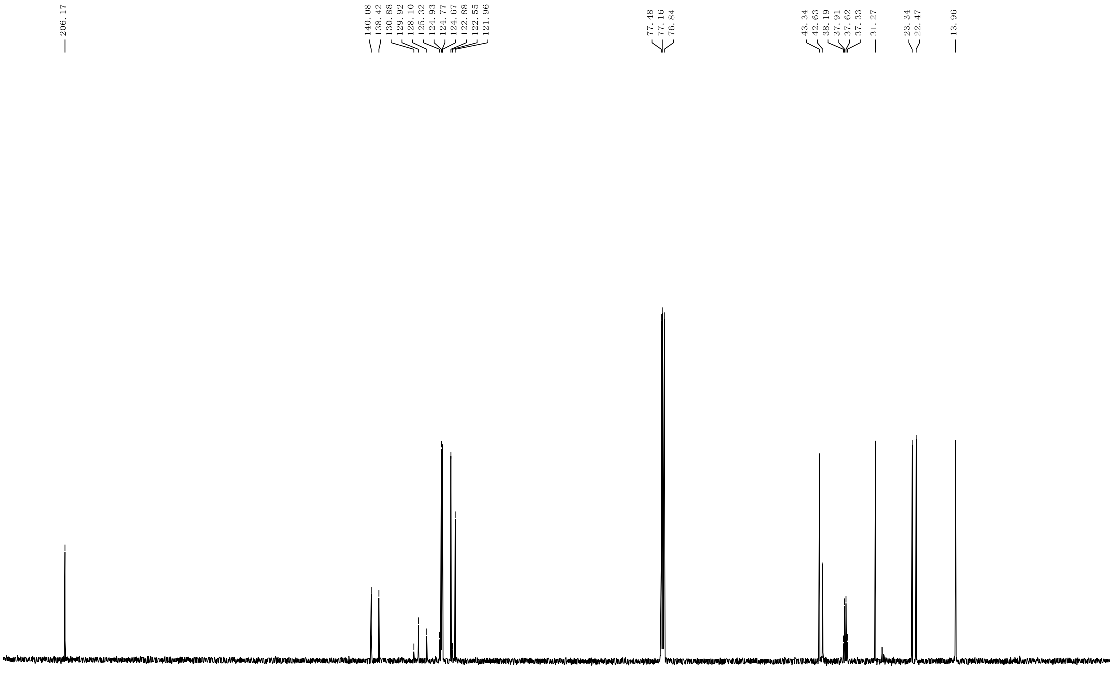


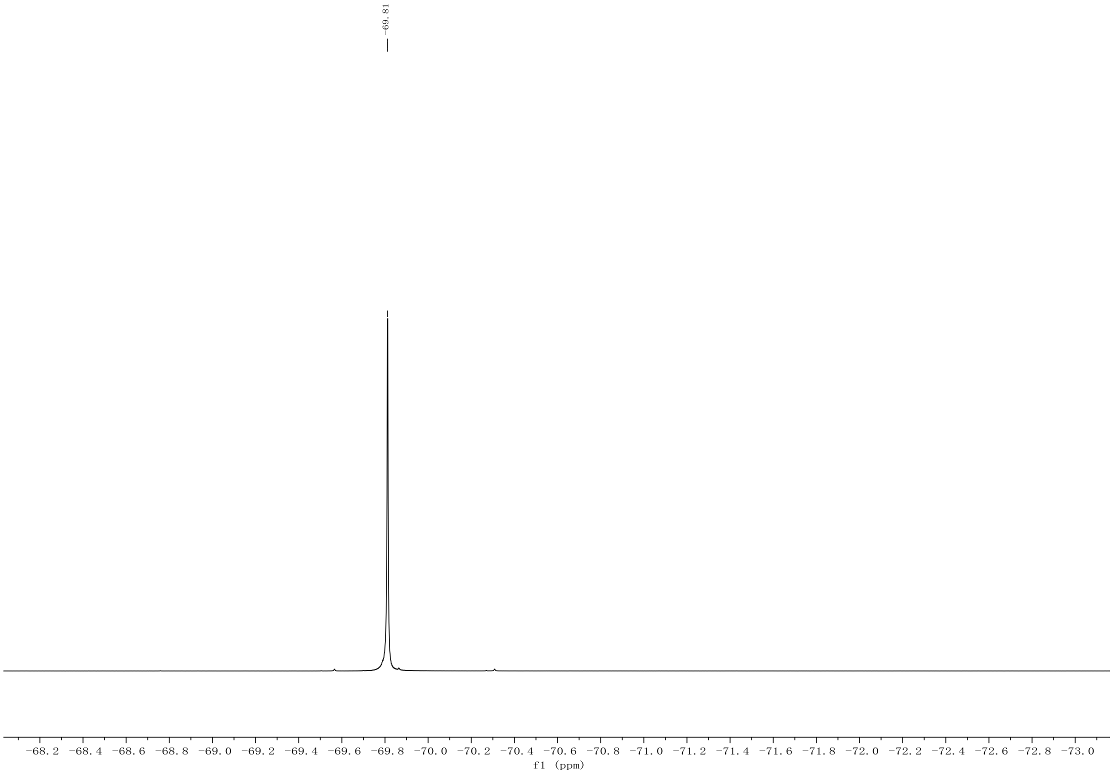

-69.50
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

2-(Benzo[b]thiophen-3-yl)-1,1,1-trifluorononan-4-one (3pa)

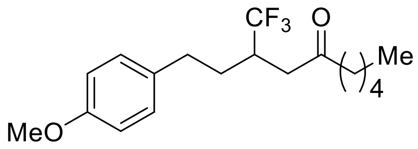


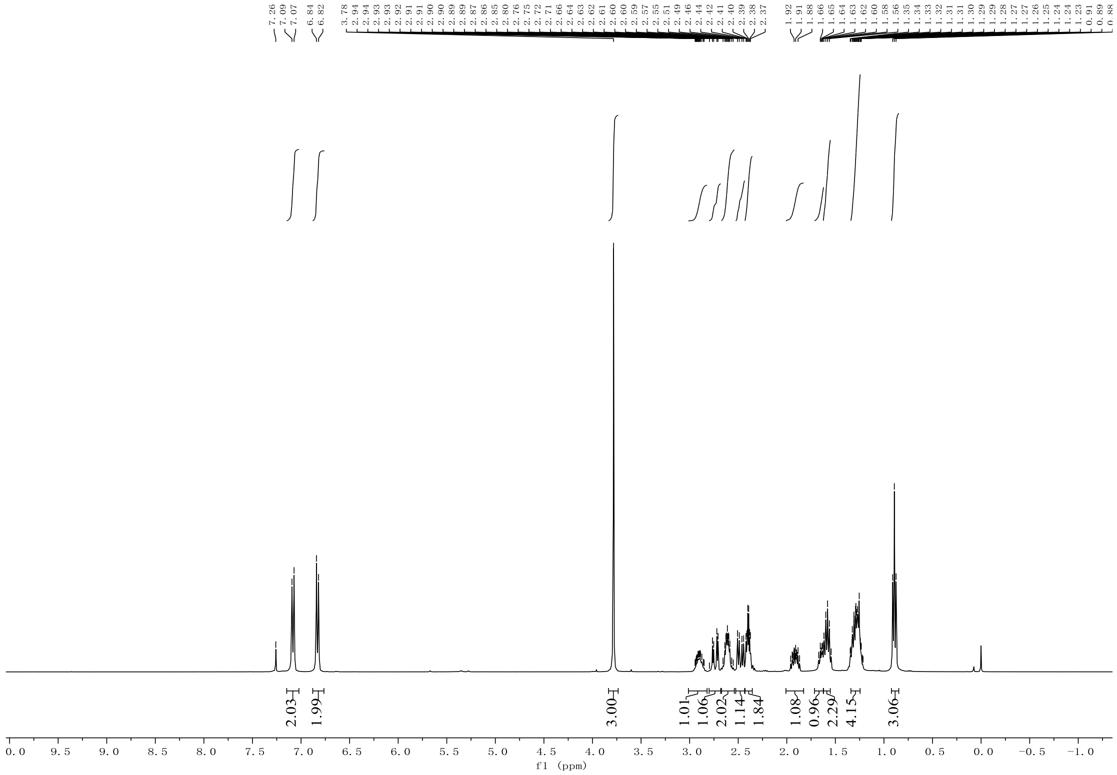


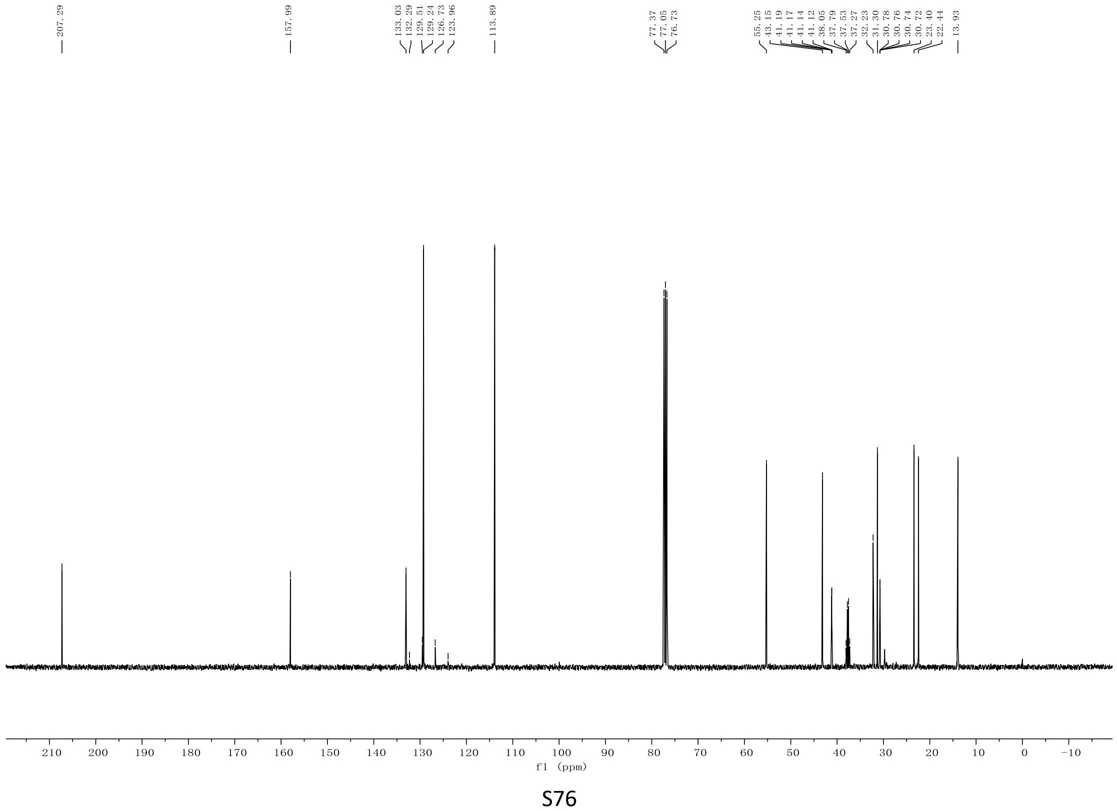


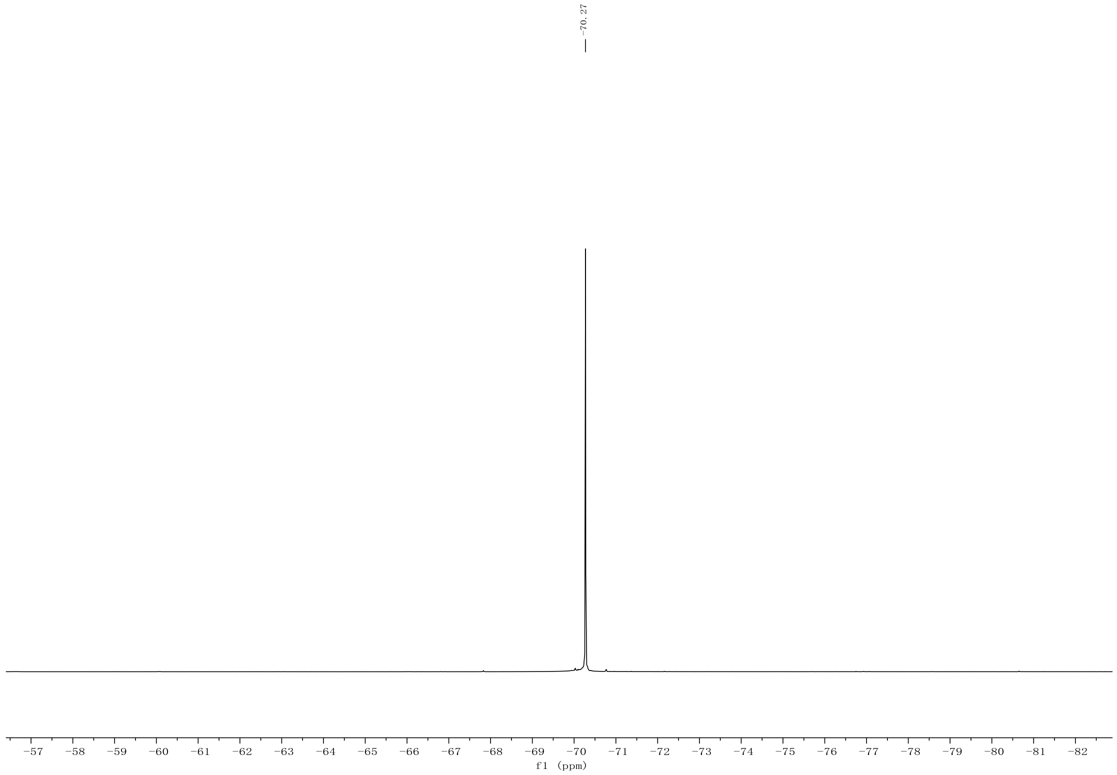

-69.81
-68.2
-68.4
-68.6
-68.8
-69.0
-69.2
-69.4
-69.6
-69.8
-70.0
-70.2
-70.4
-70.6
-70.8
-71.0
-71.2
-71.4
-71.6
-71.8
-72.0
-72.2
-72.4
-72.6
-72.8
-73.0
f1 (ppm)

1-(4-Methoxyphenyl)-3-(trifluoromethyl)decan-5-one (3qa)



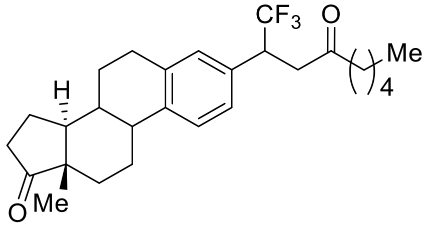


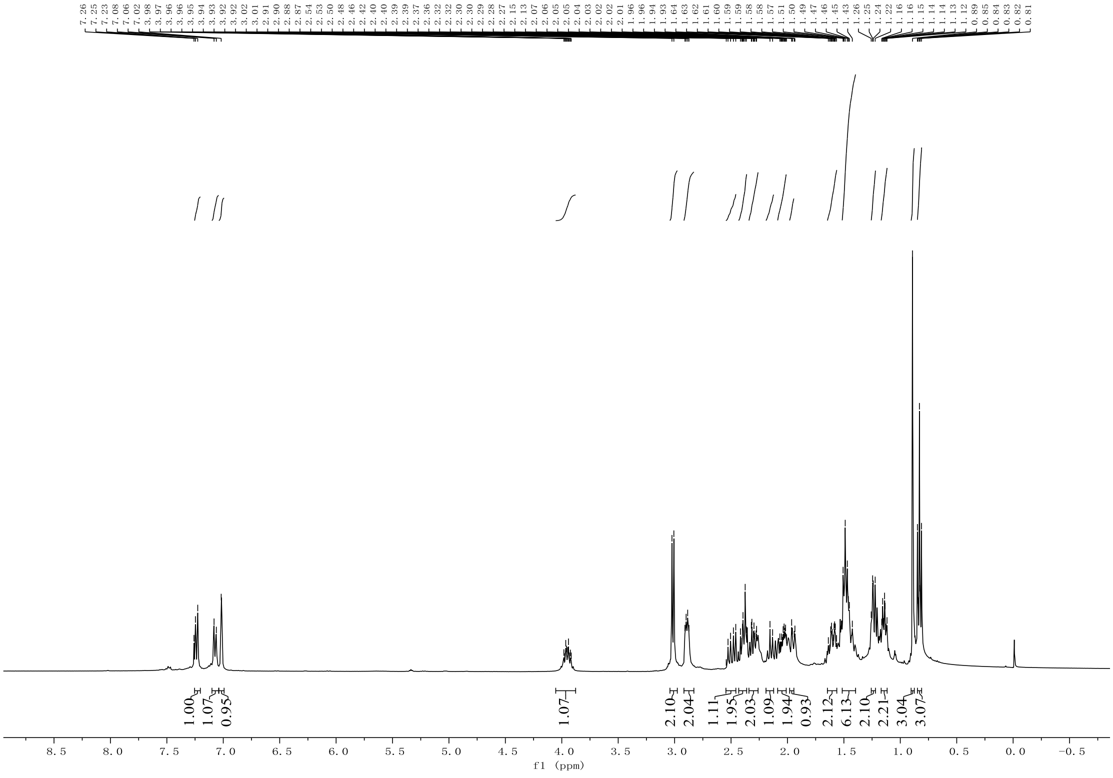


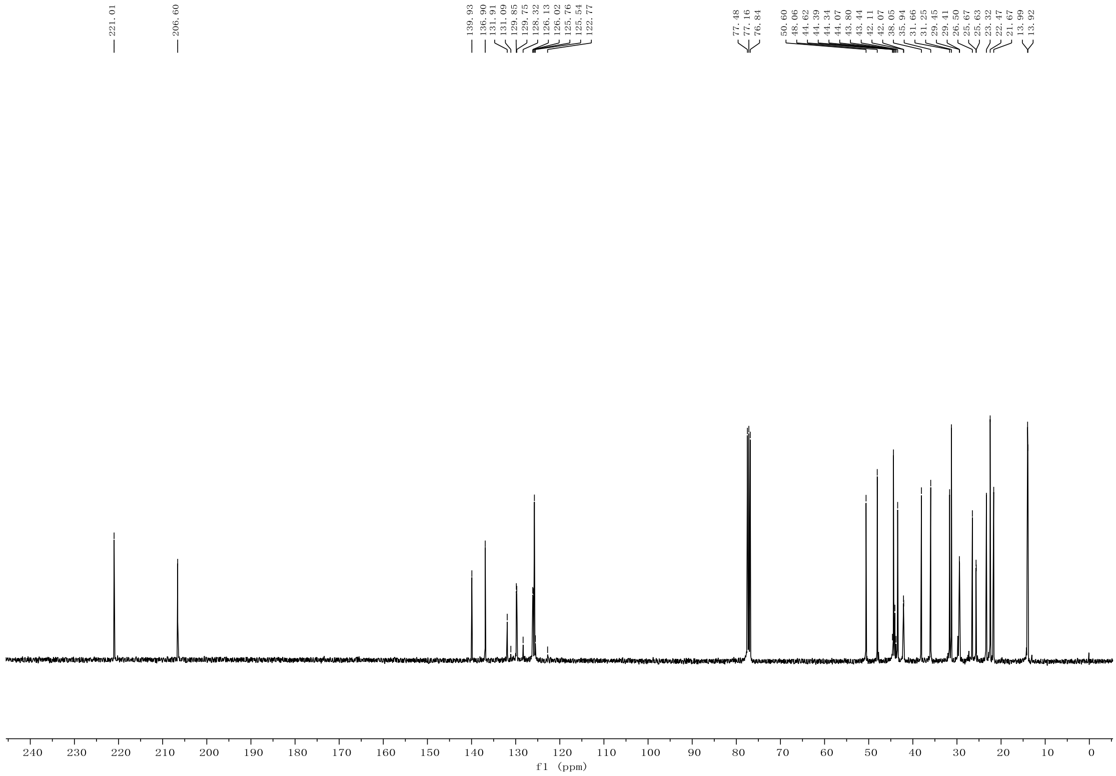


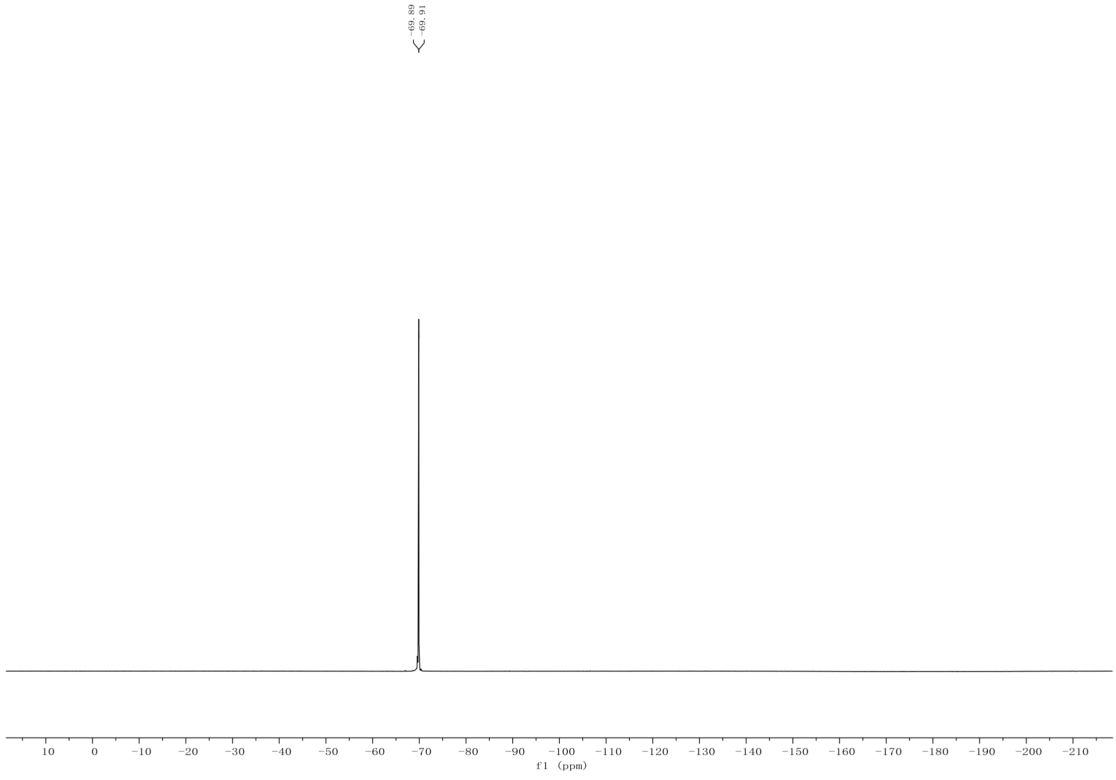
-70.27
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
-77
-78
-79
-80
-81
-82
f1 (ppm)

(13*S*,14*S*)-13-methyl-3-(1,1,1-trifluoro-4-oxononan-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (3ra)

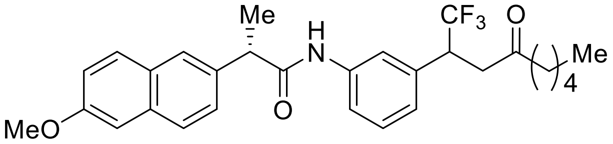


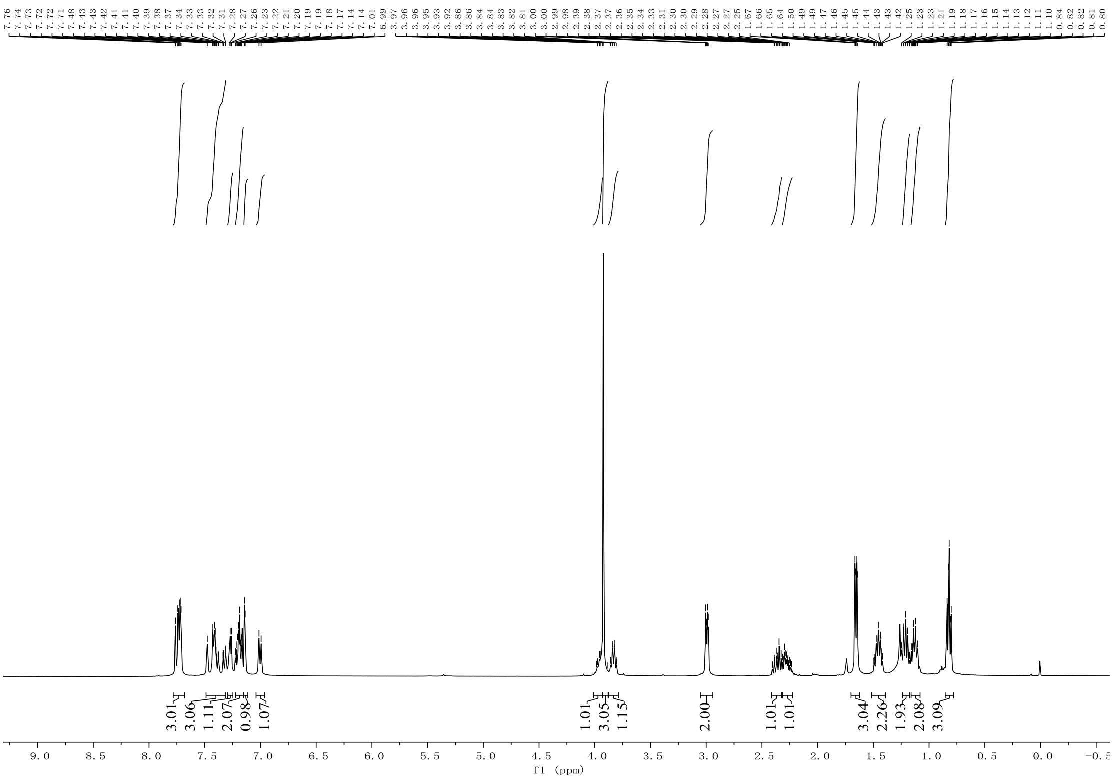


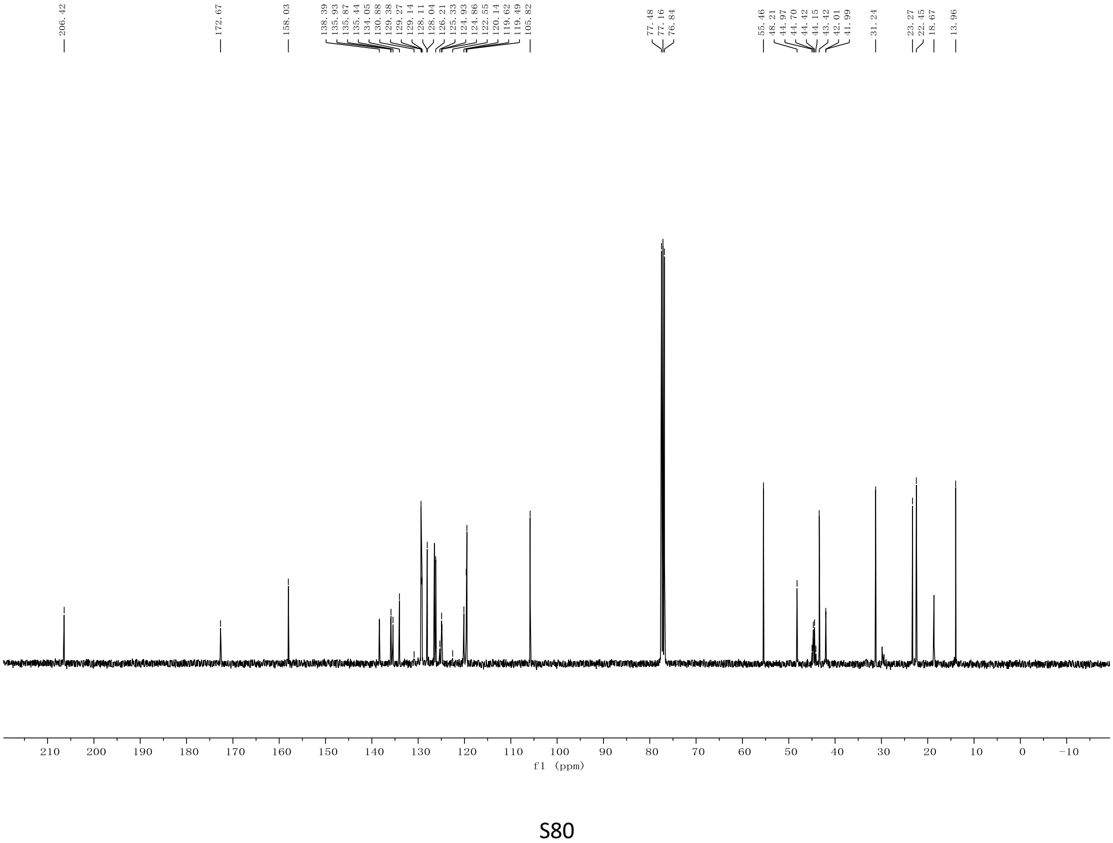

221.01
206.60
139.93
136.90
131.91
131.09
129.85
129.75
128.32
126.13
126.02
125.76
125.54
122.77
77.48
77.16
76.84
50.60
48.06
44.62
44.39
44.34
44.07
43.80
43.44
42.11
42.07
38.05
35.94
31.66
31.25
29.45
29.41
26.50
25.67
25.63
23.32
22.47
21.67
13.99
13.92
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

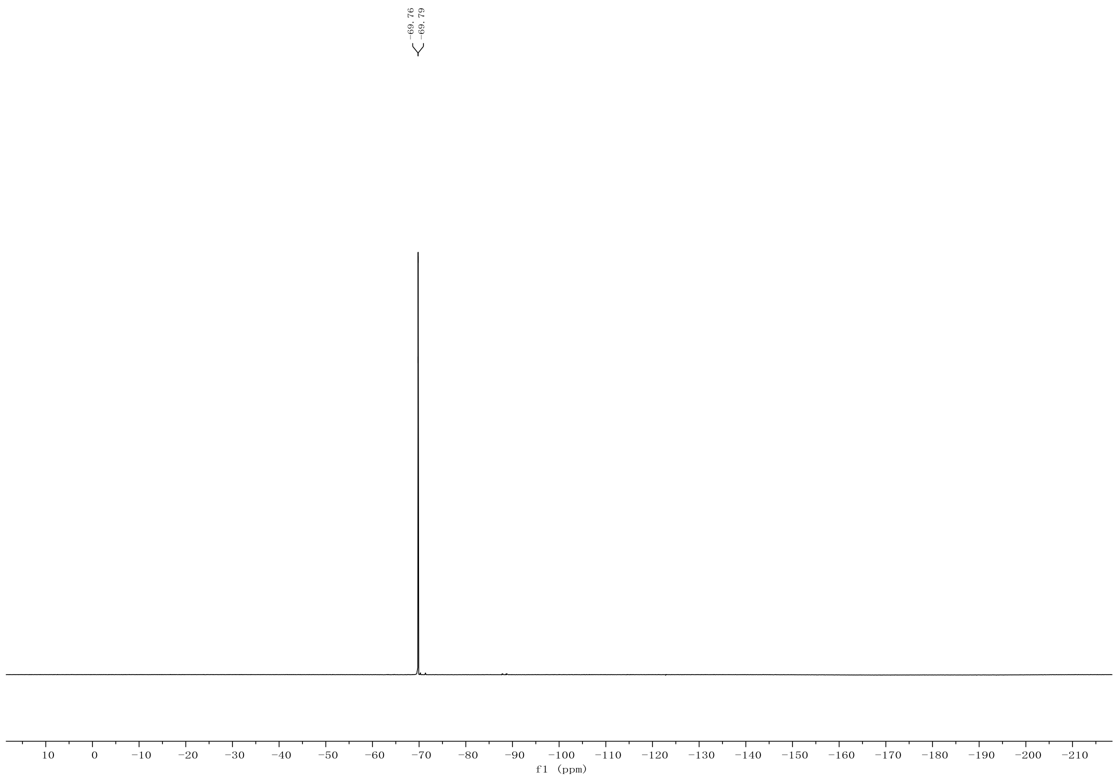

-69.89
-69.91
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

(2*S*)-2-(6-Methoxynaphthalen-2-yl)-*N*-(3-(1,1,1-trifluoro-4-oxononan-2-yl)phenyl)propanamide (3sa)

