Supporting Information

Direct Oxidation of Aryl Malononitriles Enabling a Copper-Catalyzed Intermolecular Alkene Carbochlorination

Prakash Basnet, Gang Hong, Charles E. Hendrick, and Marisa C. Kozlowski*

Table of Contents

1. General Considerations

All non-aqueous reactions were carried out under an atmosphere of dry argon unless otherwise noted. Commercial reagents were used as received without additional purification unless otherwise noted. MeCN was distilled from CaH_2. All glassware including 8 mL microwave vials were cleaned and dried in oven before use. $CuCl_2$ was acquired from Lancaster. $Cu(OTf)_2$ and 4,4'-di-tert-butyl-2,2'-bipyridine were acquired from Aldrich. All the alkenes were acquired from commercial vendors and used as received unless noted otherwise. KCl was acquired from Fisher scientific which was dried under vacuum at 100 °C for 2 h and stored inside a glovebox.

^1H NMR, and ^{13}C NMR, spectra were recorded on a Fourier transform NMR spectrometer at 500 MHz or 600 MHz, and 126 MHz or 151 MHz, respectively. Chemical shifts are reported relative to the solvent resonance peak δ 7.26 ($CDCl_3$) for ^1H NMR spectra and δ 77.16 ($CDCl_3$) for ^{13}C NMR spectra. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, b = broad singlet, m = multiplet), coupling constants, and number of protons. Accurate mass measurement analyses were conducted on either a GCMS with electron ionization (EI) or an LCMS with electrospray ionization (ESI). The signals were mass measured (TOF) against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS, and leucine enkephalin for ESI-LCMS. Waters software calibrates the instruments, and reports measurements, by use of neutral atomic masses; the mass of the electron is not subtracted (positive ions) or added (negative ions). Unless otherwise noted, yields refer to isolated material based on product purity ($\geq$95%) determined by ^1H NMR spectroscopy following silica gel chromatography with Silica-P flash silica gel (50-63 μm mesh particle size).

2. Experimental Procedures and characterization

Preparation of starting materials: 1-(But-3-en-1-yl)-4-methoxybenzene[1], arylmalononitriles[2,3], 2-(2,3-dihydrobenzofuran-5-yl)malononitrile[4] and 2-(but-3-en-1-yl)isoindoline-1,3-dione[5] were prepared following literature procedures.

General procedure for optimization (Table 1)

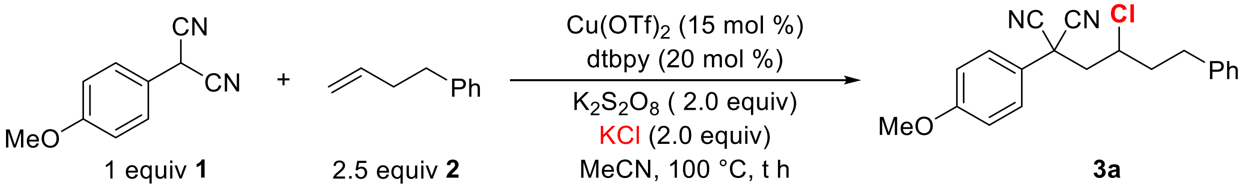
A flame dried 8 mL microwave vial equipped with a stirbar was charged with aryl malononitrile (0.1 mmol, 1 equiv) and the vial was brought into a glovebox where copper salt or $FeCl_3$ was added. The vial was capped with a rubber septum and removed from the glovebox. Under an argon atmosphere, alkene (0.25 mmol, 2.5 equiv) and the solvent (0.5 ml, 0.2 M) were added to the vial. The vial was then carefully sealed with a Teflon cap with ca rimper and placed in a heating block preheated to 100 °C with stirring. After the indicated time, the reaction vial was removed from the heating block and allowed to cool to ambient temperature. The reaction mixture was diluted with EtOAc (3 mL) followed by water (2 mL). The layers were separated, and the organic layer was transferred to another flask. The aqueous layer was extracted with ethyl acetate (2 x 2 mL). The combined ethyl acetate layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The resultant material was analyzed by ^{1}H-NMR spectroscopy with CH_2Br_2 (7 µL) as internal standard.

