

Supporting Information for

**Visible-light-induced N-Alkylation of Anilines with
4-Hydroxybutan-2-one**

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1. UV-vis spectroscopic of **1a** and NH₄Br in MeOH

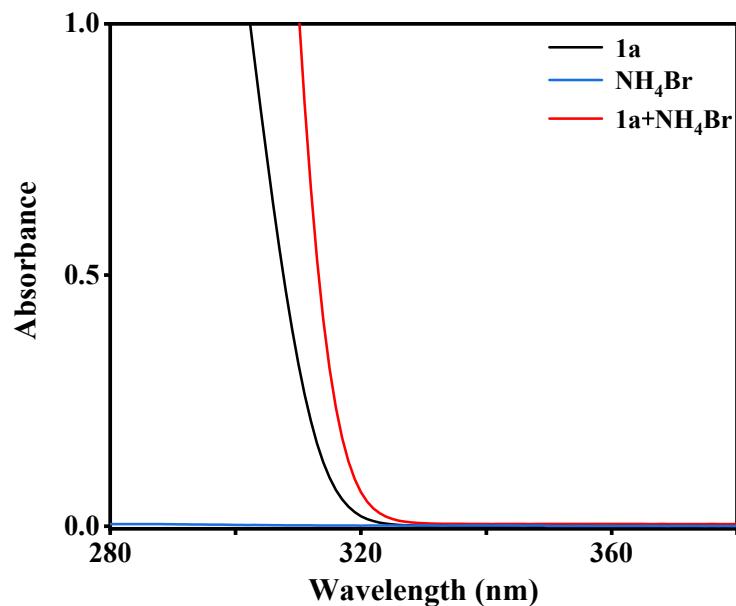


Figure S1. UV-vis spectroscopic of **1a** and NH₄Br in MeOH.

2. Reactions setup

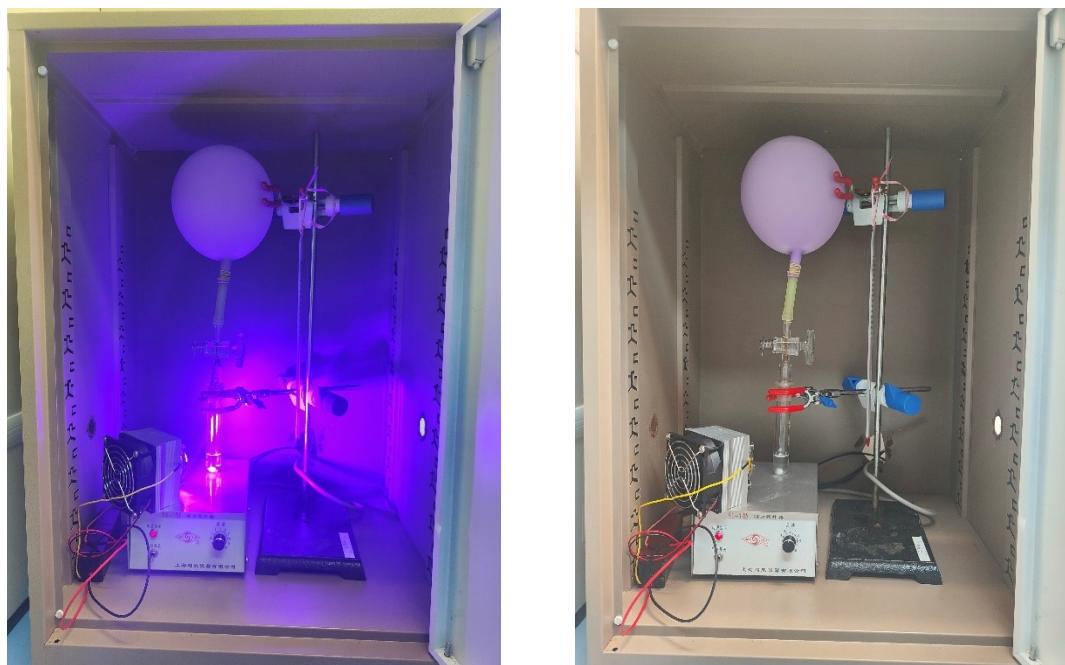
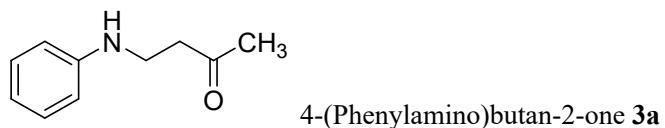
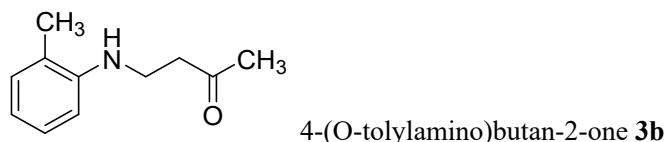


Figure S2. Reactions setup.

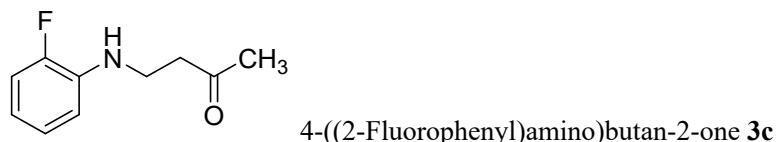
3. ^1H , ^{13}C and ^{19}F NMR Data



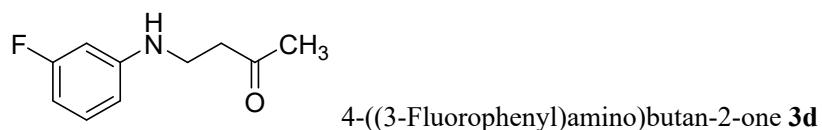
^1H NMR (500 MHz, CDCl_3) δ 7.21 - 7.16 (m, 2H), 6.72 (t, $J = 7.3$ Hz, 1H), 6.61 (d, $J = 8.5$ Hz, 2H), 4.01 (s, 1H), 3.41 (t, $J = 6.2$ Hz, 2H), 2.74 (t, $J = 6.1$ Hz, 2H), 2.16 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 208.1, 147.7, 129.3, 117.6, 113.0, 42.6, 38.3, 30.3. Known compound.¹



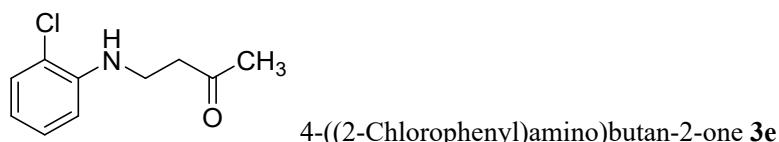
^1H NMR (500 MHz, CDCl_3) δ 7.14 (t, $J = 7.7$ Hz, 1H), 7.07 (d, $J = 7.2$ Hz, 1H), 6.69 (t, $J = 7.3$ Hz, 1H), 6.63 (d, $J = 8.0$ Hz, 1H), 3.89 (s, 1H), 3.48 (t, $J = 6.1$ Hz, 2H), 2.80 (t, $J = 6.1$ Hz, 2H), 2.18 (s, 3H), 2.13 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 208.4, 145.7, 130.3, 127.2, 122.6, 117.2, 109.6, 42.6, 38.3, 30.4, 17.5. Known compound.¹



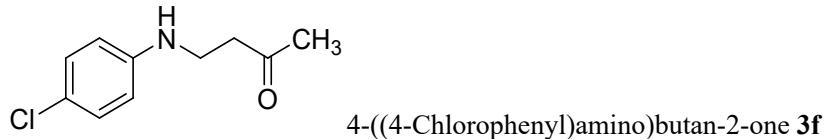
^1H NMR (500 MHz, CDCl_3) δ 7.01 - 6.93 (m, 2H), 6.68 (t, $J = 8.2$ Hz, 1H), 6.63 (dd, $J = 7.8, 4.9$ Hz, 1H), 4.20 (dd, $J = 18.9, 12.7$ Hz, 1H), 3.45 (t, $J = 6.3$ Hz, 2H), 2.77 (t, $J = 6.3$ Hz, 2H), 2.18 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 207.7, 151.9 (d, $J = 238.8$ Hz), 136.7, 124.7 (d, $J = 3.5$ Hz), 117.0 (d, $J = 7.2$ Hz), 114.7 (d, $J = 18.4$ Hz), 112.2 (d, $J = 3.0$ Hz), 42.8, 38.1, 30.5. ^{19}F NMR (471 MHz, CDCl_3) δ -136.1 (s). Known compound.²



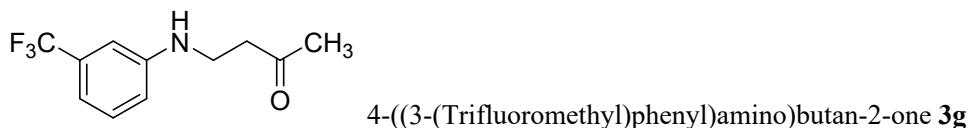
^1H NMR (500 MHz, CDCl_3) δ 7.07 (td, $J = 8.2, 6.8$ Hz, 1H), 6.39 - 6.32 (m, 2H), 6.27 (dd, $J = 11.6, 2.3$ Hz, 1H), 4.14 (s, 1H), 3.37 (t, $J = 6.0$ Hz, 2H), 2.72 (t, $J = 6.0$ Hz, 2H), 2.15 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 208.0, 164.3 (d, $J = 242.7$ Hz), 149.6 (d, $J = 10.8$ Hz), 130.4 (d, $J = 10.2$ Hz), 108.9 (d, $J = 2.4$ Hz), 104.0, 99.5, 77.1, 42.4, 38.3, 30.4. ^{19}F NMR (471 MHz, CDCl_3) δ -112.8 (s). Known compound.¹



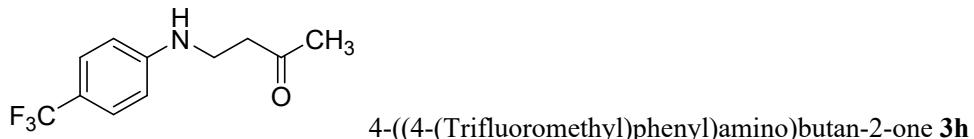
¹H NMR (500 MHz, CDCl₃) δ 7.24 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.13 (m, 1H), 6.69 - 6.59 (m, 2H), 4.56 (d, *J* = 6.8 Hz, 1H), 3.45 (t, *J* = 6.4 Hz, 2H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.16 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 206.9, 143.0, 128.7, 127.2, 118.9, 116.8, 110.5, 42.0, 37.5, 29.7. Known compound.¹



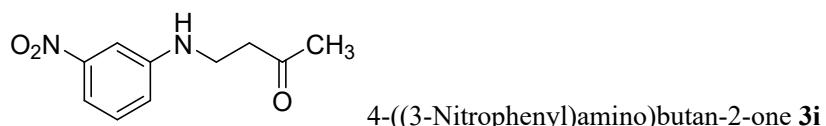
¹H NMR (500 MHz, CDCl₃) δ 7.10 (d, *J* = 8.9 Hz, 2H), 6.51 (d, *J* = 8.9 Hz, 2H), 4.02 (s, 1H), 3.36 (s, 2H), 2.72 (s, 2H), 2.16 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 207.8, 146.0, 128.9, 121.8, 113.8, 42.1, 38.2, 30.1. Known compound.¹



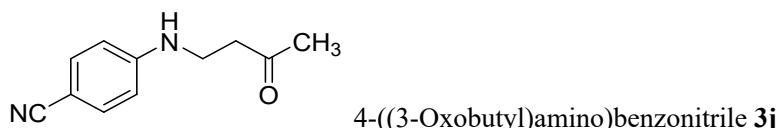
¹H NMR (500 MHz, CDCl₃) δ 7.24 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.78 (s, 1H), 6.73 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.17 (s, 1H), 3.42 (t, *J* = 6.0 Hz, 2H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.17 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 207.9, 148.0, 131.7, 129.8, 124.4 (q, *J* = 272.7 Hz), 116.1, 114.0 (d, *J* = 3.8 Hz), 108.9 (d, *J* = 4.0 Hz), 42.3, 38.1, 30.3. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.8. Known compound.¹



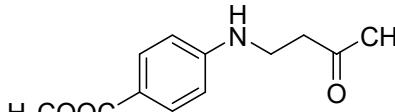
¹H NMR (500 MHz, CDCl₃) δ 7.39 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 4.38 (s, 1H), 3.44 (t, *J* = 6.0 Hz, 2H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.17 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 207.8, 150.2, 126.7 (q, *J* = 3.7 Hz), 125.1 (q, *J* = 262.7 Hz), 119.1 (q, *J* = 32.5 Hz) 112.0, 42.3, 37.9, 30.4. ¹⁹F NMR (471 MHz, CDCl₃) δ -60.9 (s). Known compound.¹



¹H NMR (500 MHz, CDCl₃) δ 7.49 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.36 (s, 1H), 7.25 (t, *J* = 7.0 Hz, 1H), 6.84 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.47 (s, 1H), 3.45 (t, *J* = 5.9 Hz, 2H), 2.78 (t, *J* = 5.9 Hz, 2H), 2.18 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 208.1 (s), 149.7 (s), 148.9 (s), 130.1 (s), 119.4 (s), 112.4 (s), 106.4 (s), 42.4 (s), 38.3 (s), 30.6 (s). Known compound.¹

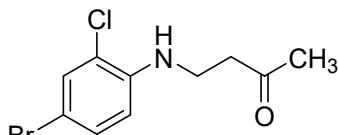


¹H NMR (500 MHz, CDCl₃) δ 7.39 (dd, *J* = 8.8, 1.4 Hz, 2H), 6.53 (d, *J* = 8.7 Hz, 2H), 4.63 (s, 1H), 3.44 (dd, *J* = 8.6, 3.3 Hz, 2H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.17 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 207.6, 150.9, 133.8, 120.5, 112.3, 98.9, 42.2, 37.5, 30.4. Known compound.²



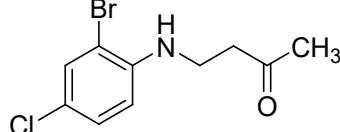
Methyl 4-((3-oxobutyl)amino)benzoate **3k**

¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 8.7 Hz, 2H), 4.54 (s, 1H), 3.83 (s, 3H), 3.44 (t, *J* = 6.0 Hz, 2H), 2.74 (t, *J* = 6.0 Hz, 2H), 2.15 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 207.7, 167.3, 151.5, 131.6, 118.5, 111.5, 51.6, 42.4, 37.7, 30.3. Known compound.²



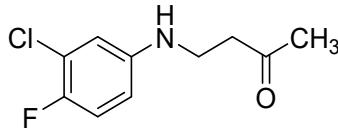
4-((4-Bromo-2-chlorophenyl)amino)butan-2-one **3l**

¹H NMR (500 MHz, CDCl₃) δ 7.29 (s, 1H), 7.15 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.46 (d, *J* = 8.7 Hz, 1H), 4.54 (s, 1H), 3.34 (t, *J* = 6.3 Hz, 2H), 2.69 (t, *J* = 6.3 Hz, 2H), 2.11 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 207.0, 142.7, 131.2, 130.4, 119.8, 112.0, 107.5, 42.1, 37.9, 30.1. Known compound.²



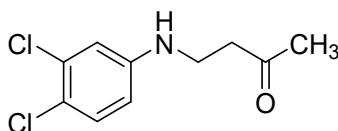
4-((2-Bromo-4-chlorophenyl)amino)butan-2-one **3m**

