Radical-Mediated Hydroalkylation of Alkenes *via* Fe-Catalysed Hydrogen Atom Transfers

(Supporting Information)

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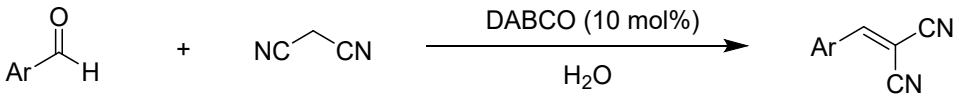
1. General Information.

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. All new compounds were fully characterized. NMR-spectra were recorded on Bruker ARX-400 MHz or a ARX-600 Associated. ^{1}H NMR spectra data were reported as δ values in ppm relative to chloroform (δ 7.26) if collected in $CDCl_3$. ^{13}C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.00). ^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doublet of quartets); app (apparent); br (broad). Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). All reactions were carried out in flame-dried 25-mL Schlenk tubes with Teflon screw caps under argon. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Preparation of Starting Materials.

2.1 Prearation of alkenes 2.

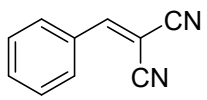


2

Alkenes **2** was prepared according to the reported procedure[1]. A 10-mL round bottomed flask was charged with the carbonyl compound (2.0 mmol), active methylene compound (2.0 mmol), catalyst DABCO (22.4 mg, 10 mol %) and water (2 mL). The reaction mixture was stirred at the room temperature. The formation of the products was monitored by TLC. After completion of the reaction, the reaction mixture often solidified in the round bottomed flask. The solid mixture was filtered and washed with

cold water to remove impurities, and then dried to obtain the products. In general, no further purification method was required.

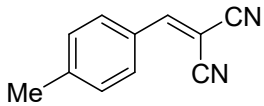
2-Benzylidenemalononitrile (2a)



2a

According to the general procedure, **2a** was prepared from the corresponding aldehyde (10 mmol) as a white solid (1.43 g, 93 %). The spectral data are in accordance with previous reported literature[2].

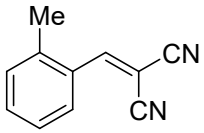
2-(4-Methylbenzylidene)malononitrile (2b)



2b

According to the general procedure, **2b** was prepared from the corresponding aldehyde (2 mmol) as a white solid (295.7 mg, 88 %). The spectral data are in accordance with previous reported literature[2].

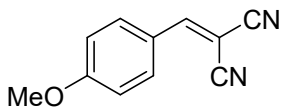
2-(2-Methylbenzylidene)malononitrile (2c)



2c

According to the general procedure, **2c** was prepared from the corresponding aldehyde (2 mmol) as a white solid (302.4 mg, 90 %). The spectral data are in accordance with previous reported literature[3]

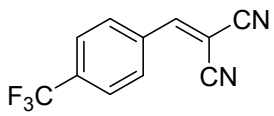
2-(4-Methoxybenzylidene)malononitrile (2d)



2d

According to the general procedure, **2d** was prepared from the corresponding aldehyde (2 mmol) as a white solid (331.2 mg, 90 %). The spectral data are in accordance with previous reported literature[2].

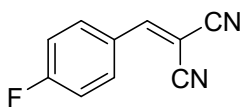
2-(4-(Trifluoromethyl)benzylidene)malononitrile (2e)



2e

According to the general procedure, **2e** was prepared from the corresponding aldehyde (2 mmol) as a white solid (368.5 mg, 83 %). The spectral data are in accordance with previous reported literature[5].

2-(4-Fluorobenzylidene)malononitrile (2f)

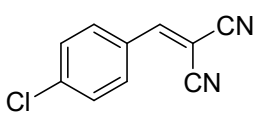


2f

According to the general procedure, **2f** was prepared from the

corresponding aldehyde (2 mmol) as a white solid (316.5 mg, 92 %). The spectral data are in accordance with previous reported literature[2].

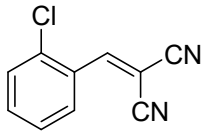
2-(4-Chlorobenzylidene)malononitrile (2g)



2g

According to the general procedure, **2g** was prepared from the corresponding aldehyde (2 mmol) as a yellow solid (336.4 mg, 89 %). The spectral data are in accordance with previous reported literature[2].

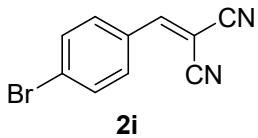
2-(2-Chlorobenzylidene)malononitrile (2h)



2h

According to the general procedure, **2h** was prepared from the corresponding aldehyde (2 mmol) as a yellow solid (297.0 mg, 79 %). The spectral data are in accordance with previous reported literature[3].

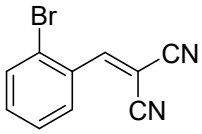
2-(4-Bromobenzylidene)malononitrile (2i)



2i

According to the general procedure, **2i** was prepared from the corresponding aldehyde (2 mmol) as a yellow solid (419.4 mg, 90 %). The spectral data are in accordance with previous reported literature[2].

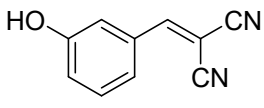
2-(2-Bromobenzylidene)malononitrile (2j)



2j

According to the general procedure, **2j** was prepared from the corresponding aldehyde (2 mmol) as a brown solid (382.1 mg, 82 %). The spectral data are in accordance with previous reported literature[4].

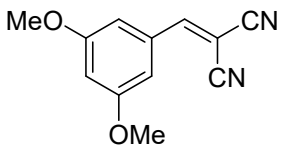
2-(3-Hydroxybenzylidene)malononitrile (2k)



2k

According to the general procedure, **2k** was prepared from the corresponding aldehyde (2 mmol) as a yellow solid (238.0 mg, 70 %). The spectral data are in accordance with previous reported literature[6].

2-(3,5-Dimethoxybenzylidene)malononitrile (2l)

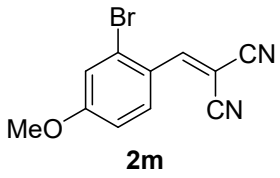


2l

According to the general procedure, **2l** was prepared from the

corresponding aldehyde (2 mmol) as a yellow solid (355.2 mg, 83 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (s, 1H), 7.04 (d, *J* = 2.2 Hz, 2H), 6.70 (t, *J* = 2.3 Hz, 1H), 3.84 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.3, 160.1, 132.4, 113.6, 112.6, 108.2, 107.2, 83.2, 55.7; **HRMS m/z (ESI)** calcd for $C_{12}H_{11}N_2O_2$ $(M + H)^+$ 215.0815, found 215.0818.

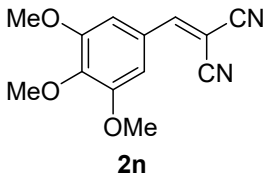
2-(2-Bromo-4-methoxybenzylidene)malononitrile (2m)



2m

According to the general procedure, **2m** was prepared from the corresponding aldehyde (2 mmol) as a white solid (426 mg, 81 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 8.9 Hz, 1H), 8.15 (s, 1H), 7.25 (s, 1H), 7.01 – 6.98 (m, 1H), 3.90 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.4, 131.1, 123.3, 119.5, 117.1, 115.5, 114.4, 113.9, 112.6, 56.1; **HRMS m/z (ESI)** calcd for $C_{11}H_8BrN_2O$ $(M + H)^+$ 262.9815, found 262.9820.

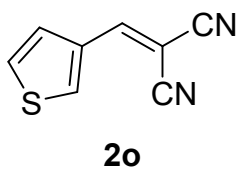
2-(3,4,5-Trimethoxybenzylidene)malononitrile (2n)



2n

According to the general procedure, **2n** was prepared from the corresponding aldehyde (2 mmol) as a yellow solid (405.0 mg, 83 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (s, 1H), 7.19 (s, 2H), 3.98 (s, 3H), 3.91 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.4, 153.4, 153.0, 126.0, 114.0, 108.3, 61.3, 56.4; **HRMS m/z (ESI)** calcd for $C_{13}H_{13}N_2O_3$ $(M + H)^+$ 245.0921, found 245.0922.

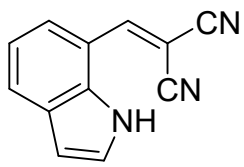
2-(Thiophen-3-ylmethylene)malononitrile (2o)



2o

According to the general procedure, **2o** was prepared from the corresponding aldehyde (2 mmol) as a gray solid (256.0 mg, 80 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 – 8.17 (m, 1H), 7.80 – 7.78 (m, 1H), 7.76 (s, 1H), 7.52 – 7.50 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.2, 136.8, 134.0, 128.5, 126.9, 113.8, 77.2; **HRMS m/z (ESI)** calcd for $C_8H_4N_2NaS$ $(M + Na)^+$ 182.9987, found 182.9989.

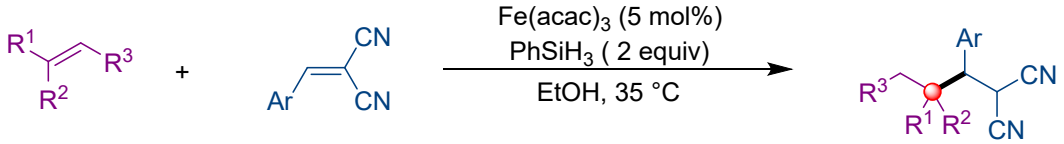
2-((1*H*-Indol-7-yl)methylene)malononitrile (2p)



2p

According to the general procedure, **2p** was prepared from the corresponding aldehyde (2 mmol) as a white solid (308.8 mg, 90 %).**^{1}H NMR (600 MHz, DMSO)** δ 11.83 (s, 1H), 8.90 (s, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 2.8 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 6.62 (dd, *J* = 3.2, 1.8 Hz, 1H); **^{13}C NMR (151 MHz, DMSO)** δ 156.6, 136.1, 129.8, 128.4, 127.6, 121.4, 112.0, 115.7, 115.4, 114.4, 102.9, 79.3; **HRMS m/z (ESI)** calcd for $C_{12}H_{18}N_3$ $(M + H)^+$ 194.0713, found 194.0715.

3. General Procedures for the Fe-catalysed Hydroalkylation of Alkenes.

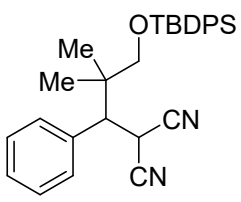


1 **2** **3**

Flame-dried 10 mL Schlenk tube filled with N_2, alkenes **2** (0.2 mmol, 1.0 equiv), $Fe(acac)_3$ (0.01 mmol, 5 mol%) were added under N_2, evacuated and purged with N_2 for three times, then alkenes **1** (0.3 mmol, 1.5 equiv), $PhSiH_3$ (0.4 mmol, 2 equiv), and EtOH (1.0 mL) were added. The formed mixture was stirred at 35 ºC under N_2 for 12 h as monitored by TLC. The solvent was removed under vaccum directly. The crude product was purified by flash column chromatography on silica gel (eluent: PE/EA) to afford the product **3**.

4. Characterization Data of the Products 3.

2-(3-((*tert*-Butyldiphenylsilyl)oxy)-2,2-dimethyl-1-phenylpropyl)malononitrile (3ba)

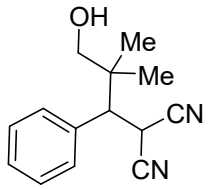


3ba

Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **3ba** was obtained as a colorless oil (85.9 mg, 92 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.67 (m, 2H), 7.63 – 7.61 (m, 2H), 7.50 – 7.40 (m, 8H), 7.38 – 7.36 (m, 3H), 4.56 (d, *J* = 5.4 Hz, 1H), 3.42

– 3.37 (m, 3H), 1.17 (s, 9H), 1.10 (s, 3H), 0.95 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.7, 135.6, 132.4, 130.2, 130.0, 129.6, 128.7, 128.6, 128.0, 127.8, 113.5, 113.2, 71.3, 52.1, 39.5 , 27.0 , 24.8, 24.1, 22.3, 19.2; **HRMS m/z (ESI)** calcd for $C_{30}H_{35}N_2OSi$ $(M + H)^+$ 467.2513, found 467.2511.

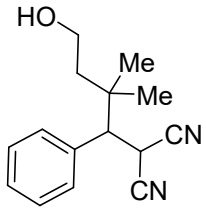
2-(3-Hydroxy-2,2-dimethyl-1-phenylpropyl)malononitrile (3ca)



3ca

Eluent in chromatography: petroleum ether/ethyl acetate 5:1, **3ca** was obtained as a white solid (38.7 mg, 85 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33– 7.30 (m, 2H), 7.27 – 7.24 (m, 1H), 7.19 – 7.17 (m, 2H), 4.46 (s, 2H), 3.84 (d, *J* = 10.7 Hz, 1H), 3.70 (d, *J* = 10.6 Hz, 1H), 3.31 (s, 1H), 1.05 (s, 3H), 0.61 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.3, 139.8, 129.4, 127.9, 127.1, 121.4, 74.7, 58.5, 48.6, 32.2, 25.1, 21.3; **HRMS m/z (ESI)** calcd for $C_{14}H_{17}N_2O$ $(M + H)^+$ 229.1335, found 229.1336.

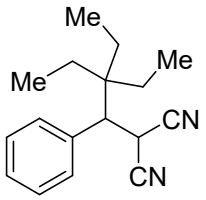
2-(4-Hydroxy-2,2-dimethyl-1-phenylbutyl)malononitrile (3da)



3da

Eluent in chromatography: petroleum ether/ethyl acetate 3:1, **3da** was obtained as a colorless oil (32.3 mg, 67 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.38 (m, 5H), 4.68 (d, *J* = 5.1 Hz, 1H), 3.84 – 3.81 (m, 2H), 3.26 (d, *J* = 5.1 Hz, 1H), 1.84 – 1.80 (m, 1H), 1.62 – 1.57 (m, 2H), 1.20 (s, 3H), 0.99 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.9, 129.7, 128.7, 128.5, 113.7, 113.3, 59.0, 54.7, 42.6, 37.2, 26.5, 25.4, 24.9; **HRMS m/z (ESI)** calcd for $C_{15}H_{19}N_2O$ $(M + H)^+$ 243.1492, found 243.1495.

2-(2,2-Diethyl-1-phenylbutyl)malononitrile (3ea)

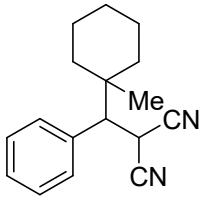


3ea

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3ea** was obtained as a colorless oil (25.7 mg, 51 %). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45 – 7.37 (m,5H), 4.21 (d, *J* = 5.5 Hz, 1H), 3.23 (d, *J* = 5.5 Hz, 1H), 1.60 – 1.48 (m, 6H), 0.83 (t, *J* = 7.5 Hz, 9H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.0, 130.0, 128.7, 128.6, 113.4, 113.3 , 53.1, 42.0, 27.7, 25.1, 8.6; **HRMS m/z (ESI)** calcd for $C_{17}H_{22}N_2Na$ $(M + Na)^+$ 277.1675,

found 277.1677.

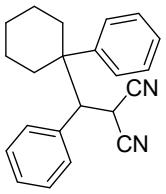
2-((1-methylcyclohexyl)(phenyl)methyl)malononitrile (3fa)



3fa

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3fa** was obtained as a colorless oil (35.9 mg, 71 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.37 (m, 5H), 4.25 (d, *J* = 5.4 Hz, 1H), 3.06 (d, *J* = 5.3 Hz, 1H), 1.58 – 1.37 (m, 6H), 1.29 – 1.23 (m, 4H), 1.16 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.7, 129.7, 128.6, 128.5, 113.4, 113.2, 56.8, 37.3, 36.8, 36.5, 25.6, 24.2, 21.7, 21.4, 20.3; **HRMS m/z (ESI)** calcd for $C_{17}H_{21}N_2$ $(M + H)^+$ 253.1699, found 253.1695.

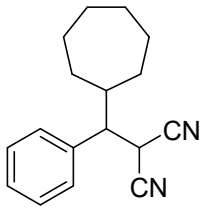
2-(Phenyl(1-phenylcyclohexyl)methyl)malononitrile (3ga)



3ga

Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **3ga** was obtained as a colorless oil (56.8 mg, 90 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 – 7.32 (m, 10H), 3.61 (d, *J* = 5.7 Hz, 1H), 3.12 (d, *J* = 5.7 Hz, 1H), 2.59 – 2.63 (m, 1H), 2.36 – 2.40(m, 1H), 1.70 – 1.59 (m, 2H), 1.51 – 1.35 (m, 4H), 1.14 – 1.07(m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.7, 135.0, 130.1, 129.3, 128.7, 128.5, 127.8, 127.3, 113.3, 113.0, 59.4, 46.5, 36.5, 30.6, 25.8, 25.2, 22.3, 21.9; **HRMS m/z (ESI)** calcd for $C_{22}H_{23}N_2$ $(M + H)^+$ 315.1856, found 315.1859.

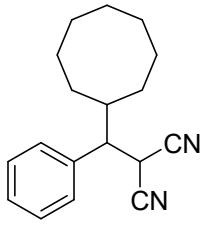
2-(Cycloheptyl(phenyl)methyl)malononitrile (3ha)



3ha

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3ha** was obtained as a colorless oil (24.4 mg, 48 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.31 (m, 5H), 4.19 (d, *J* = 5.9 Hz, 1H), 3.01 – 2.98 (m, 1H), 2.31 – 2.23 (m, 1H), 1.95 – 1.90 (m,1H), 1.74 – 1.45 (m, 7H), 1.36 – 1.10 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.9, 129.1, 128.7, 128.4, 112.2, 111.9, 52.1, 40.4, 32.6, 30.6, 28.6, 27.8, 27.7, 25.9, 25.8; **HRMS m/z (ESI)** calcd for $C_{17}H_{20}N_2Na$ $(M + Na)^+$ 275.1519, found 275.1525.

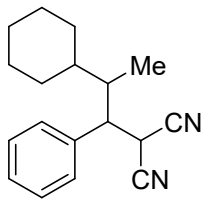
2-(Cyclooctyl(phenyl)methyl)malononitrile (3ia)



3ia

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3ia** was obtained as a colorless oil (28.9 mg, 54 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.34 (m, 5H), 4.20 (d, *J* = 5.3 Hz, 1H), 2.96 (dd, *J* = 10.3, 5.3 Hz, 1H), 2.37 – 2.30 (m, 1H), 1.86 – 1.44 (m, 12H), 1.30 – 1.18 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.0, 129.1, 128.8, 128.5, 112.3, 111.9, 52.1, 38.2, 30.6, 28.6, 27.8, 27.4, 26.6, 26.3, 25.7, 24.3; ; **HRMS m/z (ESI)** calcd for $C_{18}H_{22}N_2Na$ $(M + Na)^+$ 289.1675, found 289.1677.

2-(2-Cyclohexyl-1-phenylpropyl)malononitrile (3ja)

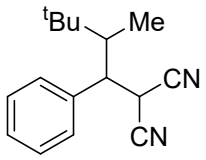


3ja

Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **3ja** was obtained as a colorless oil (46.4 mg 87 % dr = 1/1.1): Major: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.34 (m, 5H), 4.14 – 4.12 (m, 1H), 3.11 (dd, *J* = 10.1, 5.5 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.85 – 1.63 (m, 3H), 1.34 – 1.03 (m, 8H), 0.69 (d, *J* = 6.9 Hz, 3H); Minor: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.34 (m, 5H), 4.14 – 4.12 (m, 1H), 3.03 (dd, *J* = 11.5, 4.4 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.85 – 1.63 (m, 3H), 1.34 – 1.03 (m, 11H); All isomers: **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.1, 137.0, 129.2, 129.1, 128.8, 128.7, 128.3, 128.1, 112.2, 111.9, 111.8, 50.1, 48.9, 39.7, 39.6, 39.1, 38.6, 32.1, 32.0, 28.2, 27.5, 26.7, 26.6, 26.5, 26.4, 26.3, 26.2, 26.0, 25.4, 12.8, 12.5; **HRMS m/z (ESI)** calcd for $C_{18}H_{23}N_2$ $(M + H)^+$ 267.1856, found 267.1853.

2-(2,3,3-Trimethyl-1-phenylbutyl)malononitrile (3ka)

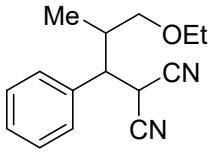
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **3ka** was obtained as a colorless oil (30.3 mg, 63 %, dr = 1/8): Major: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.37 (m, 5H), 4.11 (d, *J* = 4.2 Hz, 1H), 3.23 (dd, *J* = 8.1, 4.2 Hz, 1H), 2.28 – 2.22 (m, 1H), 1.25 (d, *J* = 7.1 Hz, 3H), 0.82 (s, 9H); Minor: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.37 (m, 5H), 4.05 (d, *J* = 10.7 Hz, 1H), 3.69 (dd, *J* = 10.7, 3.1 Hz, 1H), 2.05 – 2.02 (m, 1H), 1.11 (d, *J* = 7.2 Hz, 3H), 0.86 (s, 9H); All isomers: **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.0, 129.4, 129.03, 128.95, 128.6, 128.6, 128.5, 112.6, 112.4, 112.22,



3ka

112.20, 48.1, 47.7, 45.0, 44.3, 34.7, 29.5, 29.12, 28.4, 28.0, 13.7, 10.6; **HRMS m/z (ESI)** calcd for $C_{16}H_{21}N_2$ $(M + H)^+$ 241.1699, found 241.1705.

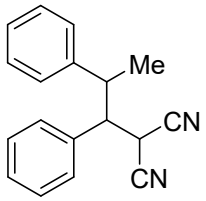
2-(3-Ethoxy-2-methyl-1-phenylpropyl)malononitrile (3la)



3la

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3la** was obtained as a colorless oil (21.2 mg, 44 %, dr = 1/1.3): Major: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.34 (m, 5H), 4.80 (d, *J* = 9.5 Hz, 1H), 3.61 – 3.46 (m, 2H), 3.43 – 3.34 (m, 1H), 3.24 (dd, *J* = 9.5, 5.4 Hz, 1H), 3.19 – 3.13 (m, 1H), 2.63 – 2.56 (m, 1H), 1.28 – 1.20 (m, 3H), 0.94 (d, *J* = 6.9 Hz, 3H); Minor: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.34 (m, 5H), 4.72 (d, *J* = 5.4 Hz, 1H), 3.61 – 3.46 (m, 2H), 3.43 – 3.34 (m, 1H), 3.19 – 3.13 (m, 1H), 3.09 (dd, *J* = 9.9, 5.4 Hz, 1H), 2.54 – 2.45 (m, 1H), 1.28 – 1.20 (m, 3H), 0.77 (d, *J* = 6.9 Hz, 3H); All isomers: **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.6, 134.4, 129.1, 129.0, 128.8, 128.7, 128.7, 128.4, 113.0, 112.6, 112.4, 74.4, 72.3, 66.9, 66.7, 50.81, 50.5, 35.0, 34.7, 28.0, 27.7, 15.9, 15.7, 15.2, 15.1; **HRMS m/z (ESI)** calcd for $C_{15}H_{18}N_2NaO$ $(M + Na)^+$ 265.1311, found 265.1315.

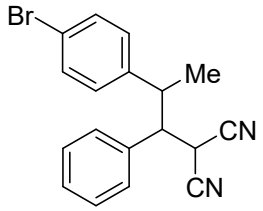
2-(1,2-Diphenylpropyl)malononitrile (3ma) [8]



3ma

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3ma** was obtained as a white solid (26.7 mg, 51 %, dr ＞ 20/1): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.33 (m, 10H), 3.61 (d, *J* = 4.1 Hz, 1H), 3.45 – 3.34 (m, 1H), 3.21 (dd, *J* = 11.7, 4.1 Hz, 1H), 1.15 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.4, 135.5, 129.7, 129.3, 129.1, 128.5, 128.1, 127.1, 112.1, 111.4, 53.6, 42.0, 28.7, 20.6; **HRMS m/z (ESI)** calcd for $C_{18}H_{16}N_2Na$ $(M + Na)^+$ 283.1206, found 283.1211.

2-(2-(4-Dromophenyl)-1-phenylpropyl)malononitrile (3na)

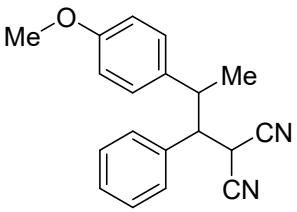


3na

Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **3na** was obtained as a white solid (27.5 mg, 40 %, dr ＞ 20/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.43 (m, 5H), 7.27 – 7.25 (m, 2H), 3.61 (d, *J* = 4.3 Hz, 1H), 3.42 – 3.37 (m, 1H), 3.17 (dd, *J* = 11.6, 4.3 Hz, 1H), 1.12 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.3, 135.2, 132.8, 129.4, 129.3, 128.8, 128.4, 121.9, 111.8, 111.3, 53.3, 41.6, 28.6, 20.5; **HRMS m/z (ESI)** calcd for $C_{18}H_{15}BrN_2Na$ $(M + Na)^+$ 361.0311, found 361.0312.

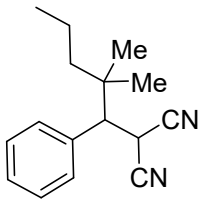
2-(2-(4-Methoxyphenyl)-1-phenylpropyl)malononitrile (3oa)



3oa

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3oa** was obtained as a colorless oil (36.1 mg, 62 %, dr = 1/10)：Major: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 – 7.27 (m, 3H), 6.98 – 6.95 (m, 2H), 6.87 – 6.85 (m, 2H), 6.75 – 6.73 (m, 2H), 4.04 (d, *J* = 8.1 Hz, 1H), 3.70 (s, 3H), 3.50 – 3.48 (m, 2H), 1.39 (d, *J* = 6.9 Hz, 3H); Minor: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.27 (m, 7H), 6.98 – 6.95 (m, 2H), 3.68 (s, 3H), 3.64 (d, *J* = 4.1 Hz, 1H), 3.29 (d, *J* = 6.9 Hz, 2H); 1.12 (d, *J* = 6.8 Hz, 3H); All isomers: **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.7, 134.8, 132.3, 129.3, 129.2, 128.9, 128.6, 128.6, 128.1, 115.0, 113.8, 112.6, 112.0, 55.4, 55.2, 53.9, 52.7, 41.3, 40.7, 28.1, 27.5, 20.7, 20.2; **HRMS m/z (ESI)** calcd for $C_{19}H_{18}N_2NaO$ $(M + Na)^+$ 313.1311, found 313.1313.

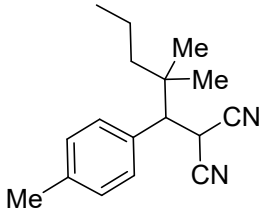
2-(2,2-Dimethyl-1-phenylpentyl)malononitrile (3aa)[7]



3aa

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3aa** was obtained as a colorless oil (39.4 mg, 82 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.39 (m, 5H), 4.21 (d, *J* = 5.4 Hz, 1H), 3.08 (d, *J* = 5.4 Hz, 1H), 1.35 – 1.26 (m, 4H), 1.14 (s, 3H), 1.00 (s, 3H), 0.93 – 0.87 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.0, 129.5, 128.7, 128.6, 113.3, 113.1, 55.3, 43.5, 37.5, 25.4 , 25.0, 24.8, 17.0, 14.6; **HRMS m/z (ESI)** calcd for $C_{16}H_{21}N_2$ $(M + H)^+$ 241.1699, found 241.1702.

2-(2,2-Dimethyl-1-(p-tolyl)pentyl)malononitrile (3ab)

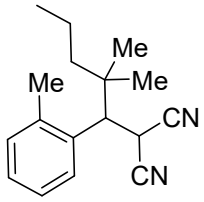


3ab

Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **3ab** was obtained as a colorless oil (46.3 mg, 91%): **^{1}H NMR**

(400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 4.19 (d, *J* = 5.4 Hz, 1H), 3.04 (d, *J* = 5.4 Hz, 1H), 2.37 (s, 3H), 1.31 – 1.28 (m, 4H), 1.12 (s, 3H), 0.99 (s, 3H), 0.91 – 0.88 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.3, 132.9, 129.39, 129.35, 113.4, 113.2, 55.0, 43.5, 37.4, 25.4, 25.0, 24.9, 21.1, 17.0, 14.6; **HRMS m/z (ESI)** calcd for $C_{17}H_{23}N_2$ $(M + H)^+$ 255.1856, found 255.1855.

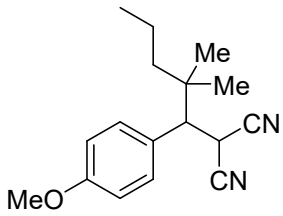
2-(2,2-Dimethyl-1-(o-tolyl)pentyl)malononitrile (3ac)



3ac

Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **3ac** was obtained as a colorless oil (36.9 mg, 73%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 – 7.55 (m, 1H), 7.26 – 7.24 (m, 3H), 4.18 (d, *J* = 6.2 Hz, 1H), 3.56 (d, *J* = 6.2 Hz, 1H), 2.41 (s, 3H), 1.36 – 1.34 (m, 4H), 1.16 (s, 3H), 0.95 (s, 3H), 0.94 – 0.91 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.6, 135.0, 131.3, 128.2, 127.4, 126.4, 113.2, 113.1, 48.3, 43.5, 38.3, 25.2, 24.9, 24.8, 20.7, 17.1, 14.6; **HRMS m/z (ESI)** calcd for $C_{17}H_{23}N_2$ $(M + H)^+$ 255.1856, found 255.1858.

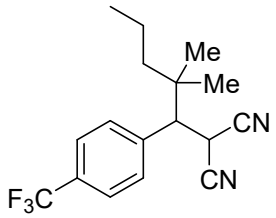
2-(1-(4-Methoxyphenyl)-2,2-dimethylpentyl)malononitrile (3ad)



3ad

Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **3ad** was obtained as a colorless oil (49.1 mg, 91 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.31 (m, 2H), 6.94 – 6.90 (m, 2H), 4.18 (d, *J* = 5.3 Hz, 1H), 3.82 (s, 3H), 3.03 (d, *J* = 5.3 Hz, 1H), 1.33 – 1.26 (m, 4H), 1.11 (s, 3H), 0.99 (s, 3H), 0.91 – 0.87 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.6, 130.6, 127.9, 114.0, 113.4, 113.2, 55.2, 54.7, 43.5, 37.5, 25.3, 25.0, 17.0, 14.6; **HRMS m/z (ESI)** calcd for $C_{17}H_{22}N_2NaO$ $(M + Na)^+$ 293.1624, found 293.1626.

2-(2,2-Dimethyl-1-(4-(trifluoromethyl)phenyl)pentyl)malononitrile (3ae)

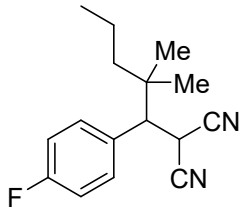


3ae

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3ae** was obtained as a colorless oil (30.2 mg, 49 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.67 (m, 2H), 7.56 (d, *J* = 8.1 Hz,

2H), 4.23 (d, *J* = 5.2 Hz, 1H), 3.14 (d, *J* = 5.2 Hz, 1H), 1.35 – 1.27 (m, 4H), 1.15 (s, 3H), 1.01 (s, 3H), 0.92 – 0.89 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.9, 130.9 (q, *J* = 32.9 Hz), 130.0, 125.7 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 272.5 Hz), 112.9, 112.6, 55.1, 43.4, 37.5, 25.4, 24.9, 24.5, 17.0, 14.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.8; **HRMS m/z (ESI)** calcd for $C_{17}H_{19}F_3N_2Na$ $(M + Na)^+$ 331.1393, found 331.1395.

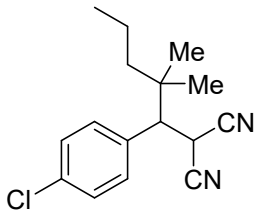
2-(1-(4-Fluorophenyl)-2,2-dimethylpentyl)malononitrile (3af)



3af

Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **3af** was obtained as a colorless oil (38.9 mg, 75 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.38 (m, 2H), 7.10 (t, *J* = 8.7 Hz, 2H), 4.19 (d, *J* = 5.2 Hz, 1H), 3.07 (d, *J* = 5.2 Hz, 1H), 1.35 – 1.24 (m, 4H), 1.12 (s, 3H), 0.99 (s, 3H), 0.91 – 0.88(m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.7 (d, *J* = 248.4 Hz), 131.7 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 8.2 Hz), 115.7 (d, *J* = 21.3 Hz), 113.1, 112.9, 54.6, 43.4, 37.5, 25.3, 24.9, 24.8, 17.0, 14.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.0; **HRMS m/z (ESI)** calcd for $C_{16}H_{19}FN_2Na$ $(M + Na)^+$ 281.1424, found 281.1428.