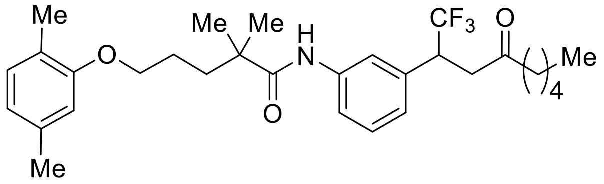


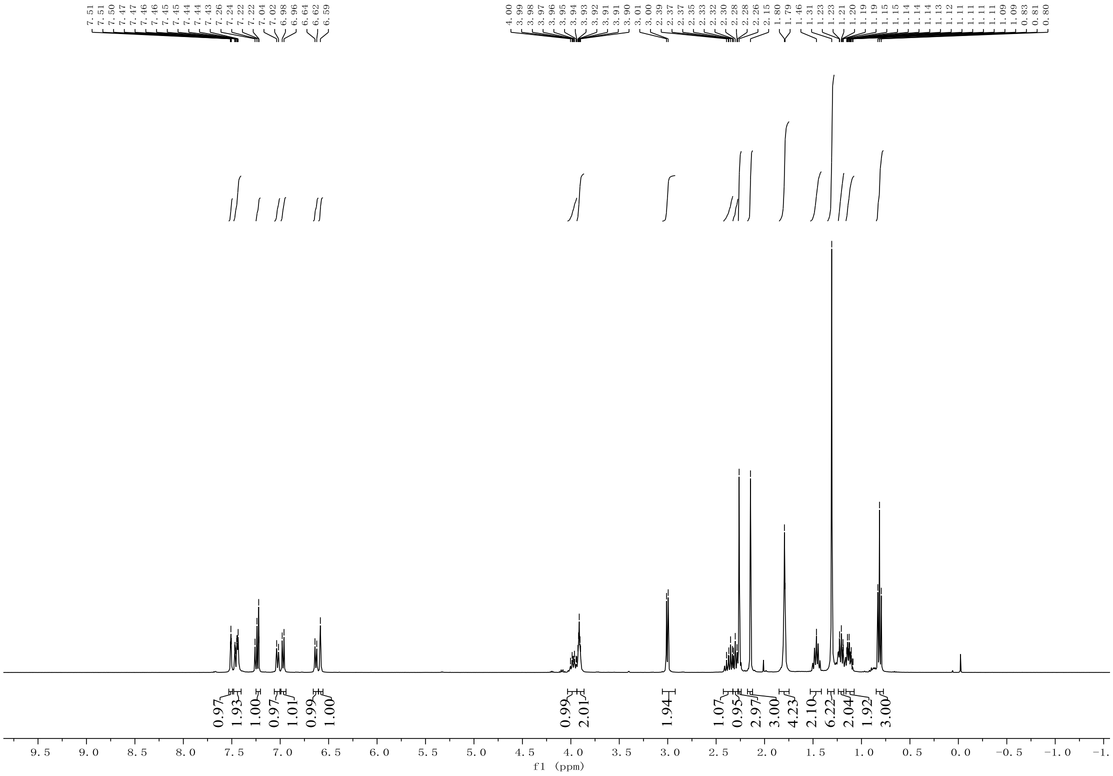


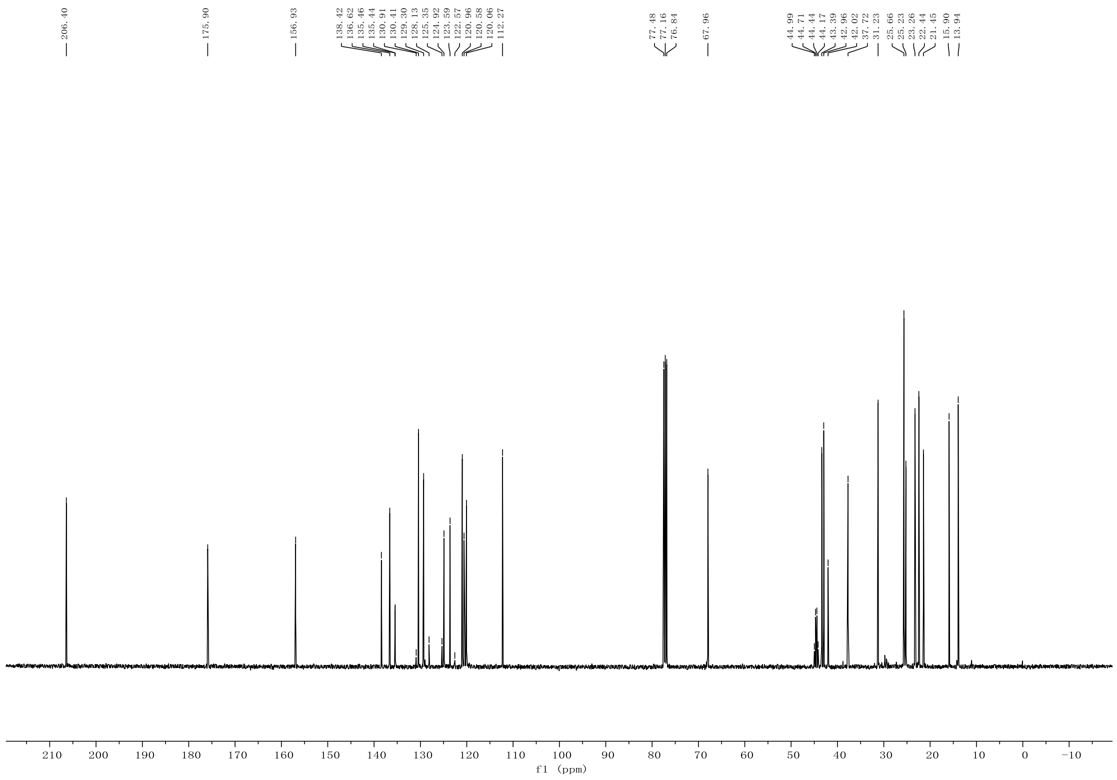


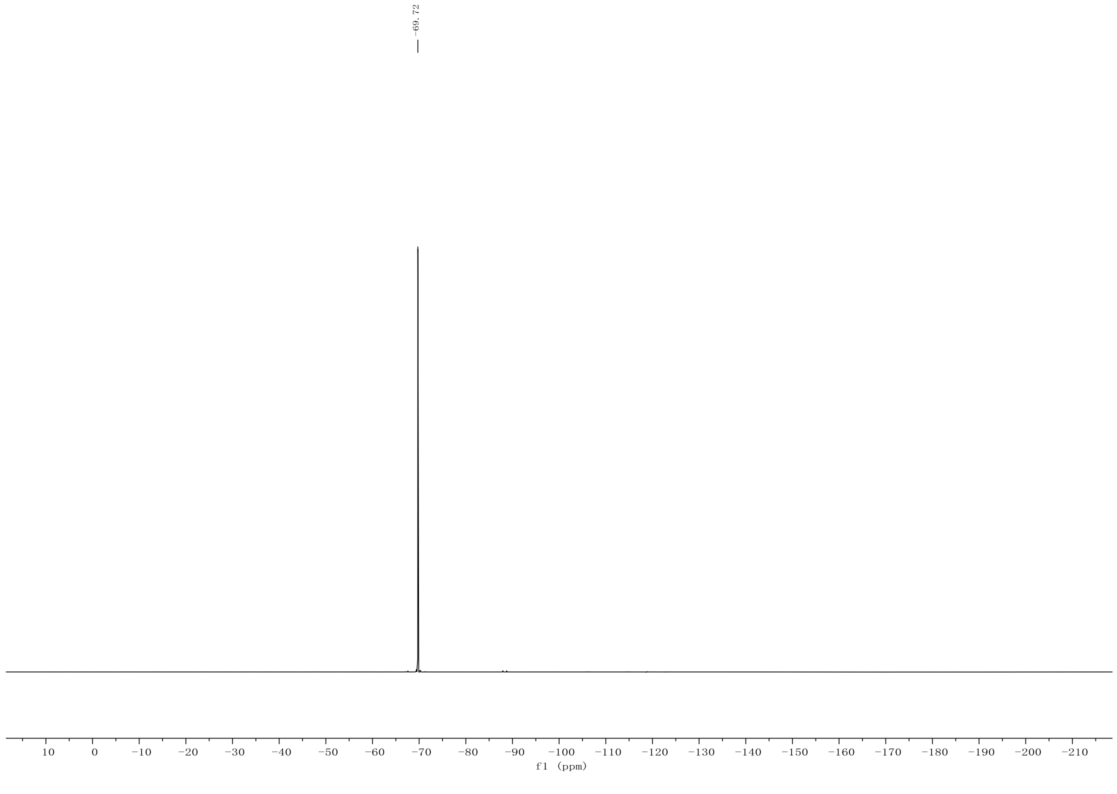

-69.76
-69.79
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

5-(2,5-Dimethylphenoxy)-2,2-dimethyl-*N*-(3-(1,1,1-trifluoro-4-oxohexan-2-yl)phenyl)pentanamide (3ta)

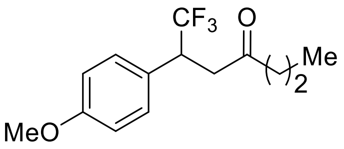


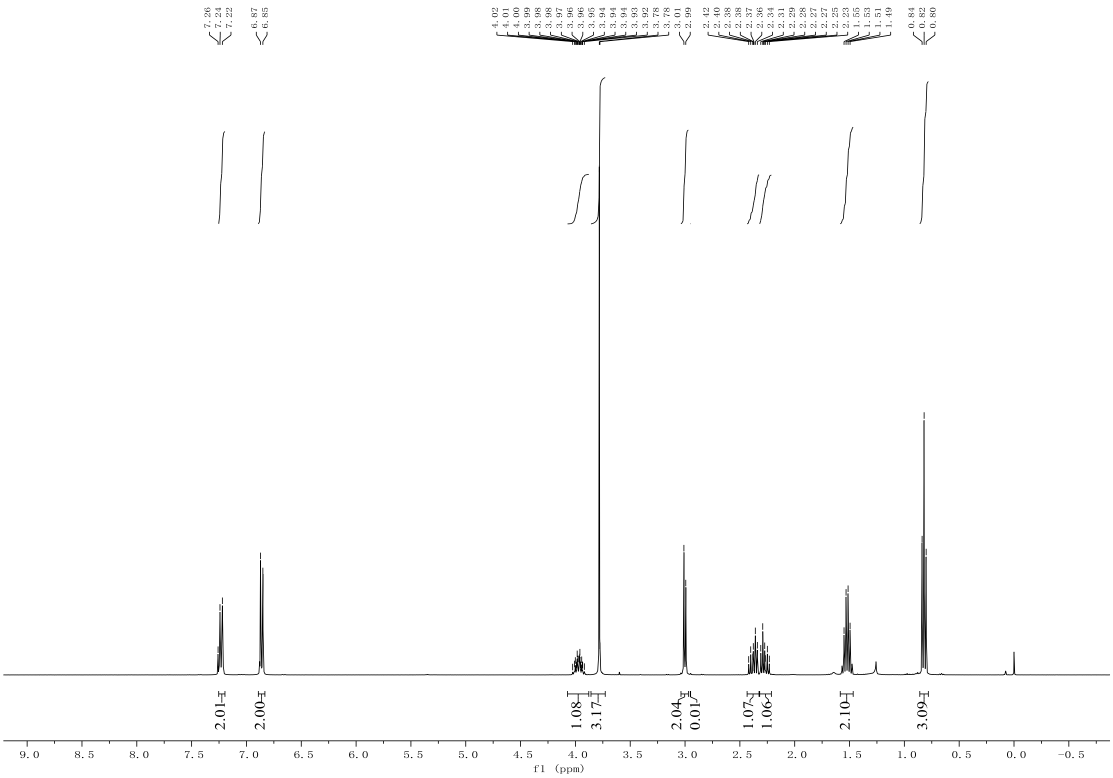


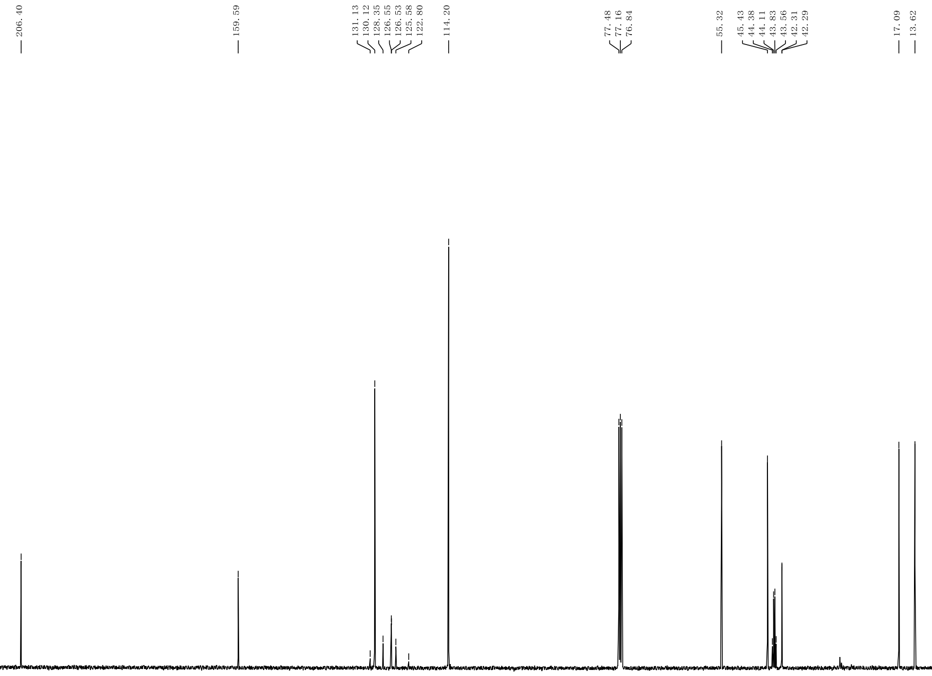

206.40
175.90
156.93
138.42
136.62
135.46
135.44
130.91
130.41
129.30
128.13
125.35
124.92
123.59
122.57
120.96
120.58
120.06
112.27
77.48
77.16
76.84
67.96
44.99
44.71
44.44
44.17
43.39
42.96
42.02
37.72
31.23
25.66
25.23
23.26
22.44
21.45
15.90
13.94
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

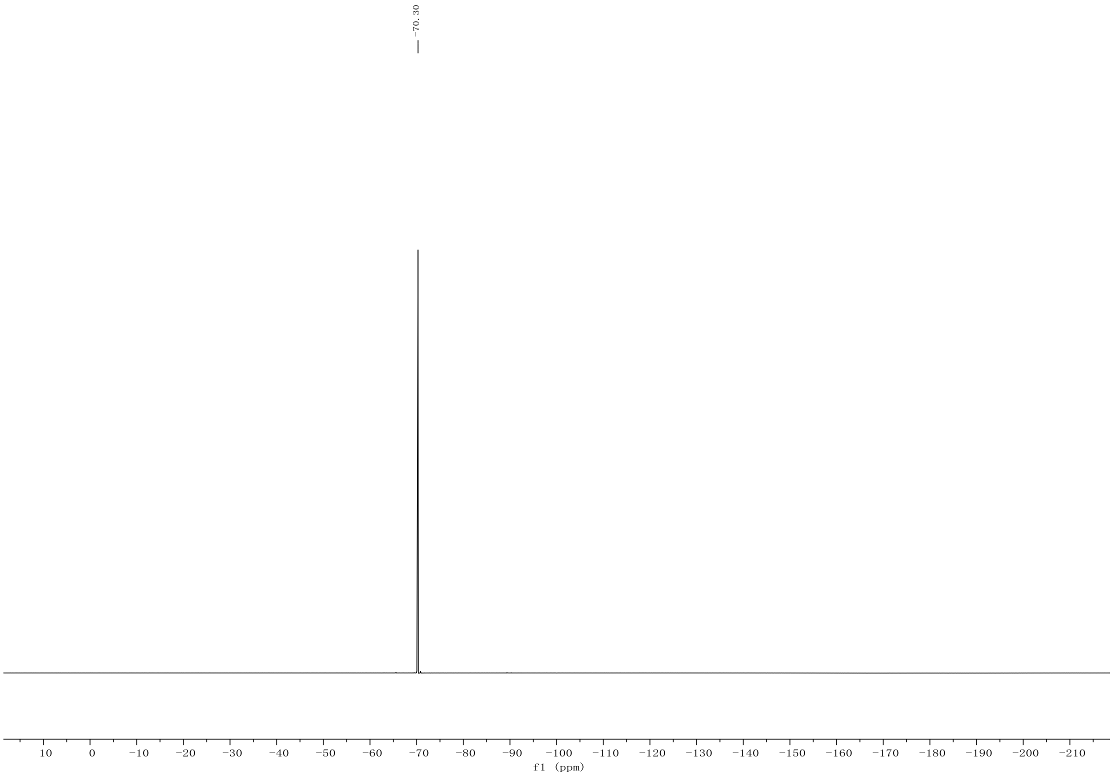

−69.72
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

1,1,1-Trifluoro-2-(4-methoxyphenyl)heptan-4-one (3ab)

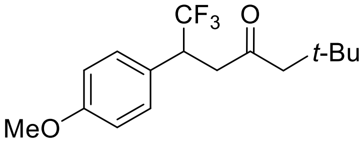


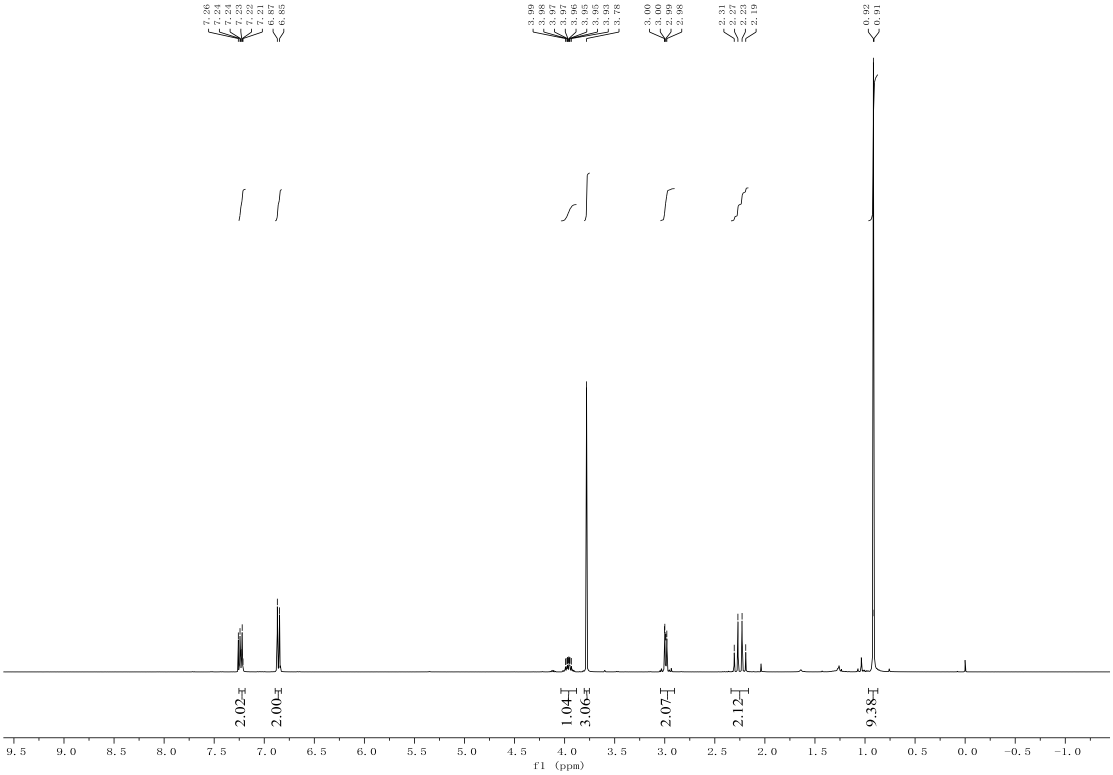


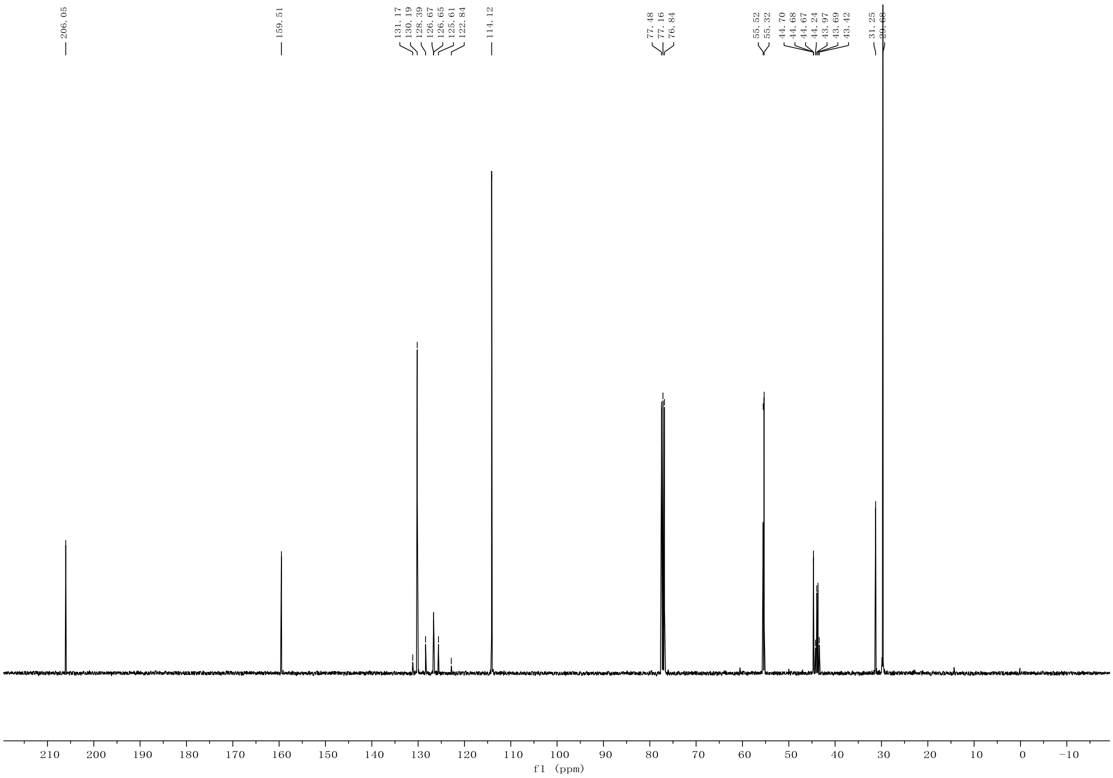


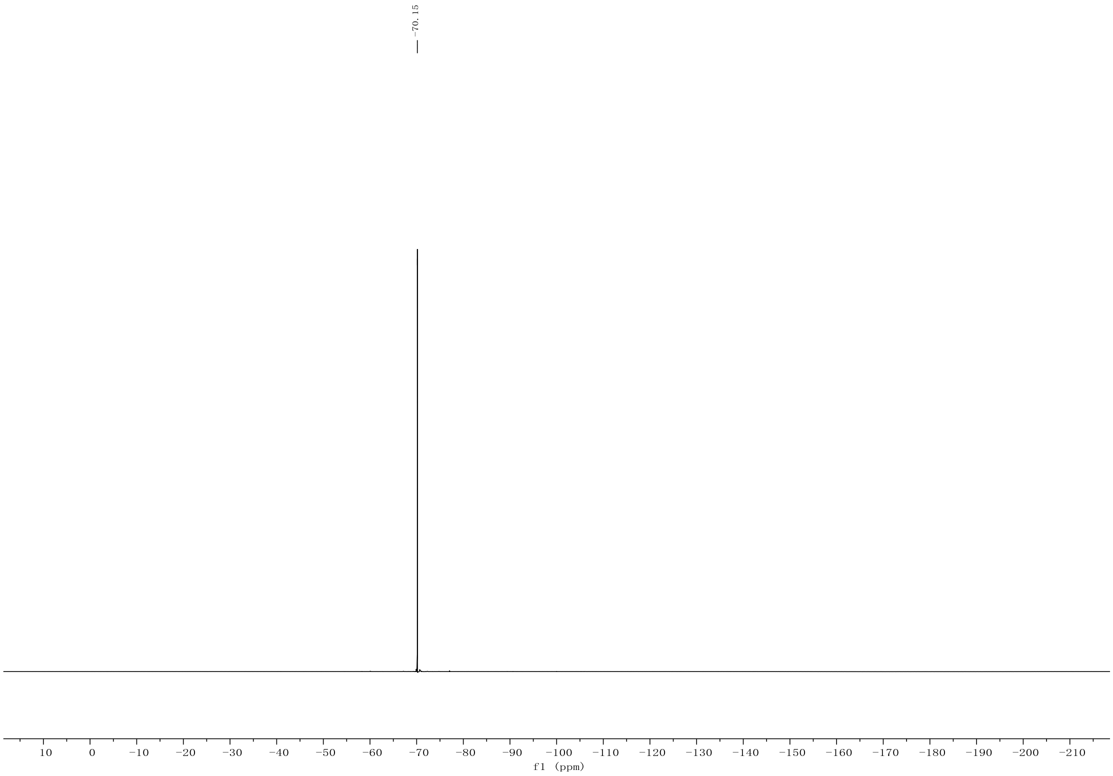

-70.30
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

1,1,1-Trifluoro-2-(4-methoxyphenyl)-6,6-dimethylheptan-4-one (3ac)

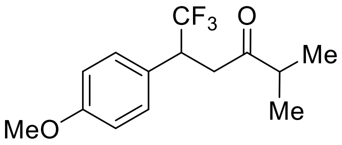


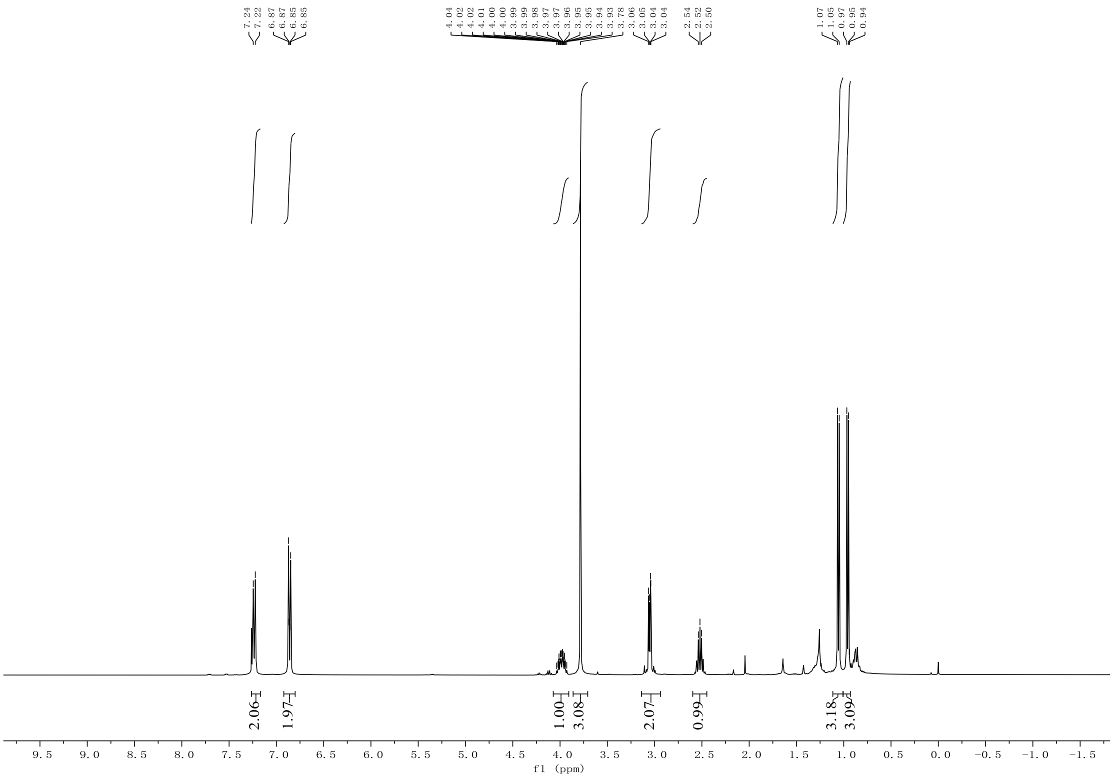


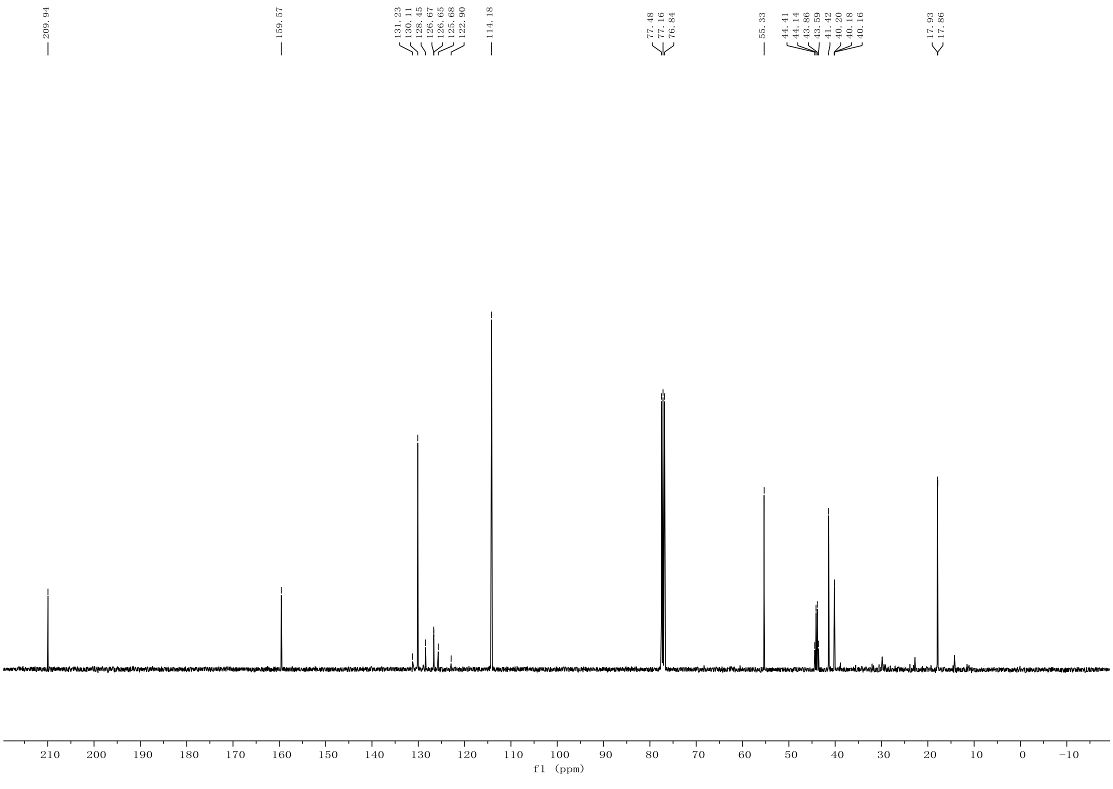


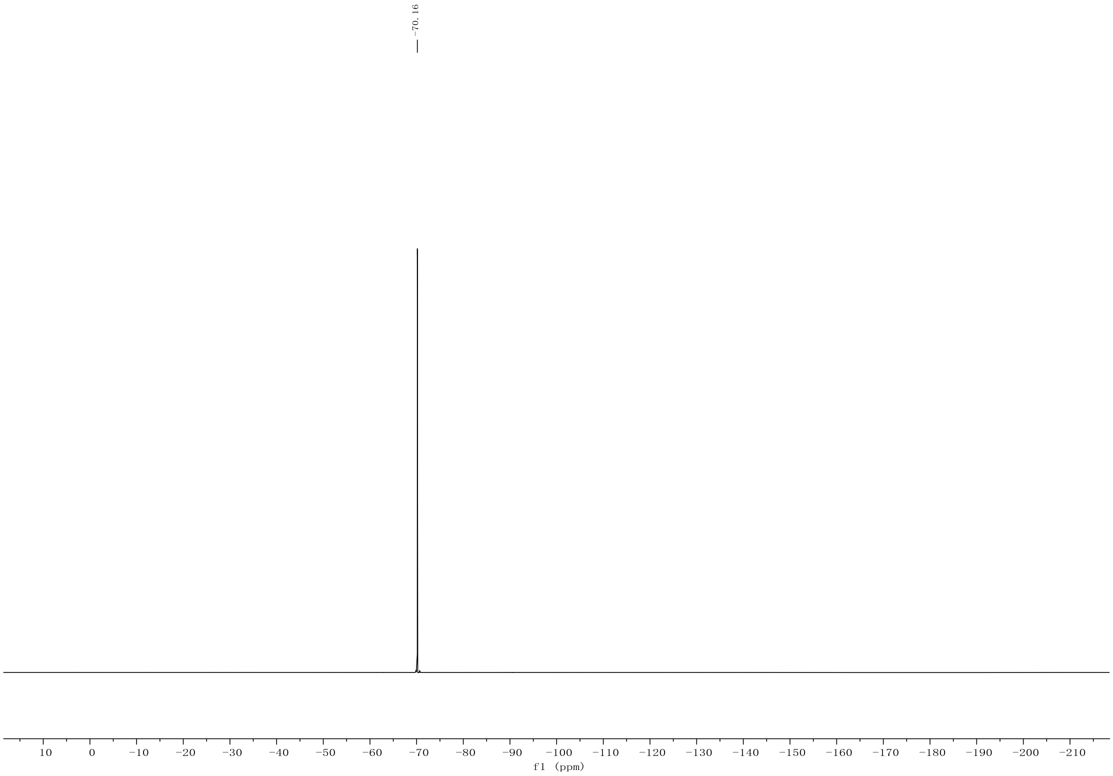

-70.15
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

6,6,6-Trifluoro-5-(4-methoxyphenyl)-2-methylhexan-3-one (3ad)