¹H NMR (500 MHz, CDCl₃) δ 7.40 (s, 1H), 7.13 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.54 (t, *J* = 7.1 Hz, 1H), 4.56 (s, 1H), 3.43 (t, *J* = 6.3 Hz, 2H), 2.77 (t, *J* = 6.3 Hz, 2H), 2.18 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 207.3, 143.5, 132.0, 128.4, 121.8, 111.6, 110.0, 42.4, 38.4, 30.5. Known compound.²



4-((3-Chloro-4-fluorophenyl)amino)butan-2-one **3n**

¹H NMR (500 MHz, CDCl₃) δ 6.89 (t, *J* = 8.9 Hz, 1H), 6.55 (dd, *J* = 6.1, 2.9 Hz, 1H), 6.38 (ddd, *J* = 8.9, 3.6, 3.0 Hz, 1H), 3.93 (s, 1H), 3.30 (t, *J* = 6.0 Hz, 2H), 2.70 (t, *J* = 6.0 Hz, 2H), 2.14 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 208.2, 151.29 (d, *J* = 237.8 Hz), 145.0 (d, *J* = 1.8 Hz), 117.1 (d, *J* = 22.0 Hz), 114.1, 112.7 (d, *J* = 6.3 Hz), 42.5, 39.0, 30.6. Known compound.²



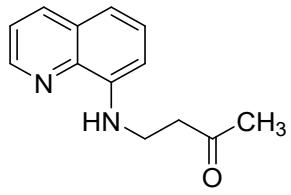
4-((3,4-Dichlorophenyl)amino)butan-2-one **3o**

¹H NMR (500 MHz, CDCl₃) δ 7.16 (d, *J* = 8.7 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 6.41 (dd, *J* = 8.7, 2.7 Hz, 1H), 4.12 (s, 1H), 3.35 (t, *J* = 6.0 Hz, 2H), 2.72 (t, *J* = 6.0 Hz, 2H), 2.16 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 207.8, 147.3, 132.9, 130.7, 120.0, 113.9, 112.9, 42.2, 38.3, 30.4. Known compound.²



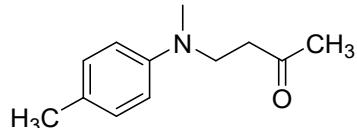
4-((2-Bromo-3-methylphenyl)amino)butan-2-one **3p**

¹H NMR (500 MHz, CDCl₃) δ 7.07 (t, *J* = 7.8 Hz, 1H), 6.61 (dd, *J* = 7.4, 0.6 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 4.68 (s, 1H), 3.46 (t, *J* = 6.4 Hz, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.37 (s, 3H), 2.17 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 207.4, 144.7, 138.6, 127.6, 119.2, 112.8, 108.6, 77.4, 77.1, 76.9, 42.6, 38.5, 30.36, 23.83. Known compound.²



4-(Quinolin-8-ylamino)butan-2-one **3q**

¹H NMR (500 MHz, CDCl₃) δ 8.70 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.05 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.38 (t, *J* = 6.2 Hz, 1H), 7.36 (dd, *J* = 6.6, 2.3 Hz, 1H), 7.06 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.70 (d, *J* = 7.0 Hz, 1H), 3.63 (t, *J* = 6.7 Hz, 2H), 2.90 (t, *J* = 6.7 Hz, 2H), 2.20 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 207.6, 147.0, 144.4, 138.3, 136.1, 128.8, 127.8, 121.5, 114.2, 104.7, 42.9, 38.0, 30.5. Known compound.²



4-(Methyl(p-tolyl)amino)butan-2-one **3r**

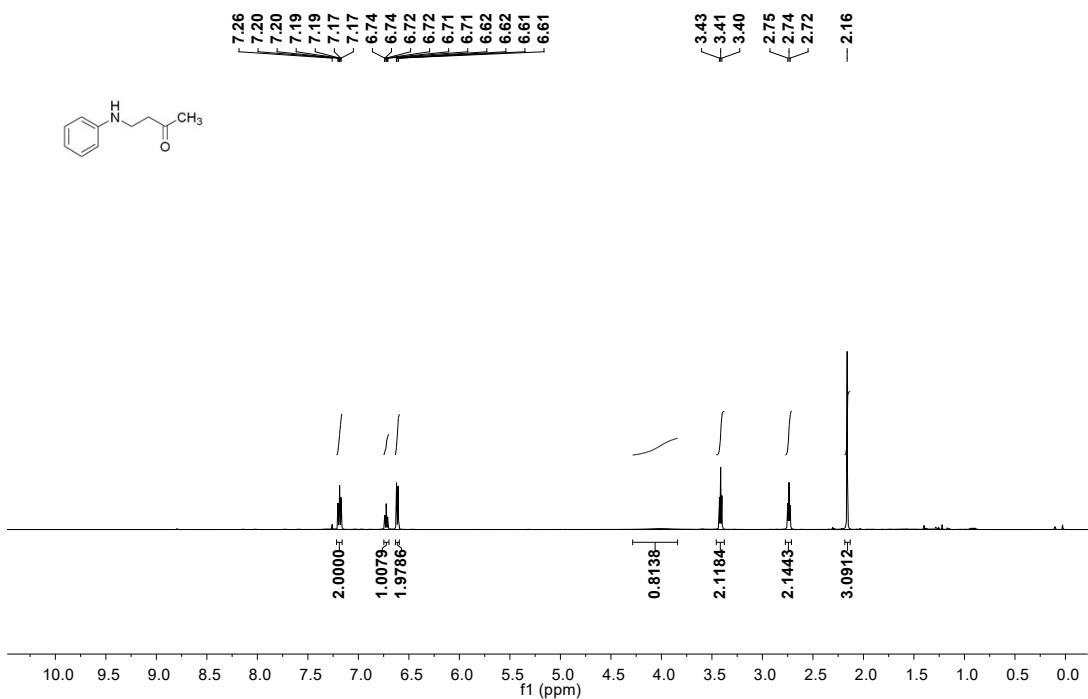
¹H NMR (500 MHz, CDCl₃) δ 7.06 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 3.65 (m, 2H), 2.89 (s, 3H), 2.69 (t, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 2.15 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 208.6, 146.9, 130.2, 130.1, 126.5, 113.4, 112.9, 48.0, 40.4, 39.0, 31.0, 20.6. Known compound.²

References

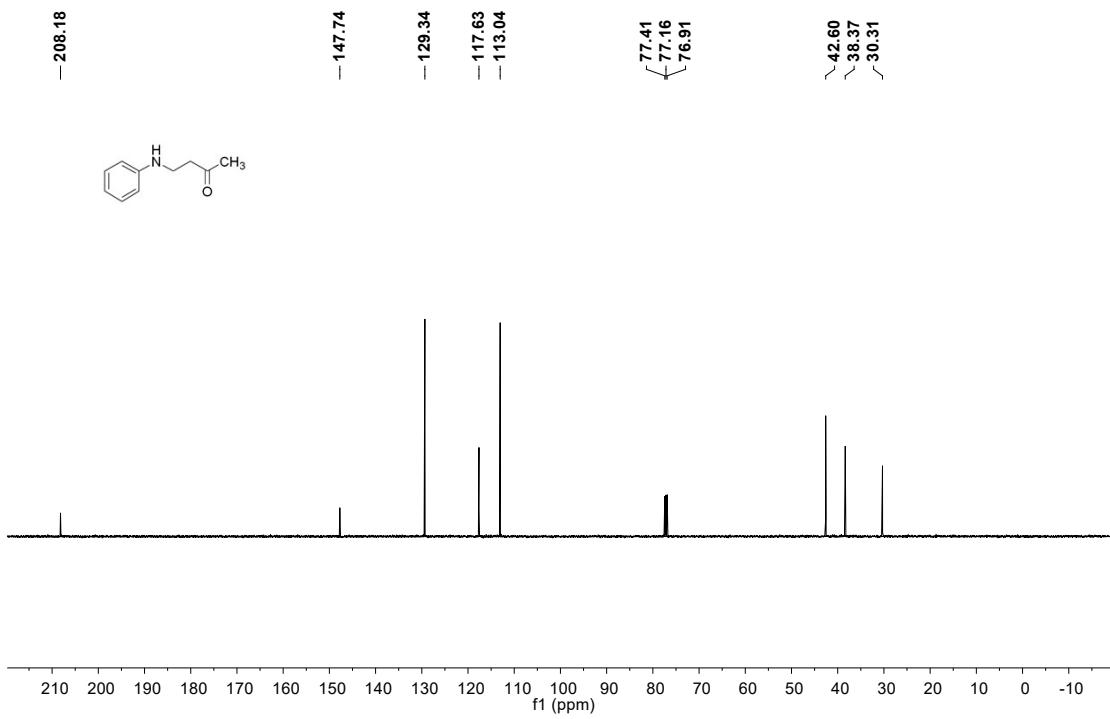
1. G. S. Kumar, D. Singh, M. Kumar and M. Kapur, *J Org Chem* 2018, **83**, 3941-3951.
2. C. Miao, L. Jiang, L. Ren, Q. Xue, F. Yan, W. Shi, X. Li, J. Sheng and S. Kai, *Tetrahedron* 2019, **75**, 2215-2228.

4. ¹H, ¹³C and ¹⁹F NMR Spectras

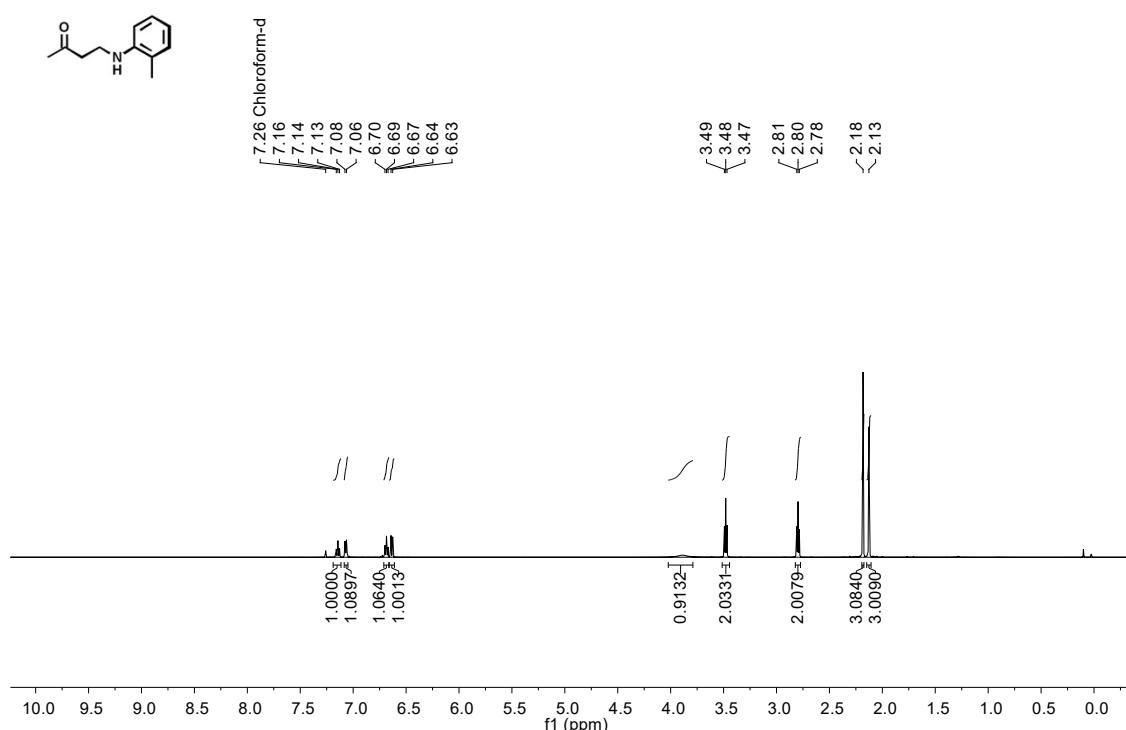
Compound 3a-1H NMR(500 MHz,CDCl₃)



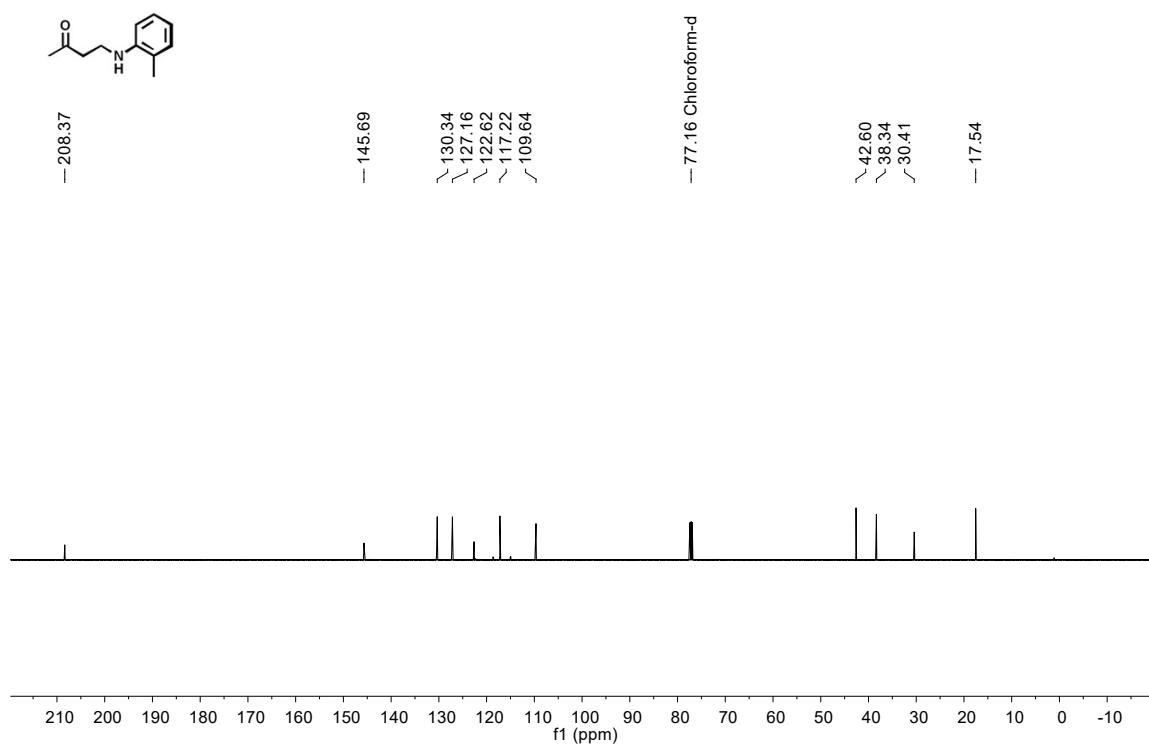
Compound 3a-13C{1H} NMR(126MHz,CDCl₃)