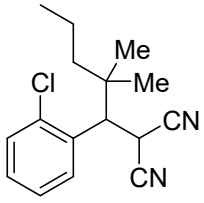
2-(1-(4-Chlorophenyl)-2,2-dimethylpentyl)malononitrile (3ag)



3ag

Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **3ag** was obtained as a colorless oil (47.6 mg, 87 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.34(m, 4H), 4.19 (d, *J* = 5.2 Hz, 1H), 3.05 (d, *J* = 5.3 Hz, 1H), 1.33 – 1.25(m, 4H), 1.12 (s, 3H), 0.99 (s, 3H), 0.91 – 0.88 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.7, 134.4, 130.9, 129.0, 113.1, 112.8, 54.7, 43.4, 37.5, 25.23, 24.9, 24.7, 16.9, 14.6; **HRMS m/z (ESI)** calcd for $C_{16}H_{20}ClN_2$ $(M + H)^+$ 275.1310, found 275.1312.

2-(1-(2-Chlorophenyl)-2,2-dimethylpentyl)malononitrile (3ah)

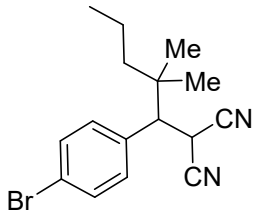


3ah

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3ah** was obtained as a colorless oil (31.0 mg, 56 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 – 7.70 (m, 1H), 7.50 – 7.48 (m, 1H), 7.36 – 7.31 (m,

2H), 4.19 (d, *J* = 5.9 Hz, 1H), 4.07 (d, *J* = 6.0 Hz, 1H), 1.41 – 1.35 (m, 4H), 1.16 (s, 3H), 0.98 (s, 3H), 0.94 – 0.91 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.0, 134.1, 130.4, 129.6, 129.0, 127.2, 113.1, 112.5, 48.1, 43.3,38.4, 25.1, 24.6, 24.5, 17.1, 14.6; **HRMS m/z (ESI)** calcd for $C_{16}H_{20}ClN_2$ $(M + H)^+$ 275.1310, found 275.1315.

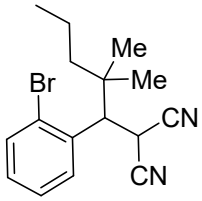
2-(1-(4-Bromophenyl)-2,2-dimethylpentyl)malononitrile (3ai)



3ai

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3ai** was obtained as a colorless oil (47.5 mg, 74 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.52 (m, 2H), 7.31 – 7.28 (m, 2H), 4.19 (d, *J* = 5.2 Hz, 1H), 3.04 (d, *J* = 5.2 Hz, 1H), 1.33 – 1.26 (m, 4H), 1.12 (s, 3H), 0.99 (s, 3H), 0.91 – 0.88 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.9, 131.9, 131.1, 122.9, 113.0, 112.8, 54.8, 43.4, 37.4, 25.3, 24.9, 24.6, 16.9, 14.6; **HRMS m/z (ESI)** calcd for $C_{16}H_{20}BrN_2$ $(M + H)^+$ 319.0804, found 319.0810; **HRMS m/z (ESI)** calcd for $C_{16}H_{20}BrN_2$ $(M + H)^+$ 319.0804, found 319.0810.

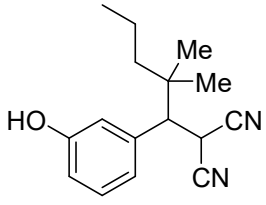
2-(1-(2-Bromophenyl)-2,2-dimethylpentyl)malononitrile (3aj)



3aj

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3aj** was obtained as a colorless oil (31.7 mg, 50%): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 – 7.67 (m, 2H), 7.42 – 7.38 (m, 1H), 7.21 – 7.25 (m, 1H), 4.18 (d, *J* = 5.9 Hz, 1H), 4.08 (d, *J* = 5.9 Hz, 1H), 1.46 – 1.34 (m, 4H), 1.17 (s, 3H), 0.98 (s, 3H), 0.95 – 0.92 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.8, 133.9, 129.9, 129.0, 127.8, 127.4, 113.0, 112.4, 50.9, 43.4, 38.5, 25.1, 24.6 , 24.5, 17.1, 14.6; **HRMS m/z (ESI)** calcd for $C_{16}H_{20}BrN_2$ $(M + H)^+$ 319.0804, found 319.0805.

2-(1-(3-Hydroxyphenyl)-2,2-dimethylpentyl)malononitrile (3ak)

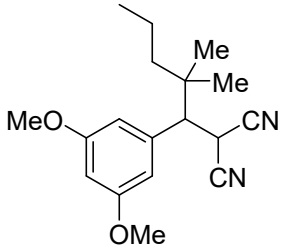


3ak

Eluent in chromatography: petroleum ether/ethyl acetate 4:1, **3ak** was obtained as a colorless oil (42.1 mg, 80 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 – 7.23 (m, 1H), 6.95 – 6.83 (m, 3H),

4.64 (br s, 1H), 4.20 (d, *J* = 5.5 Hz, 1H), 3.01 (d, *J* = 5.5 Hz,1H), 1.37 – 1.28 (m, 4H), 1.13 (s, 3H), 1.00 (s, 3H), 0.88 – 0.91 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.8, 137.6, 129.9, 122.0, 116.4, 115.7, 113.4, 113.1, 55.0, 43.5, 37.4, 25.4, 25.0, 24.8, 17.0, 14.6; **HRMS m/z (ESI)** calcd for $C_{16}H_{21}N_2O$ $(M + H)^+$ 257.1648, found 257.1652.

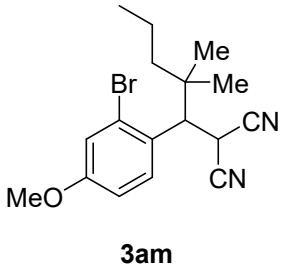
2-(1-(3,5-Dimethoxyphenyl)-2,2-dimethylpentyl)malononitrile (3al)



3al

Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **3al** was obtained as a colorless oil (31.2 mg, 52 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.54 (d, *J* = 2.2 Hz, 2H), 6.46 (d, *J* = 2.2 Hz, 1H), 4.17 (d, *J* = 5.5 Hz, 1H), 3.80 (s, 6H), 2.98 (d, *J* = 5.5 Hz, 1H), 1.34 – 1.31 (m, 4H), 1.14 (s,3H), 1.01 (s, 3H), 0.92 – 0.87 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.7, 138.1, 113.4, 113.1, 108.0, 100.0, 55.3, 55.3, 43.5, 37.4, 25.5, 25.0, 24.7, 17.0, 14.6; **HRMS m/z (ESI)** calcd for $C_{18}H_{25}N_2O_2$ $(M + H)^+$ 301.1911, found 301.1915.

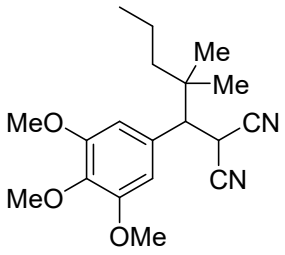
2-(1-(2-Bromo-4-methoxyphenyl)-2,2-dimethylpentyl)malononitrile (3am)



3am

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3an** was obtained as a colorless oil (58.7 mg, 85 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 2.7 Hz, 1H), 6.96 – 6.93 (m, 1H), 4.16 (d, *J* = 5.8 Hz, 1H), 3.98 (d, *J* = 5.7 Hz, 1H), 3.82 (s, 3H), 1.40 – 1.34 (m, 4H), 1.14 (s, 3H), 0.97 (s, 3H), 0.97 – 0.91 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.6, 129.3, 127.8, 127.5, 118.8, 114.0, 113.1, 112.6, 55.5, 50.3, 43.4, 38.5, 25.1, 24.7, 17.1, 14.6; **HRMS m/z (ESI)** calcd for $C_{19}H_{21}BrN_2NaO$ $(M + Na)^+$ 371.0729, found 371.0733.

2-(2,2-Dimethyl-1-(3,4,5-trimethoxyphenyl)pentyl)malononitrile (3an)

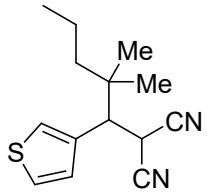


3an

Eluent in chromatography: petroleum ether/ethyl acetate 10:1, **3am**was obtained as a colorless oil (46.5 mg, 70 %): **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.62 (s, 2H), 4.20 (d, *J* = 4.8 Hz, 1H), 3.87 (s, 3H), 3.87 (s, 6H), 2.96 (d, *J* = 4.8 Hz, 1H), 1.32 – 1.30

(m, 4H), 1.14 (s, 3H), 1.01 (s, 3H), 0.93 – 0.87 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.0, 138.1, 131.3, 113.5, 113.0, 106.9, 60.9, 56.2, 55.4, 43.6, 37.6, 25.4, 25.0, 24.8, 17.0, 14.6; **HRMS m/z (ESI)** calcd for $C_{19}H_{27}N_2O_3$ $(M + H)^+$ 331.2016, found 331.2020.

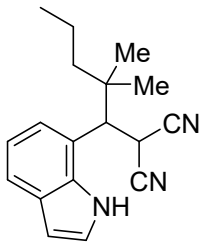
2-(2,2-Dimethyl-1-(thiophen-3-yl)pentyl)malononitrile (3ao)



3ao

Eluent in chromatography: petroleum ether/ethyl acetate 15:1, **3ao** was obtained as a white solid (41.6 mg, 84%): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 – 7.36 (m, 2H), 7.21 (dd, *J* = 4.9, 1.5 Hz, 1H), 4.15 (d, *J* = 4.4 Hz, 1H), 3.27 (d, *J* = 4.4 Hz, 1H), 1.33 – 1.24 (m,4H), 1.12 (s, 3H), 1.01 (s, 3H), 0.92 – 0.87 (m, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 135.8, 128.1, 126.1, 124.8, 113.3, 113.0, 51.1, 43.4, 37.4, 25.3, 25.0, 24.9, 16.9, 14.6; **HRMS m/z (ESI)** calcd for $C_{14}H_{19}N_2S$ $(M + H)^+$ 247.1263, found 247.1266.

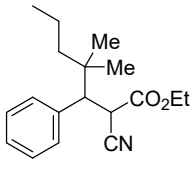
2-(1-(1*H*-Indol-7-yl)-2,2-dimethylpentyl)malononitrile (3ap)



3ap

Eluent in chromatography: petroleum ether/ethyl acetate 5:1, **3ap** was obtained as a yellow solid (35.2 mg, 63 %): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.18 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.21 – 7.17 (m, 1H), 6.60 (dd, *J* = 3.3, 1.9 Hz, 1H), 4.29 (d, *J* = 6.0 Hz, 1H), 3.48 (d, *J* = 6.0 Hz, 1H), 1.47 – 1.32 (m, 4H), 1.18 (s, 3H), 1.01 (s, 3H), 0.88 (t, *J* = 6.9 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 135.7, 128.6, 124.7, 121.0, 120.1, 112.0, 119.4, 113.5, 113.2, 103.6, 49.3, 43.2, 38.6, 25.4, 25.0, 24.9, 17.3, 14.6; **HRMS m/z (ESI)** calcd for $C_{18}H_{21}N_3Na$ $(M + Na)^+$ 302.1628, found 302.1632.

Ethyl 2-cyano-4,4-dimethyl-3-phenylheptanoate (3aq)

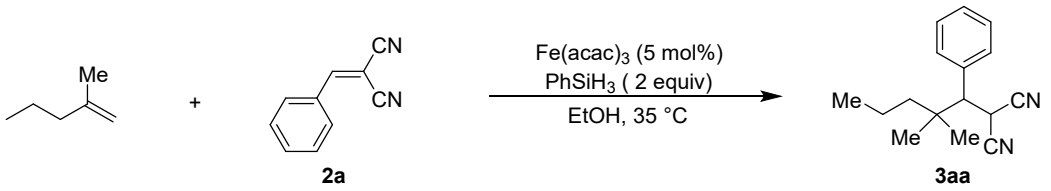


3aq

Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **3aq** was obtained as a colorless oil (30.1 mg, 52 %, dr = 1/3.5): Major: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 6.9 Hz, 2H), 7.33 – 7.24 (m, 3H), 4.02 – 3.96 (m, 3H), 3.21 (d, *J* = 4.8 Hz, 1H), 1.40 – 1.24 (m, 4H), 1.13 (s, 3H), 1.01 – 0.94 (m, 6H), 0.89 (t, *J* = 6.7 Hz, 3H); Minor: ^{1}H

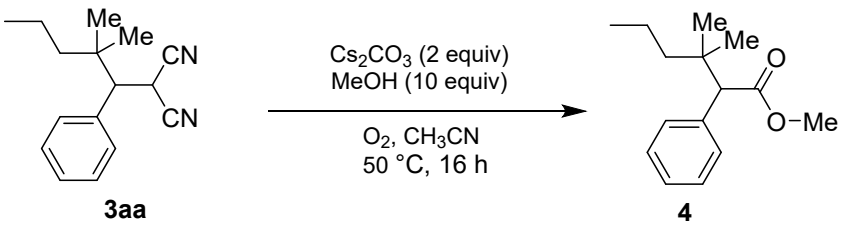
NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.24 (m, 3H), 7.18 – 7.16 (m, 2H), 3.91 (q, *J* = 7.1 Hz, 2H), 3.88 – 3.86 (m, 1H), 3.38 (d, *J* = 9.3 Hz, 1H), 1.40 – 1.24 (m, 4H), 1.08 (s, 3H), 1.01 – 0.94 (m, 6H), 0.89 (t, *J* = 6.7 Hz, 3H); All isomers: **^{13}C NMR (151 MHz, $CDCl_3$)** δ 166.2, 165.8, 138.4, 137.0, 133.3, 130.2, 128.0, 127.9, 127.6, 127.4, 117.7, 117.5, 62.6, 54.3, 43.6, 43.3, 39.5, 39.1, 37.3, 37.0, 25.7, 25.5, 25.4, 24.8, 17.03, 16.96, 14.8, 14.6, 13.6, 13.5; **HRMS m/z (ESI)** calcd for $C_{18}H_{26}NO_2$ $(M + H)^+$ 288.1958, found 288.1961.

5. Synthetic Applications.



Flame-dried 50 mL Schlenk tube filled with N_2, alkenes **2a** (4 mmol, 1.0 equiv), $Fe(acac)_3$ (0.2 mmol, 5 mol%) were added under N_2, evacuated and purged with N_2 for three times, then 2-methyl-1-pentene (6 mmol, 1.5 equiv), $PhSiH_3$ (8 mmol, 2 equiv), and EtOH (20.0 mL) were added. The formed mixture was stirred at 35 ºC under N_2 for 12 h as monitored by TLC. The solution was filtered, then concentrated and purified using column chromatography isolation on silica gel by gradient elution with petroleum ether/ethyl acetate (20:1) to give the ester **3aa** as a colorless oil (710.6 mg, 74 %).

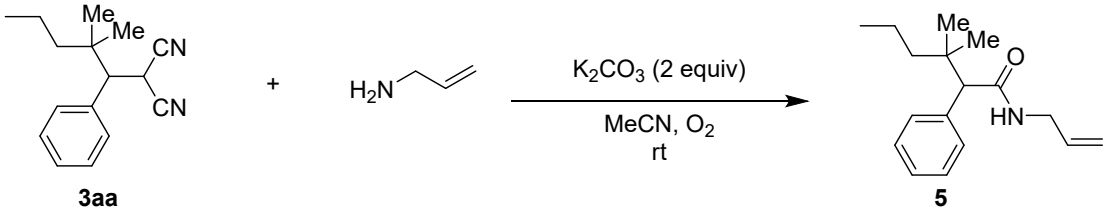
Methyl 3,3-dimethyl-2-phenylhexanoate (4)



Under O_2 atmosphere, Methanol (32 mg, 1 mmol, 10.0 equiv) was added to a solution of alkylation product **3aa** (24 mg, 0.1 mmol, 1.0 equiv) and Cs_2CO_3 (65.2 mg, 0.2 mmol, 2.0 equiv) in CH_3CN (1.0 mL). The resulting mixture was stirred at 50 °C for

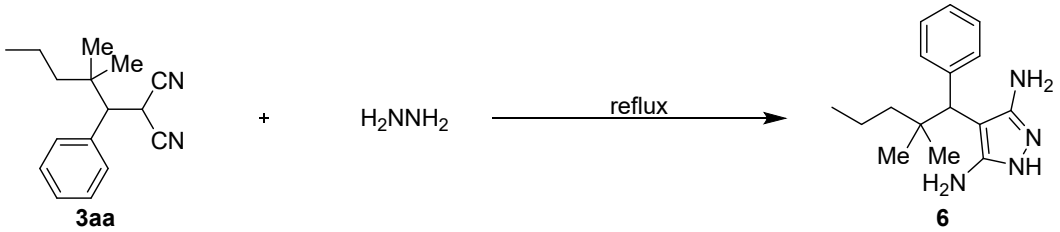
16 h. The solution was filtered, then concentrated and purified using column chromatography isolation on silica gel by gradient elution with petroleum ether/ethyl acetate (100:1) to give the ester **4** as a colorless oil (21.5 mg, 92 %).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.39 (m, 2H), 7.31 – 7.25 (m, 3H), 3.63 (s, 3H), 3.52 (s, 1H), 1.34 – 1.30 (m, 3H), 1.19 – 1.16 (m, 1H), 1.01 (s, 3H), 0.90 (s, 3H), 0.88 – 0.86 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.6, 136.0, 130.1, 127.8, 127.0, 60.2, 51.3, 43.1, 37.1, 24.6, 24.2, 17.0, 14.8; **HRMS m/z (ESI)** calcd for $C_{15}H_{23}O_2$ $(M + H)^+$ 235.1693, found 235.1696.

***N*-Allyl-3,3-dimethyl-2-phenylhexanamide (5)**



Under O_2 atmosphere, allylamine (34.2 mg, 0.6 mmol, 2.0 equiv) was added to a solution of alkylation product **3aa** (72 mg, 0.3 mmol, 1.0 equiv) and K_2CO_3 (82.8 mg, 1.0 mmol, 2.0 equiv) in CH_3CN (3.0 mL). The resulting mixture was stirred at RT until the compound **3aa** was completely consumed as monitored by TLC. The solution was filtered, then concentrated and purified using column chromatography isolation on silica gel by gradient elution with petroleum ether/ethyl acetate (20:1) to give the amide **5** as a colorless oil (71.6 mg, 92 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.44 (m, 2H), 7.29 – 7.24 (m, 3H), 5.84 (t, J = 5.9 Hz, 1H), 5.79 – 5.72 (m, 1H), 5.07 – 5.02 (m, 2H), 3.92– 3.87 (m, 1H), 3.72 – 3.67 (m, 1H) 3.15 (s, 1H), 1.43 – 1.20 (m, 4H), 1.06 (s, 3H), 0.95 (s, 3H), 0.87 (t, J = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.6, 137.2, 134.3, 130.0, 127.6, 126.8, 115.9, 62.0, 43.1, 41.6, 37.1, 24.8, 24.3, 17.1, 14.8; **HRMS m/z (ESI)** calcd for $C_{17}H_{26}NO$ $(M + H)^+$ 260.2009, found 260.2007.

4-(2,2-Dimethyl-1-phenylpentyl)-1H-pyrazole-3,5-diamine (6)



The alkylation product **3aa** (120 mg, 0.5 mmol, 1.0 equiv) was dissolved in hydrazine hydrate (150 mg, 3.0 mmol, 6.0 equiv). The mixture was heated under reflux for 4 h, and then cooled to room temperature. Ethanol was added and the precipitated was collected. Recrystallization from ethyl acetate and hexane gave the pyrazole-3,5-diamine **6** as a yellow solid (112.9 mg, 83 %). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.35 (m, 2H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.16 – 7.12 (m, 1H), 5.56 (br s, 4H), 3.48 (s, 1H), 1.49 – 1.42 (m, 1H), 1.37 – 1.19 (m, 3H), 1.10 (s, 3H), 1.02 (s, 3H), 0.81 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.2, 142.2, 129.5, 128.1, 125.8, 92.7, 50.8, 43.6, 39.1, 27.0, 25.8, 17.3, 15.0; **HRMS m/z (ESI)** calcd for $C_{16}H_{25}N_4$ $(M + H)^+$ 273.2074, found 273.2076.

6. References

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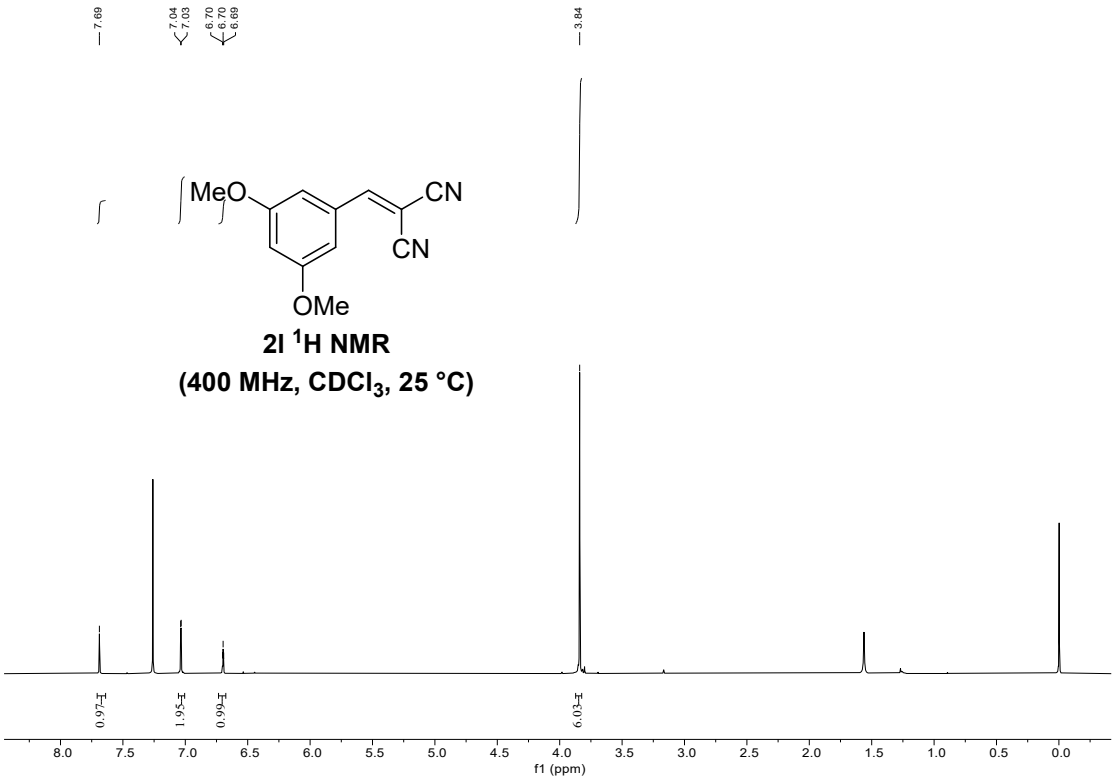
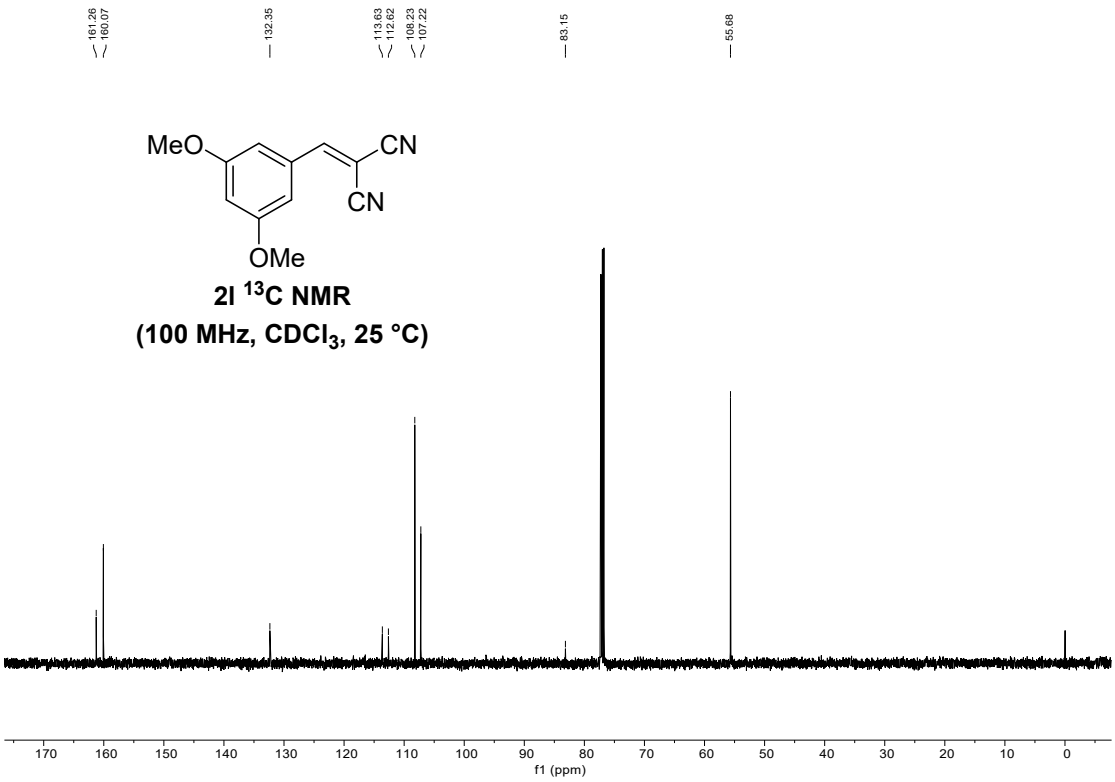
7. Copies of NMR Spectra



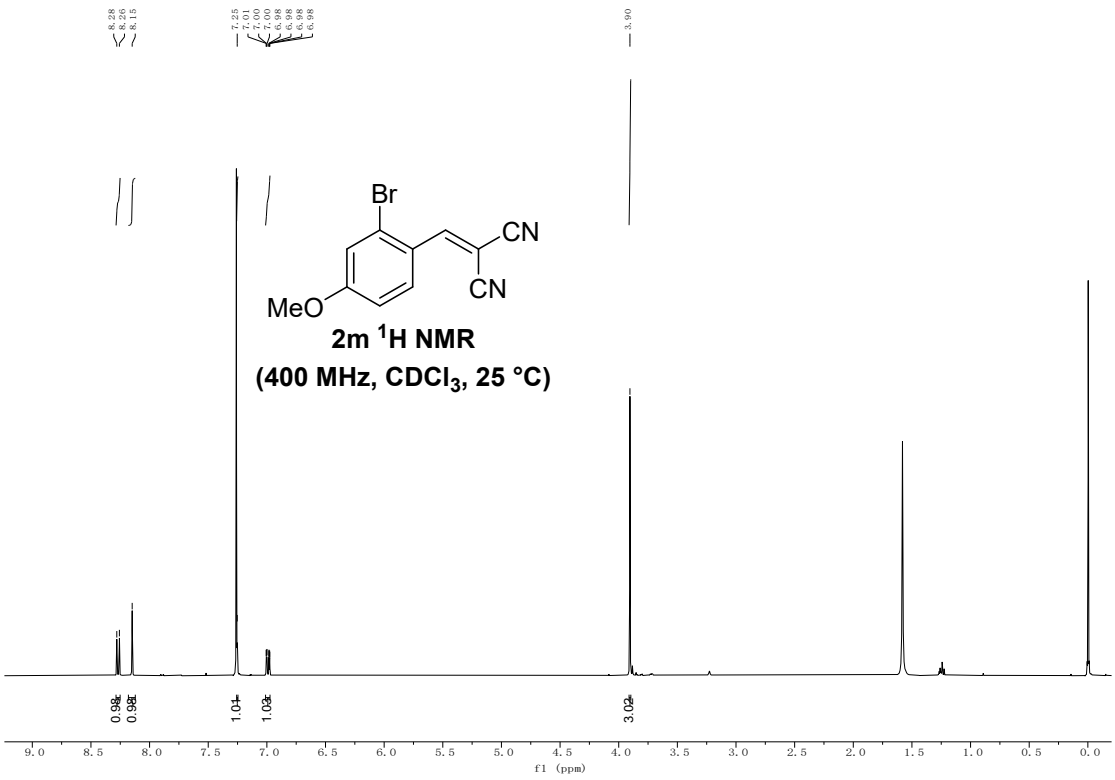
2l ^{1}H NMR

(400 MHz, $CDCl_3$, 25 °C)

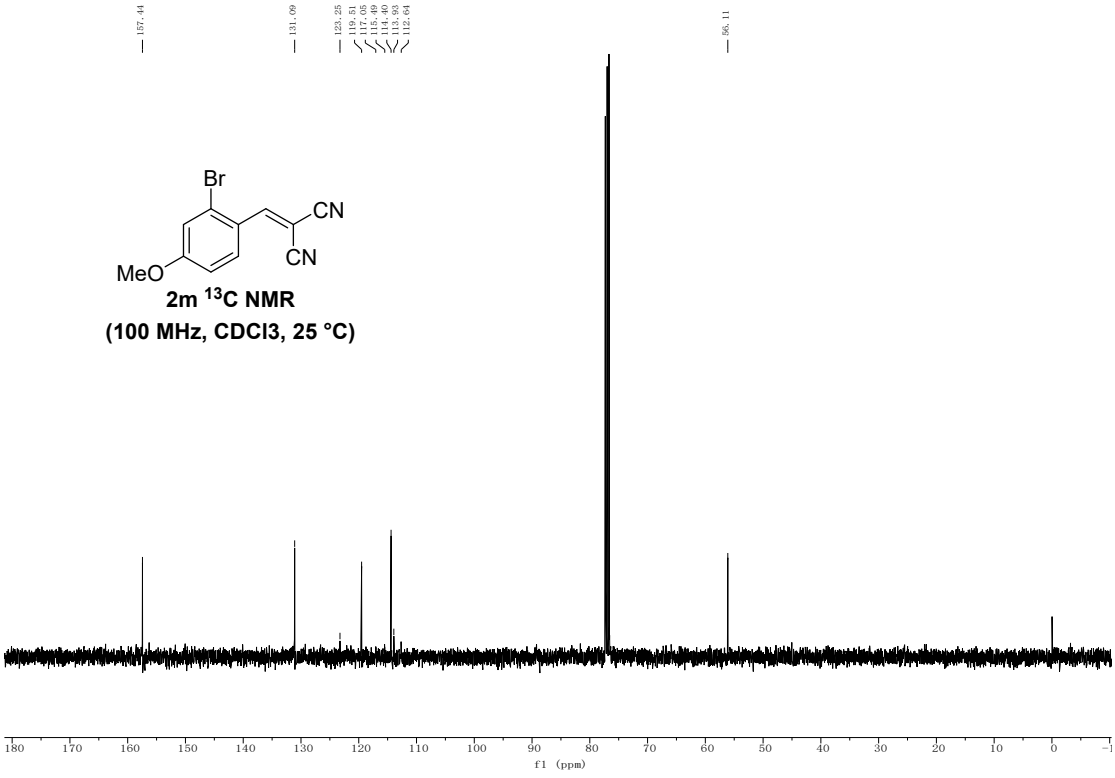


2l ^{13}C NMR

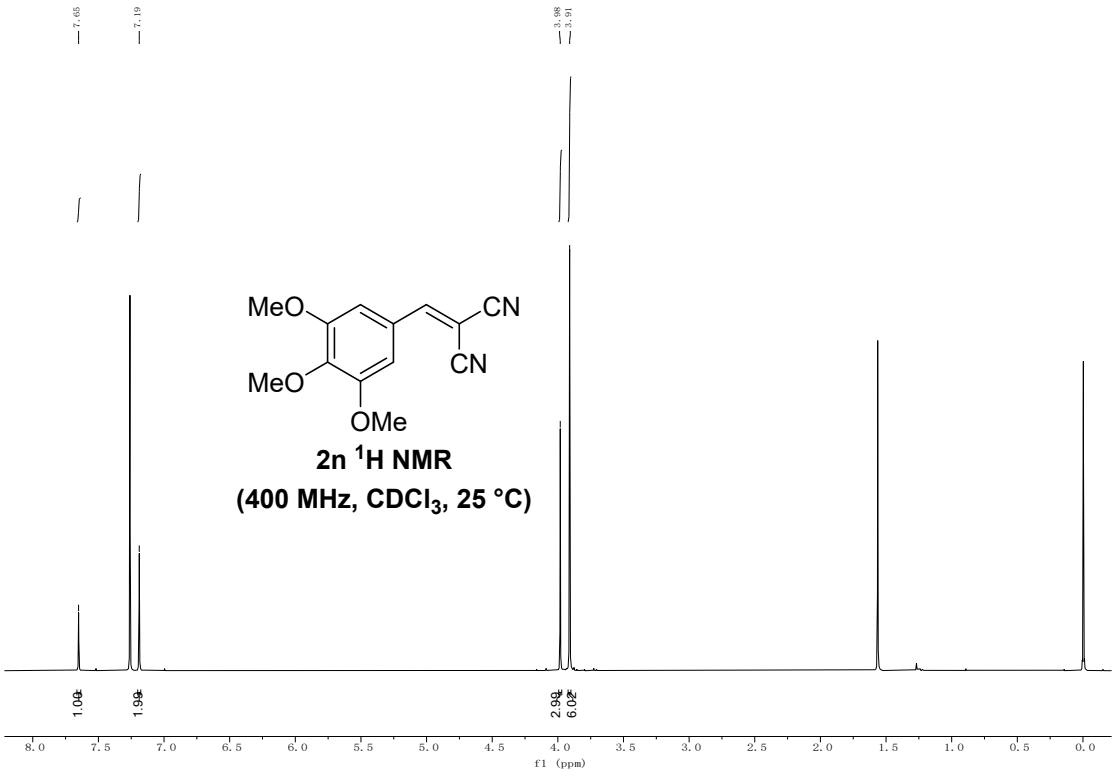
(100 MHz, $CDCl_3$, 25 °C)



