Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

AIBN for Ru-catalyzed *meta*-C_{Ar}-H alkylation

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Supporting Information

1. General Information

All commercial reagents and solvents were used directly without additional purification. Column chromatography were performed on silica gel 200-300 mesh. ^{1}H NMR and ^{13}C NMR spectra were registered on a Bruker Ascend™ 400 spectrometer (Germany). Chemical shifts were reported in units (ppm) referenced to 0.0 ppm of TMS in the ^{1}H spectrum and 77.0 ppm of $CDCl_3$ in the ^{13}C spectrum. All coupling constants were reported in Hertz (Hz). HRMS data were obtained on a Waters LCT Premierxe™ (USA), Single-crystal X-ray crystallography was carried out on a Bruker Smart Apex II diffractometer system.

2. Experimental Section

2.1. Synthesis of arenes substrates

The pyridine derivatives were prepared via Suzuki coupling of the corresponding arylboronic acids and 2-bromopyridine according to literature report.[1]

The pyrimidine derivatives were prepared via Suzuki coupling of the corresponding arylboronic acids and 2-bromopyrimidine according to literature report.[2]

2.2. Typical experimental procedure of Ru(III)-catalyzed *meta*-C-H bond alkylation of arenes with AIBN

2-Phenylpyridine (0.2 mmol), AIBN (0.6 mmol, 3.0 equiv.), $RuCl_3$ (0.02 mmol, 10 mol %), dry DMF (0.5 mL) were charged into a pre-dried 30-mL pressure tube sealed with rubber plugs under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 12 h. The reaction was cooled down to room temperature, and saturated salt water (10 mL) was added. The resulting mixture was extracted with EtOAc (5 mL×5). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under reduced pressure to provide the crude product. The purification was performed by flash column chromatography (PE/EtOAc as eluent) on silica gel.

2.3. Typical experimental procedure of intermolecular competition experiments

2-(4-Methoxyphenyl)pyridine (0.2 mmol), 2-(4-fluorophenyl)pyridine (0.2 mmol), AIBN (0.2 mmol), $RuCl_3$ (0.02 mmol, 10 mol %), dry DMF (0.5 mL) were charged into a pre-dried 30-mL pressure tube sealed with rubber plugs under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 12 h. The reaction was cooled down to

room temperature, and saturated salt water (10 mL) was added. The resulting mixture was extracted with EtOAc (5 mL×5). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under reduced pressure to provide the crude product. The purification was performed by flash column chromatography (PE/EtOAc as eluent) on silica gel.

2-Phenylpyridine (0.2 mmol), AIBN (0.2 mmol, 1.0 equiv.), 2,2'-azobis-(2,4-dimethylvaleronitrile) (0.2 mmol, 1.0 equiv.), $RuCl_3$ (0.02 mmol, 10 mol %), dry DMF (0.5 mL) were charged into a pre-dried 30-mL pressure tube sealed with rubber plugs under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 12 h. The reaction was cooled down to room temperature, and saturated salt water (10 mL) was added. The resulting mixture was extracted with EtOAc (5 mL×5). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under reduced pressure to provide the crude product. The purification was performed by flash column chromatography (PE/EtOAc as eluent) on silica gel.

3. References

1. C. Liu, N. Han, X. X. X. Song, J. S. Qiu, Eur. J. Org. Chem. 2010, 29, 5548–5551.

2. M. A. Ali, X. Y. Yao, G. G. Li, H. J. Lu, Org. Lett. 2016, 186, 1386-1389

4. Data and Spectra of ^{1}H NMR and ^{13}C NMR

2-methyl-2-(3-(pyridin-2-yl)phenyl)propanenitrile (**3a**, colorless oil, PE/EtOAc = 3:1 as eluent, 32.3 mg, 73% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.8 Hz, 1H), 8.13 (t, *J* = 1.6 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.81–7.67 (m, 2H), 7.59–7.45 (m, 2H), 7.28–7.24 (m, 1H), 1.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.78, 149.74, 142.03, 140.18, 136.91, 129.35, 126.38, 125.77, 124.55, 123.65, 122.49, 120.78, 37.34, 29.18. HRMS (ESI) Calcd. For $C_{15}H_{15}N_2$: $[M+H]^+$, 223.1230, Found: m/z 223.1234.

2-methyl-2-(2-methyl-5-(pyridin-2-yl)phenyl)propanenitrile (**3b**, colorless oil, PE/EtOAc = 3:1 as eluent, 26.9 mg, 57% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.7 Hz, 1H), 8.04 (s, 1H), 7.78 (m, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.27–7.22 (m, 1H), 2.72 (s, 3H), 1.89 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.94, 149.69, 138.56, 137.66, 137.24, 136.83, 133.15, 126.20, 124.52, 123.56, 122.18, 120.42, 35.10, 28.24, 20.98. HRMS (ESI) Calcd. For $C_{16}H_{17}N_2$:

$[M+H]^+$, 237.1386, Found: m/z 237.1388.

2-methyl-2-(4-(pyridin-2-yl)-[1,1'-biphenyl]-2-yl)propanenitrile (**3c**, colorless oil, PE/EtOAc = 3:1 as eluent, 31 mg, 52% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.2 Hz, 1H), 8.29 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 6.4 Hz, 2H), 7.48–7.36 (m, 6H), 7.32 (d, *J* = 6.3 Hz, 1H), 1.71 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.67, 149.76, 141.18, 138.33, 137.07, 133.38, 130.04, 128.71, 127.83 (d), 126.67, 125.64, 125.18, 122.56, 120.84, 115.75, 37.22, 29.98. HRMS (ESI) Calcd. For $C_{21}H_{19}N_2$: $[M+H]^+$, 299.1543, Found: m/z 299.1544.

2-(2-chloro-5-(pyridin-2-yl)phenyl)-2-methylpropanenitrile (**3d**, colorless oil, PE/EtOAc = 3:1 as eluent, 23.6 mg, 46% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.1 Hz, 1H), 8.21 (d, *J* = 2.1 Hz, 1H), 7.87 (m, 1H), 7.79 (m, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.32–7.28 (m, 1H), 1.96 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.71, 149.86, 138.45, 137.41, 136.93, 134.02, 132.18, 127.47, 125.77, 123.22, 122.65, 120.40, 36.73, 27.27. HRMS (ESI) Calcd. For $C_{15}H_{14}ClN_2$: $[M+H]^+$, 257.0840, Found: m/z 257.0843.

2-(2-bromo-5-(pyridin-2-yl)phenyl)-2-methylpropanenitrile (**3e**, colorless oil, PE/EtOAc = 3:1 as eluent, 28.2 mg, 47% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.8 Hz, 1H), 8.20 (s, 1H), 7.86–7.68 (m, 4H), 7.37–7.28 (m, 1H), 1.98 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.72, 149.87, 139.16, 138.67, 137.04, 135.91, 127.64, 125.93, 123.38 (d), 122.78, 120.47, 37.47, 27.56. HRMS (ESI) Calcd. For $C_{15}H_{14}BrN_2$: $[M+H]^+$, 301.0335, Found: m/z 301.0330.

2-(2-fluoro-5-(pyridin-2-yl)phenyl)-2-methylpropanenitrile (**3f**, colorless oil, PE/EtOAc = 3:1 as eluent, 20.6 mg, 43% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.8 Hz, 1H), 8.16 (m, 1H), 7.95 (m, 1H), 7.78 (m, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.28–7.18 (m, 2H), 1.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.18, 160.15, 155.92, 149.77, 136.93, 136.13, 128.43 (d), 125.96 (d), 123.51, 122.37, 120.38, 117.24, 117.01, 35.14, 27.22(d). HRMS (ESI) Calcd. For $C_{15}H_{14}FN_2$: $[M+H]^+$, 241.1136, Found: m/z 241.1132.

2-(2-methoxy-5-(pyridin-2-yl)phenyl)-2-methylpropanenitrile (**3g**, colorless oil, PE/EtOAc = 3:1 as eluent, 34.3 mg, 68% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70–8.61 (m, 1H), 8.05 (d, *J* = 2.2 Hz, 1H), 7.92 (m, 1H), 7.71 (m, 2H), 7.19 (m, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 3.98 (s, 3H), 1.84 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.09,

156.74, 149.61, 136.78, 132.10, 129.02, 127.82, 124.74(d), 121.71, 119.97, 112.08, 55.73, 34.46, 27.03. HRMS (ESI) Calcd. For $C_{16}H_{17}N_2O$: $[M+H]^+$, 253.1335, Found: m/z 253.1331.

2-methyl-2-(3-(4-methylpyridin-2-yl)phenyl)propanenitrile (**3h**, colorless oil, PE/EtOAc = 3:1 as eluent, 30.2 mg, 64% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.0 Hz, 1H), 8.10 (t, *J* = 1.6 Hz, 1H), 7.90 (m, 1H), 7.65–7.43 (m, 3H), 7.10 (d, *J* = 4.9 Hz, 1H), 2.44 (s, 3H), 1.81 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.73, 149.51, 147.99, 141.92, 140.35, 129.30, 126.44, 125.63, 124.62, 123.59 (d), 121.76, 37.35, 29.21, 21.27. HRMS (ESI) Calcd. For $C_{16}H_{17}N_2$: $[M+H]^+$, 237.1386, Found: m/z 237.1383.

2-methyl-2-(3-(5-methylpyridin-2-yl)phenyl)propanenitrile (**3i**, colorless oil, PE/EtOAc = 3:1 as eluent, 33.5 mg, 71% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.10 (d, *J* = 1.6 Hz, 1H), 7.88 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.58 (m, 1H), 7.51 (m, 2H), 2.38 (s, 3H), 1.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.12, 150.17, 141.94, 140.20, 137.44, 132.08, 129.31, 126.16, 125.42, 124.62, 123.39, 120.27, 37.35, 29.20, 18.22. HRMS (ESI) Calcd. For $C_{16}H_{17}N_2$: $[M+H]^+$, 237.1386, Found: m/z 237.1384.

2-(3-(1H-pyrazol-1-yl)phenyl)-2-methylpropanenitrile (**3j**, colorless oil, PE/EtOAc = 3:1 as eluent, 19.4 mg, 46% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.4 Hz, 1H), 7.86 (s, 1H), 7.76 (d, *J* = 1.3 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.48 (m, 2H), 6.51 (t, *J* = 2.0 Hz, 1H), 1.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.17, 141.40, 140.78, 130.07, 126.93, 124.25, 123.31, 118.43, 116.16, 107.98, 37.30, 29.10. HRMS (ESI) Calcd. For $C_{13}H_{14}N_3$: $[M+H]^+$, 212.1182, Found: m/z 212.1185.

2-methyl-2-(3-(pyrimidin-2-yl)phenyl)propanenitrile (**3k**, colorless oil, PE/EtOAc = 3:1 as eluent, 30.3 mg, 68% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.8 Hz, 2H), 8.58 (s, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 7.66 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 4.8 Hz, 1H), 1.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.10, 157.31, 141.92, 138.33, 129.27, 127.69 (d), 124.58 (d), 119.43, 37.30, 29.19. HRMS (ESI) Calcd. For $C_{14}H_{14}N_3$: $[M+H]^+$, 224.1182, Found: m/z 224.1187.

2-methyl-2-(2-methyl-5-(pyrimidin-2-yl)phenyl)propanenitrile (**3l**, colorless oil, PE/EtOAc = 3:1 as eluent, 26.1 mg, 55% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.8 Hz, 2H), 8.46 (d, *J* = 1.4 Hz, 1H), 8.31 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H),

7.21 (t, J = 4.8 Hz, 1H), 2.74 (s, 3H), 1.90 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.53, 157.24, 139.36, 138.42, 135.86, 133.13, 127.61, 124.54 (d), 119.10, 34.98, 28.31, 21.15. HRMS (ESI) Calcd. For $C_{15}H_{16}N_3$: $[M+H]^+$, 238.1339, Found: m/z 238.1336.

2-methyl-2-(3-(pyrimidin-2-yl)naphthalen-1-yl)propanenitrile (**3m**, white solid, PE/EtOAc = 3:1 as eluent, 30.6 mg, 56% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.88 (d, J = 4.8 Hz, 2H), 8.62 (m, 2H), 8.09 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.3 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.26 (t, J = 5.4 Hz, 1H), 2.09 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.17, 157.37, 136.26, 134.65, 133.89, 131.40, 130.94, 129.91, 127.70, 126.27, 125.07, 124.57, 122.07, 119.38, 34.70, 28.91. HRMS (ESI) Calcd. For $C_{18}H_{16}N_3$: $[M+H]^+$, 274.1339, Found: m/z 274.1332.

2-methyl-2-(3-(pyridin-2-yl)naphthalen-1-yl)propanenitrile (**3n**, colorless oil, PE/EtOAc = 3:1 as eluent, 28.3 mg, 52% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 4.7 Hz, 1H), 8.59 (d, J = 8.6 Hz, 1H), 8.41 (s, 1H), 8.29 (d, J = 1.4 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.82 (m, 1H), 7.67 (m, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.36–7.26 (m, 1H), 2.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.80, 149.82, 136.94, 136.46, 135.83, 134.80, 130.30, 127.57, 127.00, 126.25, 125.03, 124.56, 122.44, 121.94, 120.83, 34.81, 28.86. HRMS (ESI) Calcd. For $C_{19}H_{17}N_2$: $[M+H]^+$, 273.1386, Found: m/z 273.1381.