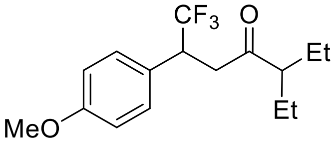


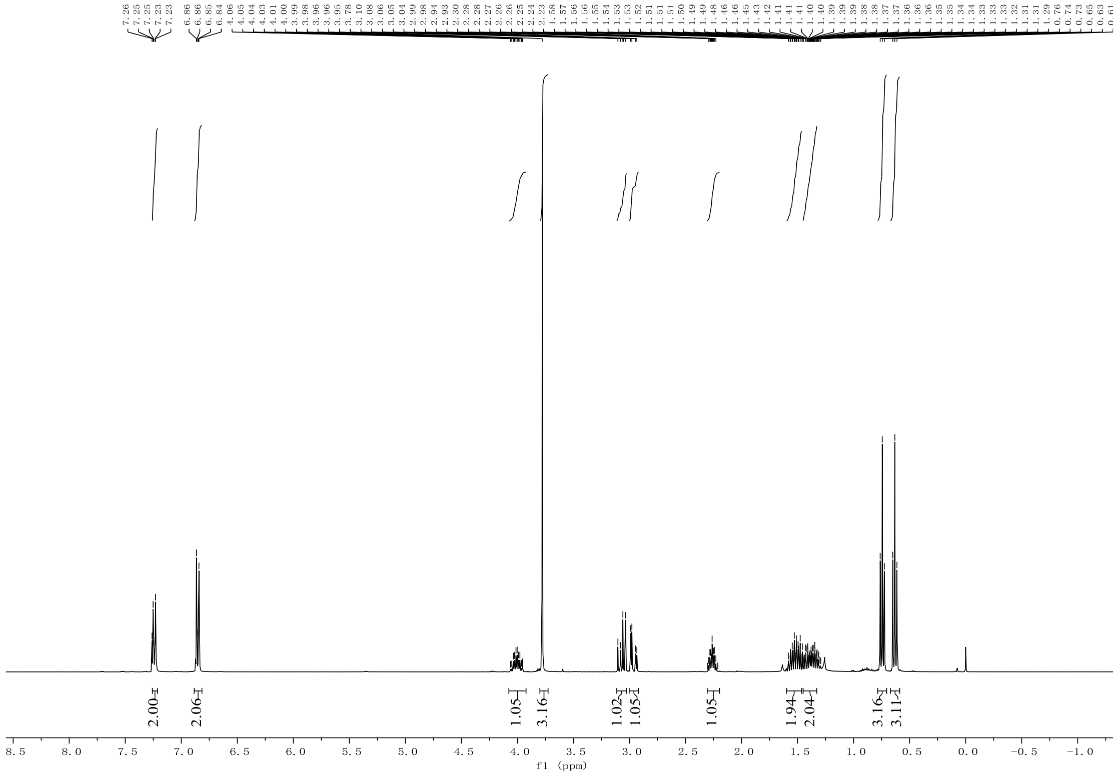


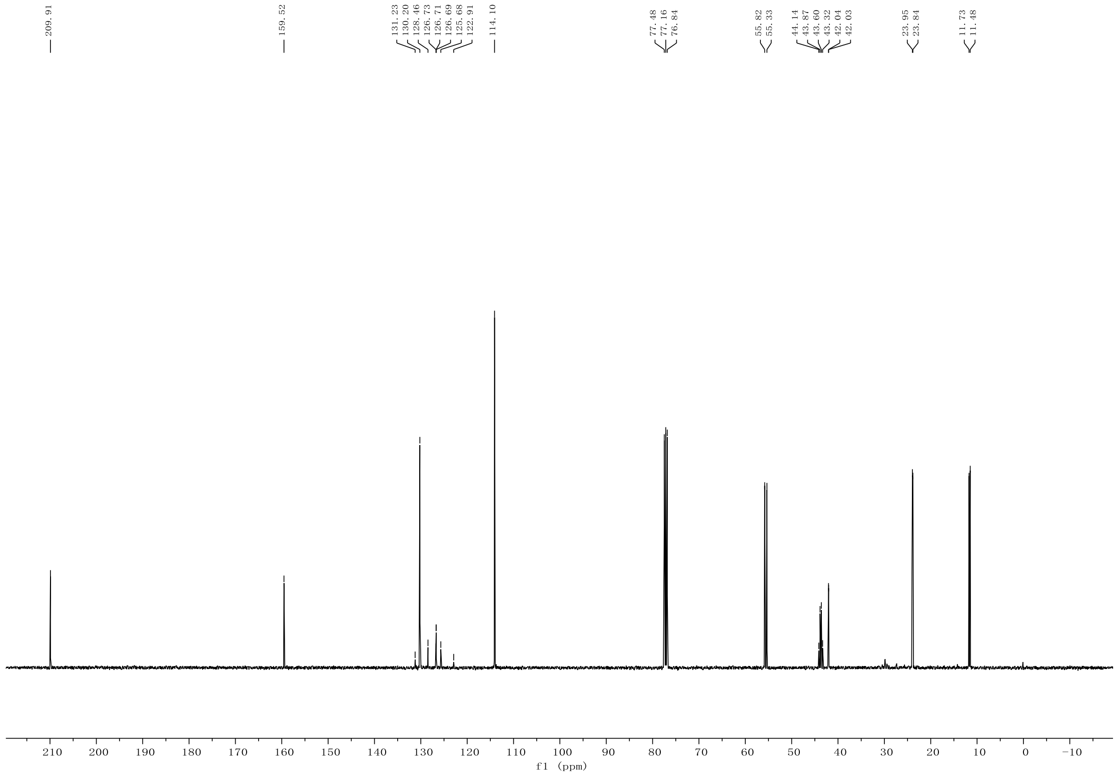


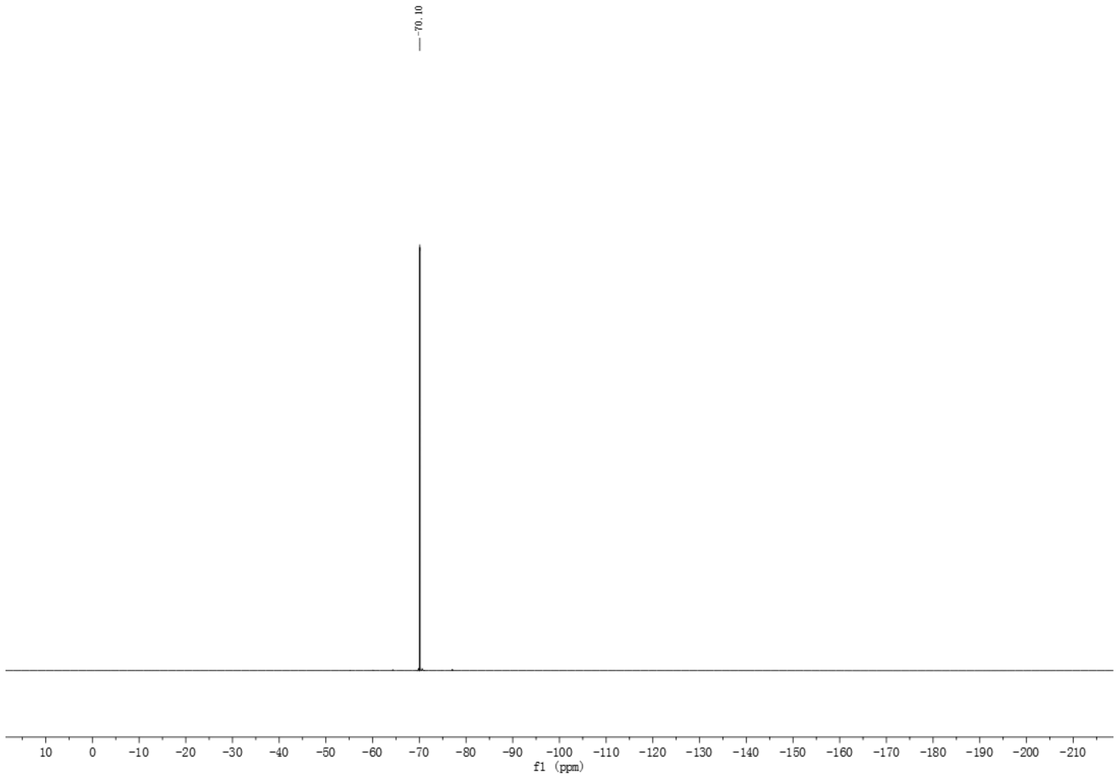
-70.16
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

5-Ethyl-1,1,1-trifluoro-2-(4-methoxyphenyl)heptan-4-one (3ae)








-70.10
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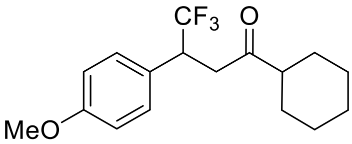
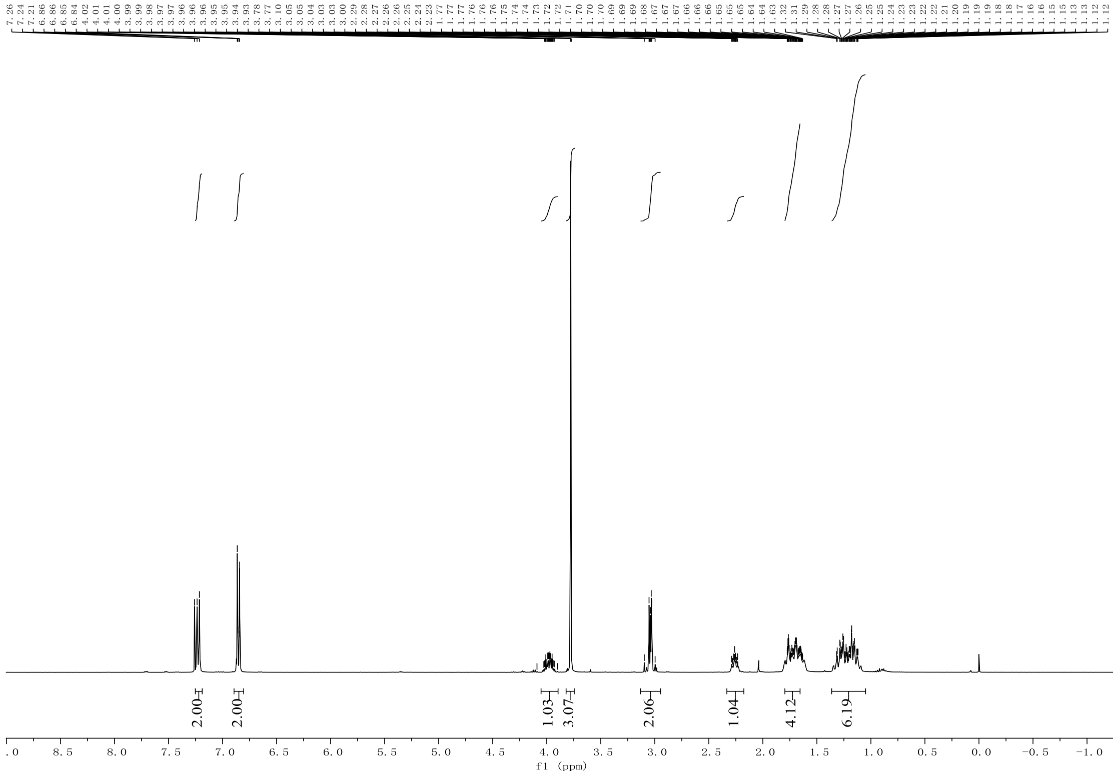
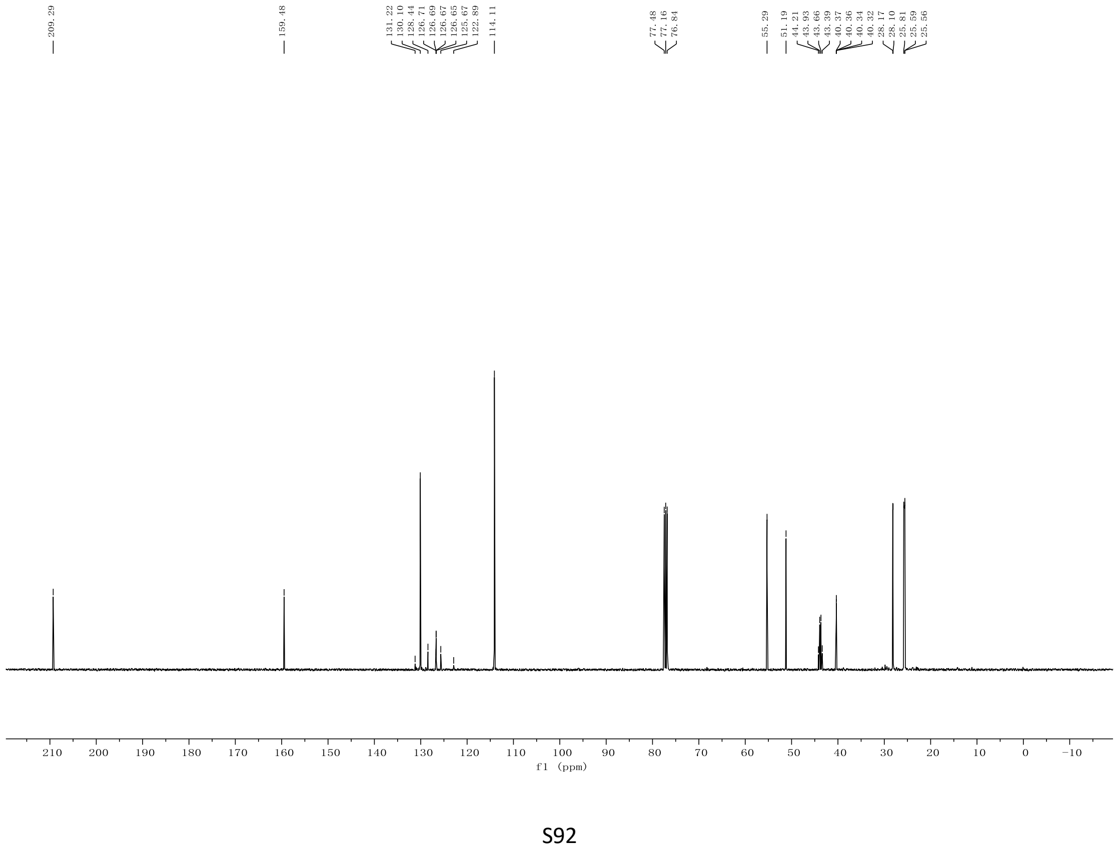
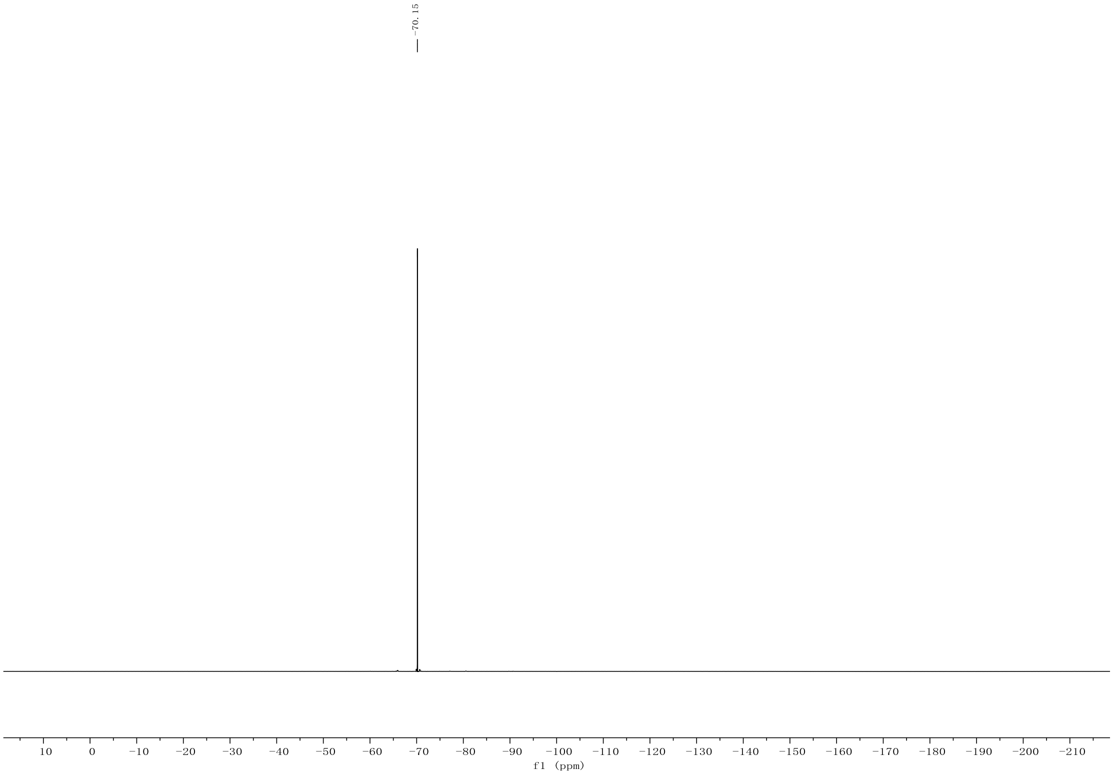
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

1-Cyclohexyl-4,4,4-trifluoro-3-(4-methoxyphenyl)butan-1-one (3af)

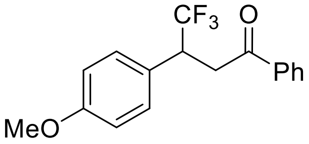


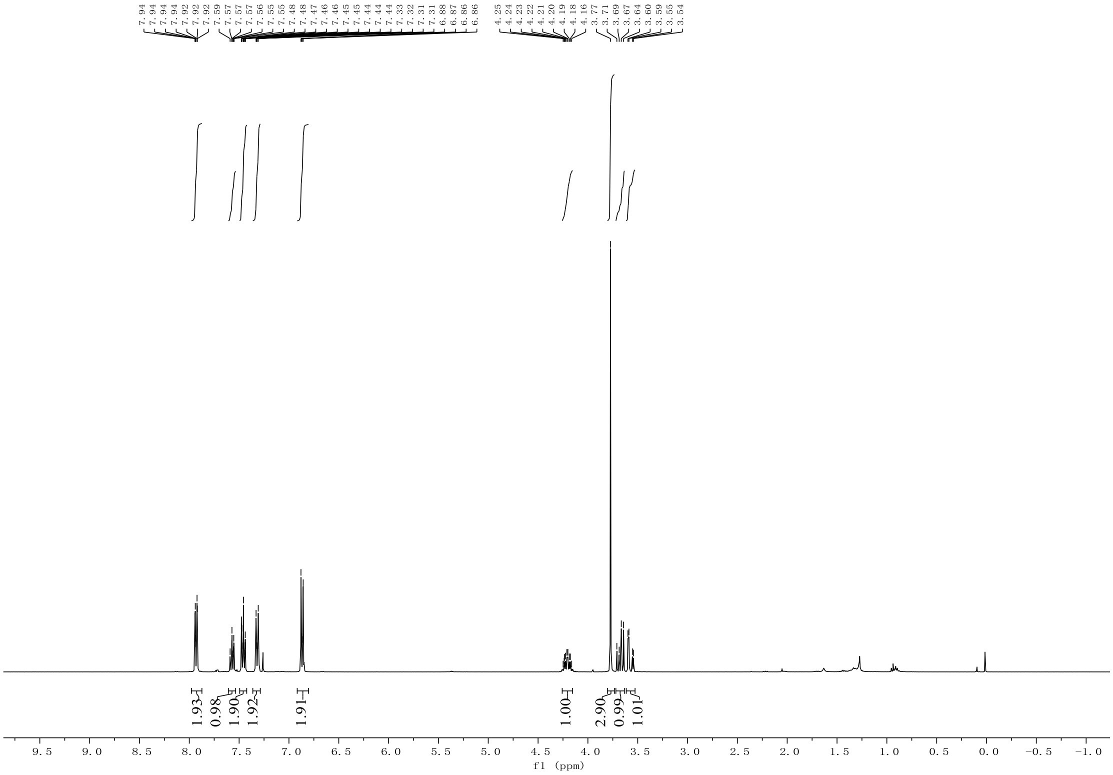


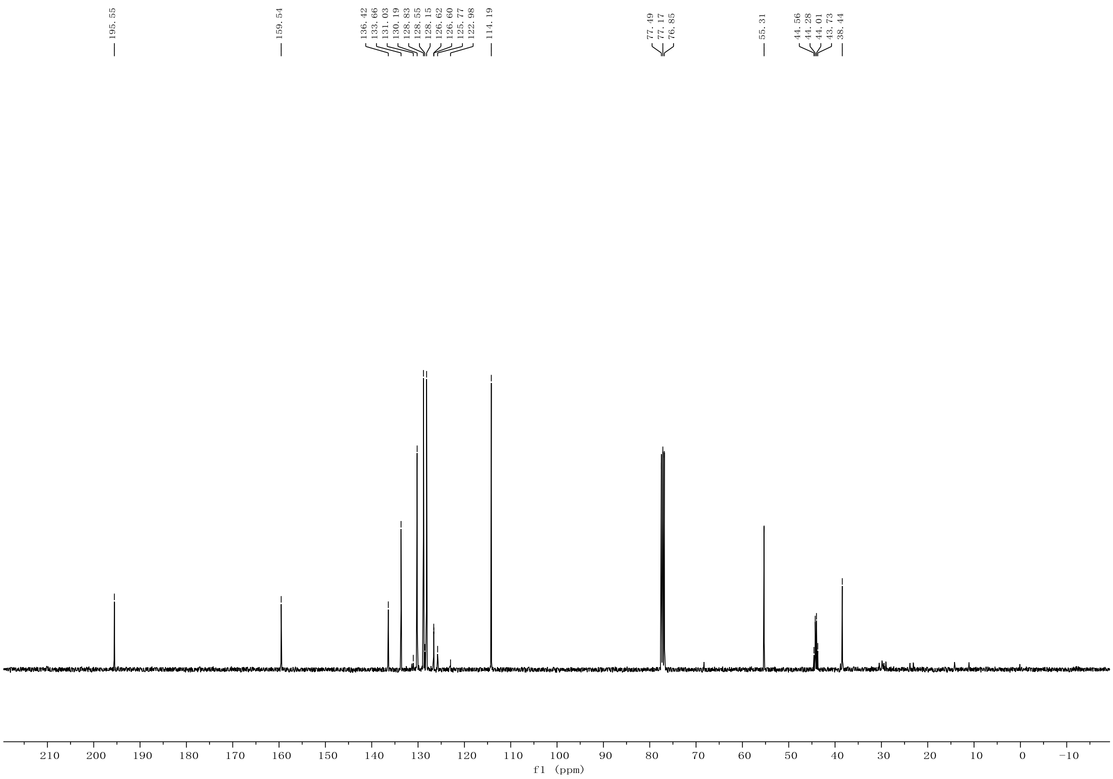


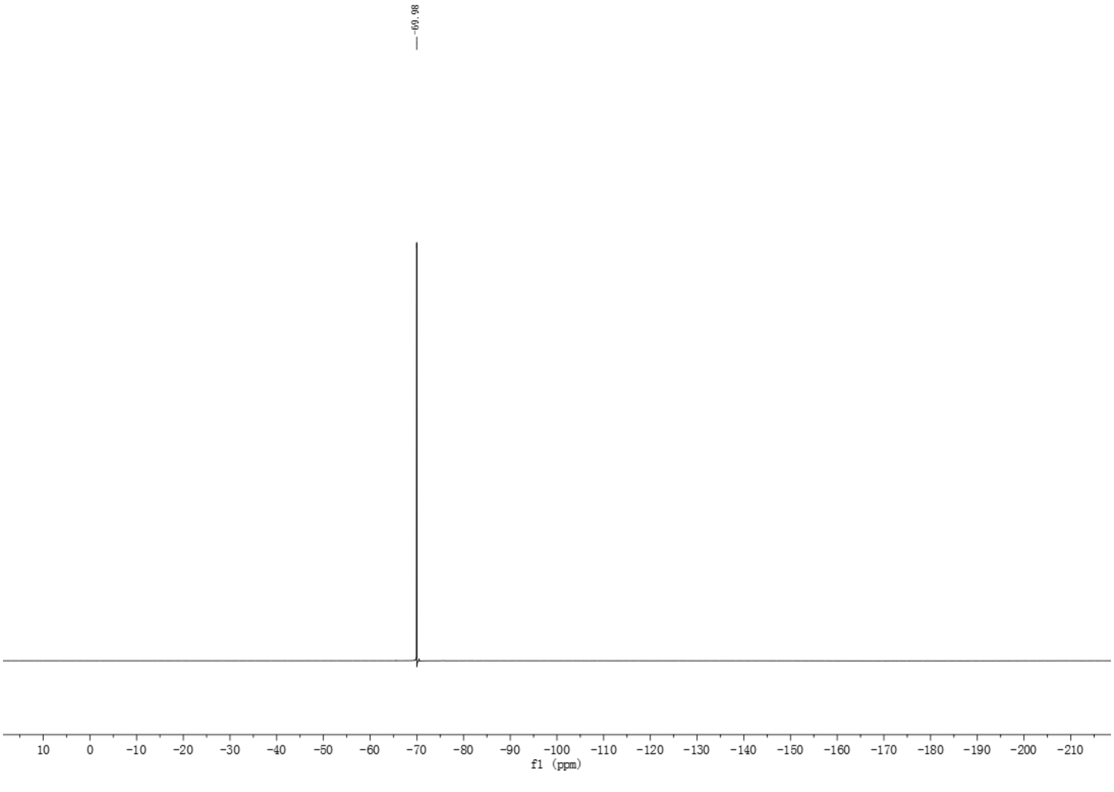

−70.15
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

4,4,4-Trifluoro-3-(4-methoxyphenyl)-1-phenylbutan-1-one (3ag)

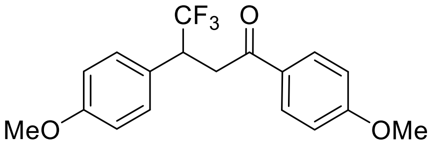


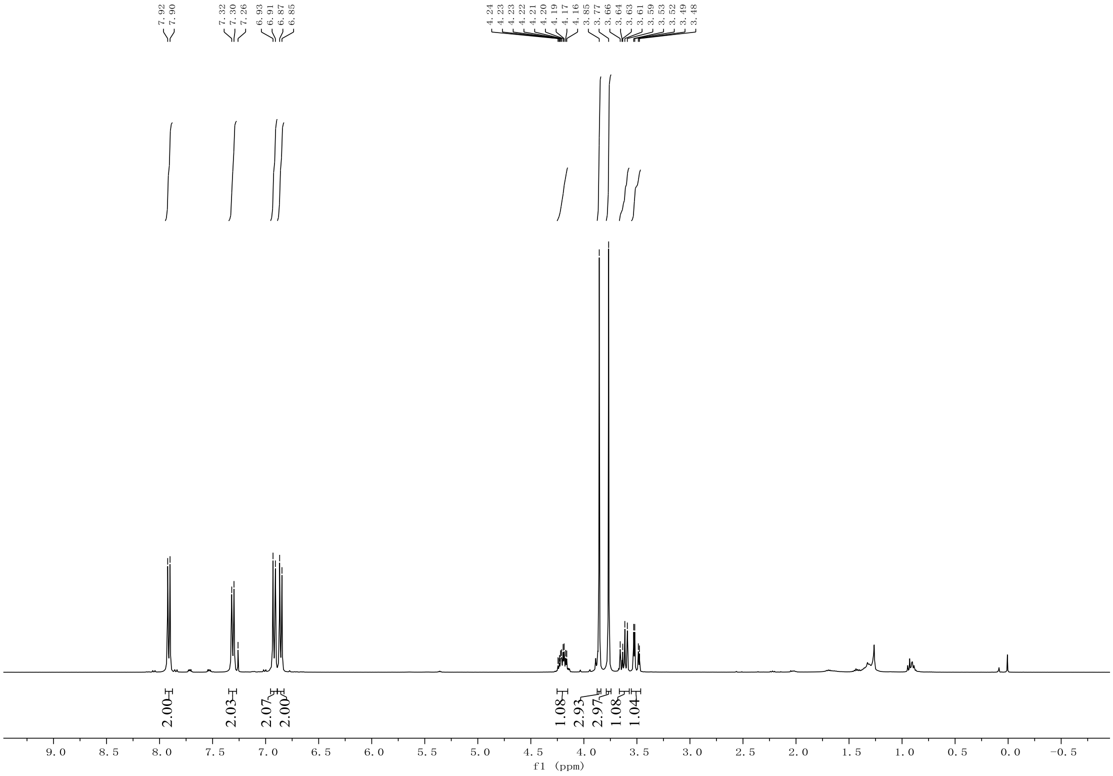


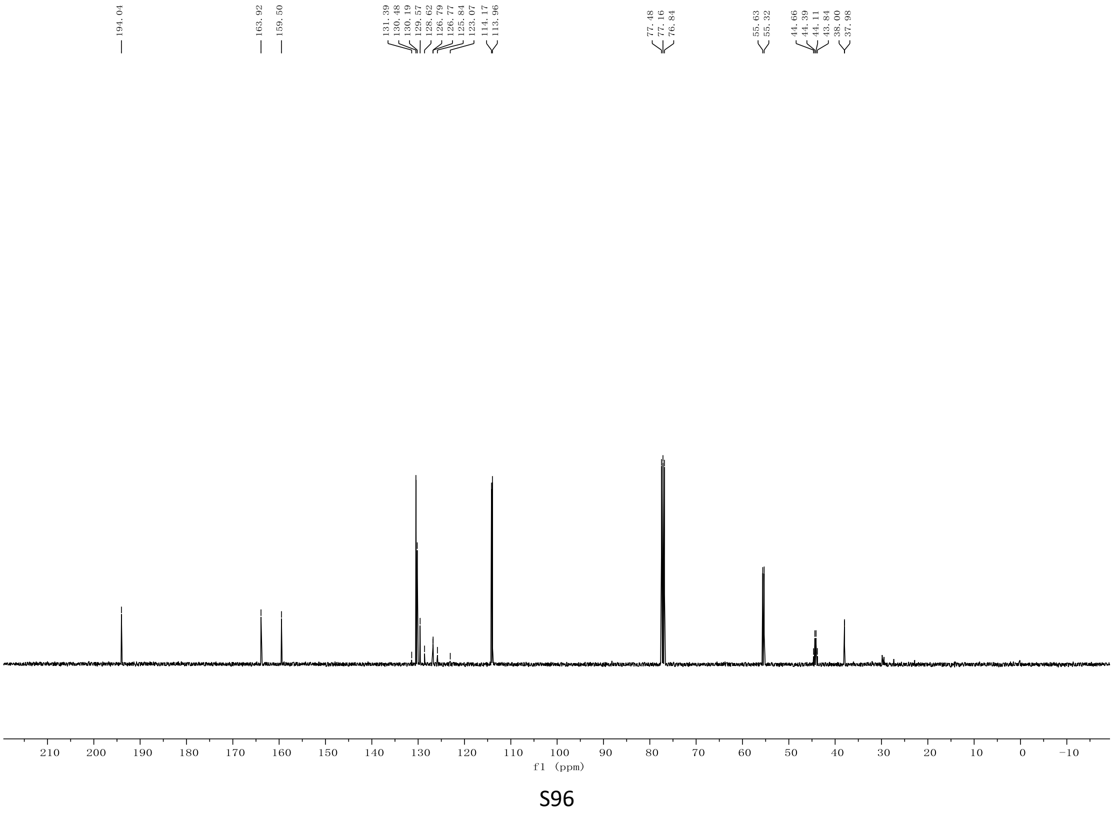

195.55
159.54
136.42
133.66
131.03
130.19
128.83
128.55
128.15
126.62
126.60
125.77
122.98
114.19
77.49
77.17
76.85
55.31
44.56
44.28
44.01
43.73
38.44
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

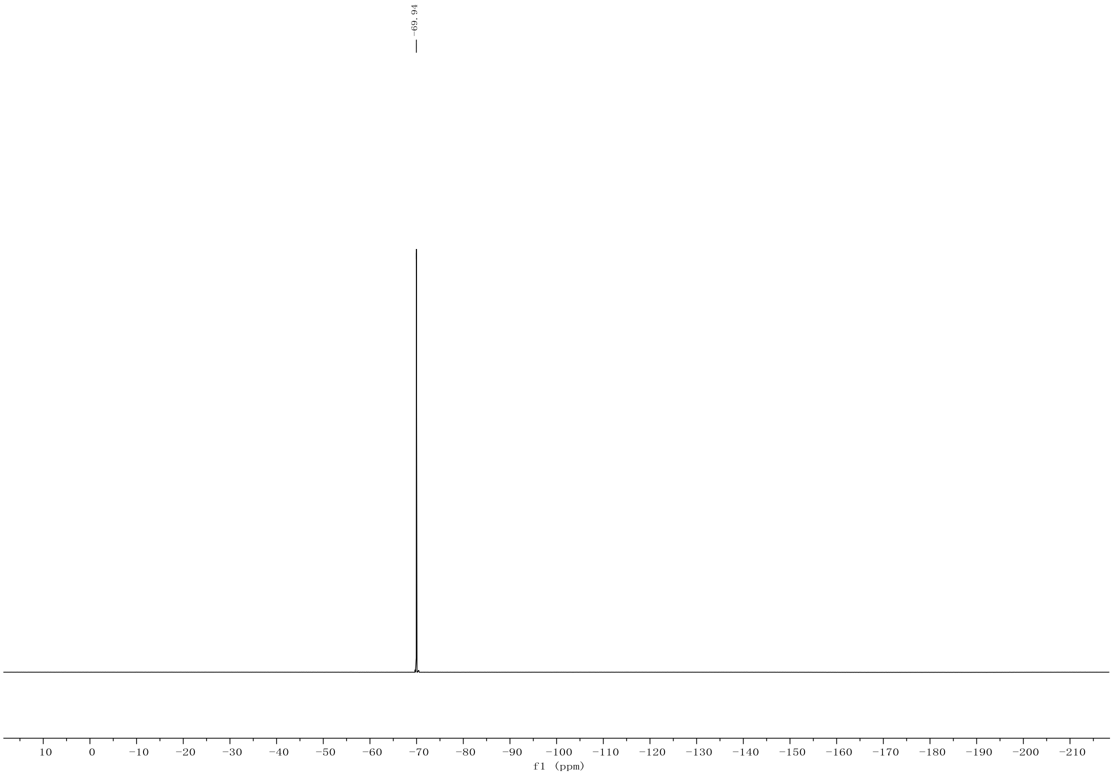

−69.98
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

4,4,4-Trifluoro-1,3-bis(4-methoxyphenyl)butan-1-one (3ah)