2m ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)

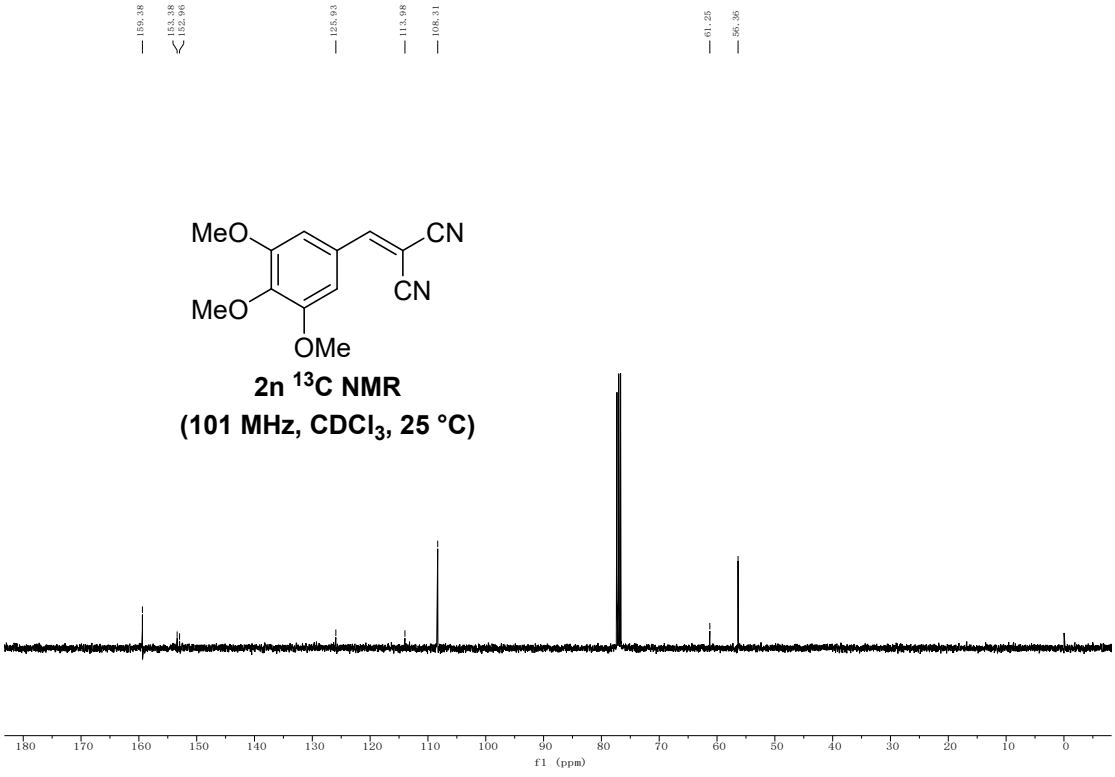


2m ^{13}C NMR
(100 MHz, CDCl3, 25 °C)



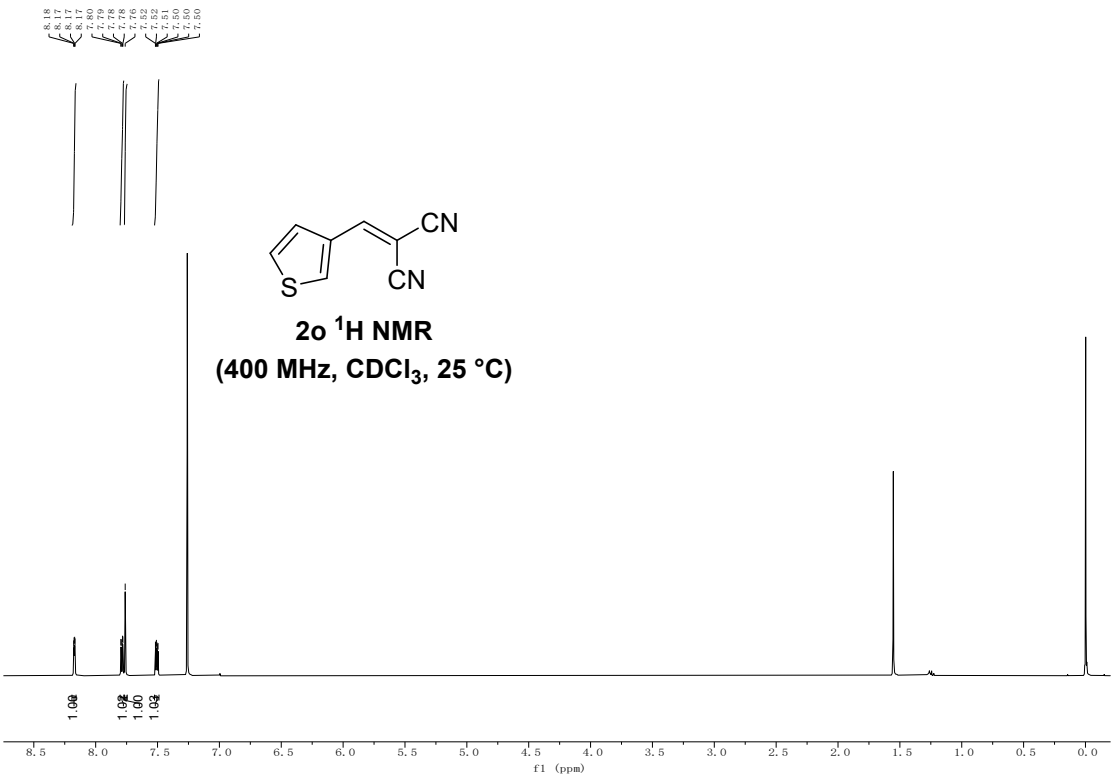
2n ^{1}H NMR

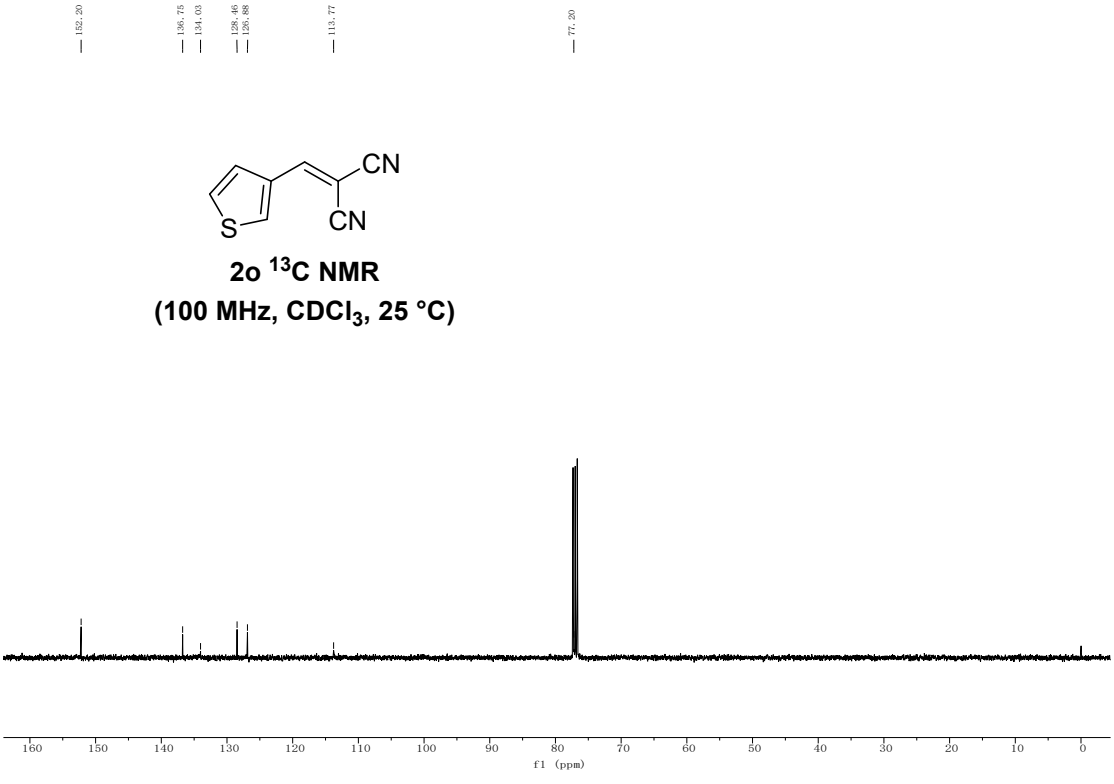
(400 MHz, $CDCl_3$, 25 °C)

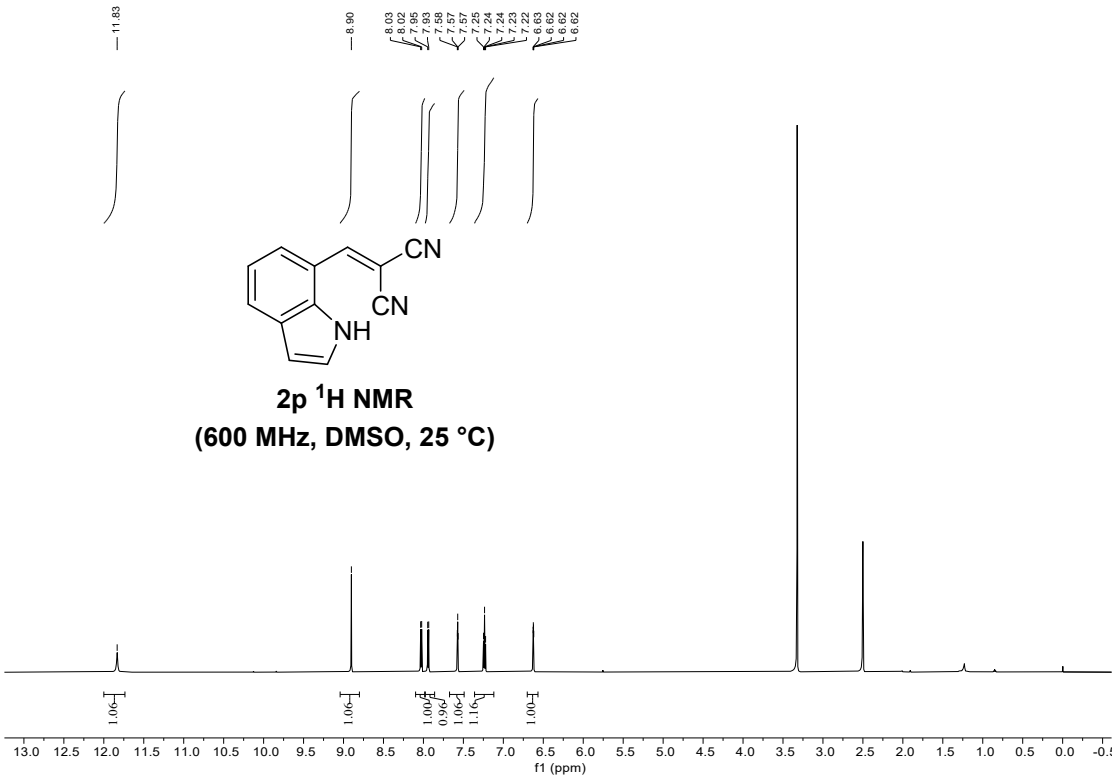


2n ^{13}C NMR

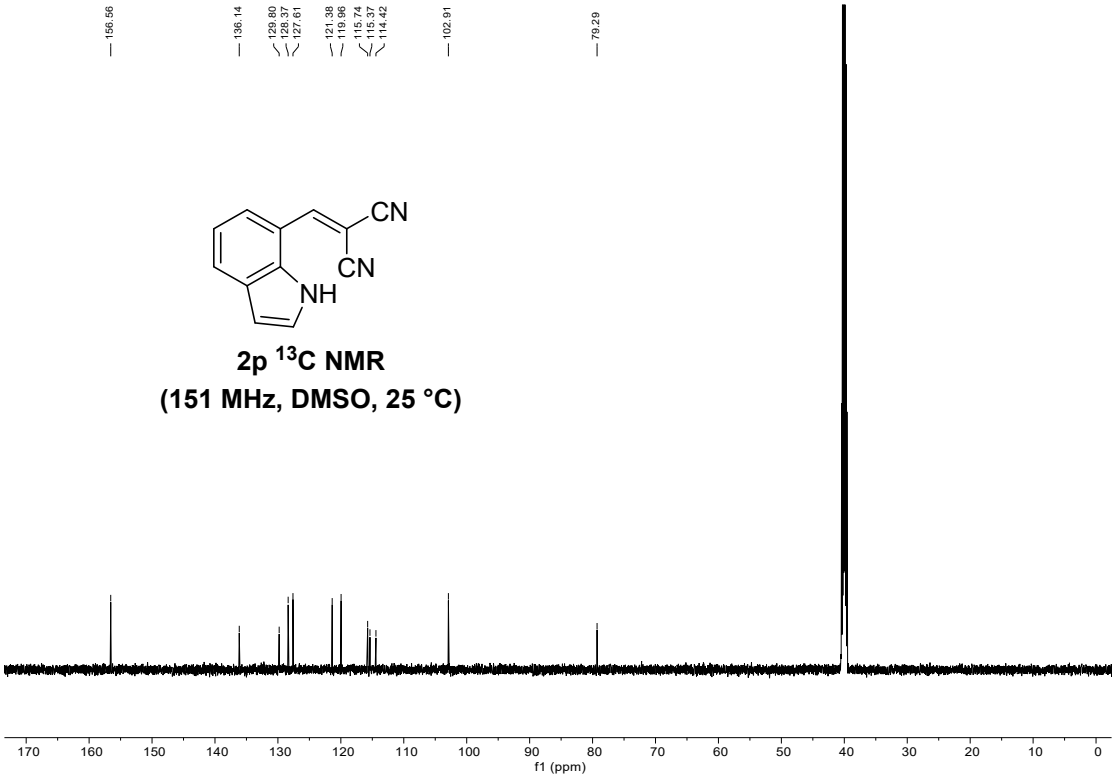
(101 MHz, $CDCl_3$, 25 °C)


8.18
8.17
8.17
8.17
7.80
7.79
7.78
7.78
7.76
7.52
7.51
7.50
7.50
7.50
CN
CN
S
2o ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)
1.00
1.02
1.00
1.03
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)

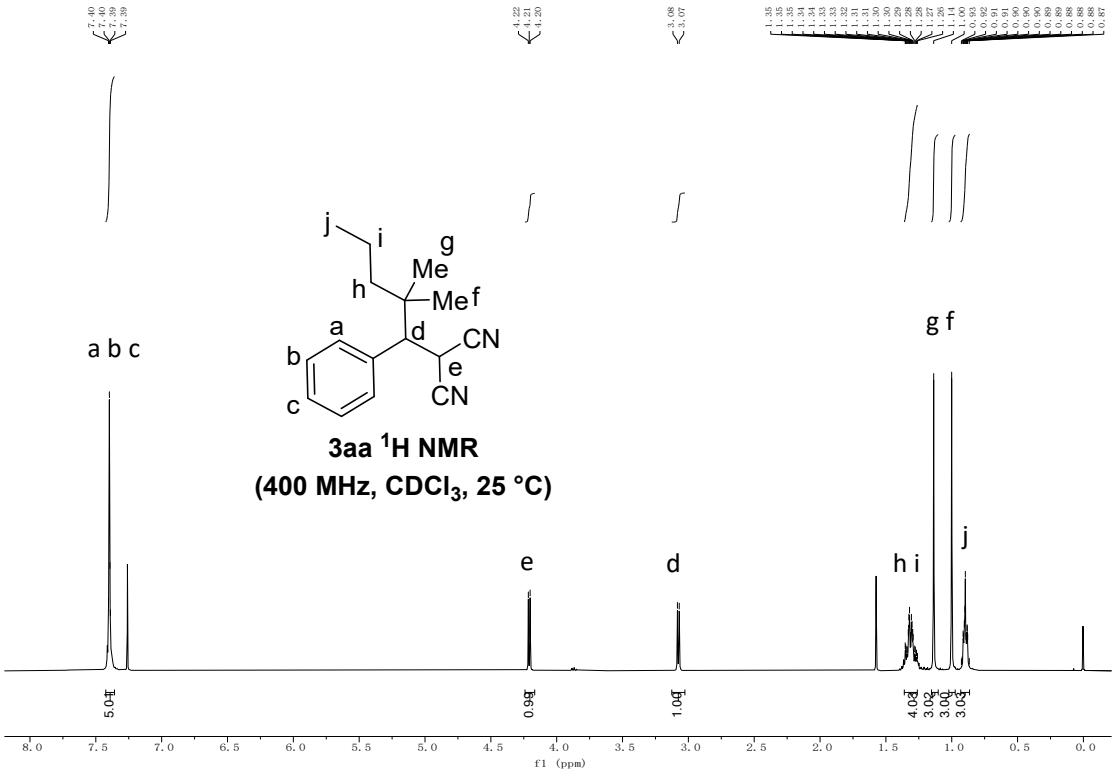

152.20
136.75
134.03
128.46
126.88
113.77
77.20
CN
CN
S
2o ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



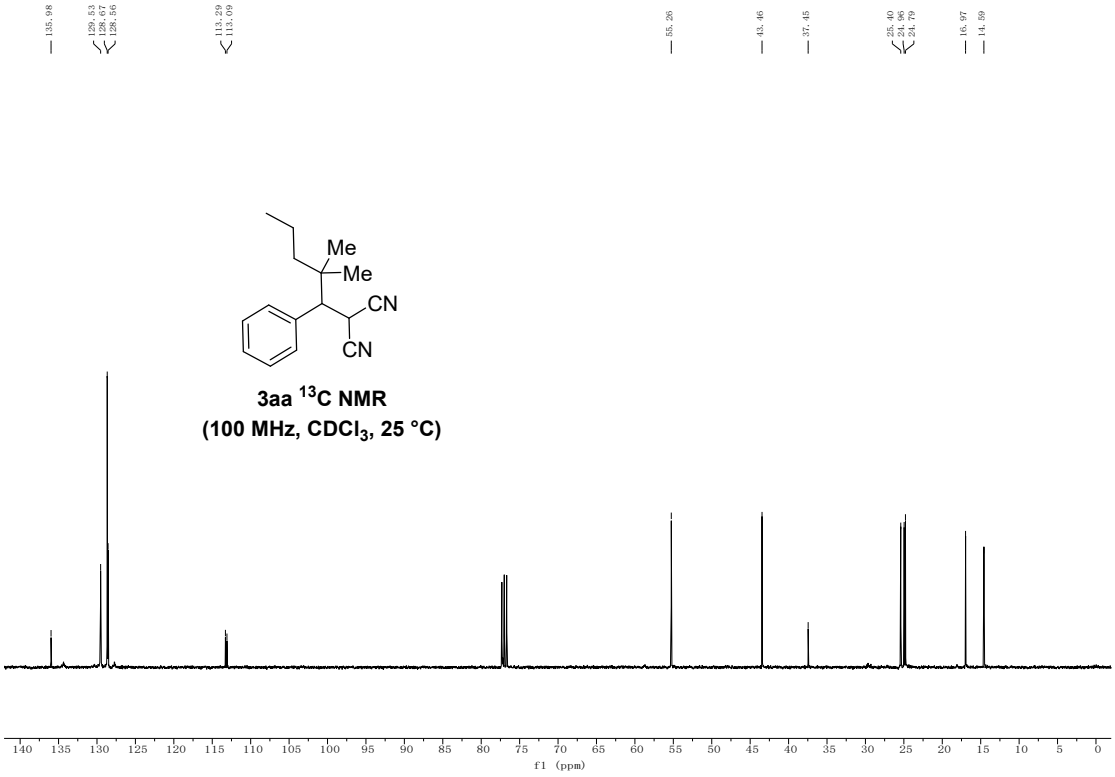
2p ^{1}H NMR
(600 MHz, DMSO, 25 °C)



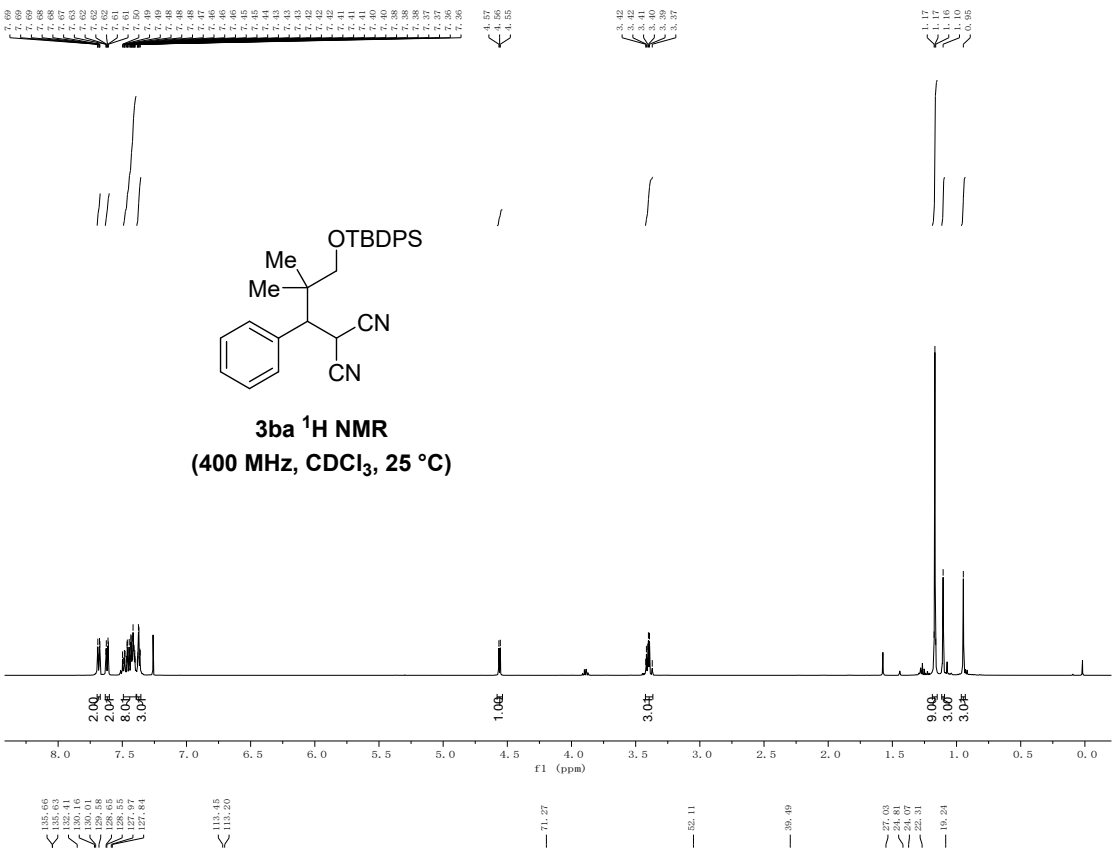
2p ^{13}C NMR
(151 MHz, DMSO, 25 °C)



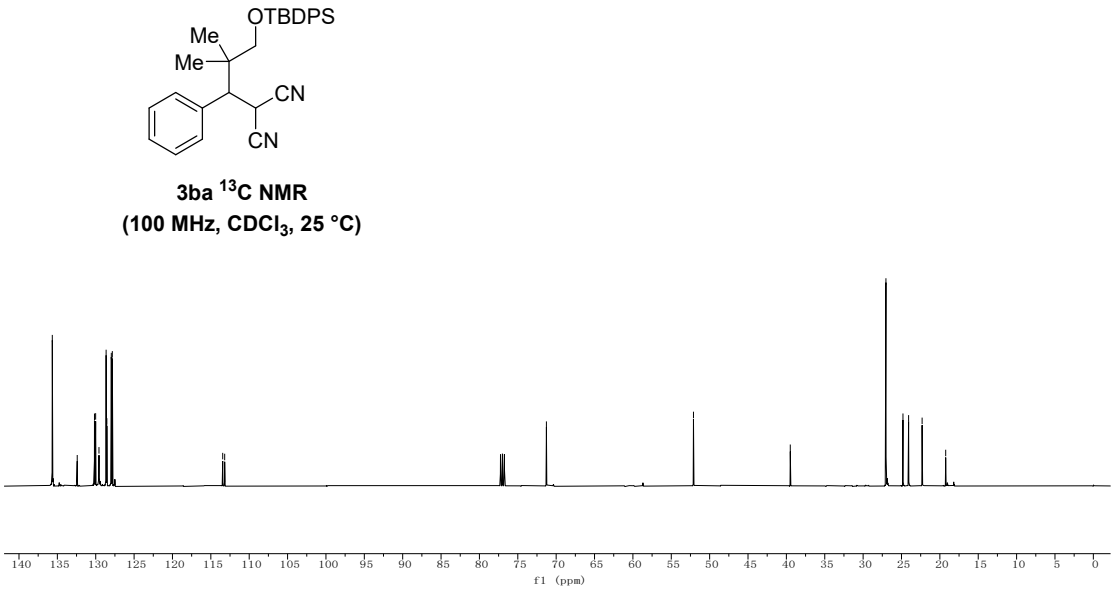
3aa ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



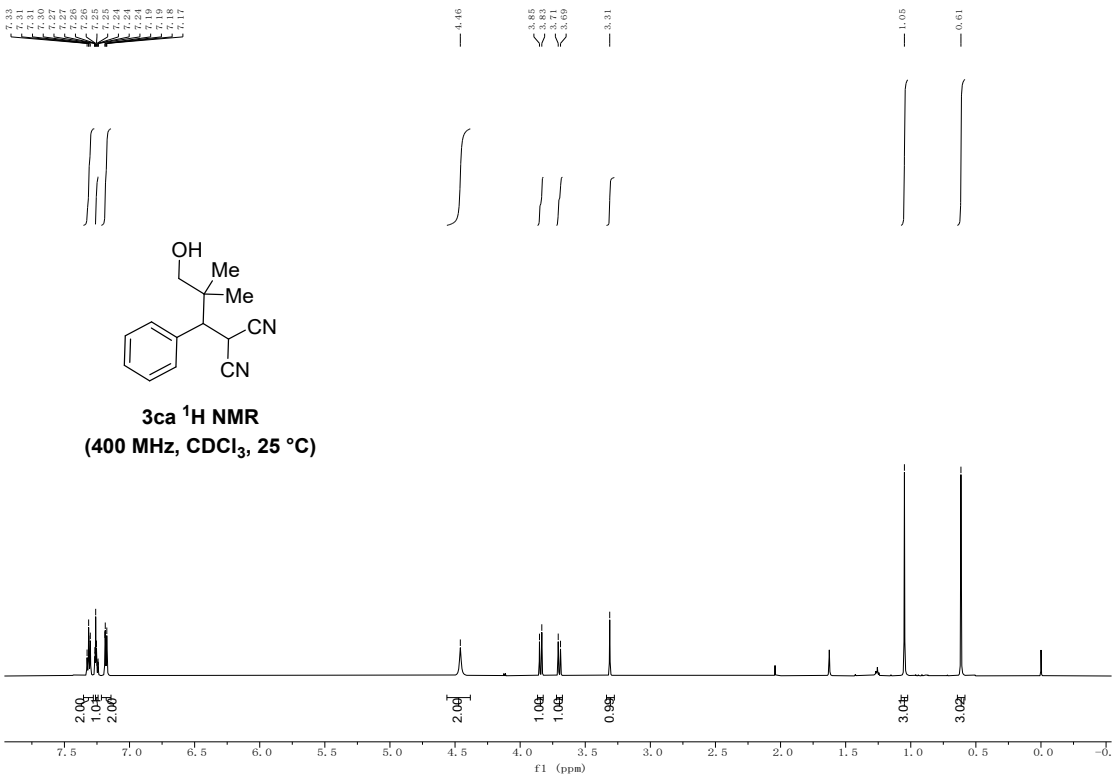
3aa ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



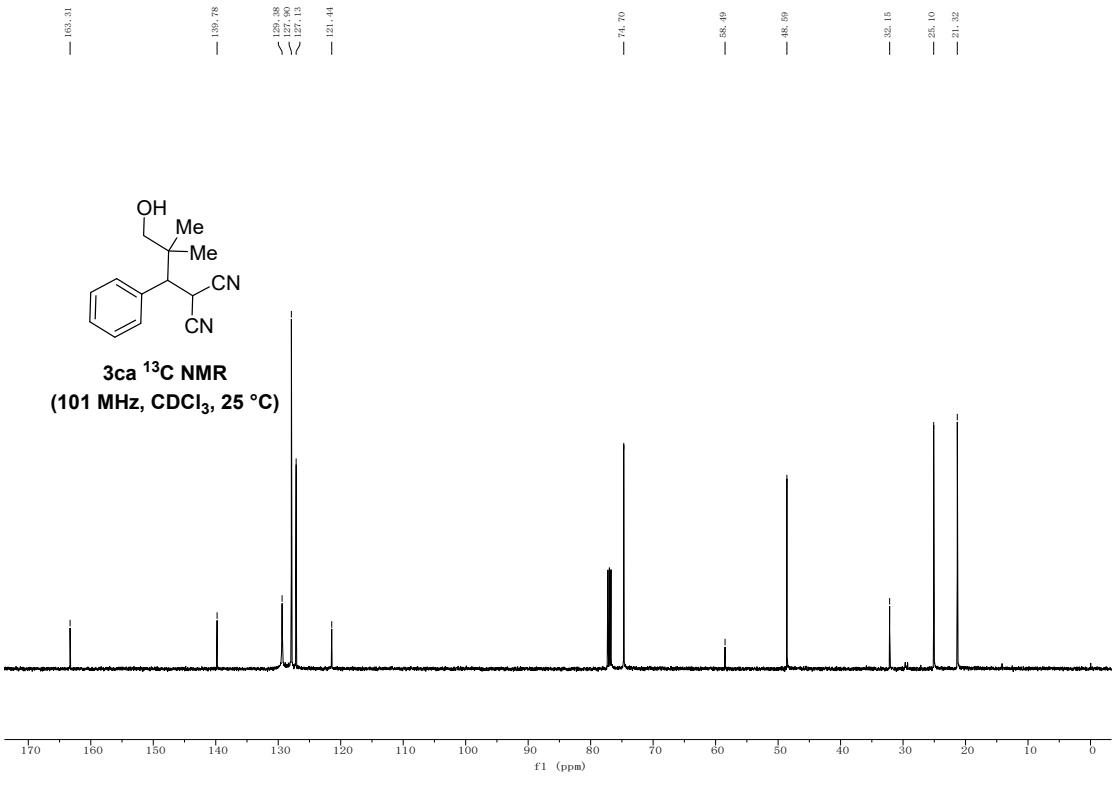
3ba ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