2-(benzo[h]quinolin-7-yl)-2-methylpropanenitrile (**3o**, colorless oil, PE/EtOAc = 3:1 as eluent, 31 mg, 63% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54–9.43 (m, 1H), 9.04 (m, 1H), 8.60 (d, J = 9.4 Hz, 1H), 8.24 (m, 1H), 7.87 (d, J = 9.4 Hz, 1H), 7.79–7.70 (m, 2H), 7.58 (m, 1H), 2.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.20, 146.73, 135.79 (d), 133.12, 130.59, 126.36, 125.77, 125.51 (d), 125.11, 124.78, 123.60, 122.30, 34.65, 29.15. HRMS (ESI) Calcd. For $C_{17}H_{15}N_2$: $[M+H]^+$, 247.1230, Found: m/z 247.1233.

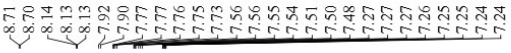
2-methyl-2-(3-(pyridin-2-yl)phenyl)butanenitrile (**3p**, colorless oil, PE/EtOAc = 3:1 as eluent, 31.2 mg, 66% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (m, 1H), 8.14–8.06 (m, 1H), 7.98–7.88 (m, 1H), 7.81–7.72 (m, 2H), 7.56–7.45 (m, 2H), 7.31–7.21 (m, 1H), 2.04 (q, J = 7.4 Hz, 2H), 1.78 (s, 3H), 1.00 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.82, 149.76, 140.73, 140.14, 136.87, 129.26, 126.26 (d), 124.05, 123.39, 122.46, 120.75, 43.40, 35.27, 27.31, 9.95. HRMS (ESI) Calcd.

For $C_{16}H_{17}N_2$: $[M+H]^+$, 237.1386, Found: m/z 237.1382.

2,4-dimethyl-2-(3-(pyridin-2-yl)phenyl)pentanenitrile (**3q**, colorless oil, PE/EtOAc = 3:1 as eluent, 32.8 mg, 62% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.8 Hz, 1H), 8.11 (s, 1H), 7.93 (d, *J* = 7.3 Hz, 1H), 7.78 (m, 2H), 7.61–7.46 (m, 2H), 7.30–7.25 (m, 1H), 1.95 (m, 2H), 1.79 (d, *J* = 8.4 Hz, 3H), 1.76–1.68 (m, 1H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.85, 149.78, 141.16, 140.10, 136.86, 129.25, 126.19 (d), 123.98 (d), 122.44, 120.74, 50.36, 41.80, 29.32, 25.91, 23.77, 23.48. HRMS (ESI) Calcd. For $C_{18}H_{21}N_2$: $[M+H]^+$, 265.1699, Found: m/z 265.1692.

1-(3-(pyridin-2-yl)phenyl)cyclohexanecarbonitrile (**3r**, colorless oil, PE/EtOAc = 3:1 as eluent, 29.3 mg, 56% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.5 Hz, 1H), 8.15 (d, *J* = 1.6 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.82–7.71 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.26 (m, 1H), 1.93–1.84 (m, 8H), 1.32 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.91, 149.74, 142.07, 140.10, 136.88, 129.30, 126.35 (d), 124.15, 122.73, 122.43, 120.77, 44.52, 37.36, 24.96, 23.62. HRMS (ESI) Calcd. For $C_{18}H_{19}N_2$: $[M+H]^+$, 263.1543, Found: m/z 263.1541.

methyl 2-methyl-2-(3-(pyridin-2-yl)phenyl)propanoate (**3s**, white solid, PE/EtOAc = 3:1 as eluent, 33.2 mg, 65% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78–8.65 (m, 1H), 8.00 (d, *J* = 1.5 Hz, 1H), 7.90–7.82 (m, 1H), 7.74 (m, 2H), 7.41 (m, 2H), 7.23 (m, 1H), 3.67 (s, 3H), 1.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.25, 157.49, 149.66, 145.18, 139.60, 136.73, 128.79, 126.46, 125.41, 124.24, 122.15, 120.76, 52.25, 46.66, 26.60. HRMS (ESI) Calcd. For $C_{16}H_{18}NO_2$: $[M+H]^+$, 256.1332, Found: m/z 256.1328.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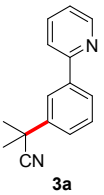
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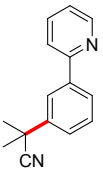
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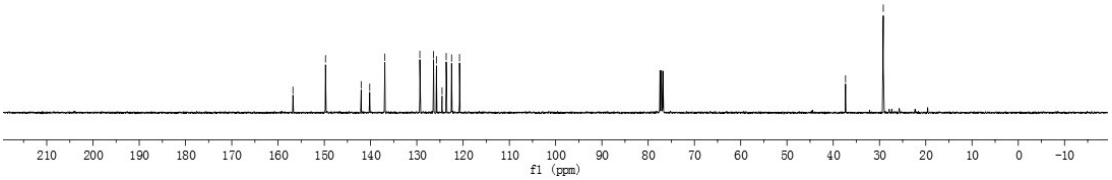
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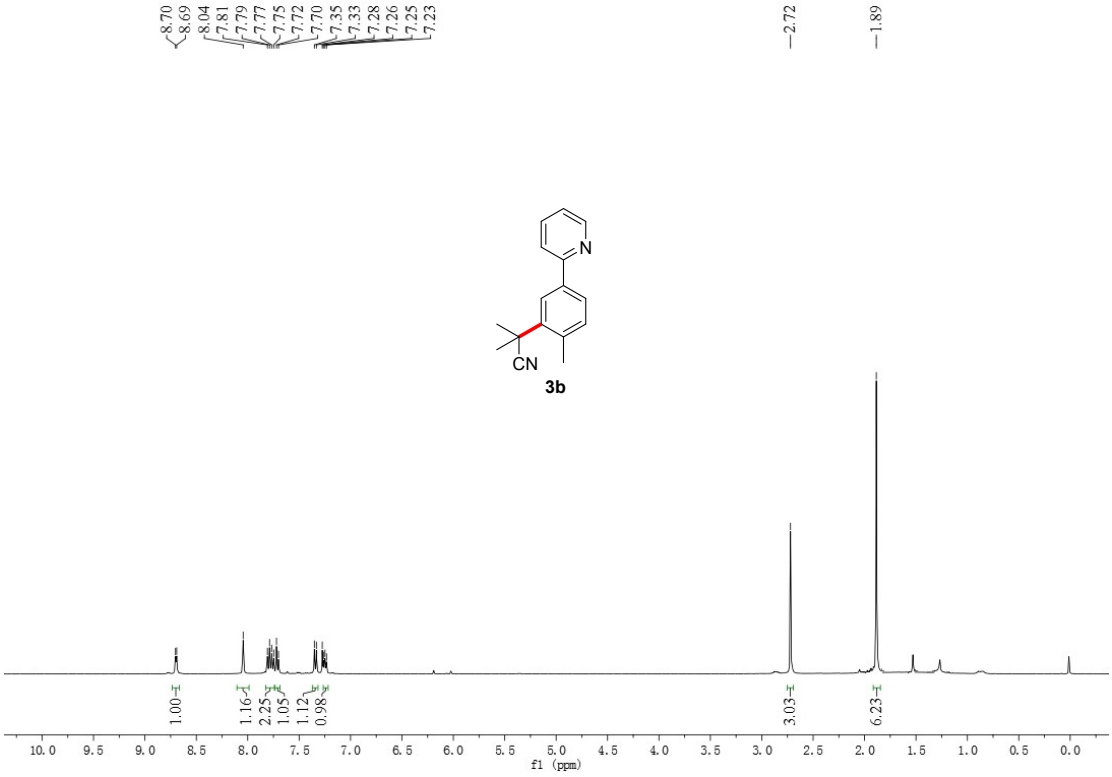
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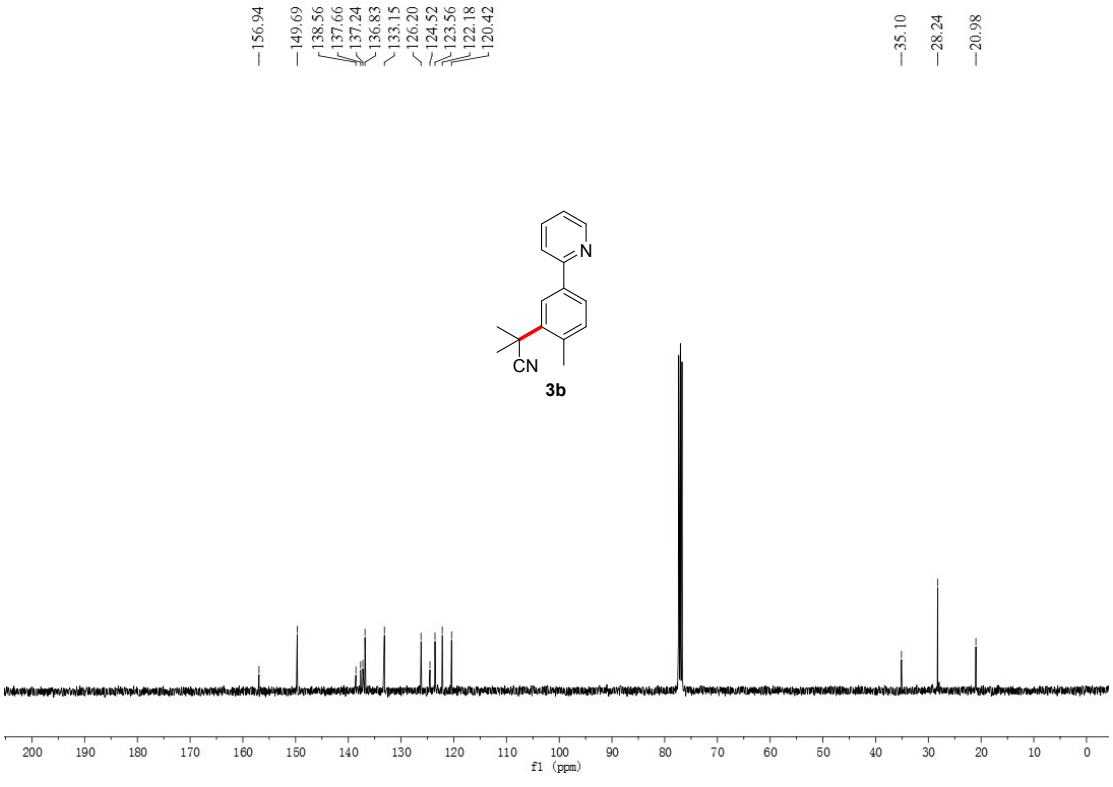
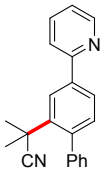
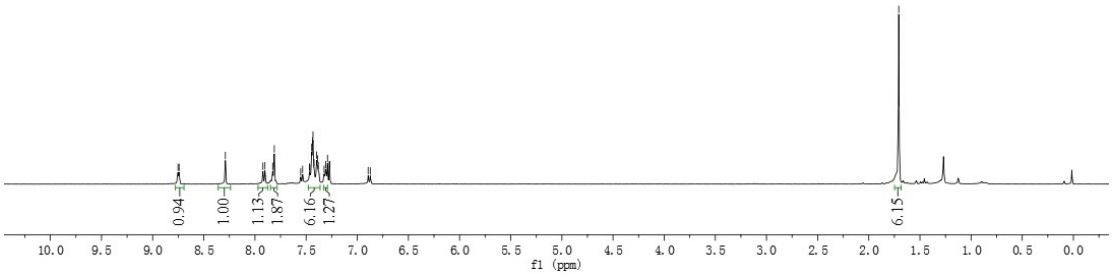
f1 (ppm)


156.94
149.69
138.56
137.66
137.24
136.83
133.15
126.20
124.52
123.56
122.18
120.42
35.10
28.24
20.98
N
CN
3b
f1 (ppm)

