

Supporting Information

A highly efficient heterogeneous copper-catalyzed chlorodeboration of arylboronic acids leading to chlorinated arenes

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The spectral data of compounds 2a-2x and compounds 3a-3i:

3-Nitrochlorobenzene 2a.¹ Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.23 (t, *J* = 1.8 Hz, 1H), 8.14 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 148.8, 135.4, 134.7, 130.4, 123.9, 121.7.

4-Biphenyl chloride 2b.¹ White solid; m.p.: 76-77 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.54 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 140.0, 139.7, 133.4, 128.9, 128.4, 127.6, 127.0.

N-(3-Chlorophenyl)acetamide 2c.¹ White solid; m.p.: 77-78 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.17 (br, 1H), 7.64 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 2.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 169.1, 139.2, 134.5, 129.9, 124.3, 120.2, 118.1, 24.4.

tert-Butyl 4-chlorophenylcarbamate 2d.² White solid; m.p.: 101-102 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.31 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H), 6.98 (s, 1H), 1.48 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.8, 137.4, 128.8, 127.6, 119.8, 40.0, 28.4.

Benzyl 4-chlorophenylcarbamate 2e.³ White solid; m.p.: 108-109 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.40-7.31 (m, 7H), 7.25 (d, J = 8.4 Hz, 2H), 6.73 (s, 1H), 5.19 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 153.4, 136.5, 135.9, 131.0, 129.1, 128.7, 128.5, 128.3, 120.1, 67.2.

N-(4-Chlorophenyl)methanesulfonamide 2f.⁴ White solid; m.p.: 123-124 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.32 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.88 (br, 1H), 3.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 135.2, 131.1, 129.8, 122.2, 39.5.

4-Chlorophenyl acetate 2g.¹ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.33 (dd, J = 6.8, 2.0 Hz, 2H), 7.02 (dd, J = 6.8, 2.0 Hz, 2H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 169.1, 149.2, 131.2, 129.5, 123.0, 21.0.

2-Chloroanisole 2h.¹ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.36 (dd, J = 7.8, 1.4 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 6.91 (t, J = 8.4 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 3.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 155.1, 130.3, 127.7, 122.5, 121.3, 112.2, 56.1.

3-Chloroanisole 2i.⁵ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.19 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.89 (s, 1H), 6.78 (d, J = 8.0 Hz, 1H), 3.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.3, 134.9, 130.2, 120.8, 114.3, 112.6,

55.4.

4-Chloroanisole 2j.⁵ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.23 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 158.3, 129.3, 125.6, 115.2, 55.5.

5-Chlorobenzo[*d*][1,3]dioxole 2k. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.83-6.77 (m, 2H), 6.72 (d, J = 8.4 Hz, 1H), 5.97 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 148.4, 146.5, 121.3, 110.2, 109.7, 108.9, 101.7; Anal. Calcd. for C₇H₅ClO₂: C 53.70, H 3.22; found: C 53.48, H 3.40.

4-Chlorobenzonitrile 2l.⁶ White solid; m.p.: 90-91 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.61 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 139.6, 133.4, 129.7, 118.0, 110.8.

3-Chlorobenzonitrile 2m.¹ White solid; m.p.: 40-41 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.63 (d, J = 1.6 Hz, 1H), 7.61-7.55 (m, 2H), 7.43 (t, J = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 135.3, 133.3, 132.0, 130.5, 130.3, 117.4, 114.1.

1-Chloro-4-(trifluoromethyl)benzene 2n.¹ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.56 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 138.1, 129.2 (q, ² J_{C-F} = 33.2 Hz), 129.1, 126.7 (q, ³ J_{C-F} = 3.7 Hz), 123.8 (q, ¹ J_{C-F} = 270.2 Hz).

4-Chlorobenzaldehyde 2o.¹ White solid; m.p.: 46-47 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.99 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 190.8, 141.0, 134.8, 130.9, 129.5.

1-(4-Chlorophenyl)ethanone 2p.¹ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ

(ppm): 7.90 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.8$ Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 196.7, 139.6, 135.5, 129.7, 128.9, 26.5.

Methyl 4-chlorobenzoate 2q.¹ White solid; m.p.: 42-43 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.97 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 166.2, 139.4, 131.0, 128.7, 128.6, 52.3.

Ethyl 4-chlorobenzoate 2r.⁷ White solid; m.p.: 71-72 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.98 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 4.37 (q, $J = 6.8$ Hz, 2H), 1.39 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 165.7, 139.2, 130.9, 129.0, 128.6, 61.2, 14.3.

(4-Chlorophenyl)methanol 2s.¹ White solid; m.p.: 69-70 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.31 (dd, $J = 6.6, 1.8$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 4.62 (d, $J = 4.8$ Hz, 2H), 2.10 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 139.3, 133.4, 128.7, 128.3, 64.5.

5-Chloro-*N,N*-dimethylpyridin-2-amine 2t. Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.08 (s, 1H), 7.37 (dd, $J = 8.8, 2.2$ Hz, 1H), 6.43 (d, $J = 8.8$ Hz, 1H), 3.06 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 157.7, 146.0, 136.8, 128.8, 106.5, 38.2; Anal. Calcd. for $\text{C}_7\text{H}_9\text{ClN}_2$: C 53.68, H 5.79, N 17.89; found: C 53.42, H 5.51, N 17.68.

1-Chloronaphthalene 2u.⁸ Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.26 (d, $J = 8.4$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.61-7.49 (m, 3H), 7.36 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 134.6, 132.0, 130.9, 128.2, 127.2, 127.0, 126.7, 126.2, 125.7, 124.4.

2-Chlorotoluene 2v.¹ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.32 (dd, J = 7.4, 1.8 Hz, 1H), 7.29-7.19 (m, 1H), 7.15-7.07 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 136.0, 134.4, 131.0, 129.1, 127.1, 126.6, 20.0.

2-Chlorobiphenyl 2w.¹ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.48-7.41 (m, 5H), 7.39-7.24 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 140.6, 139.4, 132.5, 131.4, 129.9, 129.4, 128.5, 128.0, 127.6, 126.8.

2-Chloro-1,3-dimethylbenzene 2x.¹ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.07-7.00 (m, 3H), 2.37 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 136.3, 134.7, 128.4, 125.9, 20.7.

3-Bromonitrobenzene 3a.¹ Yellow solid; m.p.: 57-58 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.39 (t, J = 1.8 Hz, 1H), 8.20-8.16 (m, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 148.9, 137.6, 130.6, 126.8, 122.9, 122.2.

4-Bromobenzonitrile 3b.⁹ White solid; m.p.: 112-113 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.64 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 133.4, 132.7, 128.0, 118.1, 111.3.

4-Bromobenzaldehyde 3c.¹⁰ White solid; m.p.: 59-60 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.98 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 191.1, 132.5, 131.0, 129.8, 128.9.

1-(4-Bromophenyl)ethanone 3d.¹⁰ White solid; m.p.: 50-51 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.82 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 2.59 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 197.0, 135.8, 131.9, 129.8, 128.3, 26.5.

Methyl 4-bromobenzoate 3e.¹⁰ White solid; m.p.: 80-81 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.90 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 166.4, 131.7, 131.1, 129.1, 128.0, 52.3.

4-Bromobiphenyl 3f.¹⁰ White solid; m.p.: 90-91 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.58-7.52 (m, 4H), 7.47-7.40 (m, 4H), 7.36 (t, J = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 140.2, 140.0, 131.9, 128.9, 128.8, 127.7, 127.0, 121.6.

2-Bromoanisole 3g.¹¹ Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.53 (dd, J = 8.0, 1.6 Hz, 1H), 7.29-7.24 (m, 1H), 6.90 (dd, J = 8.2, 1.0 Hz, 1H), 6.85-6.81 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 155.9, 133.4, 128.5, 121.8, 112.1, 111.8, 56.2.

4-Bromoanisole 3h.¹² Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.38-7.34 (m, 2H), 6.79-6.75 (m, 2H), 3.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 158.7, 132.2, 115.8, 112.8, 55.4.

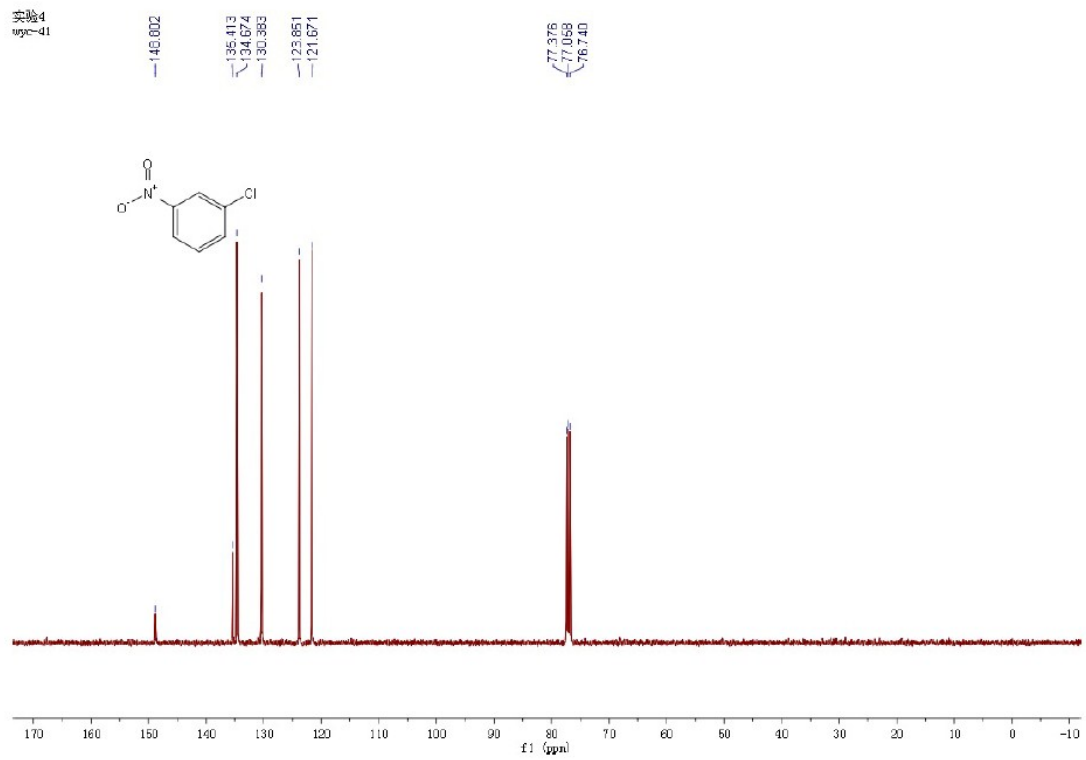
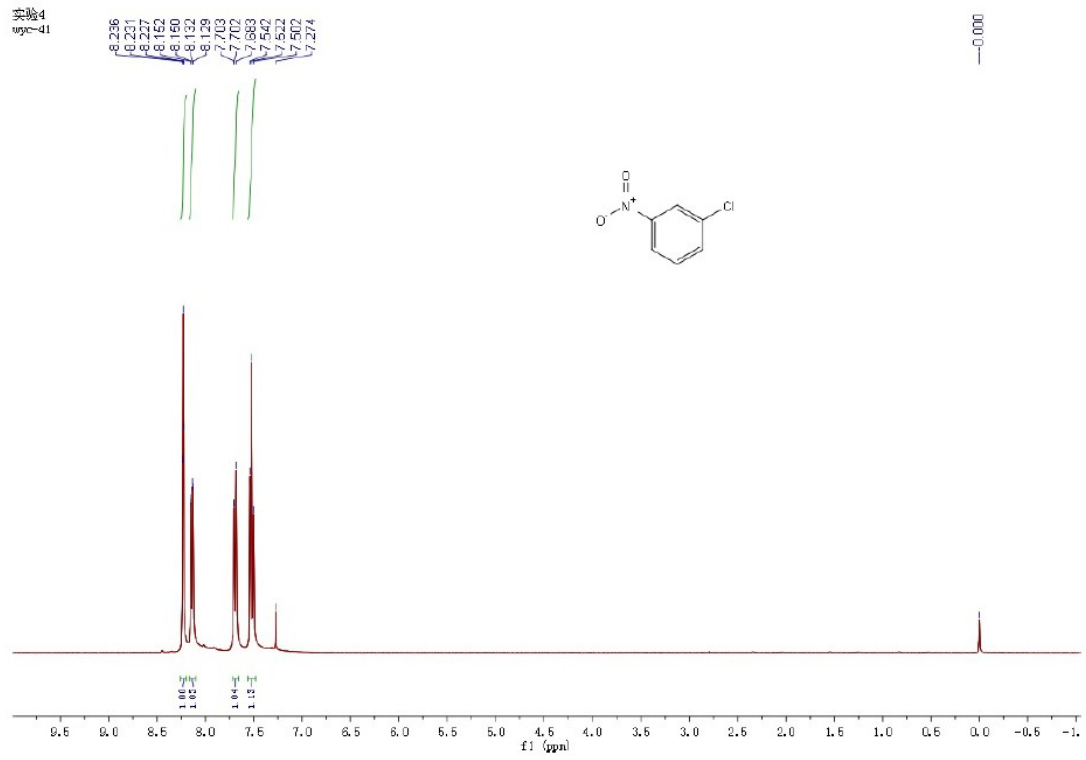
1-Bromonaphthalene 3i.¹² Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.23 (d, J = 8.4 Hz, 1H), 7.83-7.75 (m, 3H), 7.58 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 134.7, 132.1, 129.9, 128.3, 127.9, 127.3, 127.1, 126.7, 126.2, 122.9.

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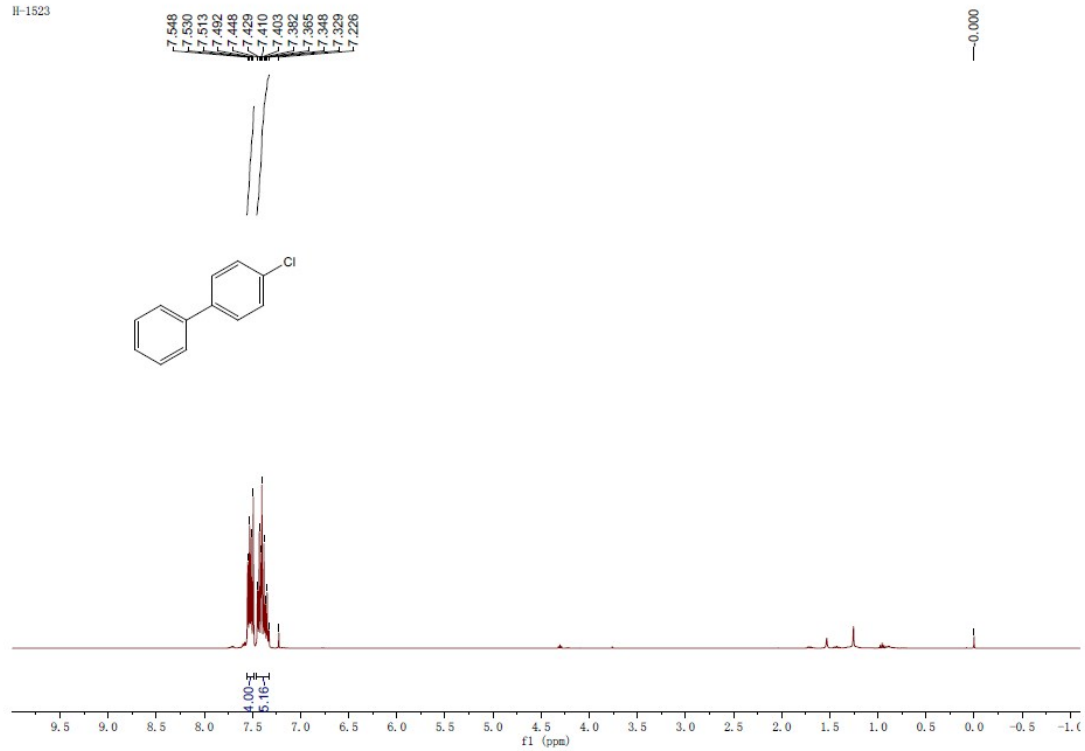
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¹H NMR and ¹³C NMR spectra of compounds 2a-2x and compounds 3a-3i