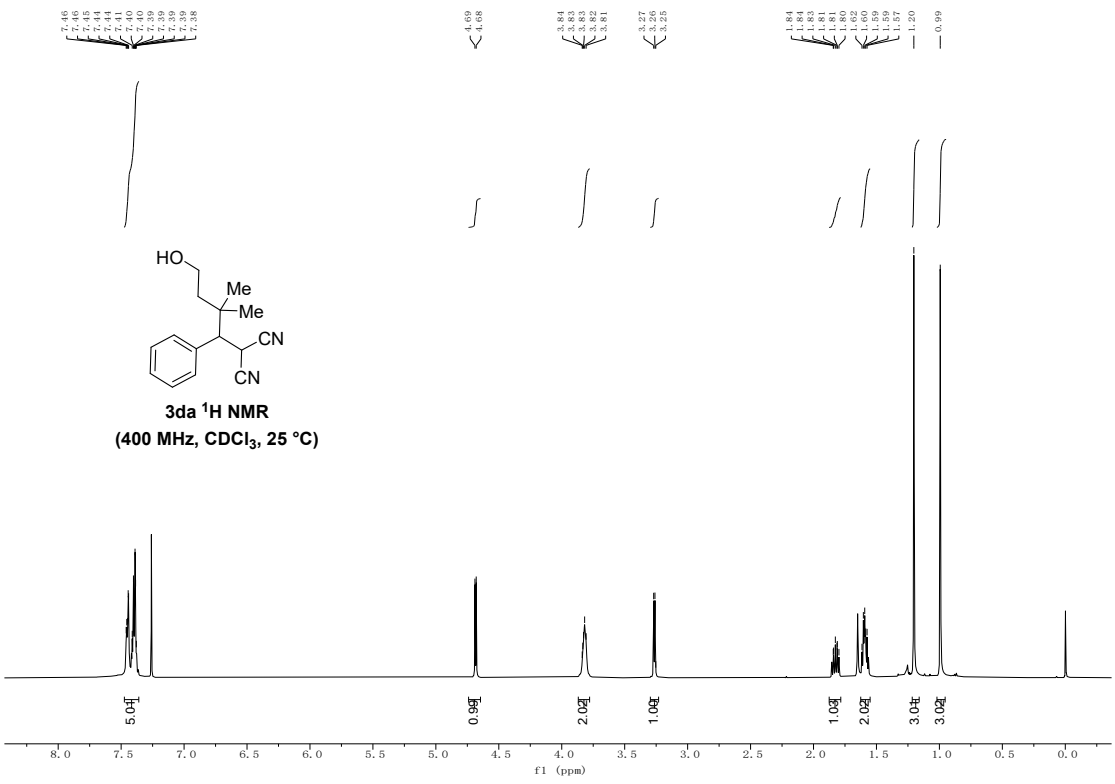
3ba ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



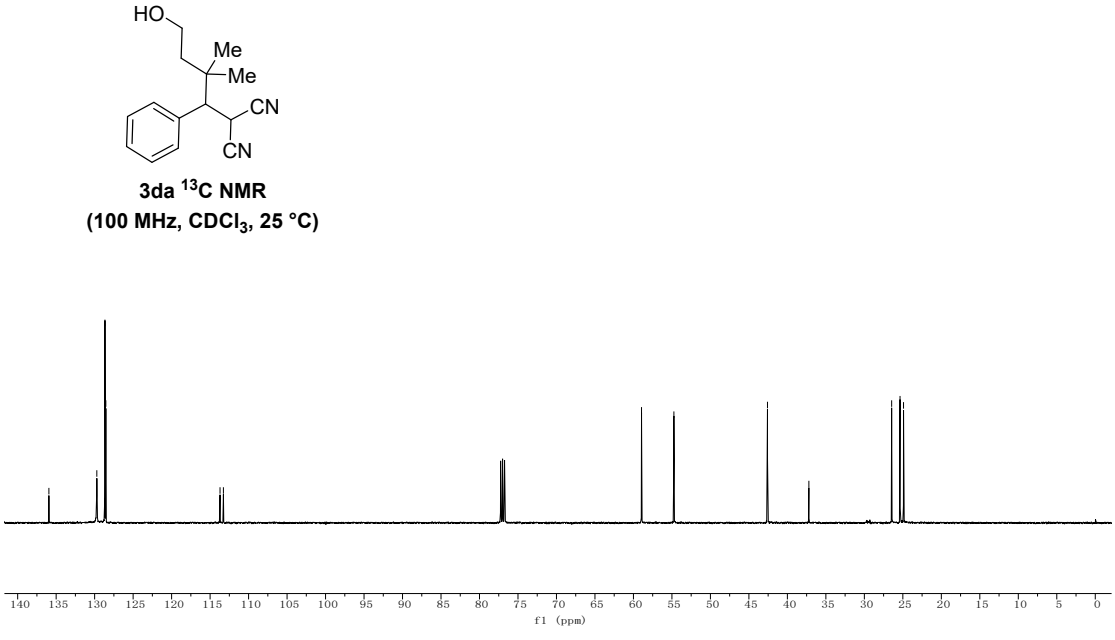
3ca ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



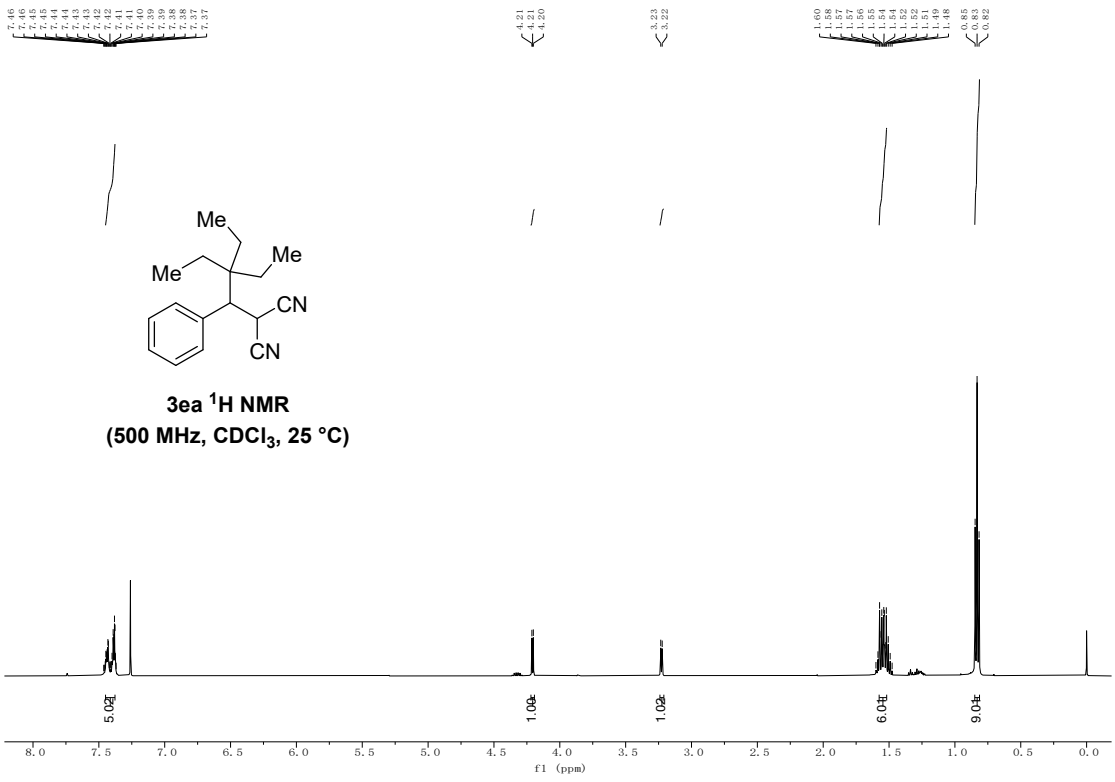
3ca ^{13}C NMR
(101 MHz, $CDCl_3$, 25 °C)



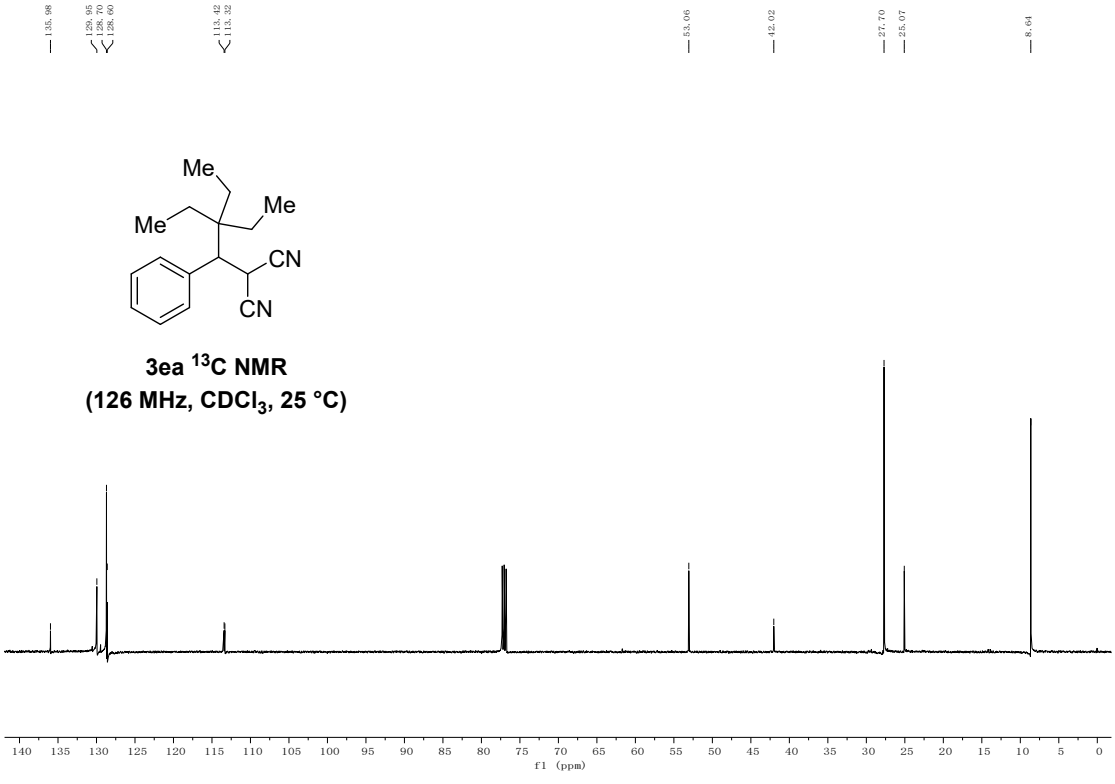
3da ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



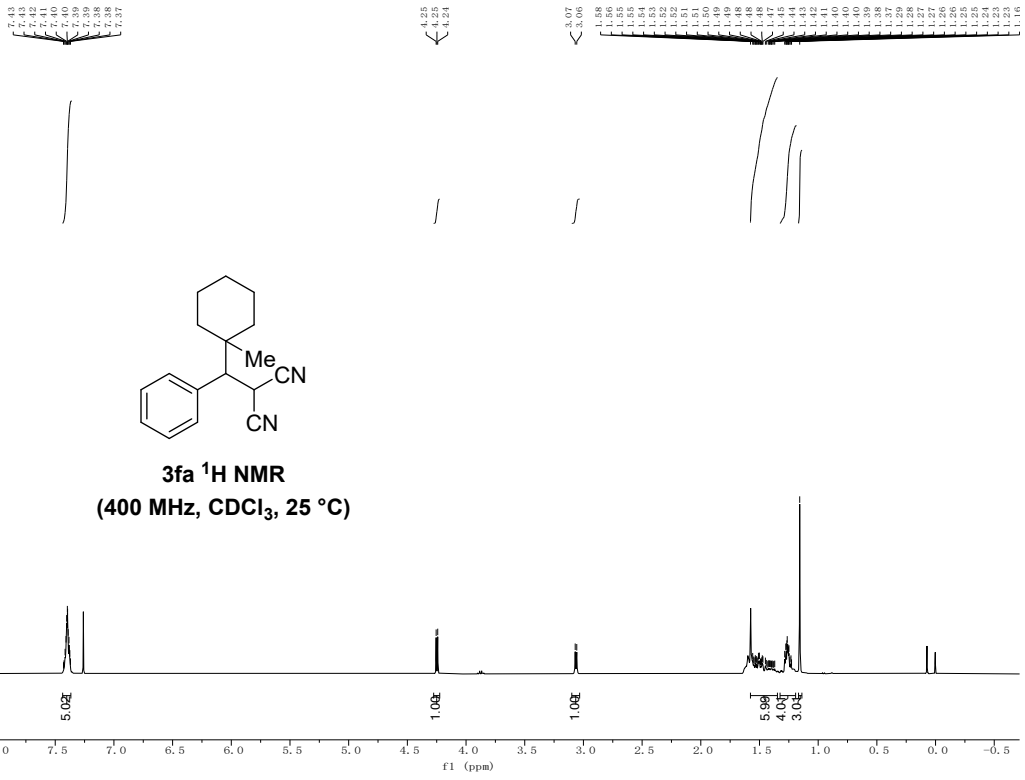
3da ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



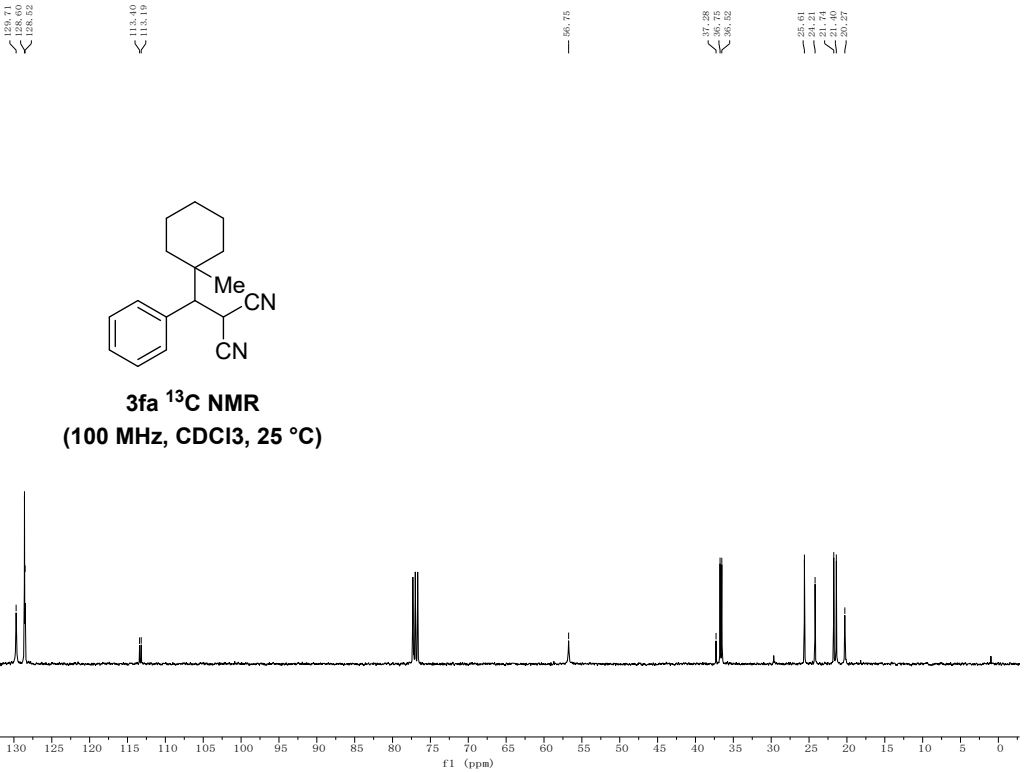
3ea ^{1}H NMR
(500 MHz, $CDCl_3$, 25 °C)



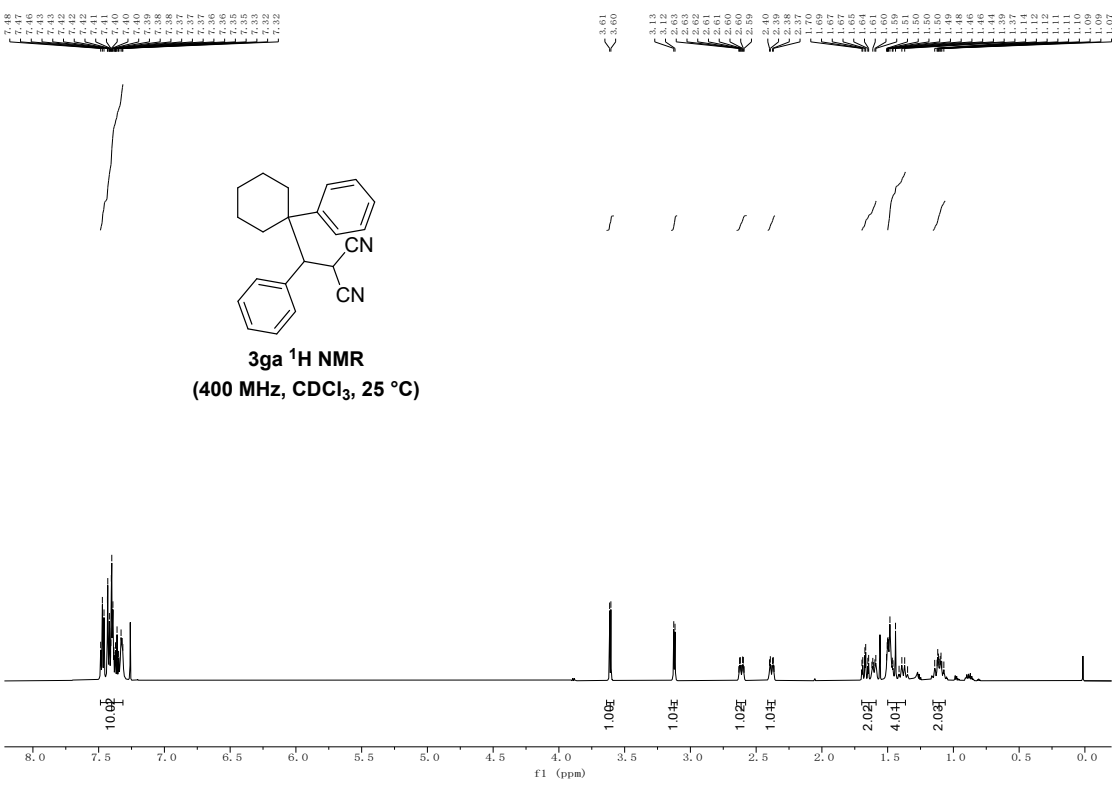
3ea ^{13}C NMR
(126 MHz, $CDCl_3$, 25 °C)



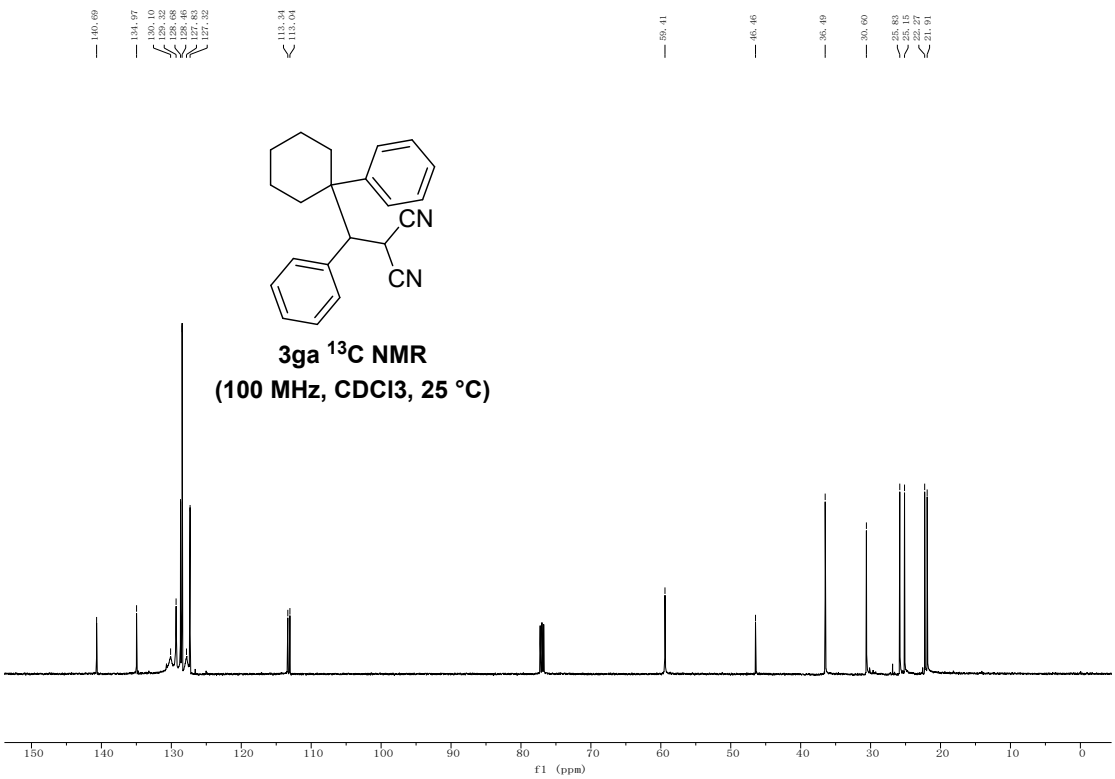
3fa ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



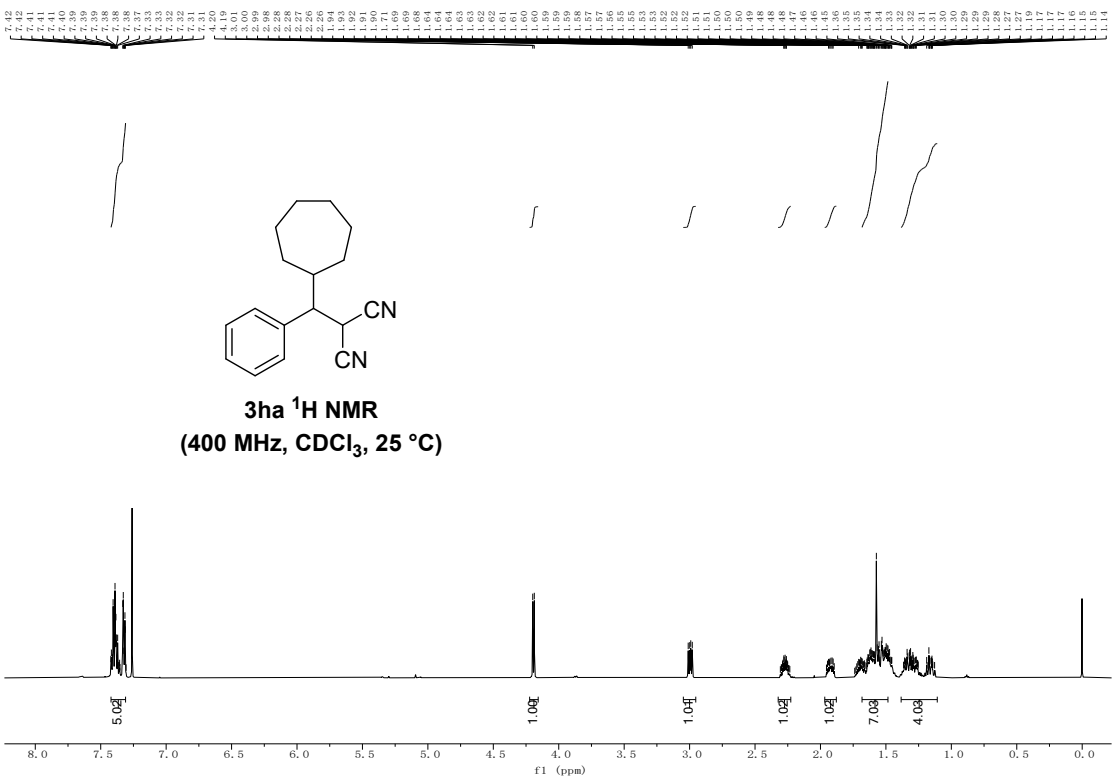
3fa ^{13}C NMR
(100 MHz, CDCl3, 25 °C)



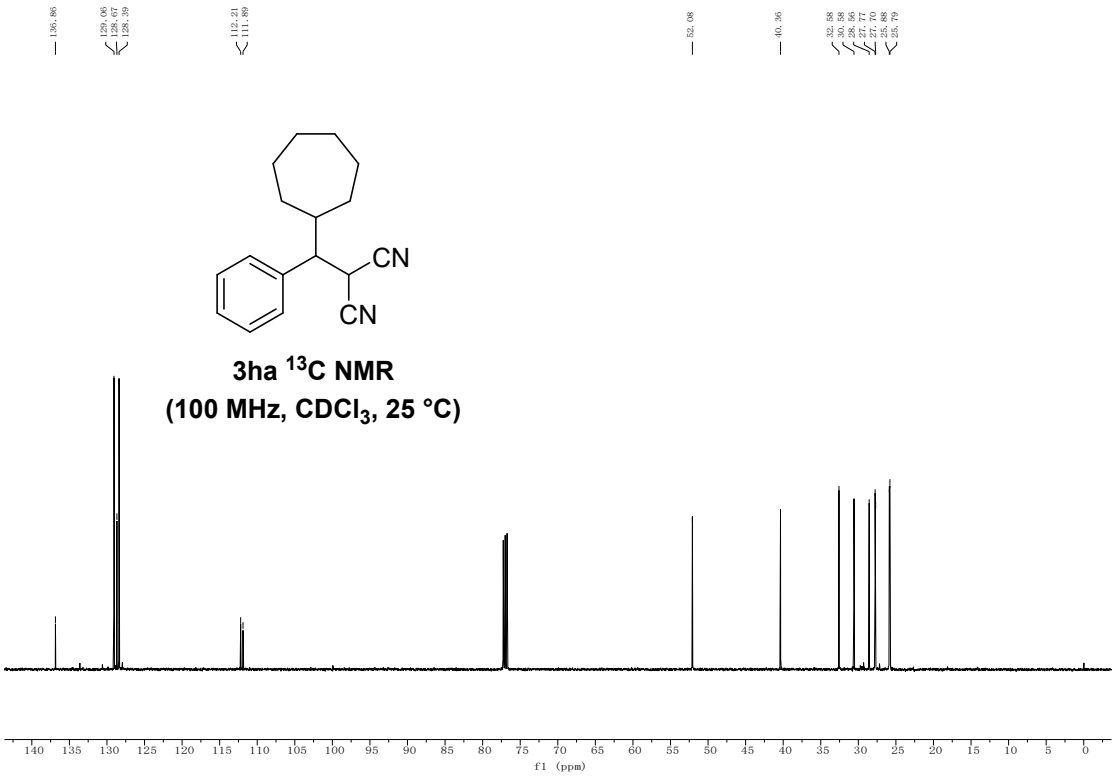
3ga ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



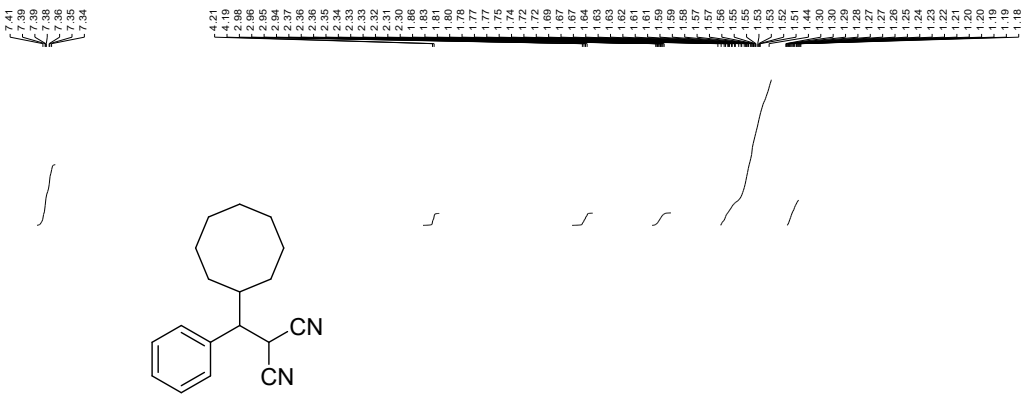
3ga ^{13}C NMR
(100 MHz, CDCl3, 25 °C)



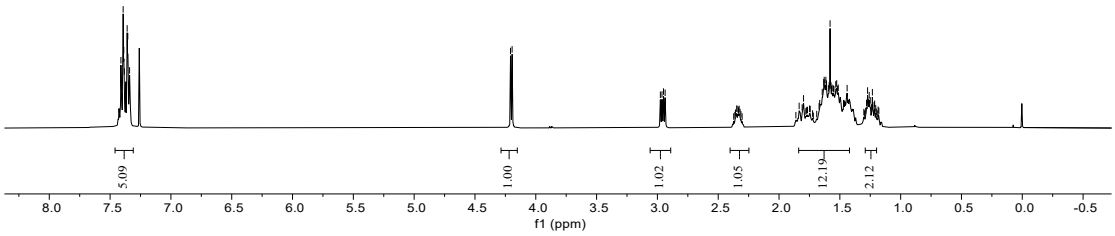
3ha ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)

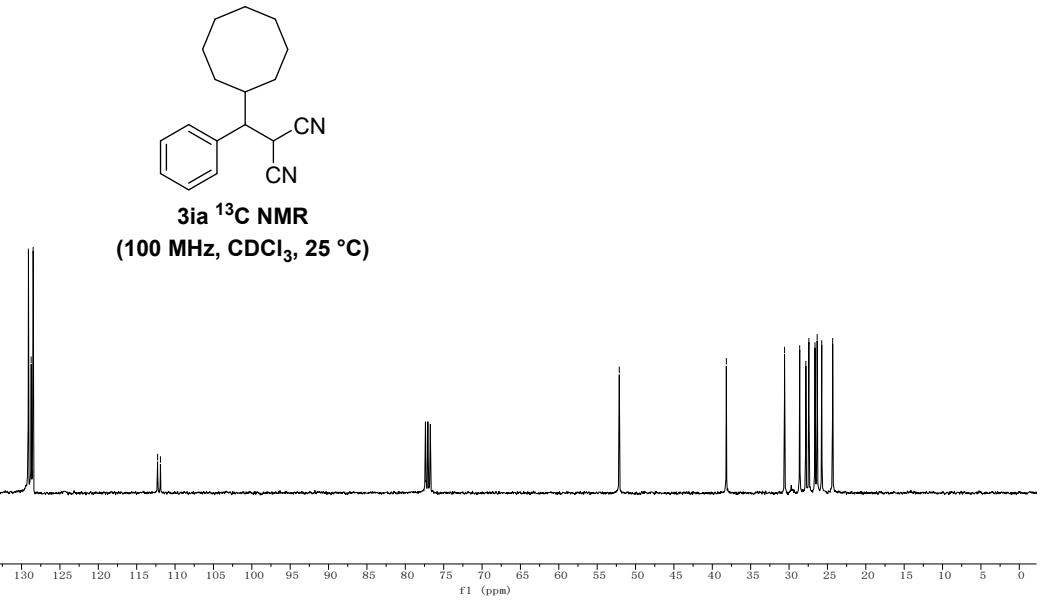


3ha ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)

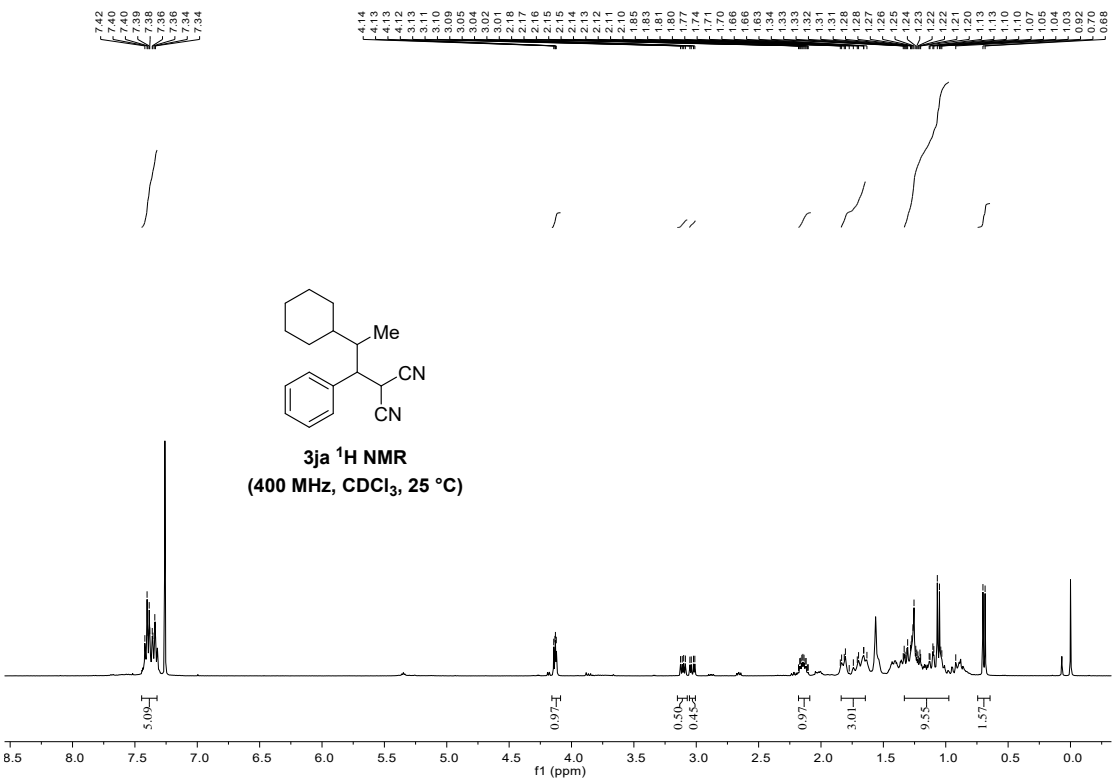


3ia ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)