General procedure A for Scheme 2

A flame dried 8 mL microwave vial equipped with a stirbar was charged with aryl malononitrile (0.2 mmol, 1 equiv) and the vial was brought into a glovebox where $CuCl_2$ (0.4 mmol, 2 equiv) was added. The vial was capped with a rubber septum and removed from the glovebox. Under an argon atmosphere, alkene (0.5 mmol, 2.5 equiv) and freshly distilled acetonitrile (1 ml, 0.2 M) were added to the vial. The vial was then carefully sealed with a Teflon cap using crimper and placed in a heating block preheated at 100 °C with stirring. After 24 h, the reaction vial was removed from the heating block and allowed to cool to room temperature. The reaction mixture was diluted with EtOAc (5 mL) followed by water (3 mL). The layers were separated, and the organic layer was transferred to another flask. The aqueous layer was extracted with ethyl acetate (2 x 2 mL). The combined ethyl acetate layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The resultant material was purified by silica gel column chromatography using EtOAc/hexanes as eluent.

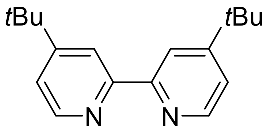
General procedure for optimization of catalytic condition

A flame dried 8 ml microwave vial equipped with stirbar was charged with aryl malononitrile (0.1 mmol, 1 equiv), $K_2S_2O_8$ (0.2 mmol, 2 equiv). The vial was brought into a glovebox where copper salt, ligand and KCl (0.2 mmol, 2 equiv) were added. The vial was capped with a rubber septum and removed from the glovebox. Under an argon atmosphere, alkene (0.25 mmol, 2.5 equiv) and freshly distilled acetonitrile (0.5 mL, 0.2 M) were added to the vial. The vial was then carefully sealed with a Teflon cap with a crimper and placed in a heating block preheated to 100 °C with stirring. After the indicated time, the reaction vial was removed from the heating block and allowed to cool to ambient temperature. The reaction mixture was diluted with EtOAc (3 mL) followed by water (2 mL). The layers were separated, and the organic layer was transferred to another flask. The aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organiclayers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The resultant material was analyzed by ^{1}H-NMR spectroscopy with CH_2Br_2 (7µL) as internal standard.

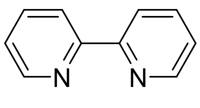


entry	change to conditions	Copper Salt (mol %)	Ligand (mol %)	Time t (h)	yield of 3a (%)[b]
1	None	$Cu(OTf)_2$ (15)	**x** (20)	24	71 (68)
2	None	$Cu(OTf)_2$ (20)	**x** (25)	18	74

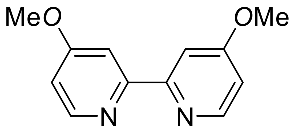
3	None	Cu(OTf)$_2$ (10)	**x** (15)	18	51
4	None	Cu(OTf)$_2$ (20)	**y** (25)	18	37
5	None	Cu(OTf)$_2$ (20)	**z** (20)	18	48
6	None	CuCl$_2$ (20)	x (25)	18	60
7	None	Cu(OTf)$_2$ (15)	-	24	38
8	None	CuCl (20)	-	20	33
9	DTBP instead of K$_2$S$_2$O$_8$	Cu(OTf)$_2$ (20)	**y** (20)	20	28
10	NaCl instead of KCl	Cu(OTf)$_2$ (20)	**y** (20)	22	38
11	LiCl instead of KCl	Cu(OTf)$_2$ (20)	**y** (20)	20	<10
12	1 equiv KCl	Cu(OTf)$_2$ (15)	**x** (20)	24	37
13	BnEt$_3$NCl instead of KCl	Cu(OTf)$_2$ (20)	**y** (20)	24	<10
14	Toluene instead of MeCN	Cu(OTf)$_2$ (15)	**x** (20)	24	55