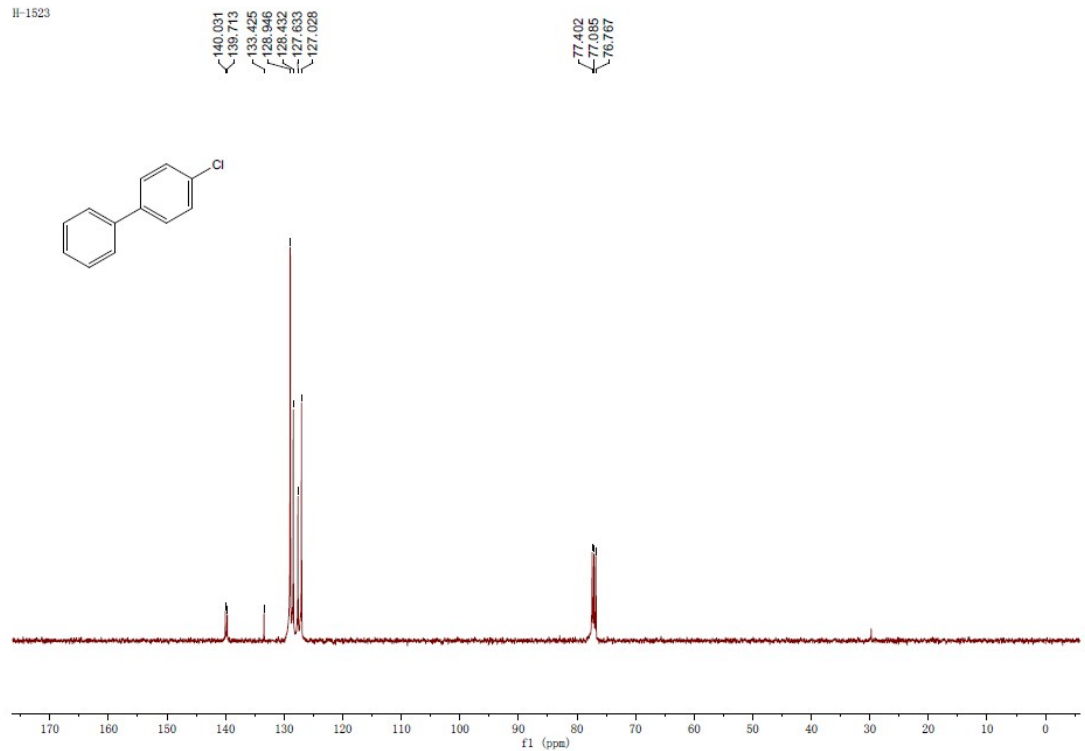


^1H NMR and ^{13}C NMR spectra of compound **2a**

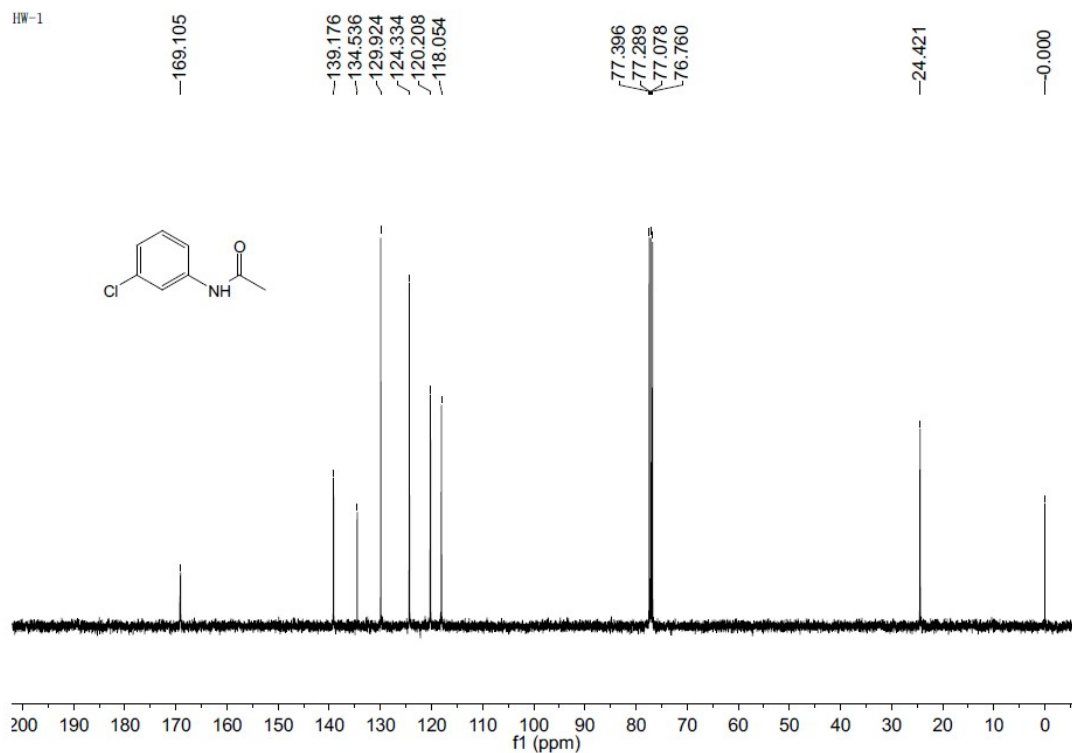
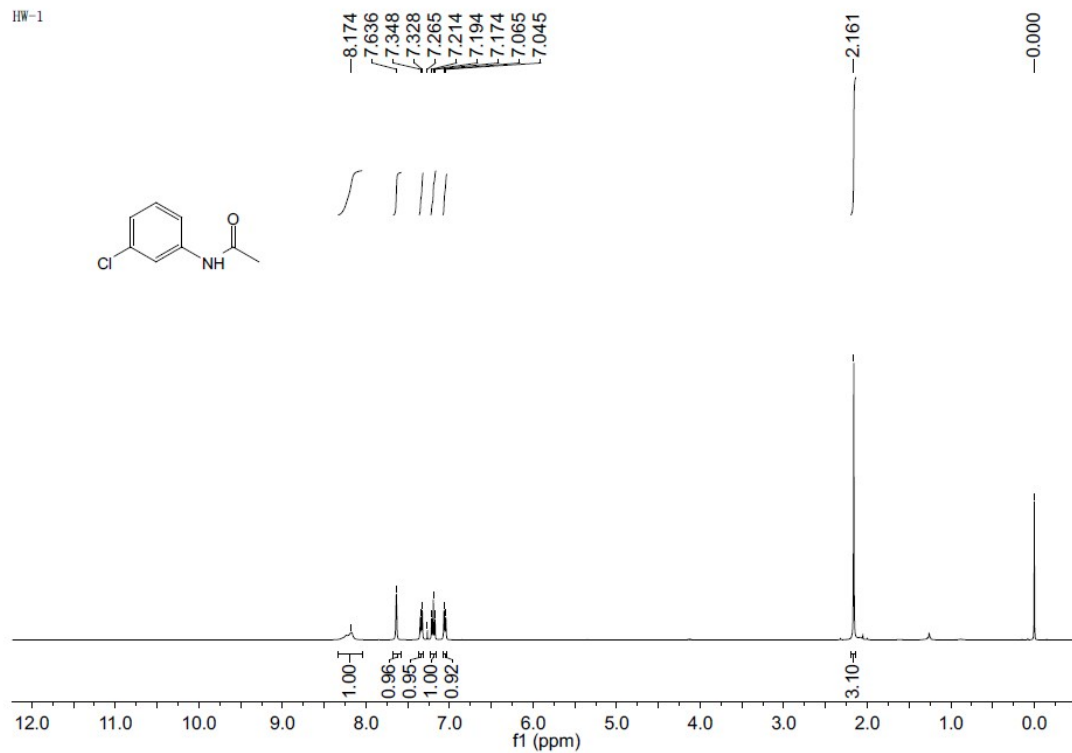
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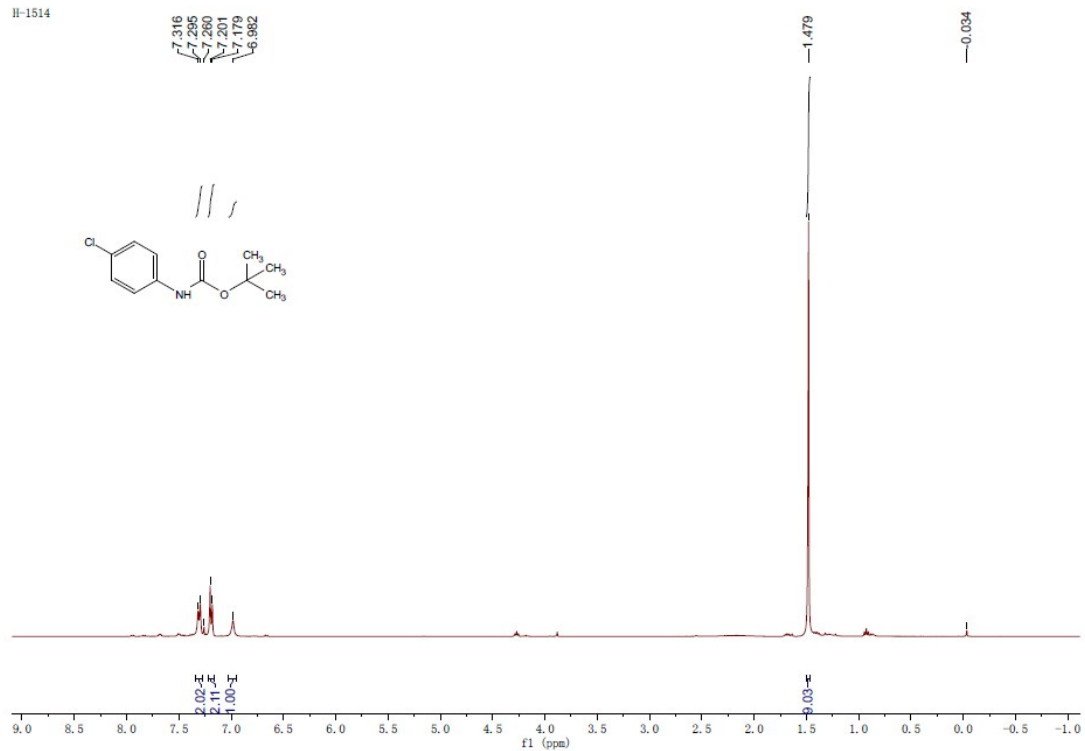


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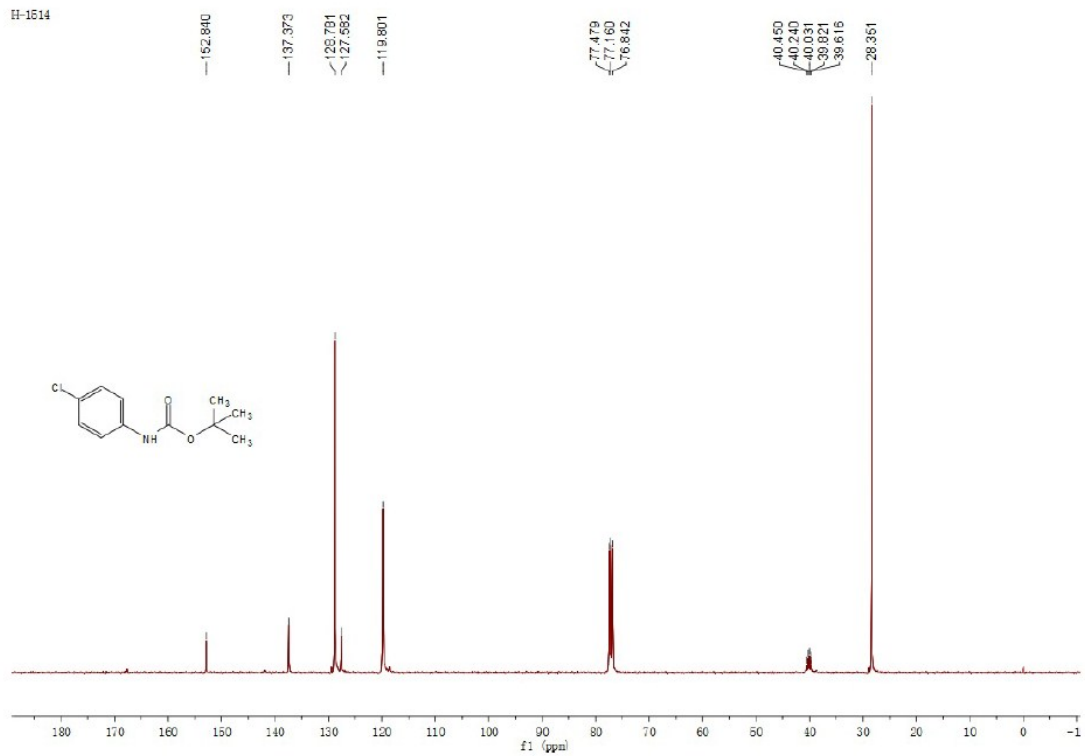


^1H NMR and ^{13}C NMR spectra of compound **2c**

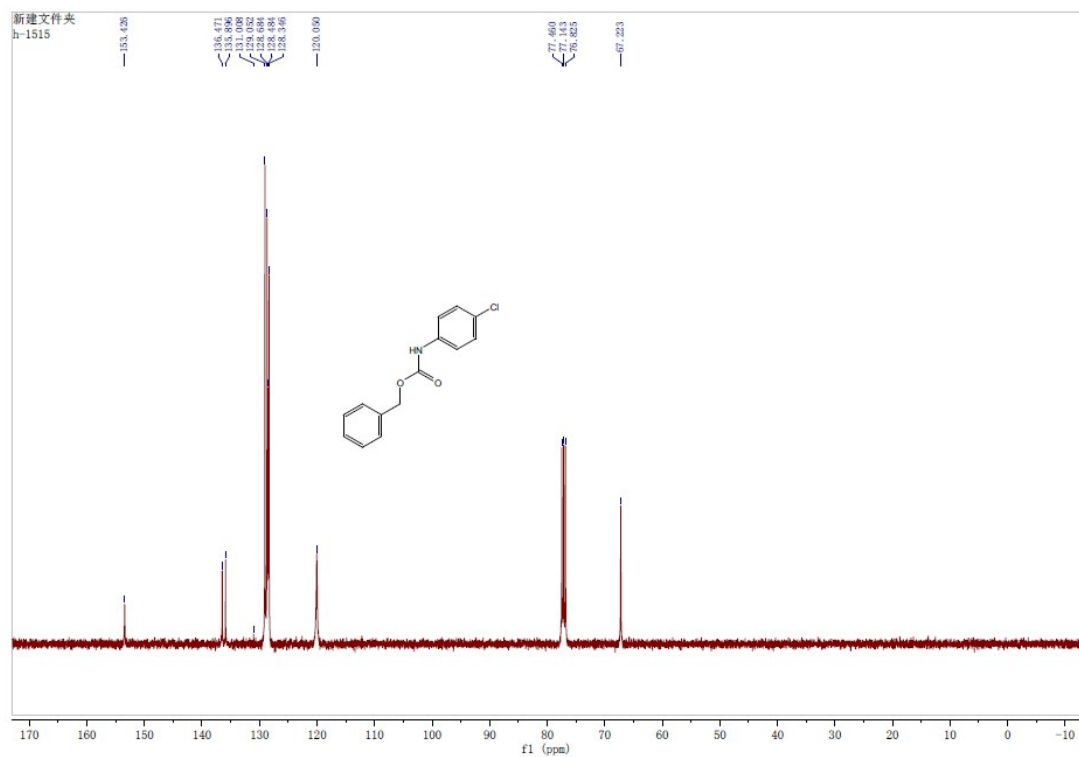
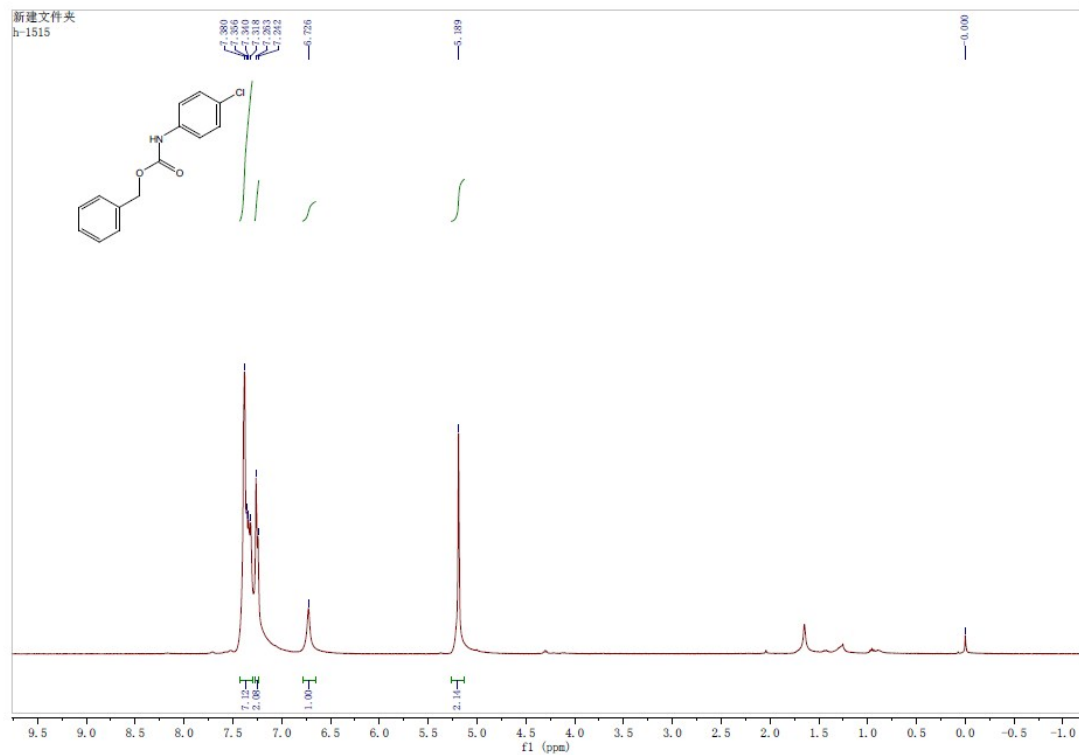
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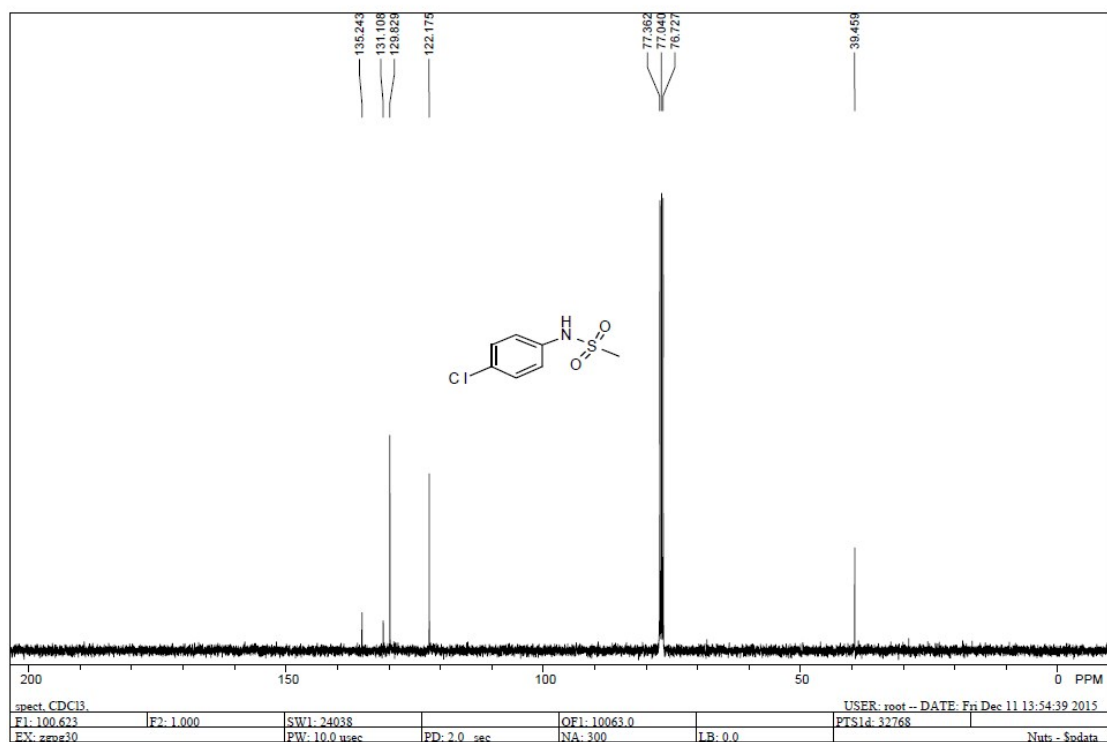
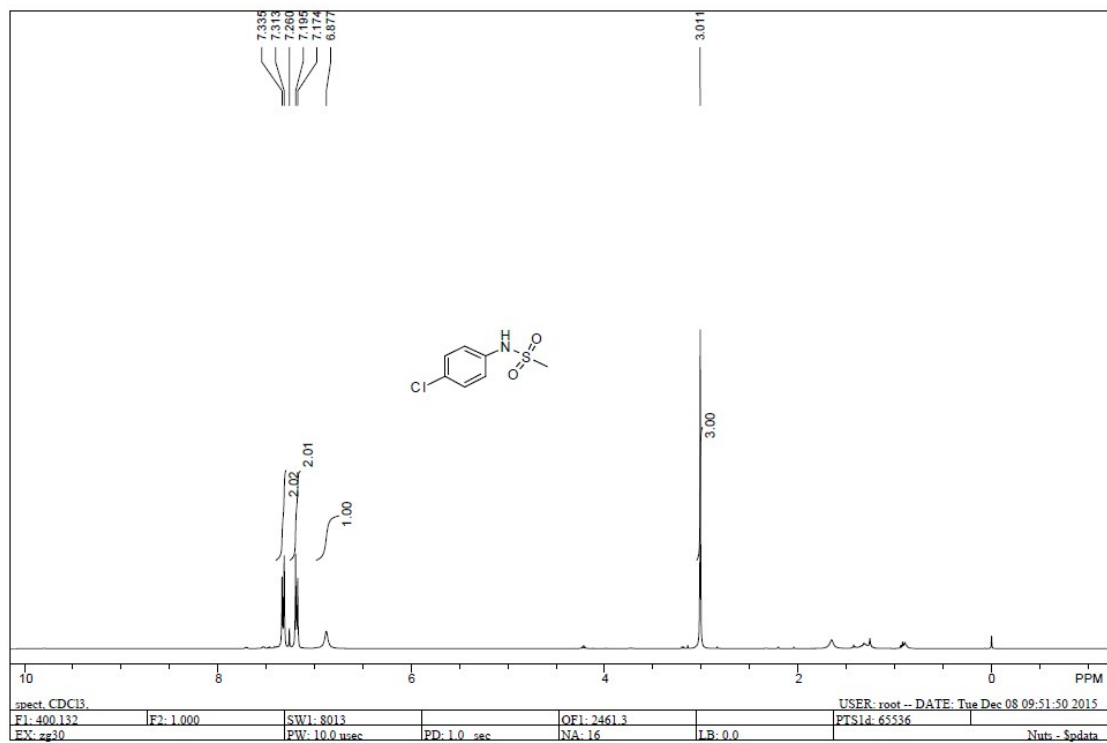
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¹H NMR and ¹³C NMR spectra of compound **2d**