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-30
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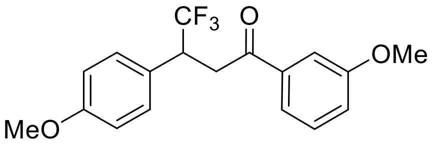
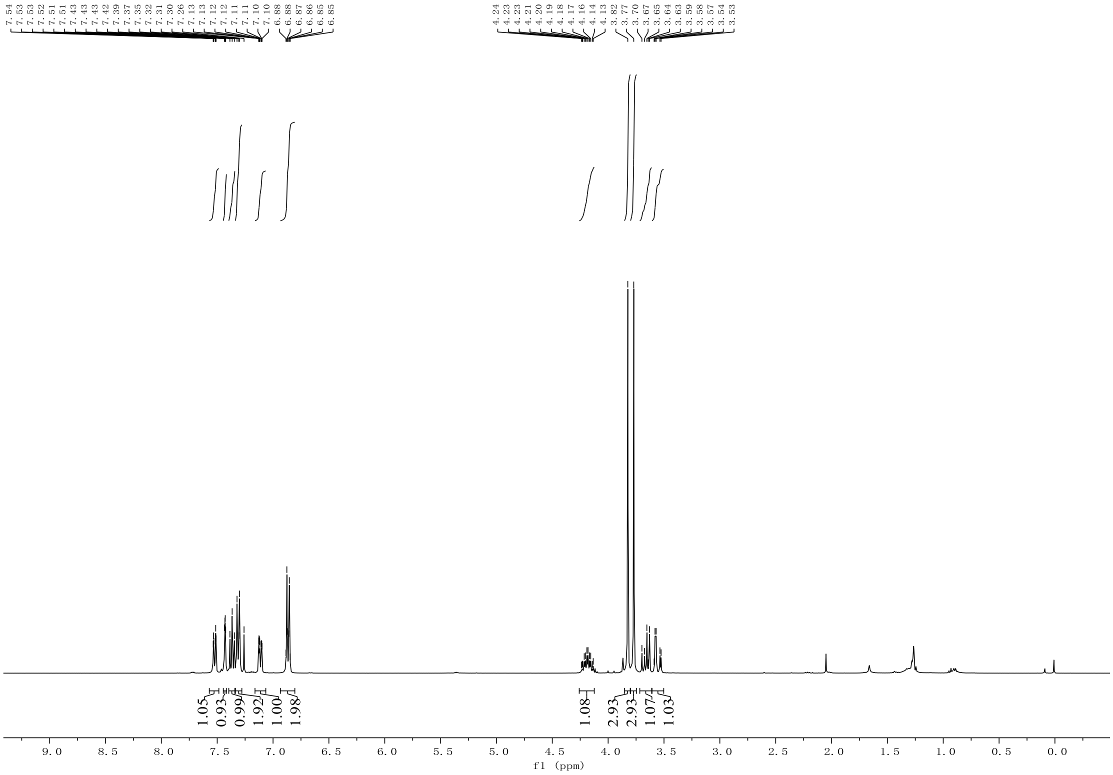
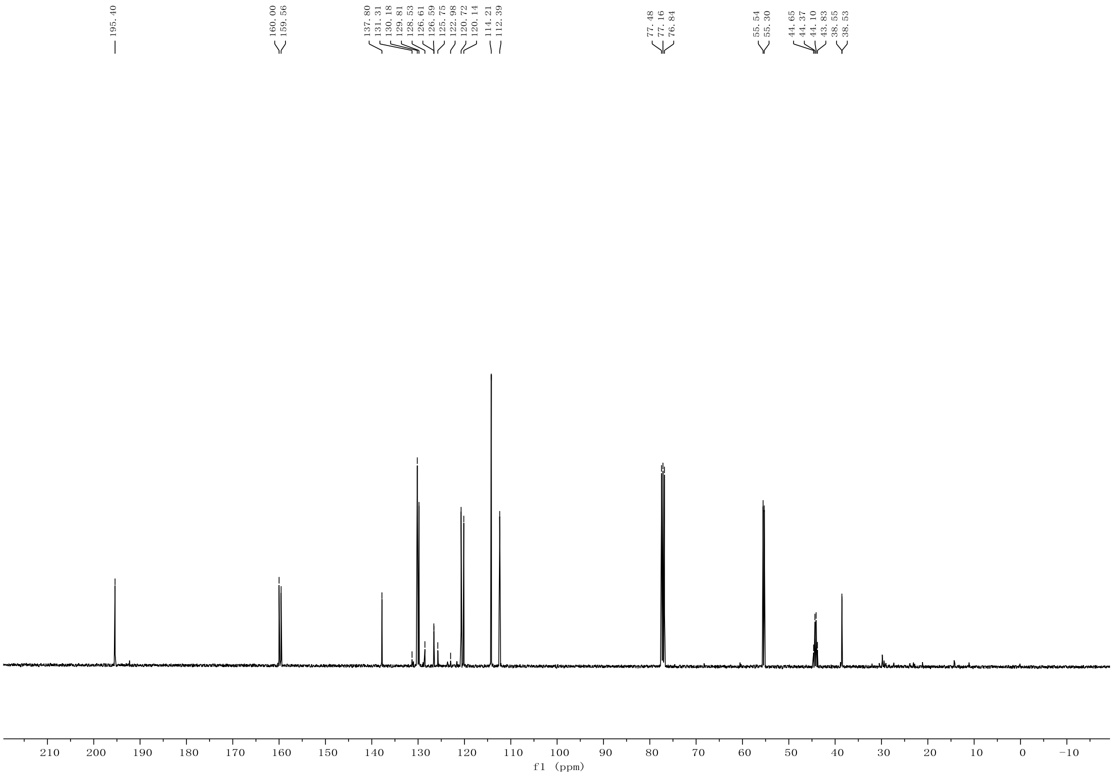
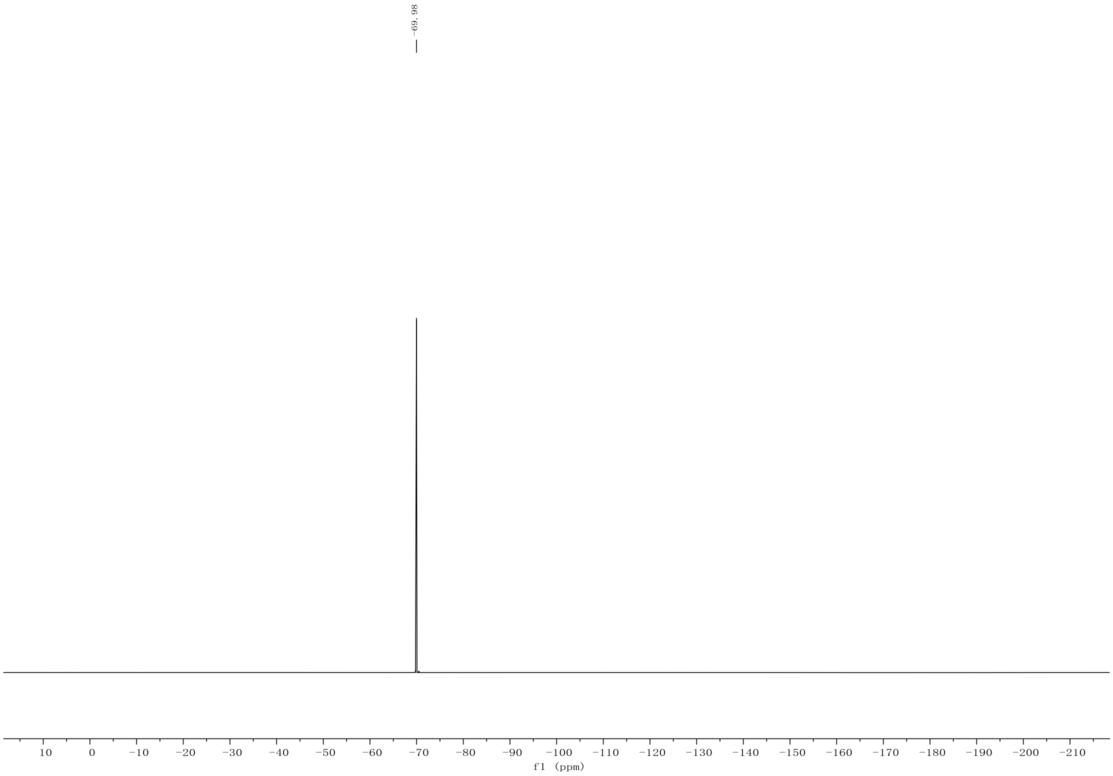
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

4,4,4-Trifluoro-1-(3-methoxyphenyl)-3-(4-methoxyphenyl)butan-1-one (3ai)

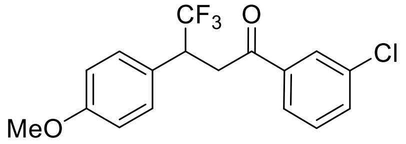


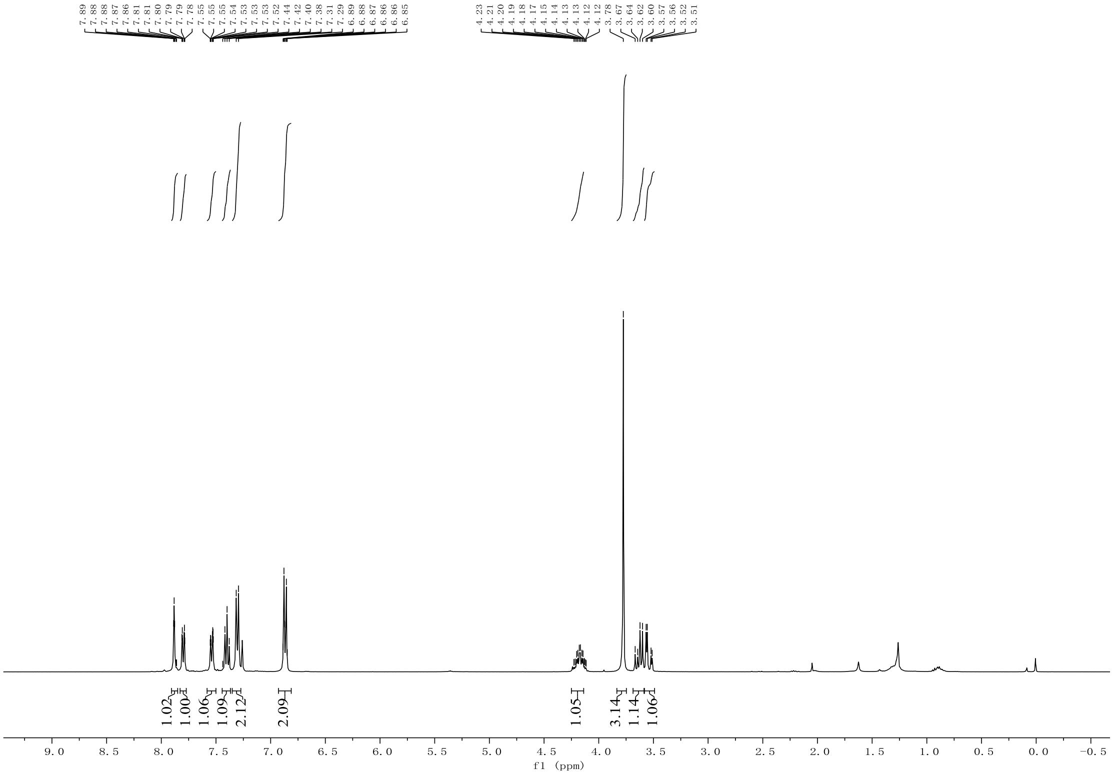


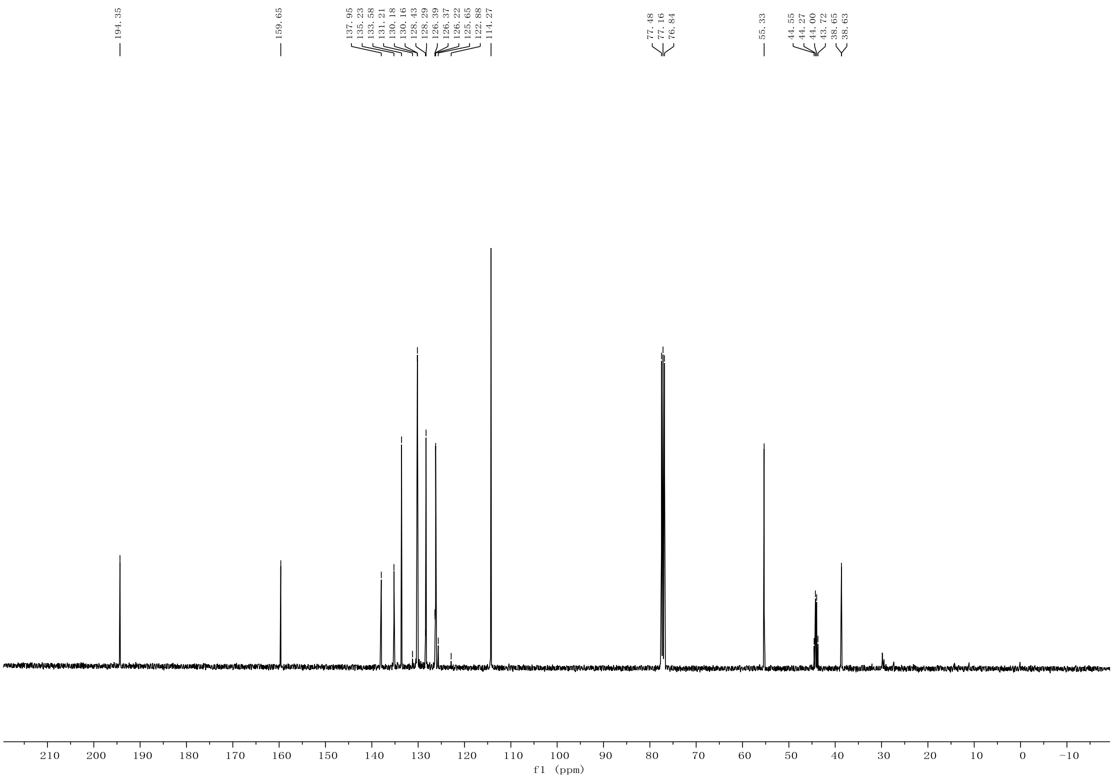


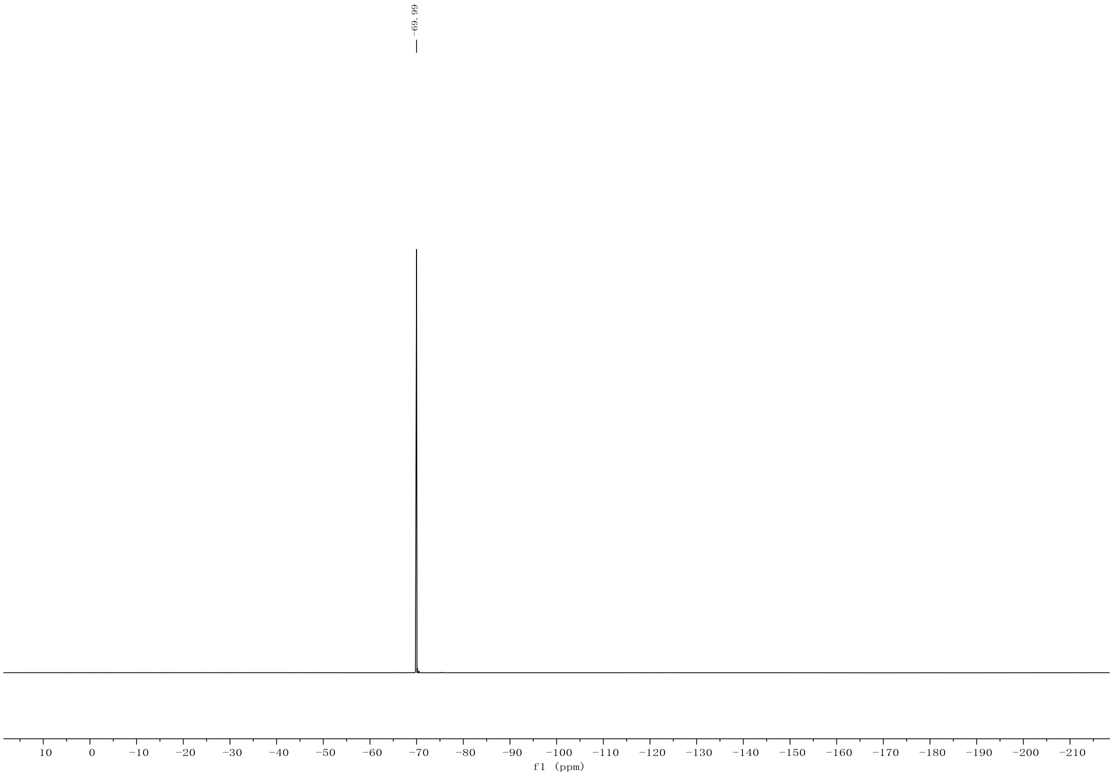

-69.98
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

1-(3-Chlorophenyl)-4,4,4-trifluoro-3-(4-methoxyphenyl)butan-1-one (3aj)






194.35
159.65
137.95
135.23
133.58
131.21
130.18
130.16
128.43
128.29
126.39
126.37
126.22
125.65
122.88
114.27
77.48
77.16
76.84
55.33
44.55
44.27
44.00
43.72
38.65
38.63
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


−69.99
10
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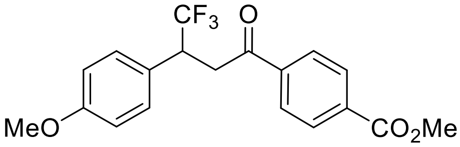
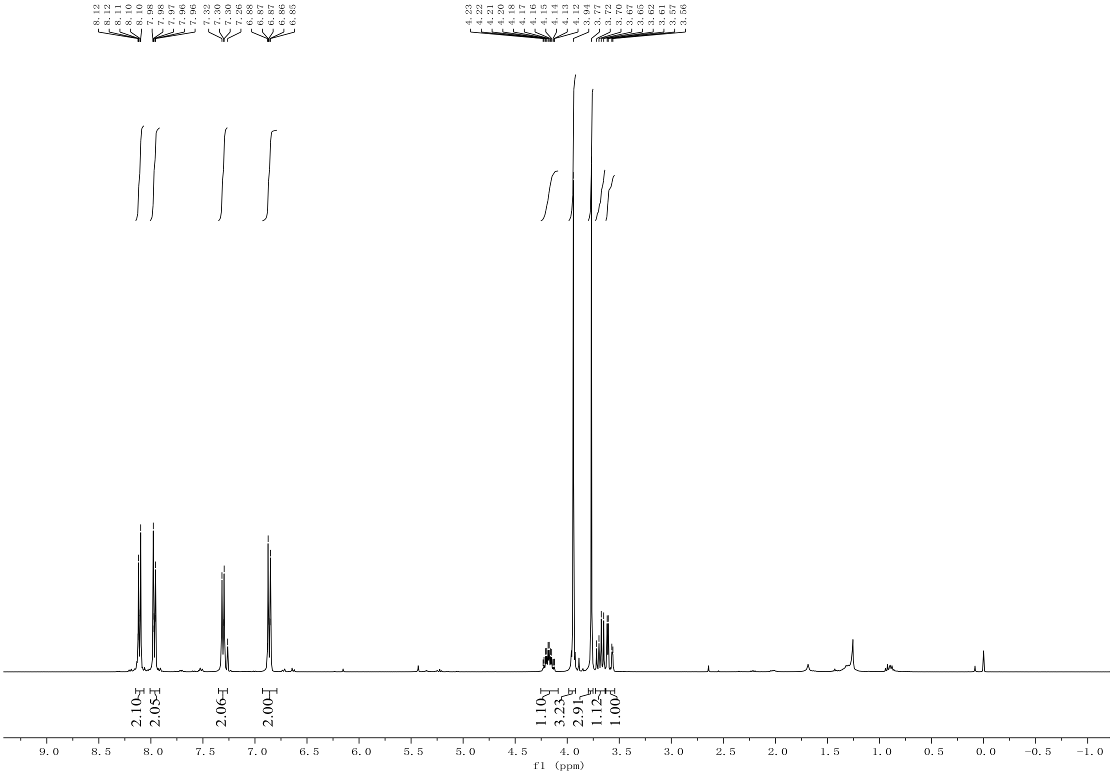
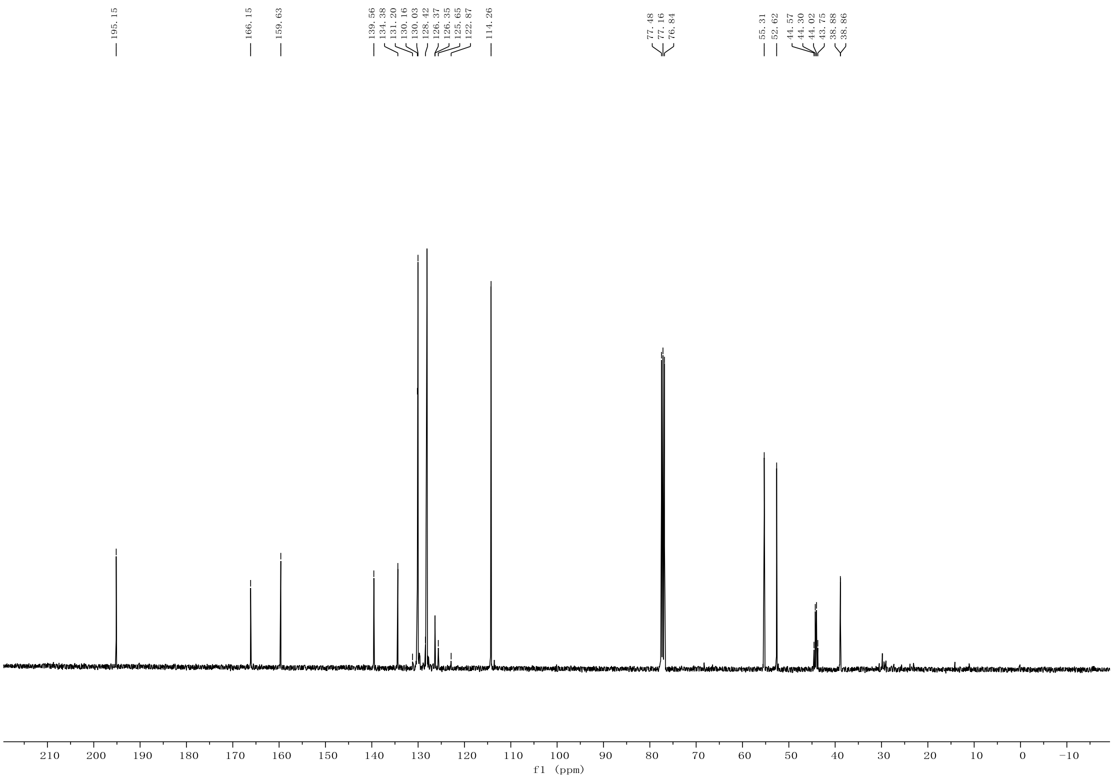
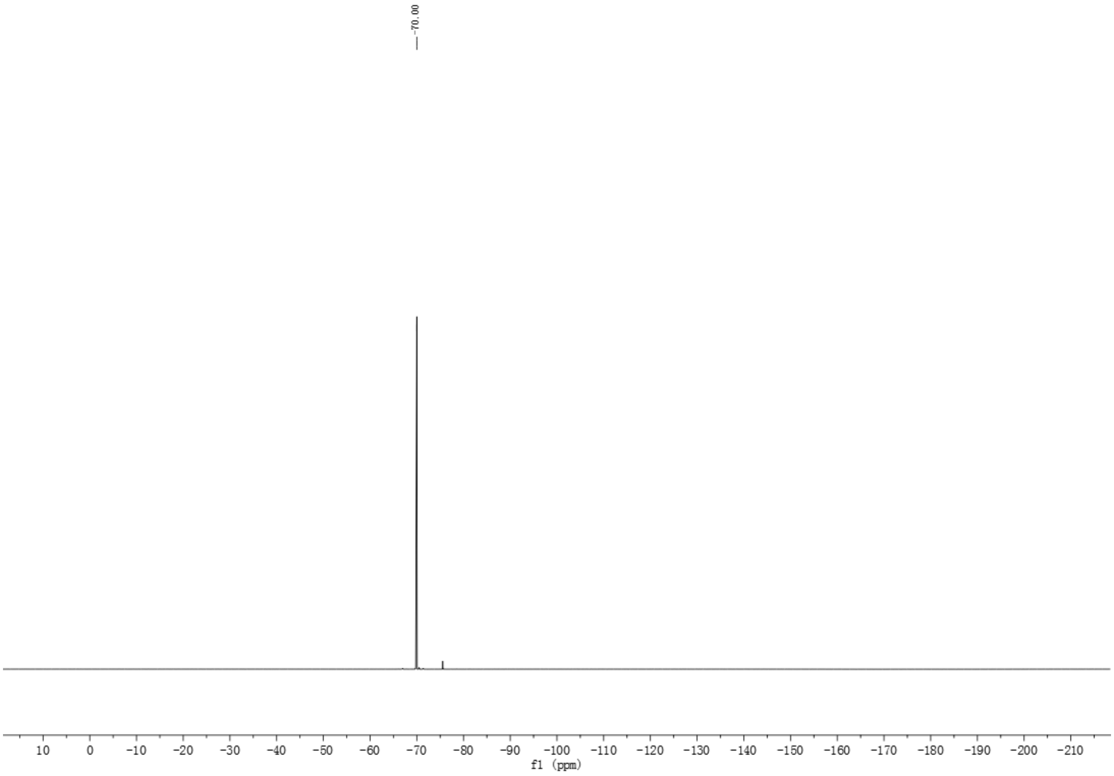
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

Methyl 4-(4,4,4-trifluoro-3-(4-methoxyphenyl)butanoyl)benzoate (3ak)






195.15
166.15
159.63
139.56
134.38
131.20
130.16
130.03
128.42
126.37
126.35
125.65
122.87
114.26
77.48
77.16
76.84
55.31
52.62
44.57
44.30
44.02
43.75
38.88
38.86
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


−70.00
10
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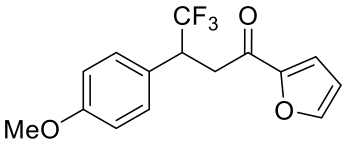
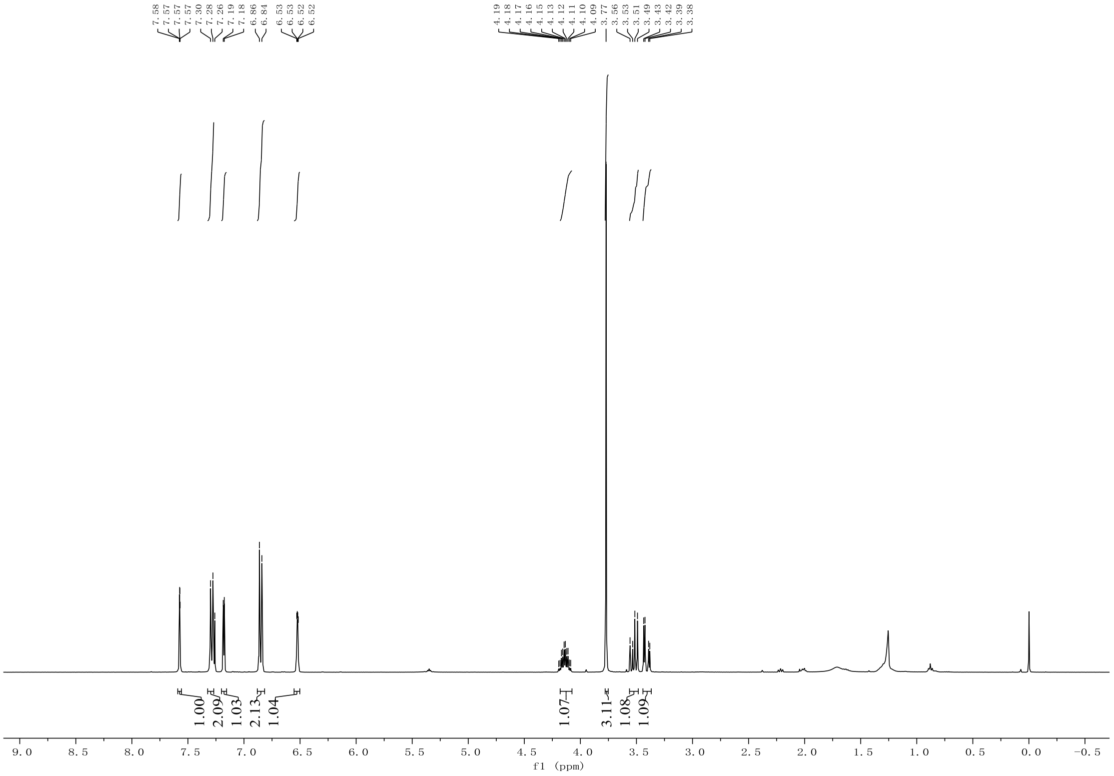
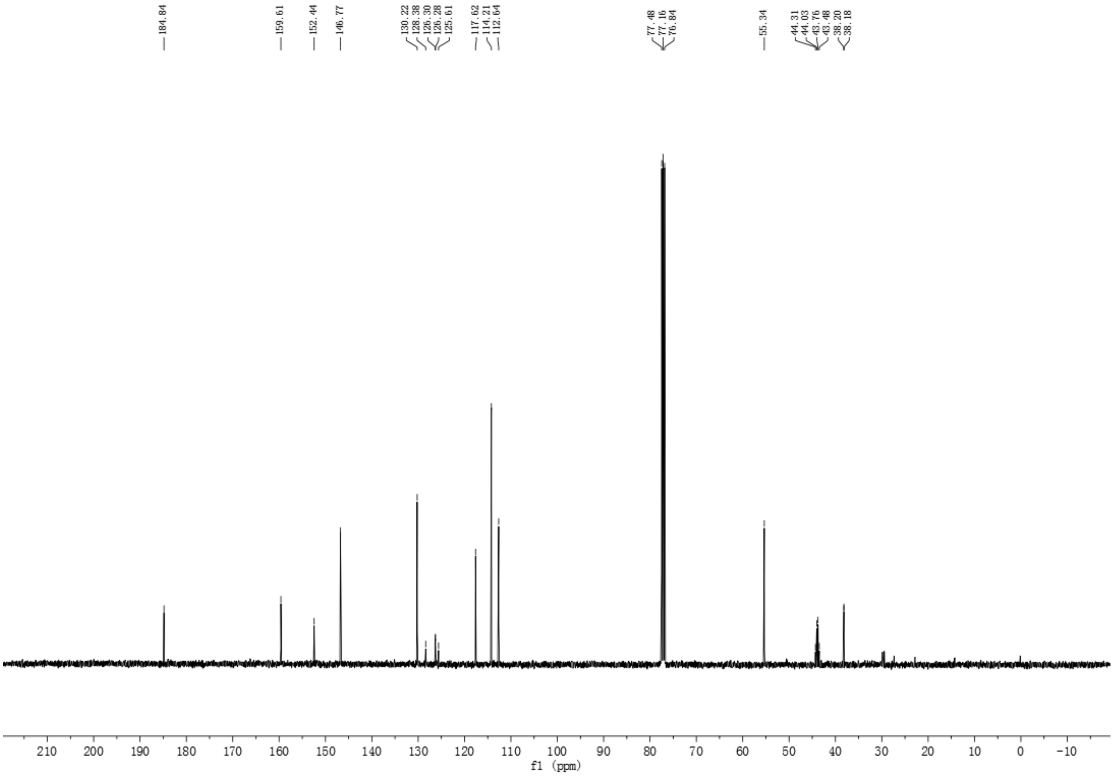
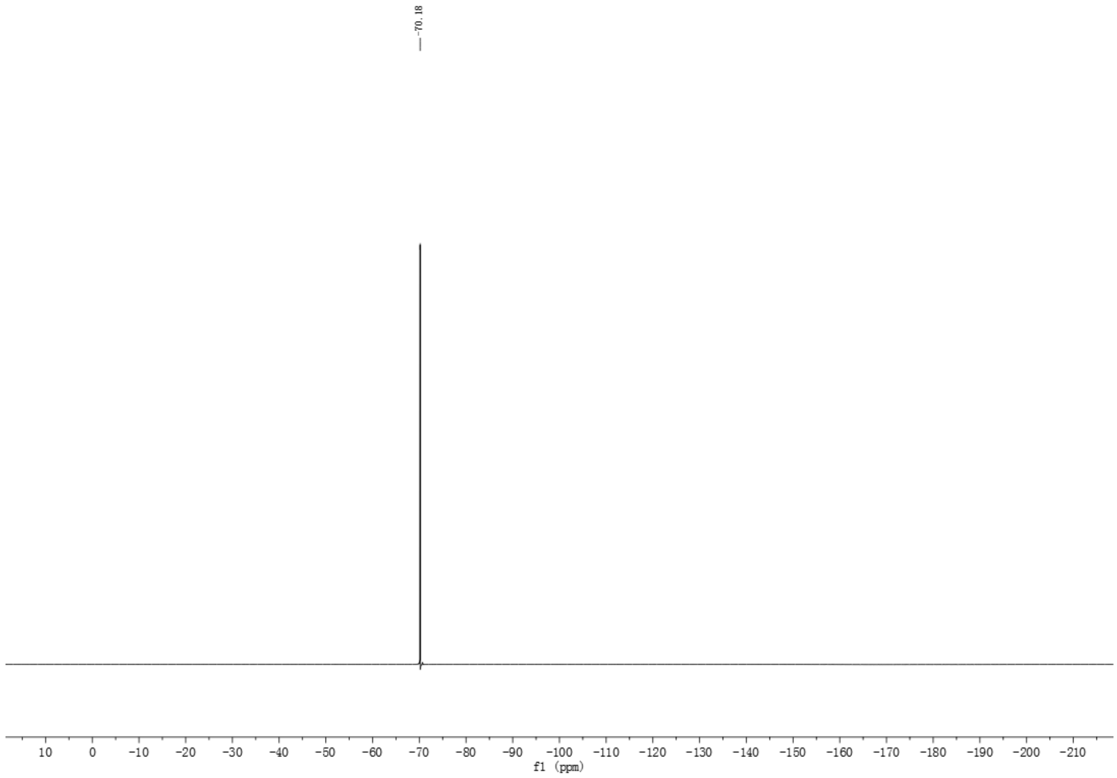
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

4,4,4-Trifluoro-1-(furan-2-yl)-3-(4-methoxyphenyl)butan-1-one (3al)