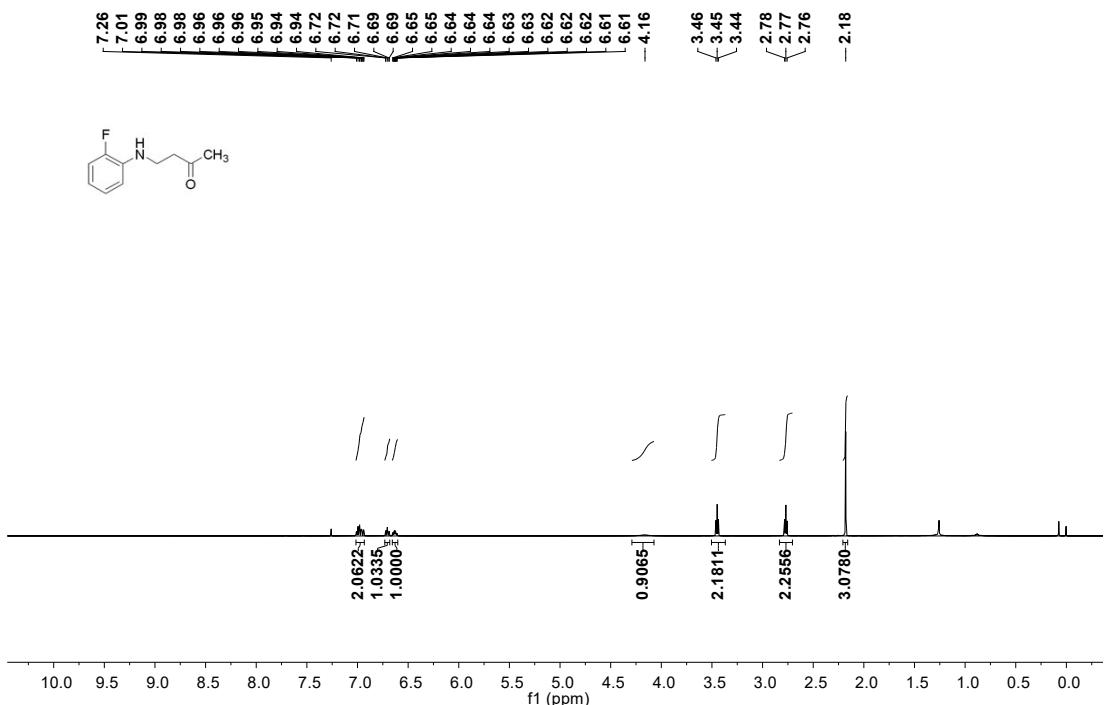
Compound 3b-1H NMR(500 MHz,CDCl₃)



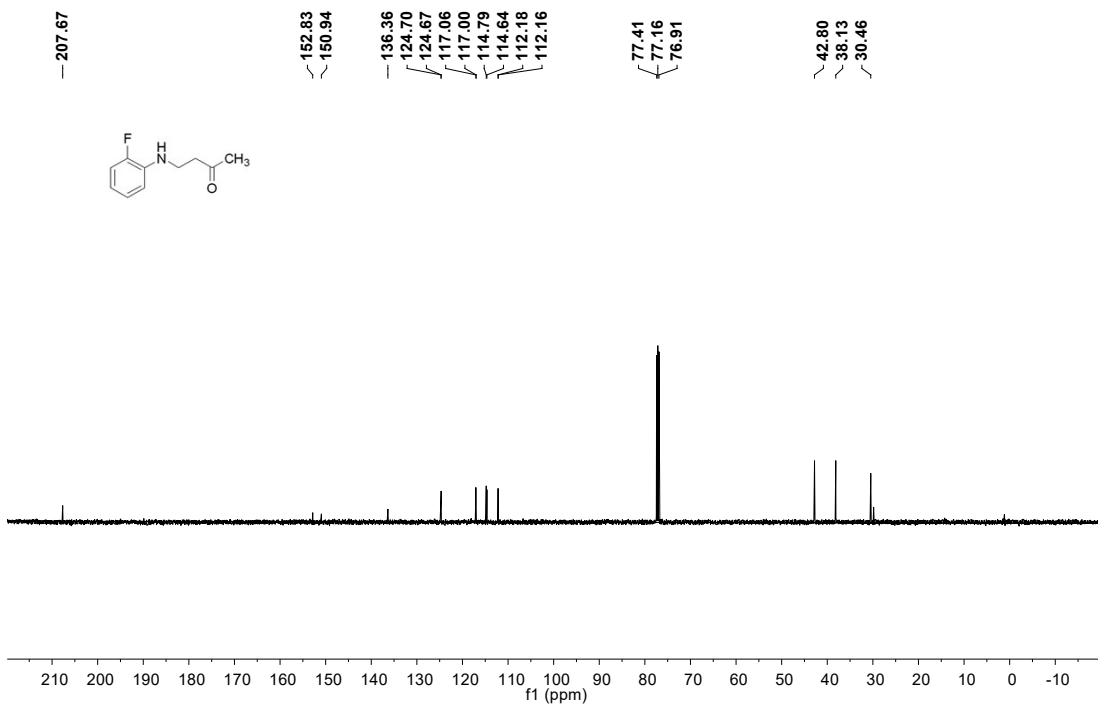
Compound 3b-¹³C{¹H} NMR(126MHz,CDCl₃)



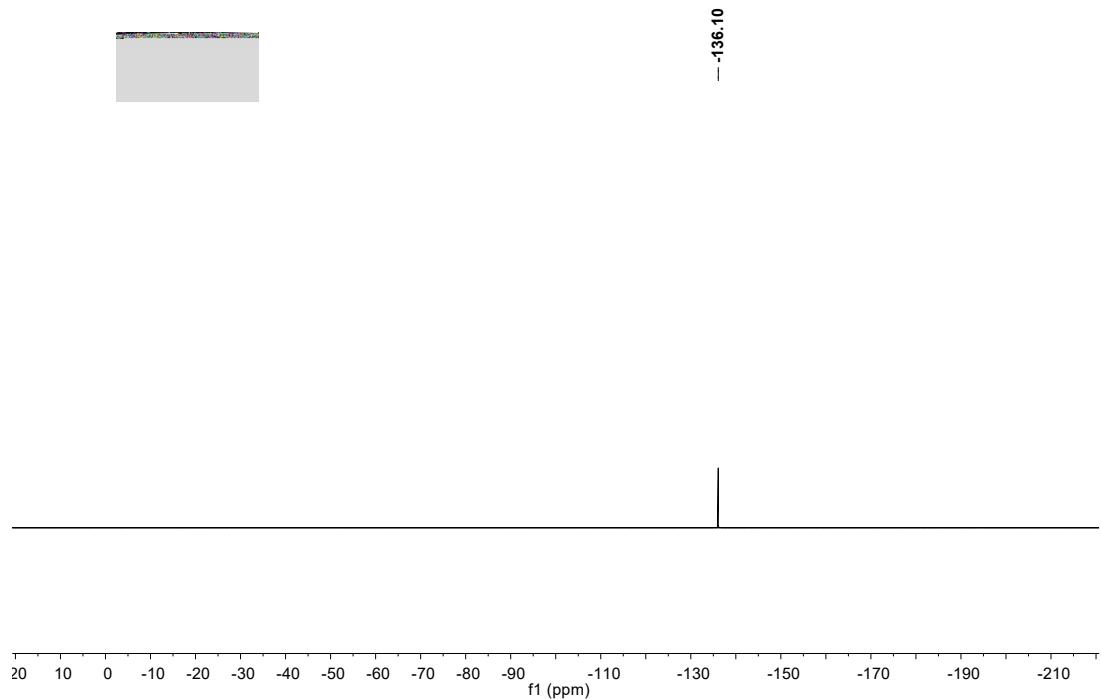
Compound 3c-¹H NMR(500 MHz, CDCl₃)



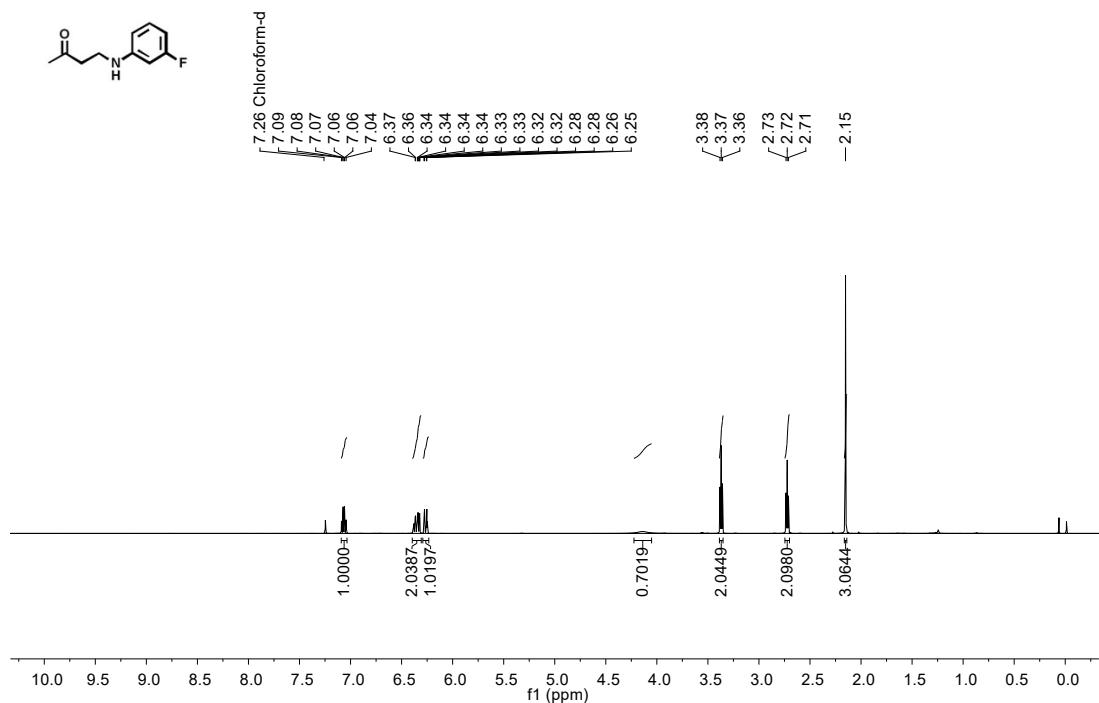
Compound 3c-¹³C{¹H} NMR(126MHz,CDCl₃)



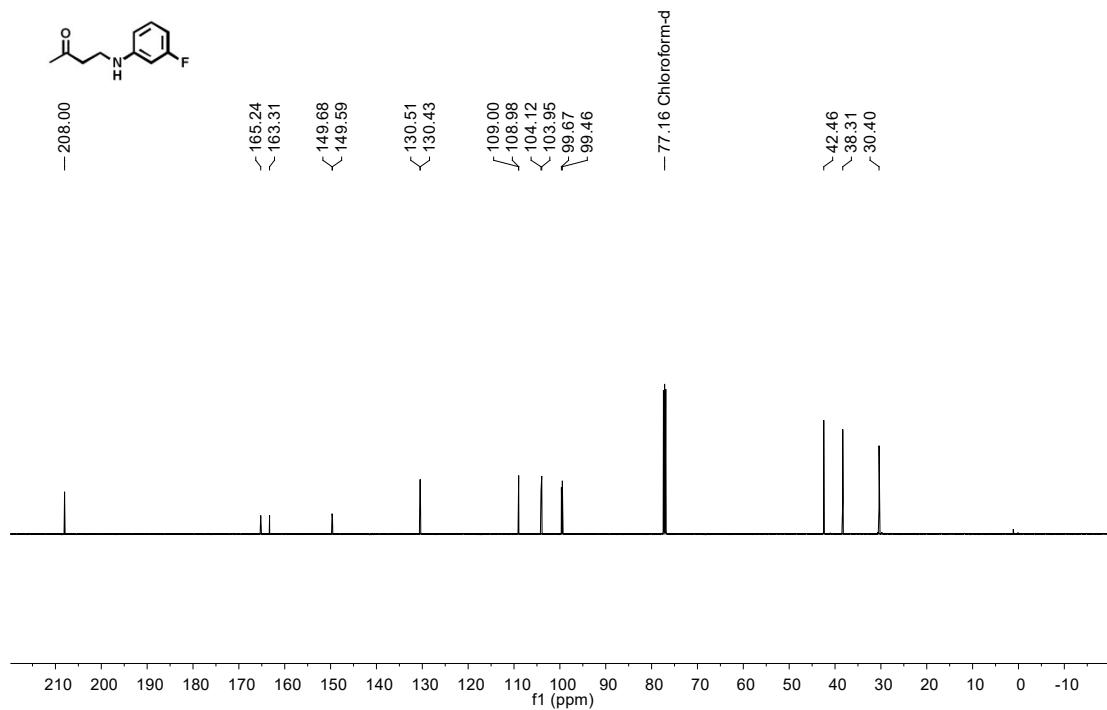
Compound 3c-19F NMR(471 MHz,CDCl₃)



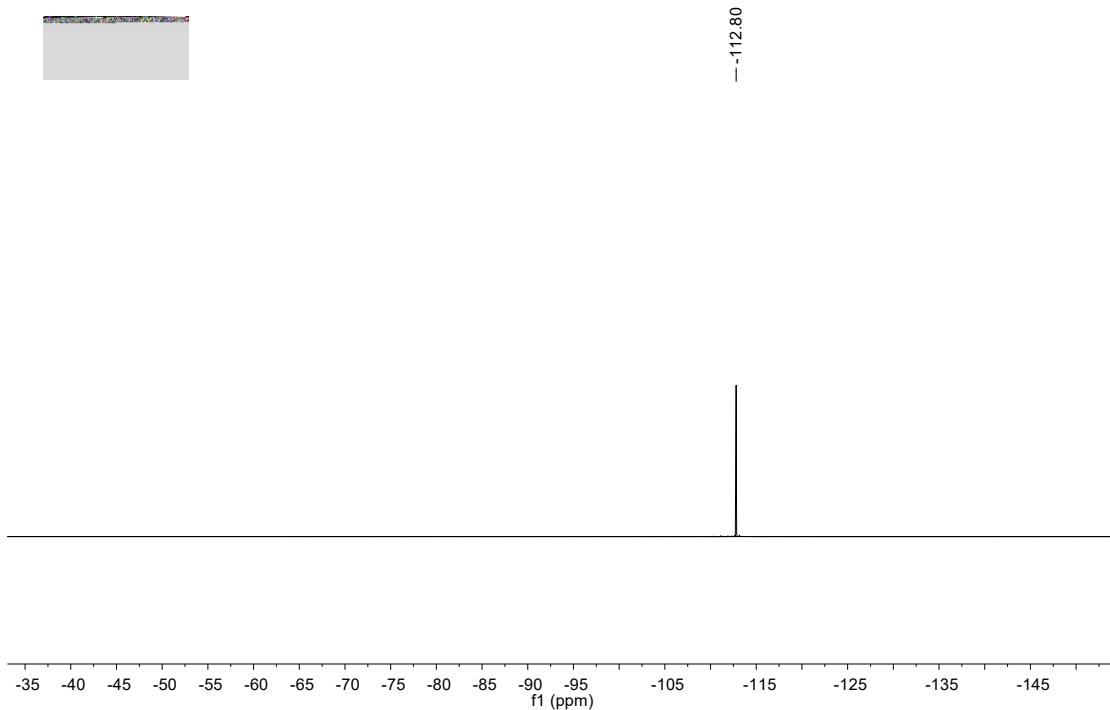
Compound 3d-¹H NMR(500 MHz,CDCl₃)