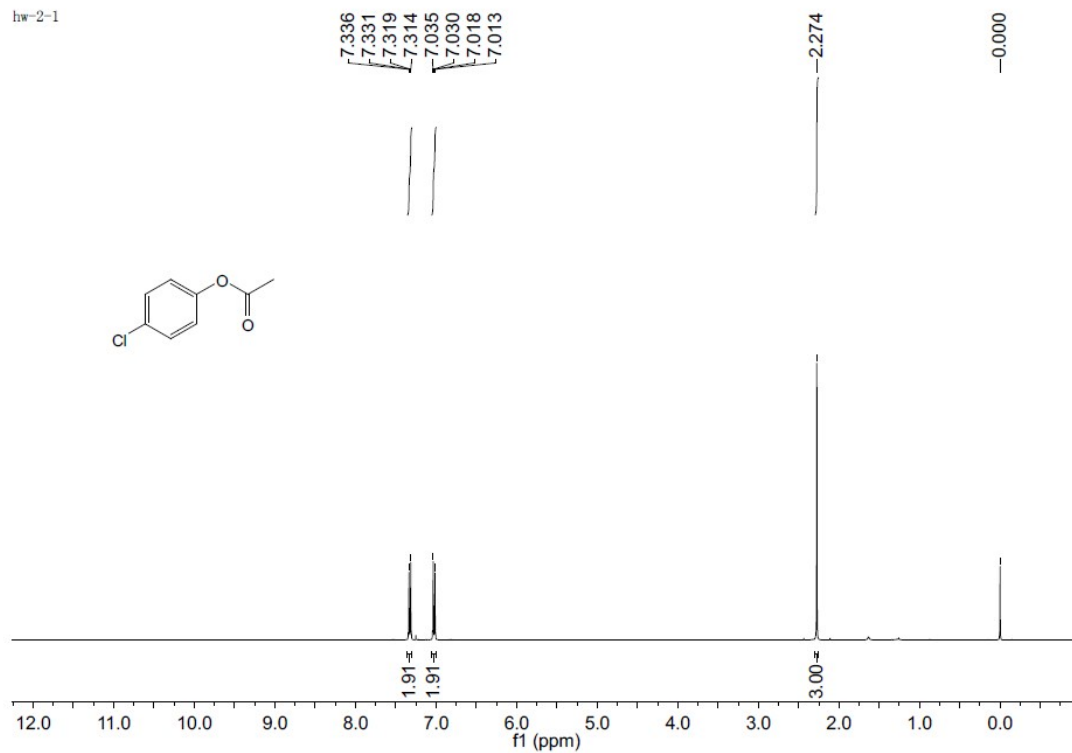


^1H NMR and ^{13}C NMR spectra of compound **2e**

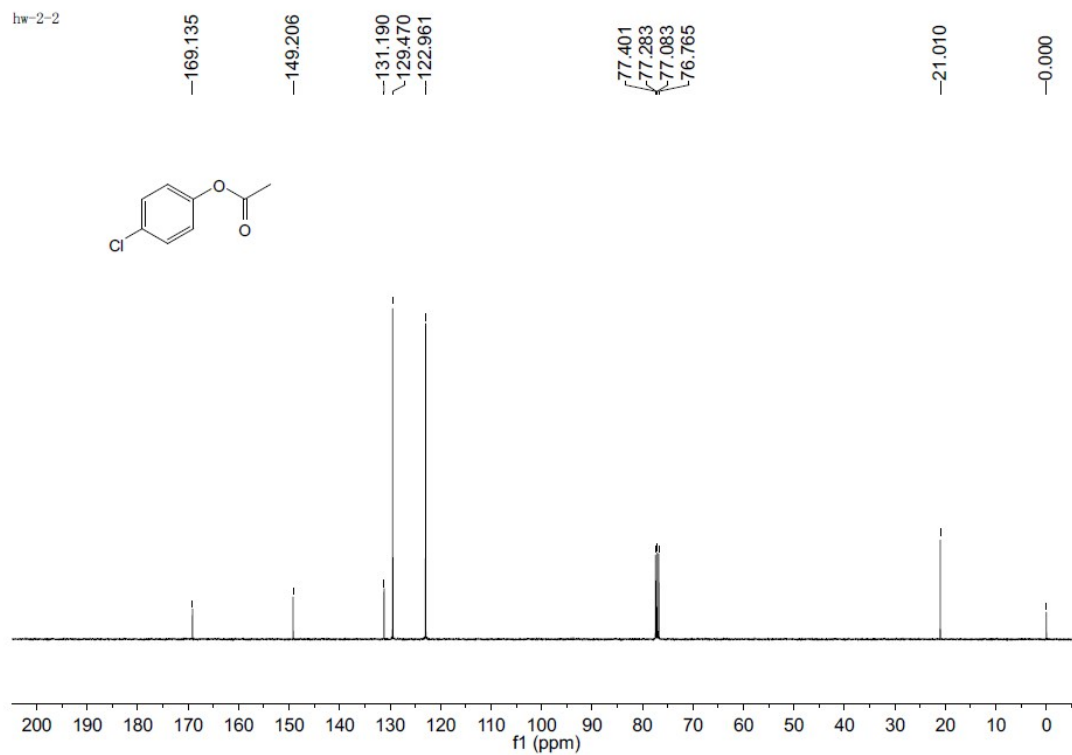


^1H NMR and ^{13}C NMR spectra of compound **2f**

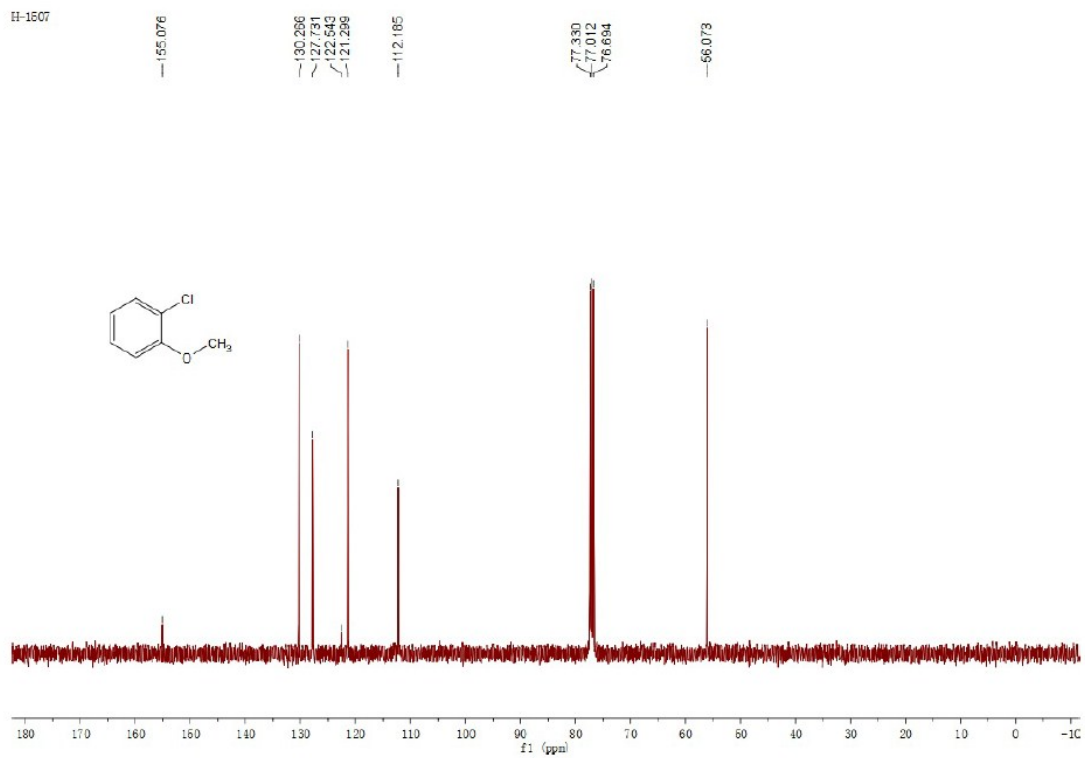
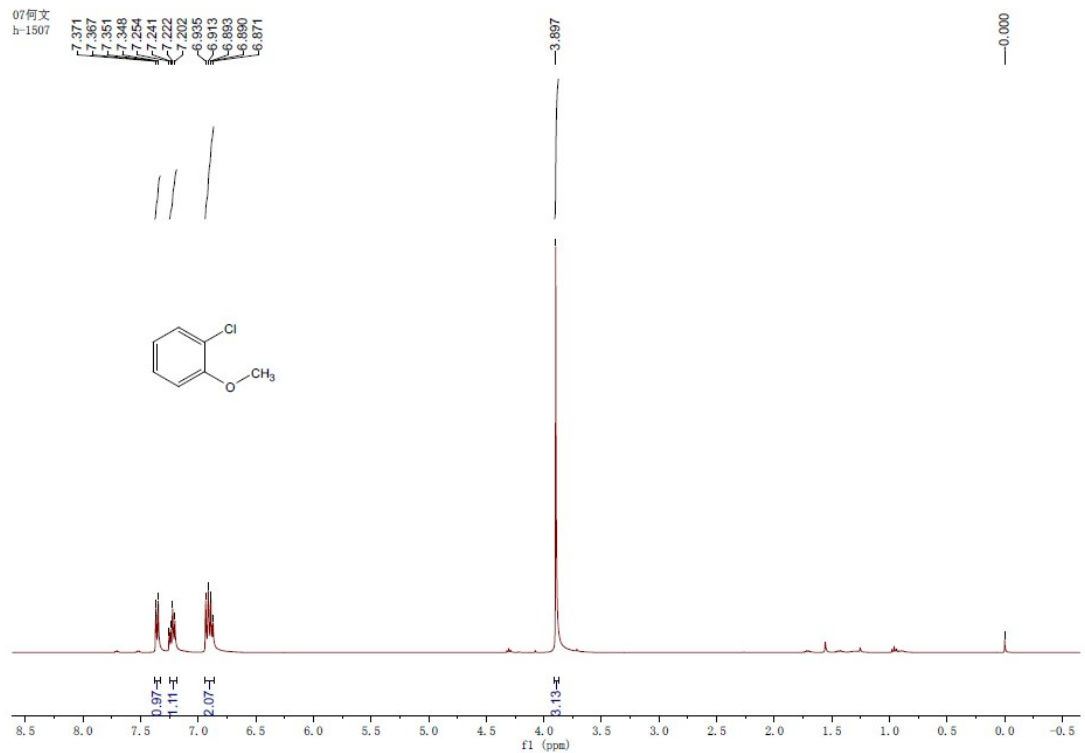
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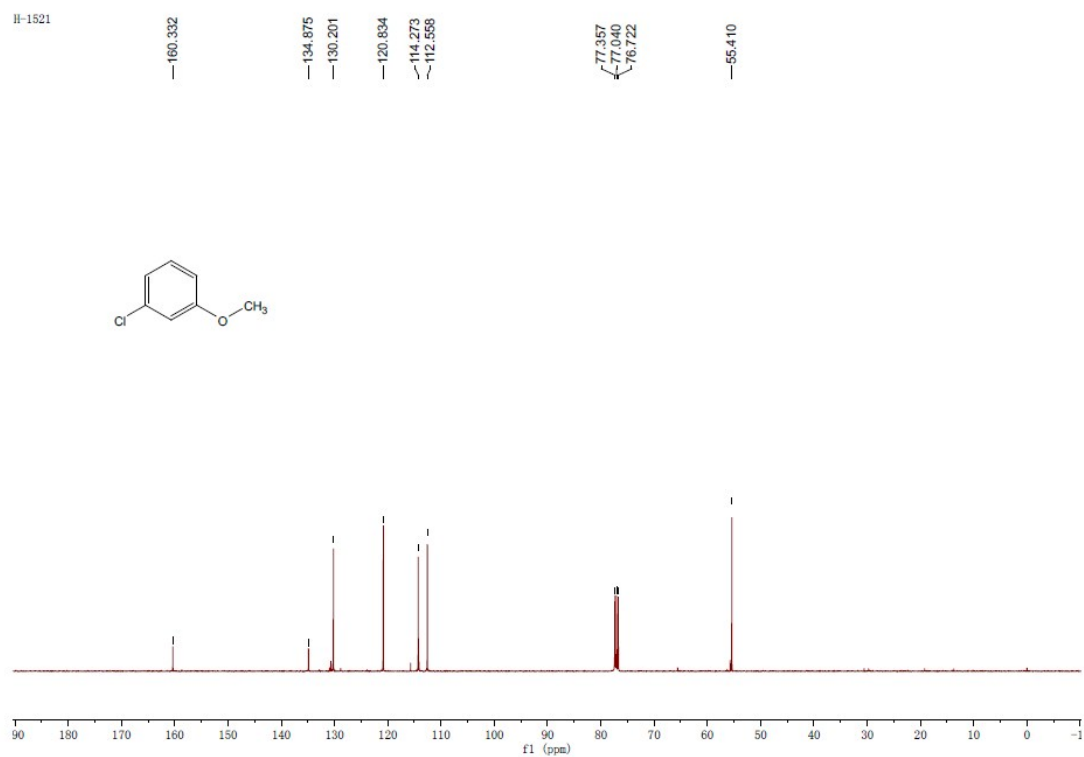
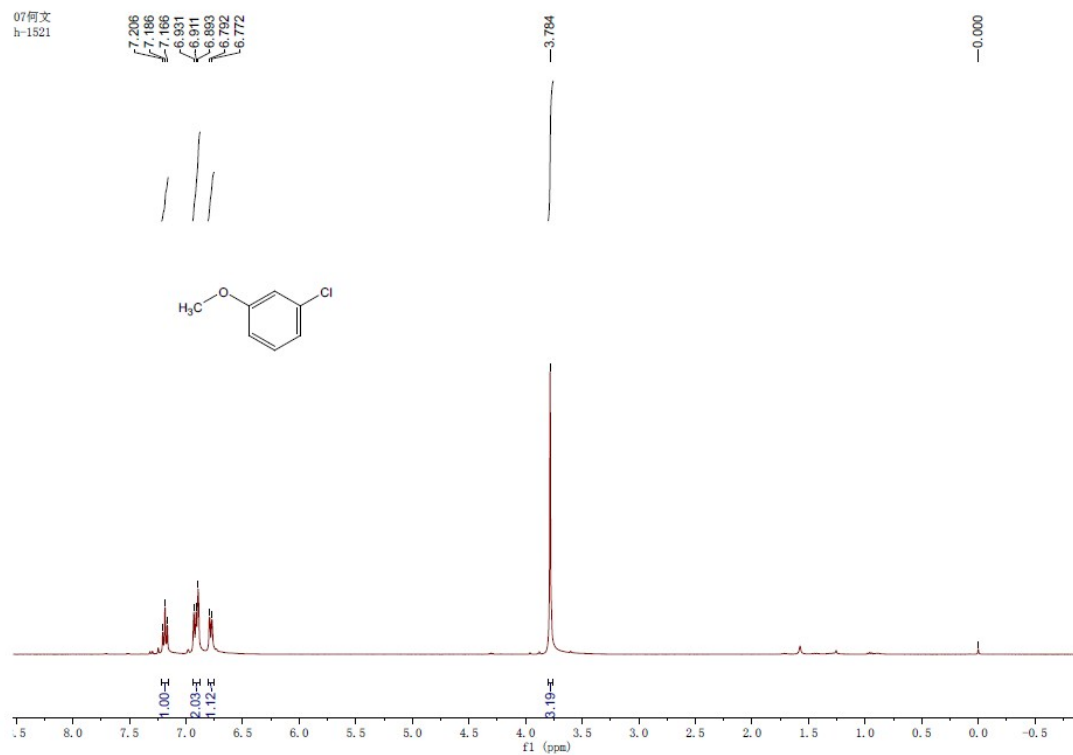
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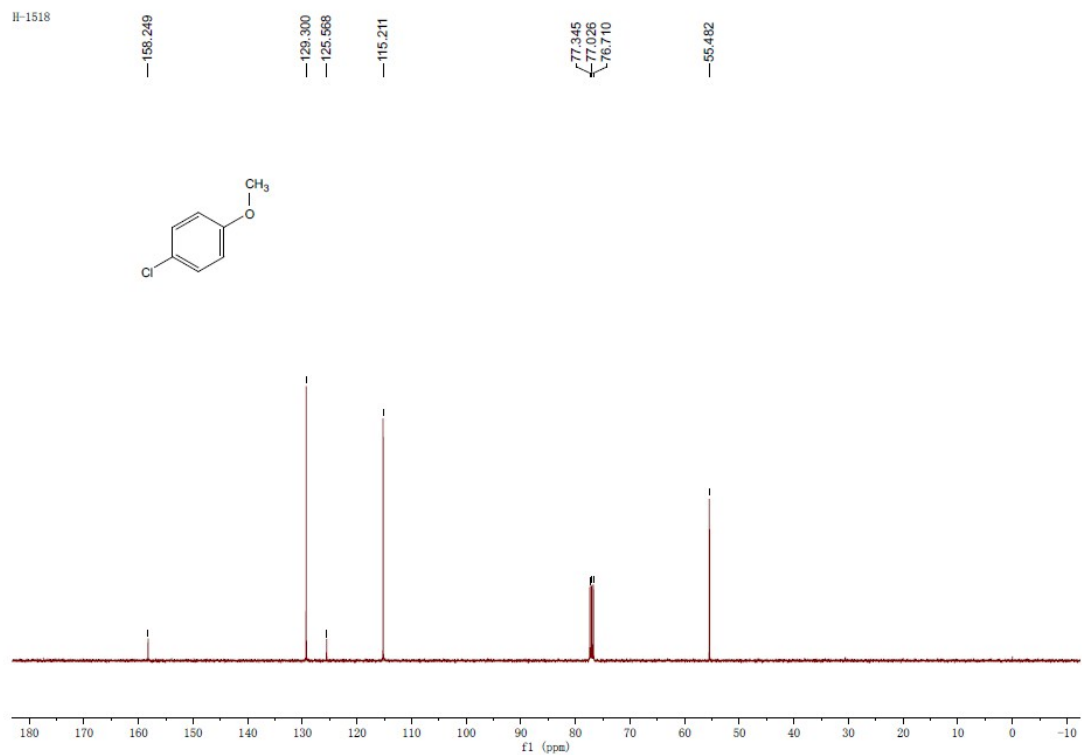
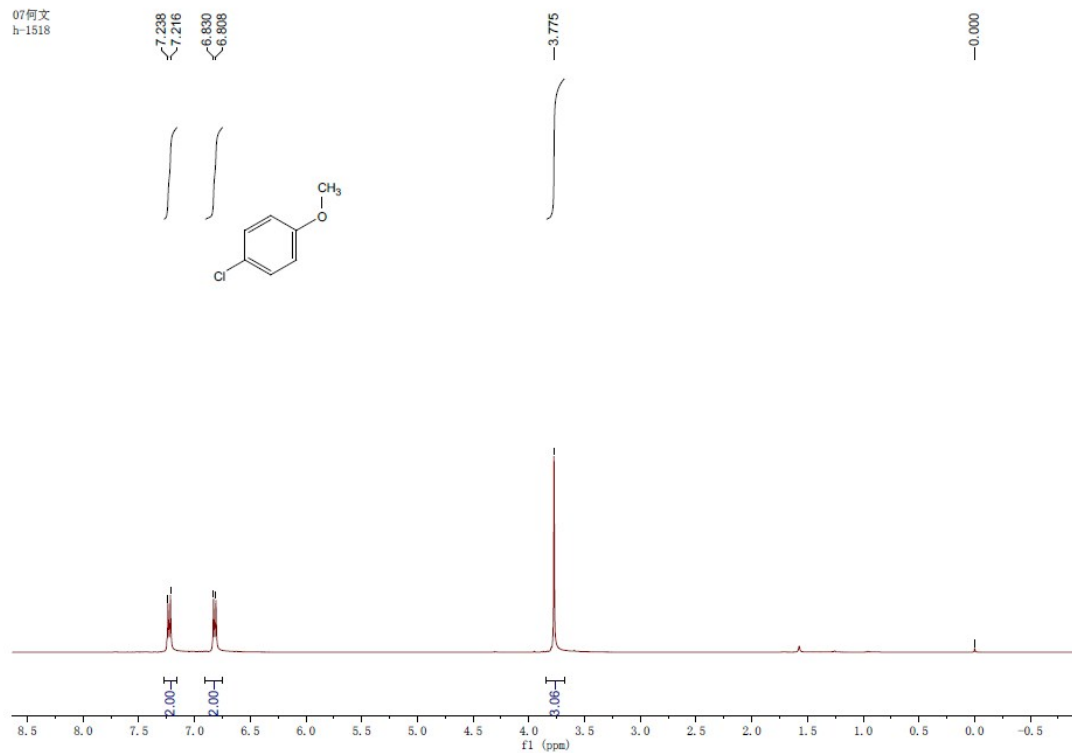
¹H NMR and ¹³C NMR spectra of compound **2g**



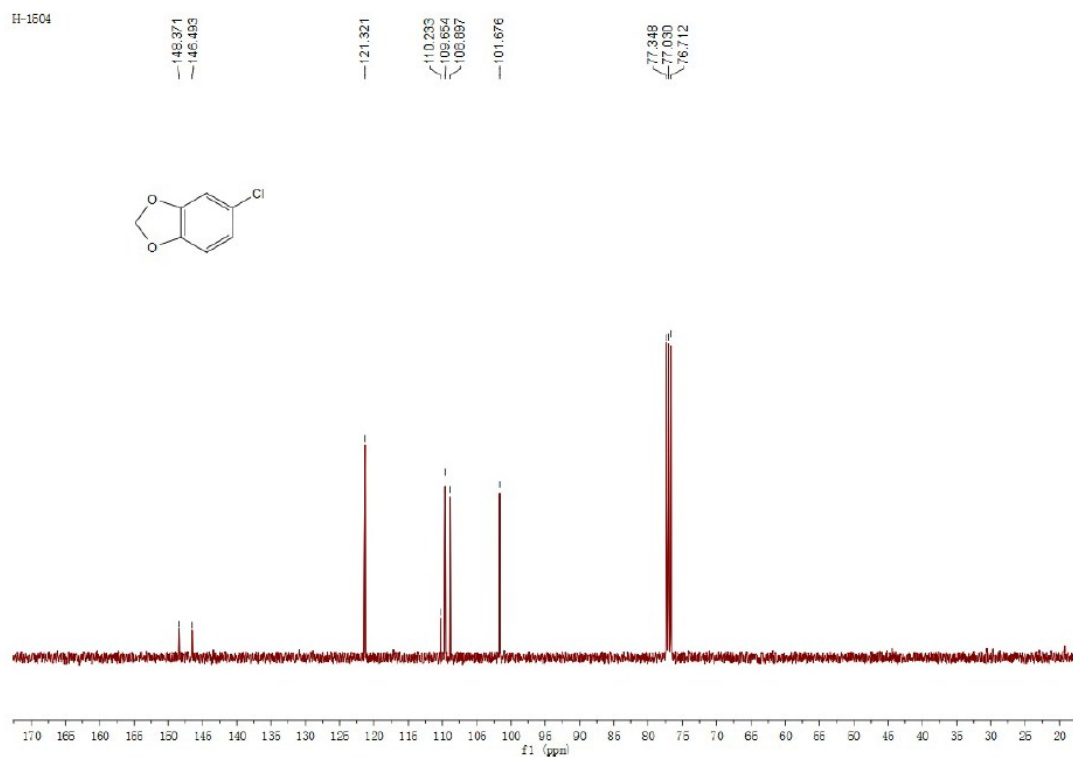
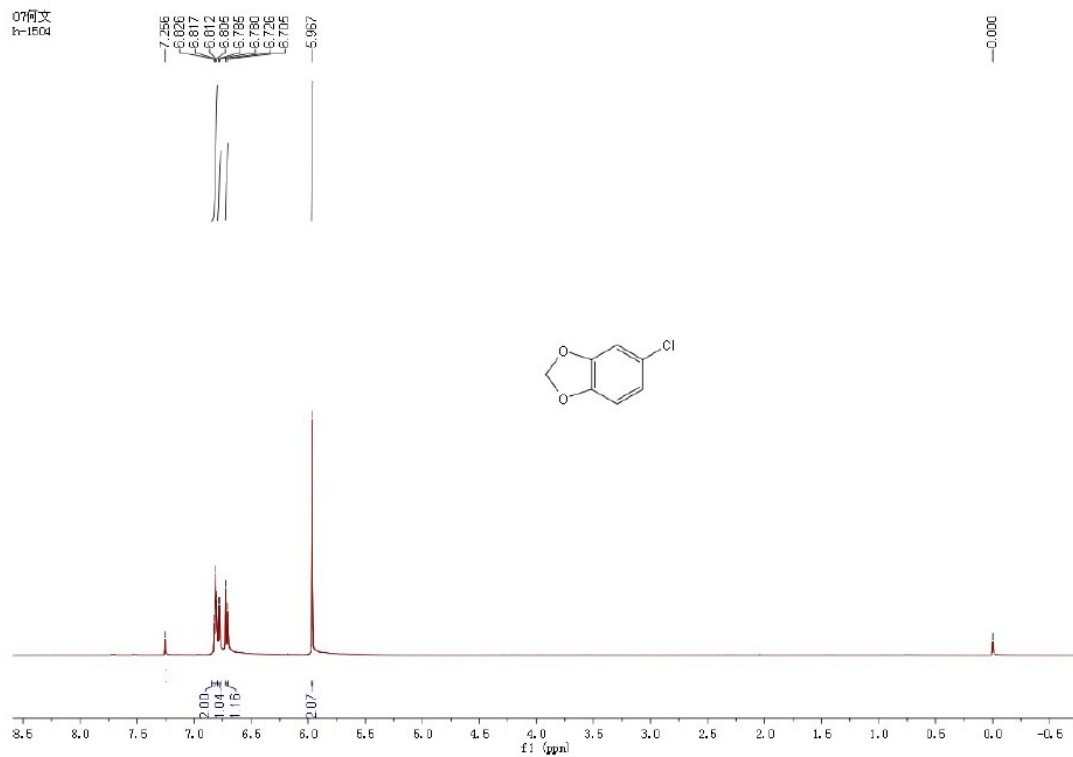
^1H NMR and ^{13}C NMR spectra of compound **2h**