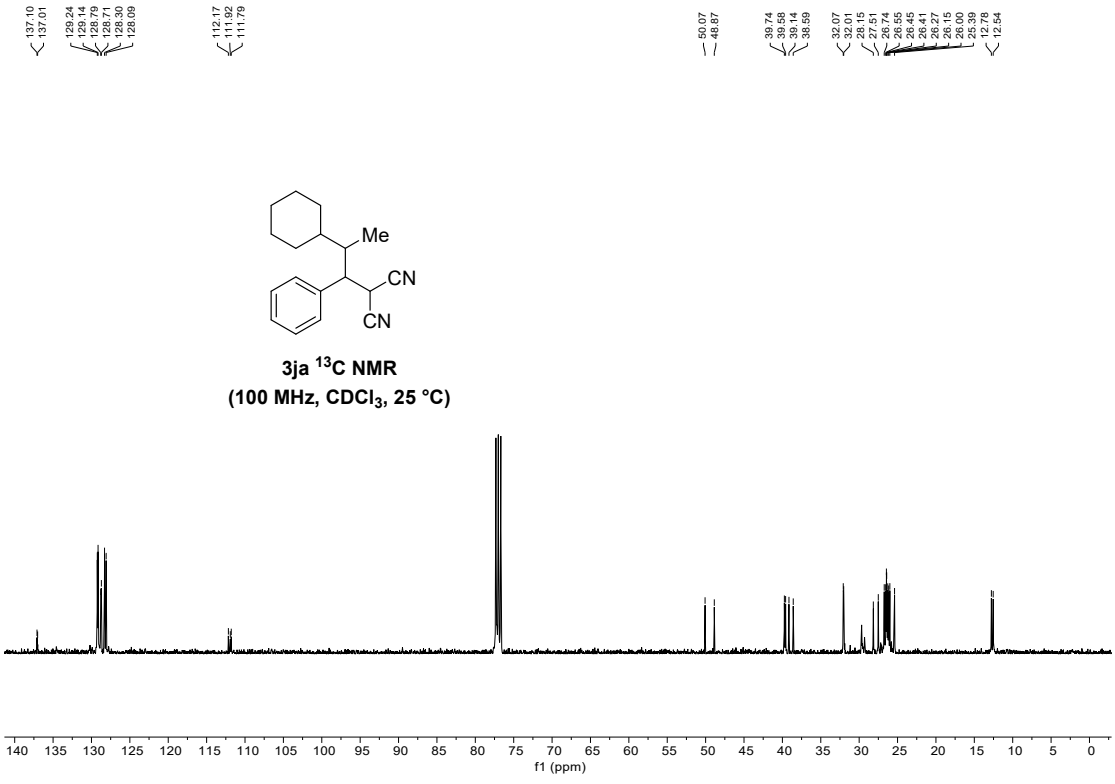




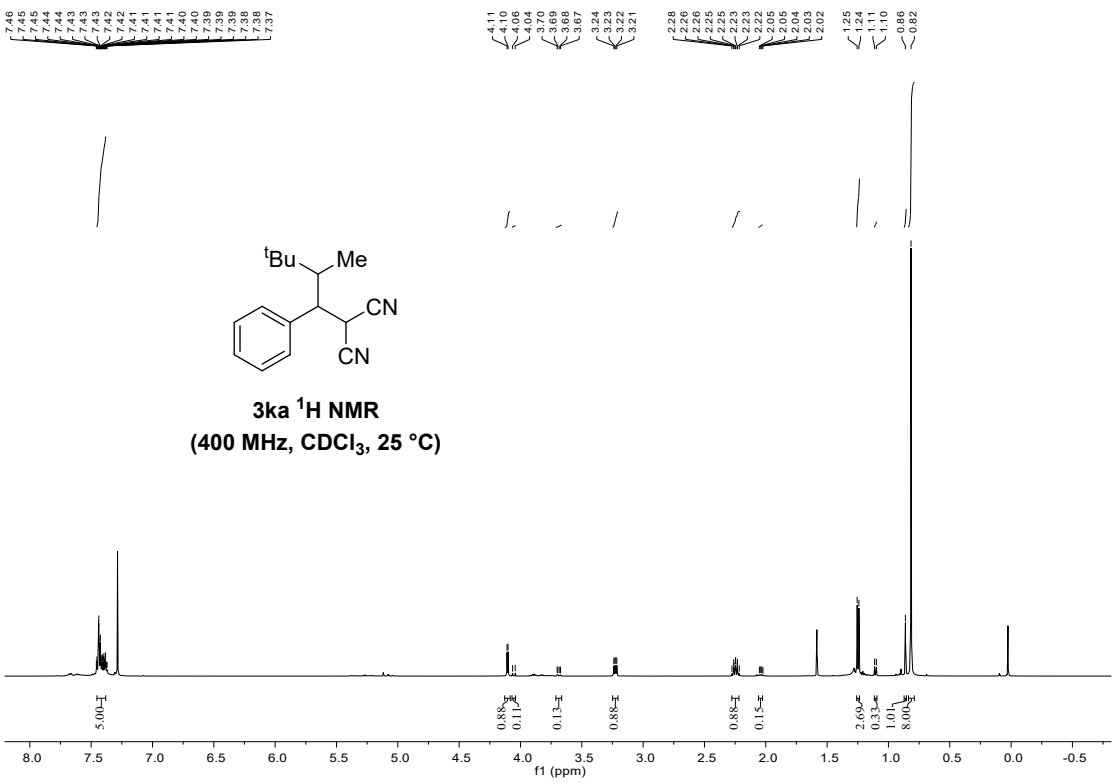
3ia ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



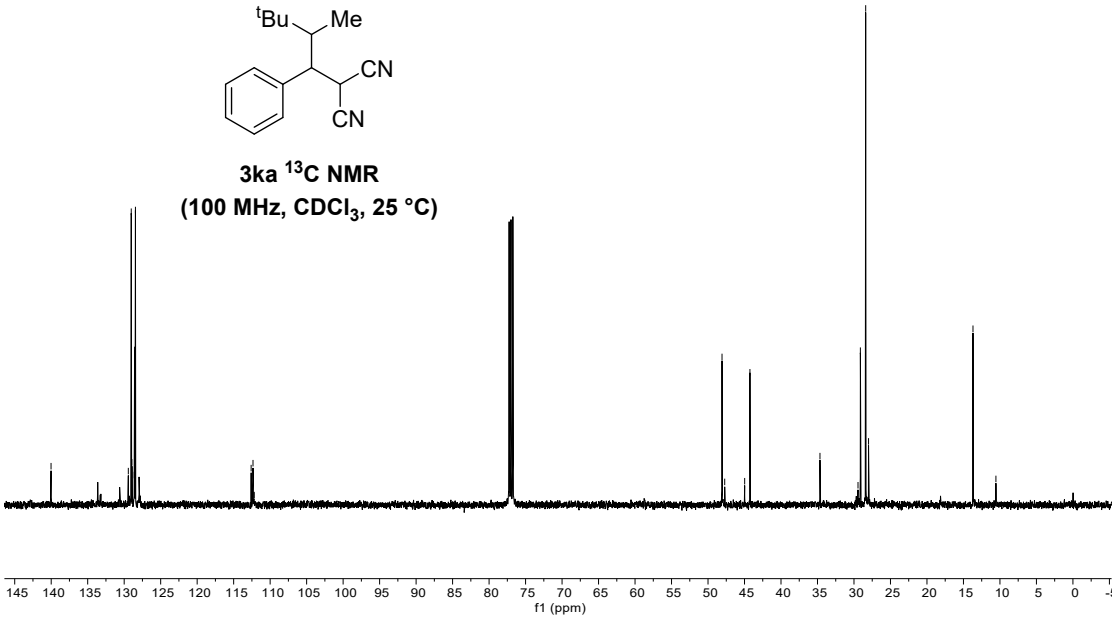
3ja ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



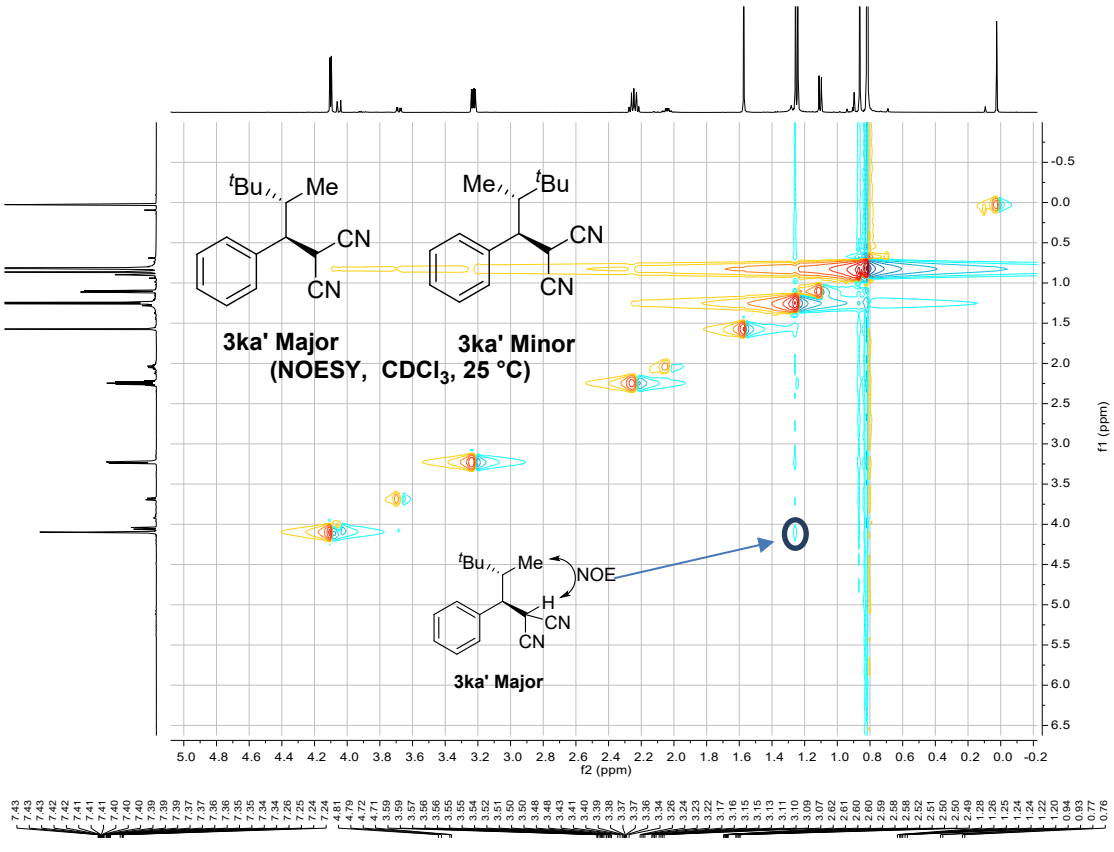
3ja ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)

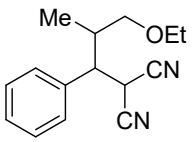


3ka ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)

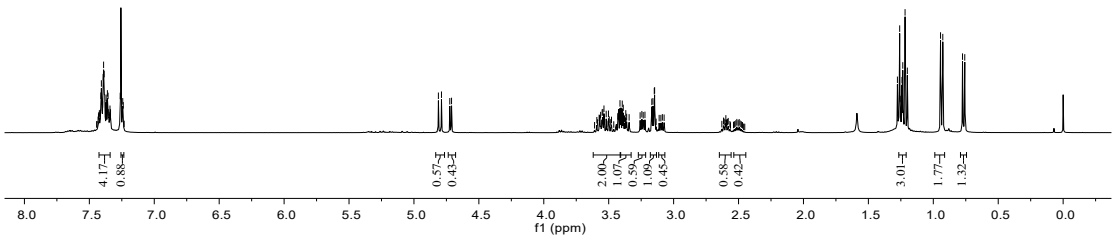


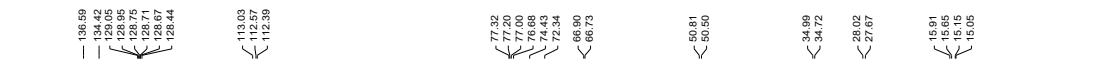
3ka ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)

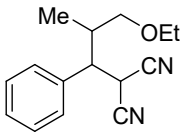




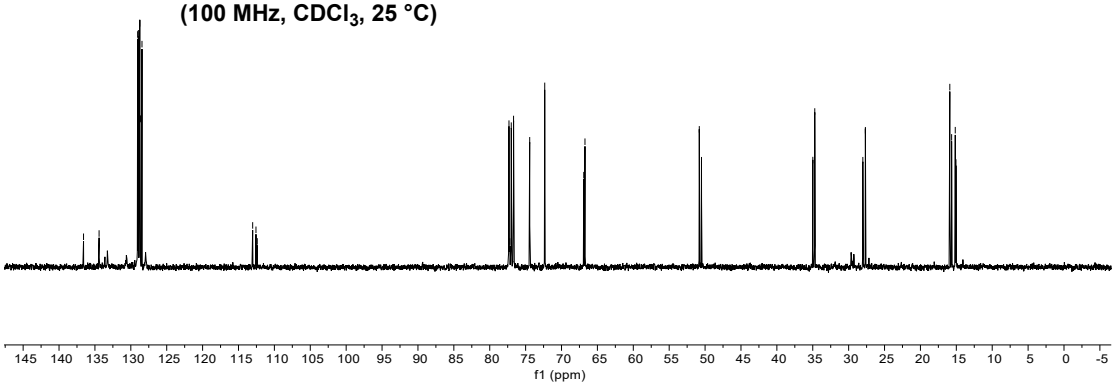
3la ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)

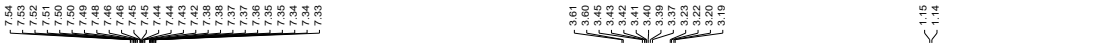


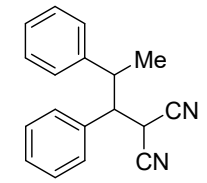




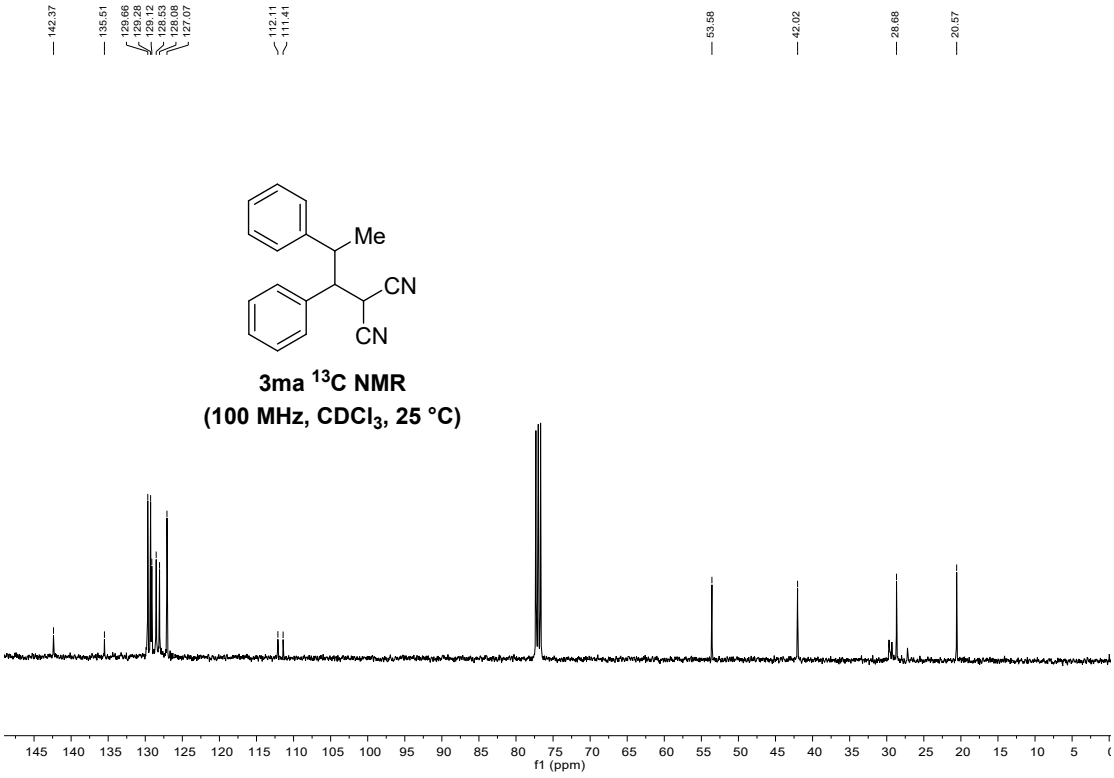
3la ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)





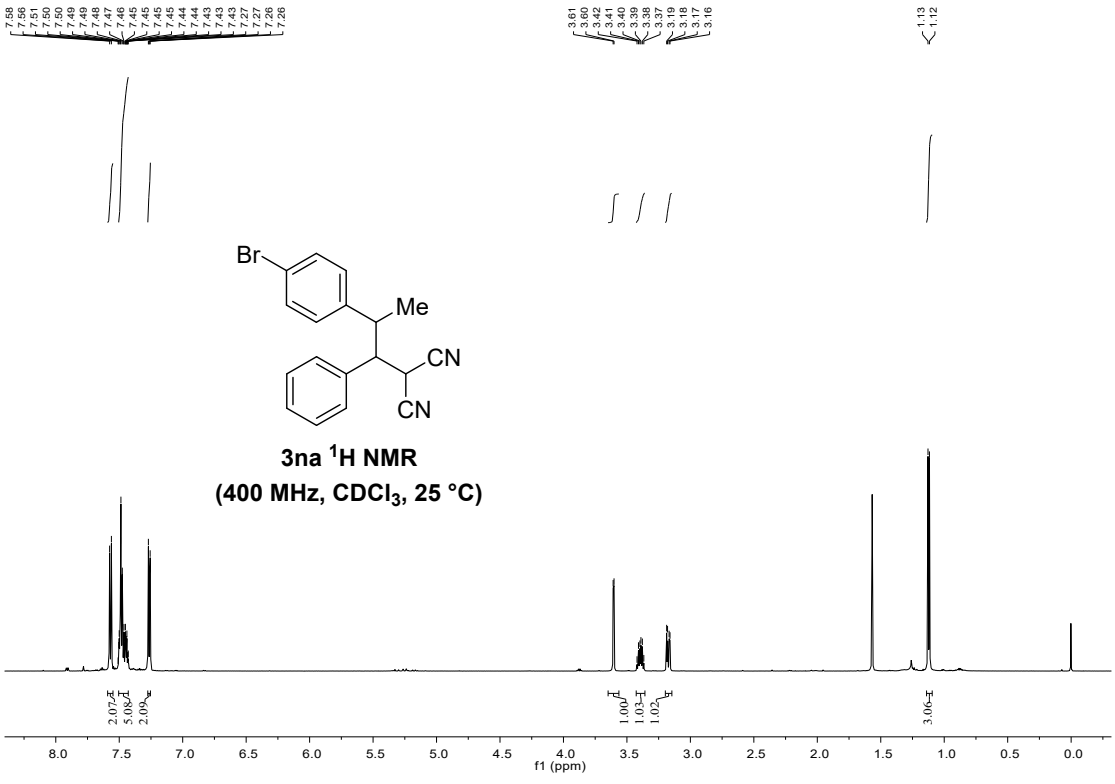


3ma ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)

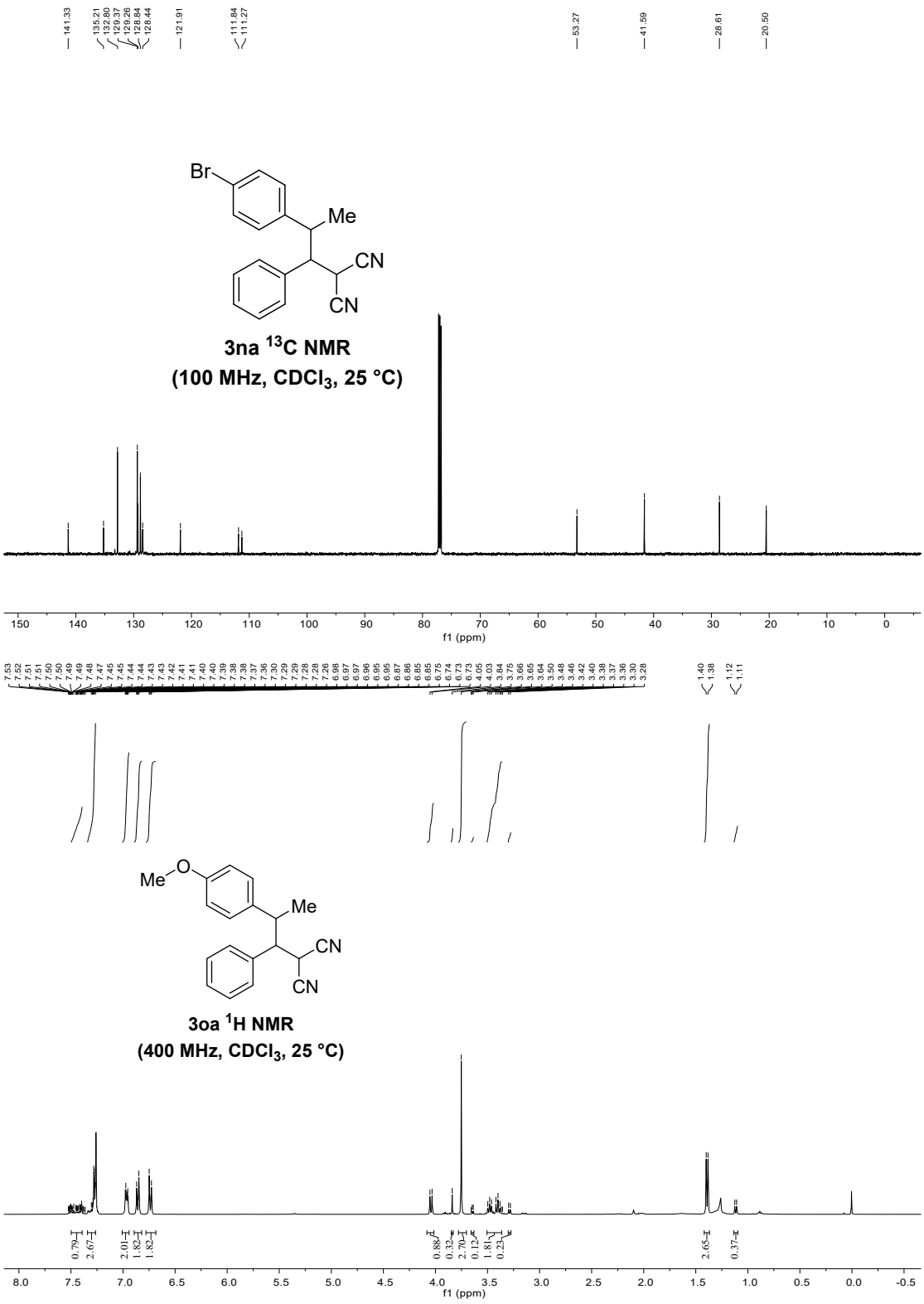


3ma ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)

,



3na ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)


141.33
135.21
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132.37
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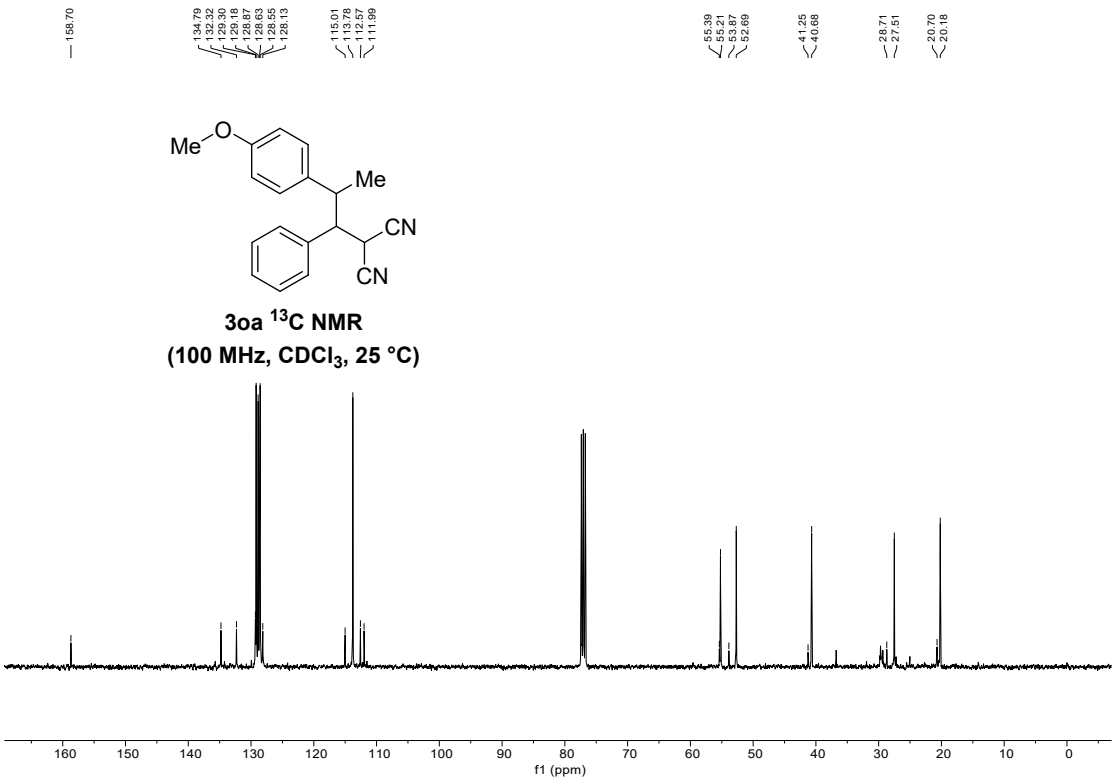
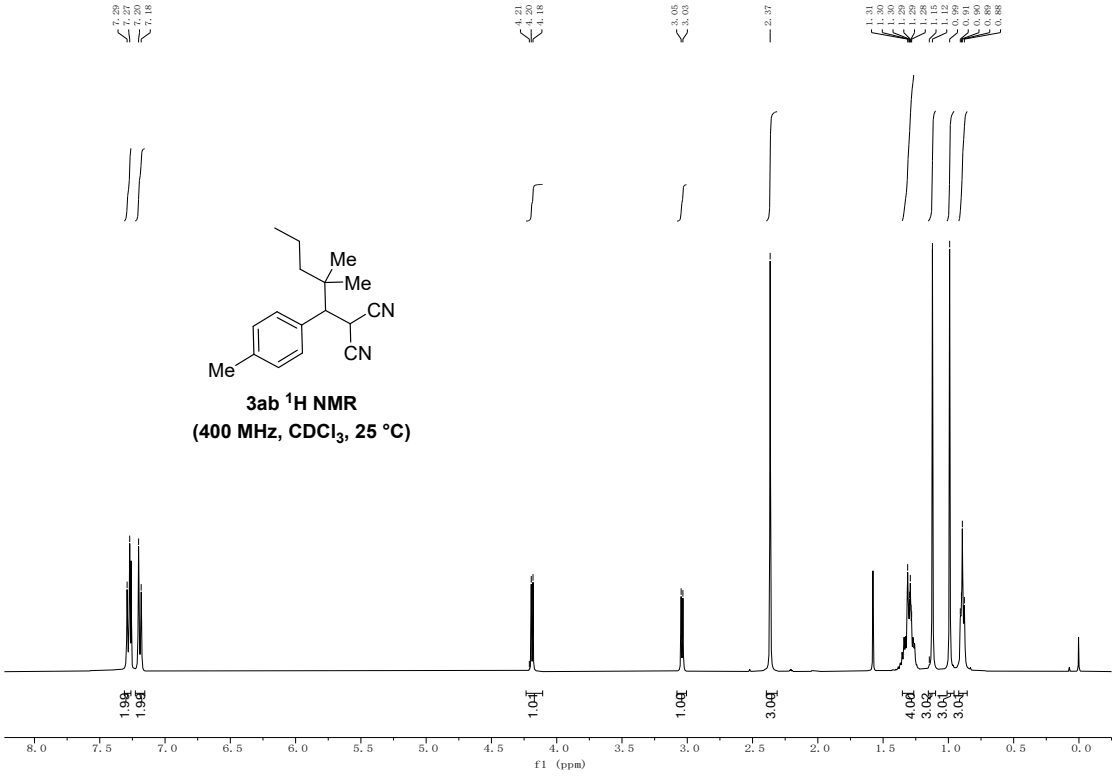
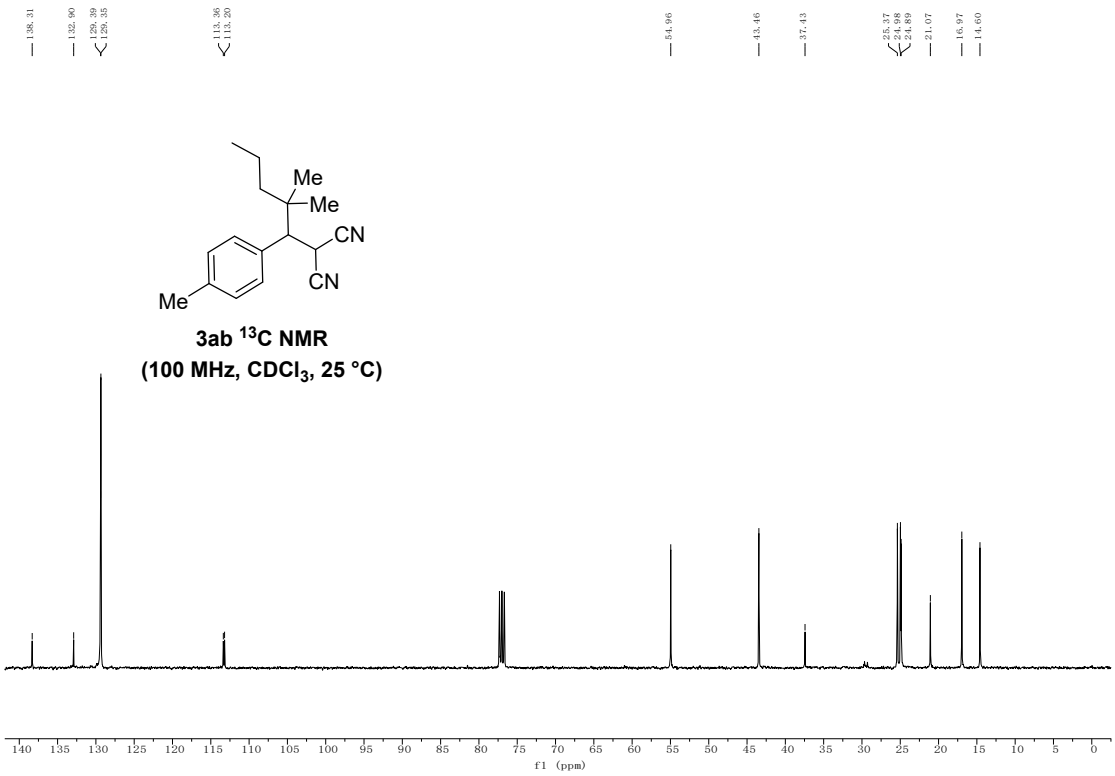
128.84
128.44
121.91
111.84
111.27
53.27
41.59
28.61
20.50
Br
Me
CN
CN
3na 13C NMR
(100 MHz, CDCl3, 25 °C)
f1 (ppm)
Me
O
Me
CN
CN
3oa 1H NMR
(400 MHz, CDCl3, 25 °C)
f1 (ppm)