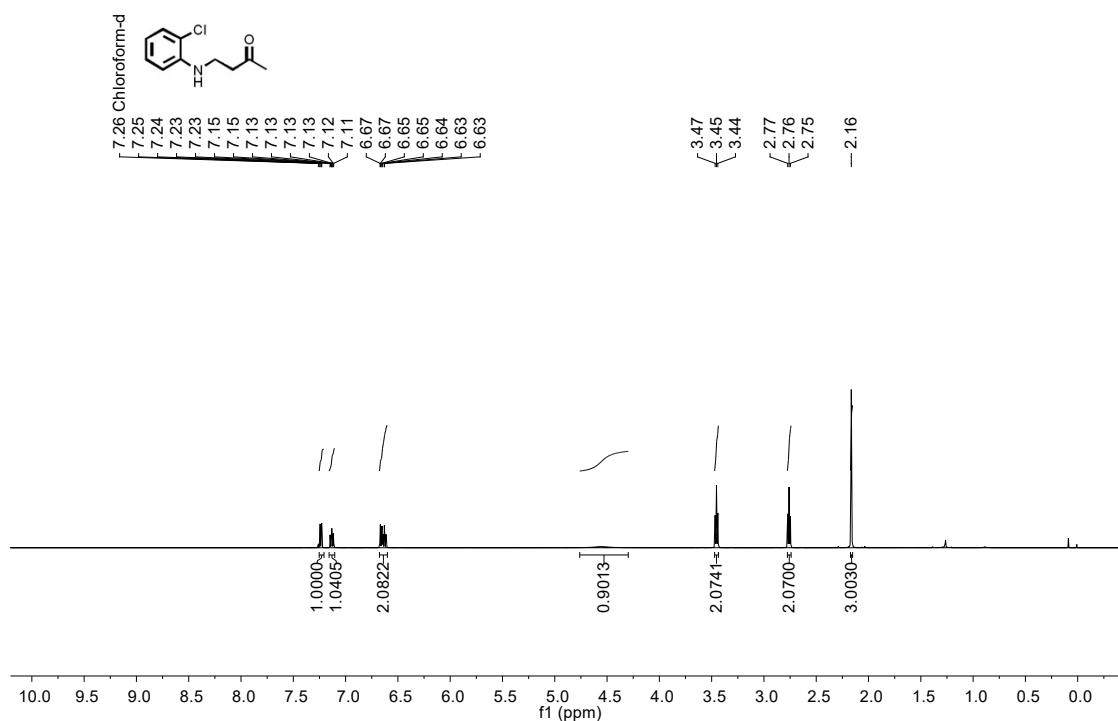
Compound 3d-¹³C{¹H} NMR(126MHz,CDCl₃)



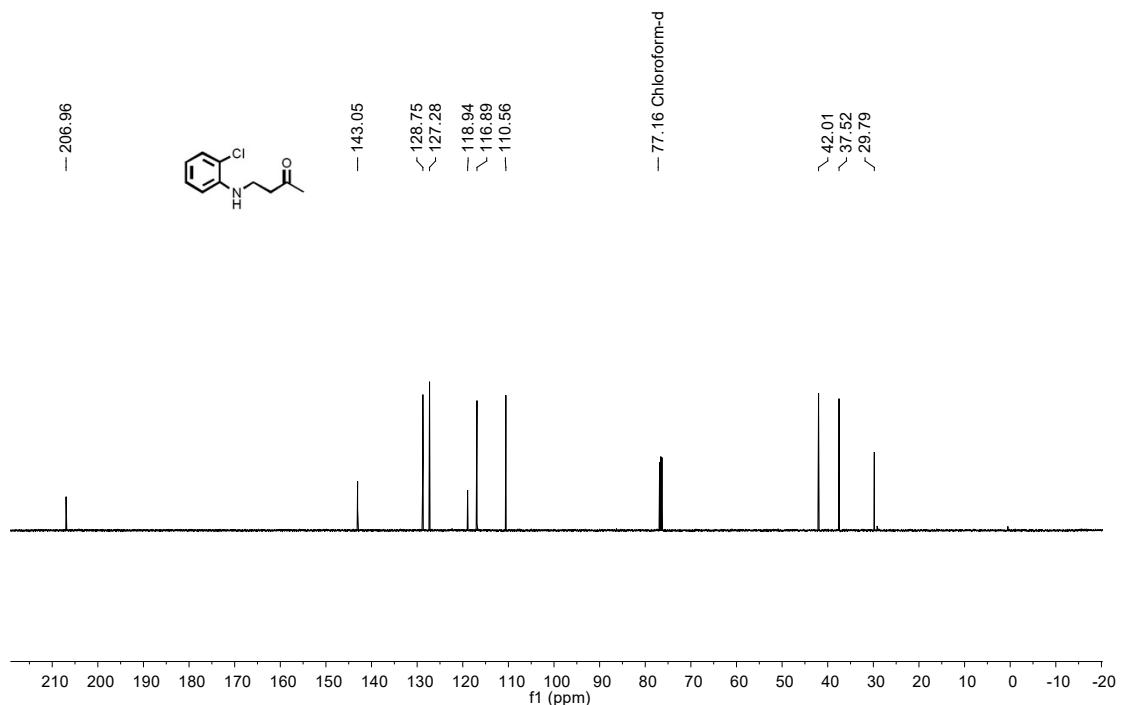
Compound 3d-¹⁹F NMR(471 MHz,CDCl₃)



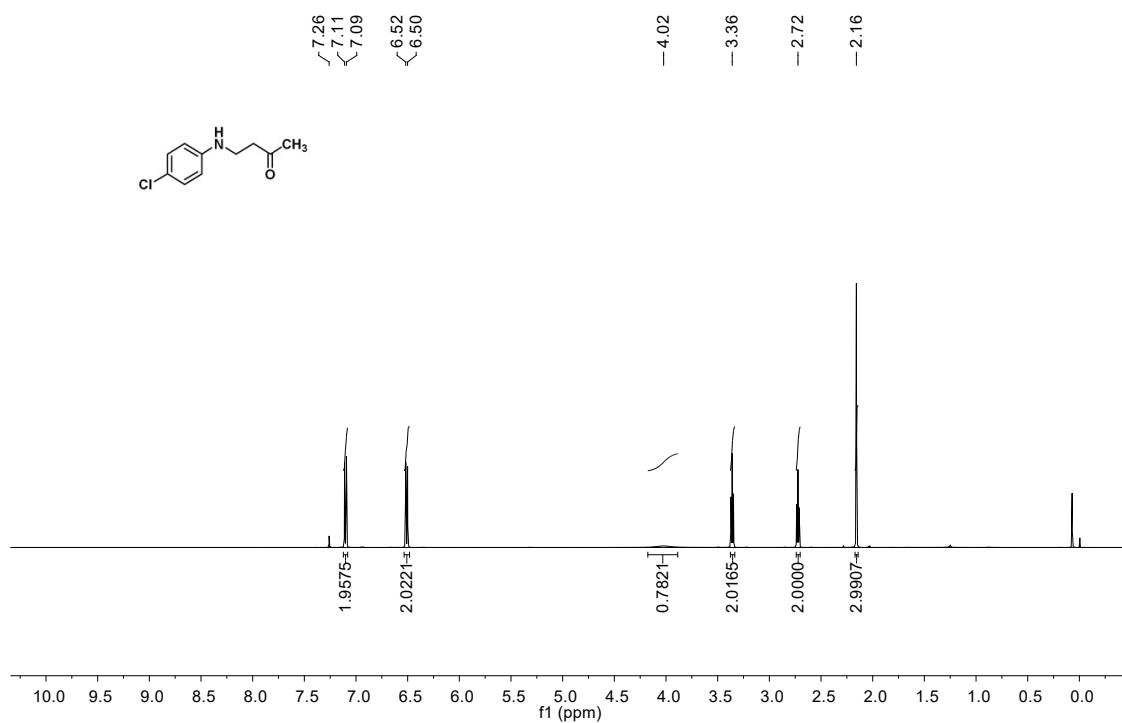
Compound 3e-1H NMR(500 MHz,CDCl₃)



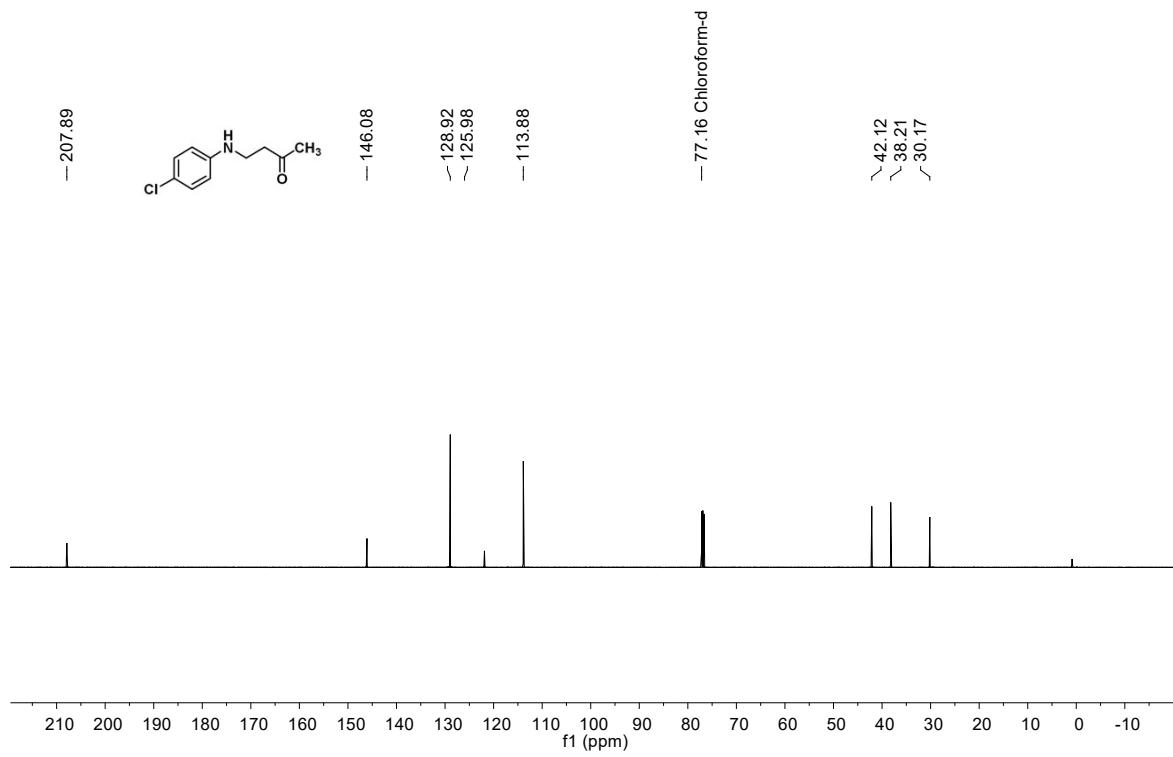
Compound 3e-13C{1H} NMR(126MHz,CDCl₃)



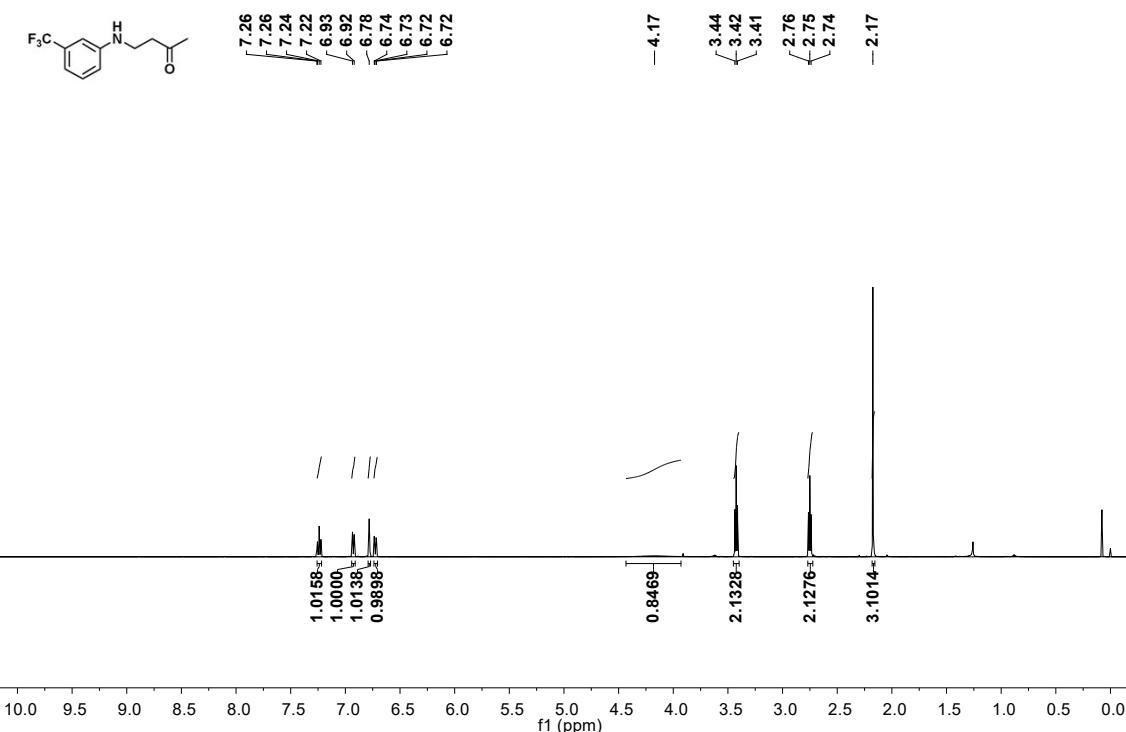
Compound 3f-1H NMR(500 MHz,CDCl₃)



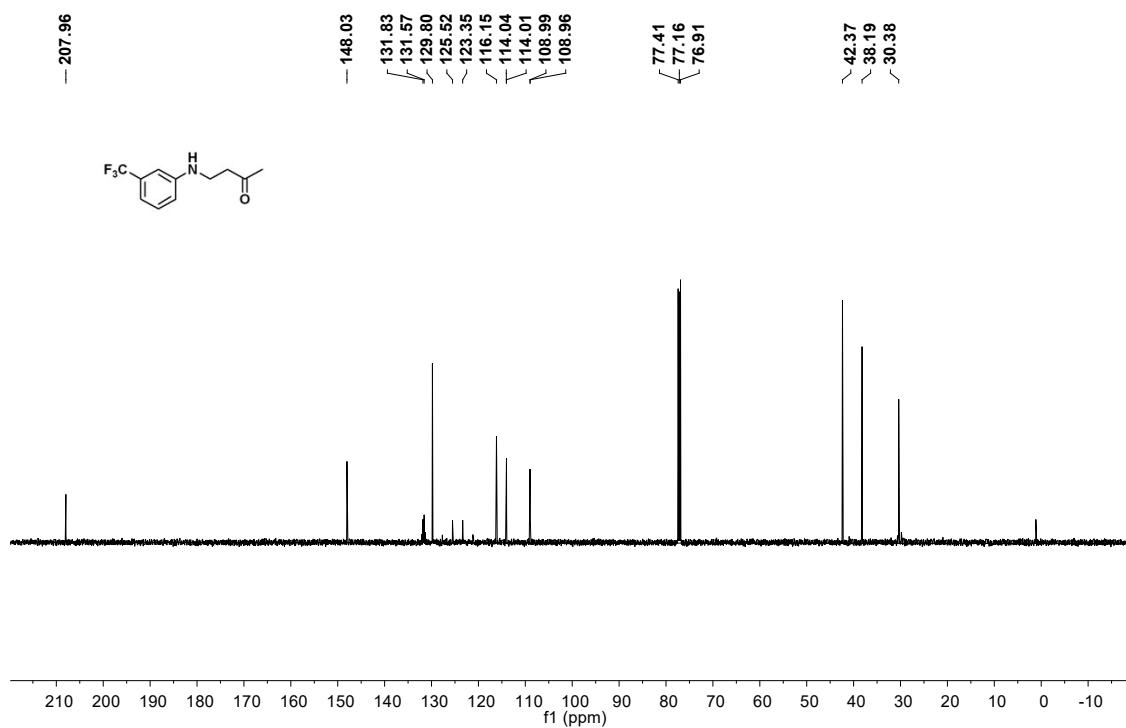
Compound 3f-13C{1H} NMR(126MHz,CDCl₃)