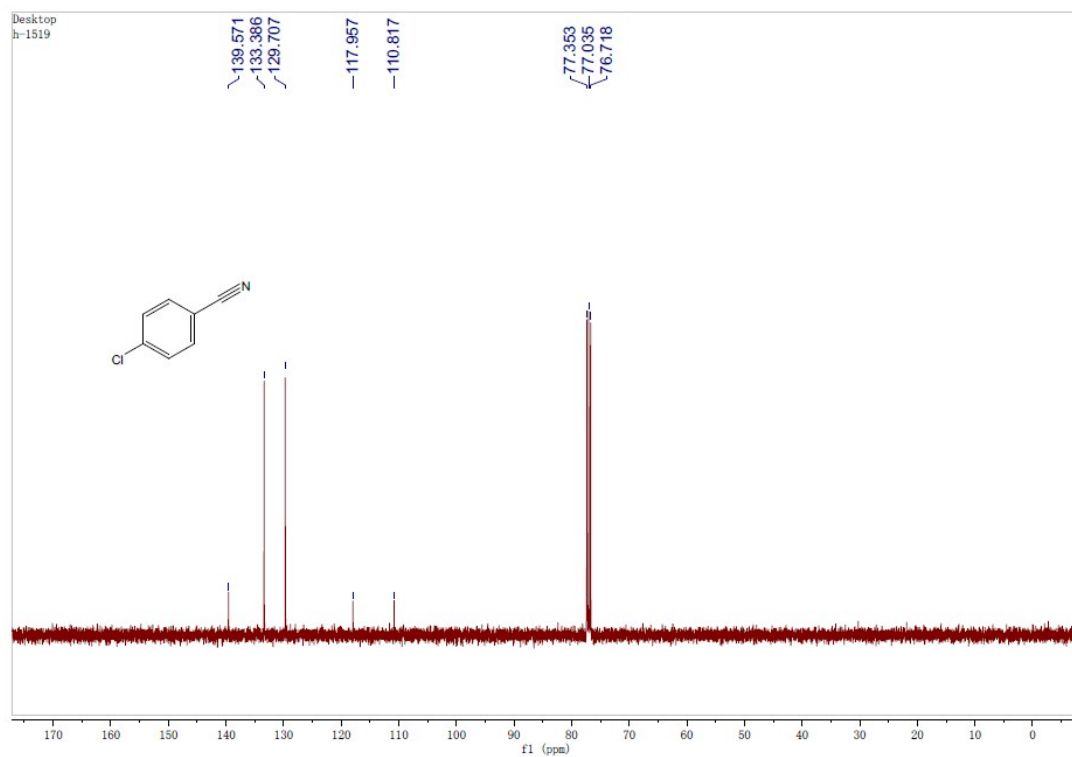
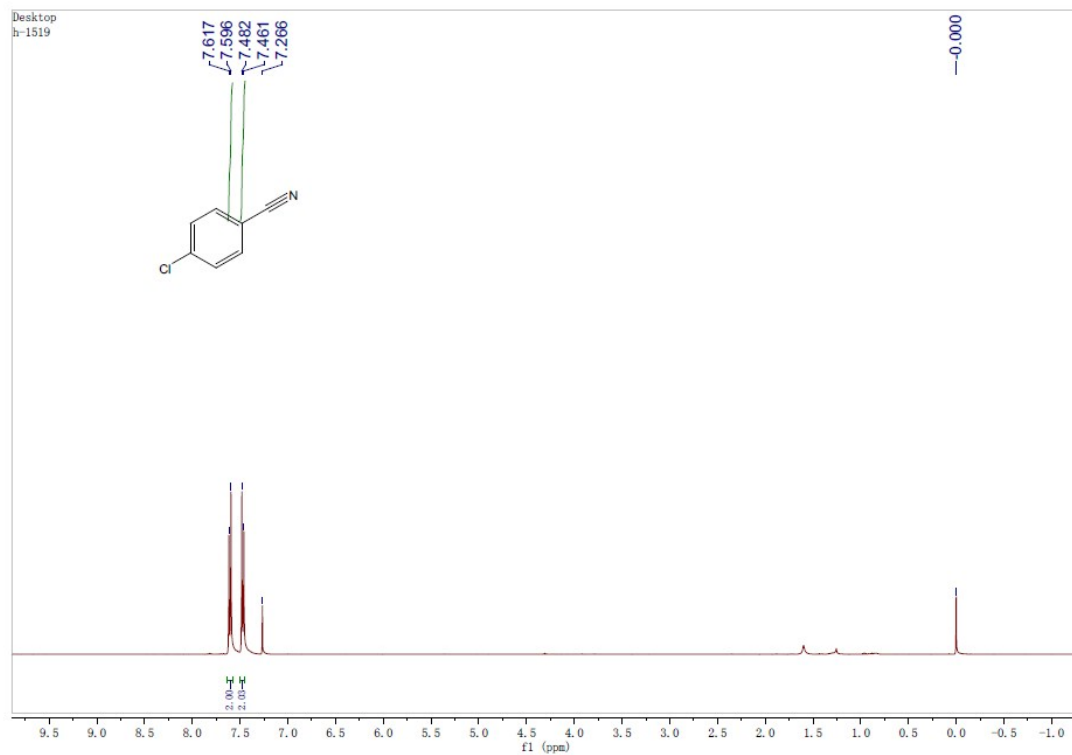
¹H NMR and ¹³C NMR spectra of compound **2i**



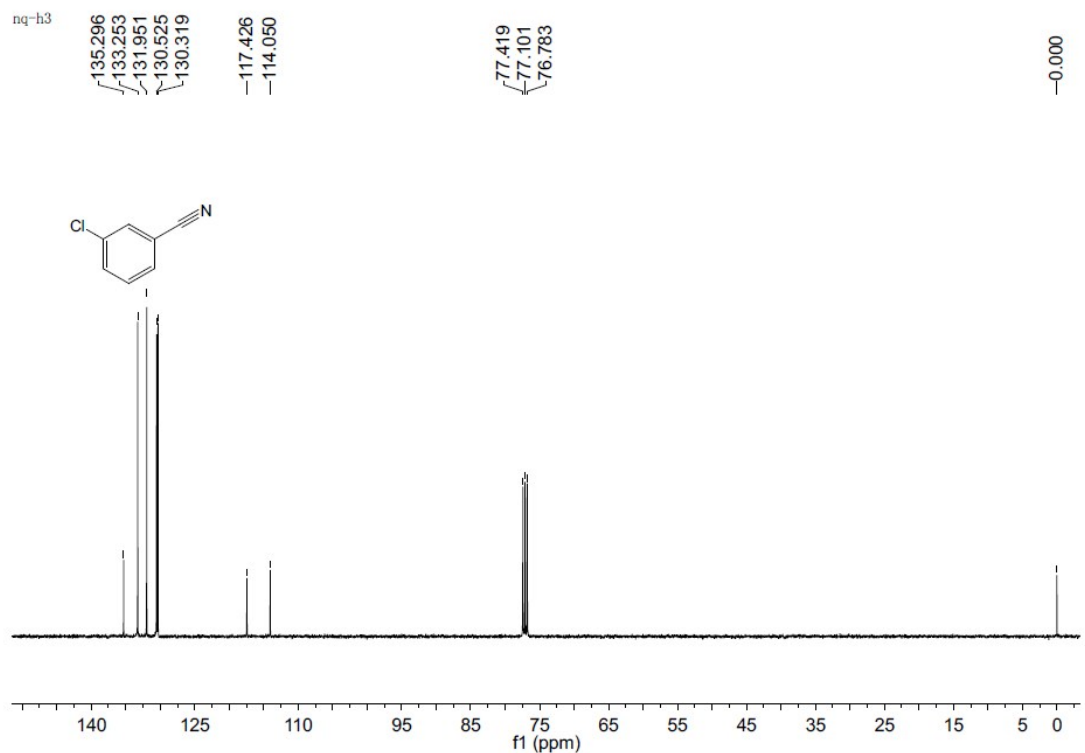
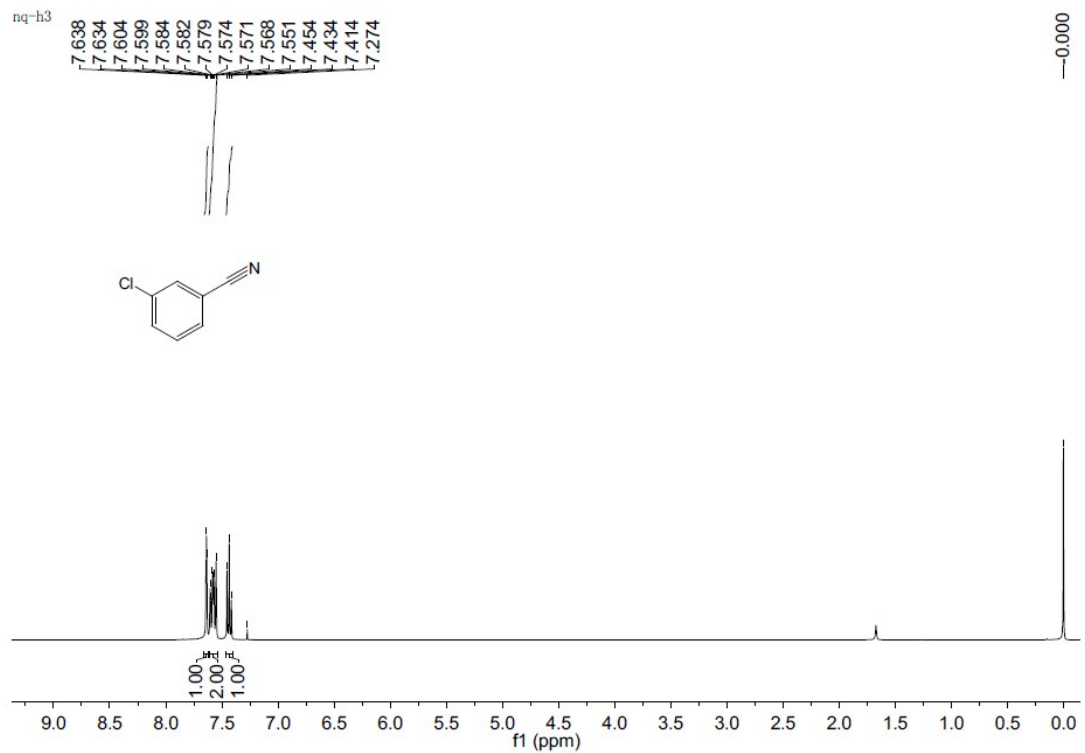
¹H NMR and ¹³C NMR spectra of compound **2j**



^1H NMR and ^{13}C NMR spectra of compound **2k**

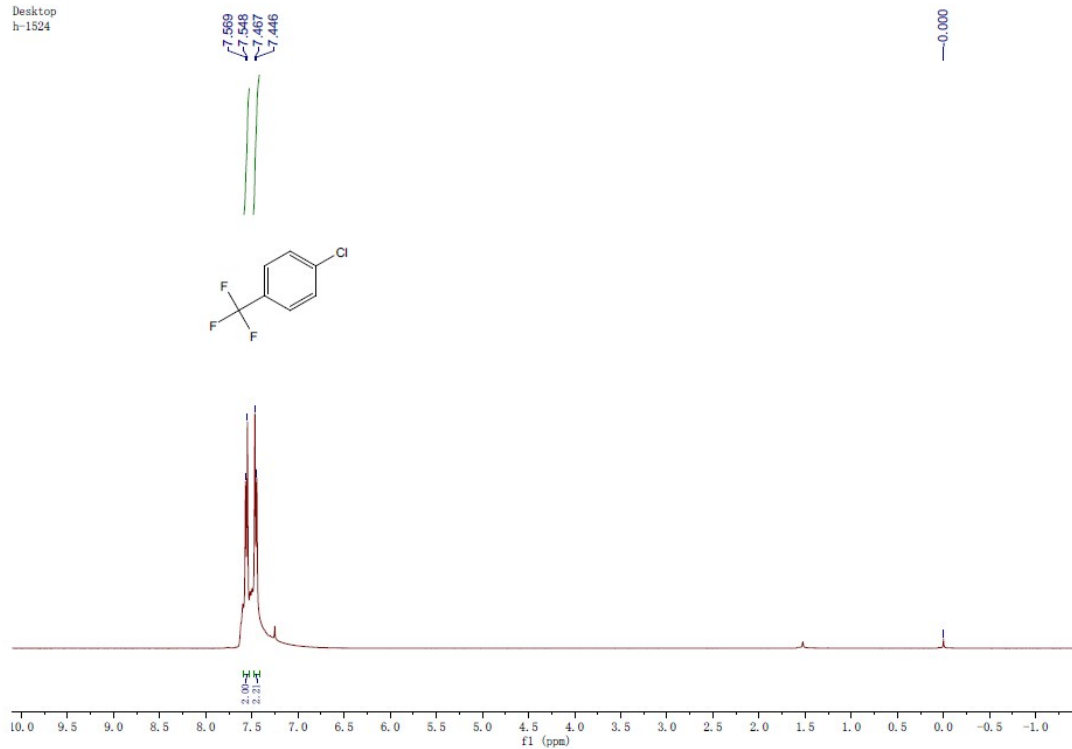


^1H NMR and ^{13}C NMR spectra of compound **21**

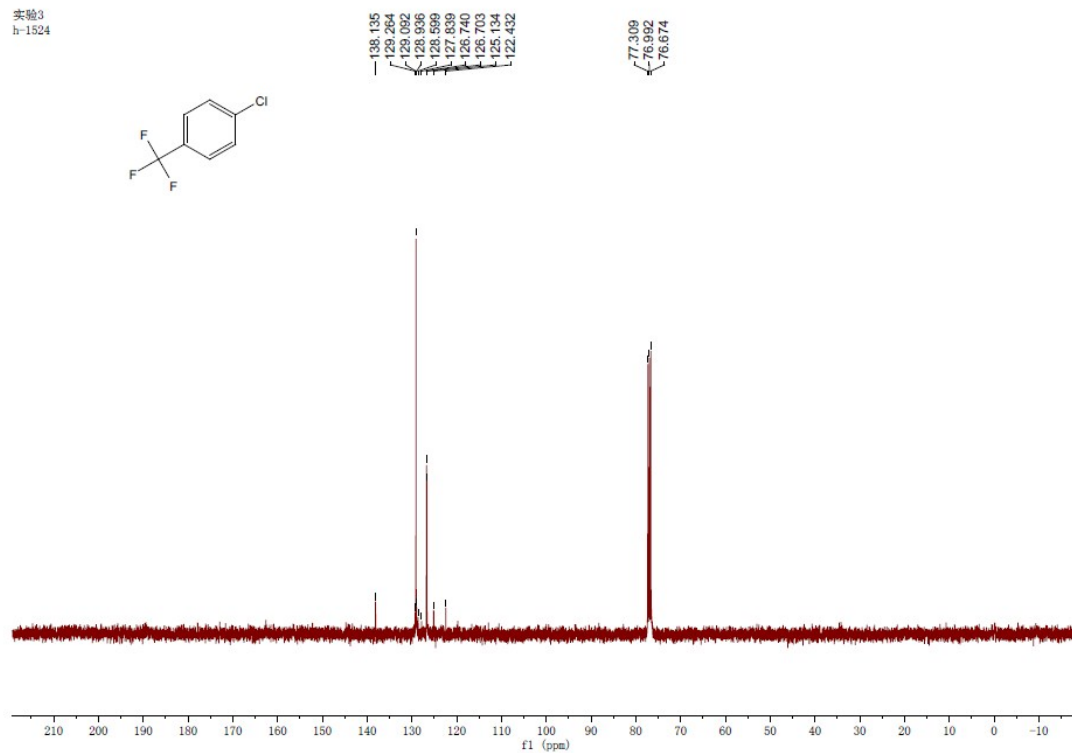


^1H NMR and ^{13}C NMR spectra of compound **2m**

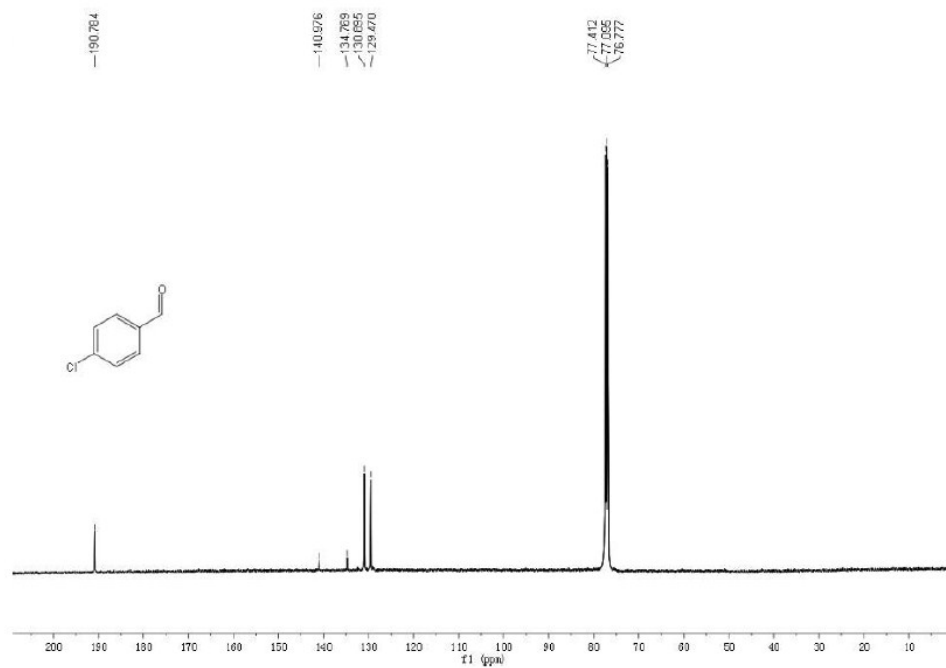
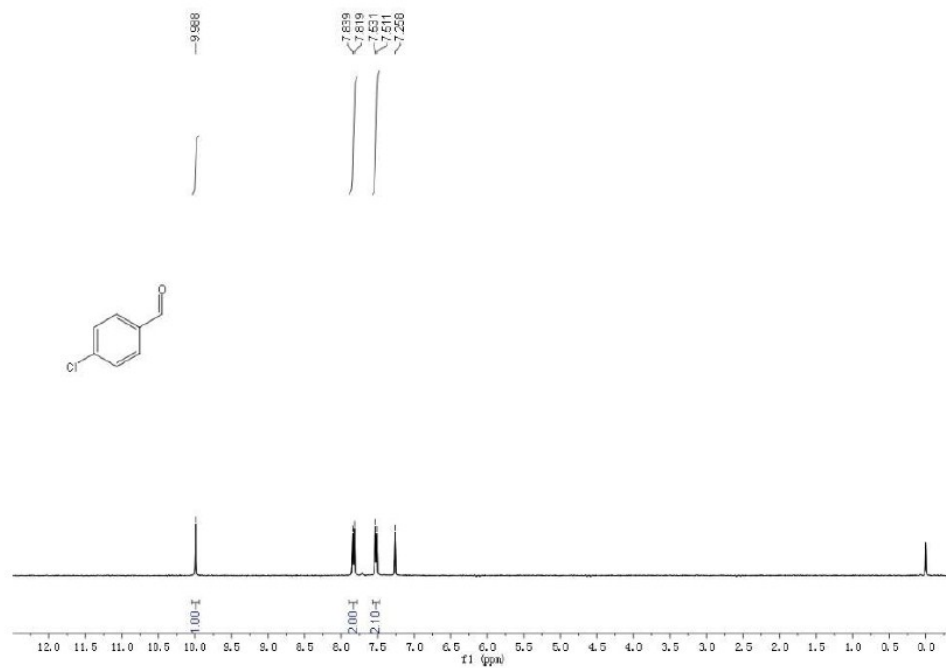
Desktop
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实验3
h-1524