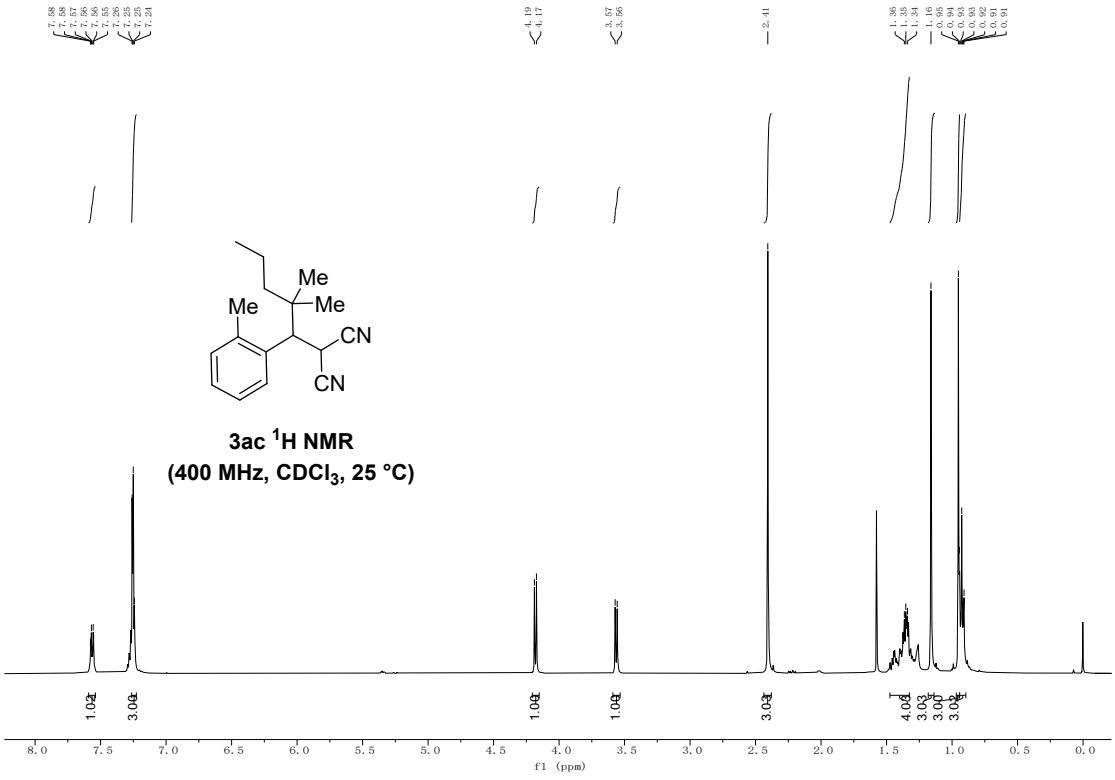
3oa ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



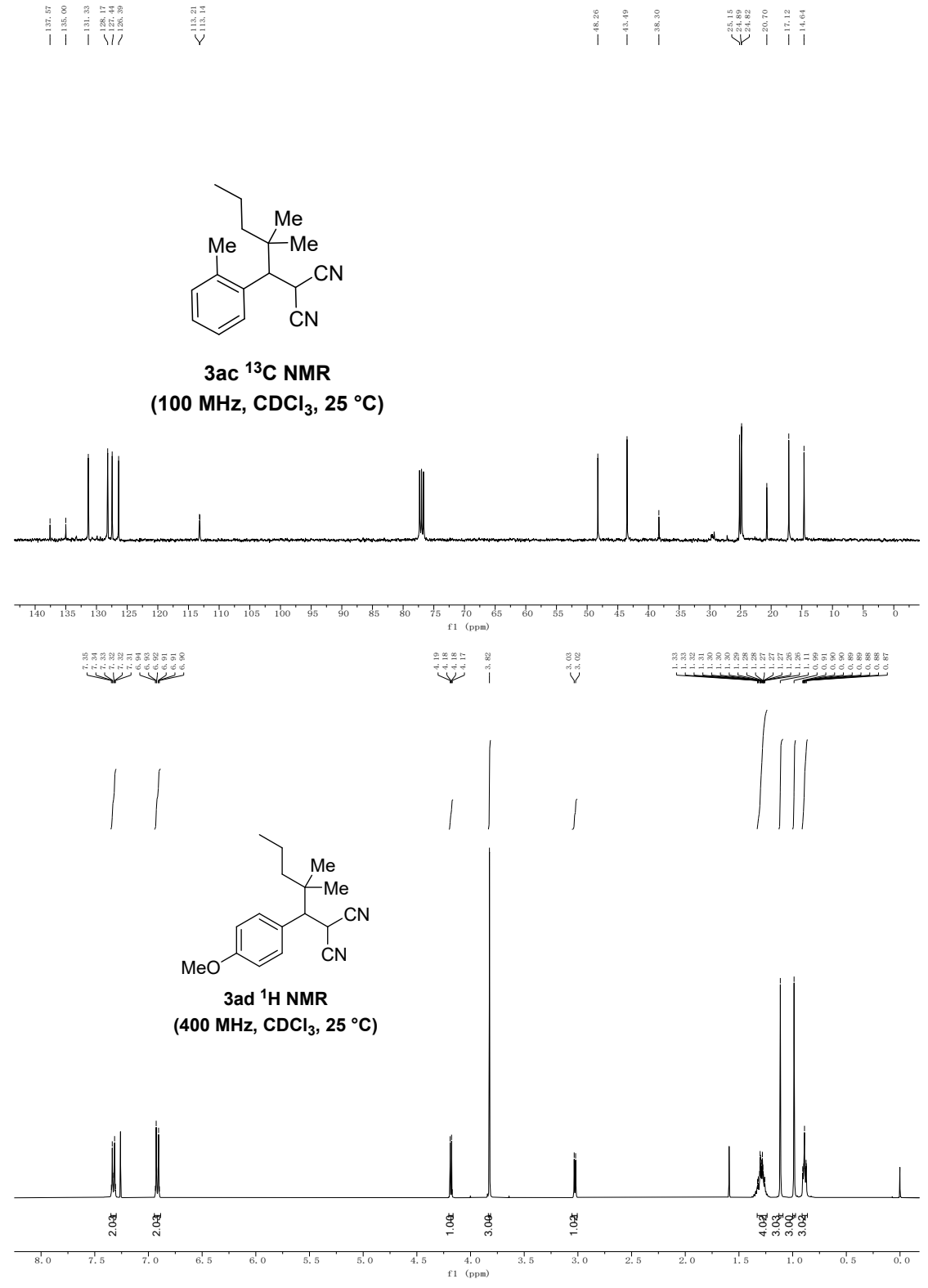
3ab ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



3ab ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



3ac ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)


137.57
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113.14
48.26
43.49
38.30
25.15
24.89
24.82
20.70
17.12
14.64
Me
Me
Me
CN
CN
3ac 13C NMR
(100 MHz, CDCl3, 25 °C)
f1 (ppm)
7.35
7.34
7.33
7.32
7.31
6.94
6.93
6.92
6.91
6.91
6.90
4.19
4.18
4.18
4.17
3.82
3.03
3.02
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1.33
1.32
1.31
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1.29
1.28
1.27
1.27
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1.26
1.26
1.11
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0.91
0.91
0.90
0.89
0.89
0.88
0.88
0.87
Me
Me
CN
CN
MeO
3ad 1H NMR
(400 MHz, CDCl3, 25 °C)
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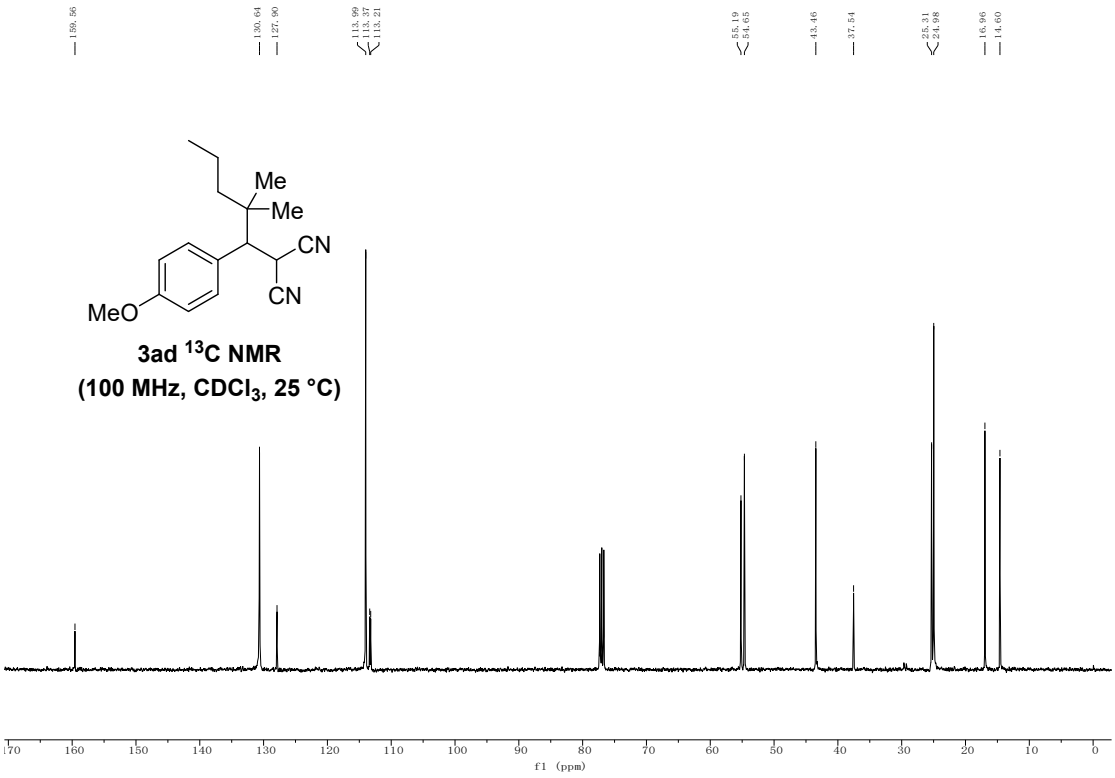
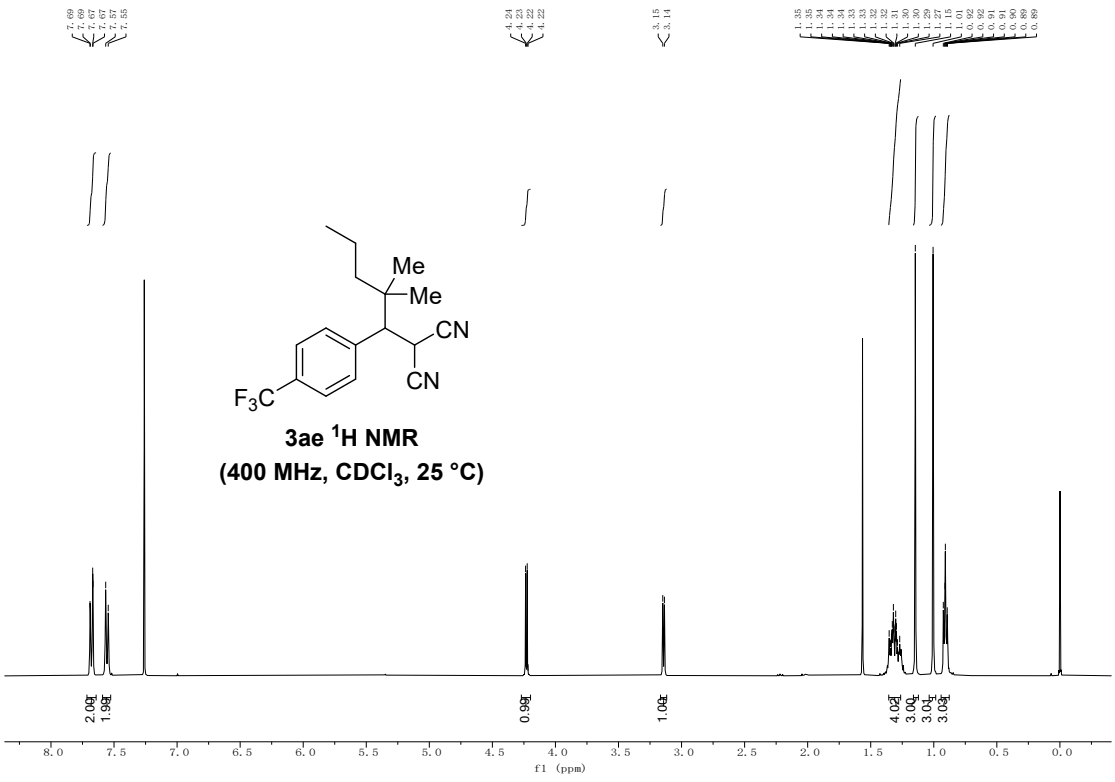
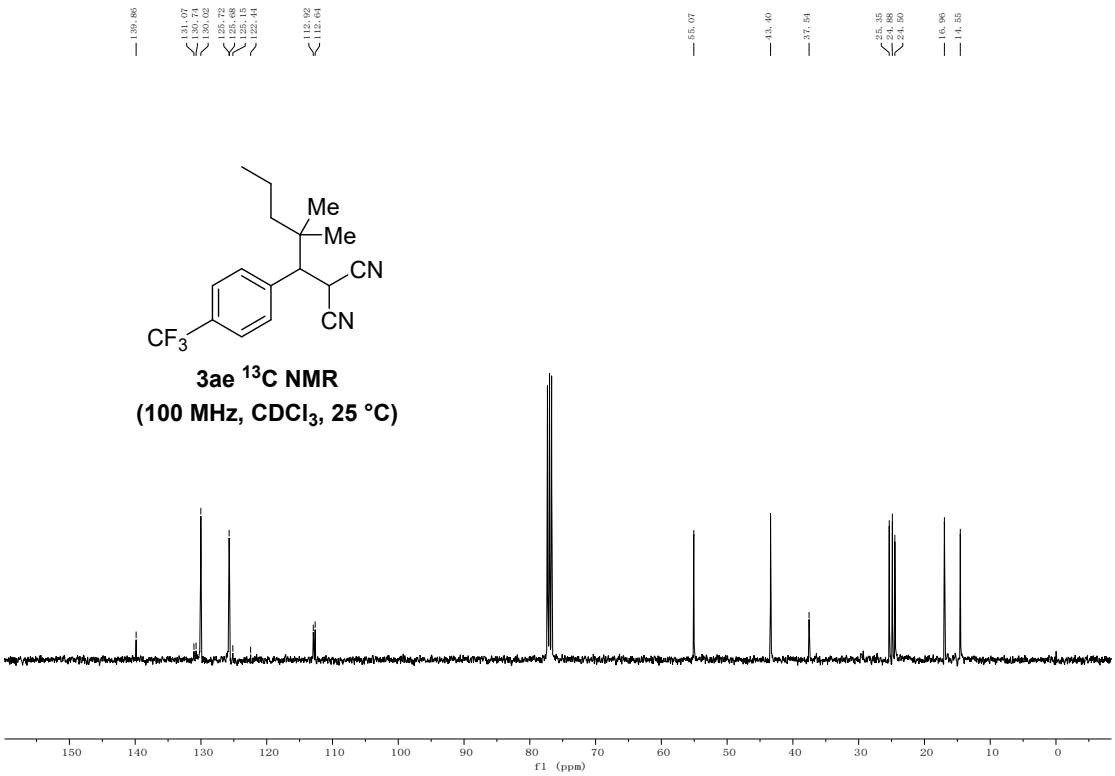
2.04
1.04
3.04
1.02
4.02
3.03
3.01
3.01
f1 (ppm)



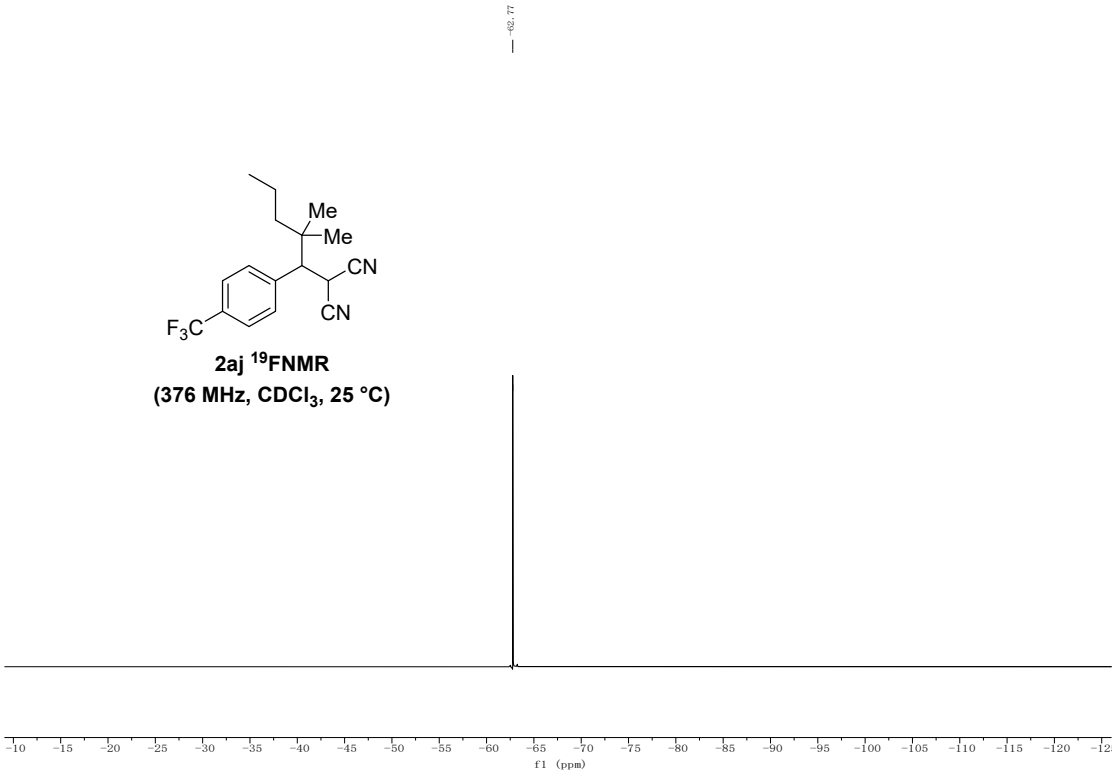
3ad ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



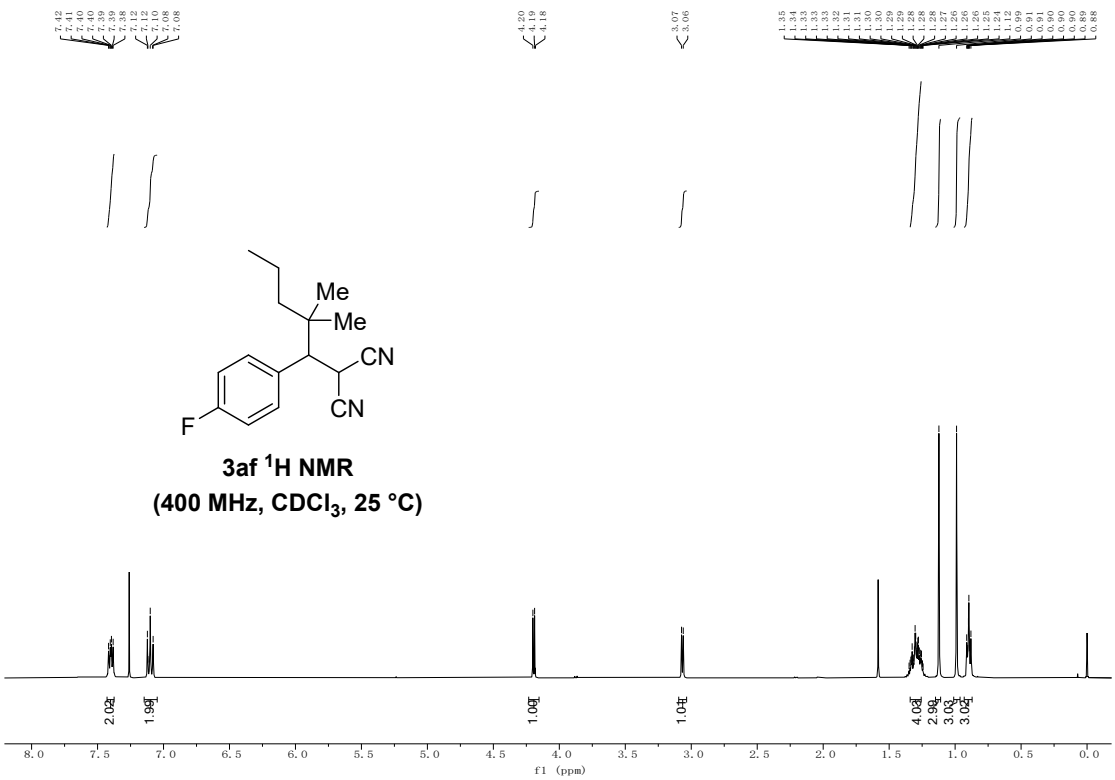
3ae ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



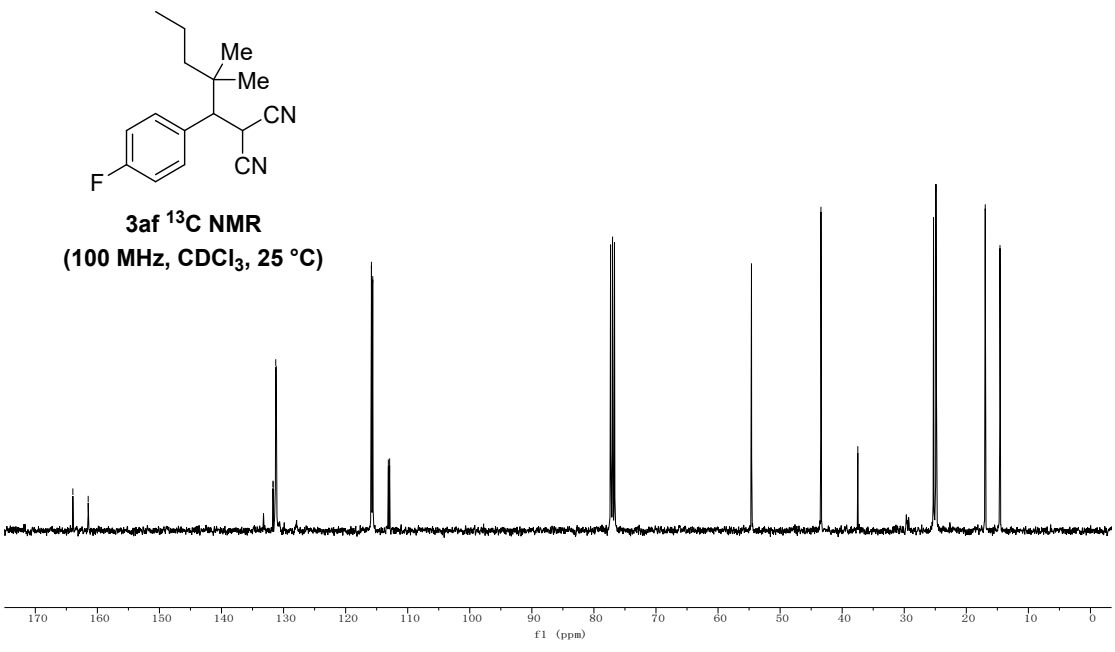
3ae ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



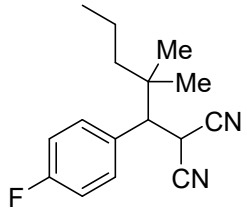
2aj ^{19}FNMR
(376 MHz, $CDCl_3$, 25 °C)



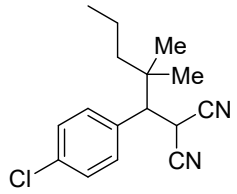
3af ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



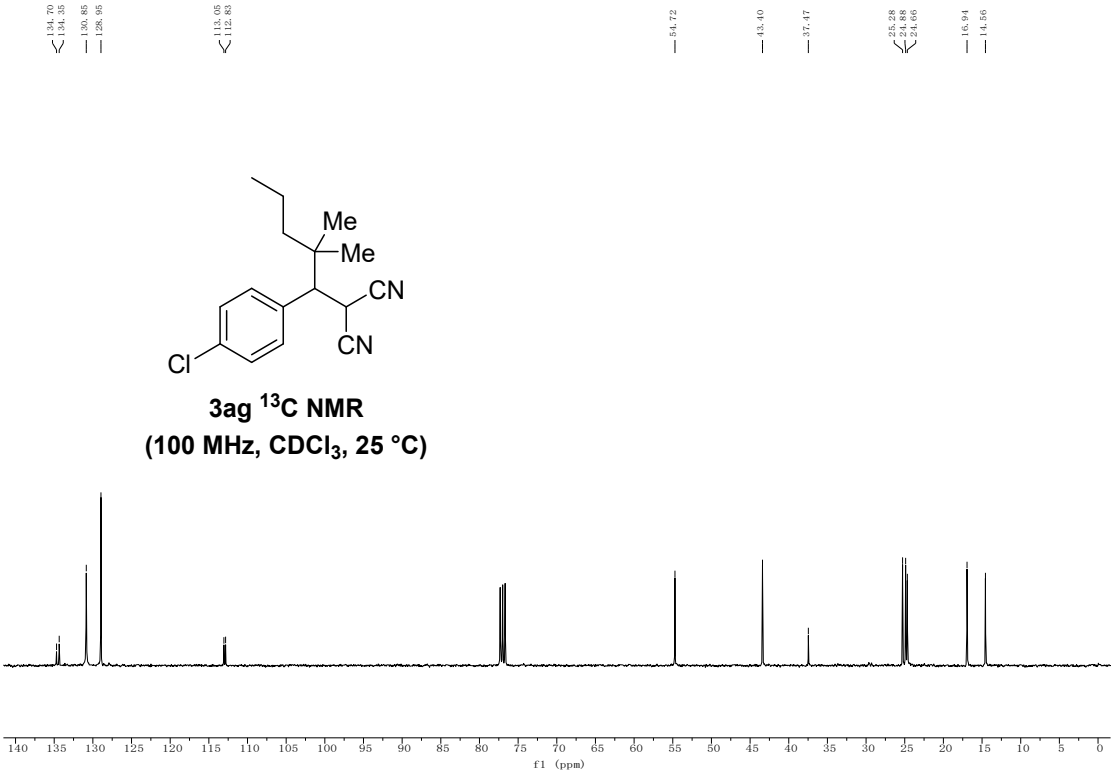
3af ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



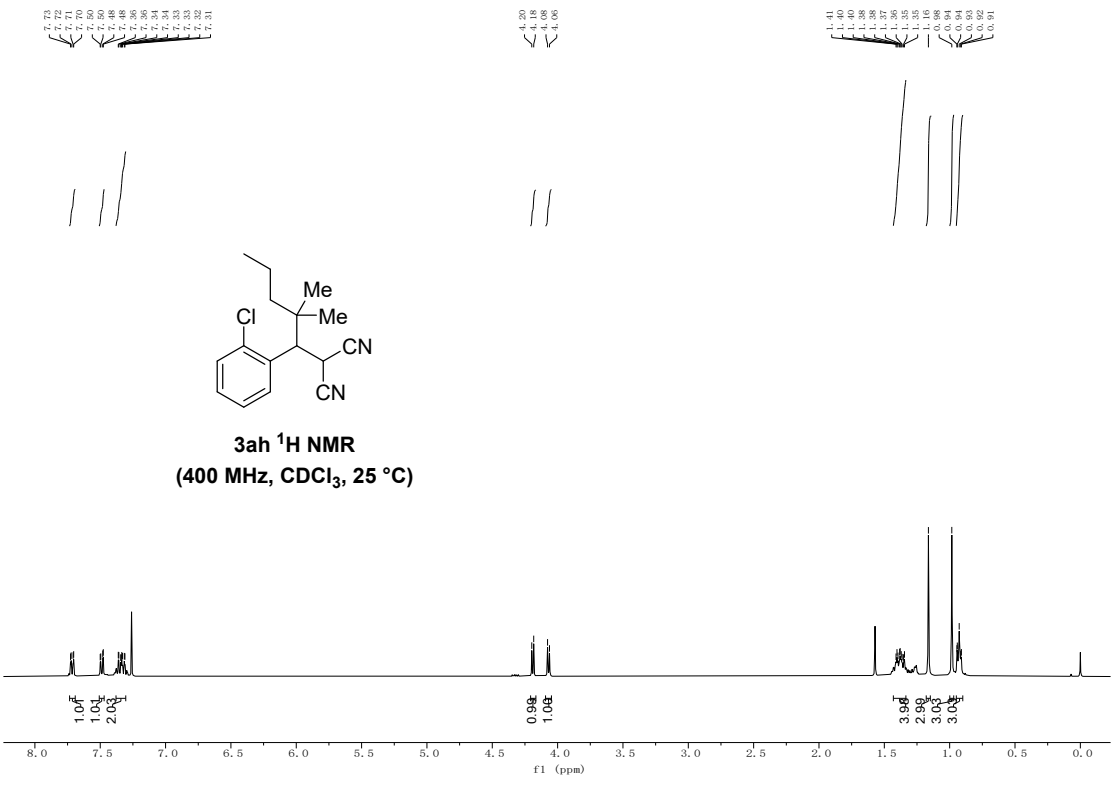
3af ^{19}F NMR
(376 MHz, $CDCl_3$, 25 °C)



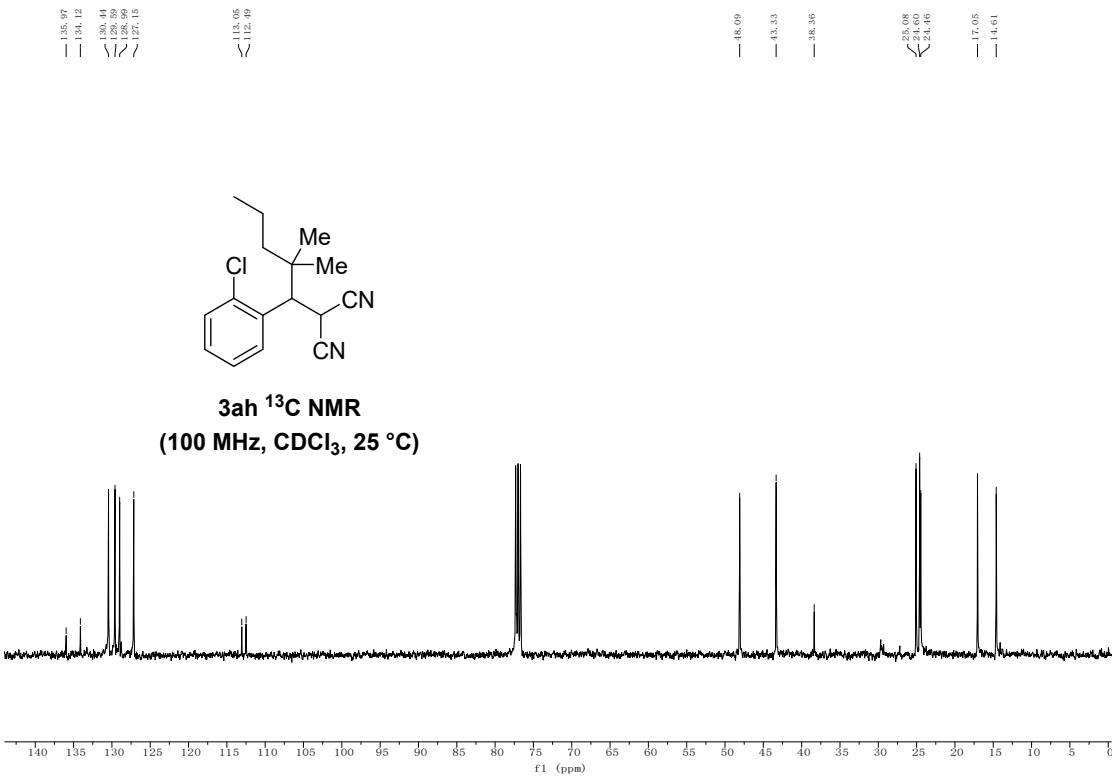
3ag ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