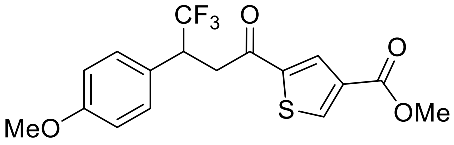


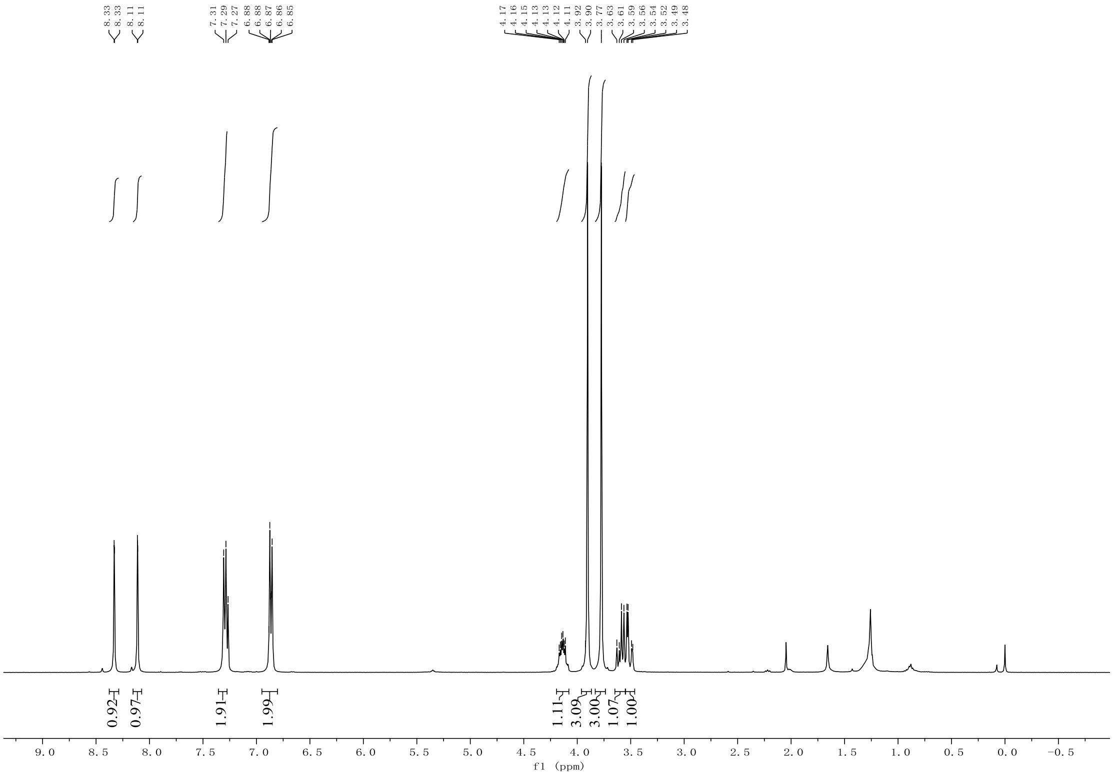


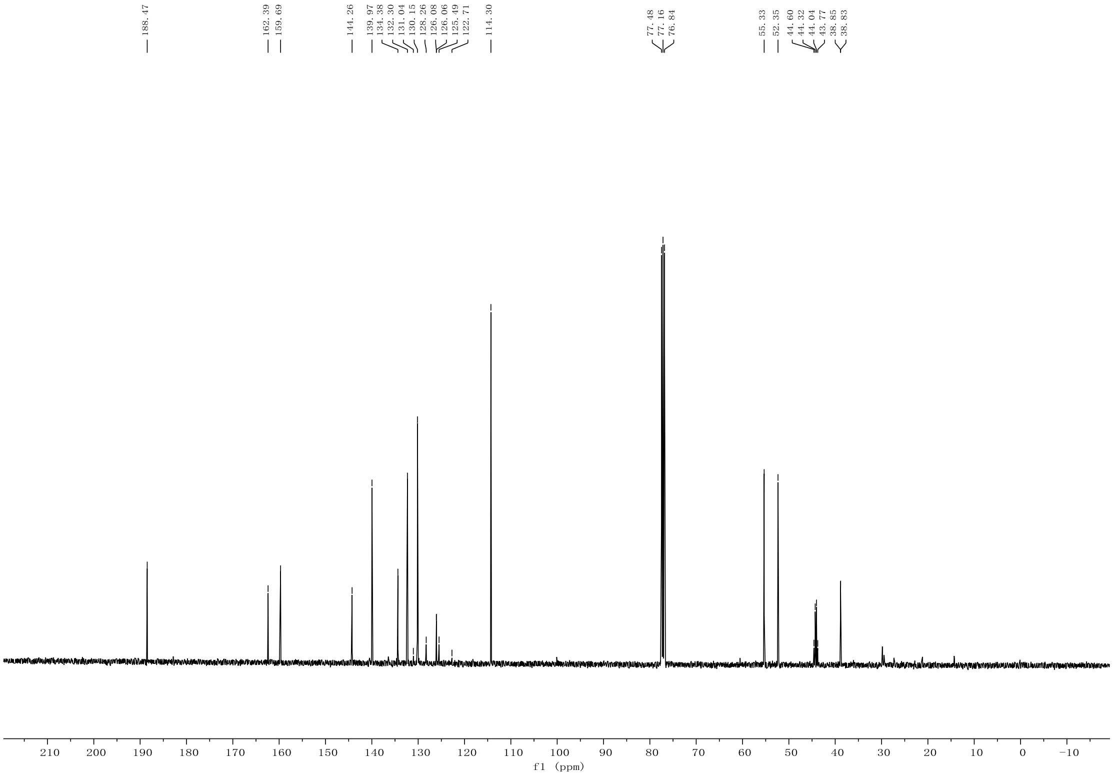


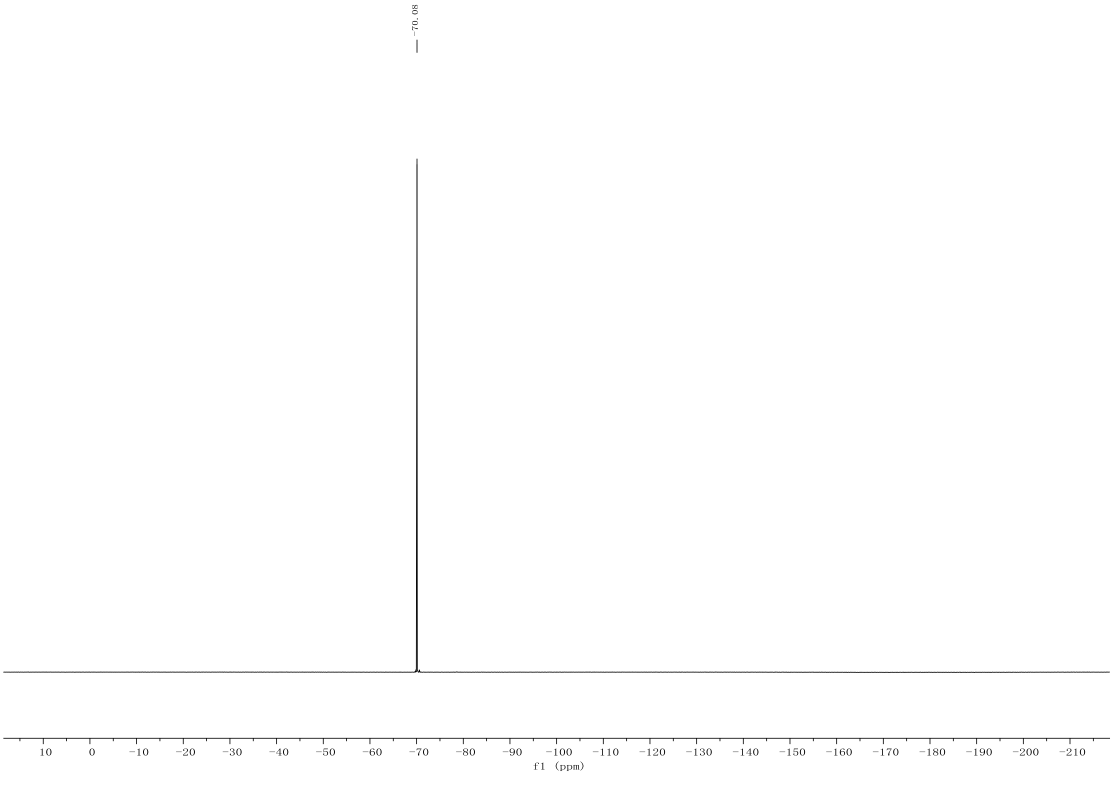

-70.18
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

Methyl 5-(4,4,4-trifluoro-3-(4-methoxyphenyl)butanoyl)thiophene-3-carboxylate (3am)

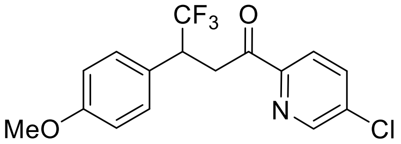


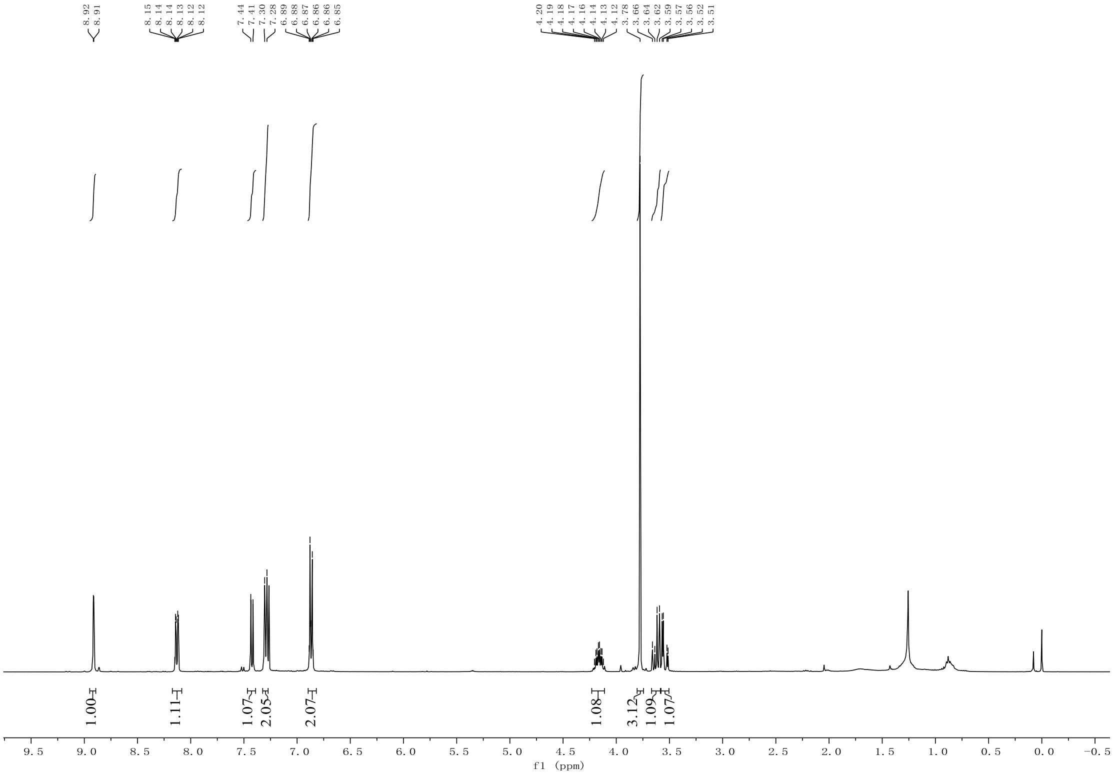


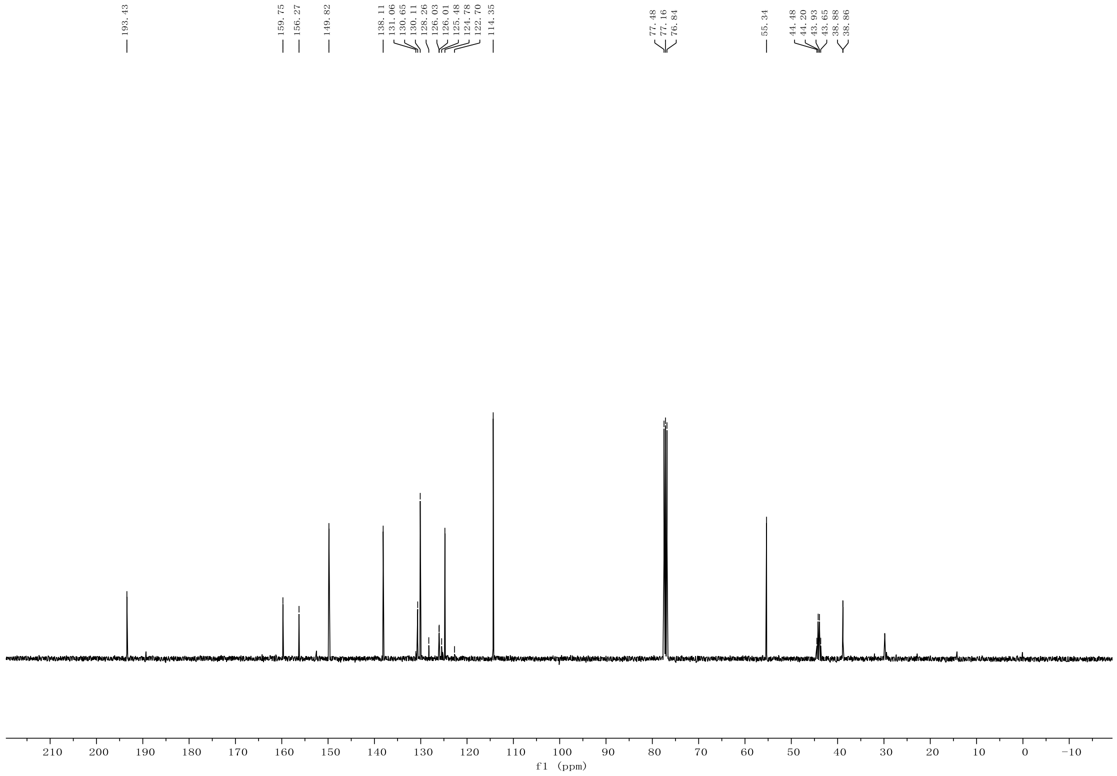

188.47
162.39
159.69
144.26
139.97
134.38
132.30
131.04
130.15
128.26
126.08
126.06
125.49
122.71
114.30
77.48
77.16
76.84
55.33
52.35
44.60
44.32
44.04
43.77
38.85
38.83
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

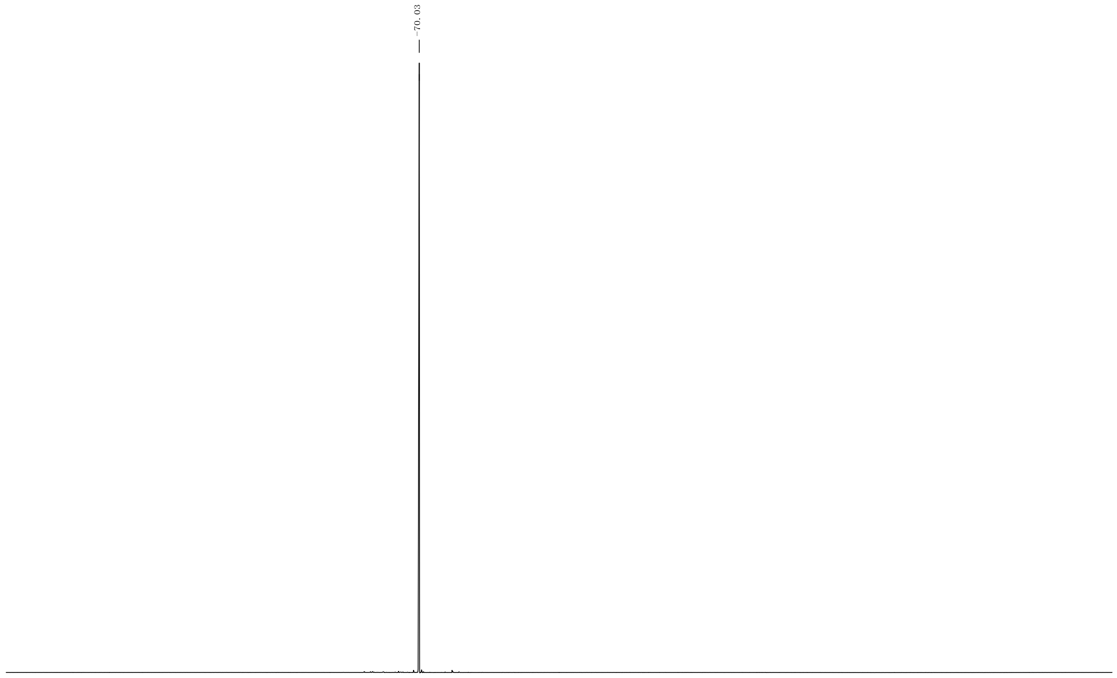

−70.08
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

1-(5-Chloropyridin-2-yl)-4,4,4-trifluoro-3-(4-methoxyphenyl)butan-1-one (3an)

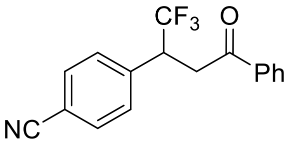


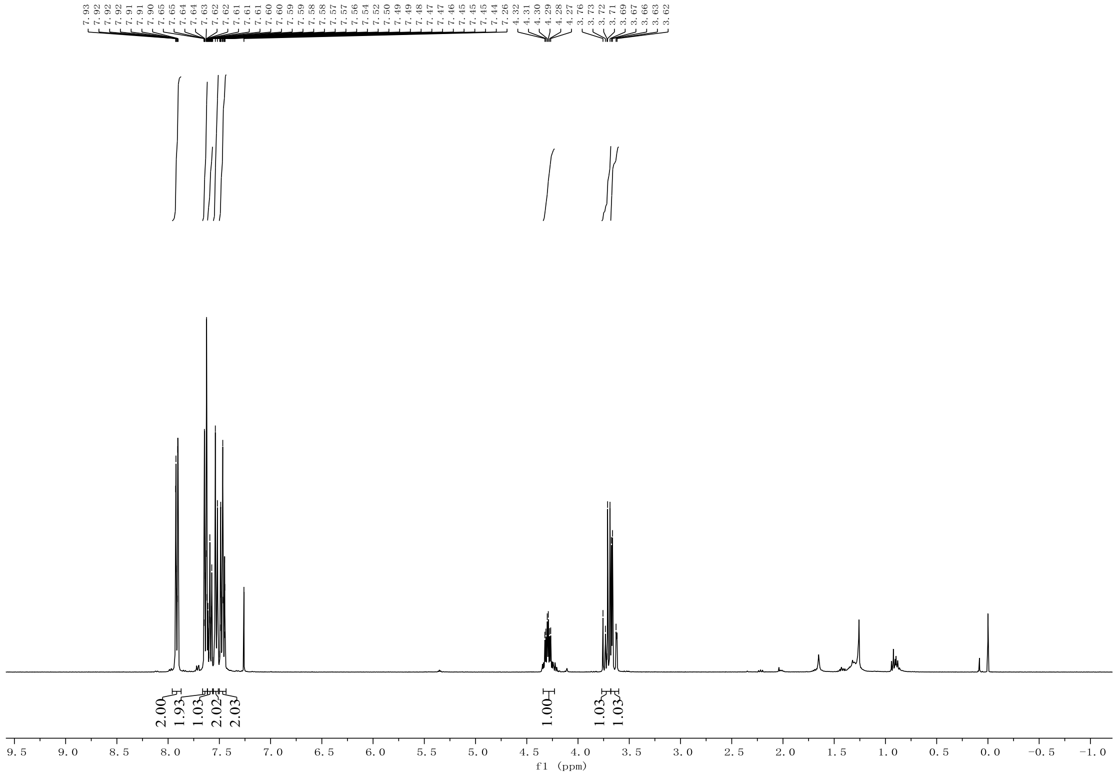


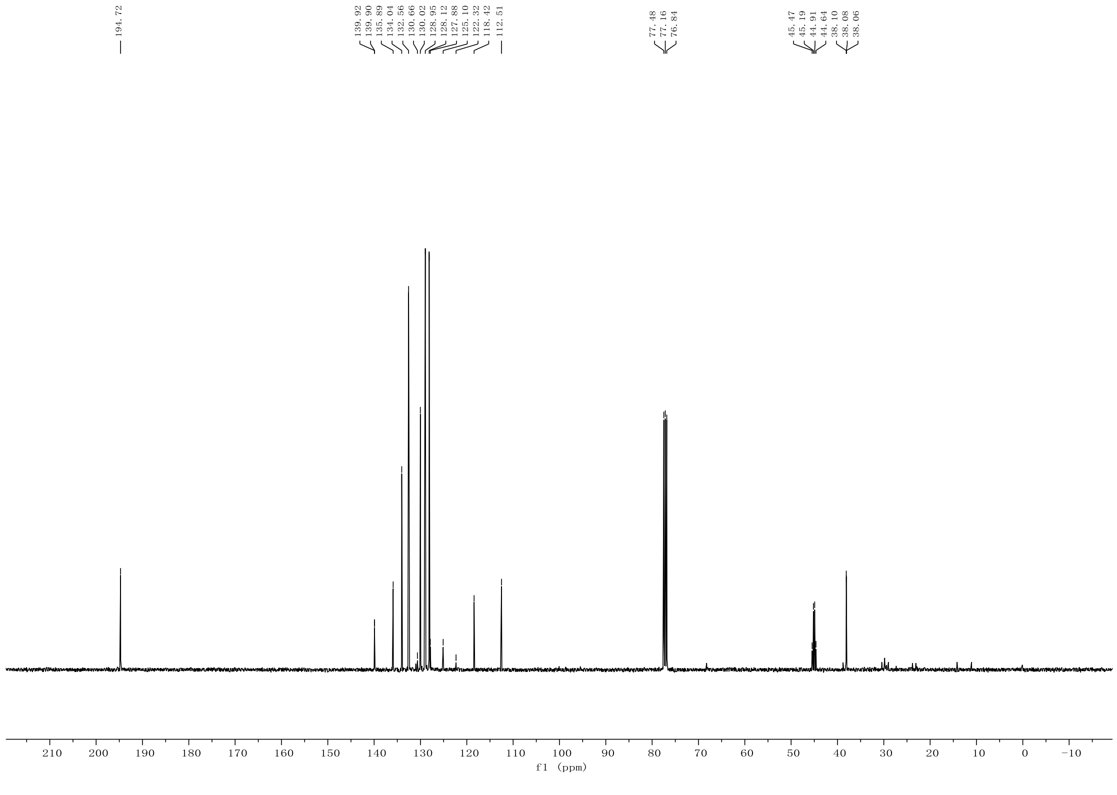

193.43
159.75
156.27
149.82
138.11
131.06
130.65
130.11
128.26
126.03
126.01
125.48
124.78
122.70
114.35
77.48
77.16
76.84
55.34
44.48
44.20
43.93
43.65
38.88
38.86
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

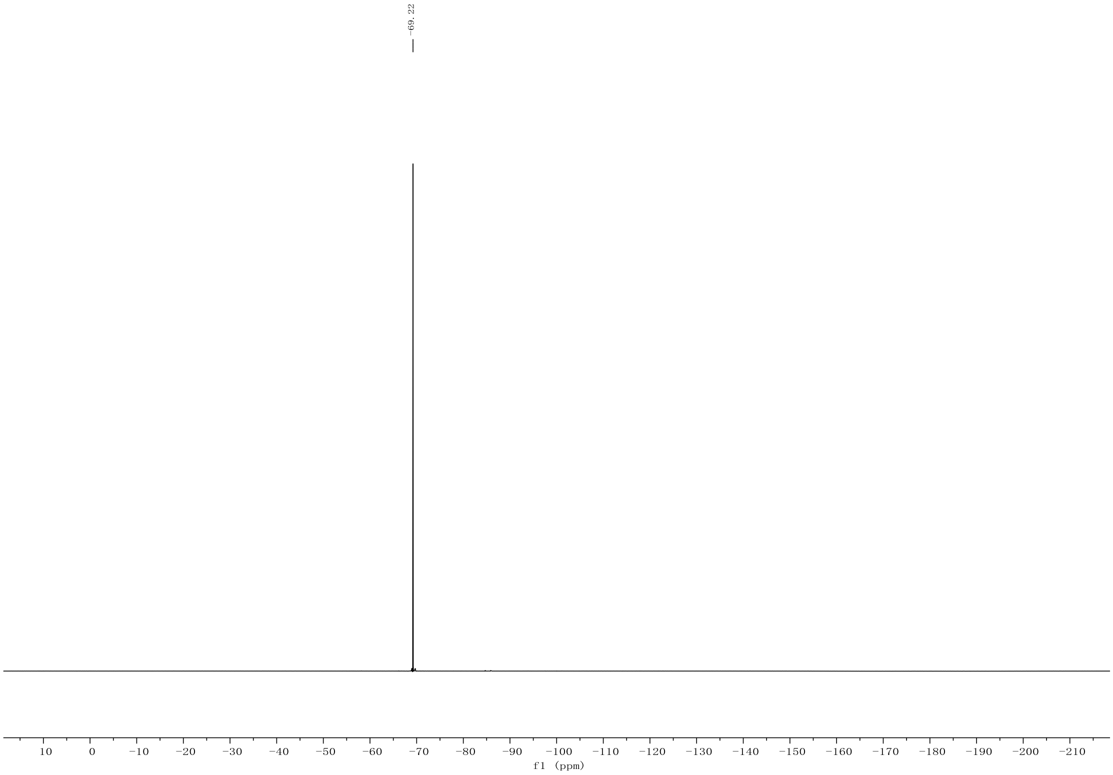

−70.03
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

4-(1,1,1-Trifluoro-4-oxo-4-phenylbutan-2-yl)benzonitrile (3kg)

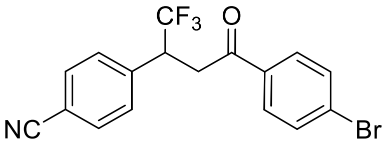


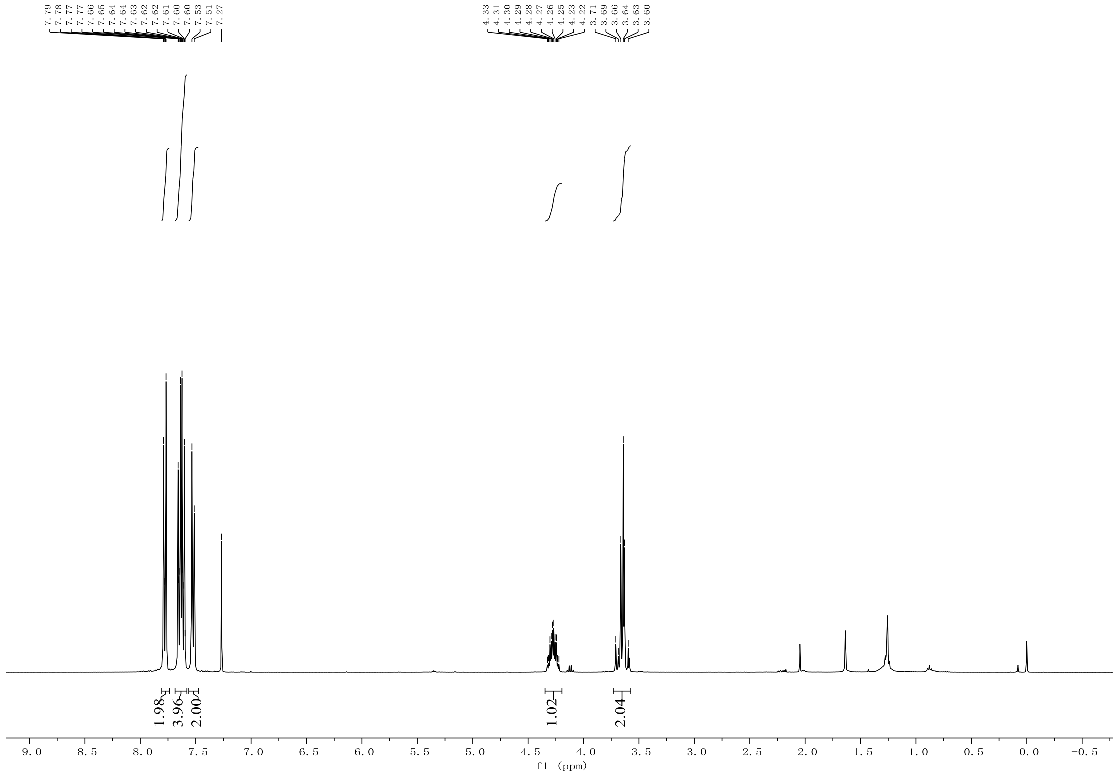


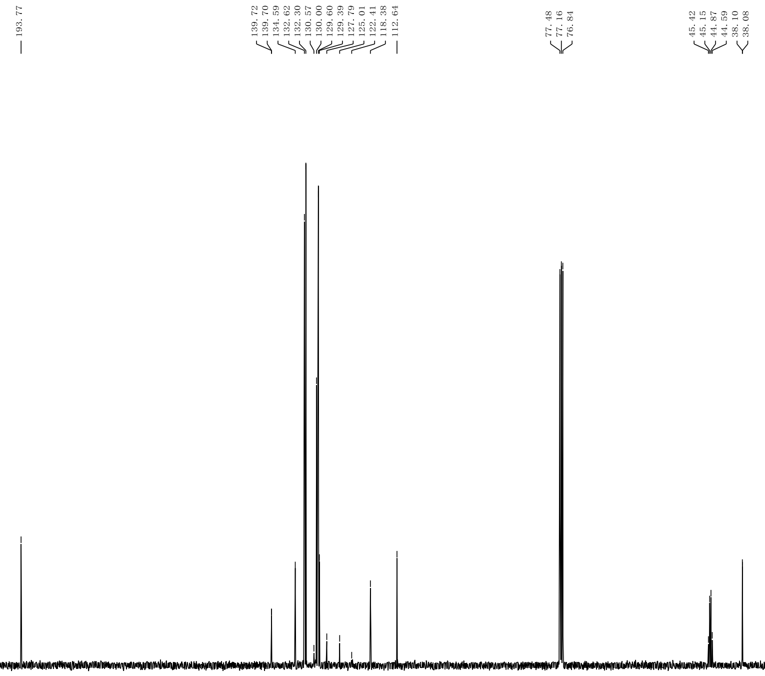


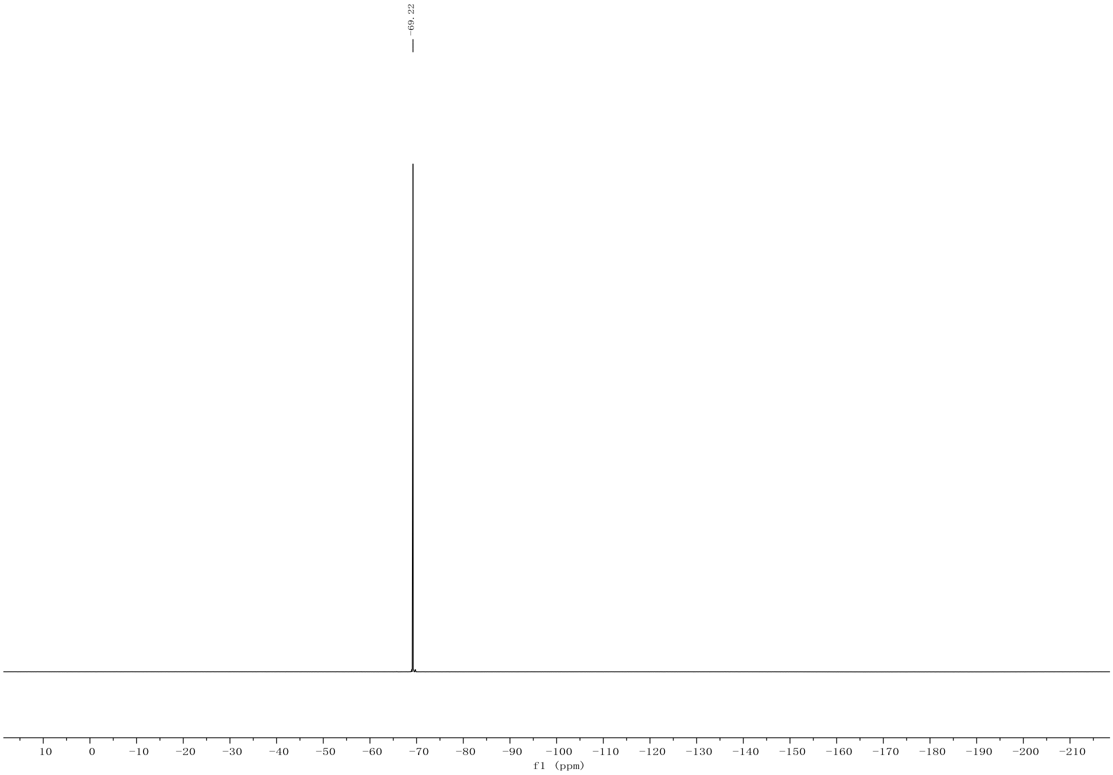

-69.22
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

4-(4-(4-Bromophenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)benzonitrile (3ko)