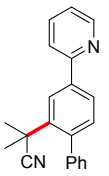

8.75
8.74
8.29
7.81
7.45
7.44
7.43
7.40
7.39
7.29
6.89
6.87
1.71


N
CN
Ph

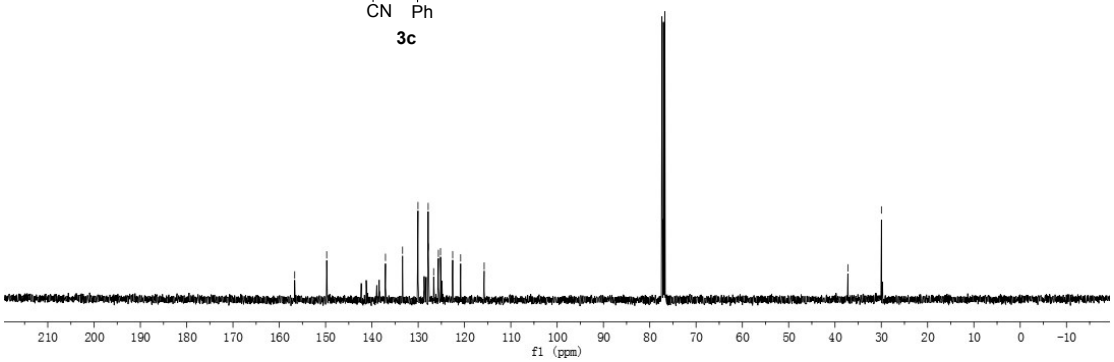
3c

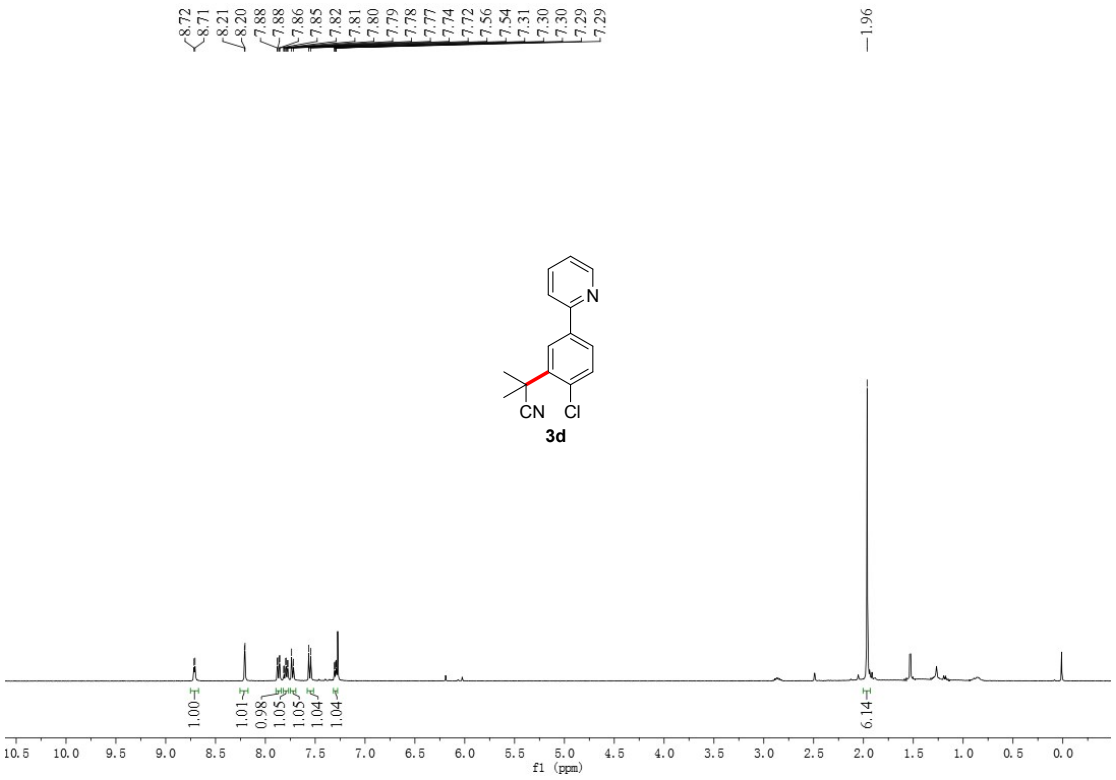

0.94
1.00
1.13
1.87
6.16
1.27
6.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

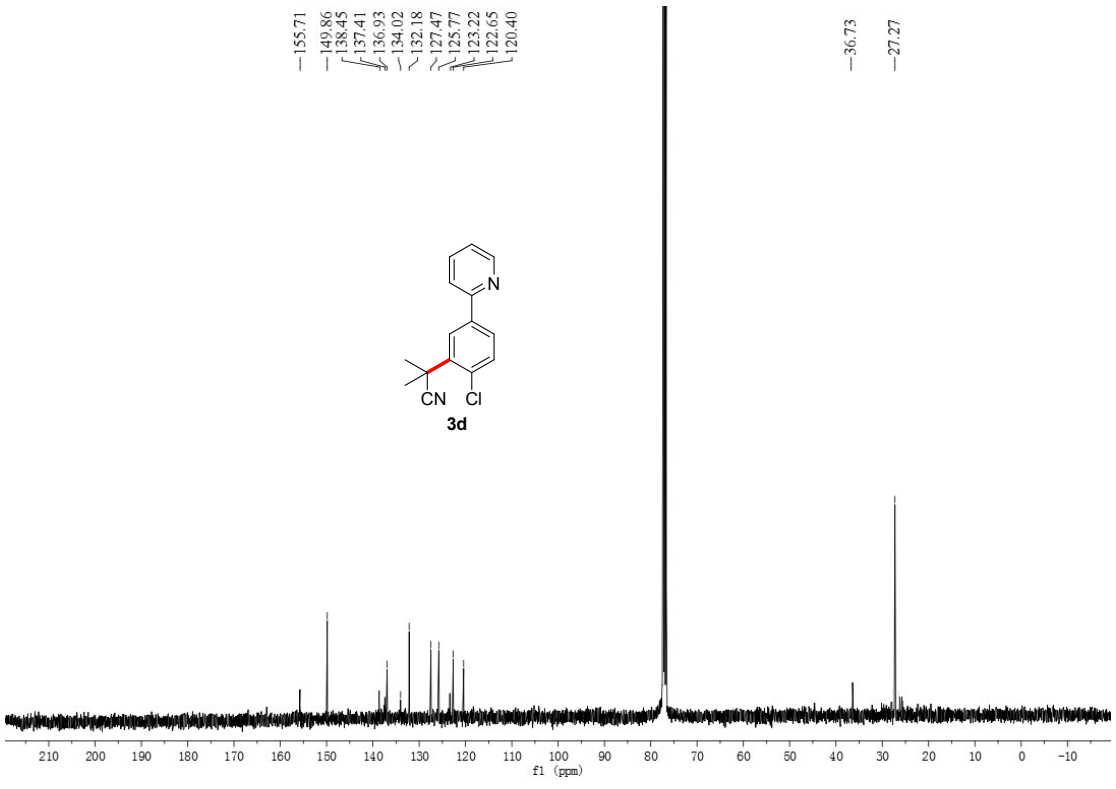

156.67
149.76
141.18
138.33
137.07
133.38
130.04
128.74
127.85
127.81
126.67
125.64
125.18
122.56
120.84
115.75
37.22
29.98