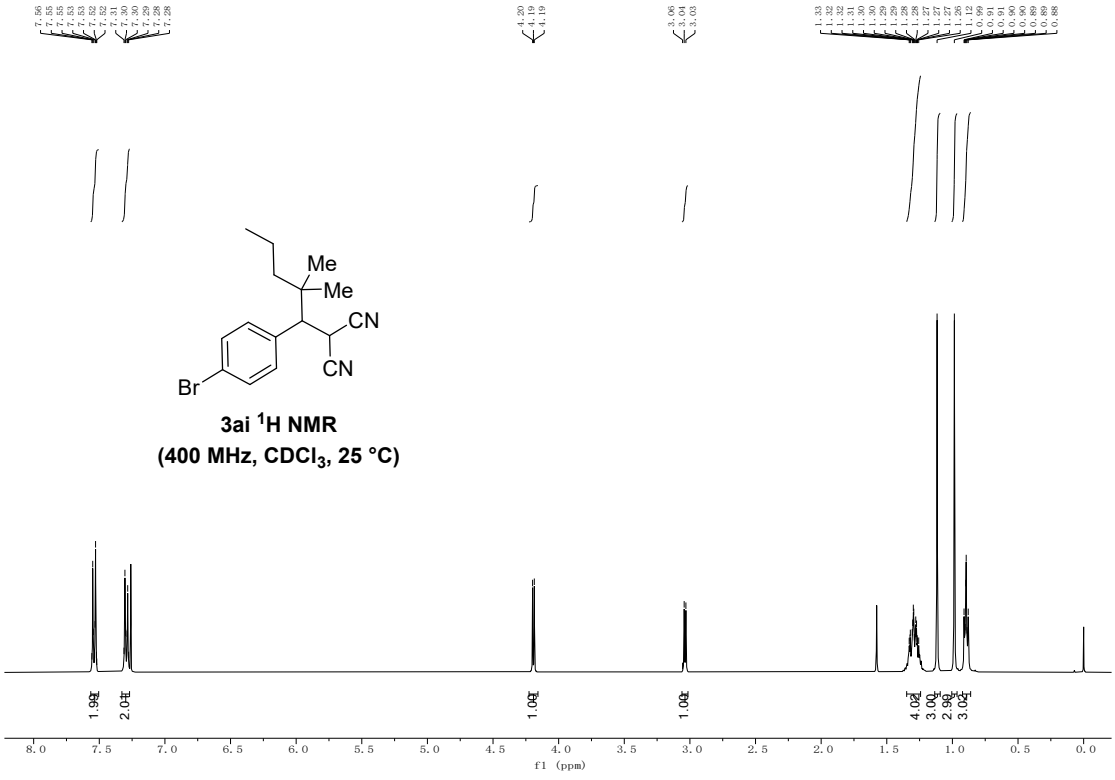
3ag ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



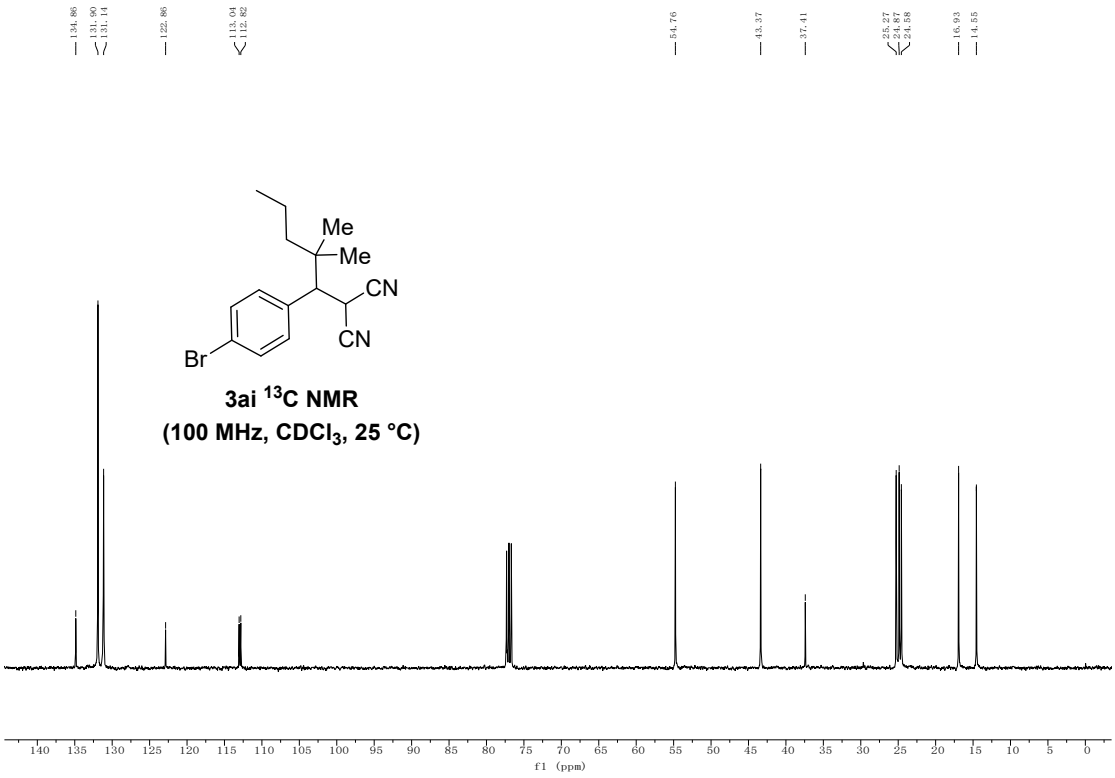
3ah ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



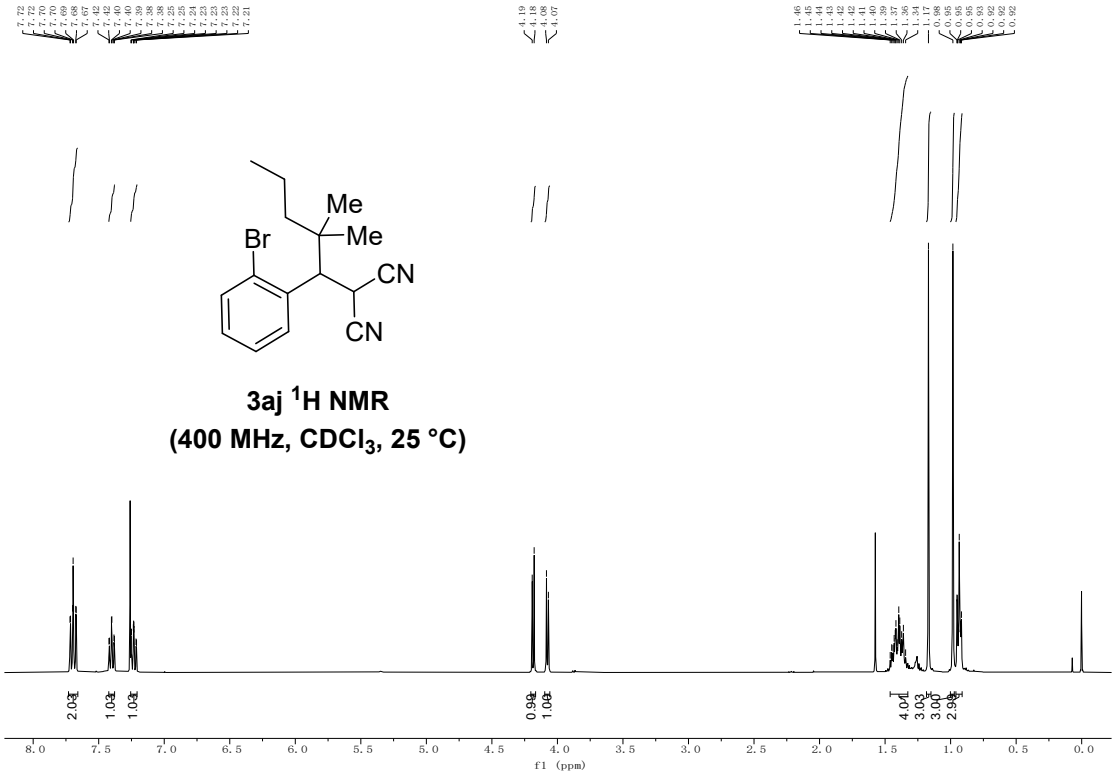
3ah ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



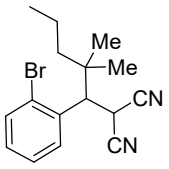
3ai ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



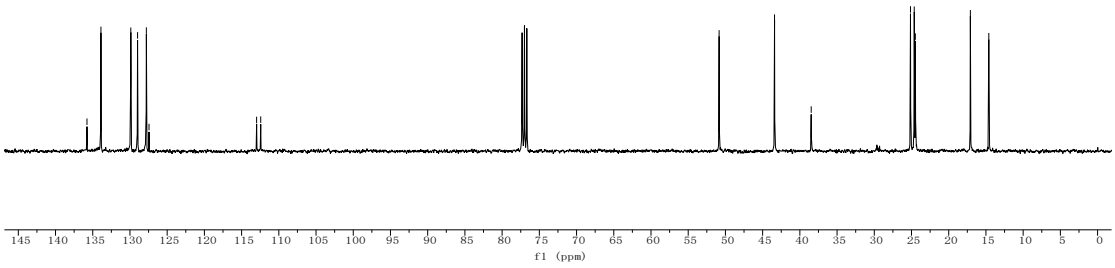
3ai ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)

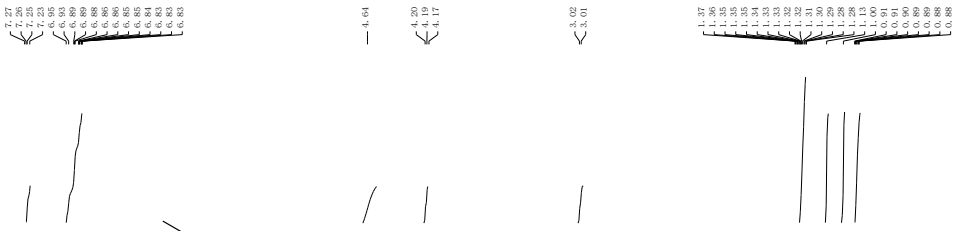


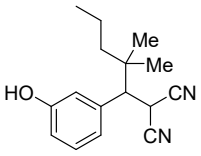
3aj ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



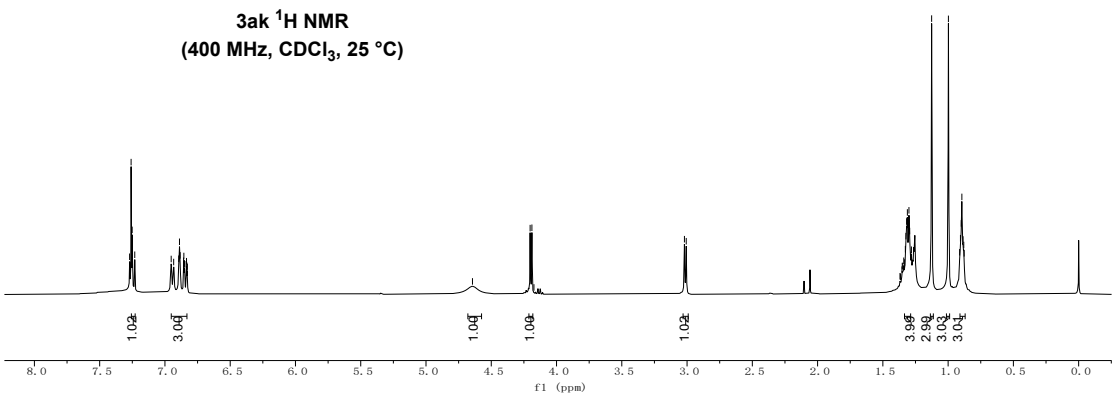
3aj ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)

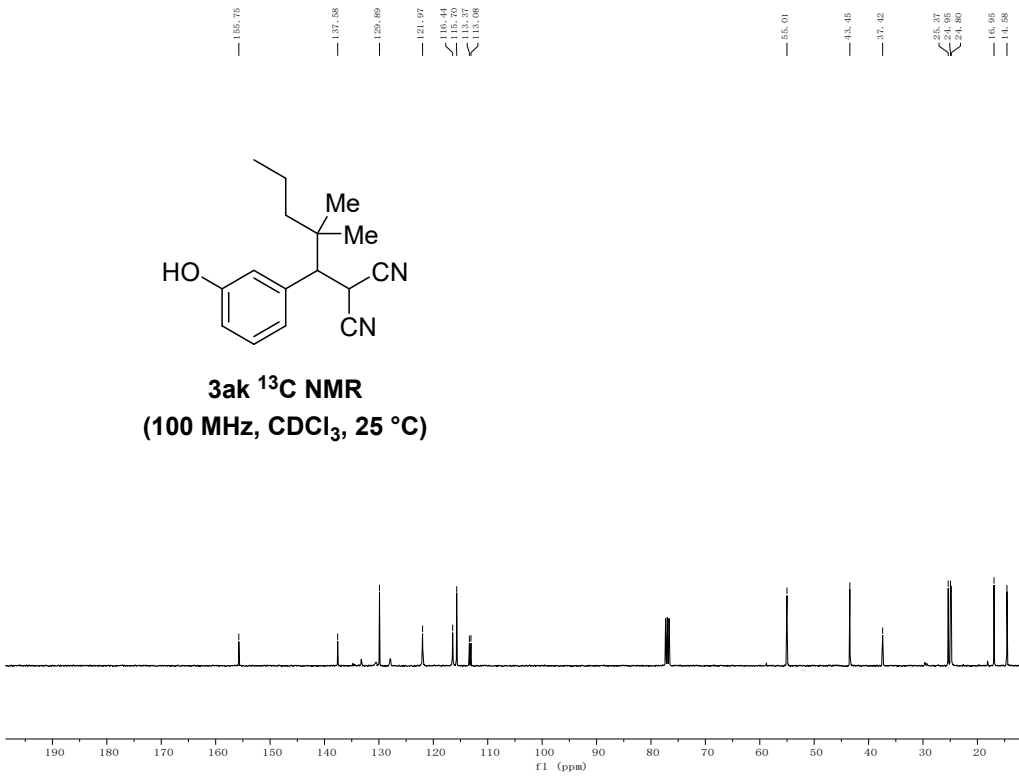




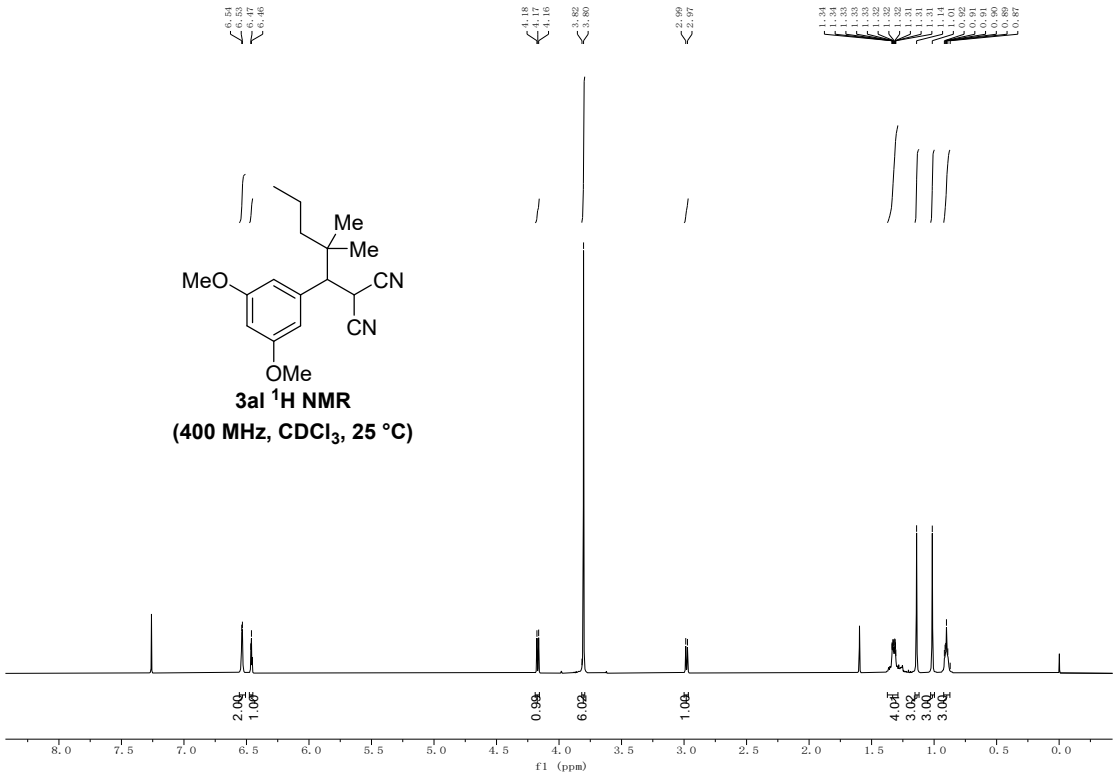


3ak ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)

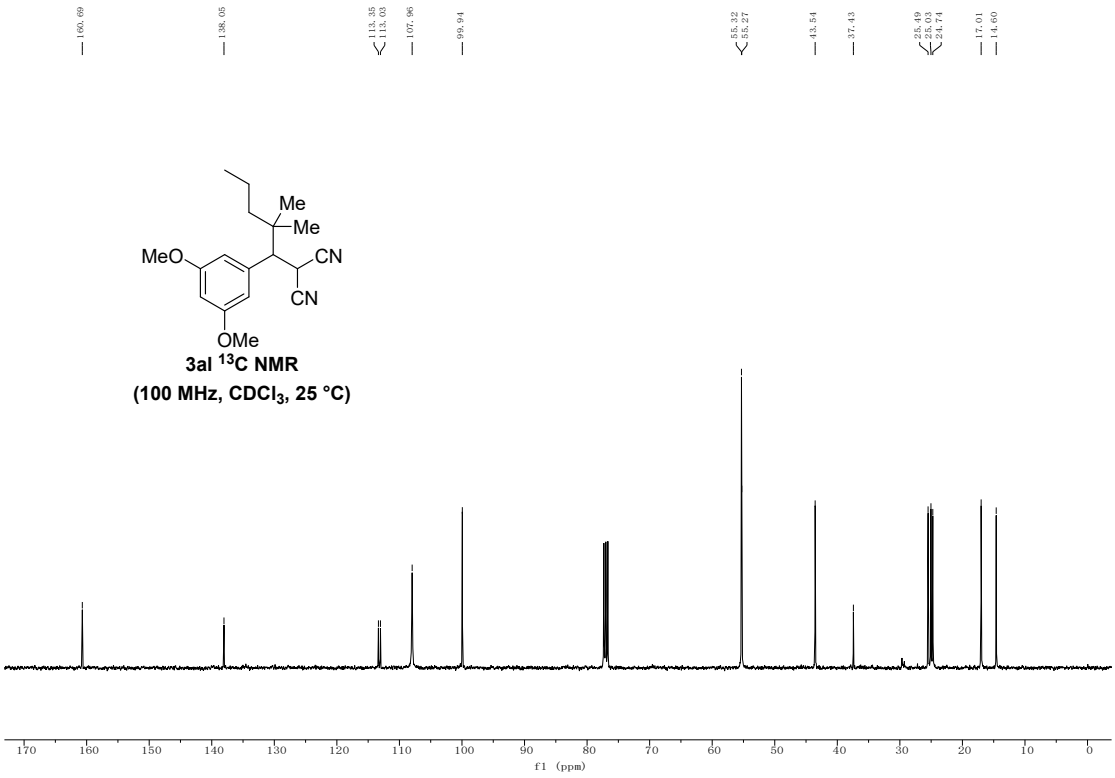




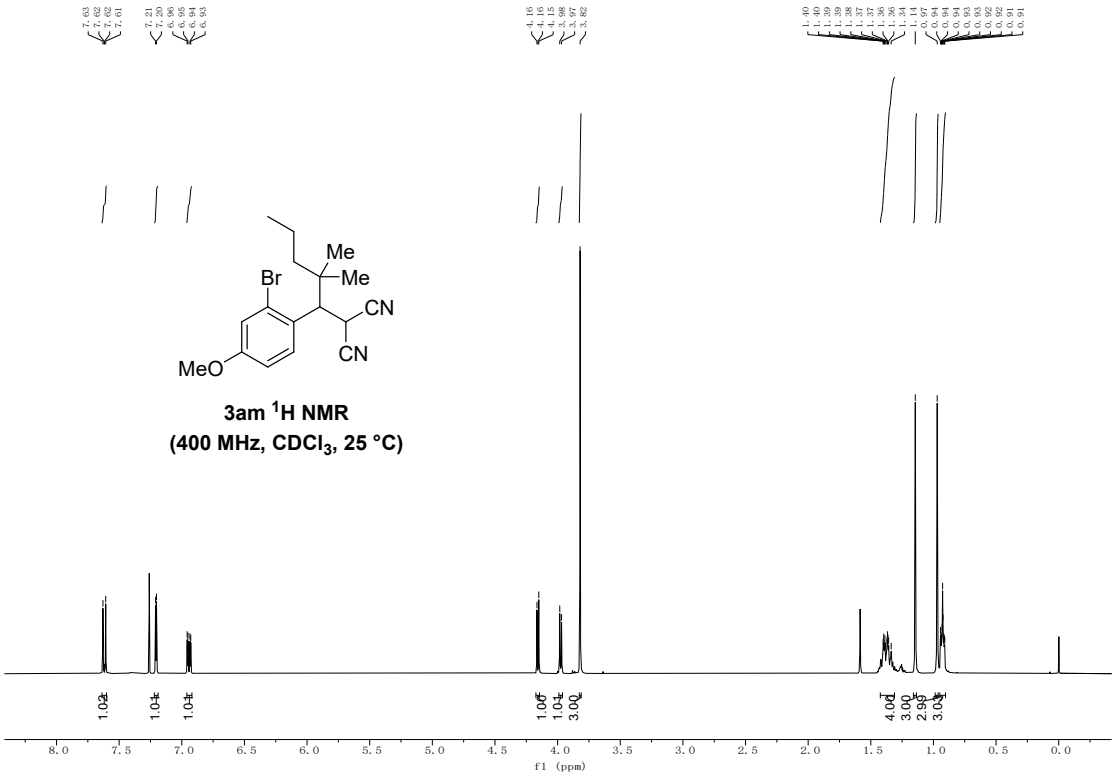
3ak ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



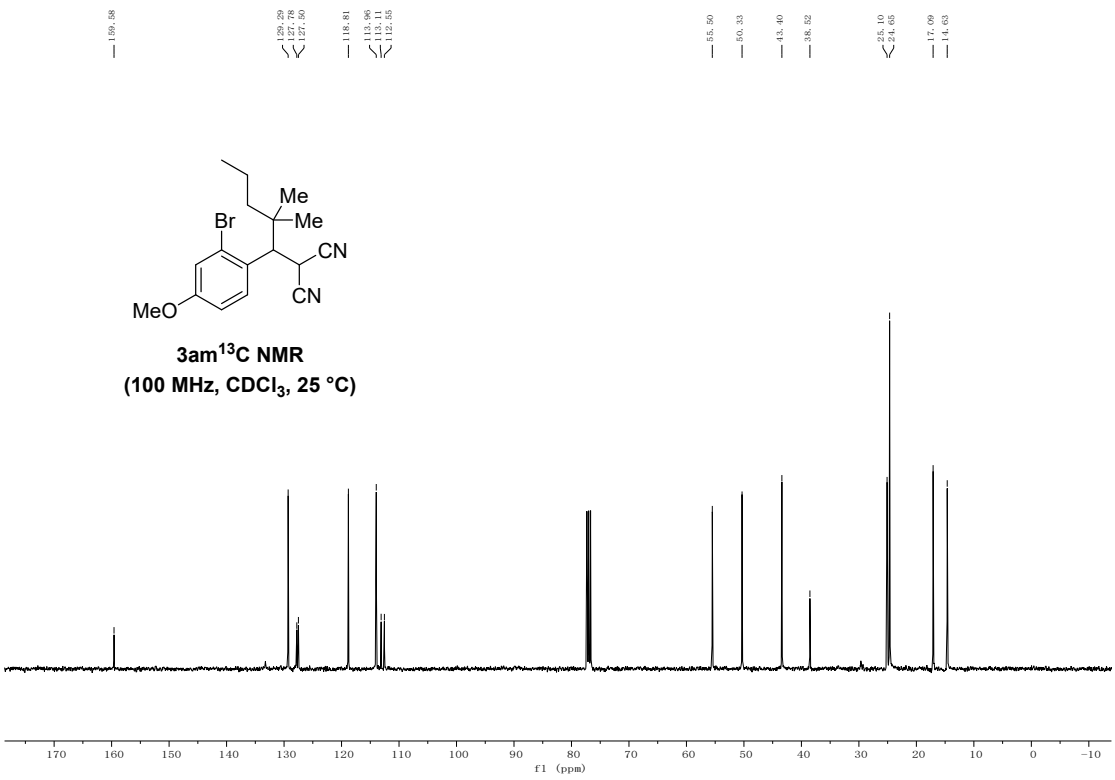
3al ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



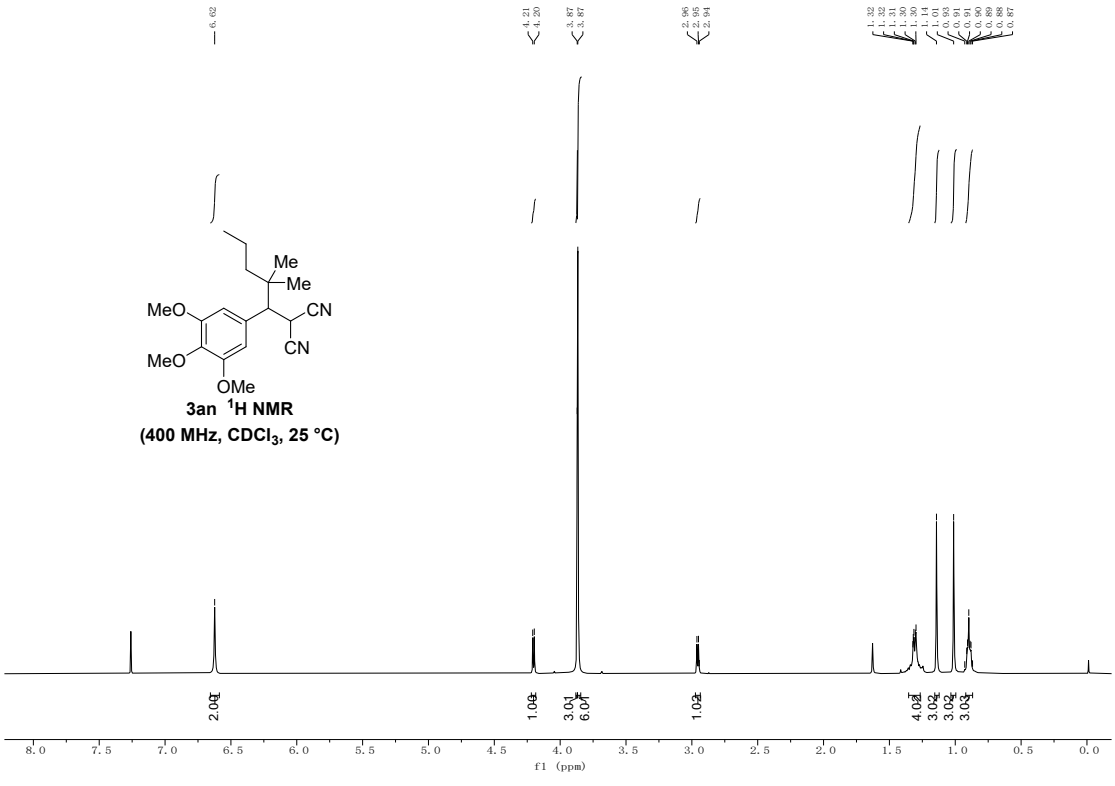
3al ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



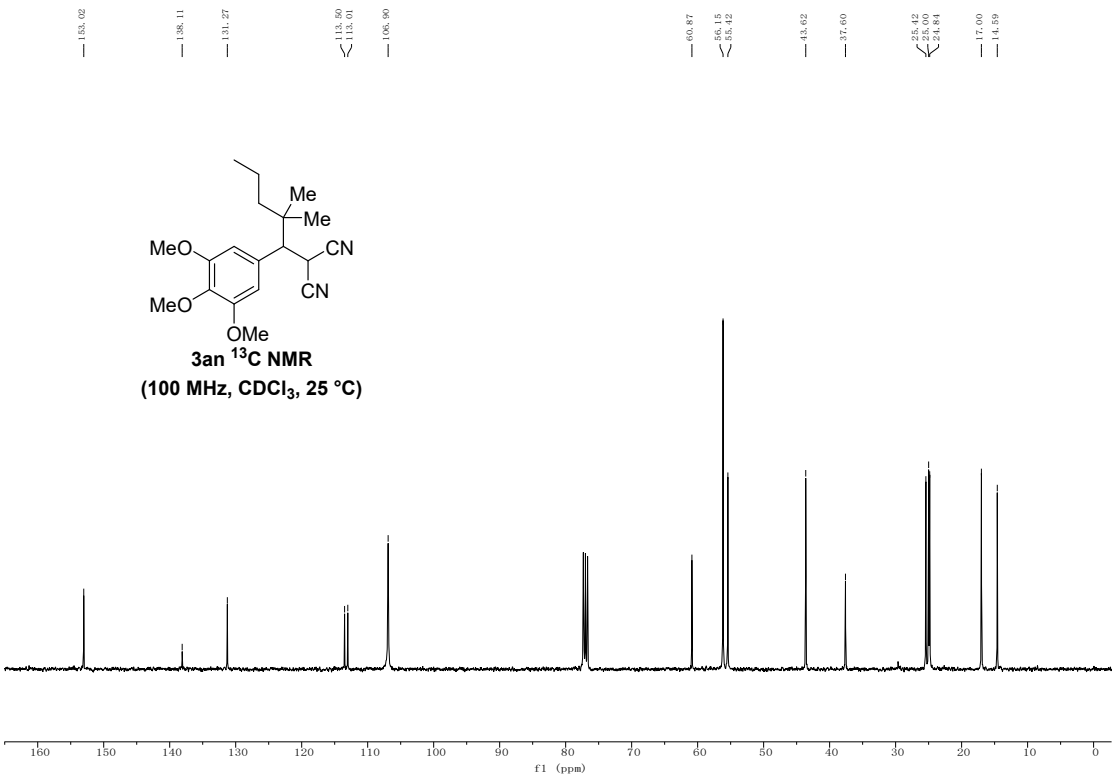
3am ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



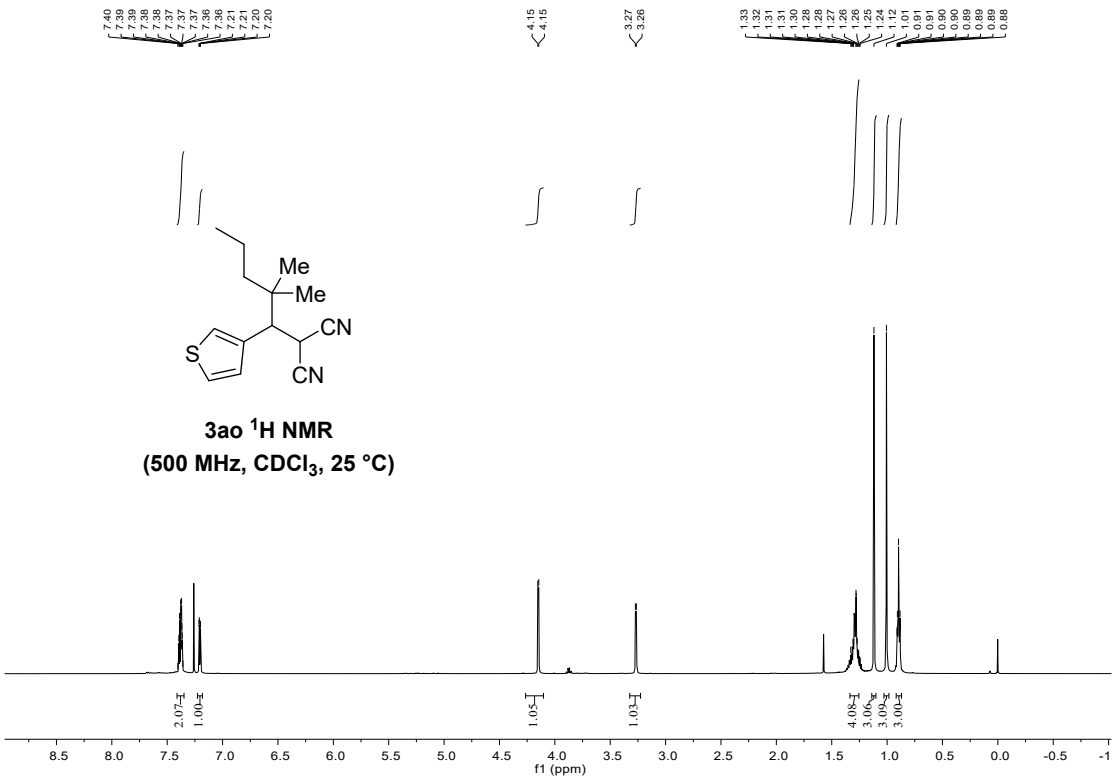
3am ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