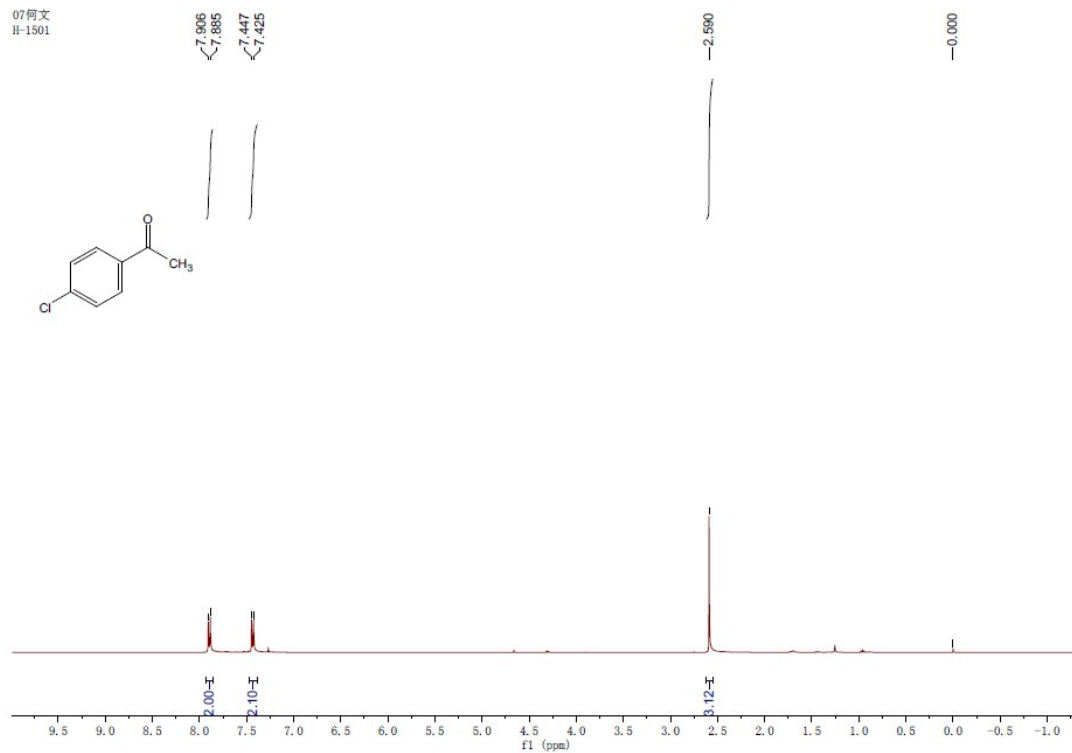


¹H NMR and ¹³C NMR spectra of compound **2n**

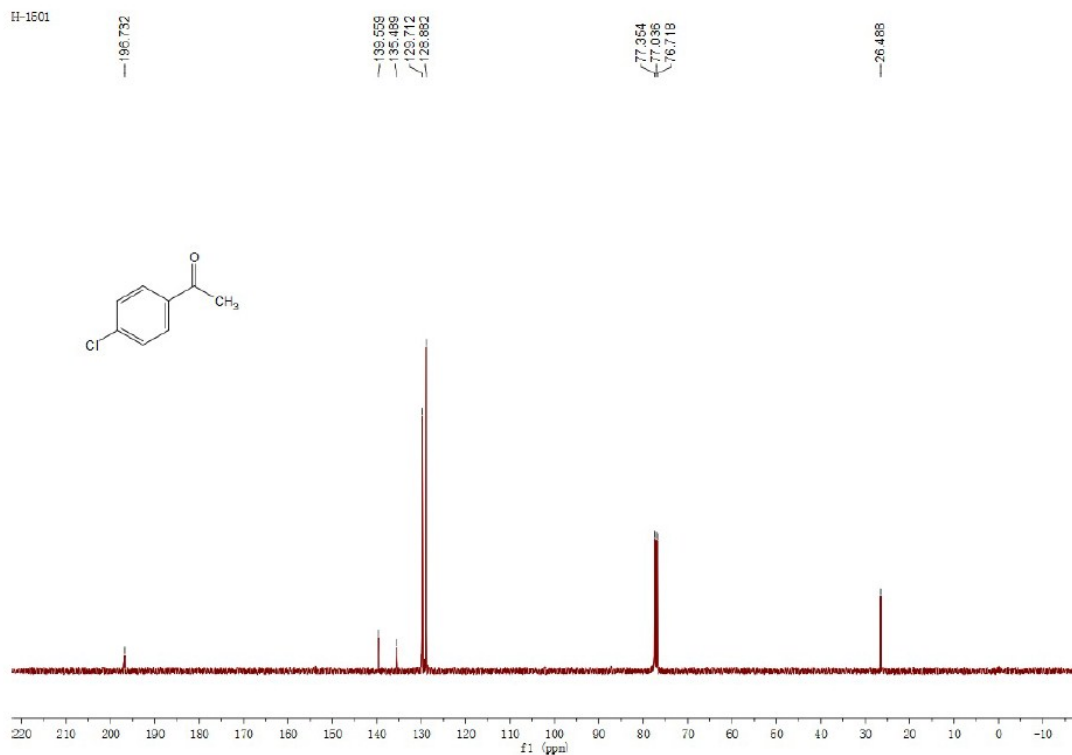


¹H NMR and ¹³C NMR spectra of compound **2o**

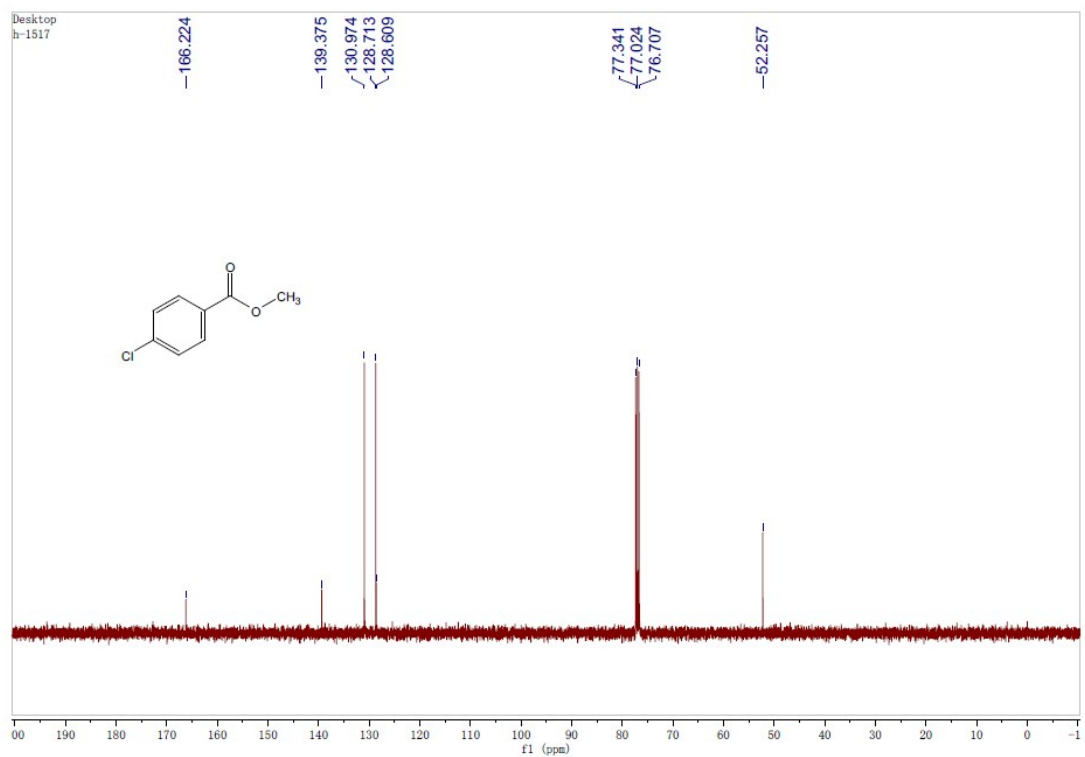
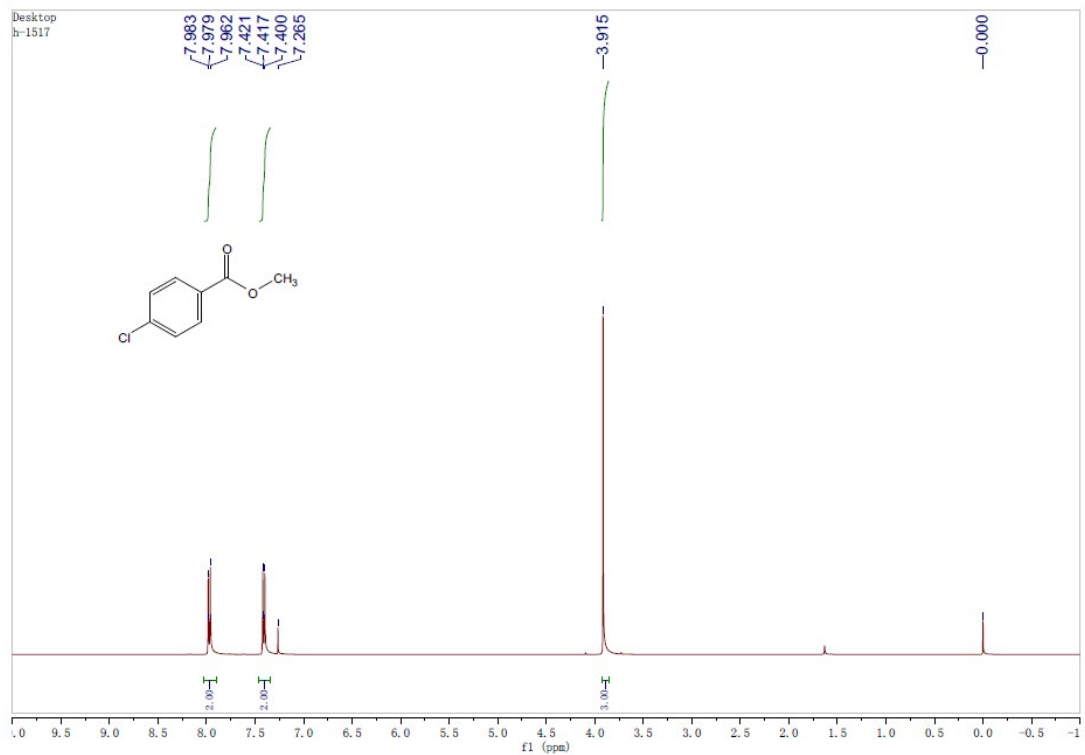
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H-1501



H-1601

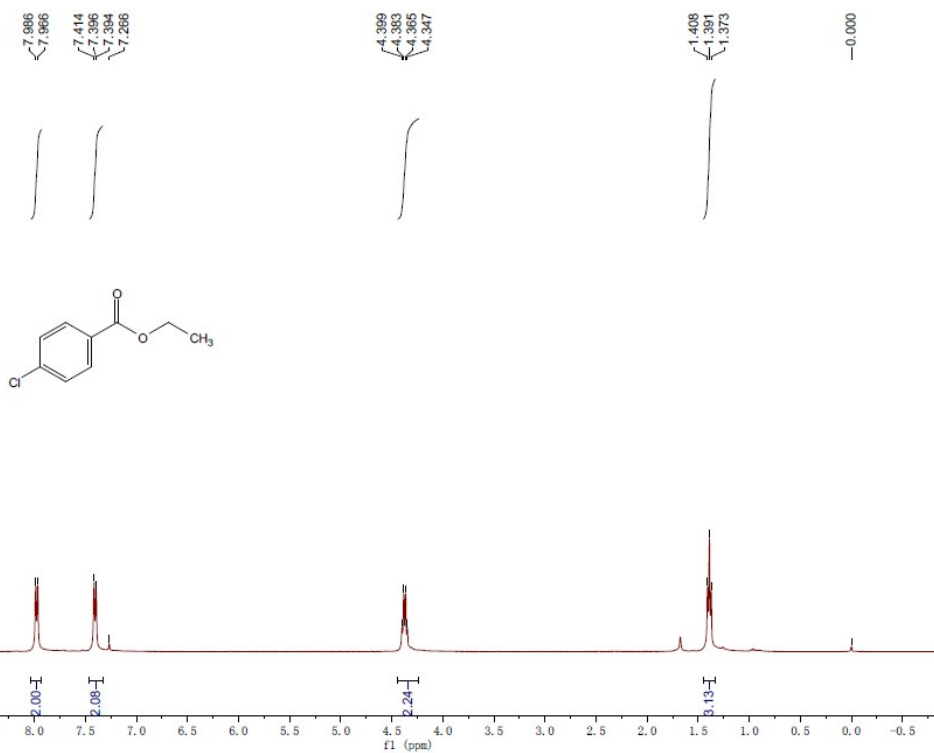


¹H NMR and ¹³C NMR spectra of compound **2p**

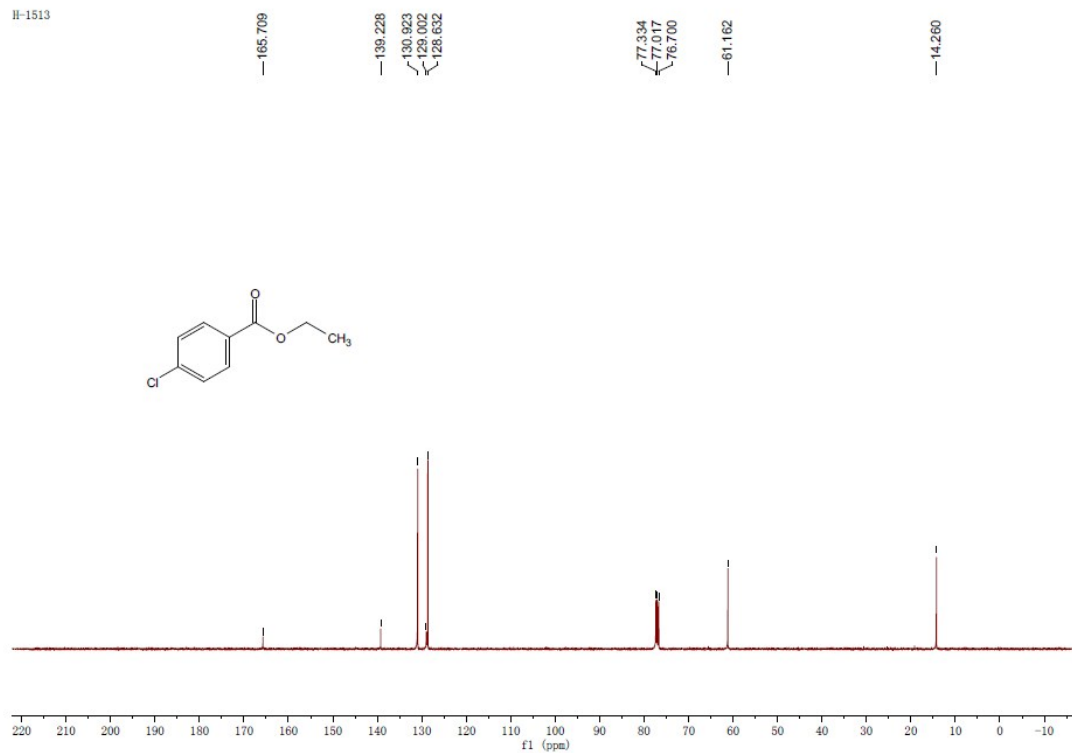


^1H NMR and ^{13}C NMR spectra of compound **2q**

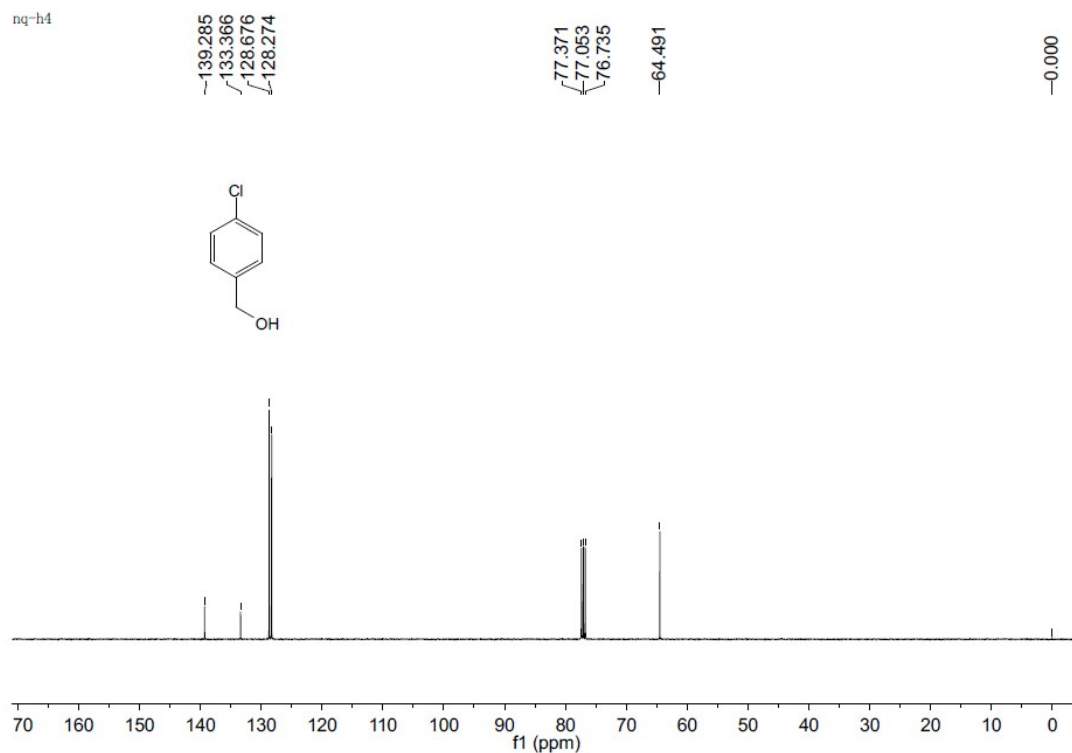
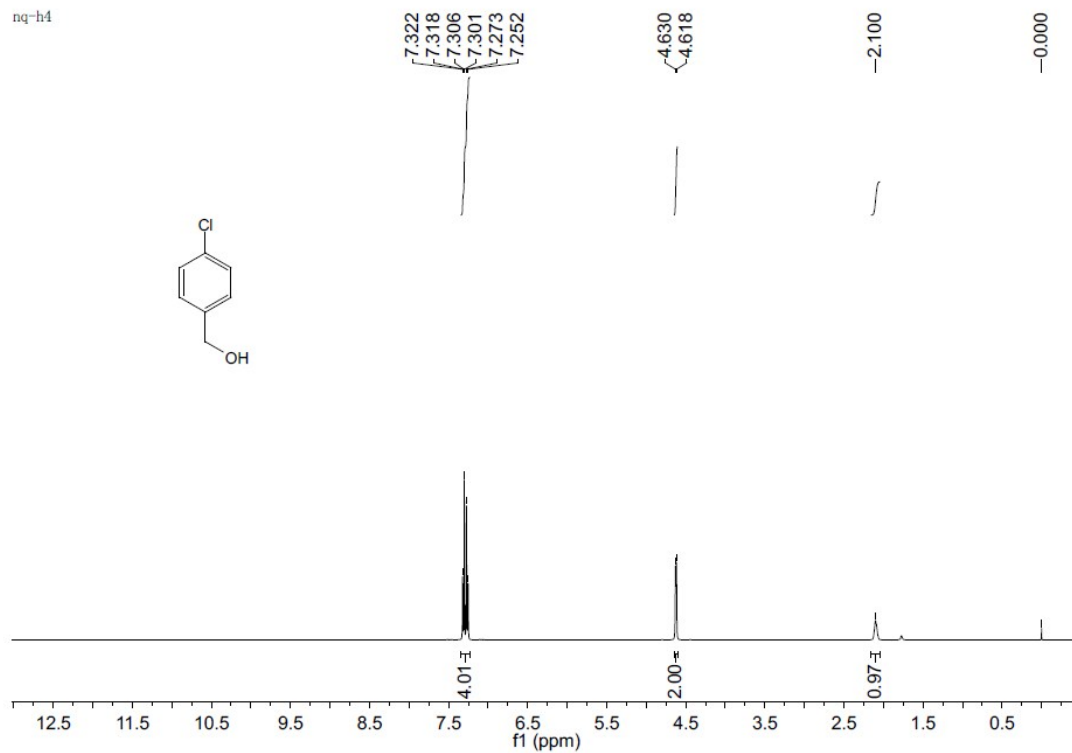
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H-1513



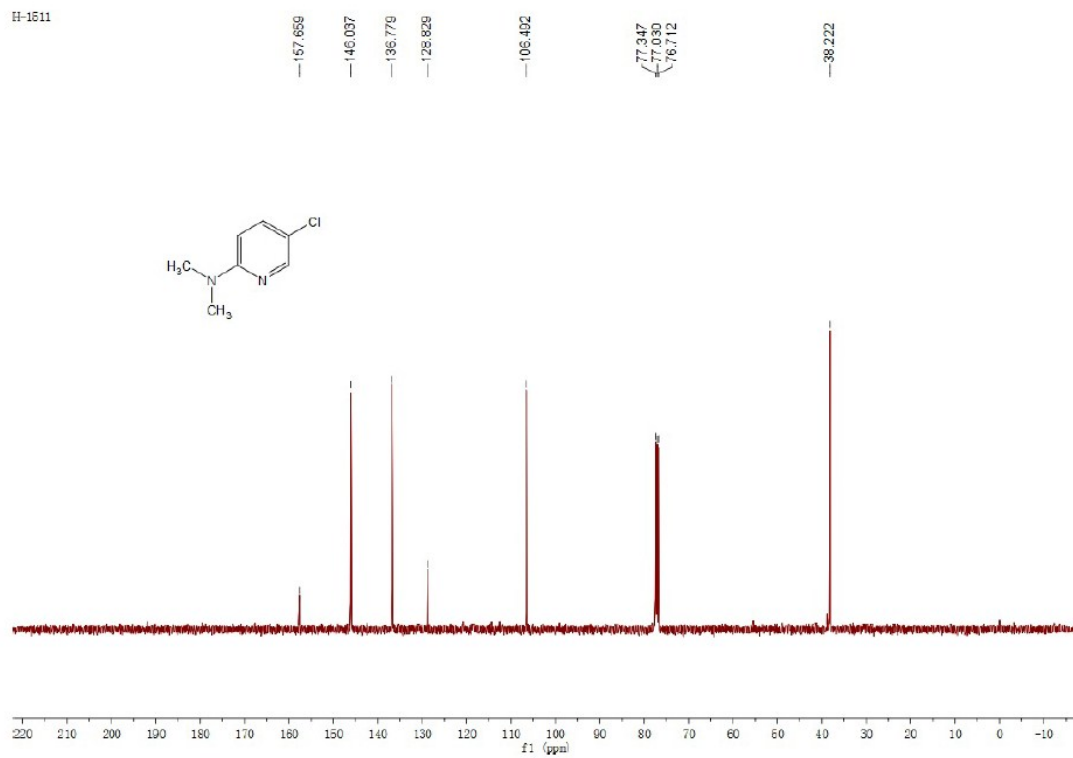
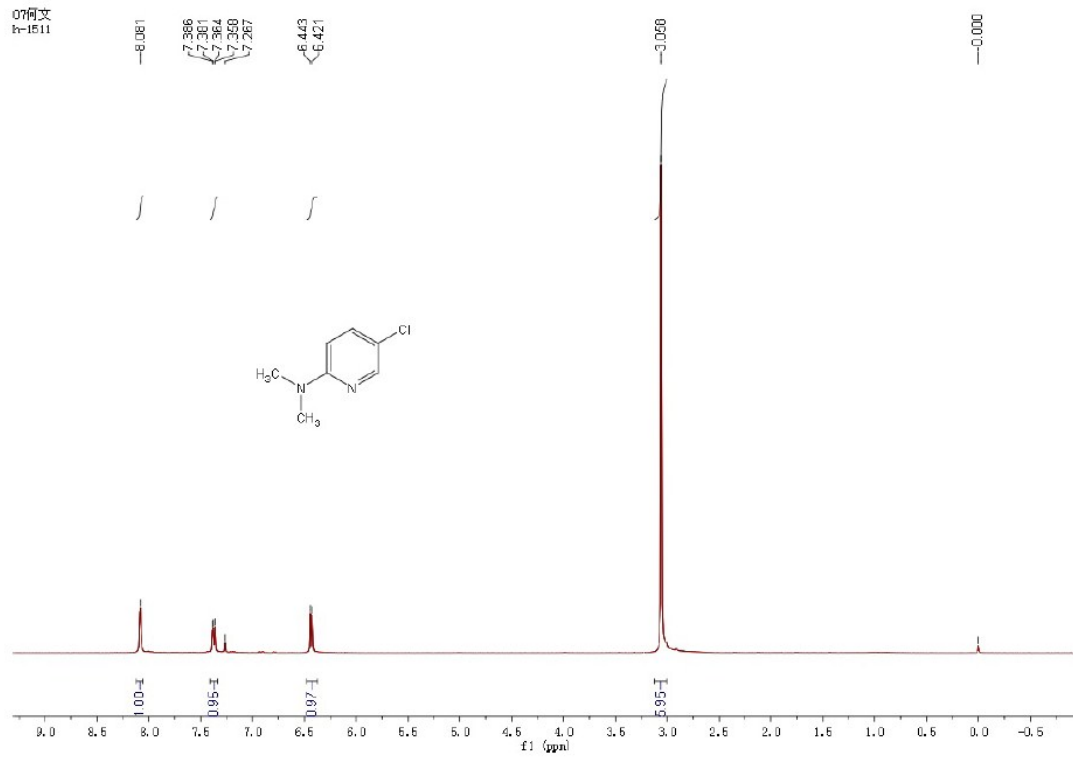
H-1513