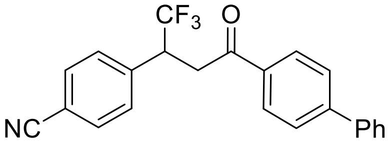


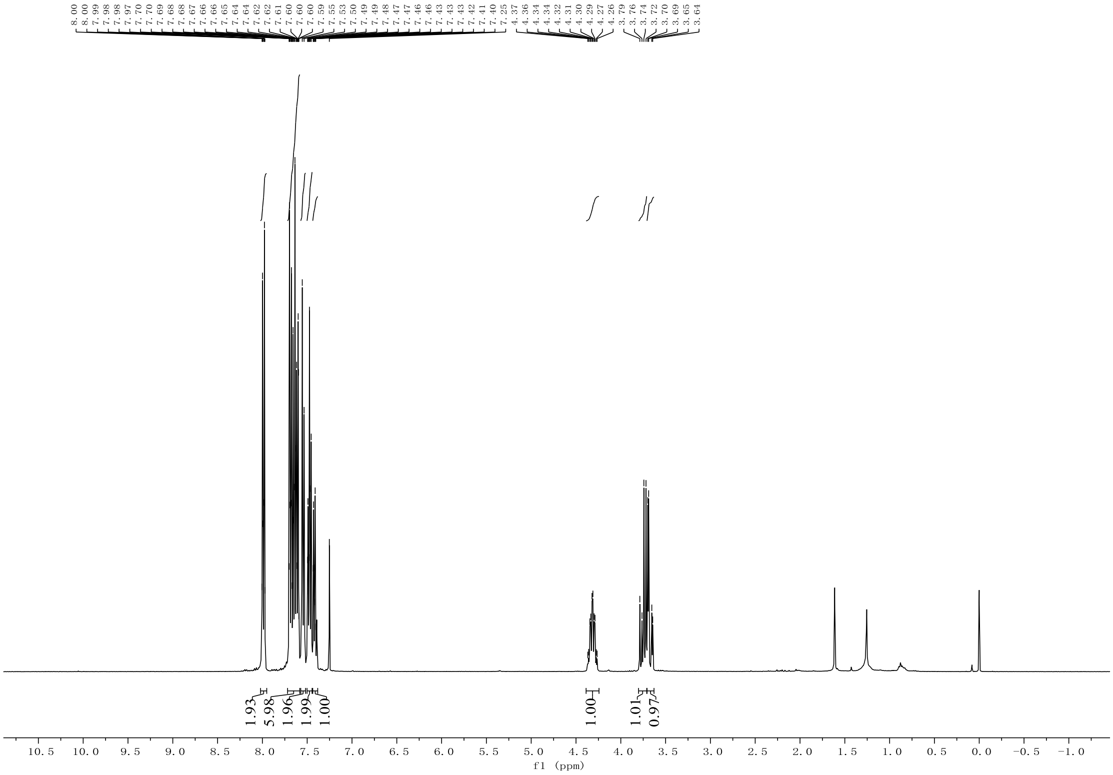


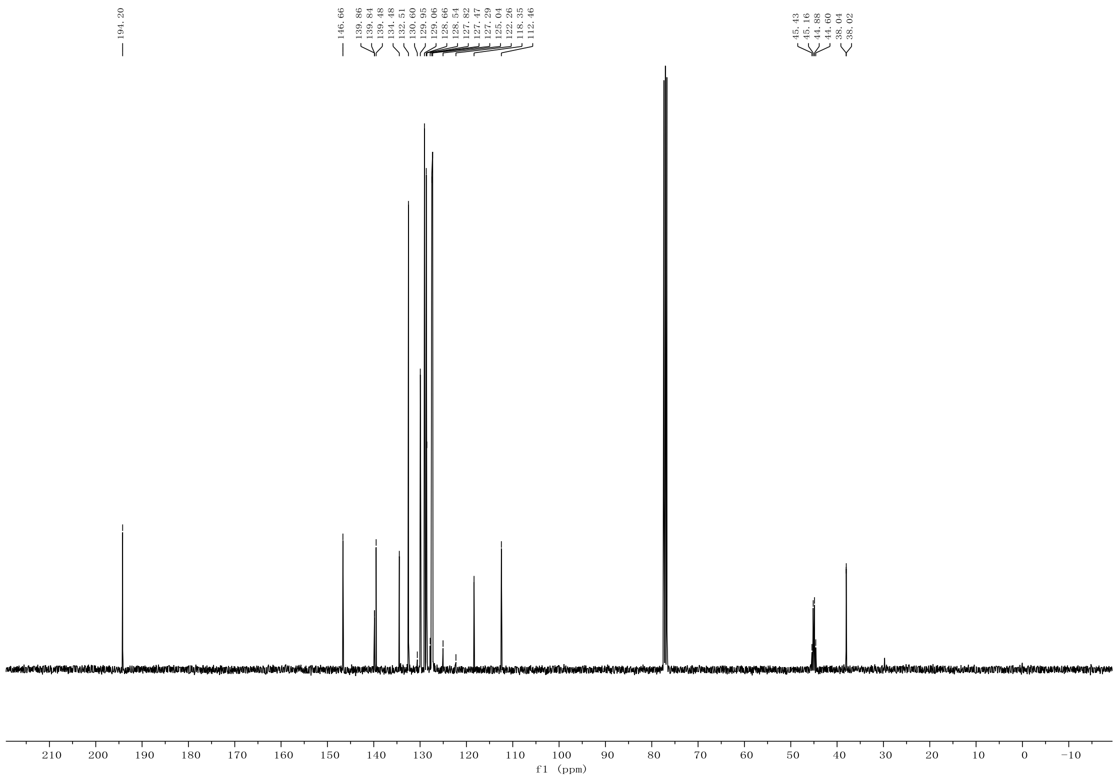


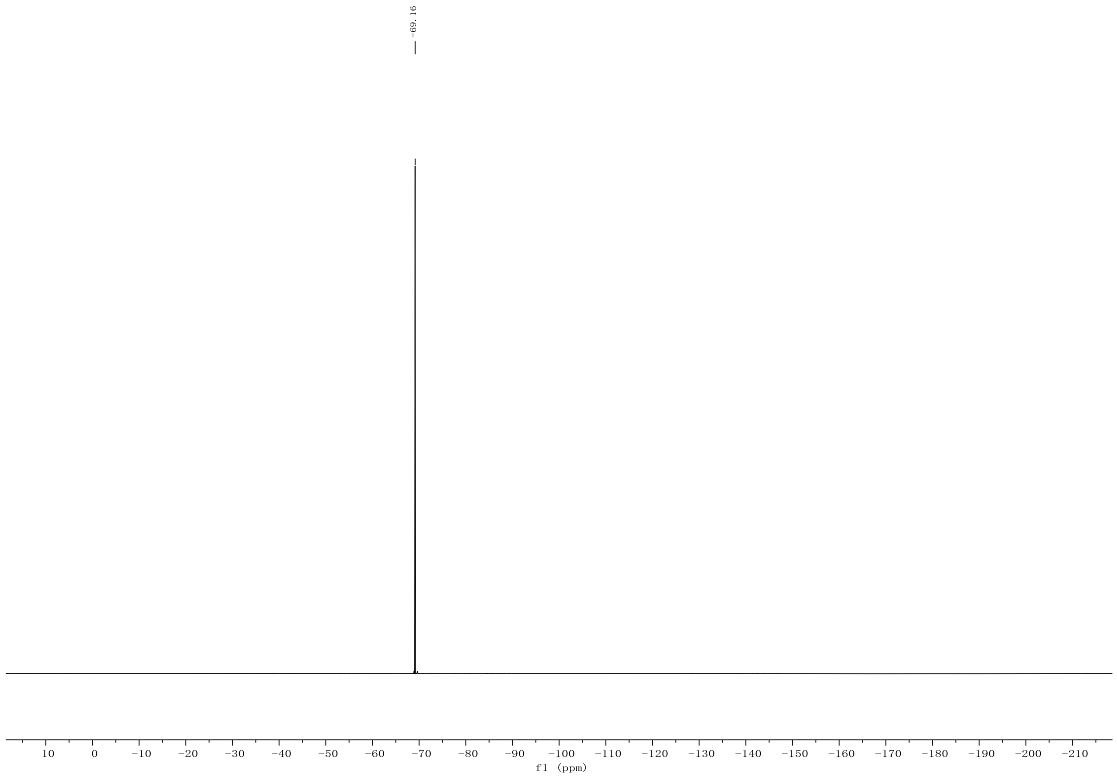

-69.22
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

4-(4-([1,1'-Biphenyl]-4-yl)-1,1,1-trifluoro-4-oxobutan-2-yl)benzonitrile (3kp)

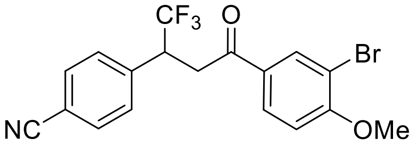


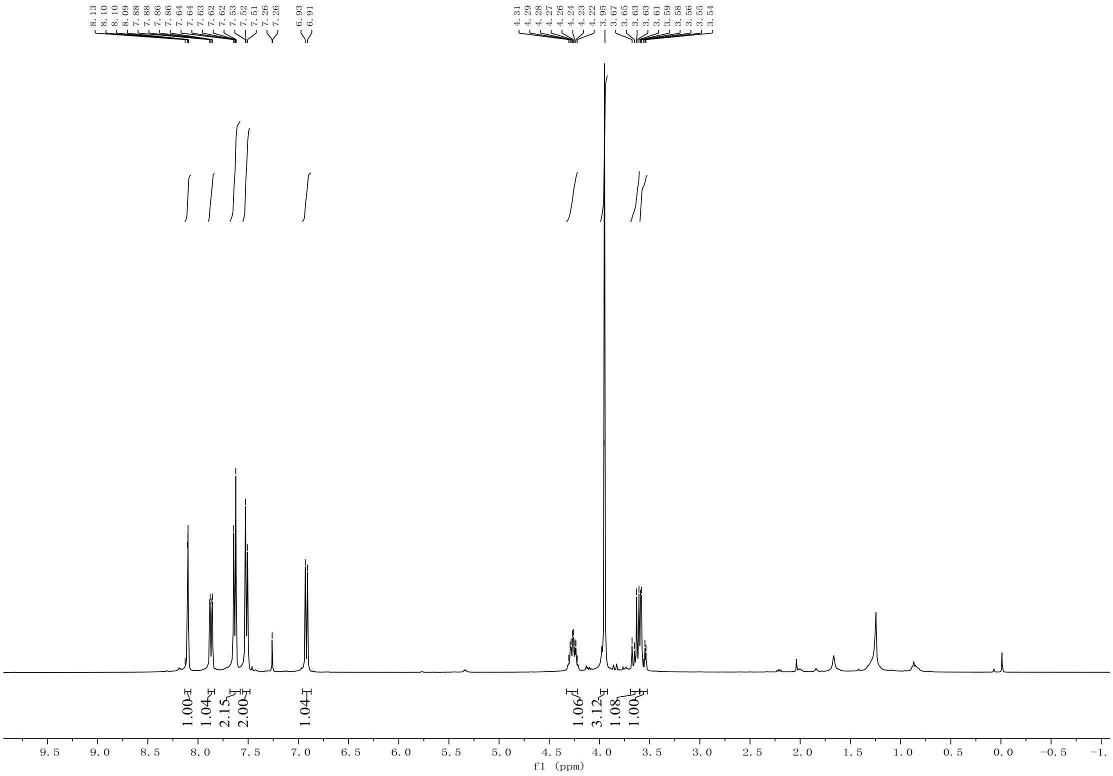


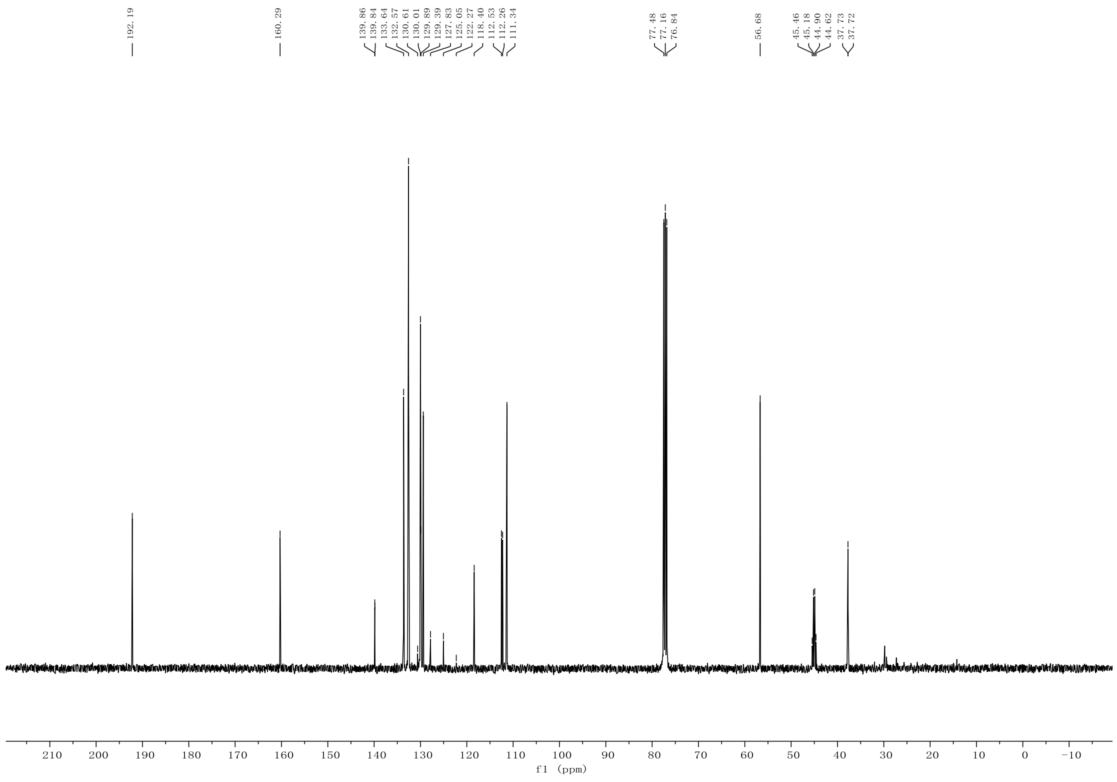

194.20
146.66
139.86
139.84
139.48
134.48
132.51
130.60
129.95
129.06
128.66
128.54
127.82
127.47
127.29
125.04
122.26
118.35
112.46
45.43
45.16
44.88
44.60
38.04
38.02
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

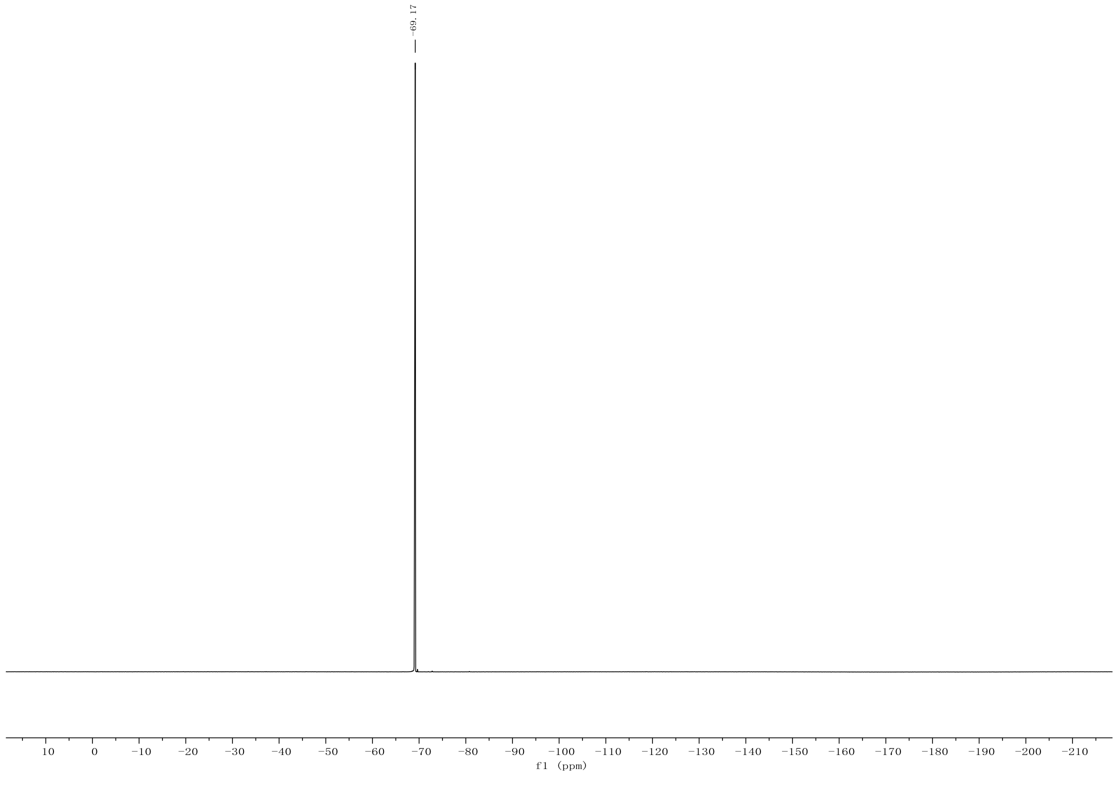

−69.16
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

4-(4-(3-Bromo-4-methoxyphenyl)-1,1,1-trifluoro-4-oxobutan-2-yl)benzonitrile (3kq)

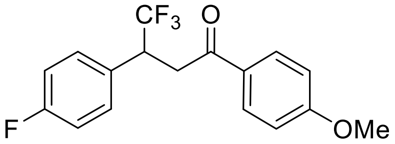


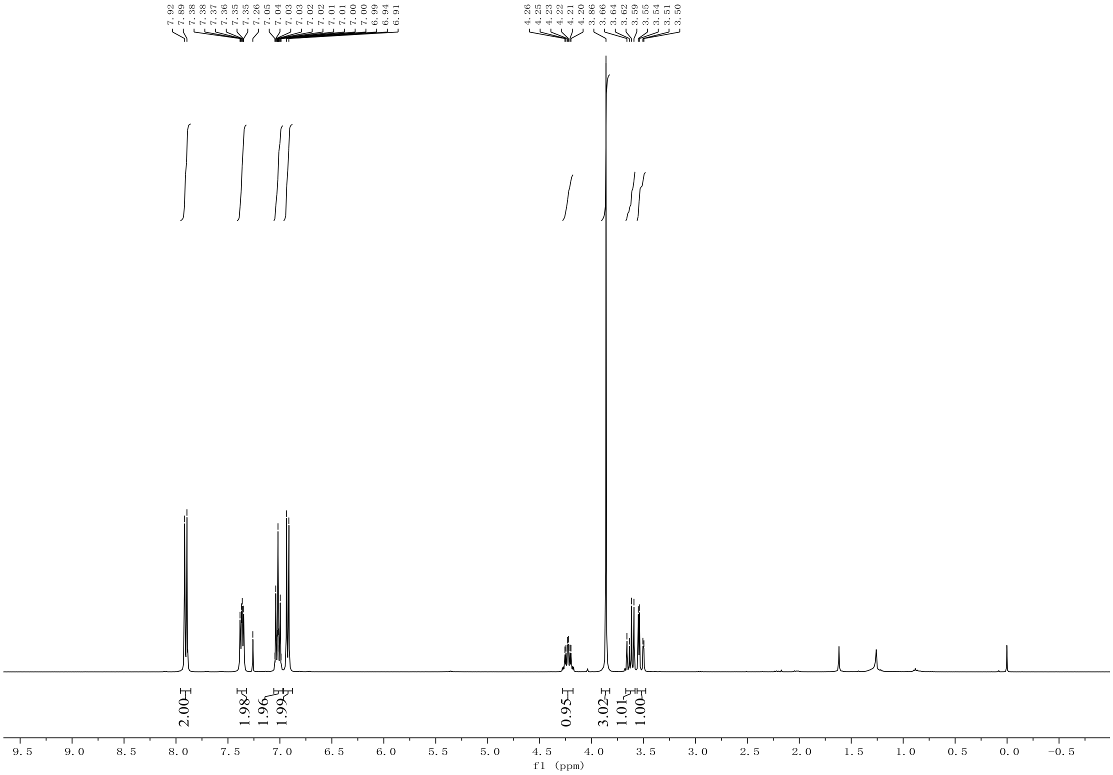


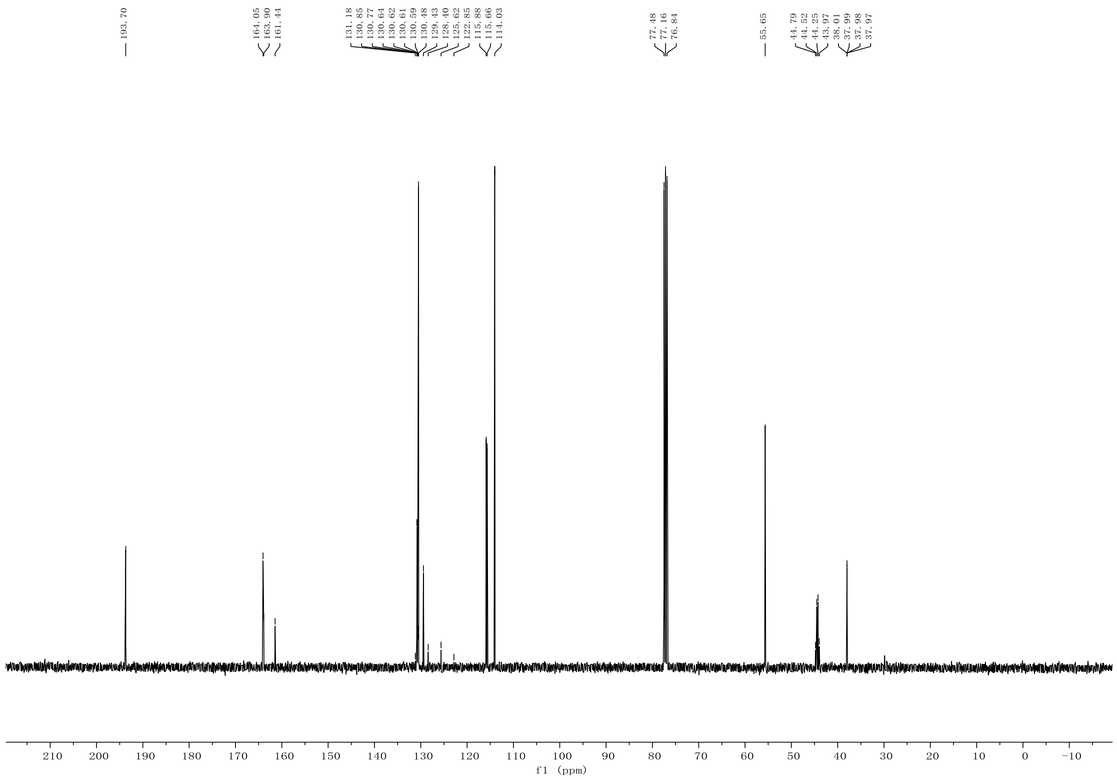

192.19
160.29
139.86
139.84
133.64
132.57
130.61
130.01
129.89
129.39
127.83
125.05
122.27
118.40
112.53
112.26
111.34
77.48
77.16
76.84
56.68
45.46
45.18
44.90
44.62
37.73
37.72
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

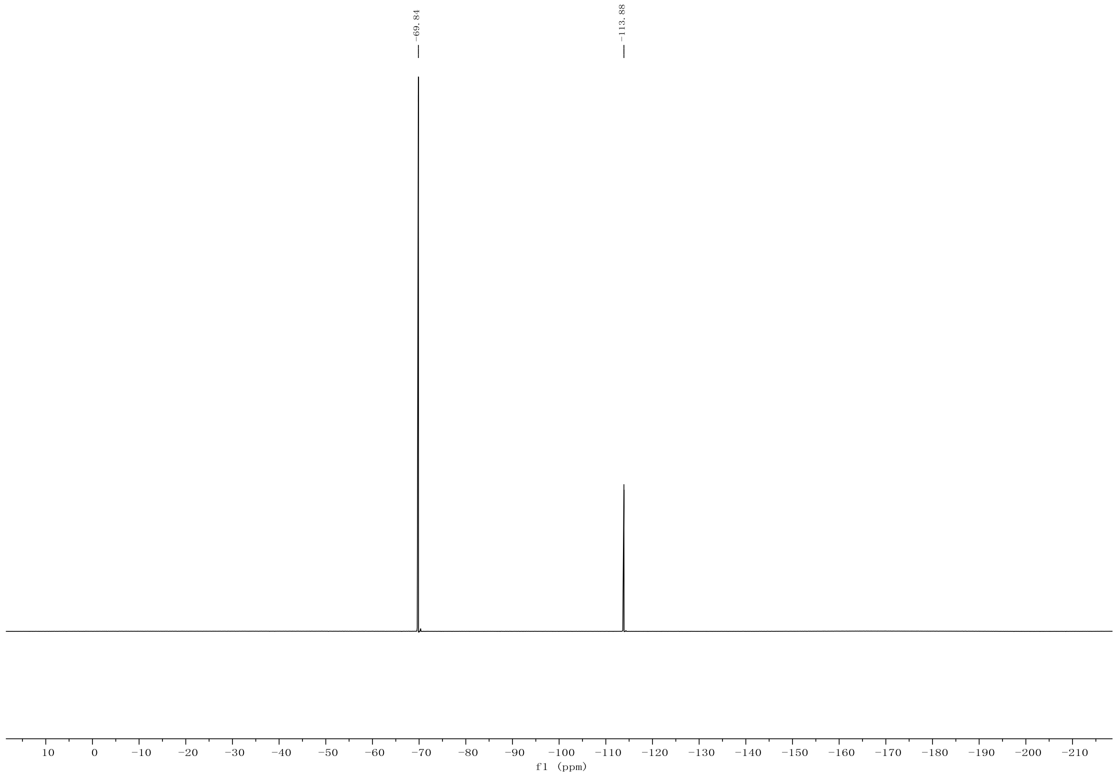

-69.17
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

4,4,4-Trifluoro-3-(4-fluorophenyl)-1-(4-methoxyphenyl)butan-1-one (3uh)

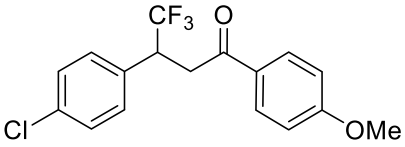


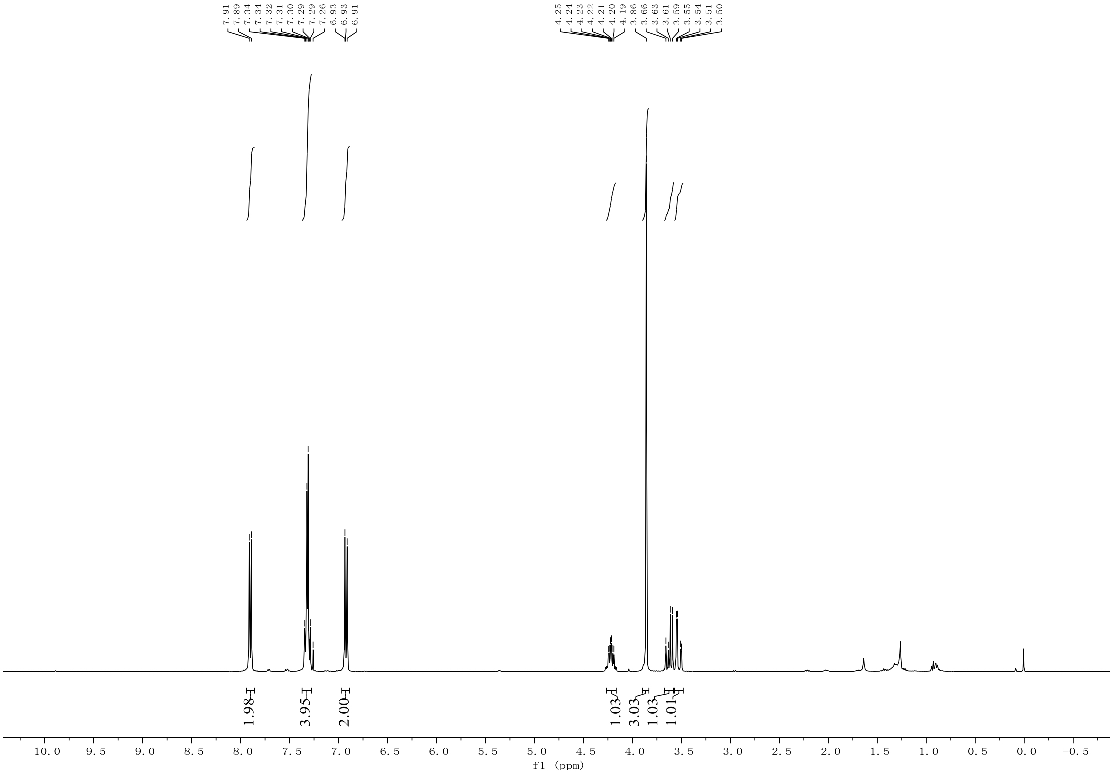


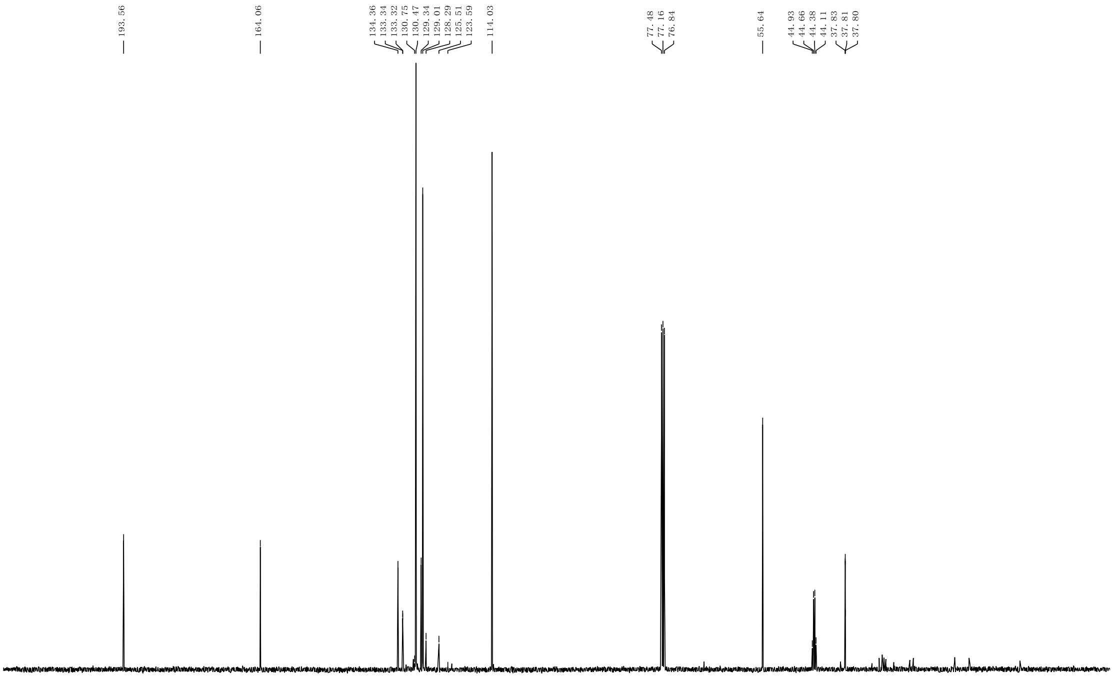

193.70
164.05
163.90
161.44
131.18
130.85
130.77
130.64
130.62
130.61
130.59
130.48
129.43
128.40
125.62
122.85
115.88
115.66
114.03
77.48
77.16
76.84
55.65
44.79
44.52
44.25
43.97
38.01
37.99
37.98
37.97
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

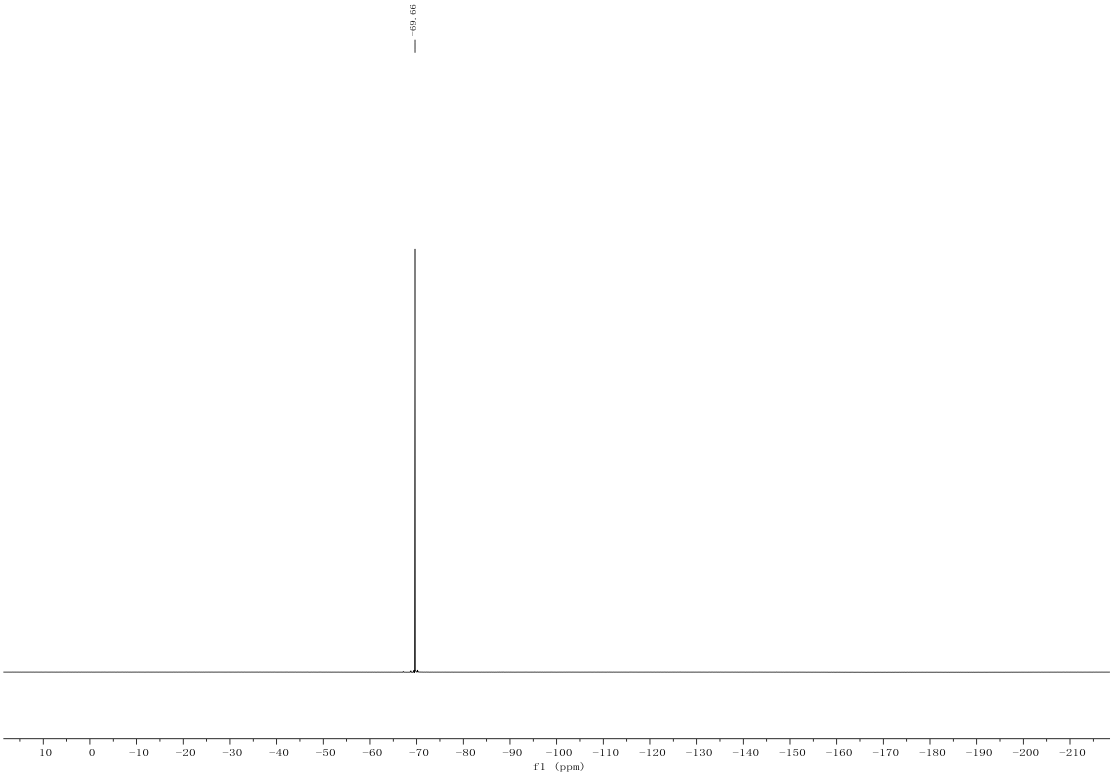

−69.84
−113.88
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

3-(4-Chlorophenyl)-4,4,4-trifluoro-1-(4-methoxyphenyl)butan-1-one (3vh)