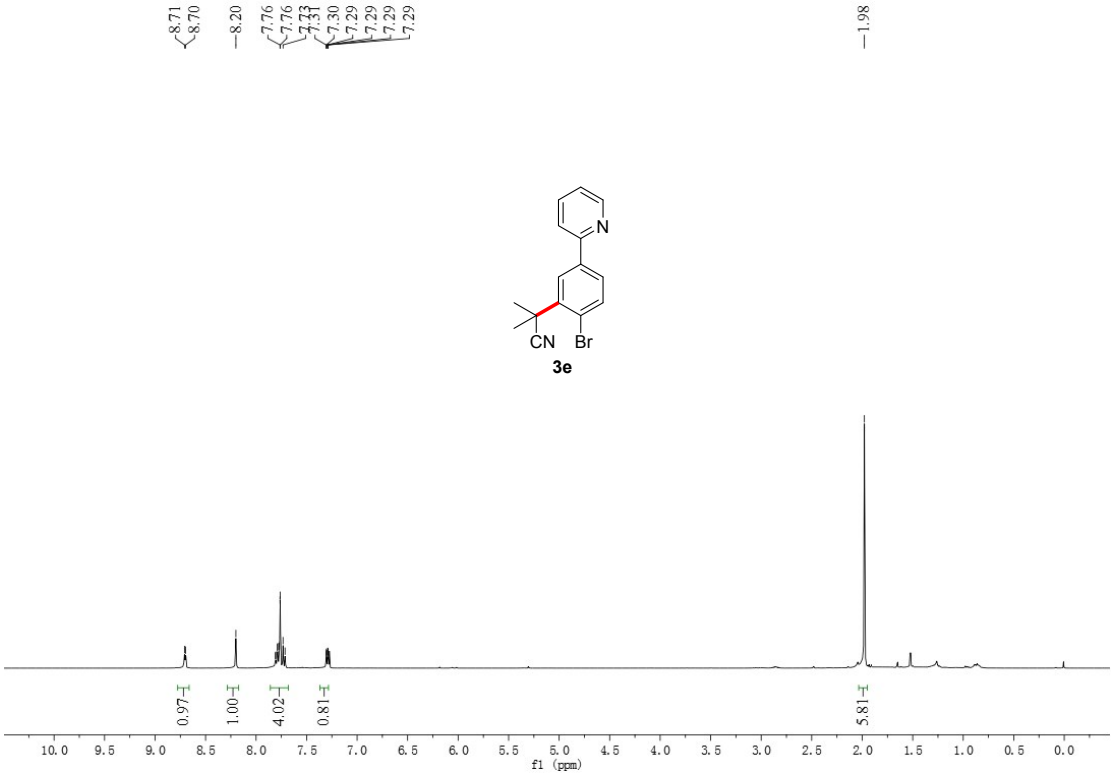

N
CN
Ph

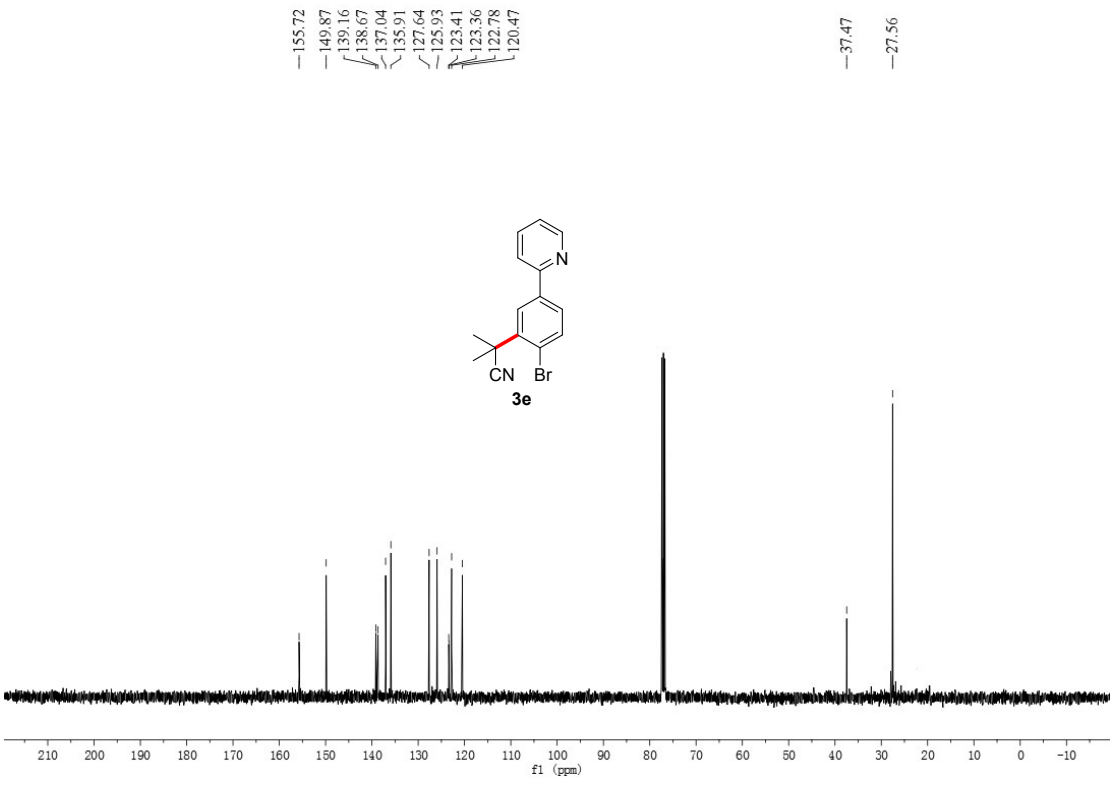
3c

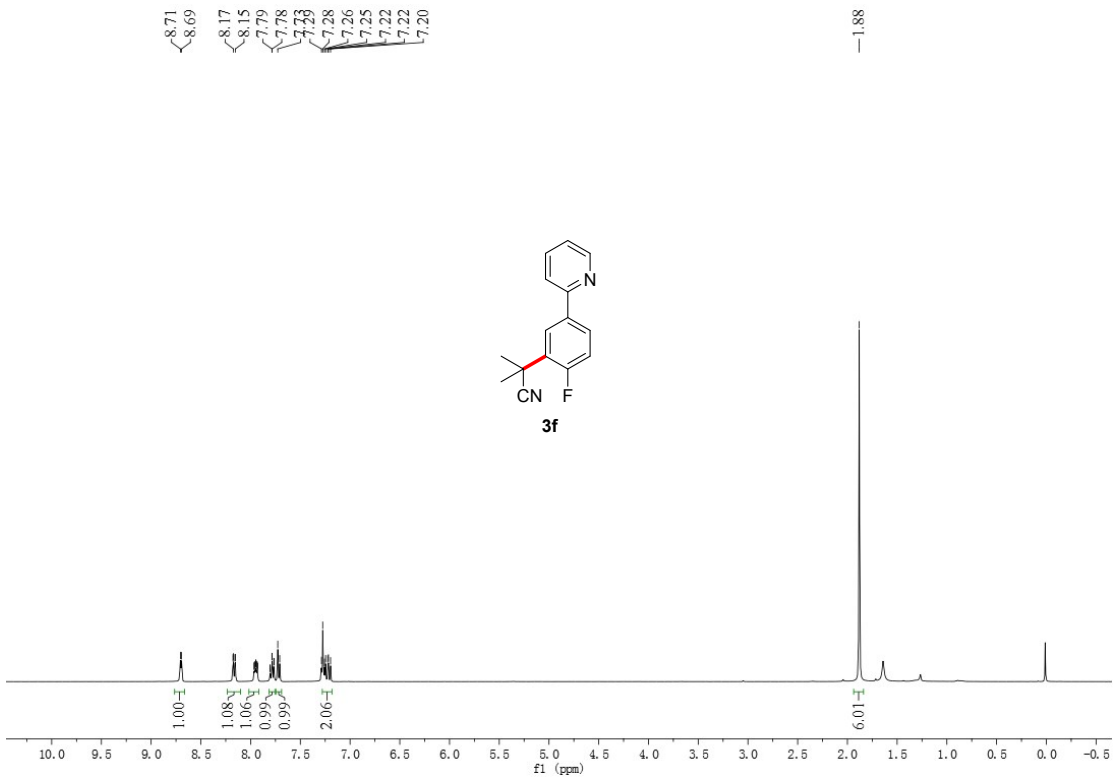

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

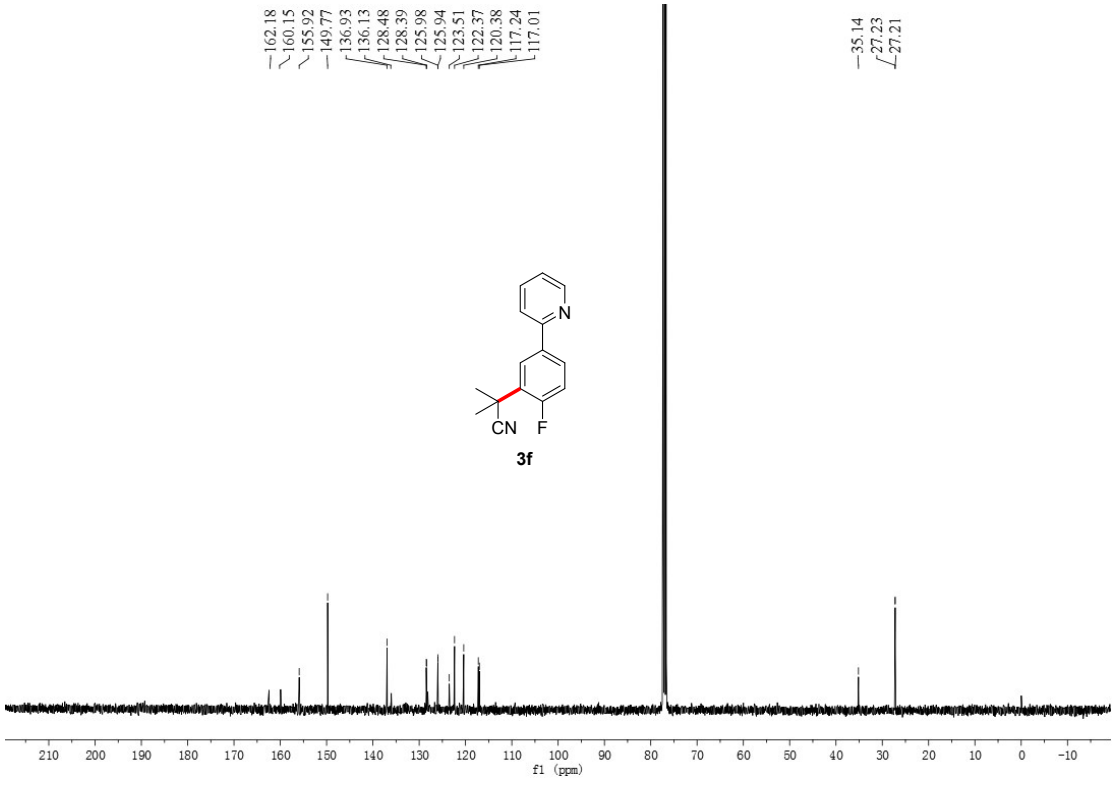

8.72
8.71
8.21
8.20
7.88
7.88
7.86
7.85
7.82
7.81
7.80
7.79
7.78
7.77
7.74
7.72
7.56
7.54
7.31
7.30
7.30
7.29
7.29
1.96
N
CN
Cl
3d
1.00
1.01
0.98
1.05
1.05
1.04
1.04
6.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.71
149.86
138.45
137.41
136.93
134.02
132.18
127.47
125.77
123.22
122.65
120.40
36.73
27.27
N
CN
Cl
3d
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)

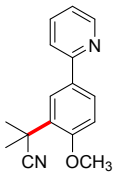

8.71
8.70
8.20
7.76
7.76
7.33
7.31
7.30
7.29
7.29
7.29
7.29
1.98
N
CN
Br
3e
0.97
1.00
4.02
0.81
5.81
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.72
149.87
139.16
138.67
137.04
135.91
127.64
125.93
123.41
123.36
122.78
120.47
37.47
27.56
N
CN
Br
3e
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)

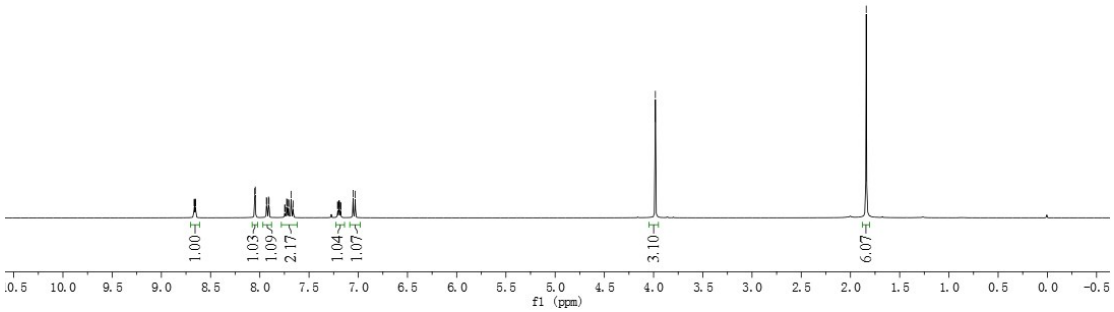

8.71
8.69
8.17
8.15
7.79
7.78
7.73
7.28
7.26
7.25
7.22
7.20
1.88
N
CN
F
3f
1.00
1.08
1.06
0.99
0.99
2.06
6.01
f1 (ppm)

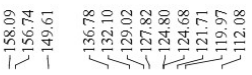

162.18
160.15
155.92
149.77
136.93
136.13
128.48
128.39
125.98
125.94
123.51
122.37
120.38
117.24
117.01
35.14
27.23
27.21
N
CN
F
3f
f1 (ppm)

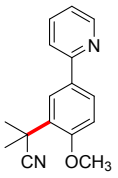

8.67
8.67
8.66
8.66
8.65
8.65
8.05
8.05
7.91
7.68
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.05
7.03
3.98
1.84


N
CN
OCH3

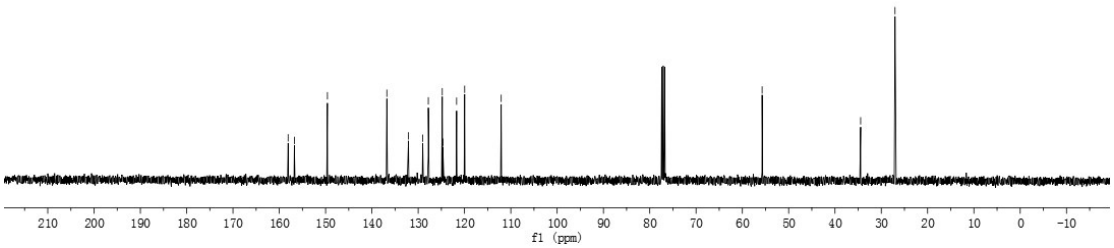
3g

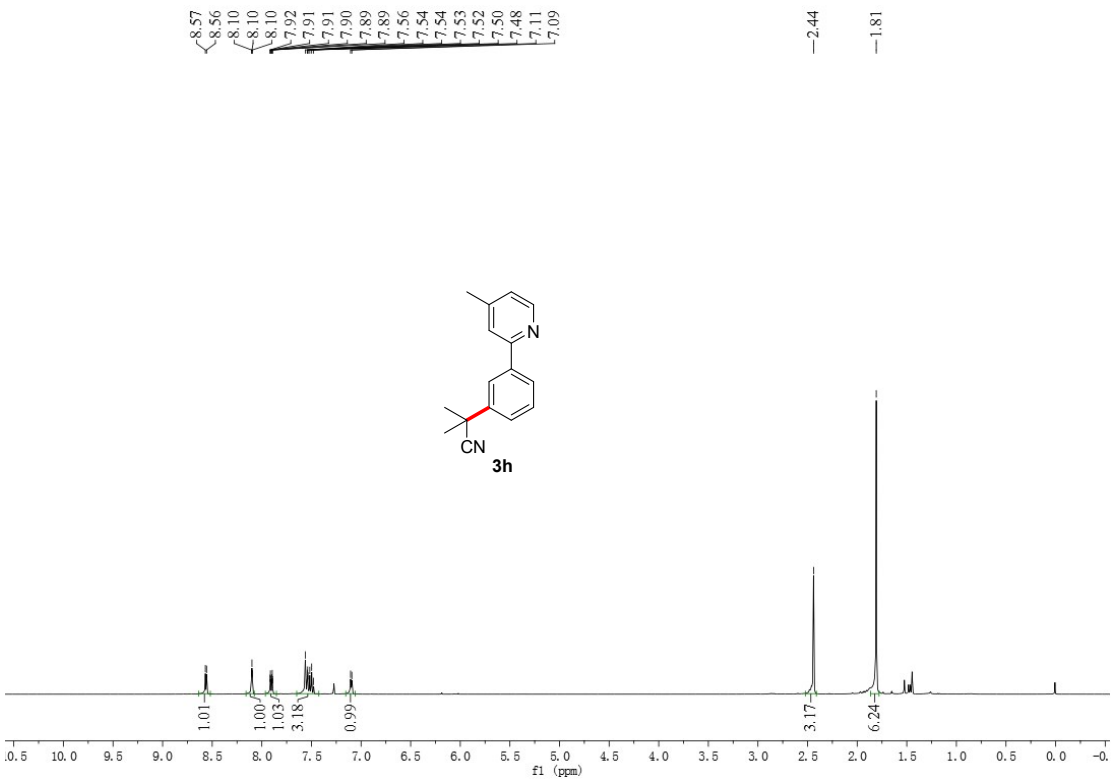

1.00
1.03
1.09
2.17
1.04
1.07
3.10
6.07
f1 (ppm)

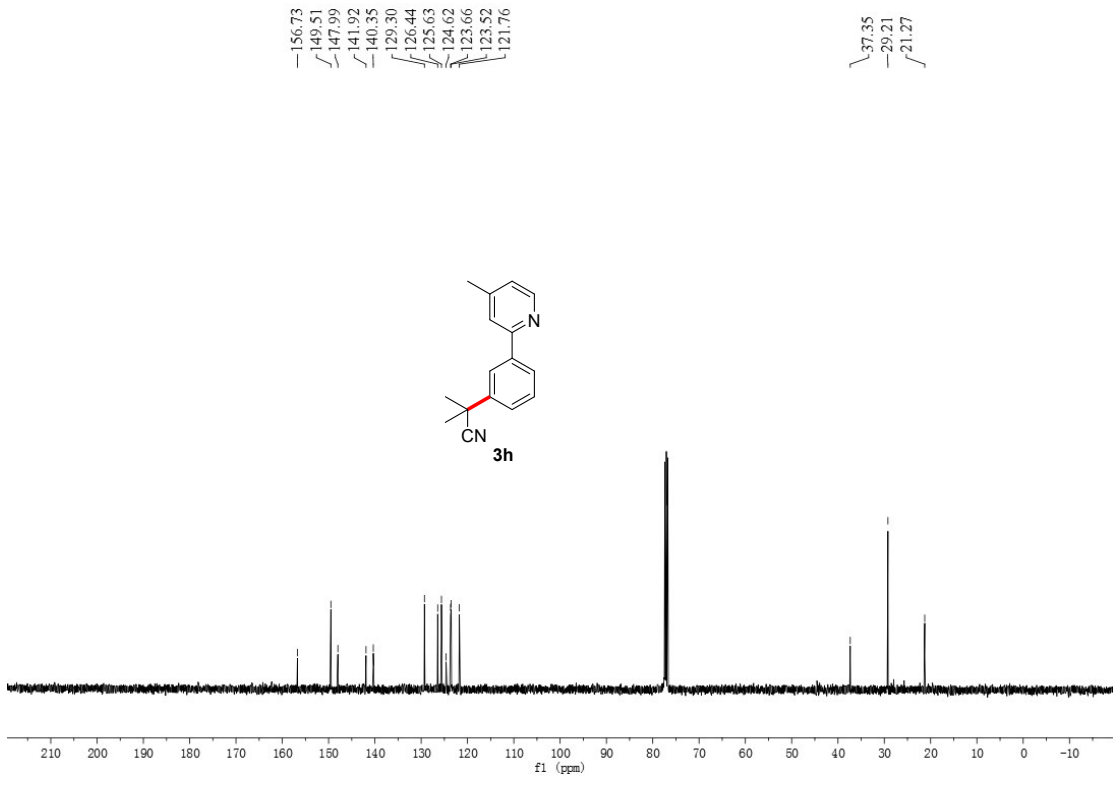

158.09
156.74
149.61
136.78
132.10
129.02
127.82
124.80
124.68
121.71
119.97
112.08
55.73
34.46
27.03