¹H NMR and ¹³C NMR spectra of compound 2r



^1H NMR and ^{13}C NMR spectra of compound **2s**

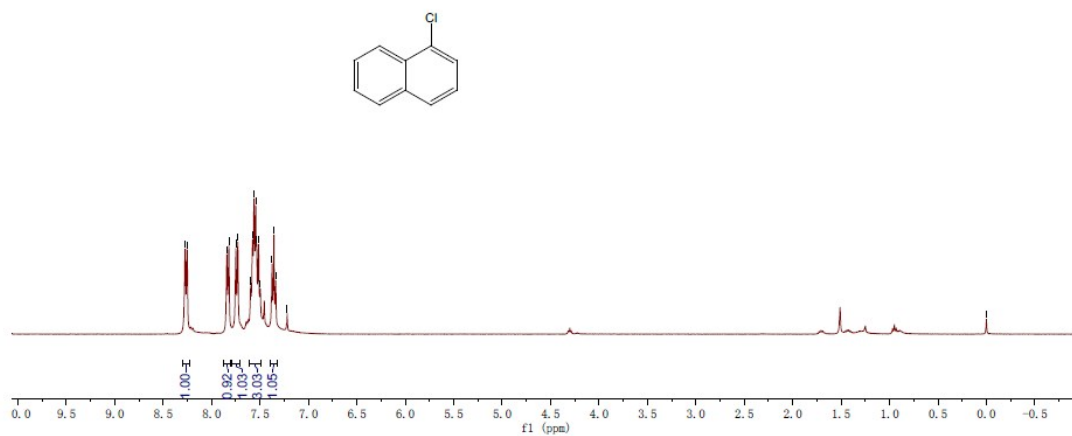


^1H NMR and ^{13}C NMR spectra of compound **2t**

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H-1520

8.273
8.252
7.842
7.822
7.749
7.729
7.595
7.578
7.544
7.537
7.516
7.498
7.376
7.356
7.337
7.220

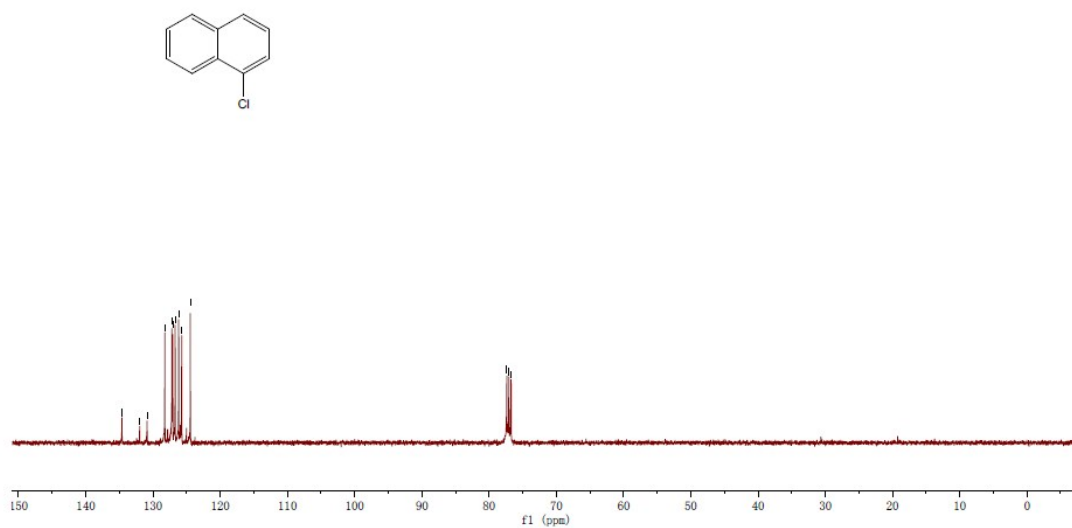
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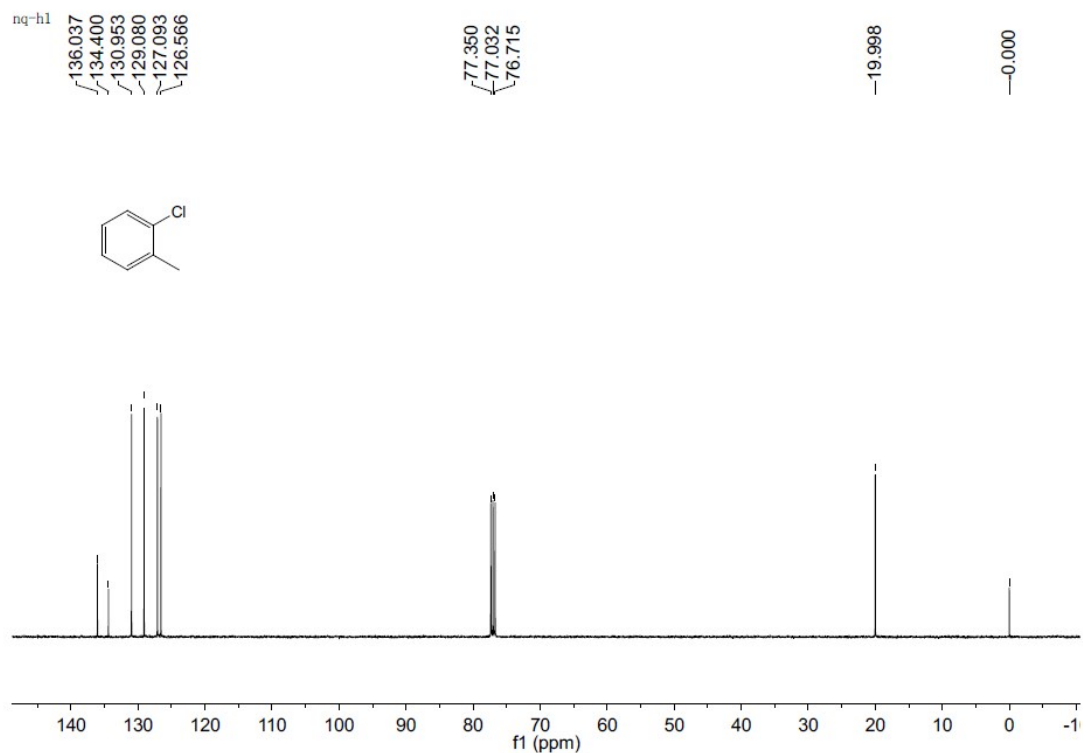
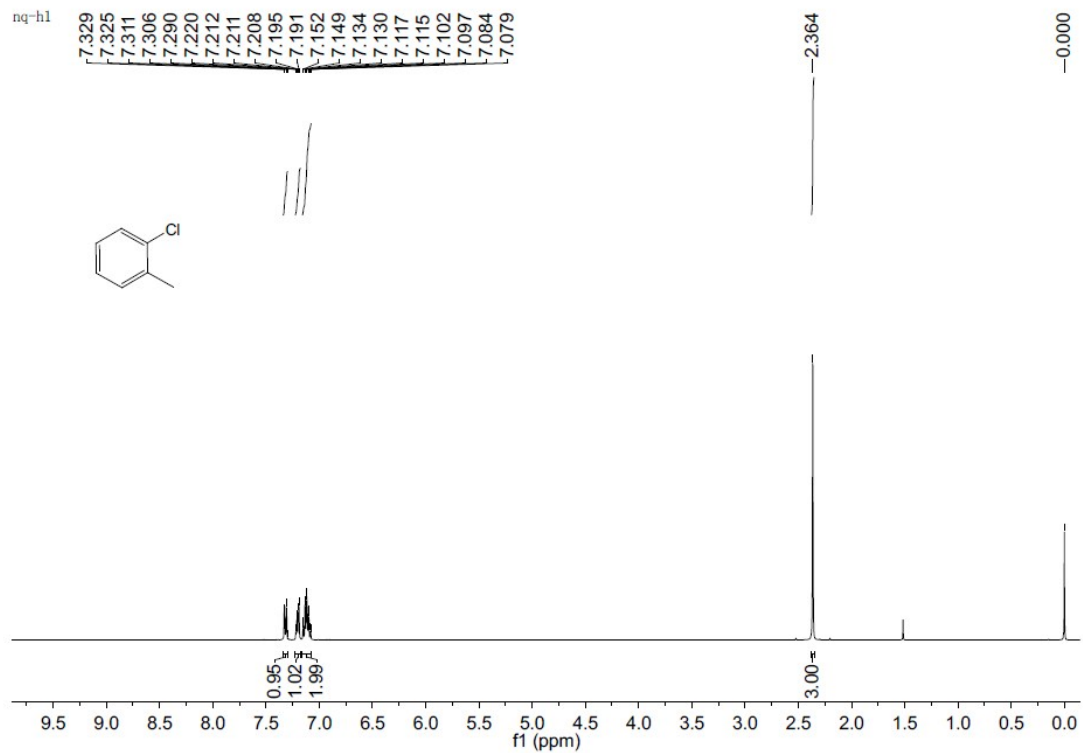
H-1520

134.623
131.982
130.877
128.236
127.178
127.052
126.698
126.176
125.724
124.444

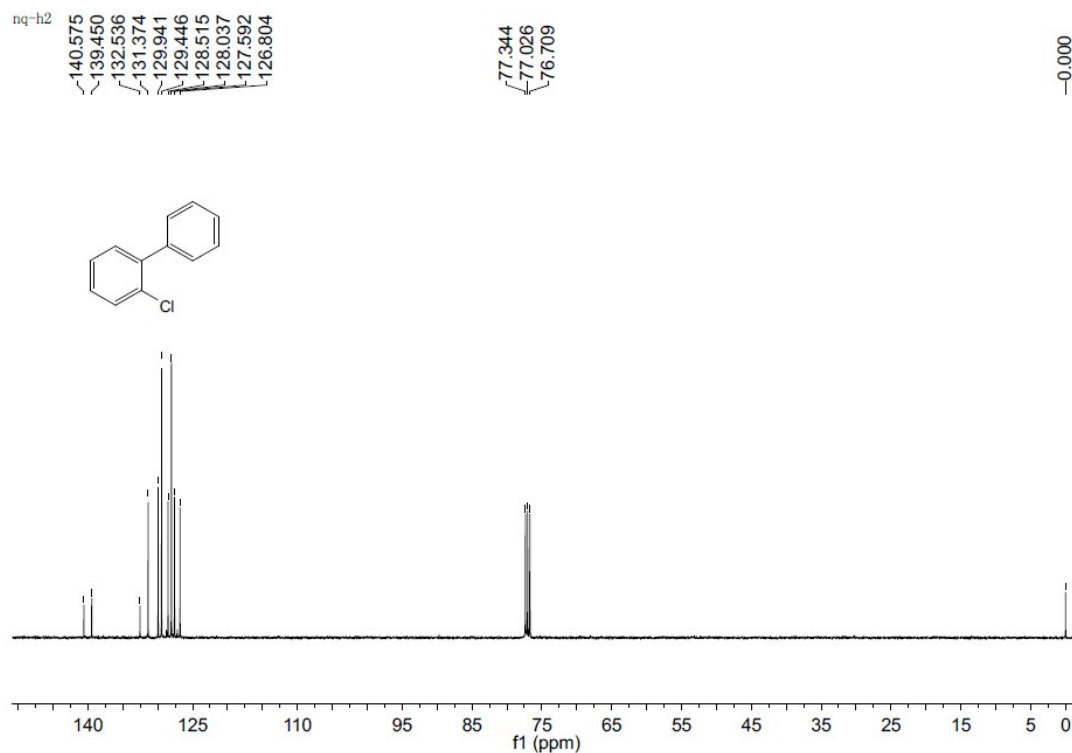
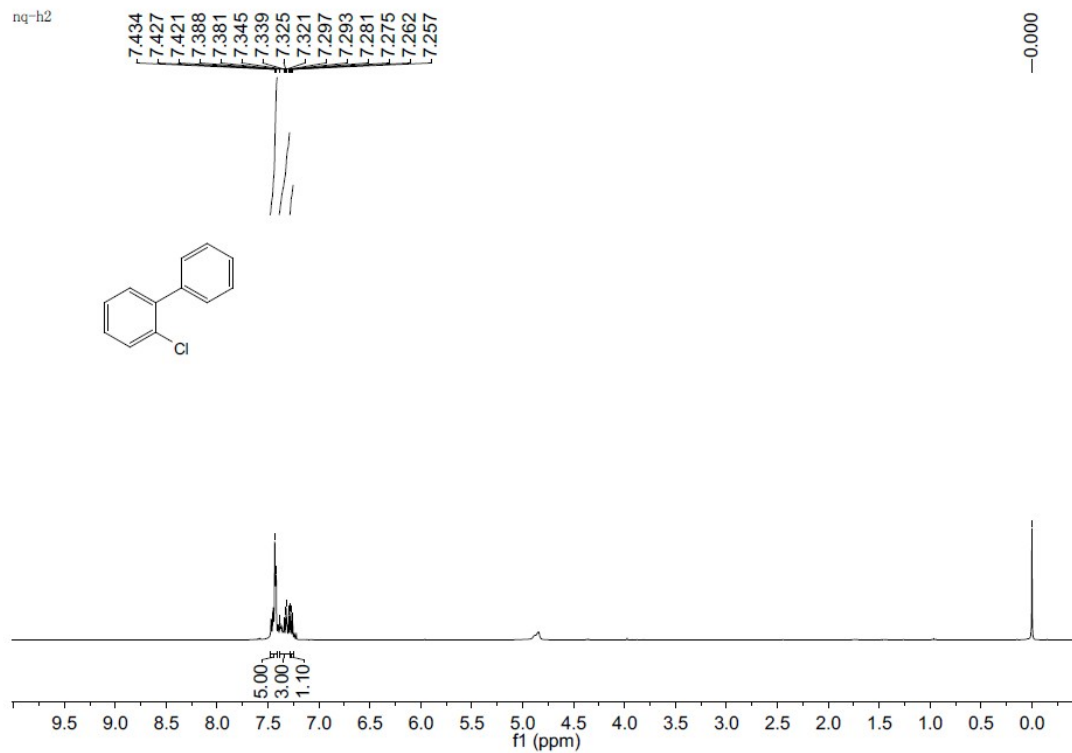
77.372
77.054
76.738



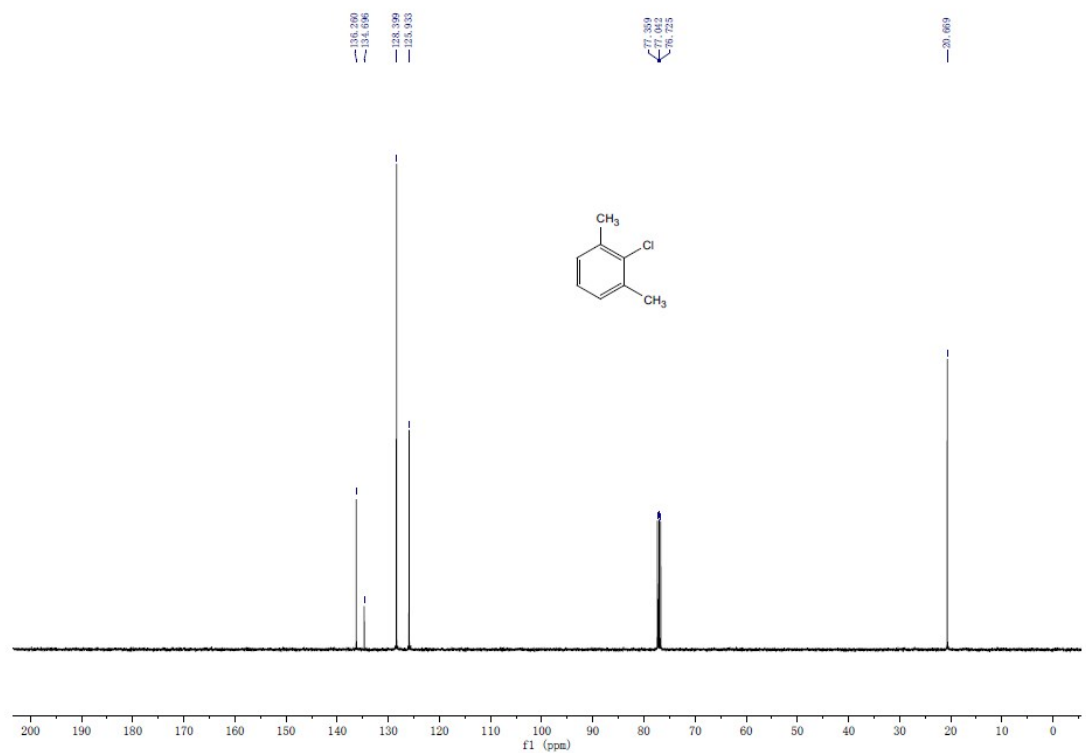
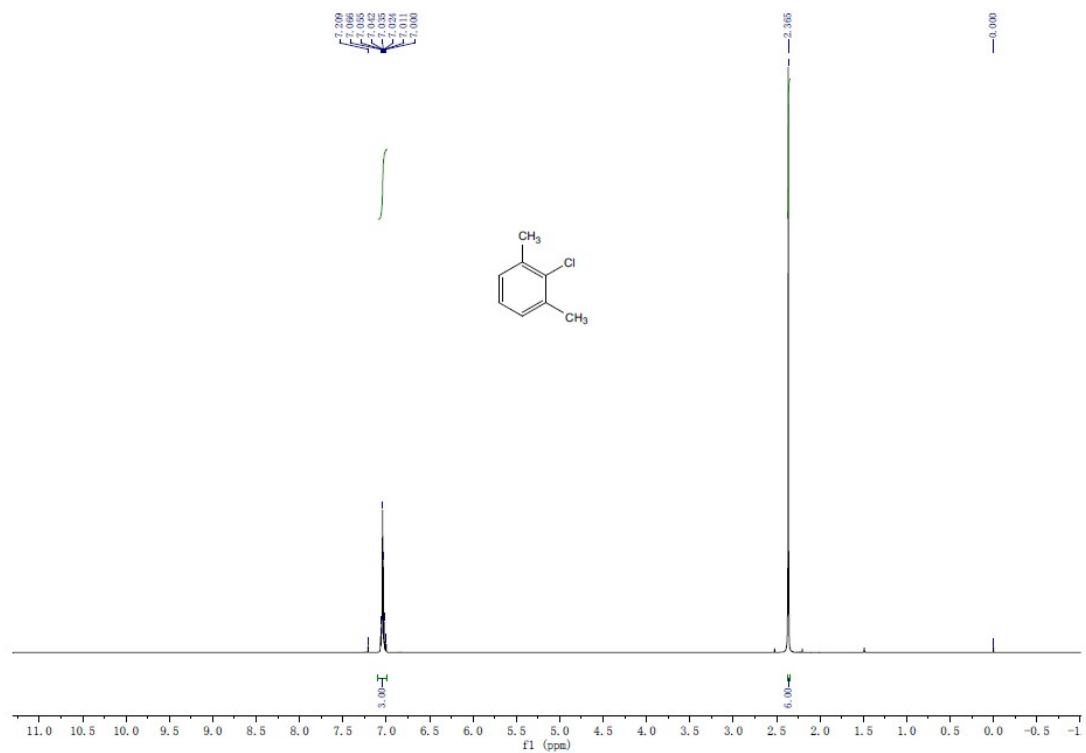
¹H NMR and ¹³C NMR spectra of compound **2u**