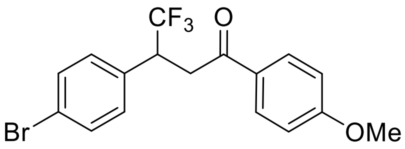


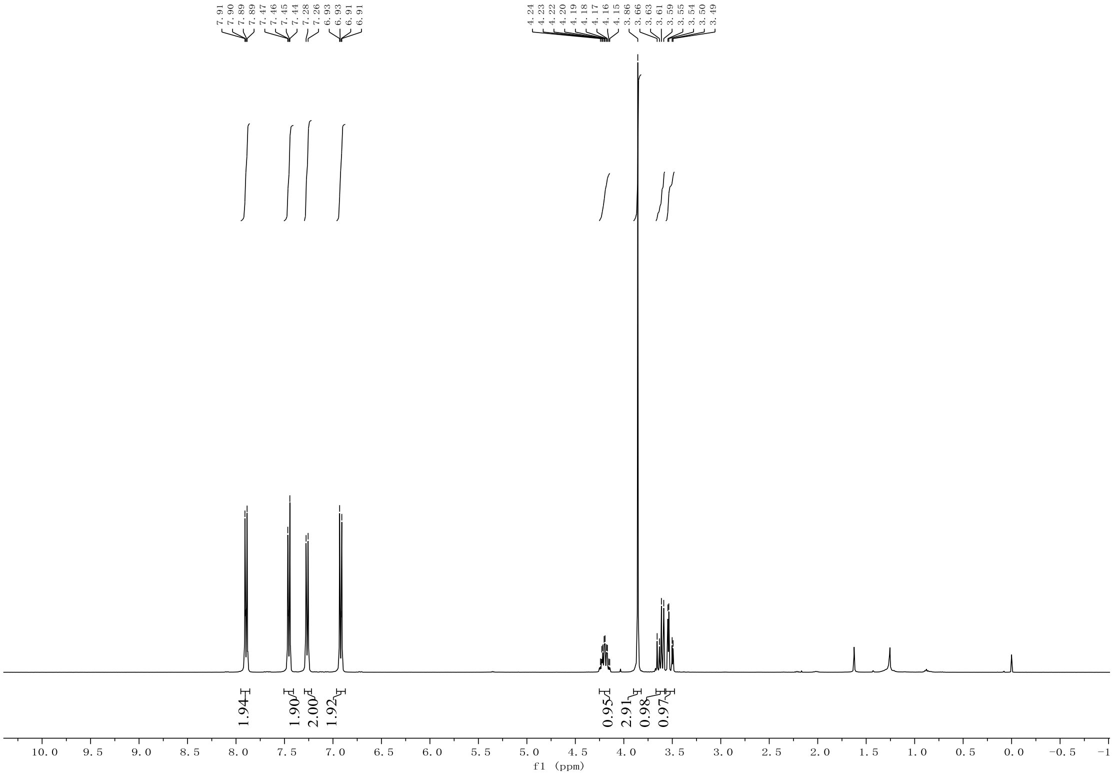


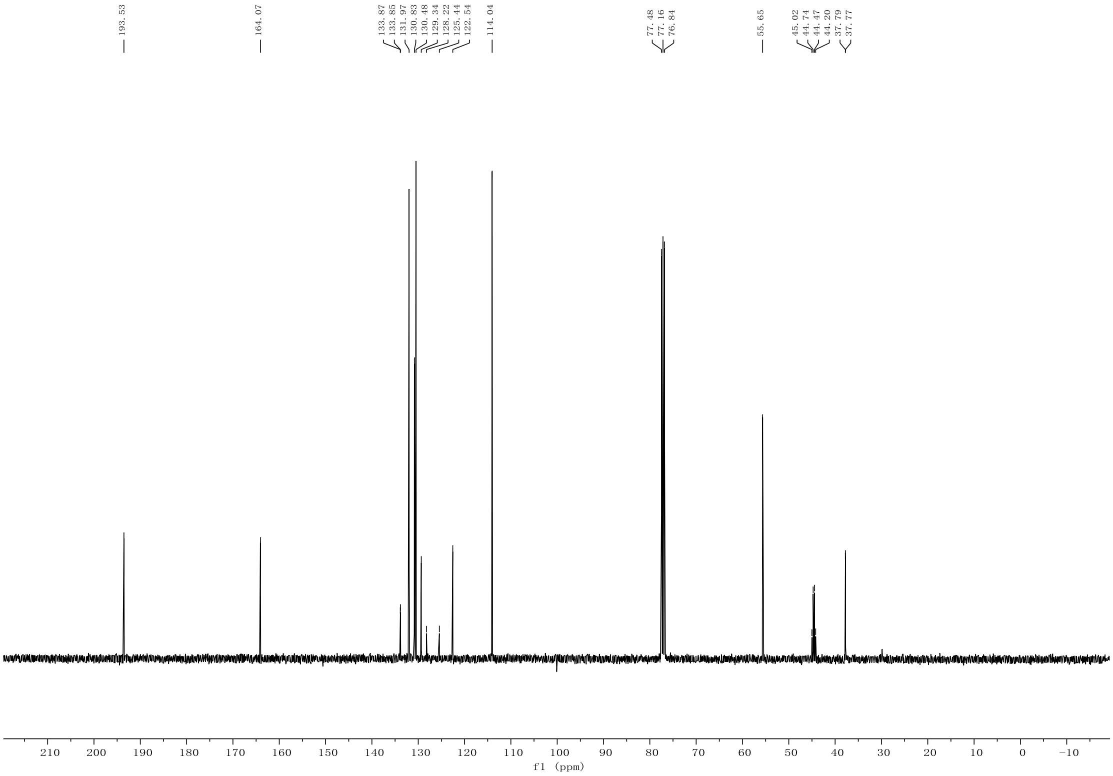


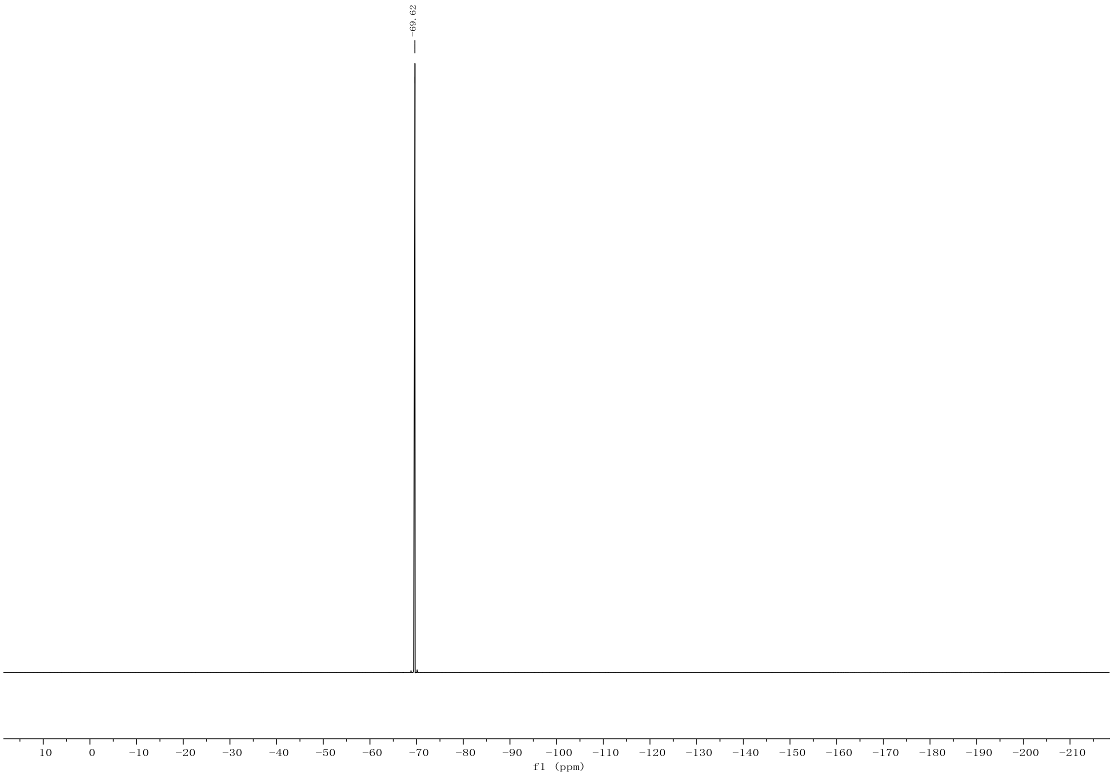

-69.66
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

3-(4-Bromophenyl)-4,4,4-trifluoro-1-(4-methoxyphenyl)butan-1-one (3wh)

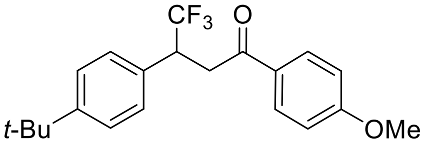


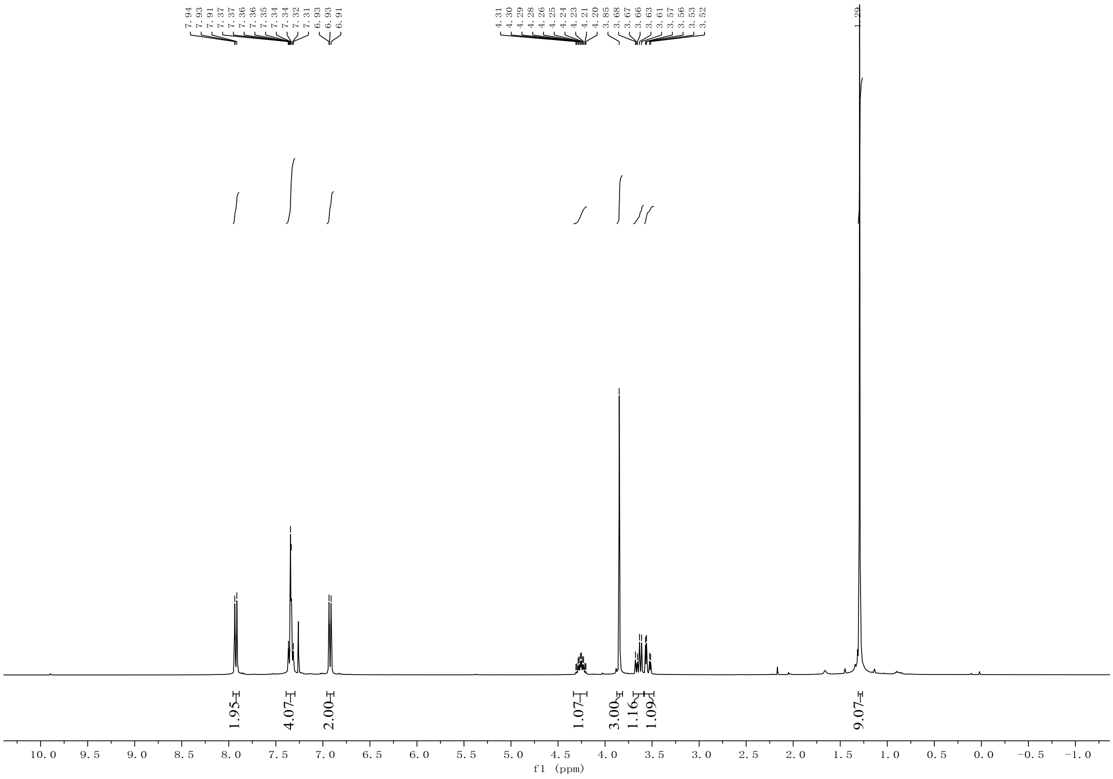


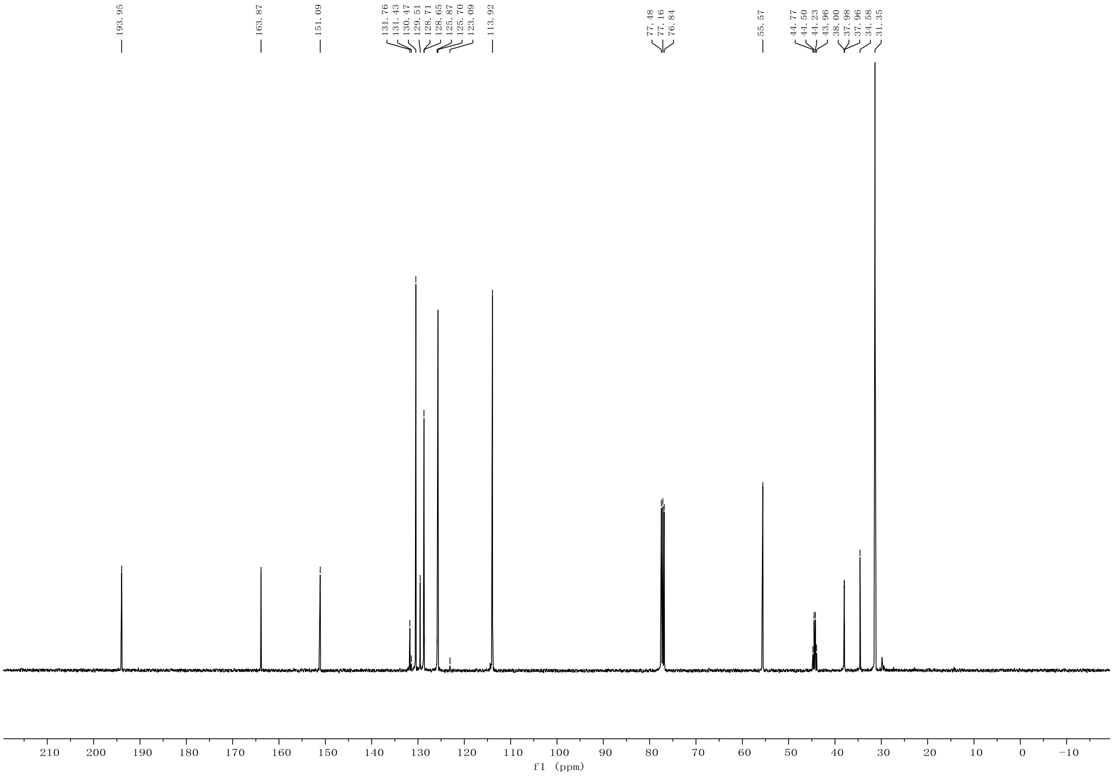


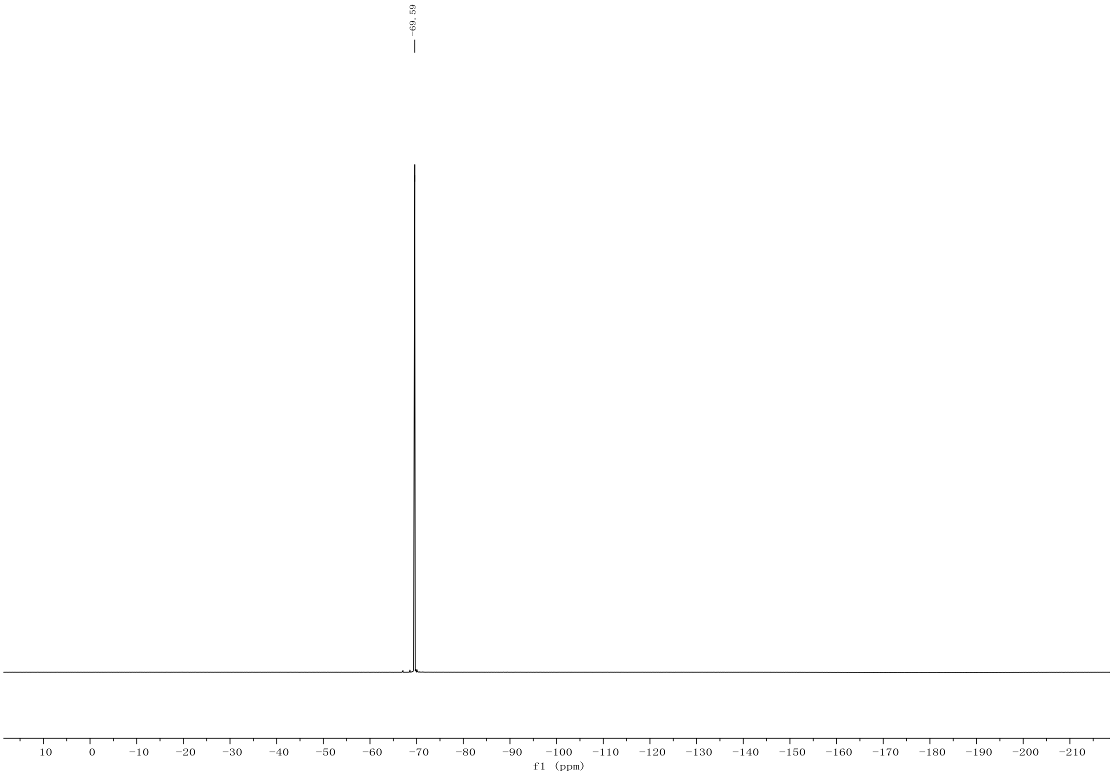

-69.62
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

3-(4-(*tert*-Butyl)phenyl)-4,4,4-trifluoro-1-(4-methoxyphenyl)butan-1-one (3xh)

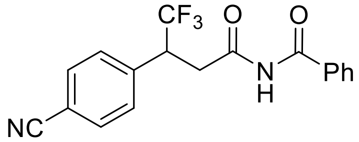


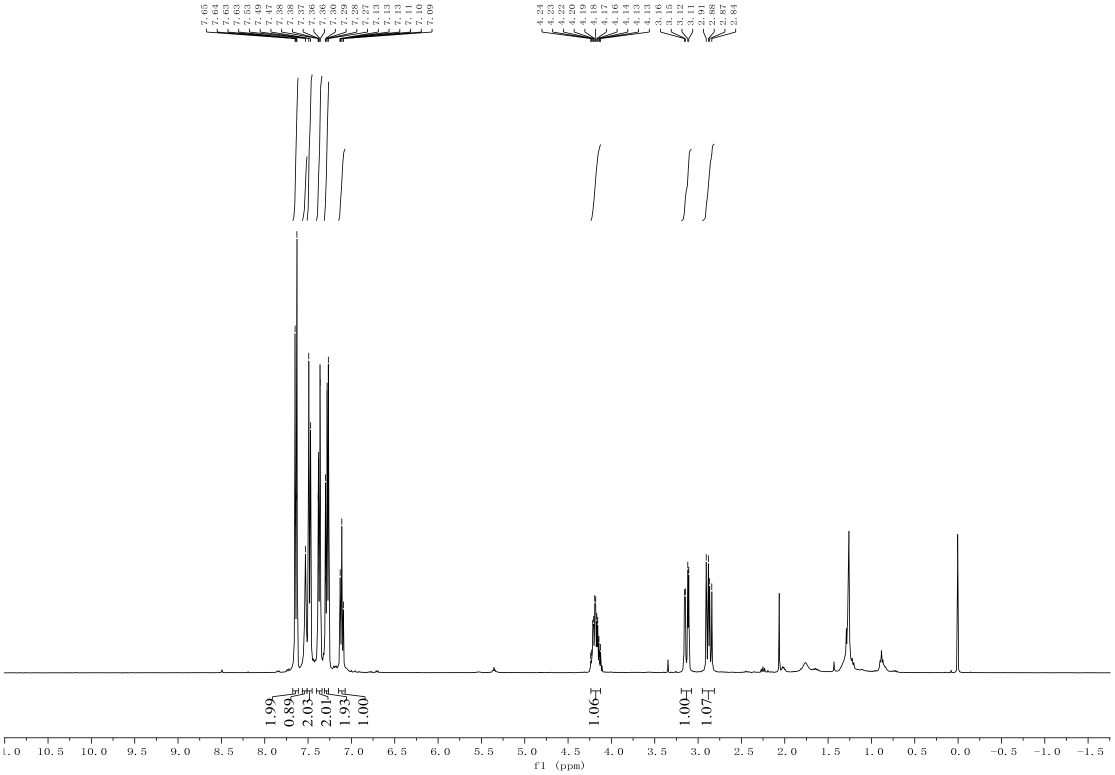


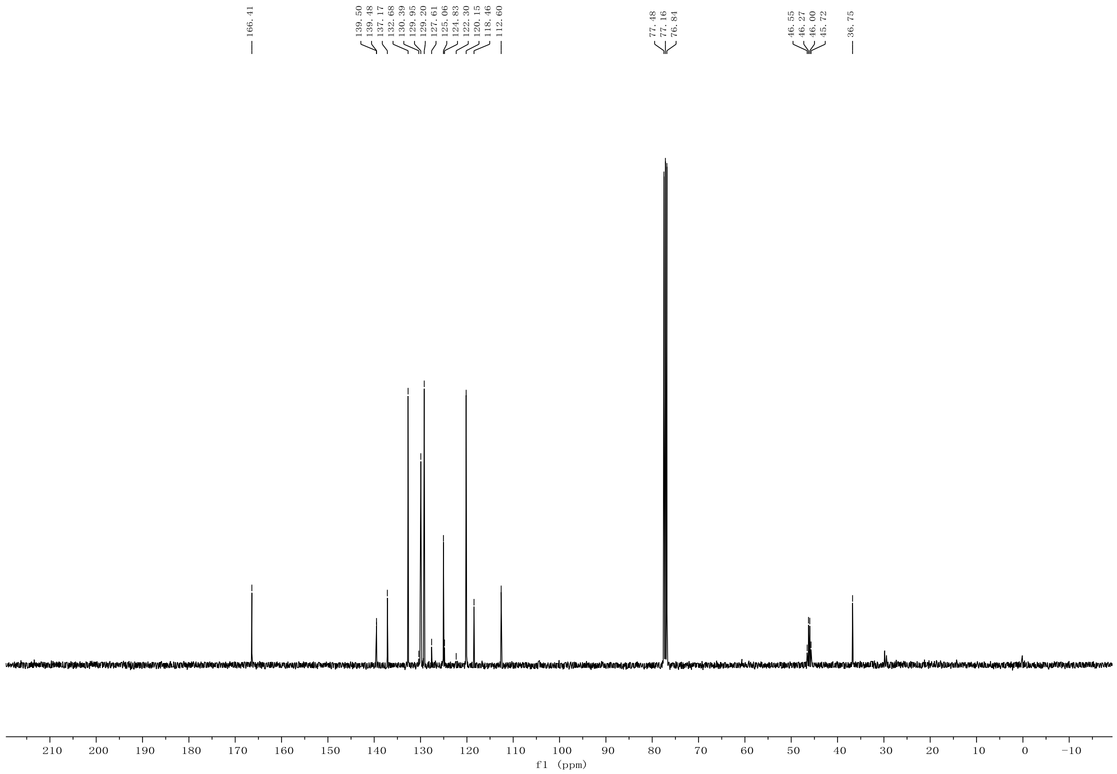

193.95
163.87
151.09
131.76
131.43
130.47
129.51
128.71
128.65
125.87
125.70
123.09
113.92
77.48
77.16
76.84
55.57
44.77
44.50
44.23
43.96
38.00
37.98
37.96
34.58
31.35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

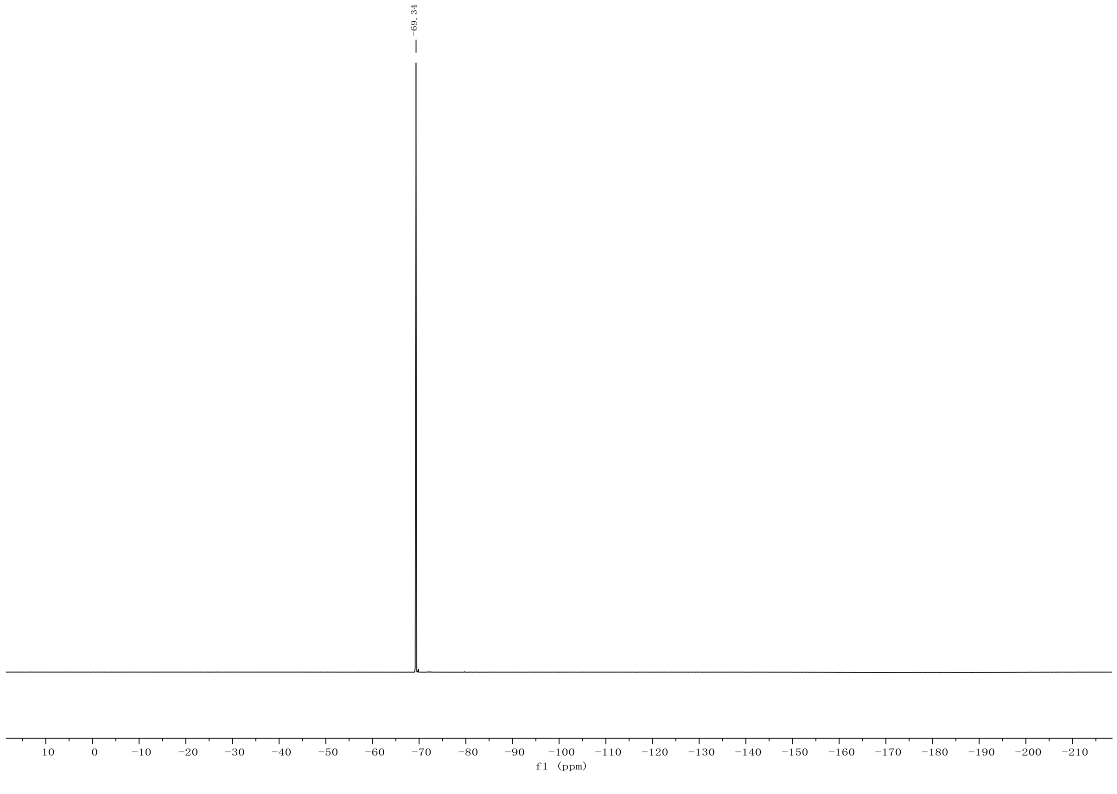

−69.59
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

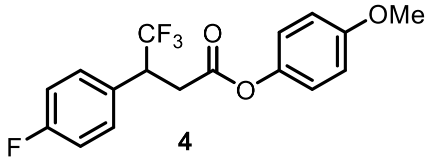
N-(3-(4-Cyanophenyl)-4,4,4-trifluorobutanoyl)benzamide (3ar)



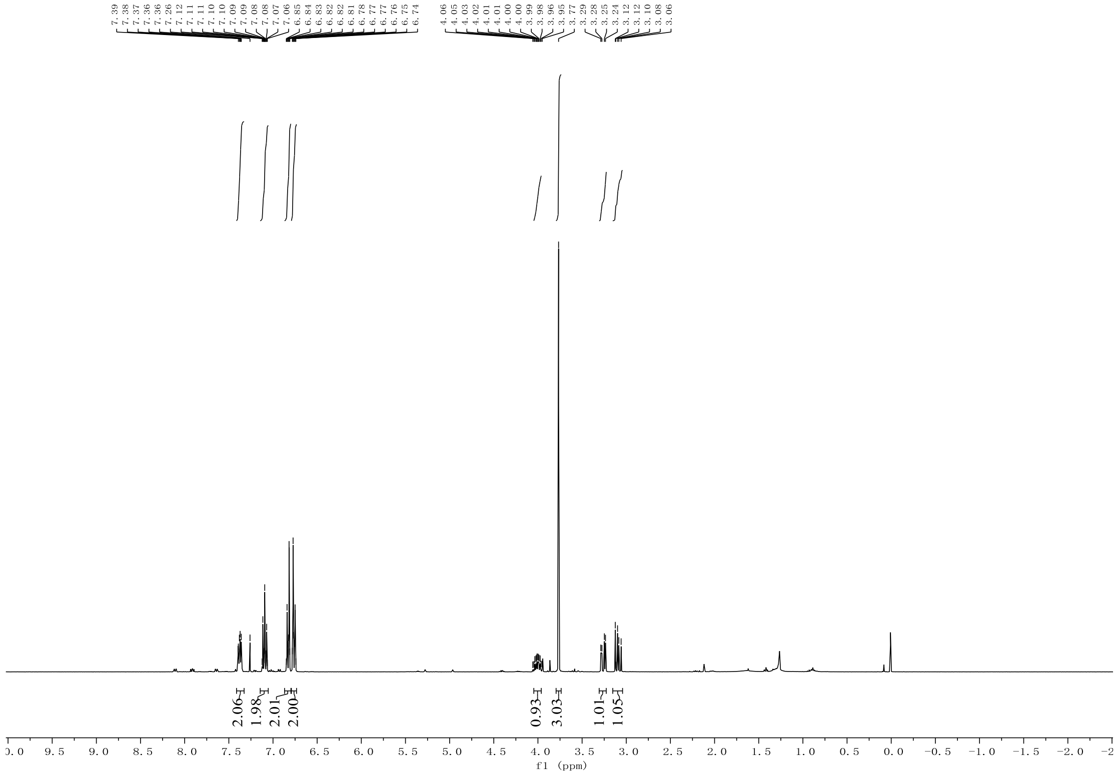


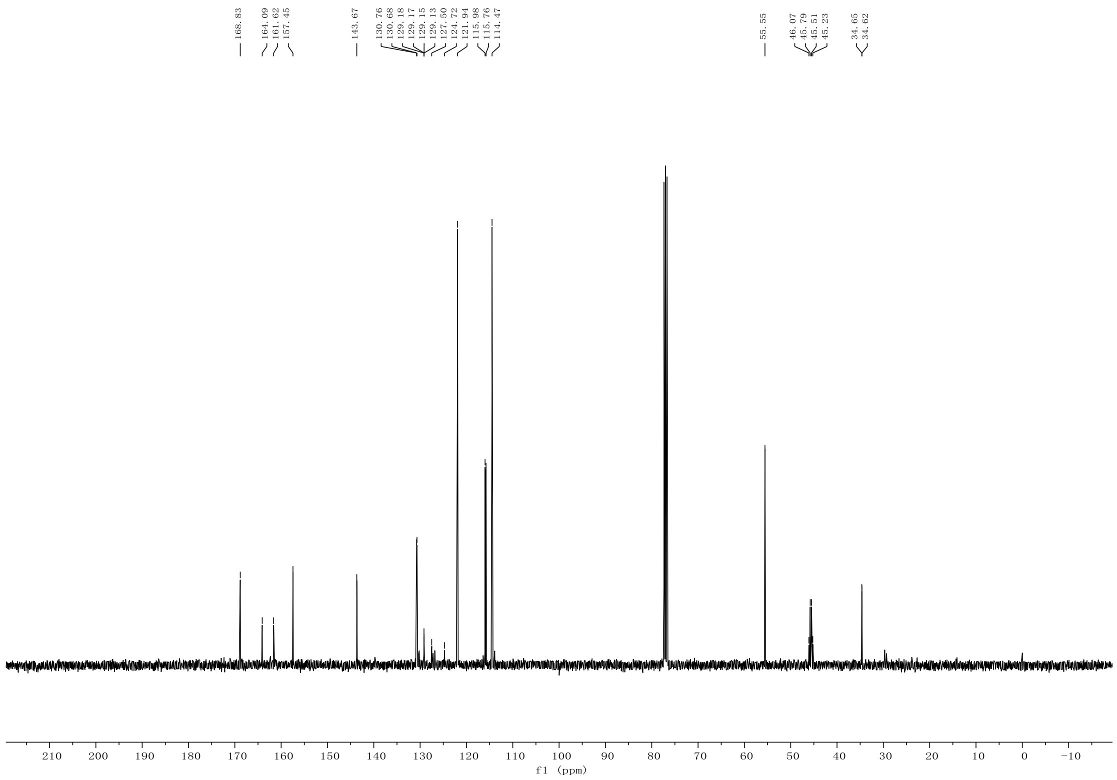

166.41
139.50
139.48
137.17
132.68
130.39
129.95
129.20
127.61
125.06
124.83
122.30
120.15
118.46
112.60
77.48
77.16
76.84
46.55
46.27
46.00
45.72
36.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

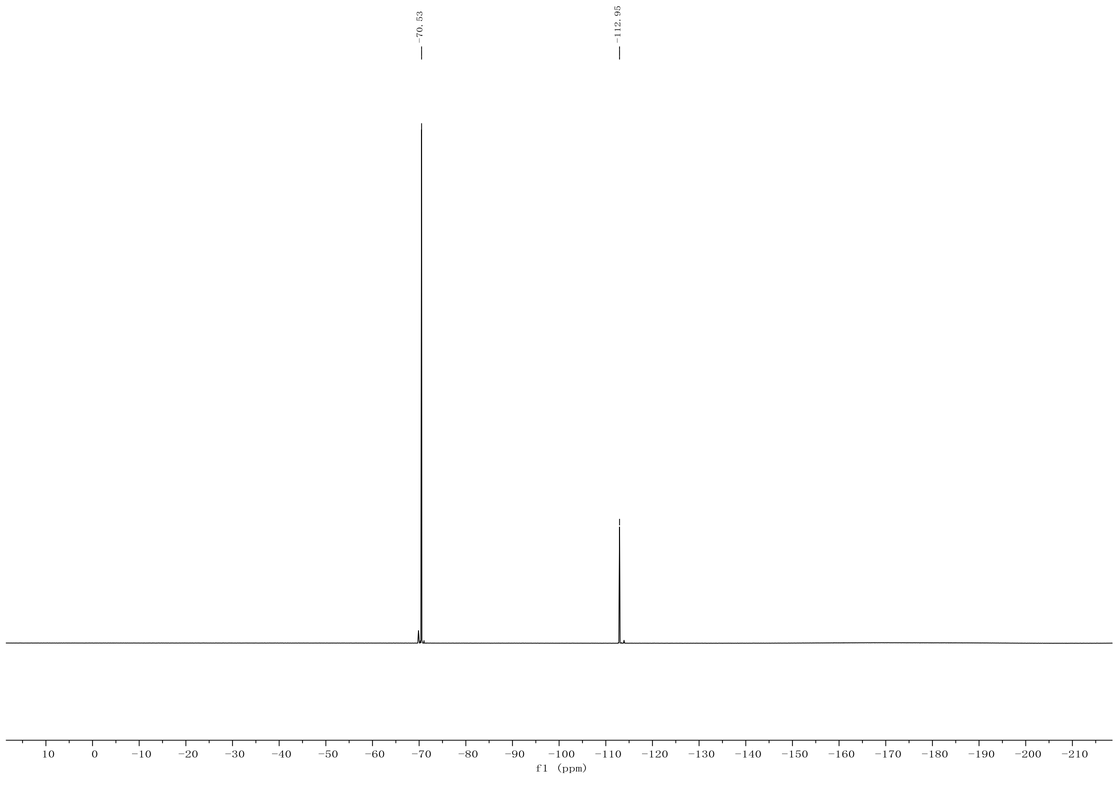

-69.34
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


CF3
O
O
OMe
F

4


7.39
7.38
7.37
7.36
7.36
7.26
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.07
7.06
6.85
6.84
6.83
6.82
6.81
6.78
6.77
6.77
6.76
6.75
6.74
4.06
4.05
4.03
4.02
4.01
4.01
4.00
4.00
3.99
3.98
3.96
3.95
3.77
3.29
3.28
3.25
3.24
3.12
3.10
3.08
3.06
2.06
1.98
2.01
2.00
0.93
3.03
1.01
1.05
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
0.0
-0.5
-1.0
-1.5
-2.0
-2
f1 (ppm)


168.83
164.09
161.62
157.45
143.67
130.76
130.68
129.18
129.17
129.15
129.13
127.50
124.72
121.94
115.98
115.76
114.47
55.55
46.07
45.79
45.51
45.23
34.65
34.62
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