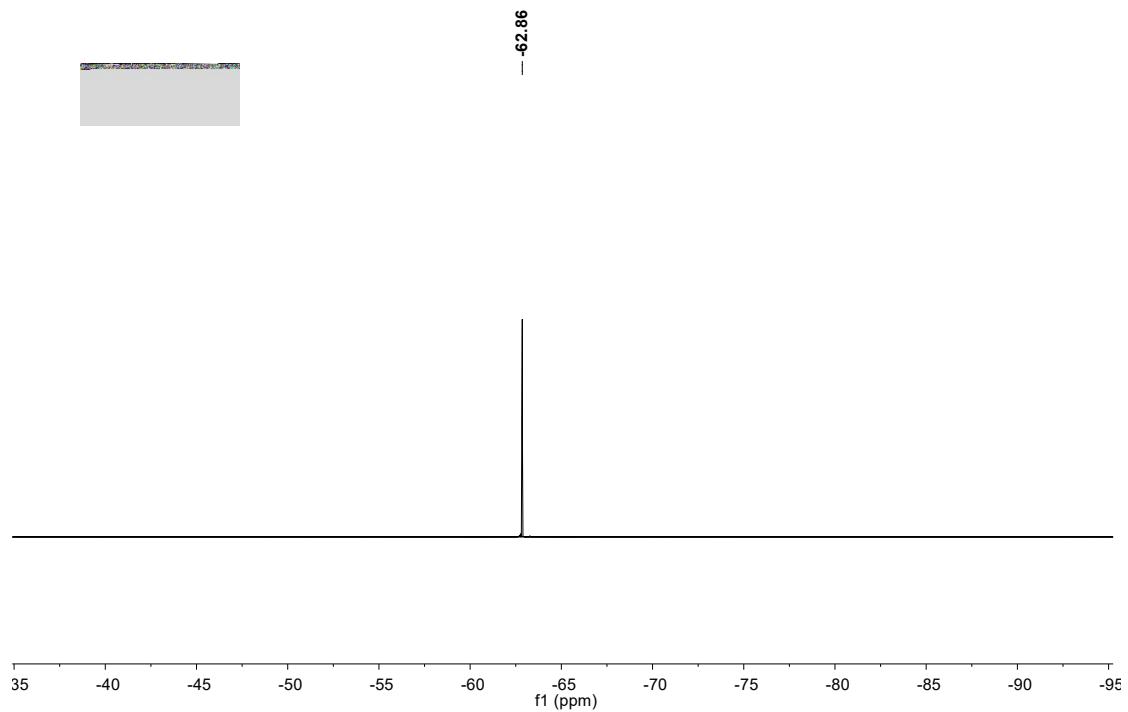
Compound 3g-¹H NMR(500 MHz,CDCl₃)



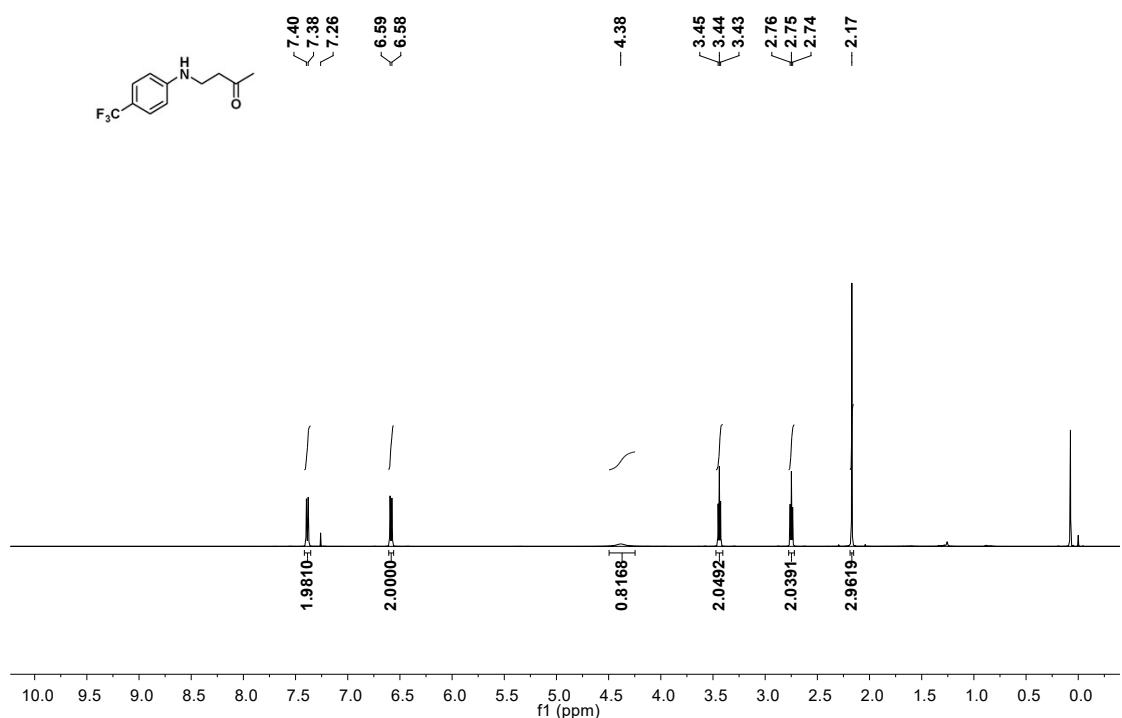
Compound 3g- $^{13}\text{C}\{^1\text{H}\}$ NMR(126MHz,CDCl₃)



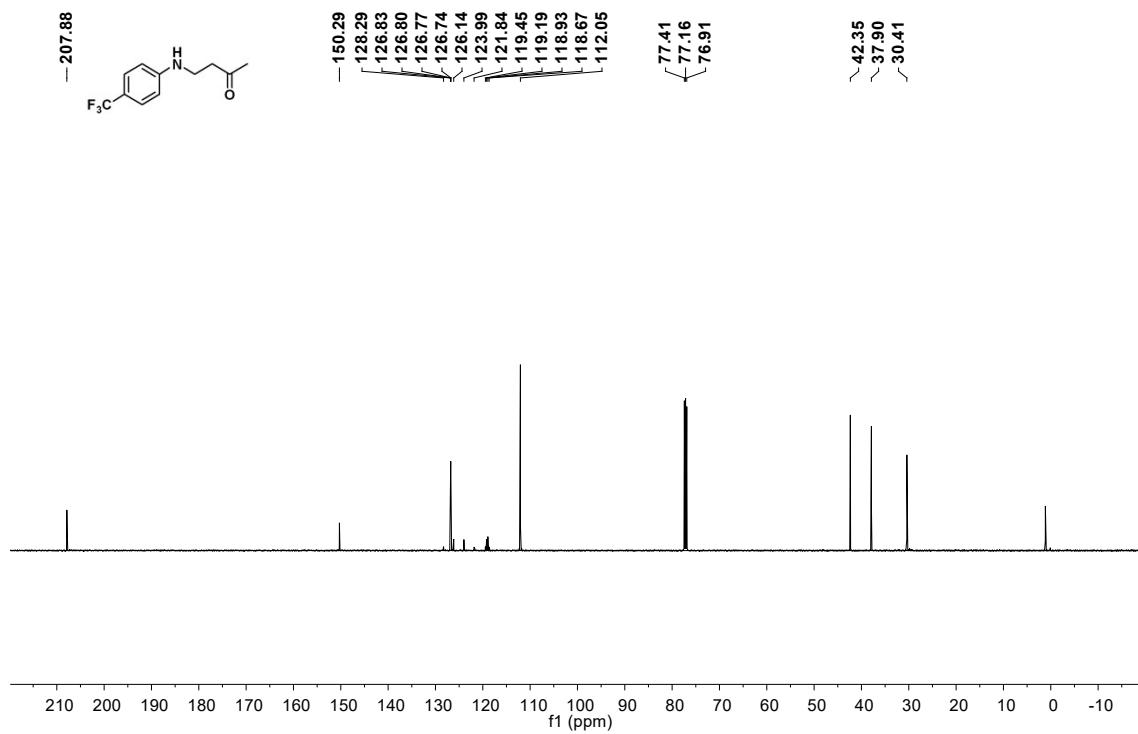
Compound 3g-19F NMR(471 MHz,CDCl₃)



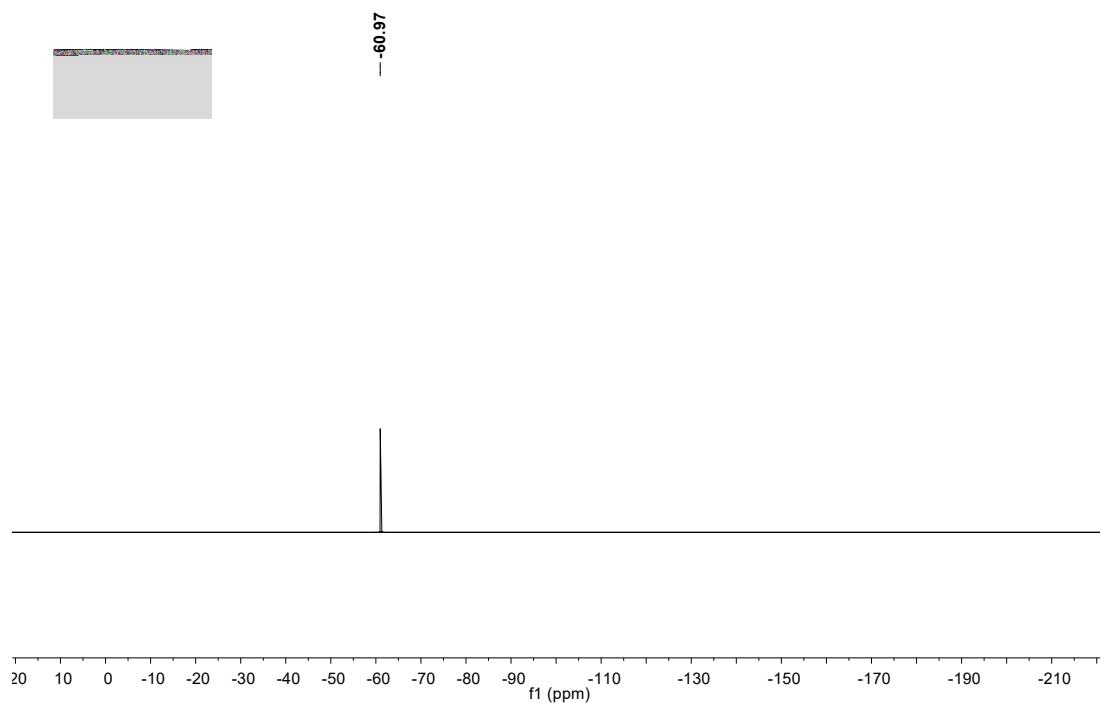
Compound 3h-1H NMR(500 MHz,CDCl₃)



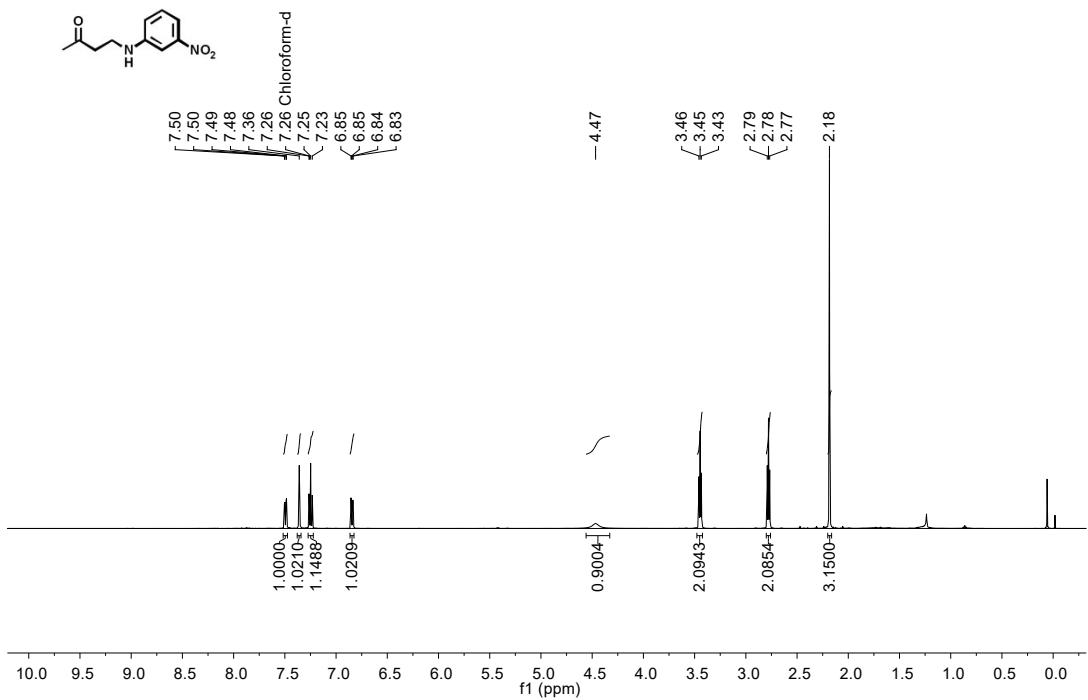
Compound 3h-13C{1H} NMR(126MHz,CDCl₃)



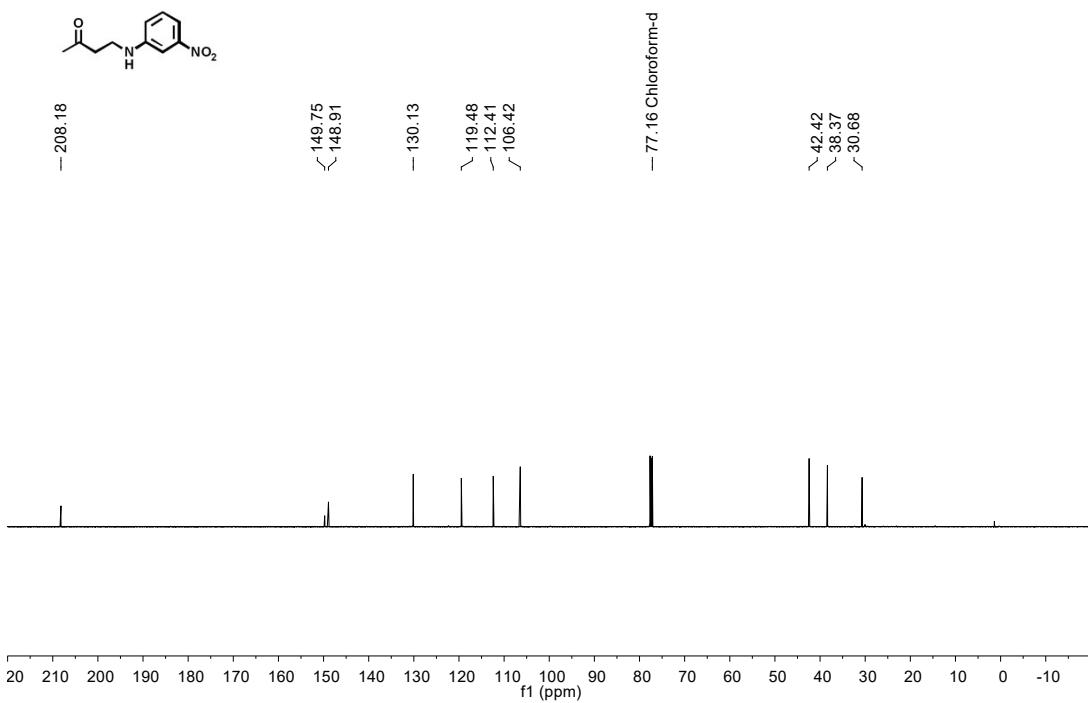
Compound 3h-19F NMR(471 MHz,CDCl₃)