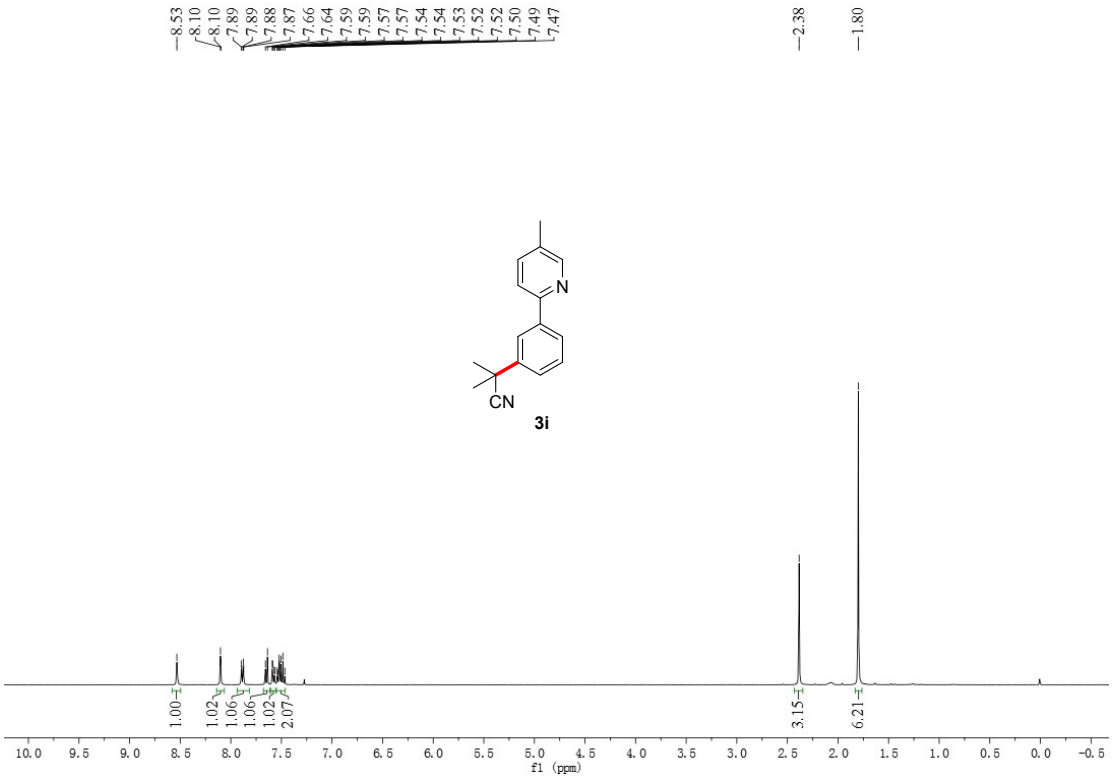

N
CN
OCH3

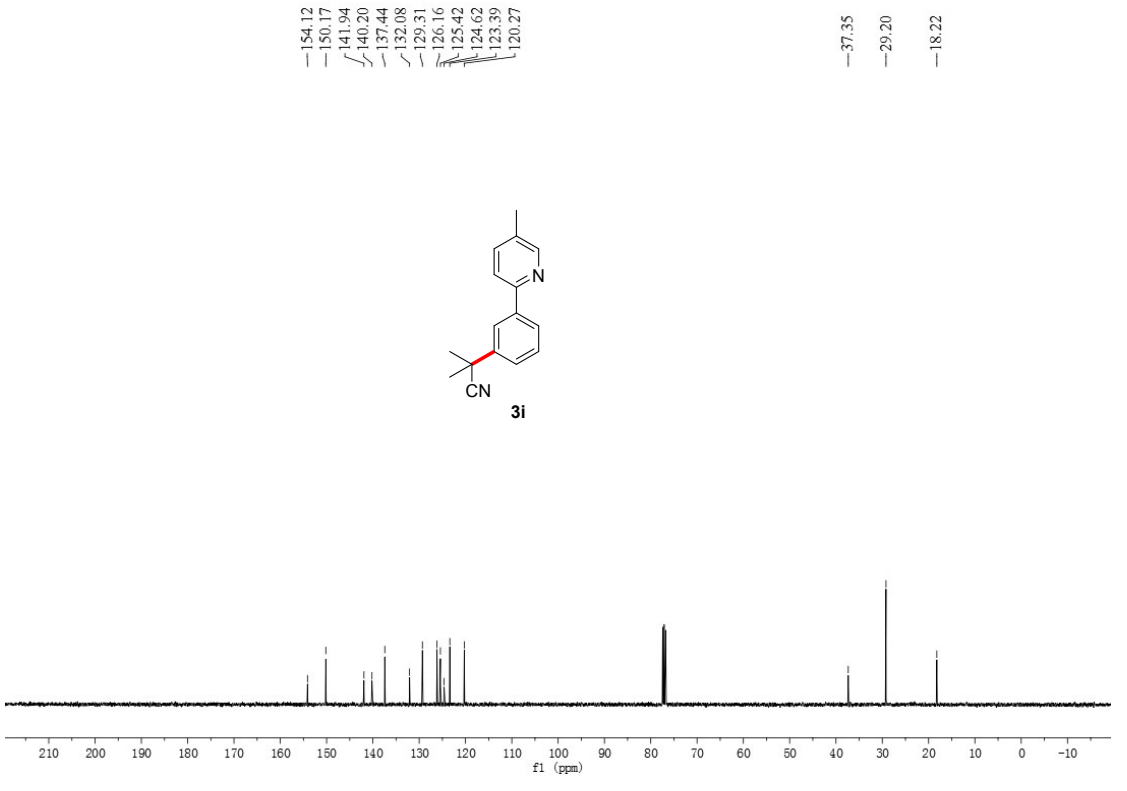
3g


f1 (ppm)

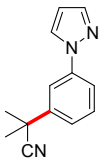

8.57
8.56
8.10
8.10
8.10
7.92
7.91
7.91
7.90
7.89
7.89
7.56
7.54
7.54
7.53
7.52
7.50
7.48
7.11
7.09
2.44
1.81
N
CN
3h
1.01
1.00
1.03
3.18
0.99
3.17
6.24
f1 (ppm)


156.73
149.51
147.99
141.92
140.35
129.30
126.44
125.63
124.62
123.66
123.52
121.76
37.35
29.21
21.27
N
CN
3h
f1 (ppm)

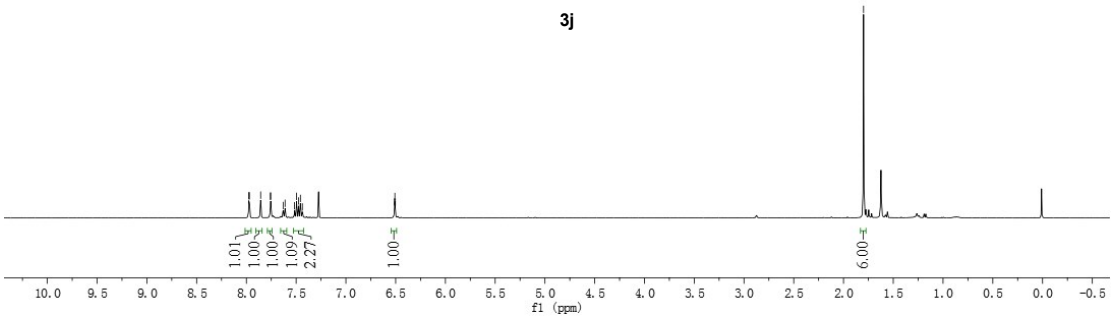

8.53
8.10
8.10
7.89
7.89
7.88
7.87
7.66
7.64
7.59
7.59
7.57
7.57
7.54
7.54
7.53
7.52
7.52
7.50
7.49
7.47
2.38
1.80
N
CN
3i
1.00
1.02
1.06
1.06
1.02
2.07
3.15
6.21
f1 (ppm)


154.12
150.17
141.94
140.20
137.44
132.08
129.31
126.16
125.42
124.62
123.39
120.27
37.35
29.20
18.22
N
CN
3i
f1 (ppm)

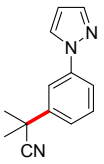

7.98
7.97
7.86
7.76
7.76
7.63
7.61
7.52
7.50
7.48
7.46
7.44
6.51
6.51
6.50
1.80


N
N
CN

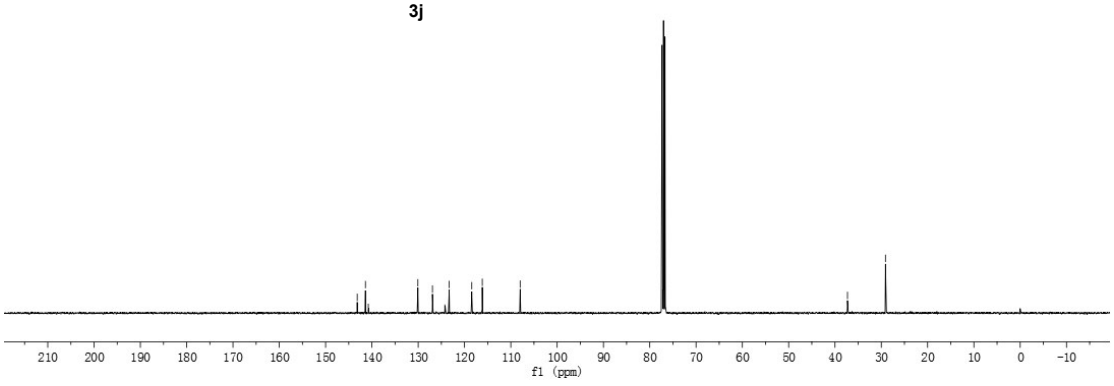
3j


1.01
1.00
1.00
1.09
2.27
1.00
6.00
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
f1 (ppm)

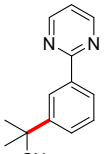

143.17
141.40
140.78
130.07
126.93
124.25
123.31
118.43
116.16
107.98
37.30
29.10