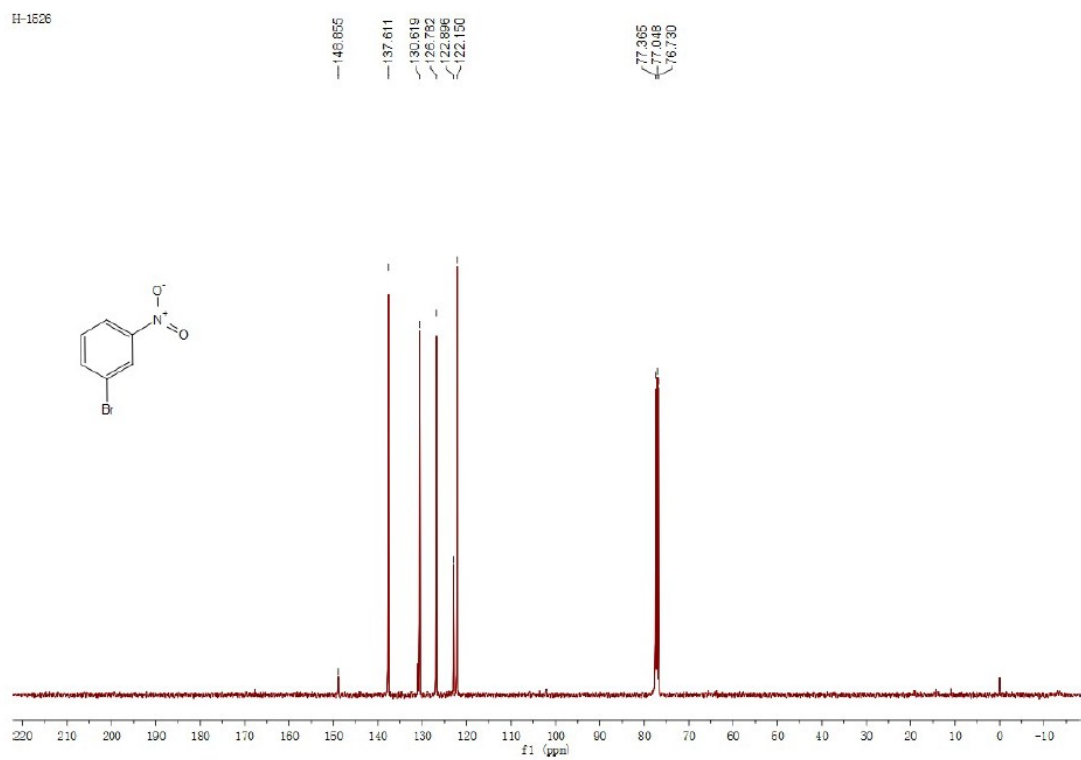
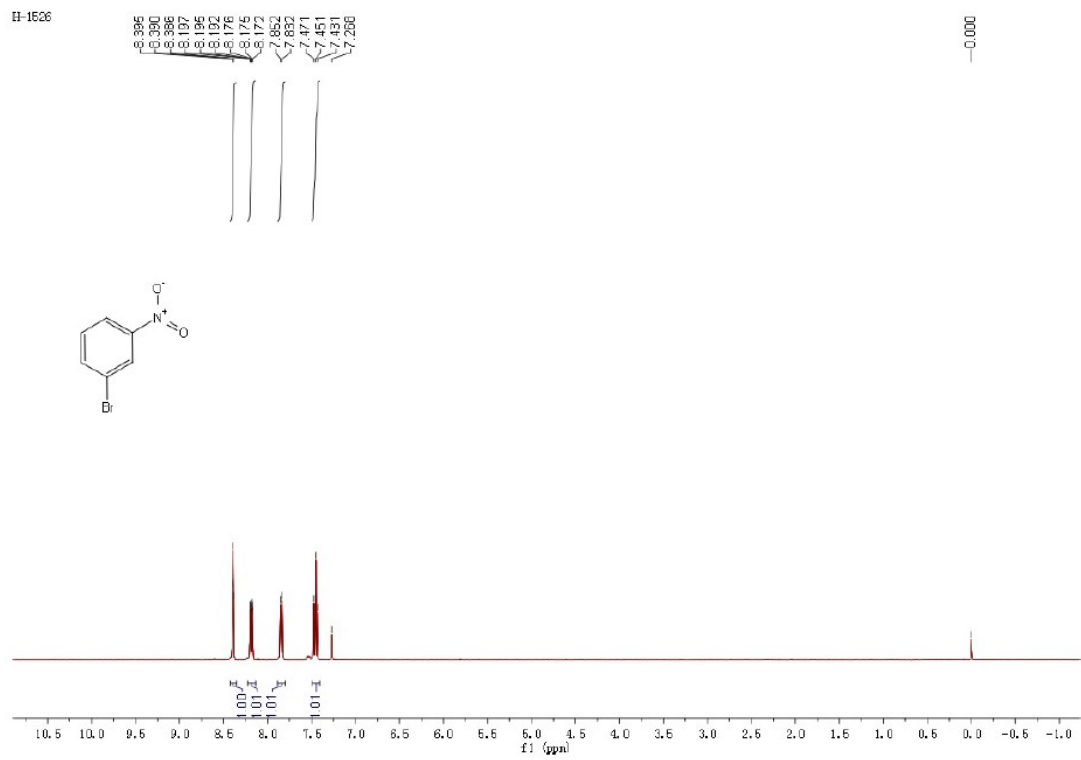
^1H NMR and ^{13}C NMR spectra of compound **2v**



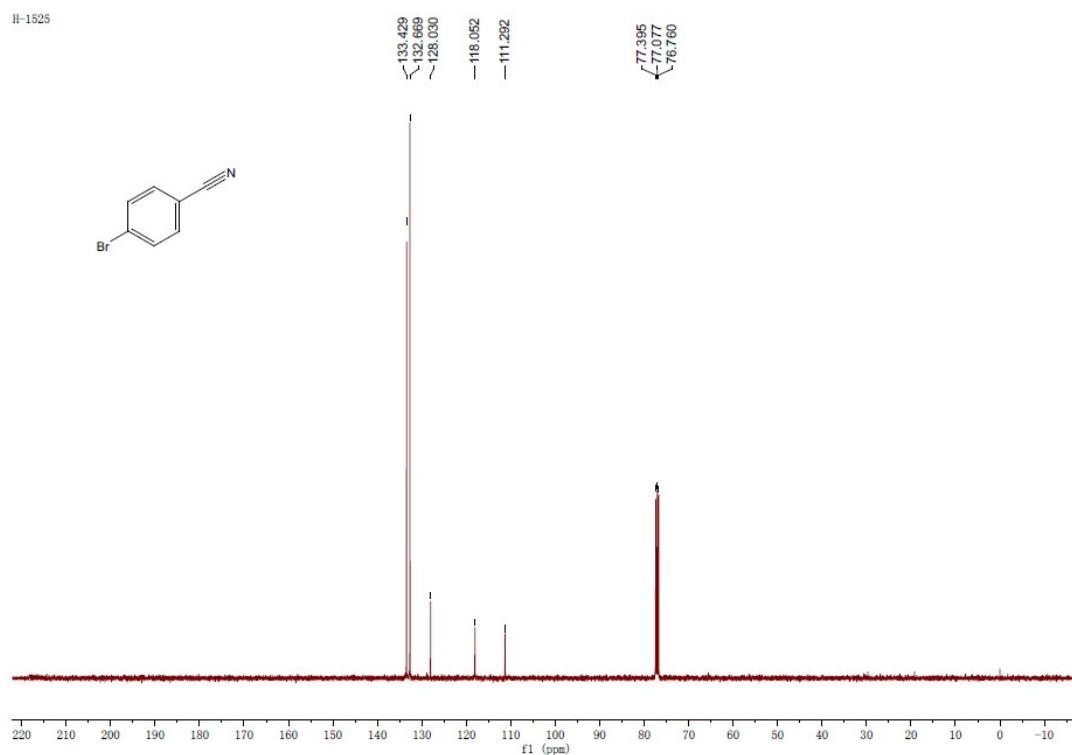
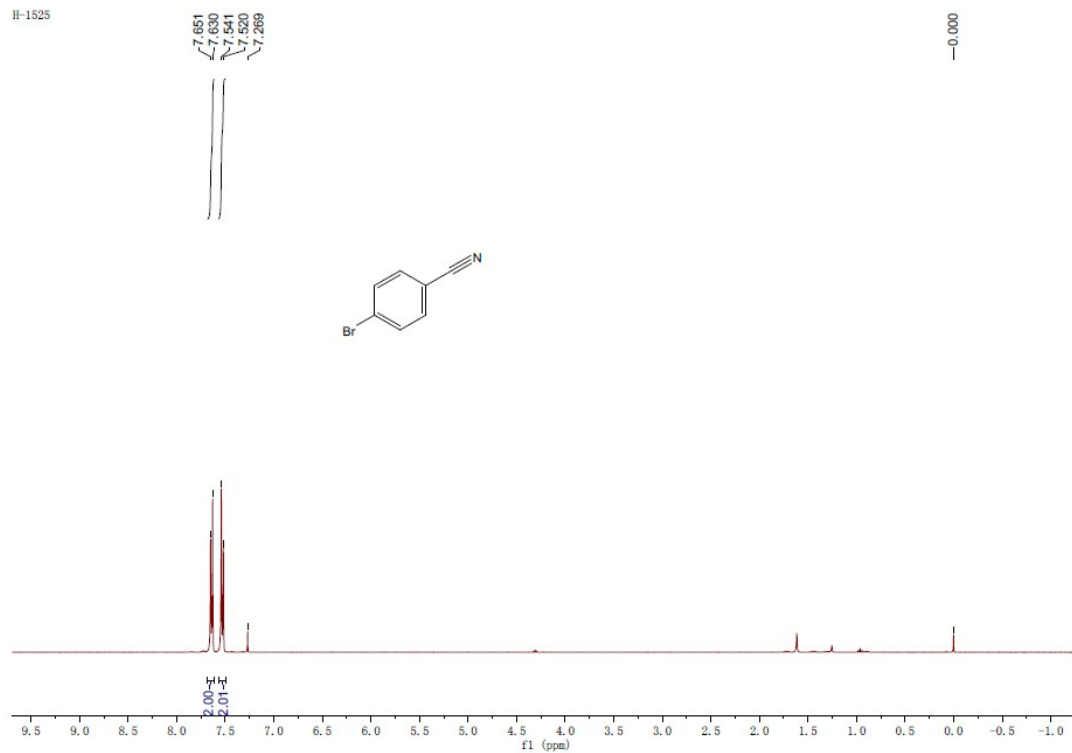
¹H NMR and ¹³C NMR spectra of compound **2w**



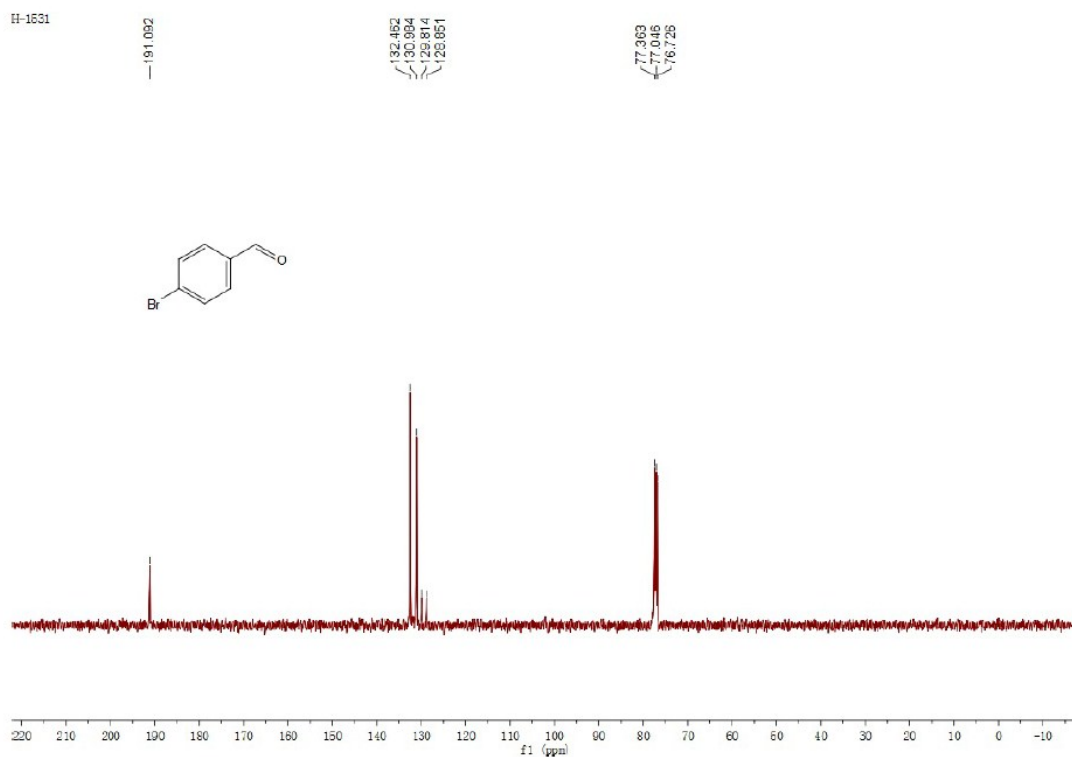
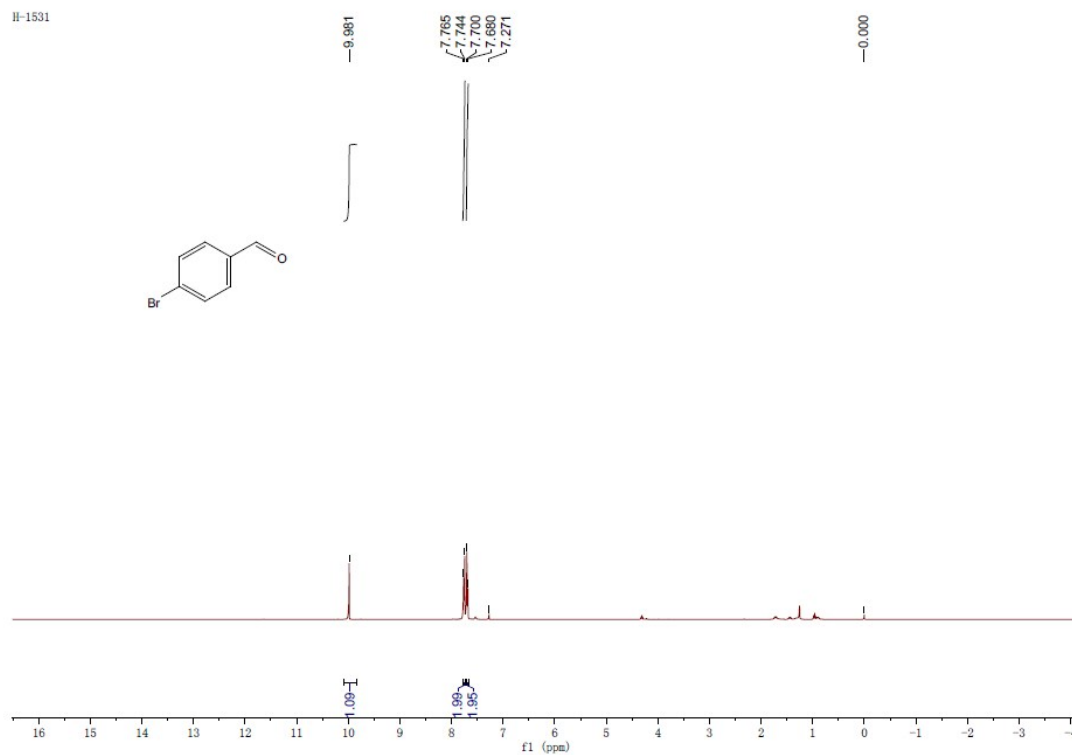
¹H NMR and ¹³C NMR spectra of compound **2x**