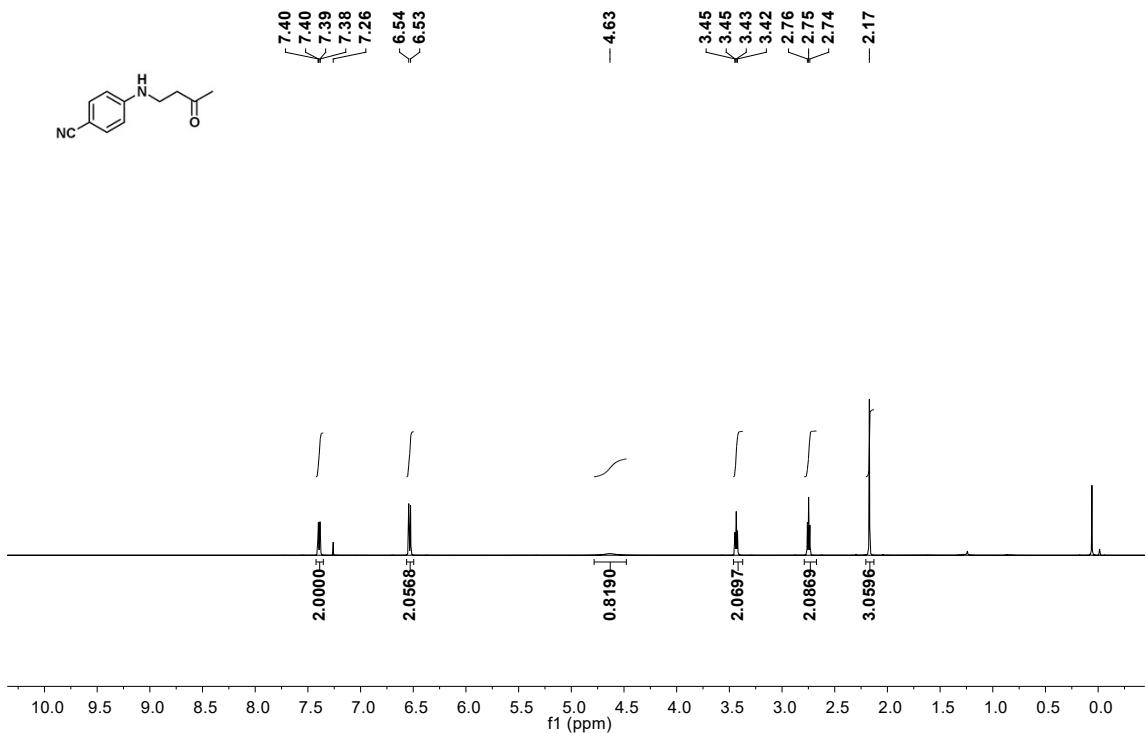
Compound 3i-¹H NMR(500 MHz,CDCl₃)



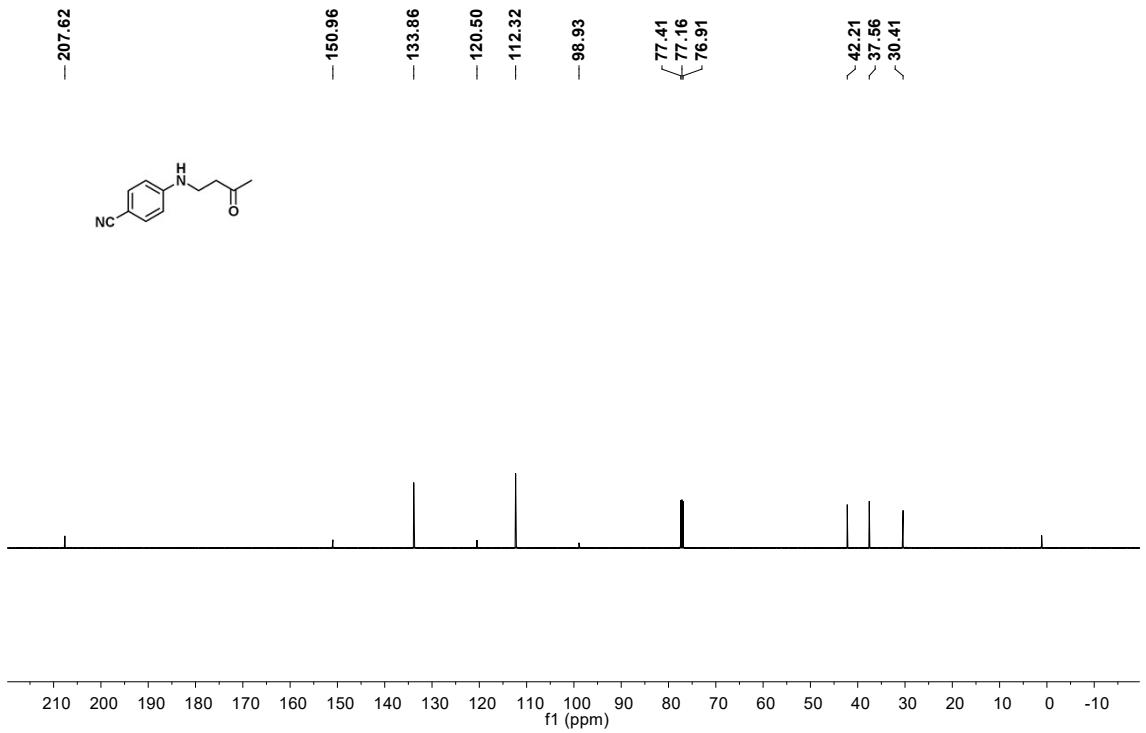
Compound 3i-13C{1H} NMR(126MHz,CDCl₃)



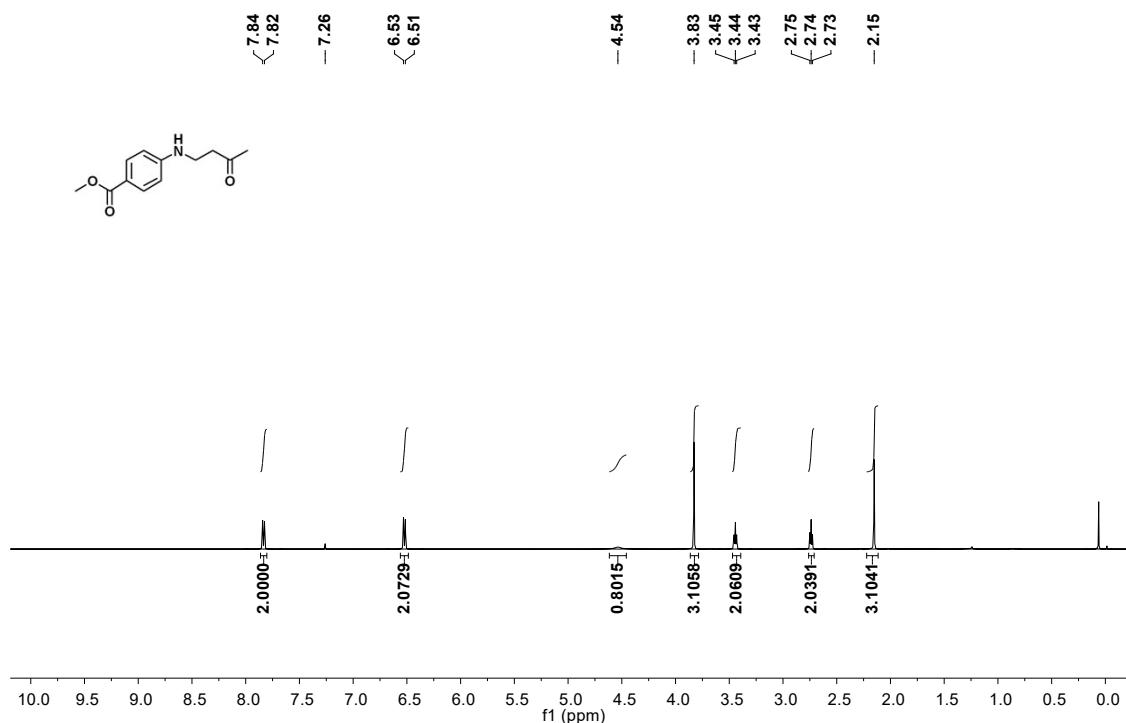
Compound 3j-1H NMR(500 MHz,CDCl₃)



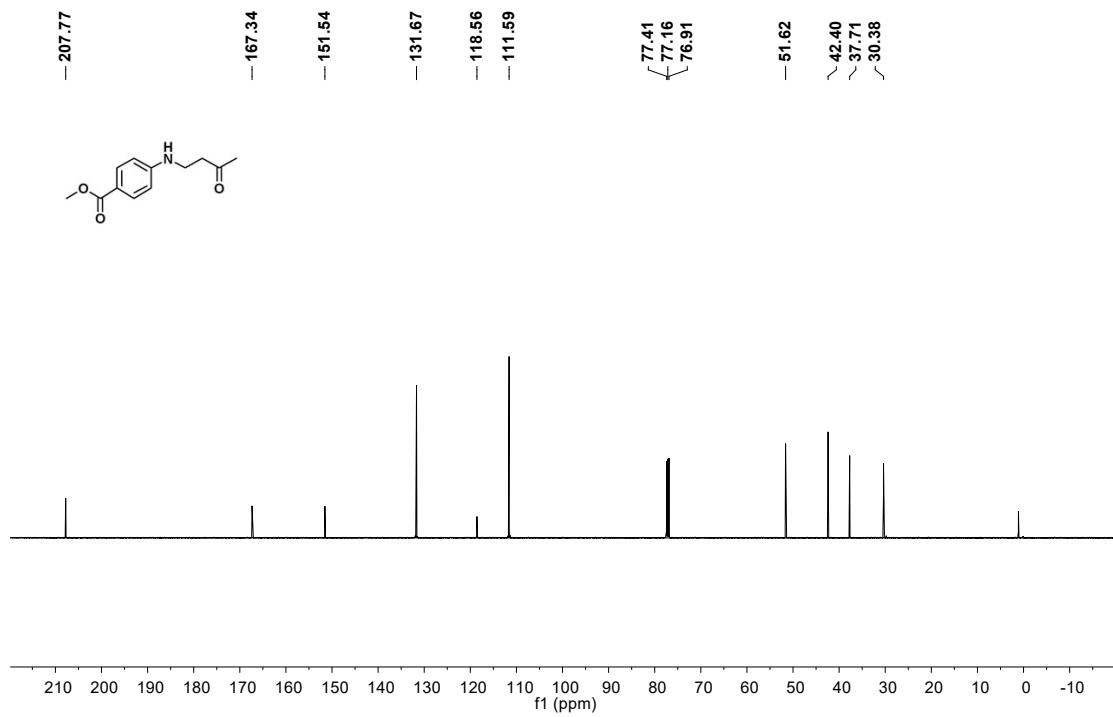
Compound 3j-13C{1H} NMR(126MHz,CDCl₃)



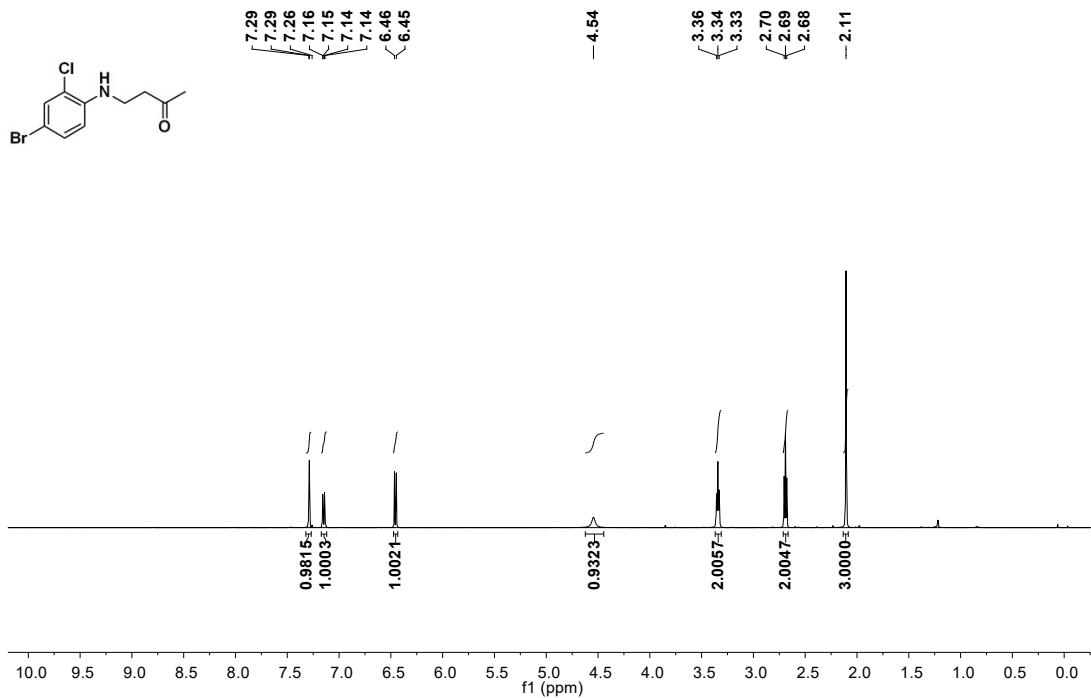
Compound 3k-1H NMR(500 MHz,CDCl₃)



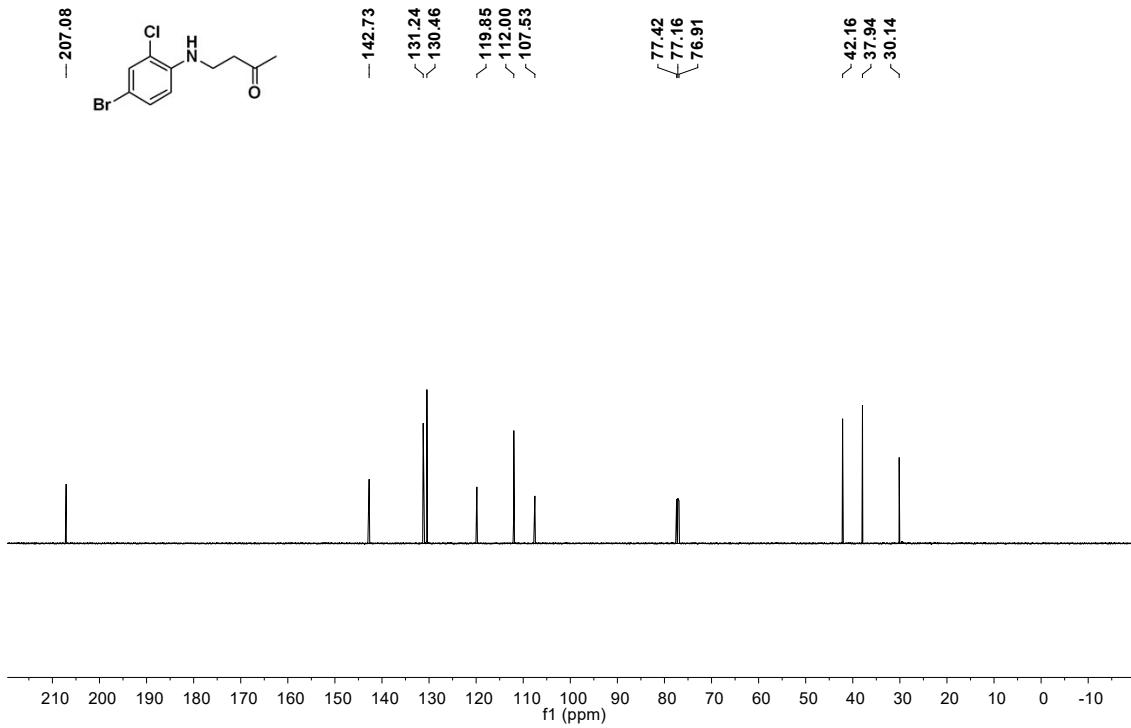
Compound 3k-13C{1H} NMR(126 MHz,CDCl₃)