N
N
CN

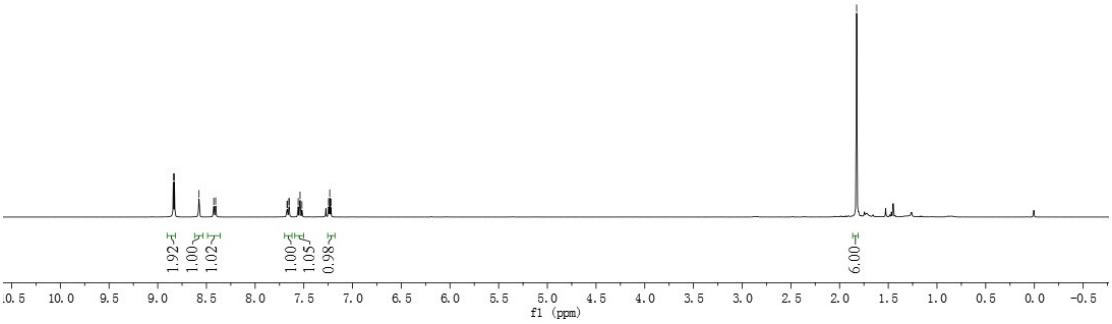
3j

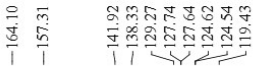

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

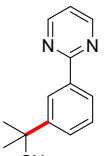

8.84
8.83
8.58
8.42
8.41
7.67
7.67
7.65
7.65
7.56
7.54
7.52
7.25
7.23
7.22
1.82


N
N
CN

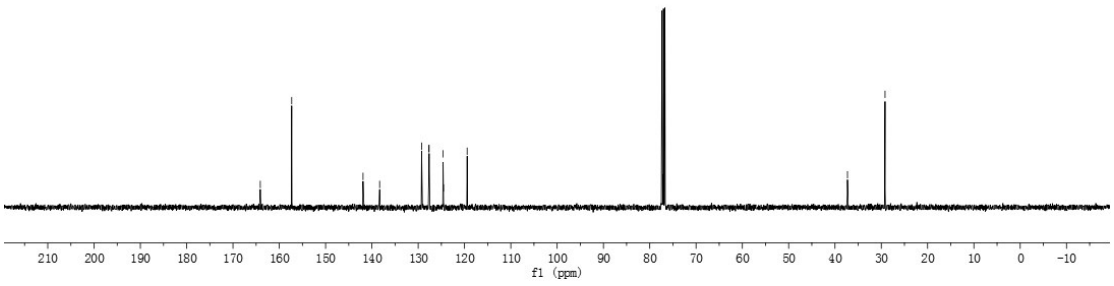
3k

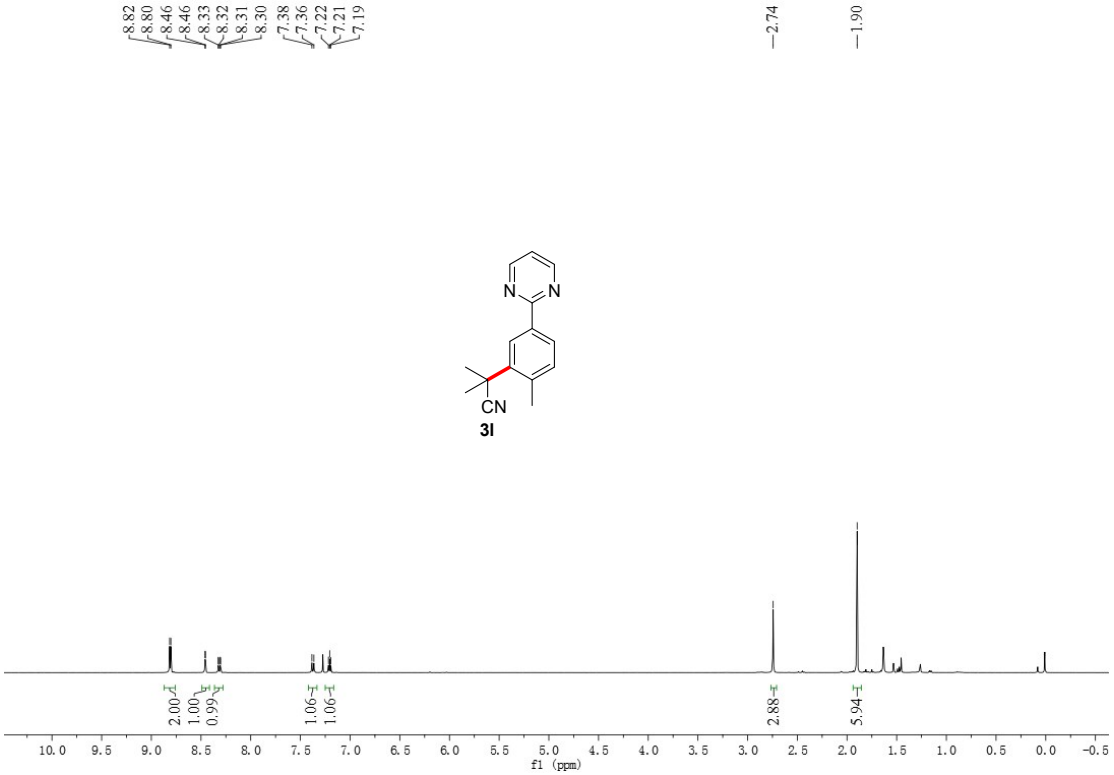

1.92
1.00
1.02
1.00
1.05
0.98
6.00
f1 (ppm)

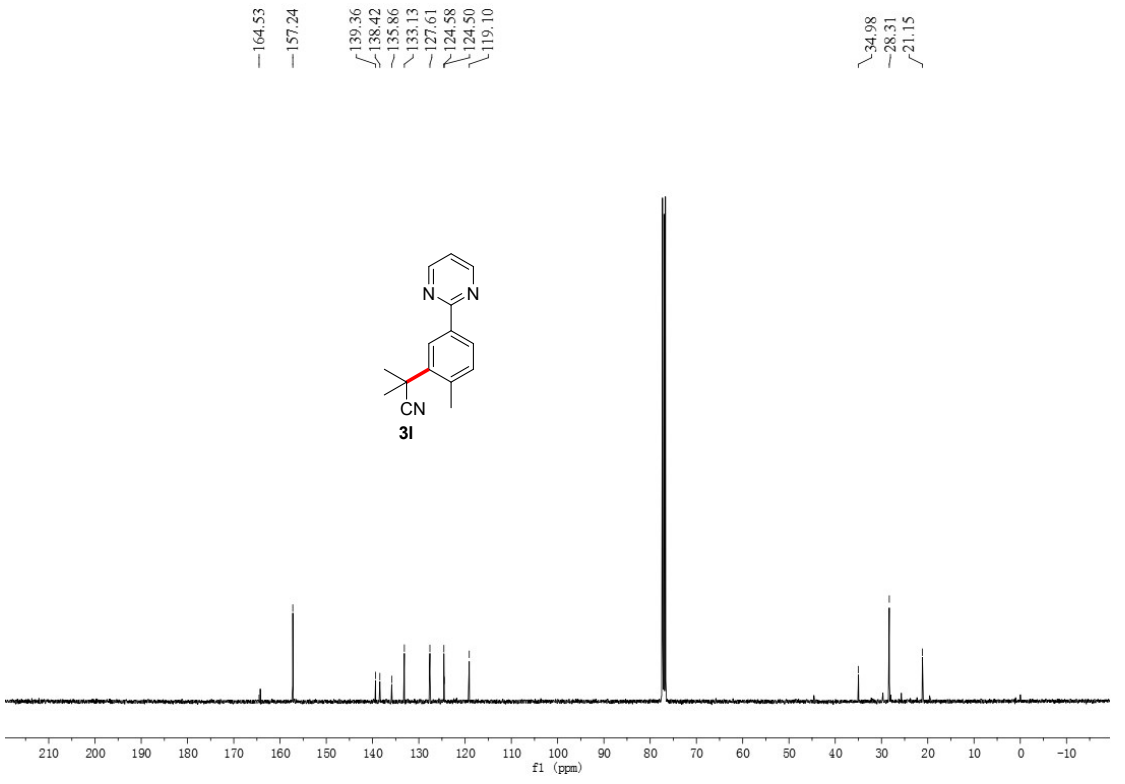

164.10
157.31
141.92
138.33
129.27
127.74
127.64
124.62
124.54
119.43
37.30
29.19

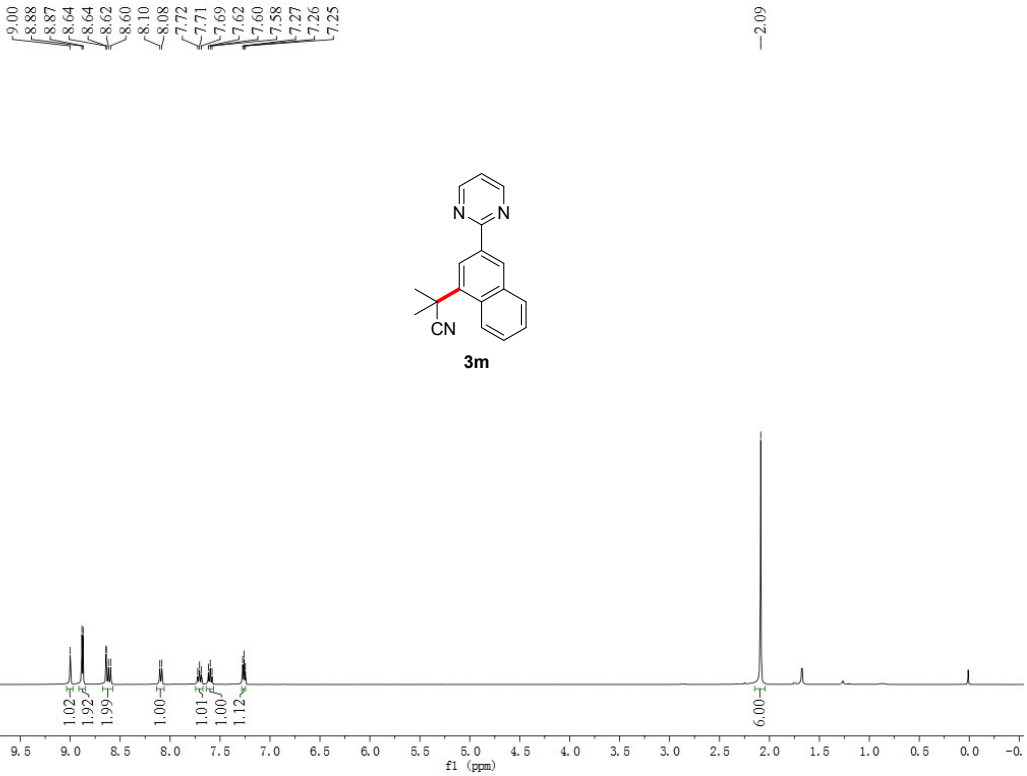

N
N
CN

3k

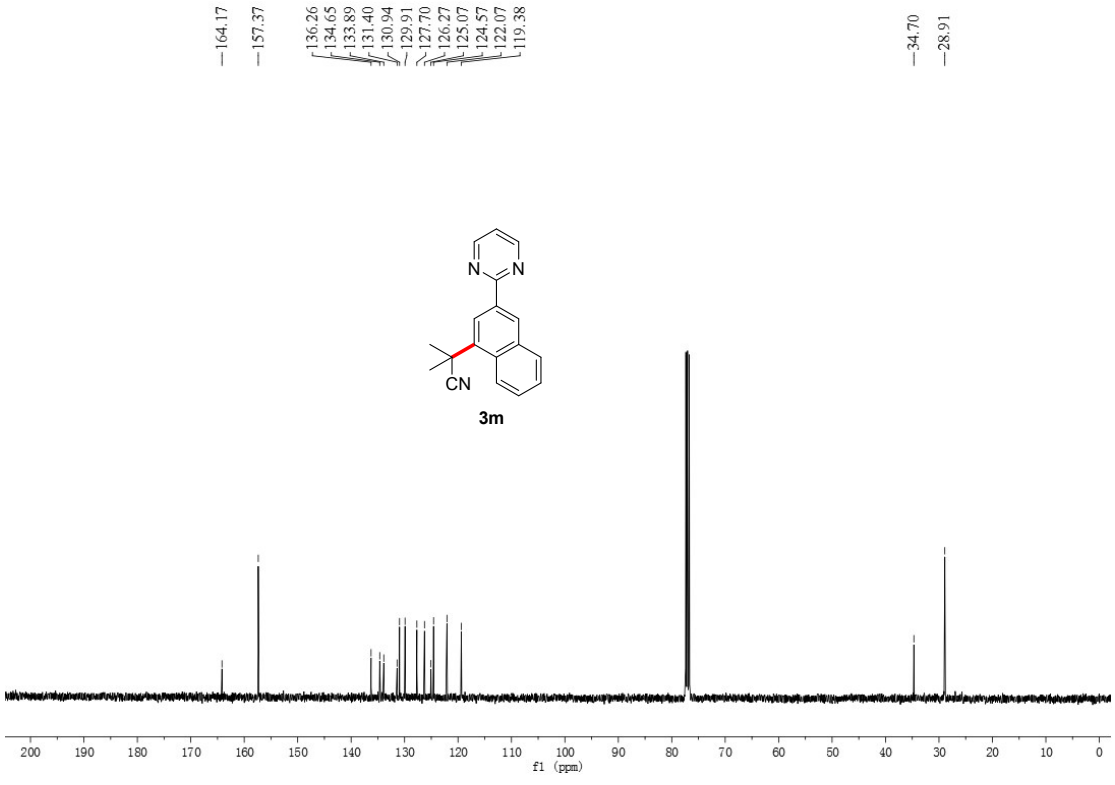

f1 (ppm)


8.82
8.80
8.46
8.46
8.33
8.32
8.31
8.30
7.38
7.36
7.22
7.21
7.19
2.74
1.90
N
N
CN
3l
2.00
1.00
0.99
1.06
1.06
2.88
5.94
f1 (ppm)


164.53
157.24
139.36
138.42
135.86
133.13
127.61
124.58
124.50
119.10
34.98
28.31
21.15
N
N
CN
3l
f1 (ppm)

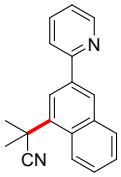

9.00
8.88
8.87
8.64
8.64
8.62
8.60
8.10
8.08
7.72
7.71
7.69
7.62
7.60
7.58
7.27
7.26
7.25
2.09
N
N
CN
1.02
1.92
1.99
1.00
1.01
1.00
1.12
6.00
f1 (ppm)

3m

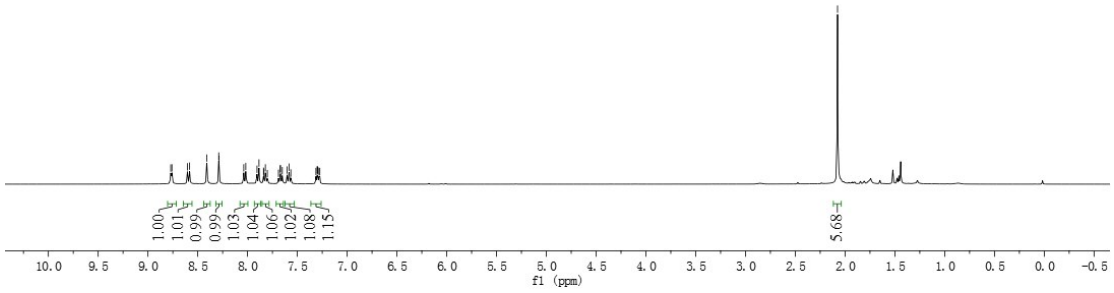

164.17
157.37
136.26
134.65
133.89
131.40
130.94
129.91
127.70
126.27
125.07
124.57
122.07
119.38
34.70
28.91
N
N
CN
f1 (ppm)