−70.53
−112.95
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
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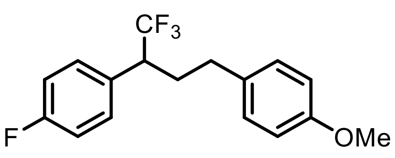
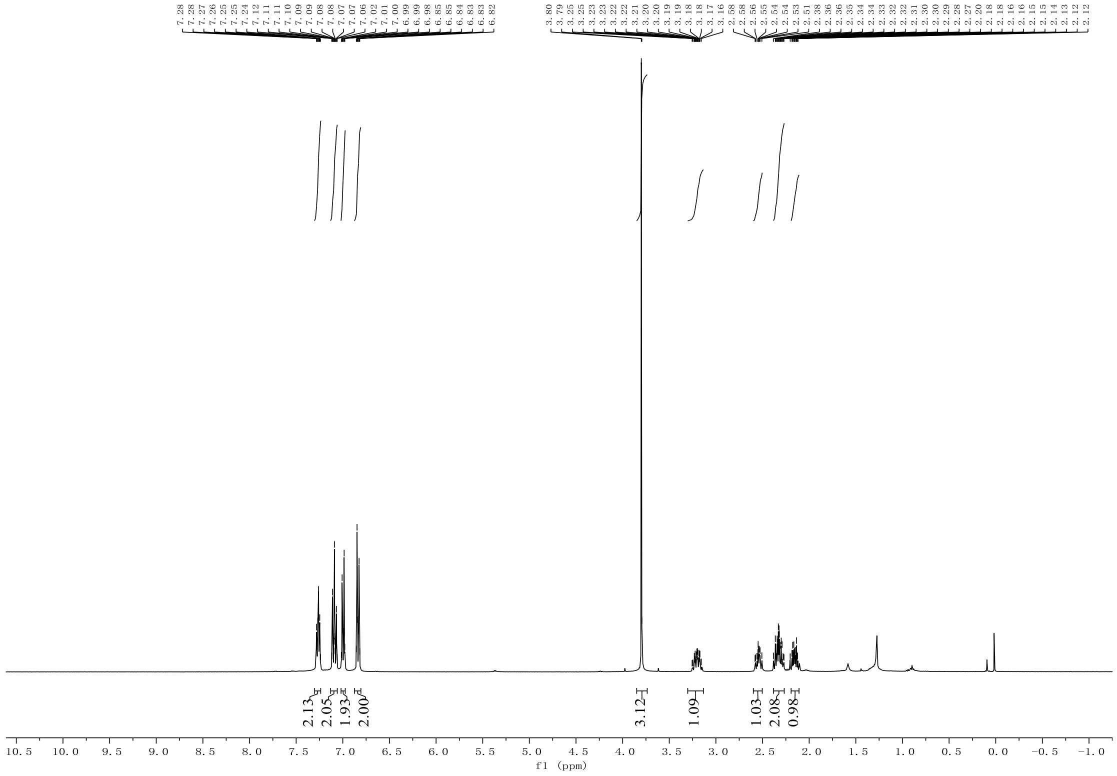
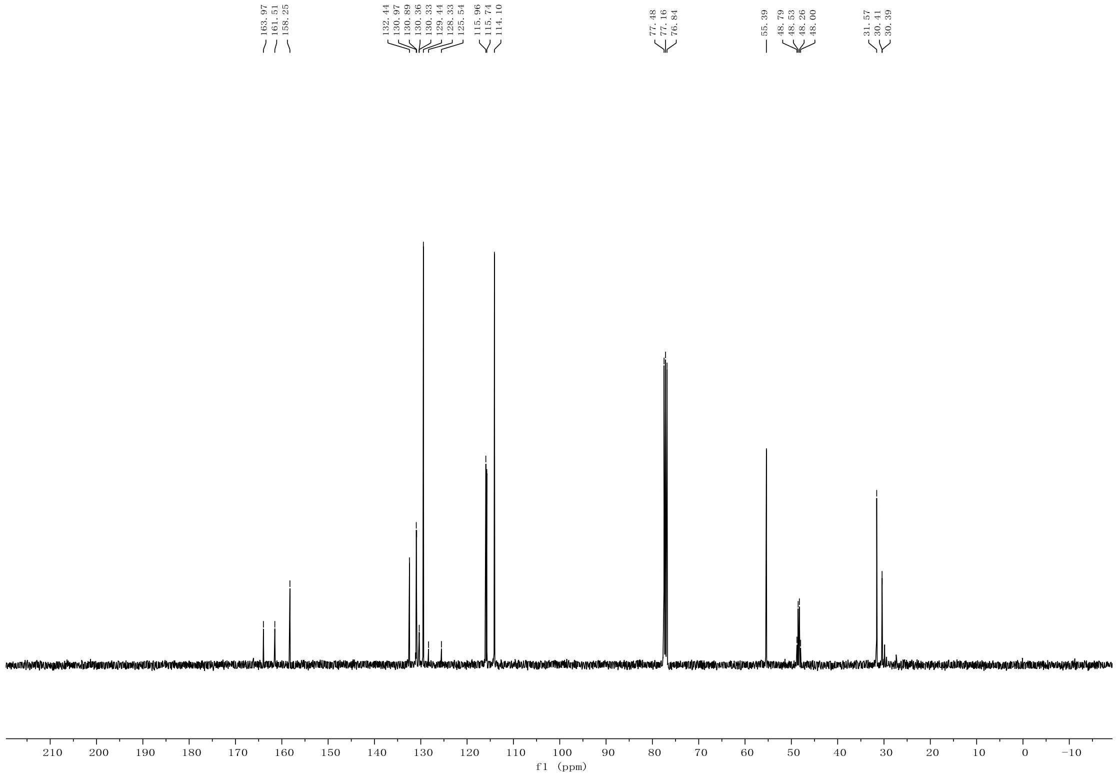
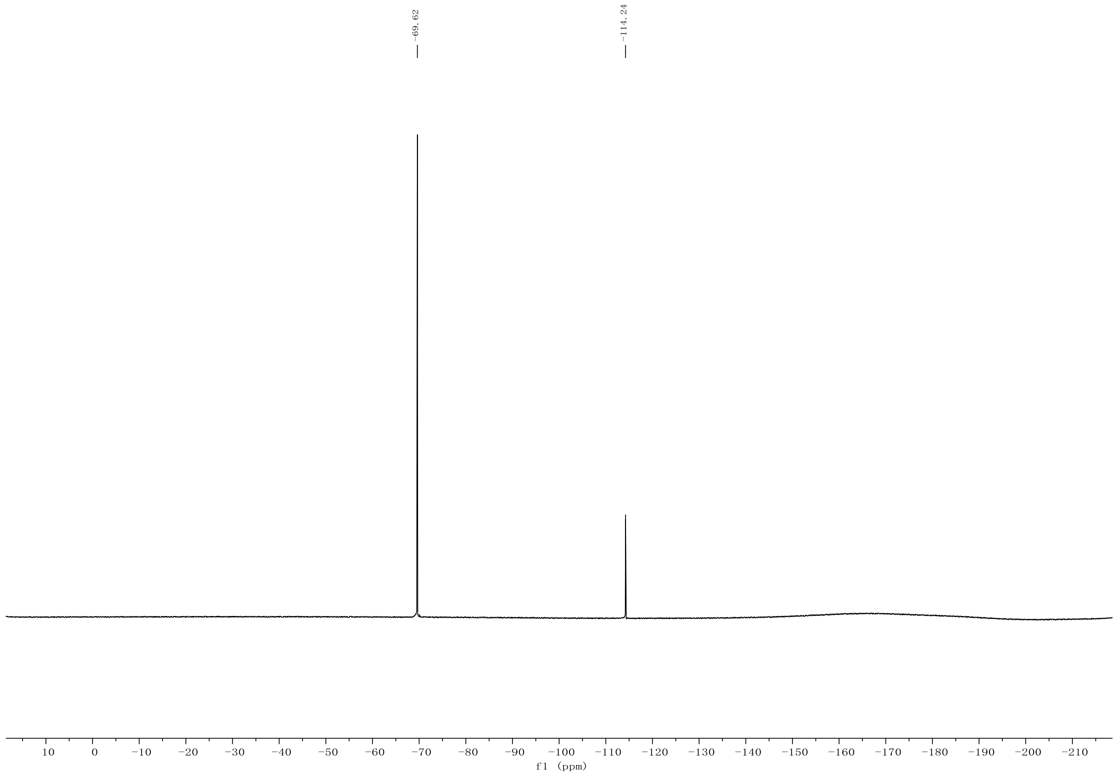
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

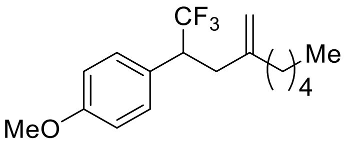

CF3
F
OMe

5

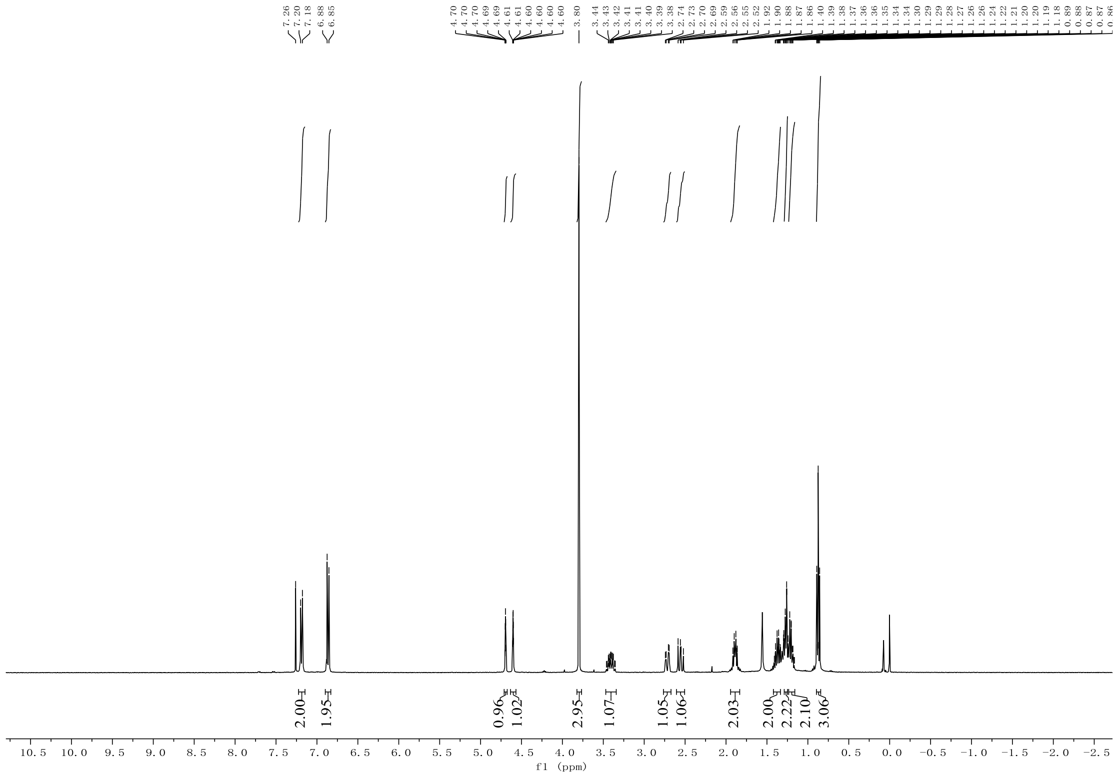

7.28
7.28
7.27
7.26
7.25
7.25
7.24
7.12
7.11
7.11
7.10
7.09
7.09
7.08
7.08
7.07
7.07
7.06
7.02
7.01
7.00
6.99
6.99
6.98
6.85
6.84
6.83
6.83
6.82
3.80
3.79
3.25
3.25
3.23
3.23
3.22
3.21
3.20
3.20
3.19
3.18
3.18
3.17
3.16
2.58
2.58
2.56
2.55
2.54
2.53
2.51
2.38
2.36
2.35
2.34
2.33
2.32
2.32
2.31
2.30
2.30
2.29
2.28
2.27
2.20
2.18
2.18
2.16
2.15
2.14
2.13
2.12
2.12
2.13
2.05
1.93
2.00
3.12
1.09
1.03
2.08
0.98
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
0.0
-0.5
-1.0
f1 (ppm)

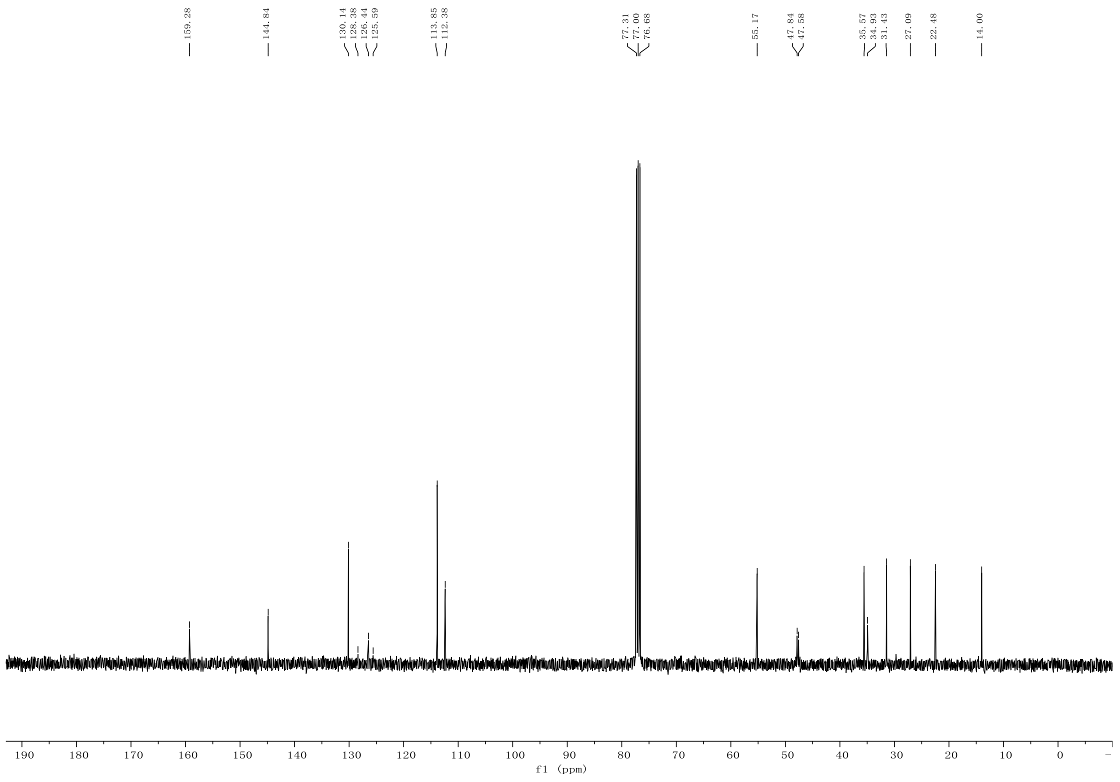

163.97
161.51
158.25
132.44
130.97
130.89
130.36
130.33
129.44
128.33
125.54
115.96
115.74
114.10
77.48
77.16
76.84
55.39
48.79
48.53
48.26
48.00
31.57
30.41
30.39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


−69.62
−114.24
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)


CF3
Me
4
MeO

6


7.26
7.20
7.18
6.88
6.85
4.70
4.70
4.70
4.69
4.69
4.61
4.61
4.60
4.60
4.60
4.60
3.80
3.44
3.43
3.42
3.41
3.41
3.40
3.39
3.38
2.74
2.73
2.70
2.69
2.59
2.56
2.55
2.52
1.92
1.90
1.88
1.87
1.86
1.40
1.39
1.38
1.37
1.36
1.36
1.35
1.34
1.34
1.30
1.29
1.29
1.28
1.27
1.26
1.26
1.24
1.22
1.21
1.20
1.20
1.19
1.18
0.89
0.88
0.87
0.87
0.86
2.00
1.95
0.96
1.02
2.95
1.07
1.05
1.06
2.03
2.00
2.22
2.10
3.06
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
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
f1 (ppm)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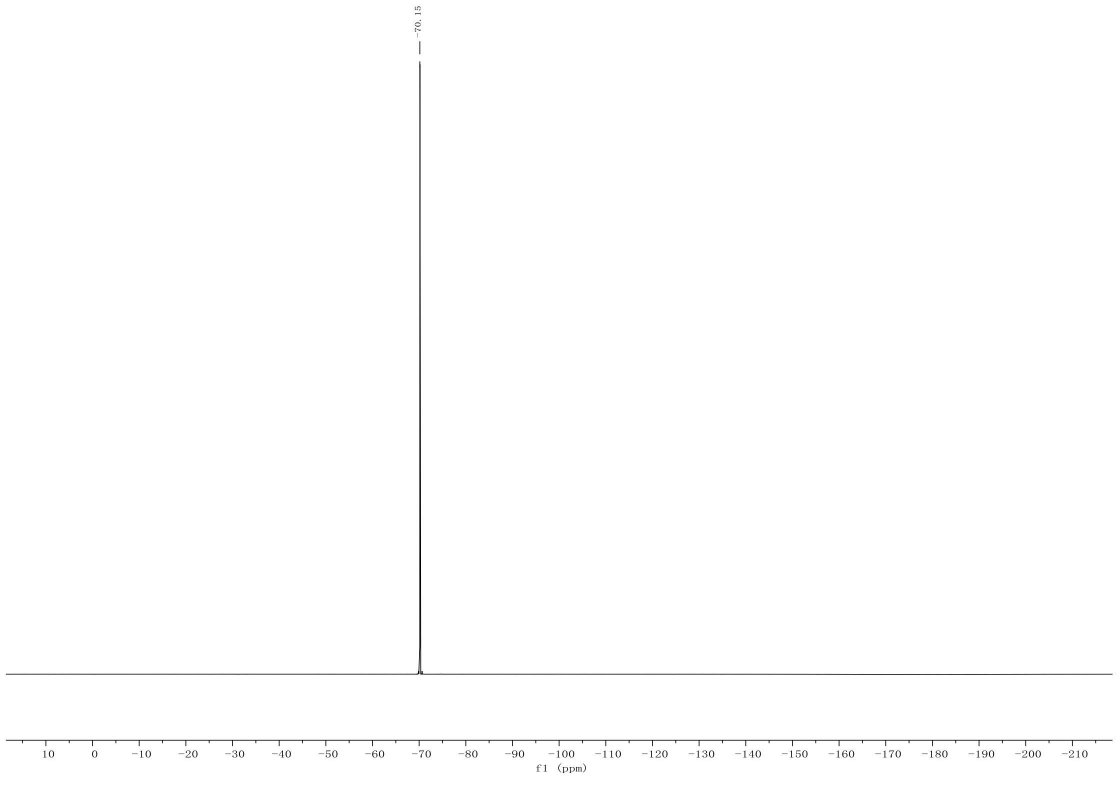
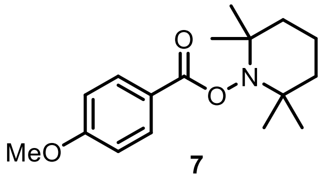
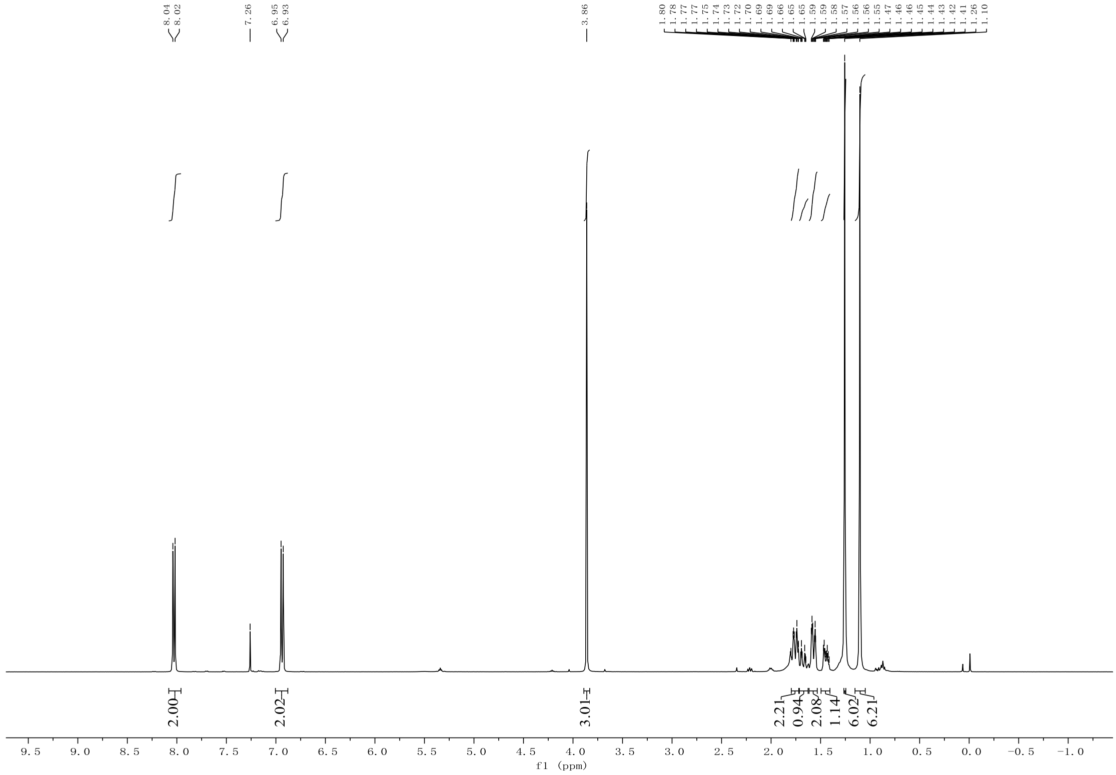
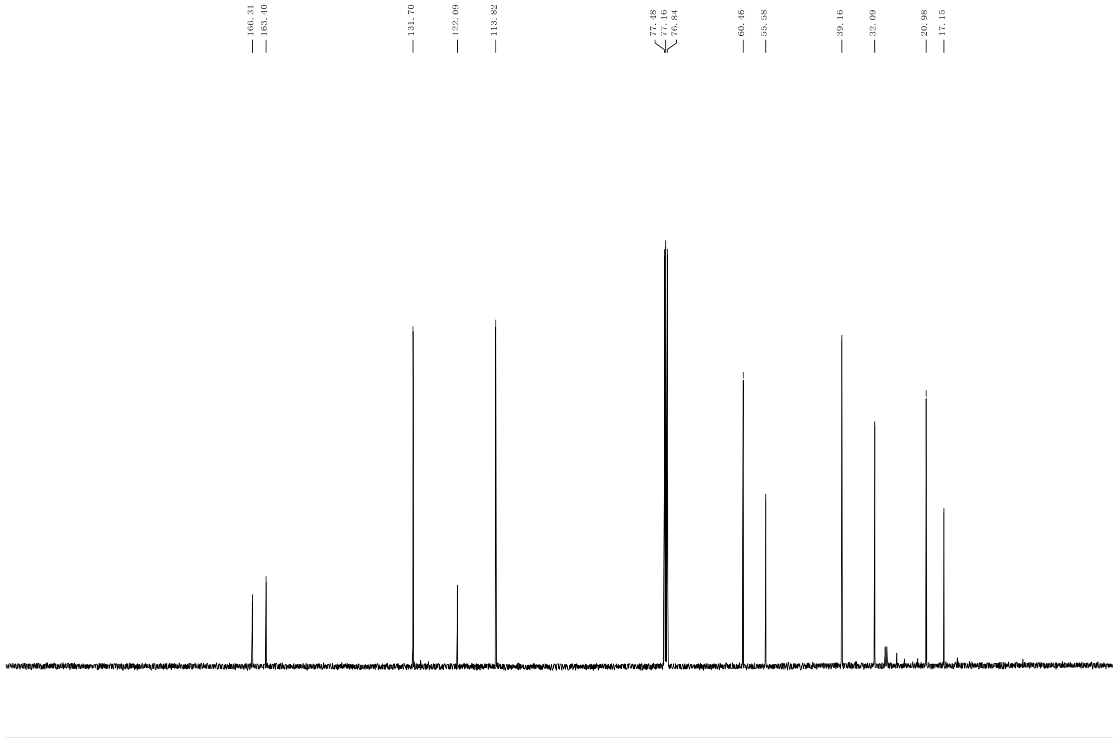
144.84
130.14
128.38
126.44
125.59
113.85
112.38
77.31
77.00
76.68
55.17
47.84
47.58
35.57
34.93
31.43
27.09
22.48
14.00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

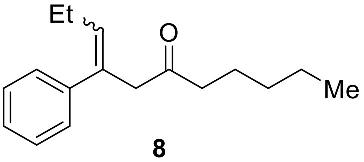

-70.15
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


O
O
N
MeO

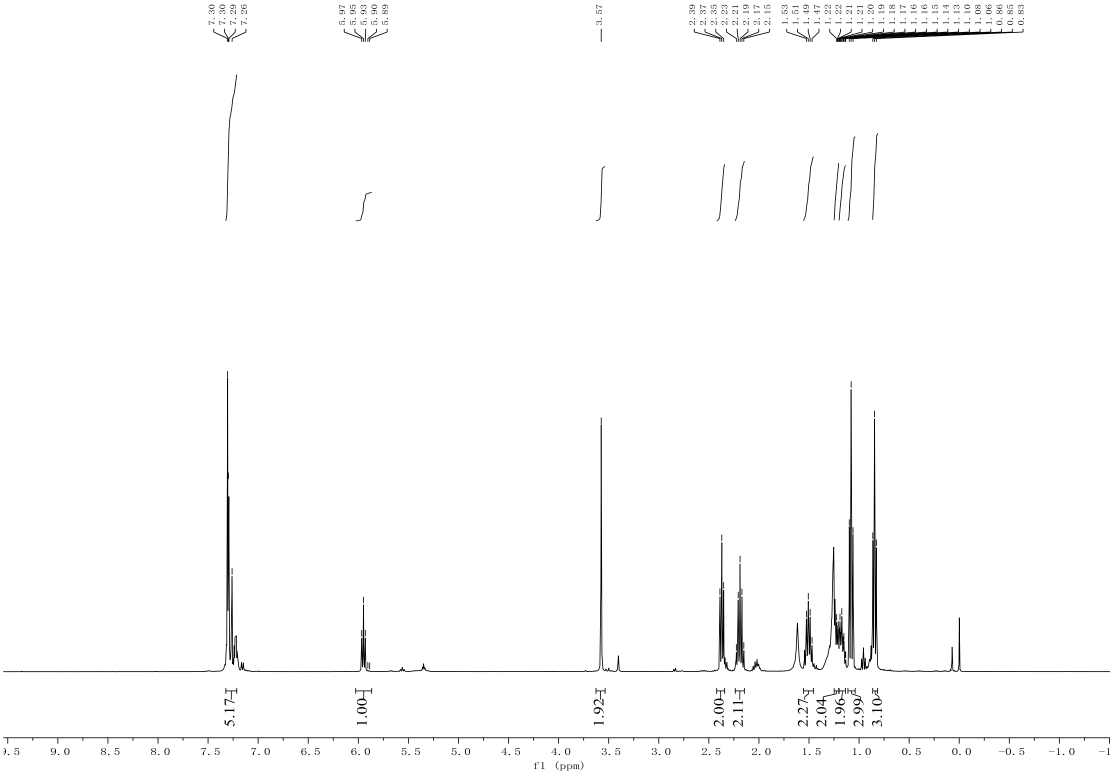
7

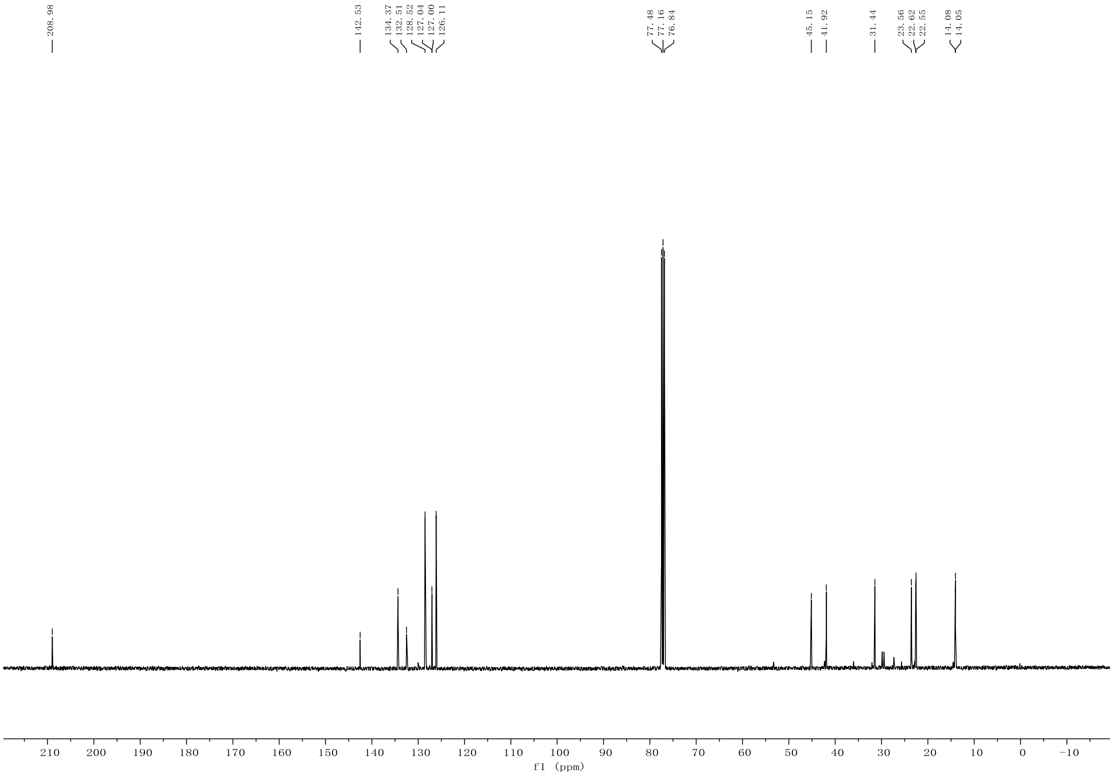

8.04
8.02
7.26
6.95
6.93
3.86
1.80
1.78
1.77
1.75
1.74
1.73
1.72
1.70
1.69
1.69
1.66
1.65
1.65
1.59
1.59
1.58
1.57
1.56
1.56
1.55
1.47
1.46
1.46
1.45
1.44
1.43
1.42
1.41
1.26
1.10
2.00
2.02
3.01
2.21
0.94
2.08
1.14
6.02
6.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

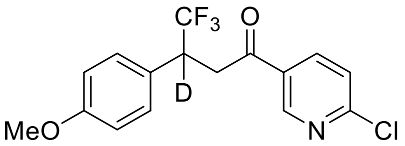

166.31
163.40
131.70
122.09
113.82
77.48
77.16
76.84
60.46
55.58
39.16
32.09
20.98
17.15
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Et
O
Me

8

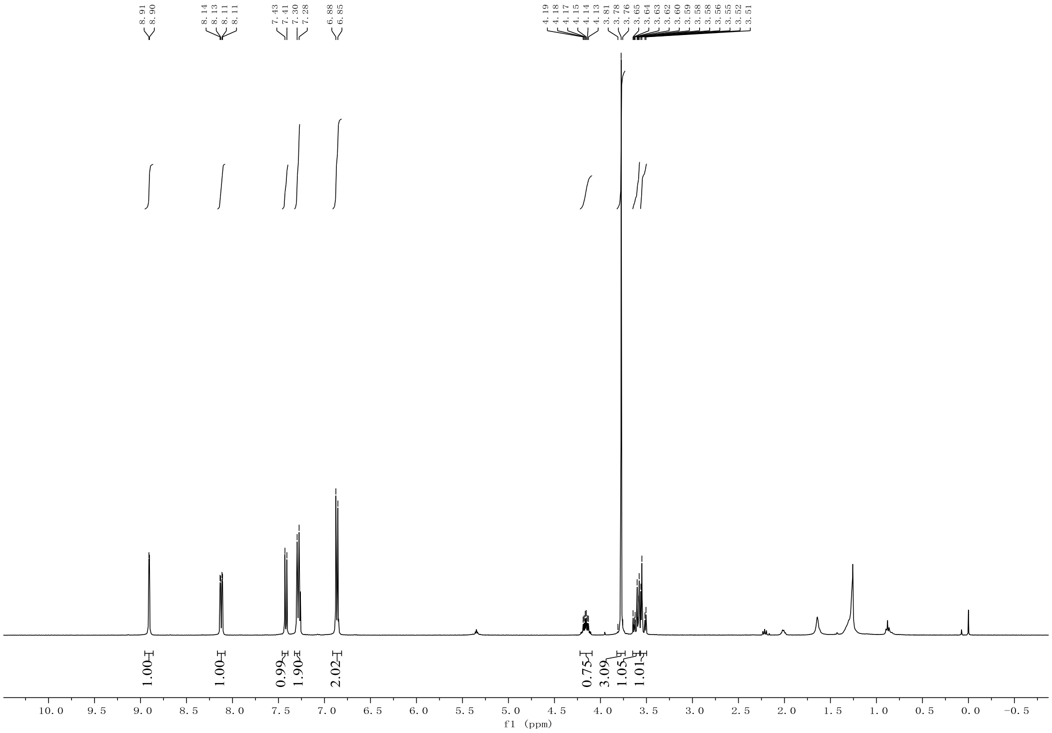

7.30
7.30
7.29
7.26
5.97
5.95
5.93
5.90
5.89
3.57
2.39
2.37
2.35
2.23
2.21
2.19
2.17
2.15
1.53
1.51
1.49
1.47
1.22
1.22
1.21
1.21
1.20
1.19
1.18
1.17
1.16
1.16
1.15
1.14
1.13
1.10
1.08
1.06
0.86
0.85
0.83
5.17
1.00
1.92
2.00
2.11
2.27
2.04
1.96
2.99
3.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
f1 (ppm)


208.98
142.53
134.37
132.51
128.52
127.04
127.00
126.11
77.48
77.16
76.84
45.15
41.92
31.44
23.56
22.62
22.55
14.08
14.05
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3an'

Spectrum for Control Experiment C



Spectrum for Control Experiment E