^1H NMR and ^{13}C NMR spectra of compound **3a**

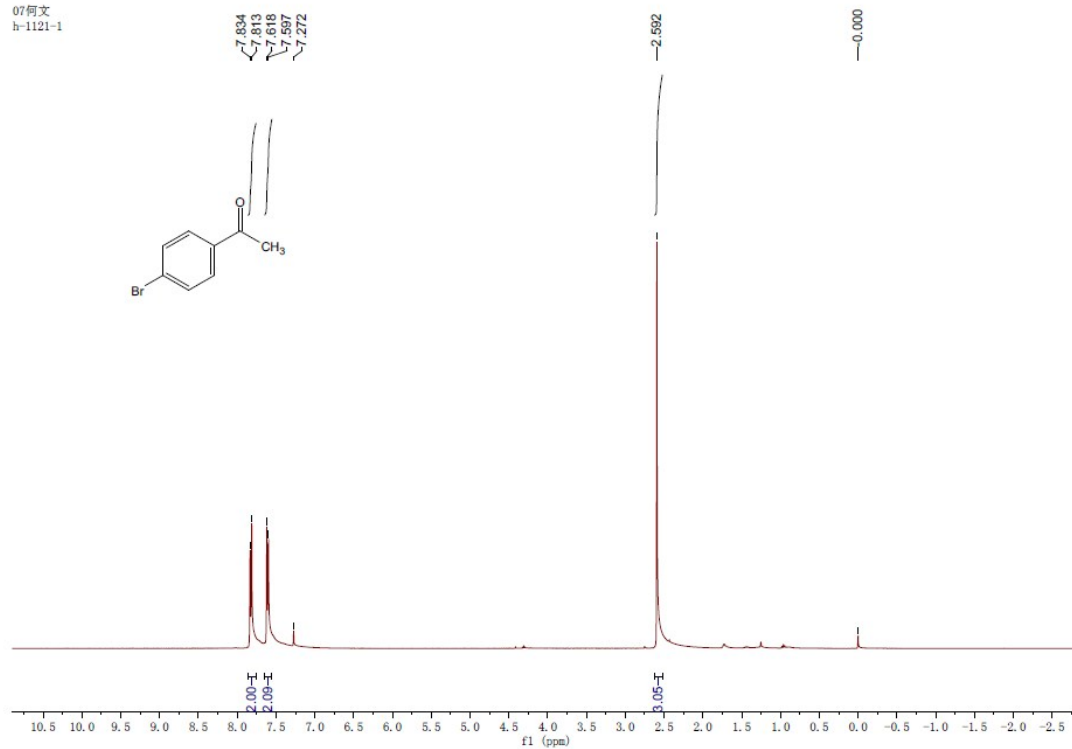


^1H NMR and ^{13}C NMR spectra of compound **3b**

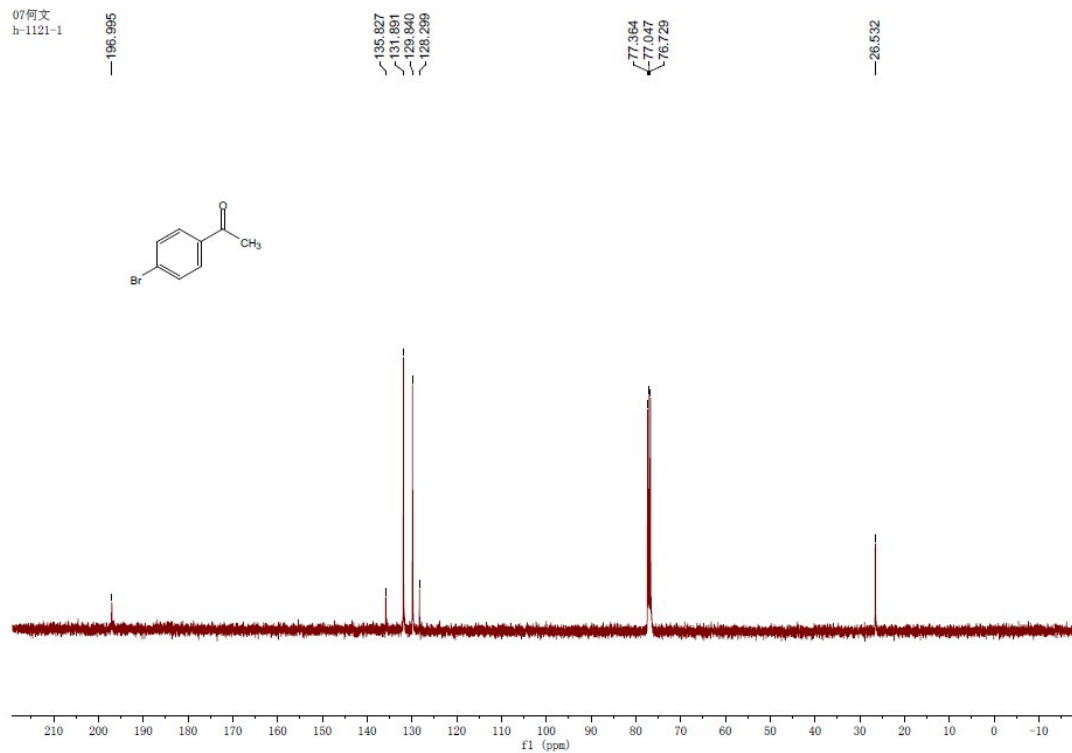


^1H NMR and ^{13}C NMR spectra of compound **3c**

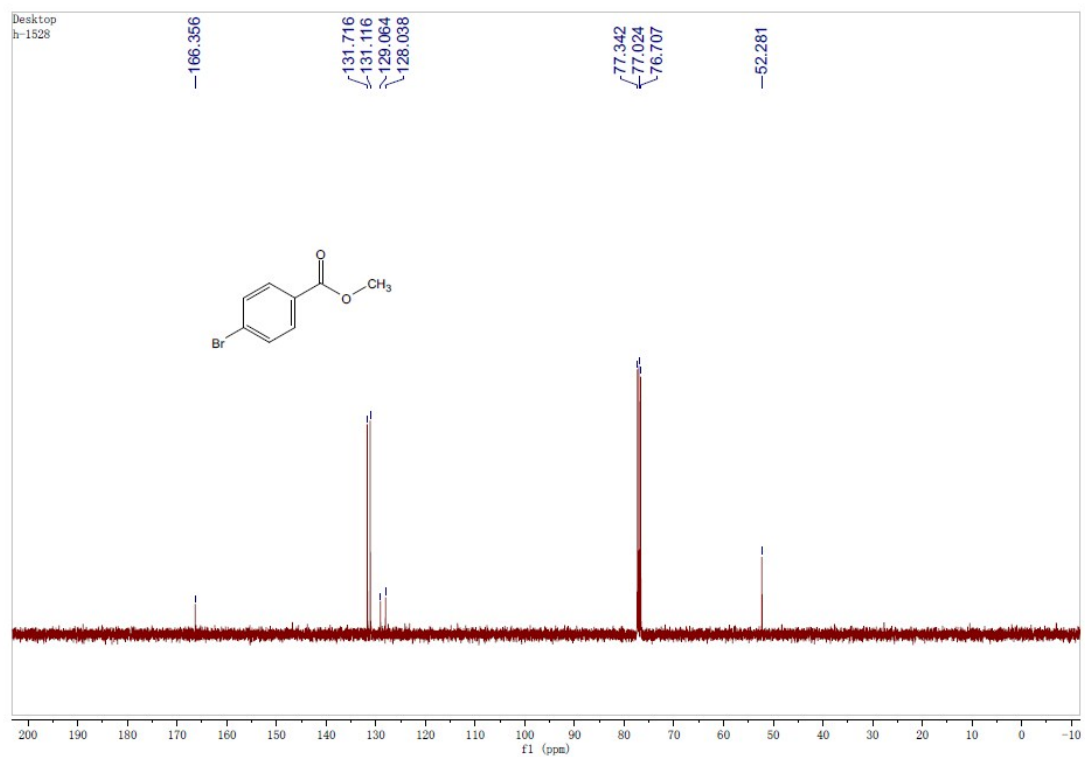
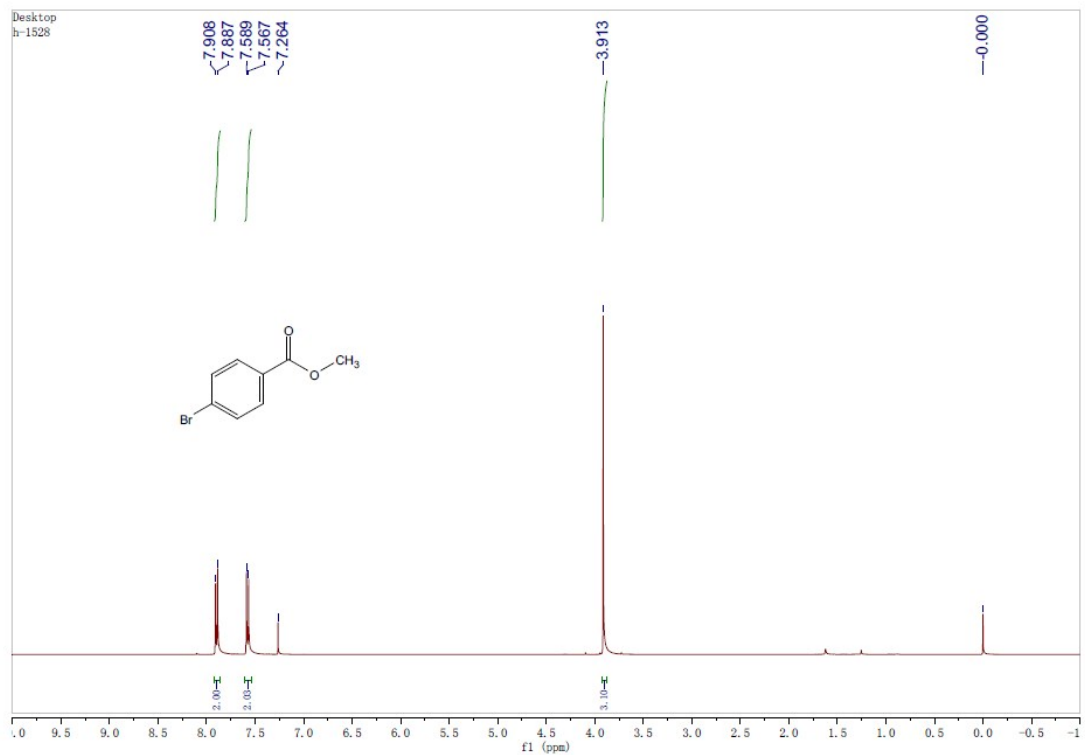
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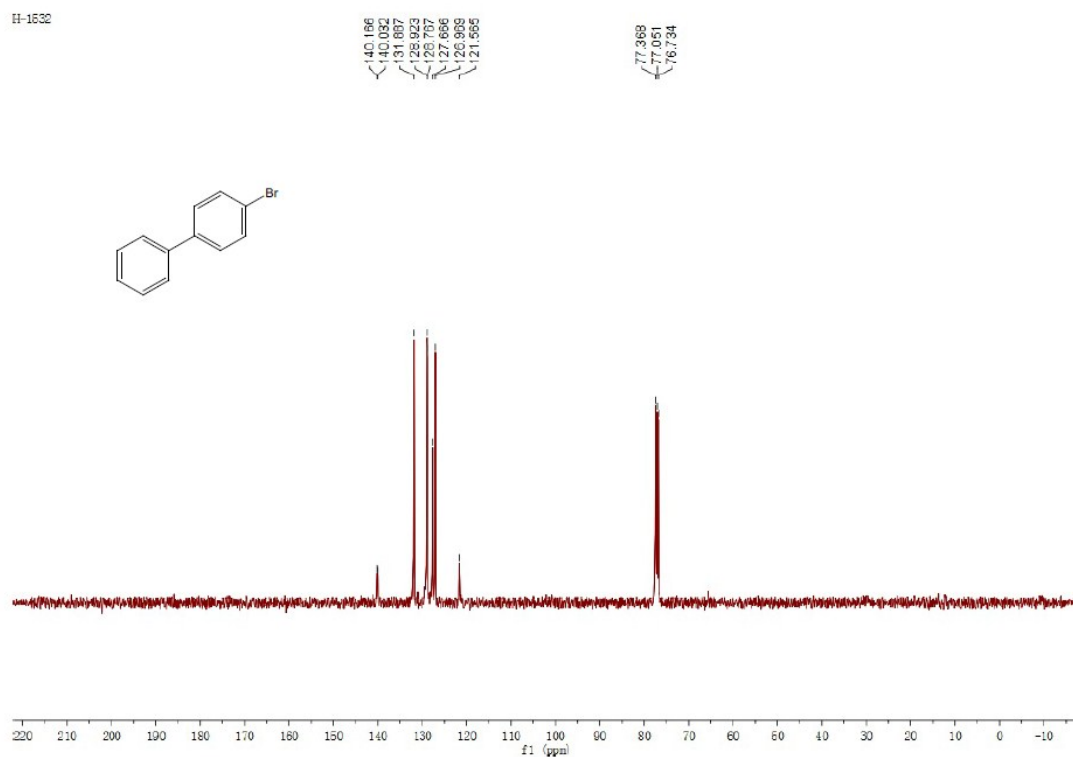
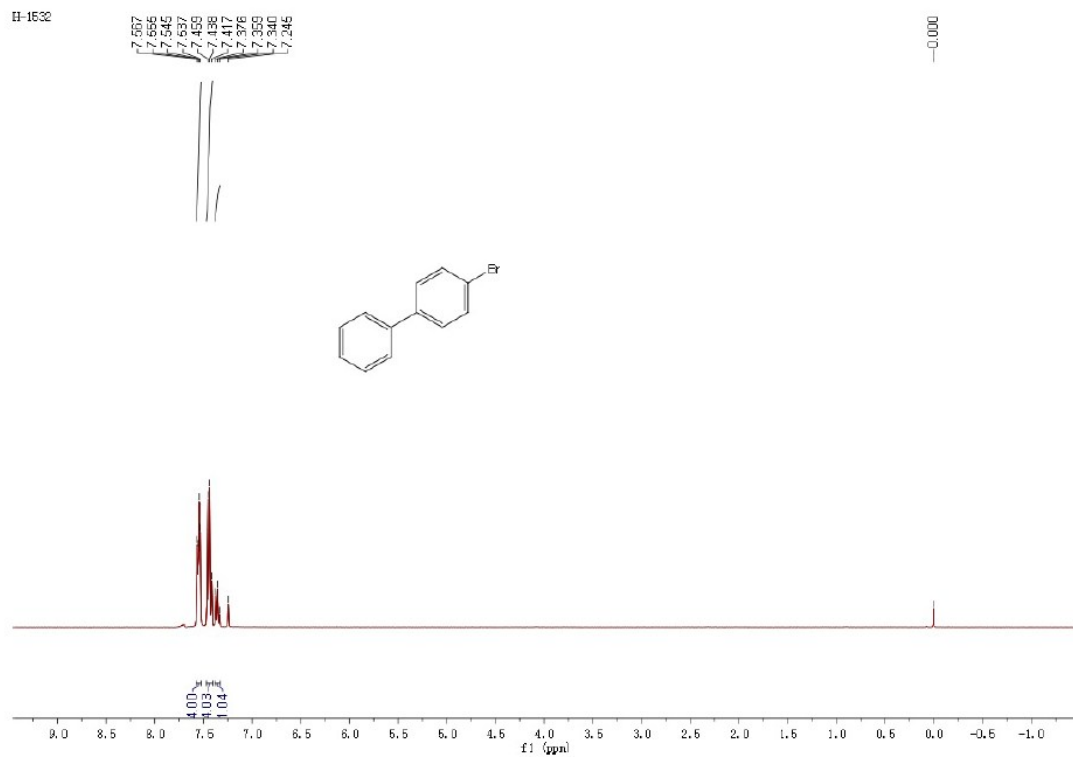
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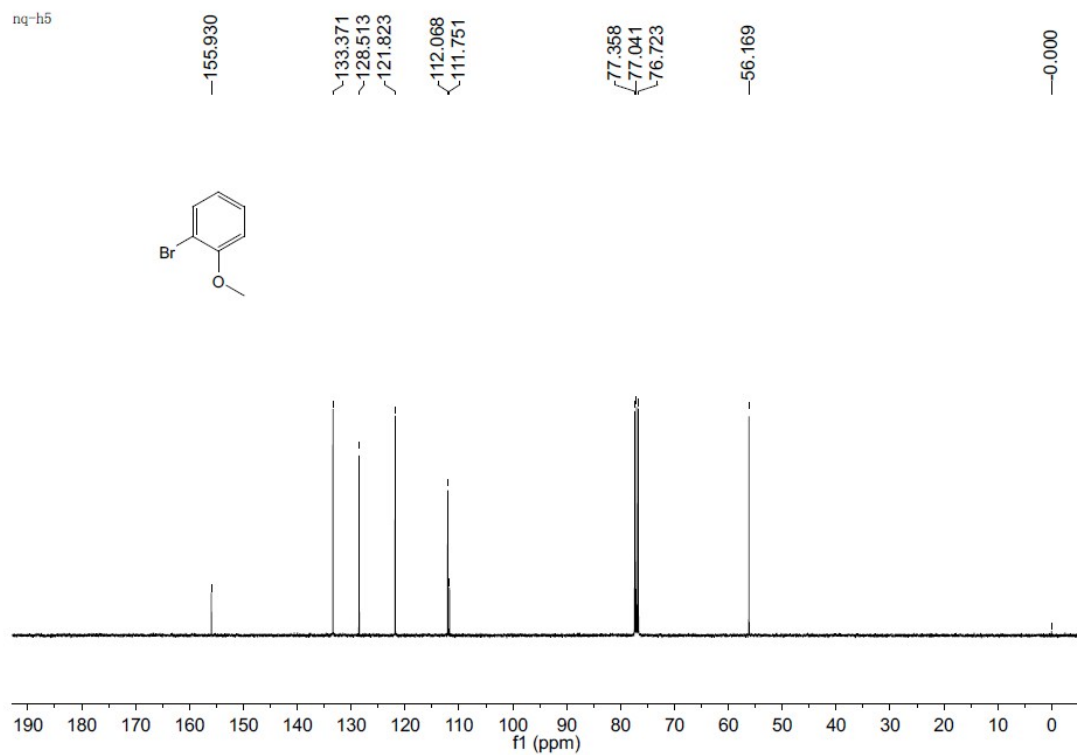
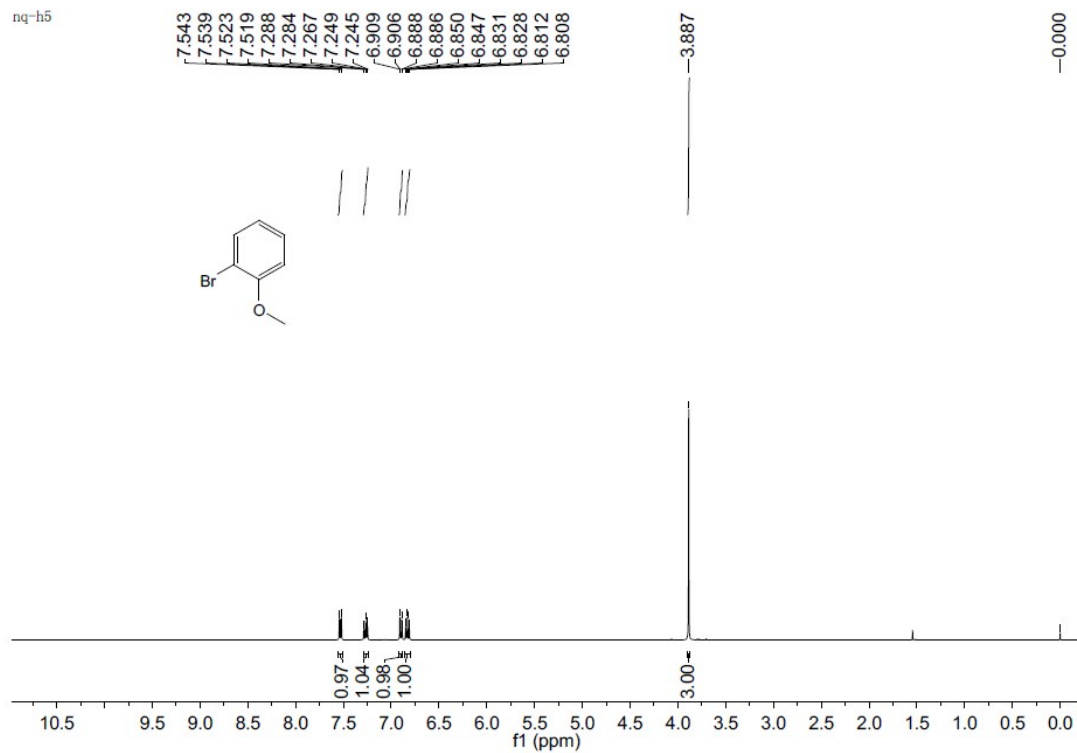
¹H NMR and ¹³C NMR spectra of compound **3d**



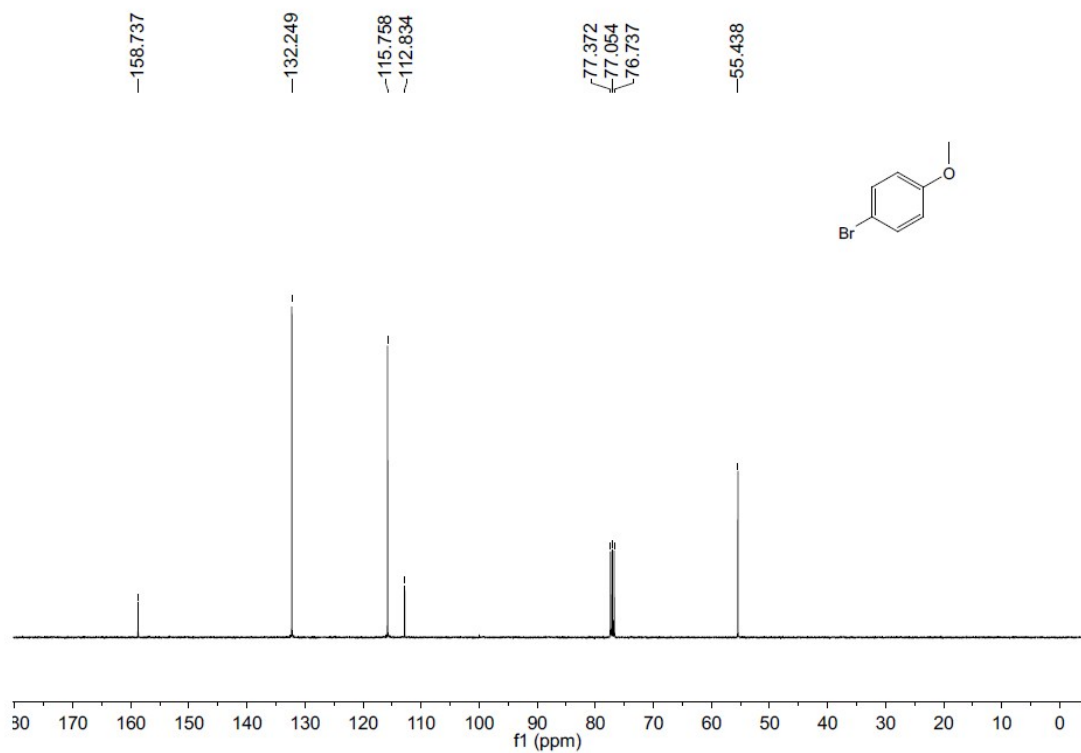
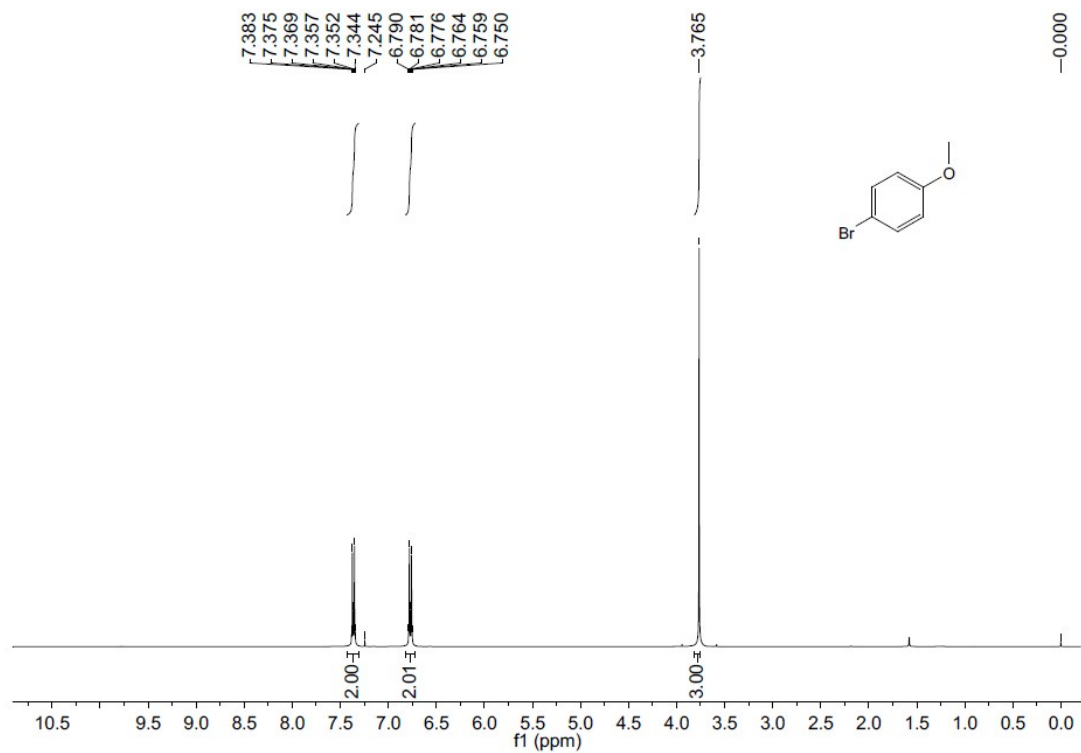
^1H NMR and ^{13}C NMR spectra of compound **3e**



¹H NMR and ¹³C NMR spectra of compound **3f**

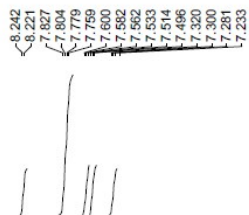


^1H NMR and ^{13}C NMR spectra of compound **3g**

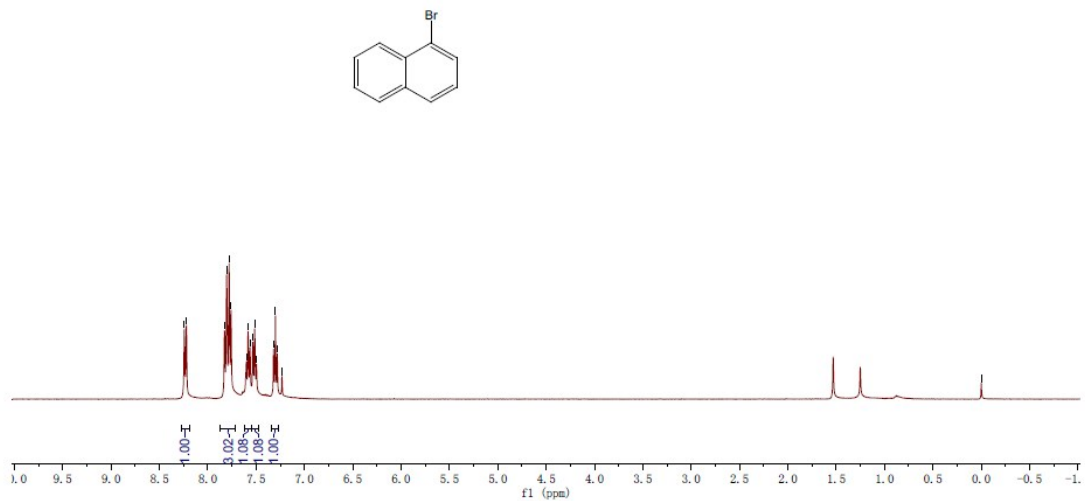


^1H NMR and ^{13}C NMR spectra of compound **3h**

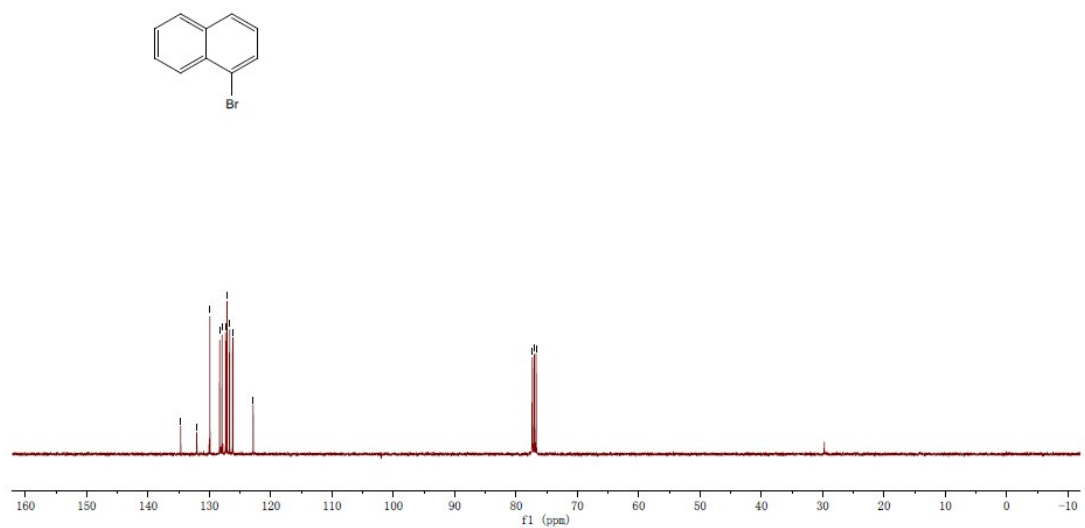
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¹H NMR and ¹³C NMR spectra of compound **3i**