3m

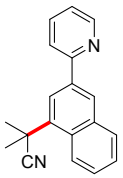

8.77
8.76
8.60
8.58
8.41
8.29
8.29
8.04
8.02
7.90
7.89
7.84
7.84
7.82
7.80
7.69
7.67
7.67
7.65
7.60
7.58
7.57
7.31
7.30
7.30
7.28
7.27
2.08


N
CN

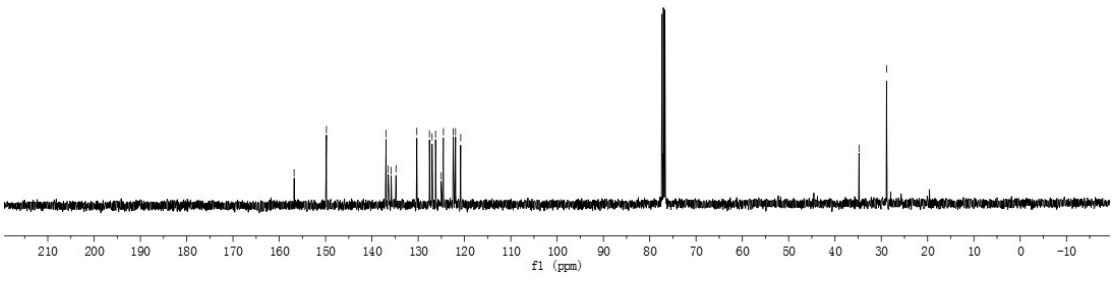
3n

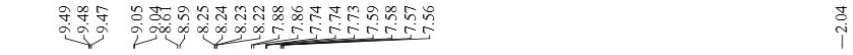

1.00
1.01
0.99
0.99
1.03
1.04
1.06
1.02
1.08
1.15
5.68
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

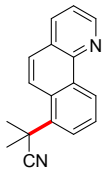

156.80
149.82
136.94
136.46
135.83
134.80
130.30
127.57
127.00
126.25
125.03
124.56
122.44
121.94
120.83
34.81
28.86


N
CN

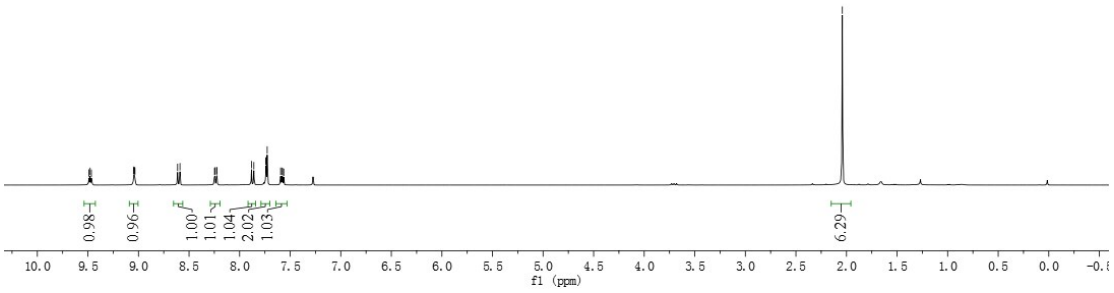
3n


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)

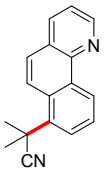

9.49
9.48
9.47
9.05
9.04
8.61
8.59
8.25
8.24
8.23
8.22
7.88
7.86
7.74
7.74
7.73
7.59
7.58
7.57
7.56
2.04


N
CN

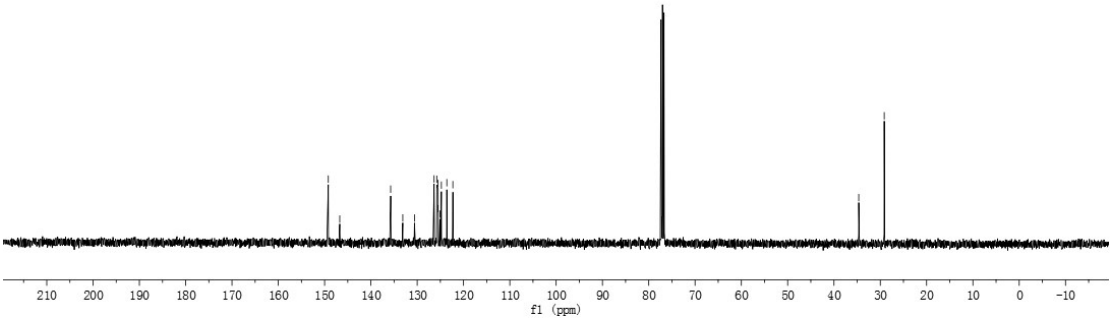
3o

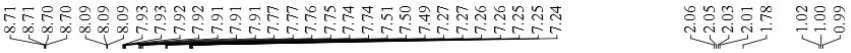

0.98
0.96
1.00
1.01
1.04
2.02
1.03
6.29
f1 (ppm)

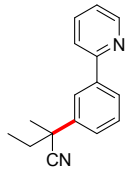

149.20
146.73
135.84
135.73
133.12
130.59
126.36
125.77
125.53
125.49
125.11
124.78
123.60
122.30
34.65
29.15


N
CN

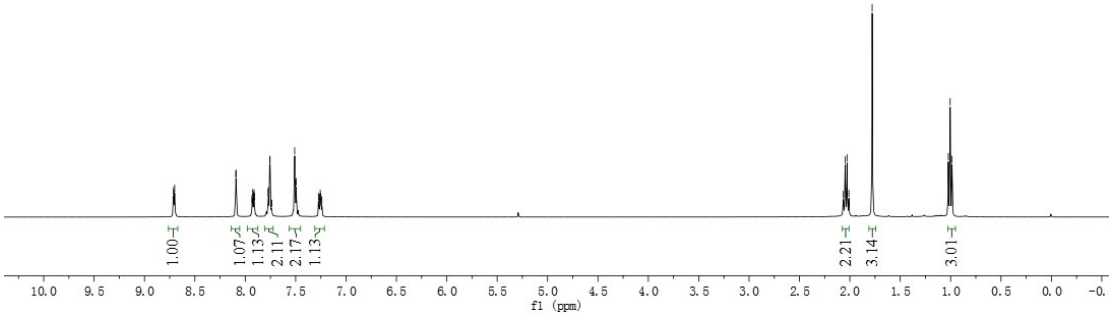
3o

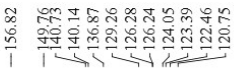

f1 (ppm)

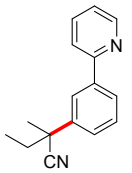

8.71
8.71
8.70
8.70
8.09
8.09
8.09
7.93
7.93
7.92
7.92
7.91
7.91
7.91
7.77
7.77
7.76
7.75
7.74
7.74
7.51
7.50
7.49
7.27
7.27
7.26
7.26
7.25
7.24
2.06
2.05
2.03
2.01
1.78
1.02
1.00
0.99


N
CN

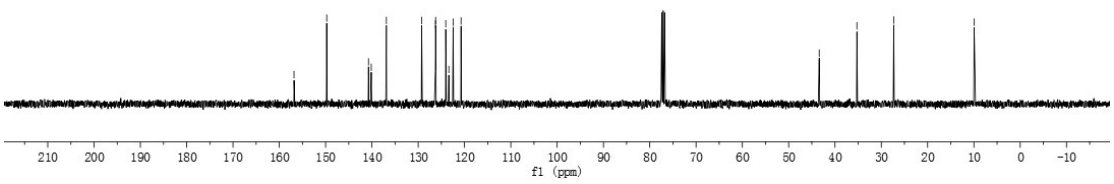
3p


1.00
1.07
1.13
2.11
2.17
1.13
2.21
3.14
3.01
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.
f1 (ppm)


156.82
148.76
140.73
140.14
136.87
129.26
126.28
126.24
124.05
123.39
122.46
120.75
43.40
35.27
27.31
9.95

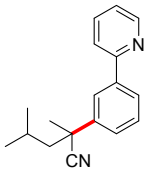

N
CN

3p

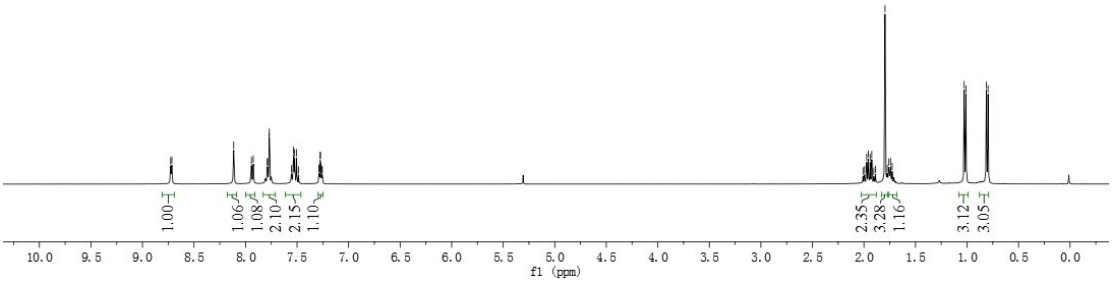

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

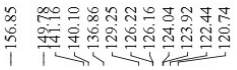

8.73
8.71
8.11
7.94
7.92
7.79
7.79
7.77
7.77
7.55
7.53
7.52
7.50
7.49
7.29
7.28
7.27
7.27
7.27
7.26
7.26

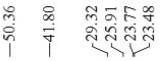

2.01
1.99
1.97
1.96
1.94
1.92
1.90
1.89
1.80
1.77
1.76
1.74
1.73
1.03
1.01
0.81
0.80

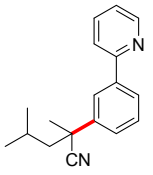

N
CN

3q

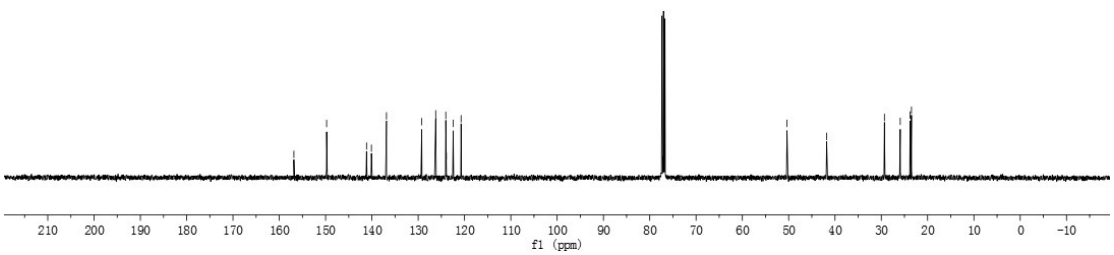

1.00
1.06
1.08
2.10
2.15
1.10
2.35
3.28
1.16
3.12
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

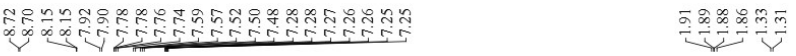

156.85
149.78
141.18
140.10
136.86
129.25
126.22
126.16
124.04
123.92
122.44
120.74

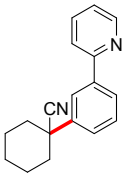

50.36
41.80
29.32
25.91
23.77
23.48


N
CN

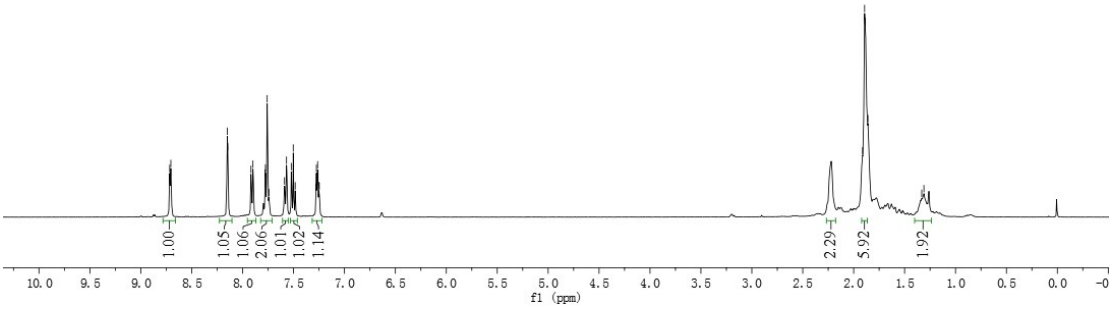
3q


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)

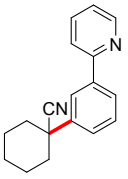

8.72
8.70
8.15
8.15
7.92
7.90
7.78
7.78
7.76
7.74
7.59
7.57
7.52
7.50
7.48
7.28
7.27
7.26
7.26
7.25
7.25
1.91
1.89
1.88
1.86
1.33
1.31