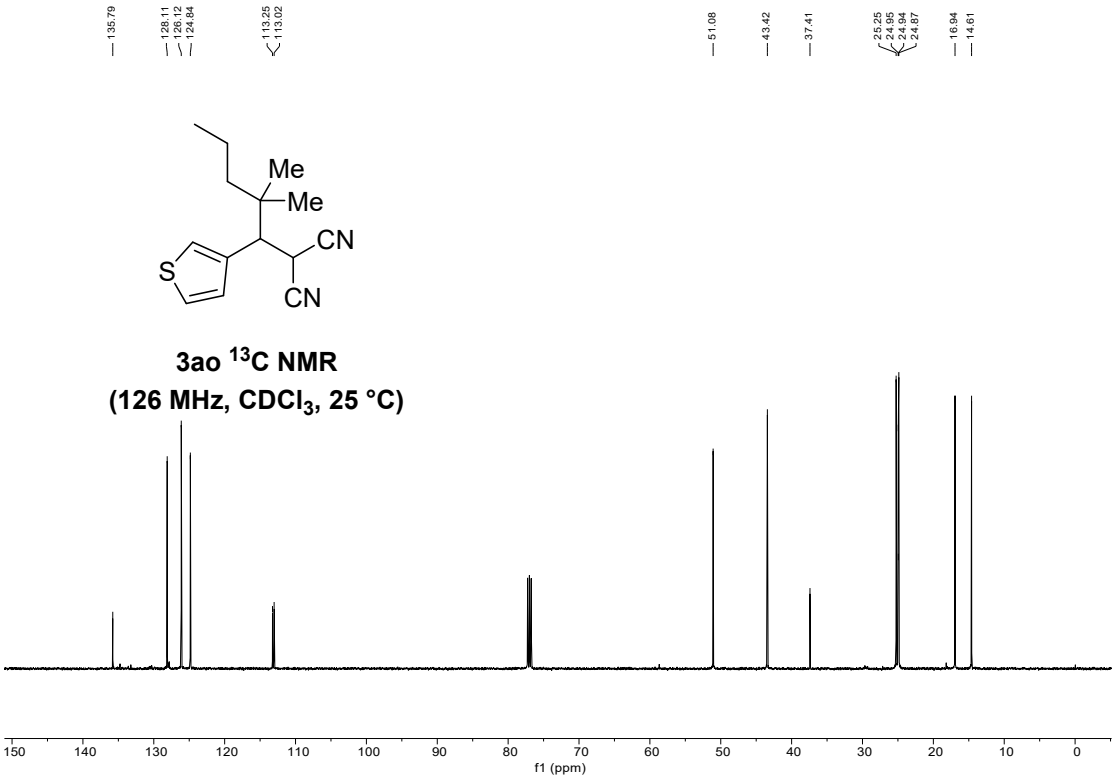
3an ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)

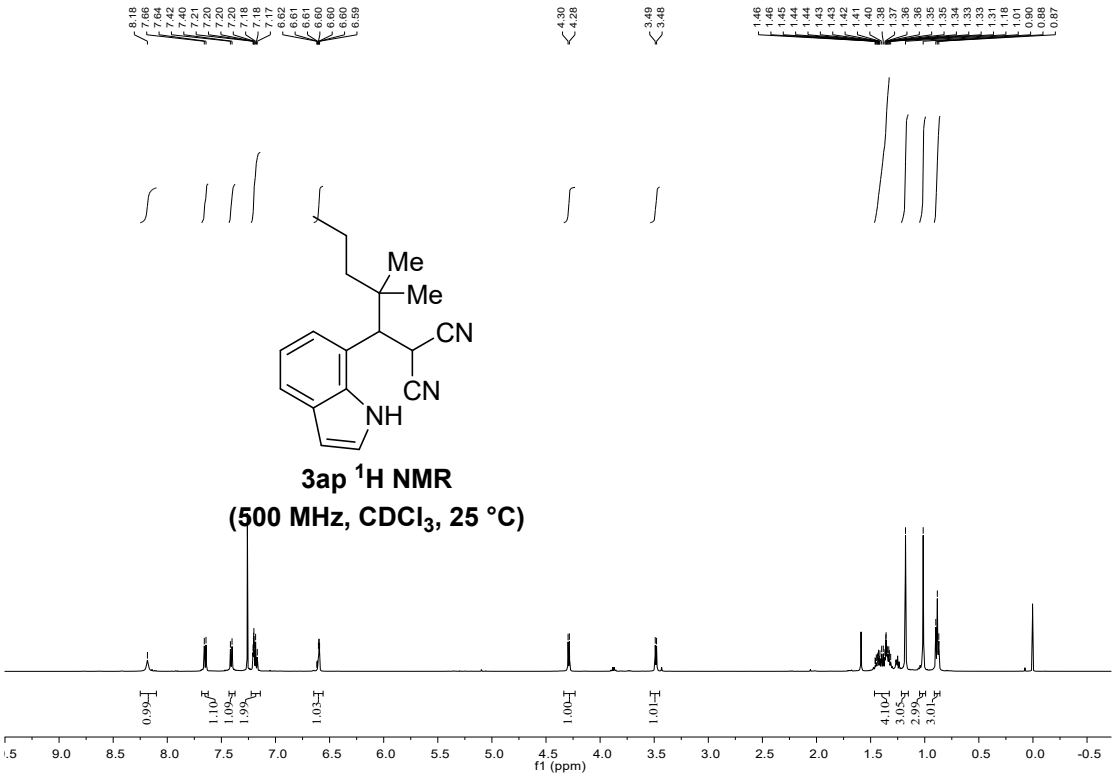


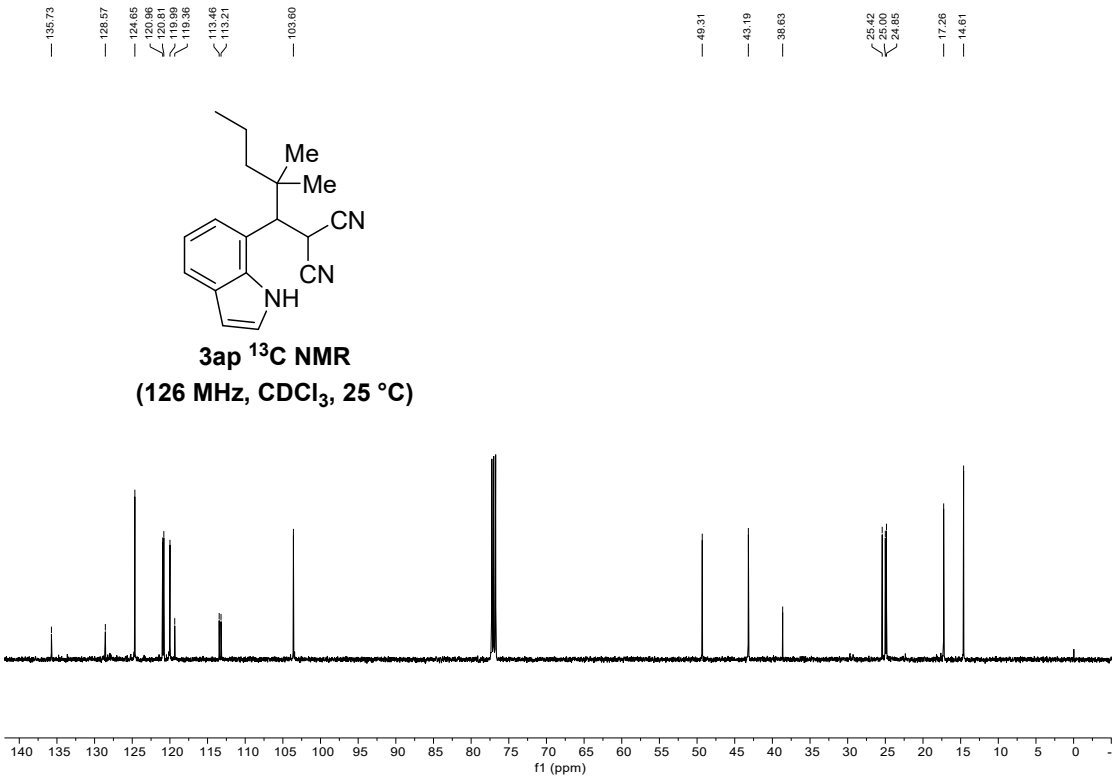
3an ^{13}C NMR
(100 MHz, $CDCl_3$, 25 °C)



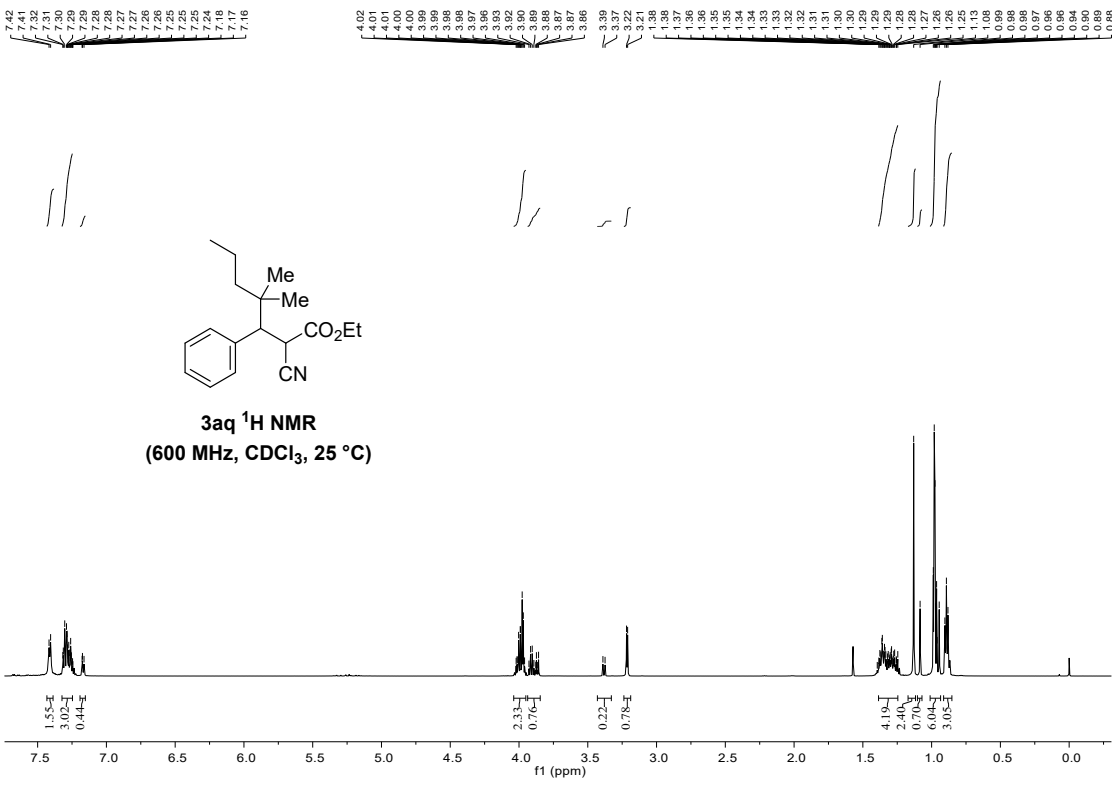
3ao ^{1}H NMR
(500 MHz, $CDCl_3$, 25 °C)


135.79
128.11
126.12
124.84
113.25
113.02
51.08
43.42
37.41
25.25
24.95
24.94
24.87
16.94
14.61
Me
Me
CN
CN
S
3ao ^{13}C NMR
(126 MHz, CDCl$_3$, 25 °C)
f1 (ppm)

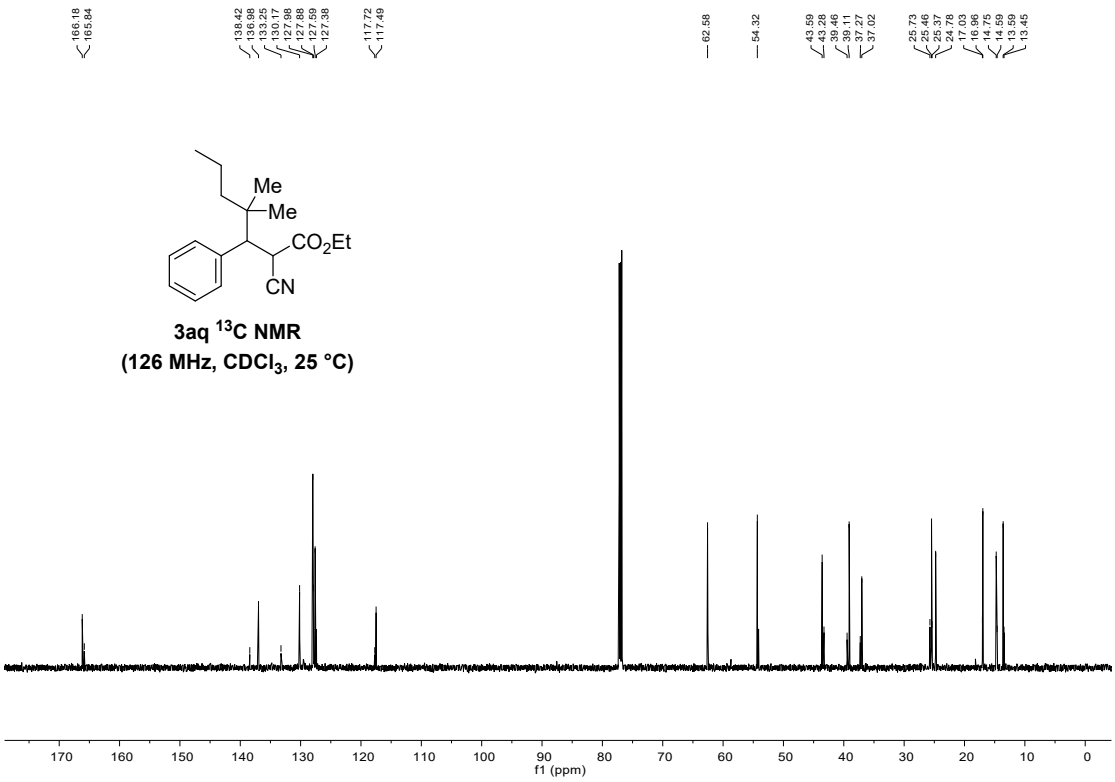

8.18
7.66
7.64
7.42
7.40
7.21
7.20
7.20
7.18
7.18
7.17
6.62
6.61
6.61
6.60
6.60
6.60
6.59
4.30
4.28
3.49
3.48
1.46
1.46
1.45
1.44
1.44
1.43
1.42
1.41
1.41
1.40
1.38
1.37
1.36
1.36
1.35
1.35
1.34
1.33
1.33
1.31
1.18
1.01
0.90
0.88
0.87
Me
Me
CN
CN
NH
3ap ^{1}H NMR
(500 MHz, CDCl$_3$, 25 °C)
0.99
1.10
1.09
1.99
1.03
1.00
1.01
4.10
3.05
2.99
3.01
f1 (ppm)



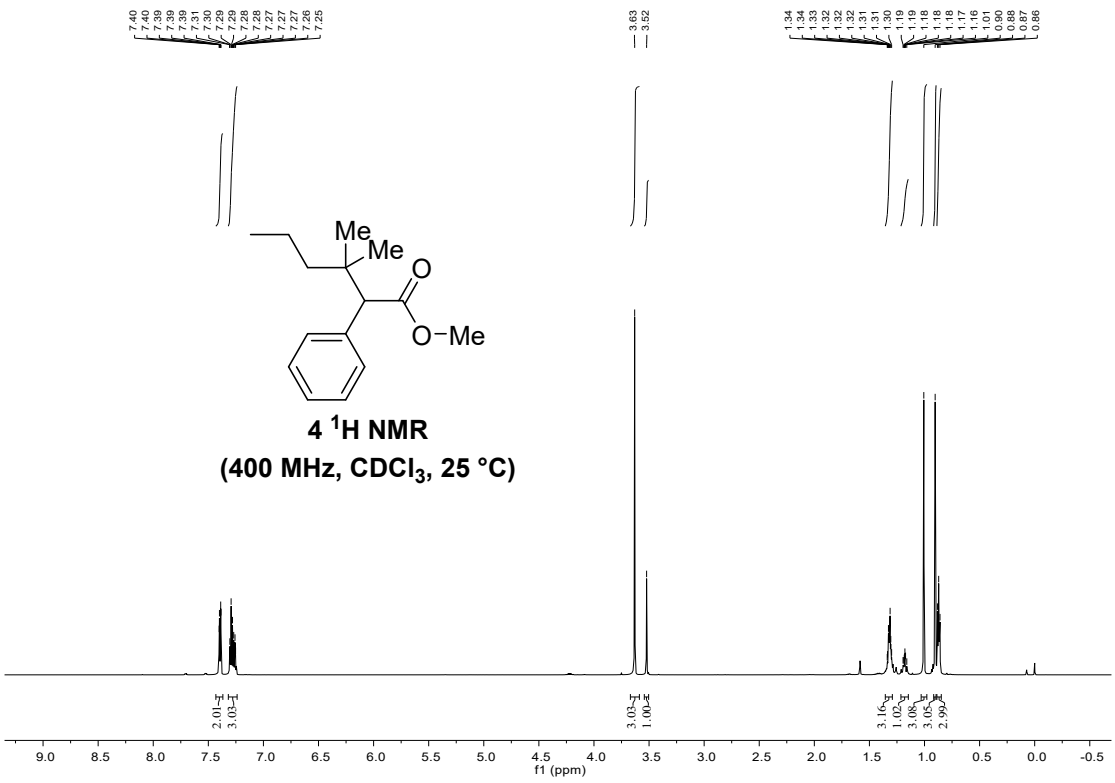
3ap ^{13}C NMR
(126 MHz, $CDCl_3$, 25 °C)



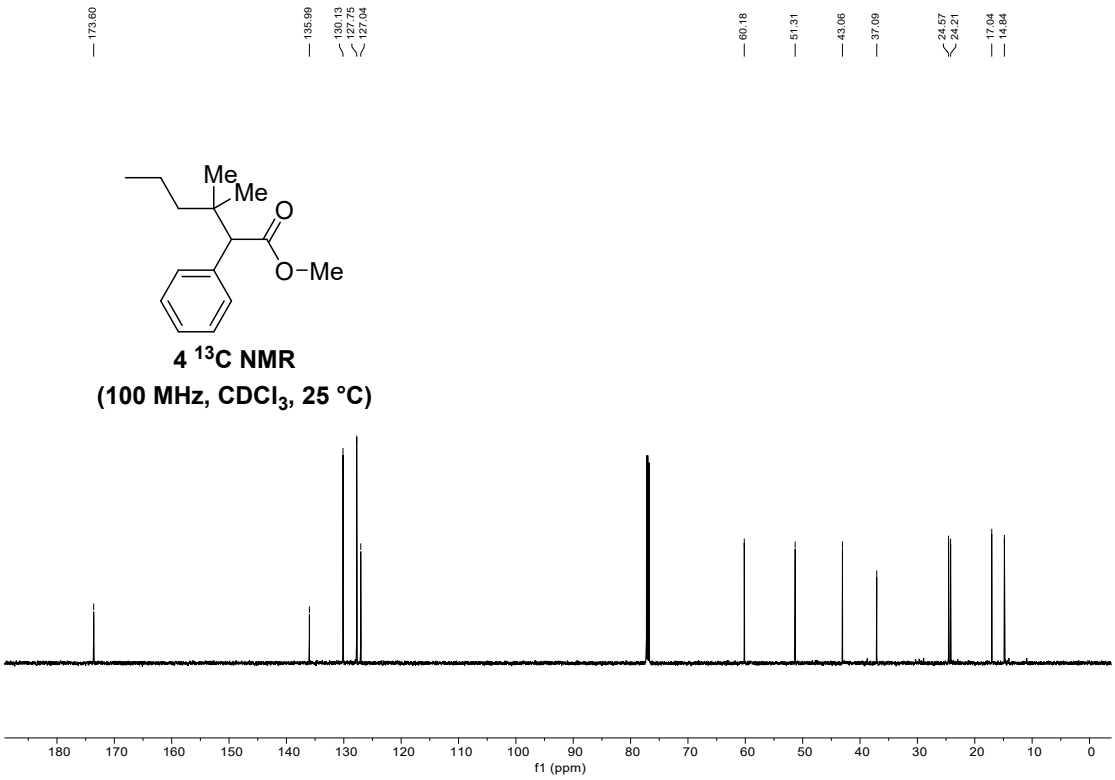
3aq ^{1}H NMR
(600 MHz, $CDCl_3$, 25 °C)



3aq ^{13}C NMR
(126 MHz, $CDCl_3$, 25 °C)

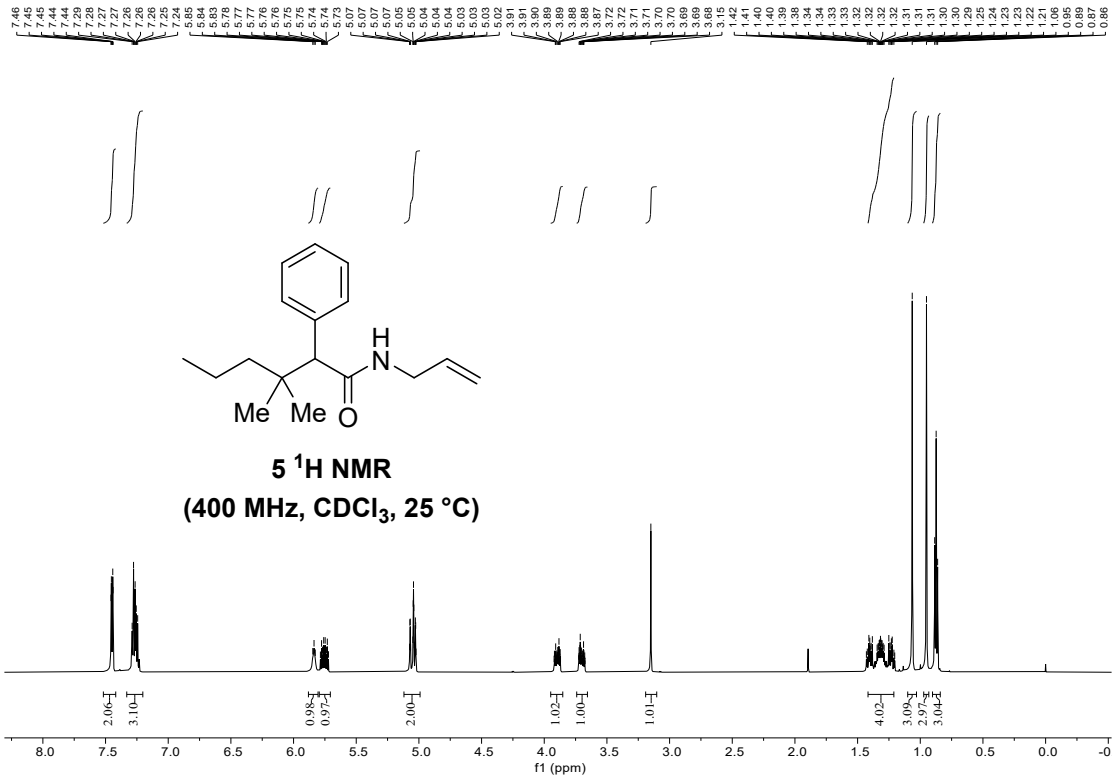


4 ^{1}H NMR
(400 MHz, $CDCl_3$, 25 °C)



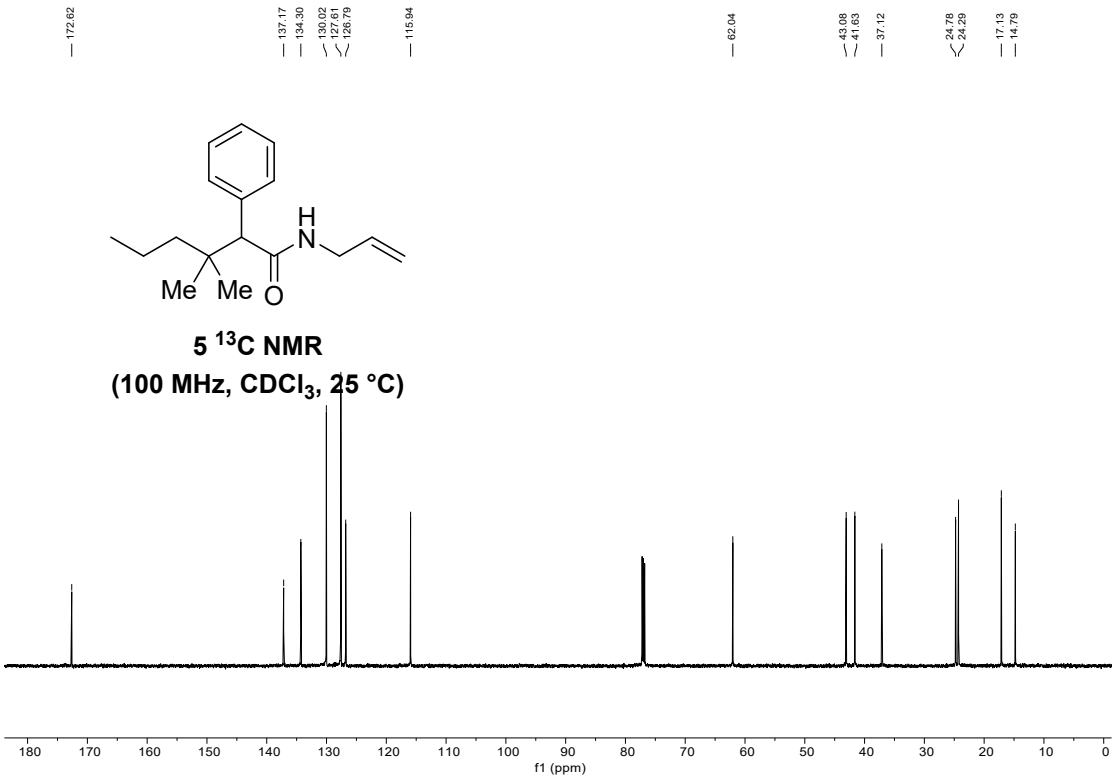
4 ^{13}C NMR

(100 MHz, $CDCl_3$, 25 °C)



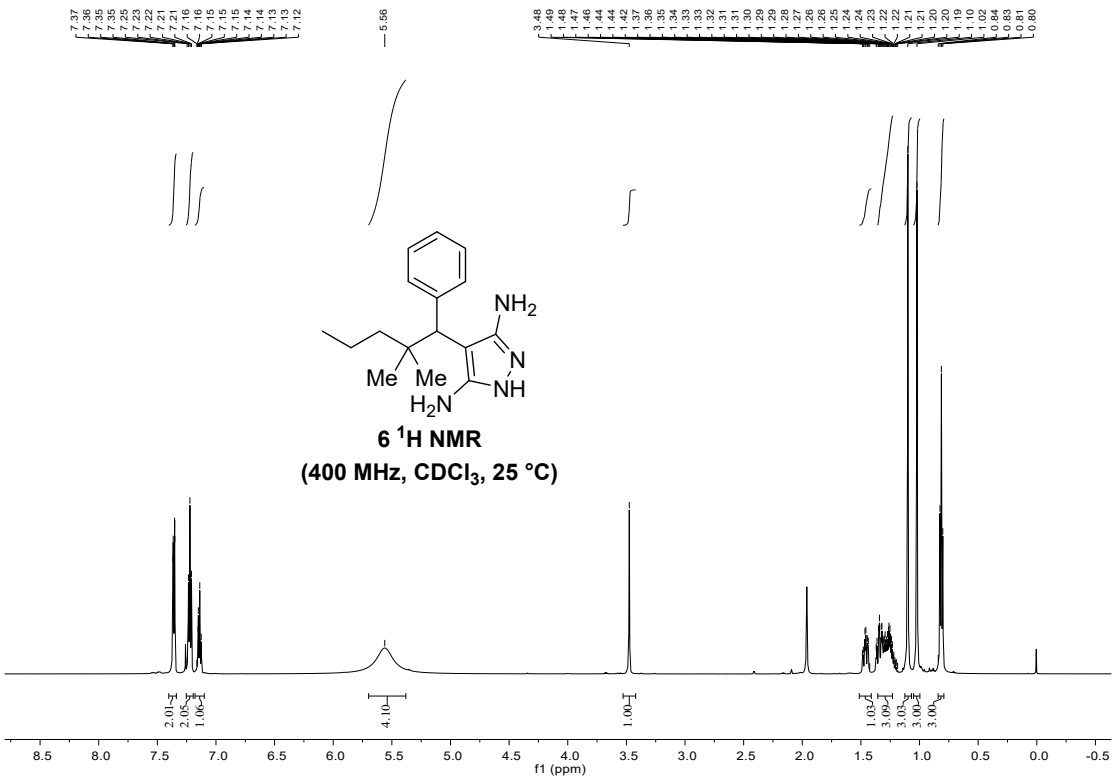
5 ^{1}H NMR

(400 MHz, $CDCl_3$, 25 °C)



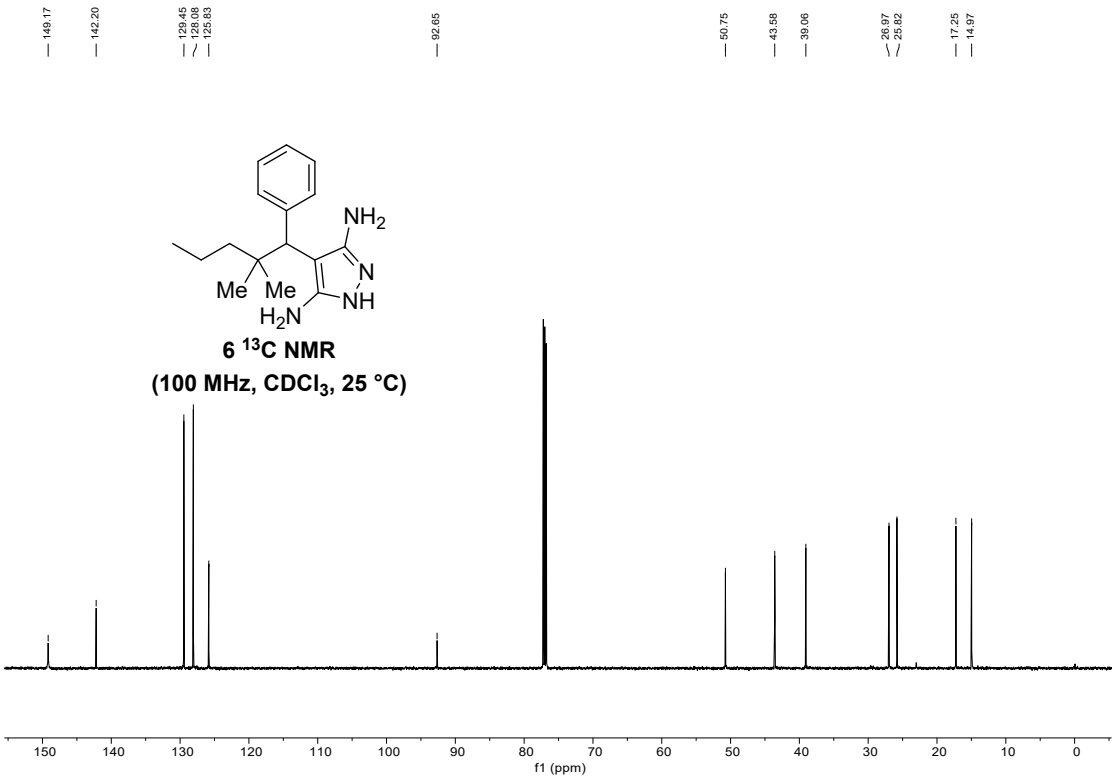
5 ^{13}C NMR

(100 MHz, $CDCl_3$, 25 °C)



6 ^{1}H NMR

(400 MHz, $CDCl_3$, 25 °C)



6 ^{13}C NMR

(100 MHz, $CDCl_3$, 25 °C)