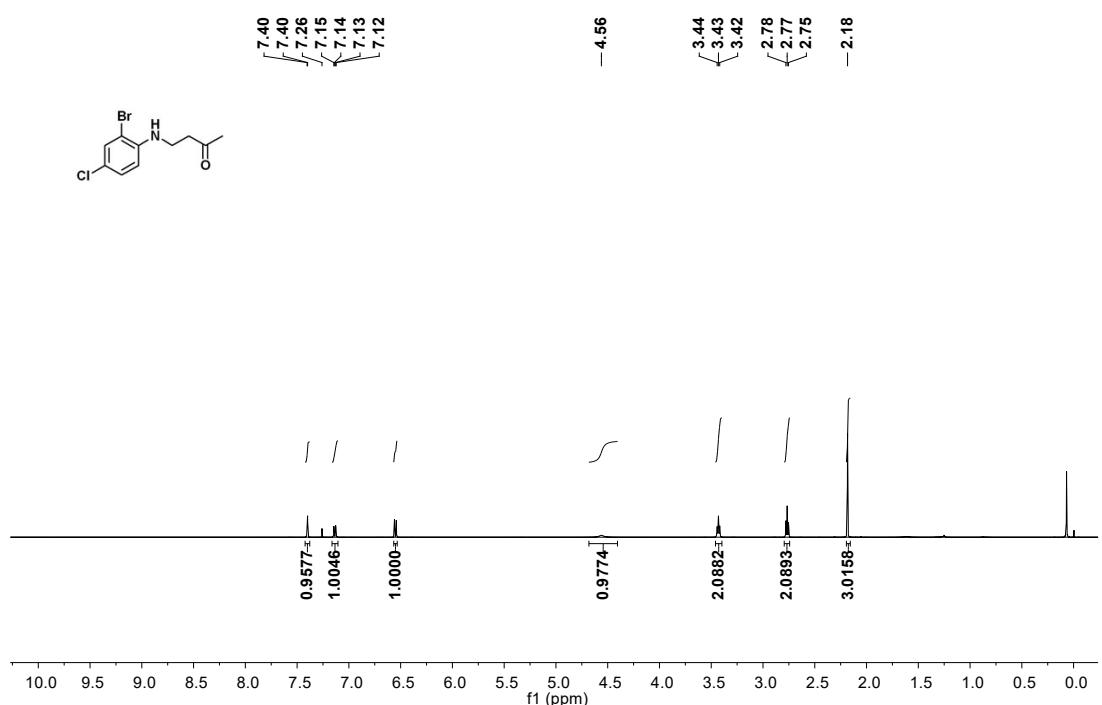
Compound 3l-1H NMR(500 MHz,CDCl₃)



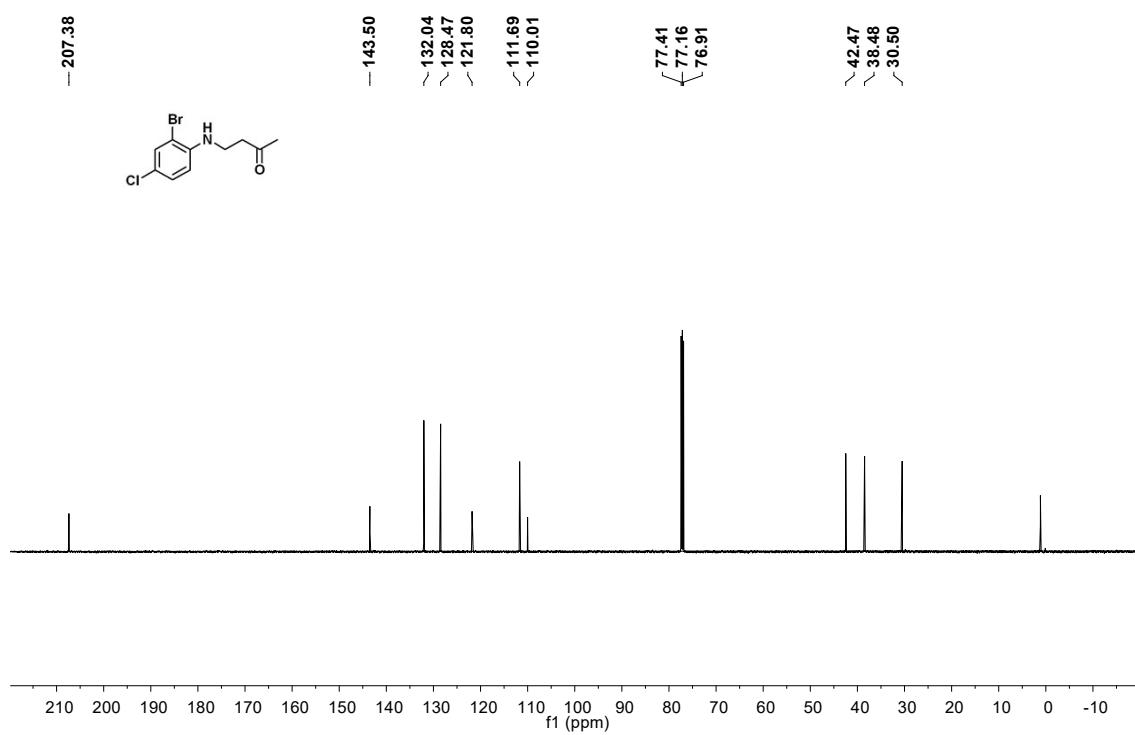
Compound 3l-13C{1H} NMR(126MHz,CDCl₃)



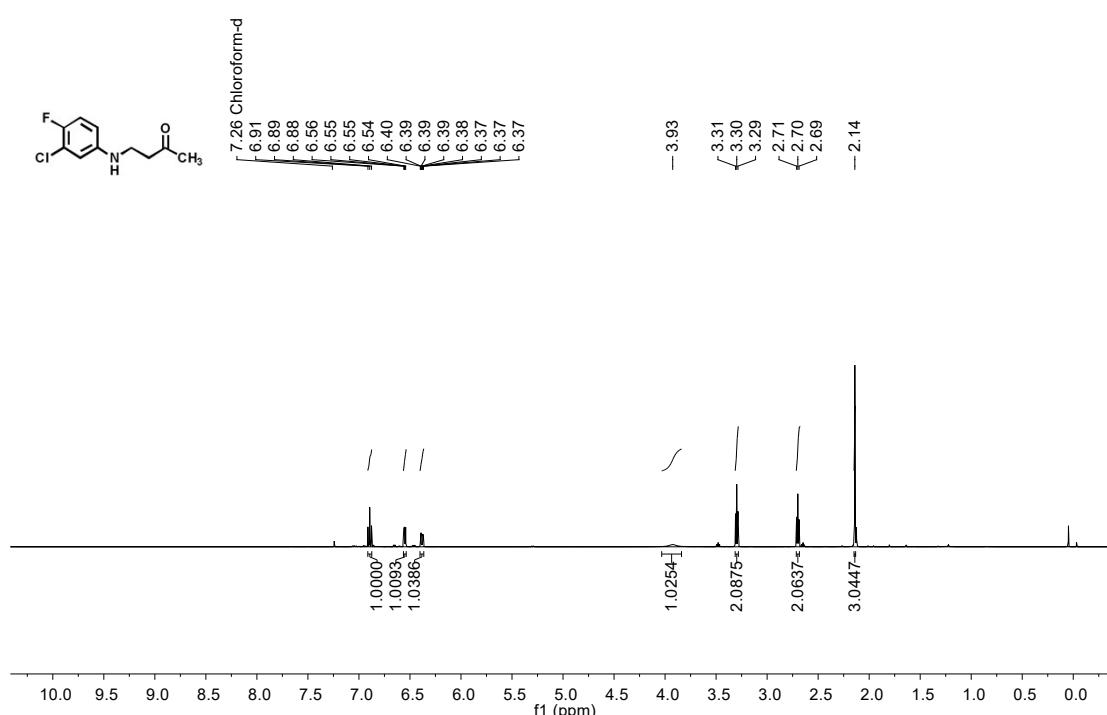
Compound 3m- ^1H NMR(500 MHz,CDCl₃)



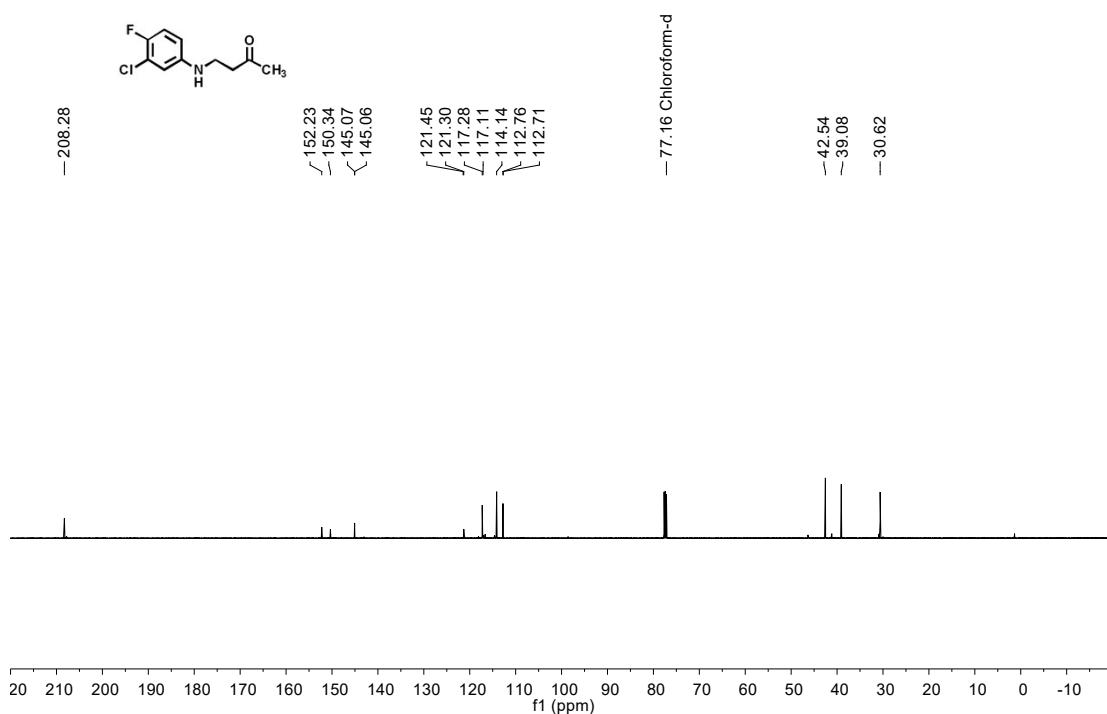
Compound 3m- $^{13}\text{C}\{^1\text{H}\}$ NMR(124 MHz,CDCl₃)



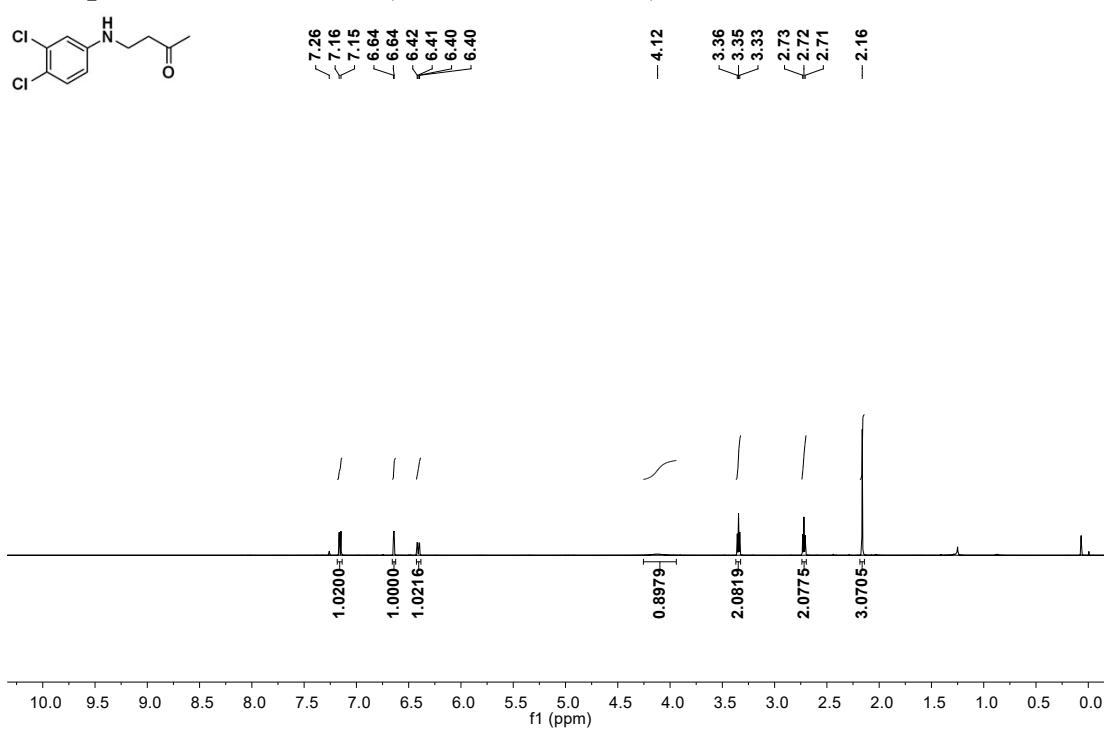
Compound 3n-1H NMR(500MHz,CDCl₃)