N
CN

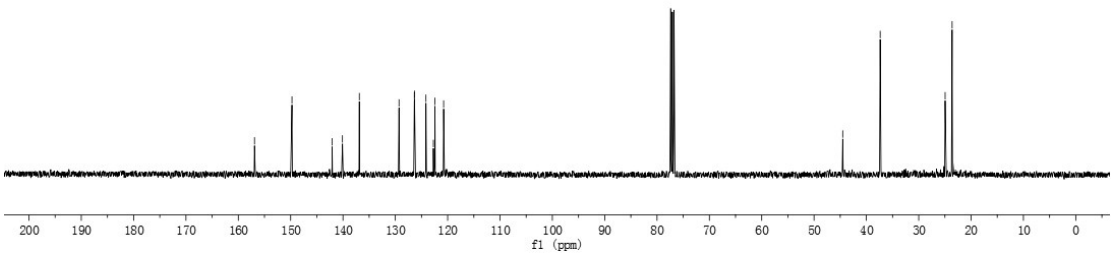
3r

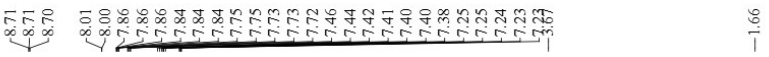

1.00
1.05
1.06
2.06
1.01
1.02
1.14
2.29
5.92
1.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

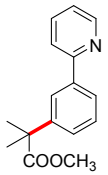

156.91
149.74
142.07
140.10
136.88
129.30
126.37
126.33
124.15
122.73
122.43
120.77
44.52
37.36
24.96
23.62


N
CN

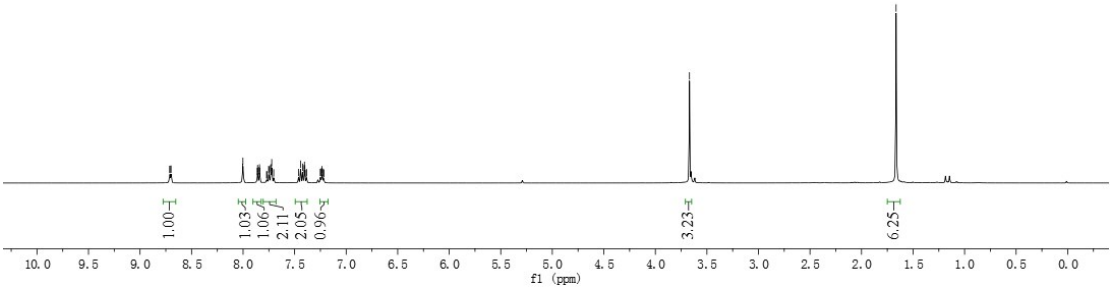
3r


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

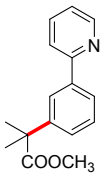

8.71
8.71
8.70
8.01
8.00
7.86
7.86
7.86
7.84
7.84
7.84
7.75
7.75
7.73
7.73
7.72
7.46
7.44
7.42
7.41
7.40
7.40
7.38
7.25
7.25
7.24
7.23
3.67
1.66


N
COOCH3

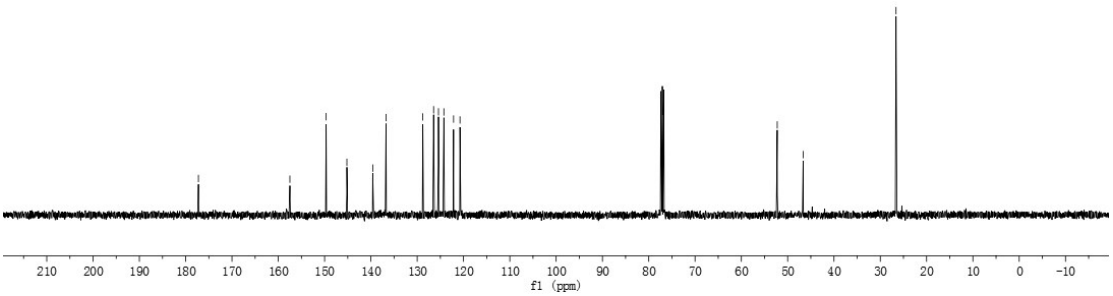
3s

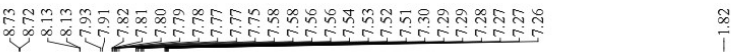

1.00
1.03
1.06
2.11
2.05
0.96
3.23
6.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

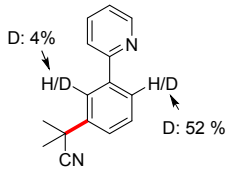

177.25
157.49
149.66
145.18
139.60
136.73
128.79
126.46
125.41
124.24
122.15
120.76
52.25
46.66
26.60

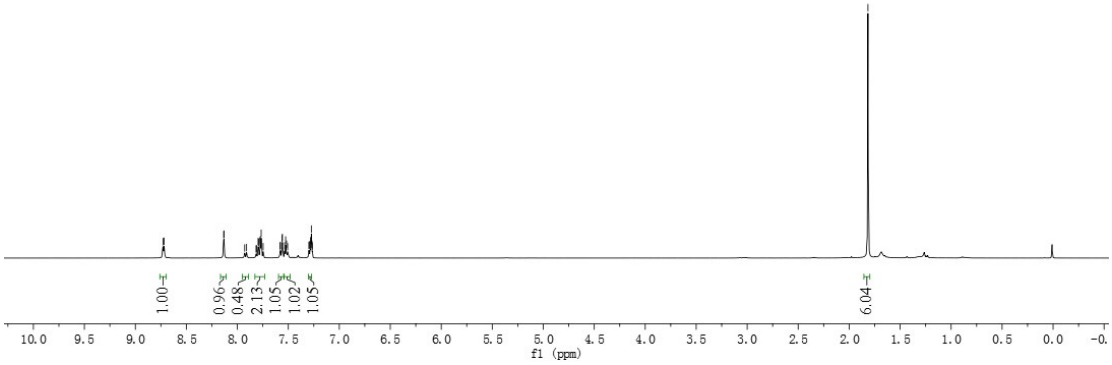

N
COOCH3

3s

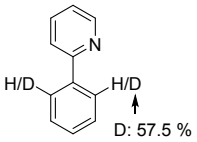

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

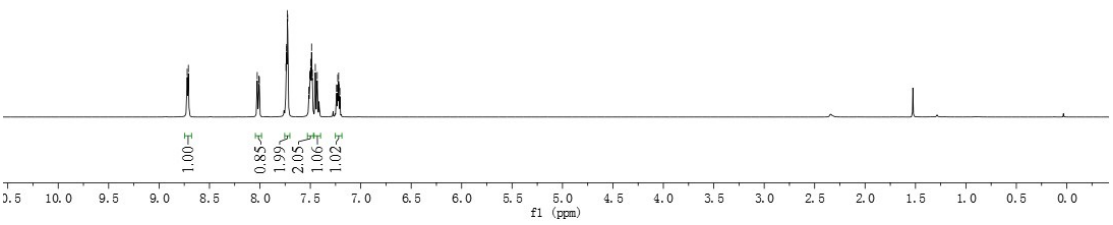

8.73
8.72
8.13
8.13
7.93
7.91
7.82
7.81
7.80
7.79
7.78
7.77
7.77
7.75
7.58
7.58
7.56
7.56
7.54
7.53
7.52
7.51
7.30
7.29
7.29
7.28
7.27
7.27
7.26
1.82

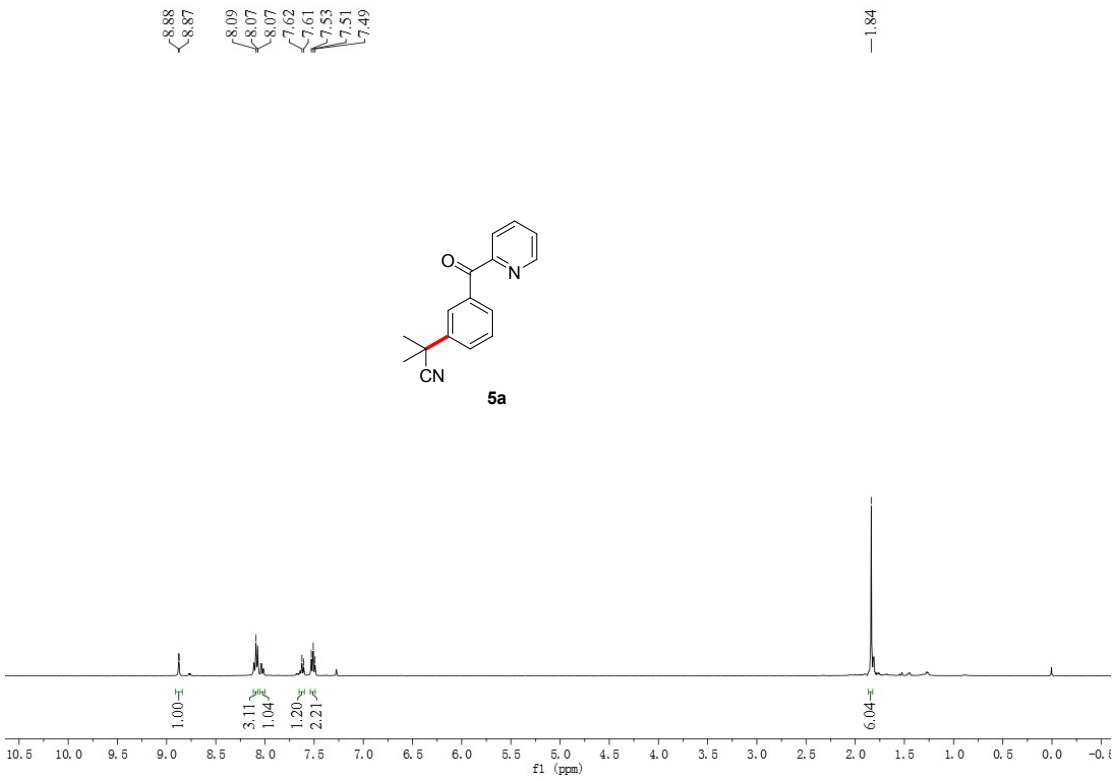

D: 4%
N
H/D
H/D
D: 52 %
CN


1.00
0.96
0.48
2.13
1.05
1.02
1.05
6.04
f1 (ppm)

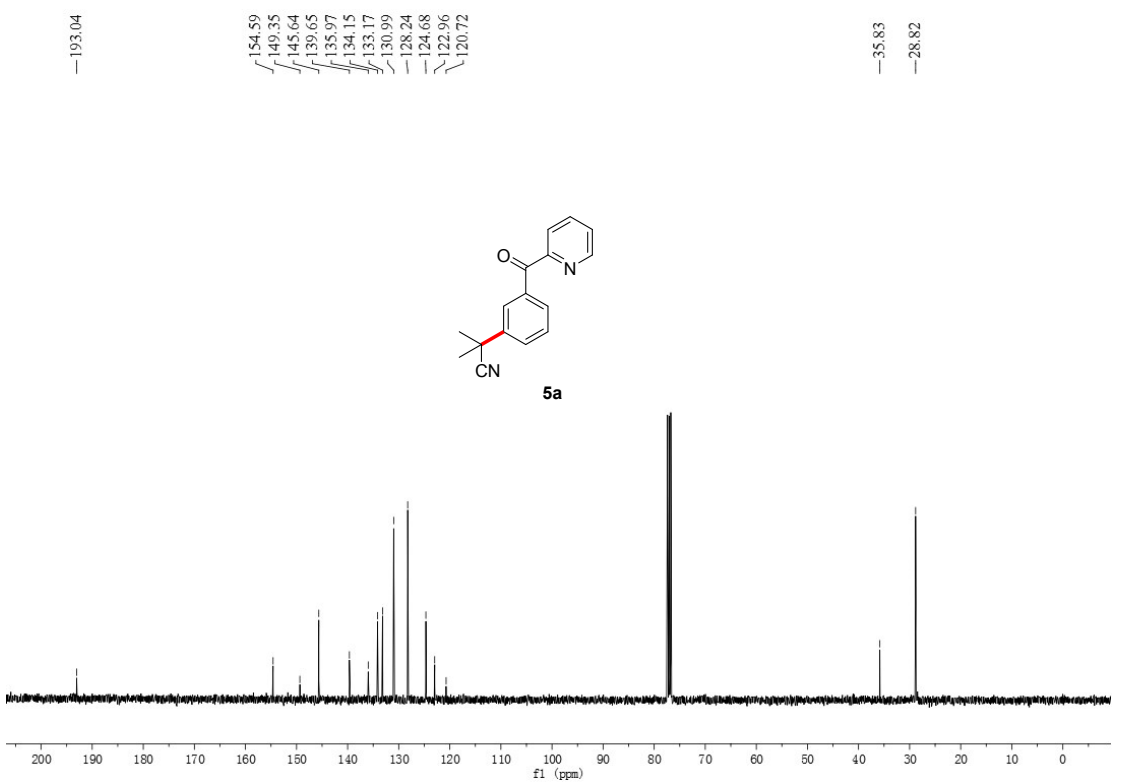

8.72
8.71
8.03
8.01
8.01
7.74
7.74
7.73
7.73
7.72
7.51
7.50
7.50
7.49
7.48
7.45
7.43
7.24
7.23
7.23
7.22
7.22
7.21


N
H/D
H/D
D: 57.5 %


1.00
0.85
1.99
2.05
1.06
1.02
f1 (ppm)


8.88
8.87
8.09
8.07
8.07
7.62
7.61
7.53
7.51
7.49
1.84
O
N
CN
1.00
3.11
1.04
1.20
2.21
6.04
f1 (ppm)

5a


193.04
154.59
149.35
145.64
139.65
135.97
134.15
133.17
130.99
128.24
124.68
122.96
120.72
35.83
28.82
O
N
CN
f1 (ppm)

5a