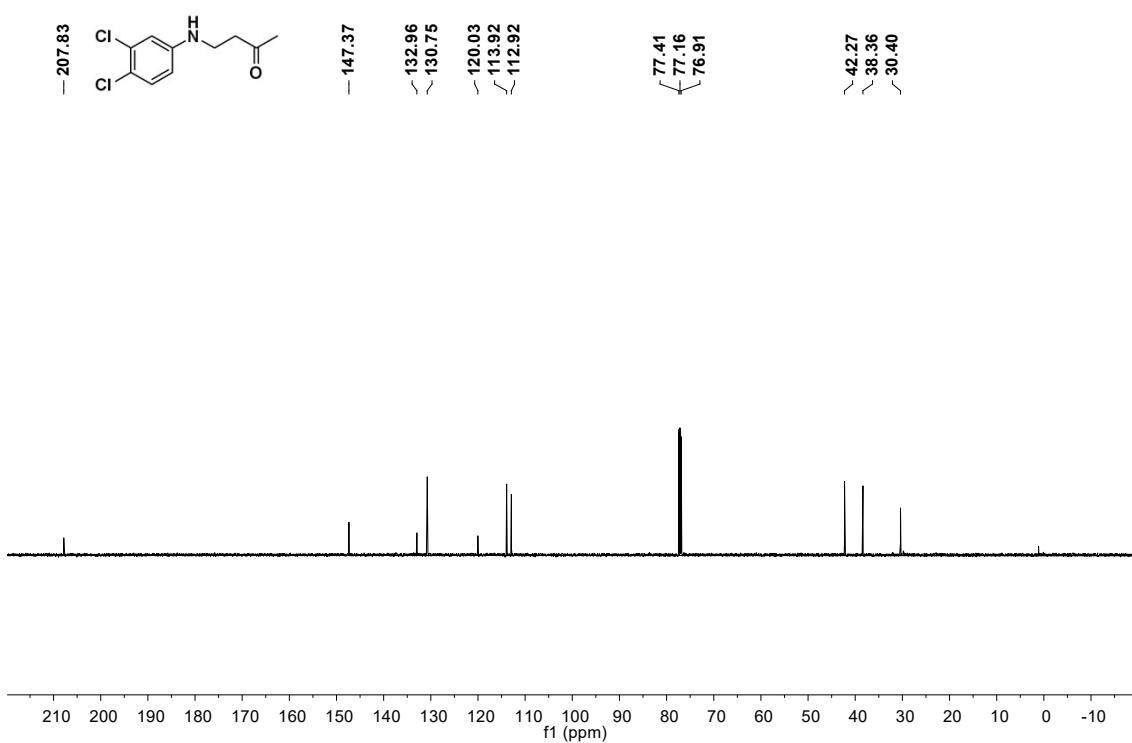
Compound 3n-13C{1H} NMR(126MHz,CDCl₃)



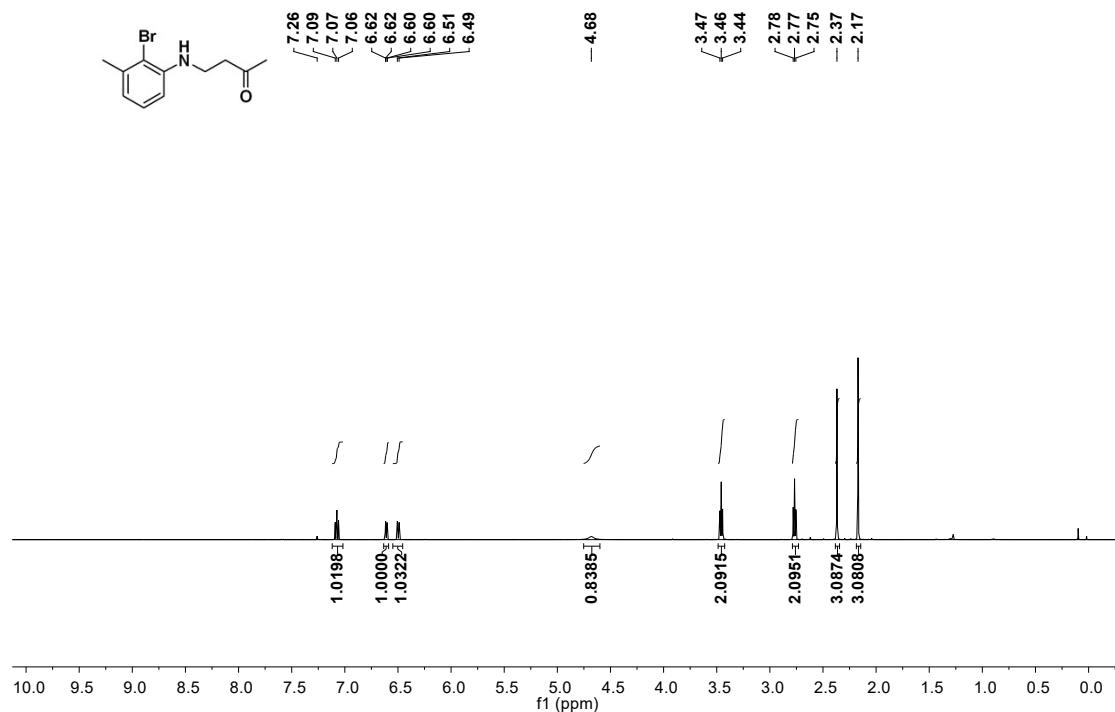
Compound 3o-1H NMR(500 MHz,CDCl₃)



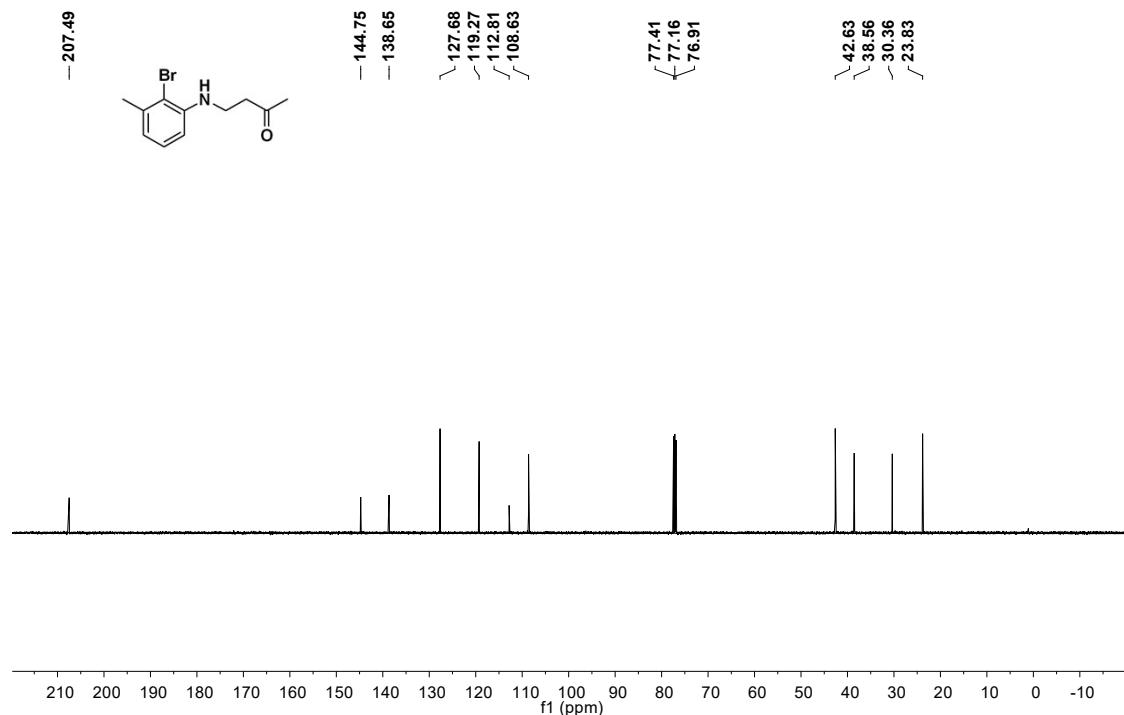
Compound 3o-13C{1H} NMR(126MHz,CDCl₃)



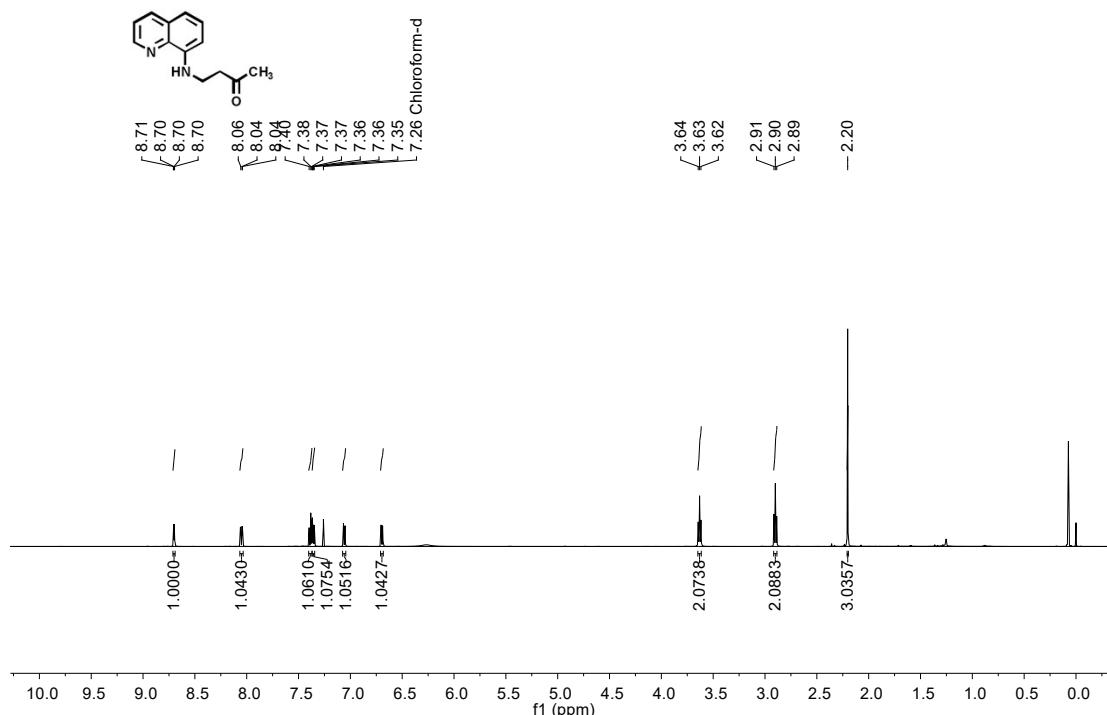
Compound 3p-¹H NMR(500 MHz,CDCl₃)



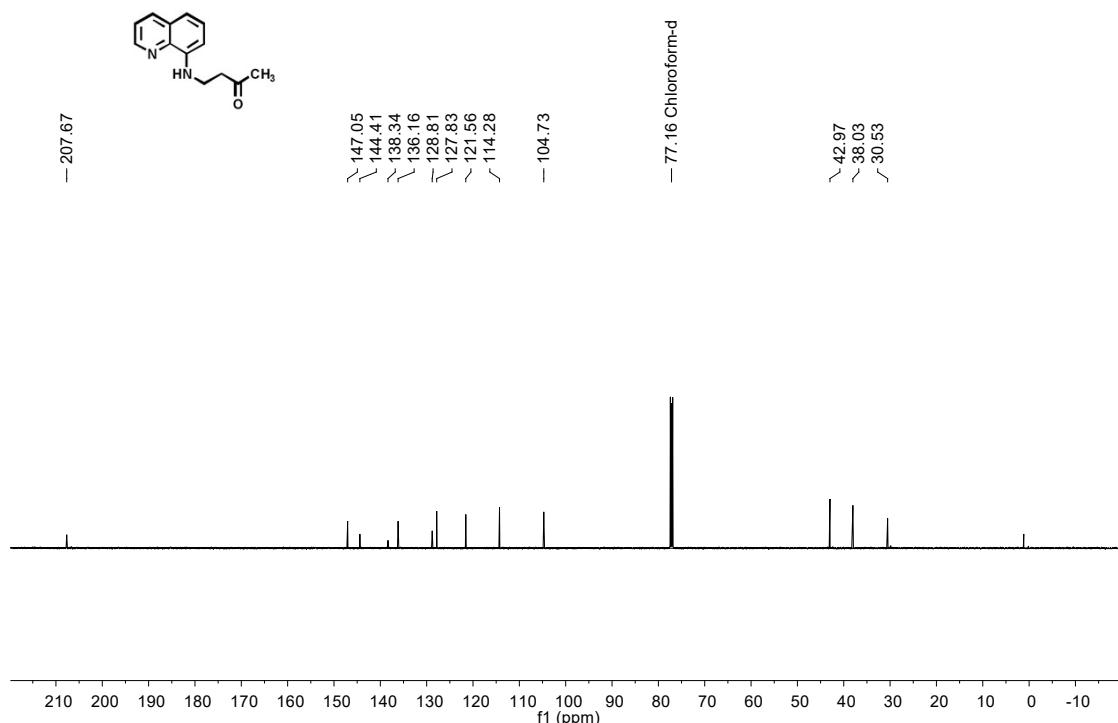
Compound 3p-¹³C{¹H} NMR(126MHz,CDCl₃)



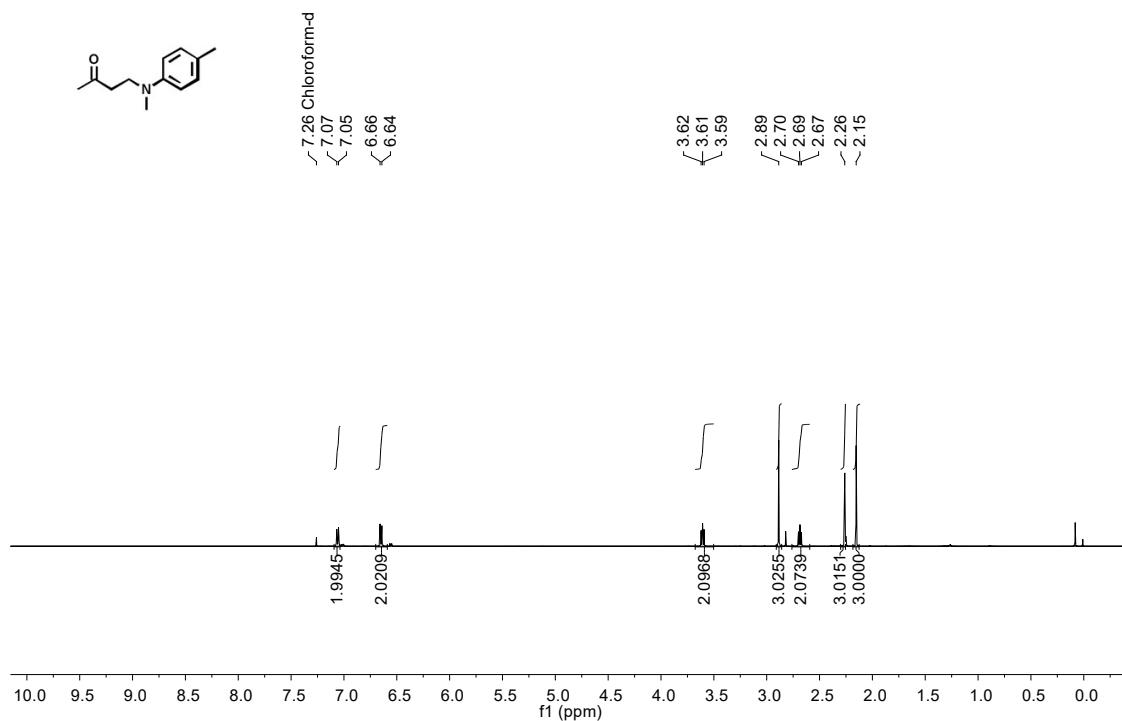
Compound 3q-¹H NMR(500MHz,CDCl₃)



Compound 3q-¹³C{¹H} NMR(126MHz,CDCl₃)



Compound 3r-1H NMR(500MHz,CDCl₃)



Compound 3r-¹³C{¹H} NMR(126MHz,CDCl₃)