x



y



z

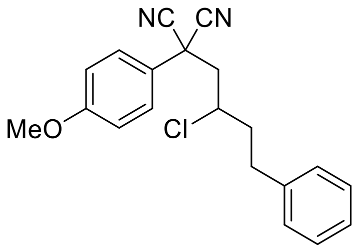
General procedure B for Scheme 3

A flame dried 8 mL microwave vial equipped with a stirbar was charged with aryl malononitrile (0.2 mmol, 1 equiv) and K$_2$S$_2$O$_8$ (0.4 mmol, 2.0 equiv). The vial was brought into a glovebox where Cu(OTf)$_2$ (0.03 mmol, 0.15 equiv) 4,4'-di-tert-butyl-2,2'-bipyridine (0.04 mmol, 0.20 equiv) and KCl (0.4 mmol, 2.0 equiv) were added. The vial was capped with a rubber septum and removed from the glovebox. Under an argon atmosphere, alkene (0.5 mmol, 2.5 equiv) and freshly distilled acetonitrile (1 ml, 0.2 M) were added into the vial. The vial was then carefully sealed with a Teflon cap with a crimper and placed in a heating block preheated to 100 °C with stirring. After the indicated time, the reaction vial was removed from the heating block and allowed to cool to room temperature. The reaction mixture was diluted with EtOAc (5 mL) followed by water (3 mL). The layers were separated, and the organic layer was transferred to another flask. The aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography using EtOAc/hexanes as eluent.

General Procedure for 1 mmol scale reaction

A flame dried 50 mL Schlenk tube equipped with a stirbar was charged with 2-(4-methoxyphenyl)malononitrile (172.2 mg, 1.0 mmol), $K_2S_2O_8$ (540 mg, 2.0 mmol), $Cu(OTf)_2$ (54.3 mg, 0.15 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (53.7 mg, 0.2 mmol) and KCl (149.1 mg, 2.0 mmol). The Schlenk tube was put under vacuum and refilled with argon three times. Under an argon atmosphere, but-3-en-1-ylbenzene (375 µL, 2.5 mmol) and freshly distilled acetonitrile (5 ml) wre added to the Schlenk tube sealed with a PTFE cap. The Schlenk tube was then placed in an oil bath preheated to 100 °C with stirring. After 28 h, the reaction vessel was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was diluted with EtOAc (10 mL) followed by water (10 mL). The layers were separated, and the organic layer was transferred to another flask. The aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography using 5% EtOAc/hexanes as eluent to get **3a** (156 mg, 46% yield) as a pale-yellow oil.

Characterization of new compounds



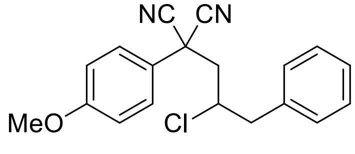
2-(1-Chloro-3-phenylpropyl)-2-(4-methoxyphenyl)malononitrile **(3a)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), but-3-en-1-ylbenzene (75.1 μL, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (6% EtOAc/hexanes) provided **3a** (58.3 mg) in 86% yield as a pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.9 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.15 (d, *J* = 6.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.96-3.92 (m, 1H), 3.85 (s, 3H), 2.87 (dt, *J* = 14.0, 7.1 Hz, 1H), 2.77 – 2.65 (m, 2H), 2.52 (dd, *J* = 14.8, 4.1 Hz, 1H), 2.08 (q, *J* = 8.1, 7.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 140.0, 128.7, 128.5, 127.3, 126.5, 123.2, 115.3, 115.1, 114.6, 56.4, 55.6, 49.5, 40.0, 39.7, 32.1.

IR (film) 2935, 2980, 2250, 1608, 1584, 1258, 1185, 1029, 830, 751 cm^{-1}.

HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{20}H_{19}ClN_2O$ 338.1186; found 338.1189.



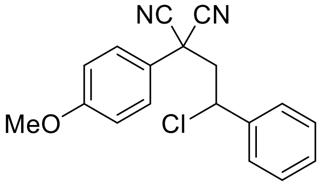
2-(2-Chloro-3-phenylpropyl)-2-(4-methoxyphenyl)malononitrile **(3b)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), allylbenzene (66.2 μL, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (6% EtOAc/hexanes) provided **3b** (43.5 mg) in 67% yield as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 9.0 Hz, 2H), 7.32-7.24 (m, 3H), 7.10 (d, *J* = 6.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.15-4.08 (m, 1H), 3.83 (s, 3H), 3.13-3.00 (m, 2H), 2.67 (dd, *J* = 15.0, 9.5 Hz, 1H), 2.52 (dd, *J* = 15.0, 3.0 Hz, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 160.7, 135.7, 129.2, 128.7, 127.4, 127.2, 122.9, 115.1, 115.0, 114.3, 56.6, 55.5, 48.0, 44.8, 39.6.

IR (film) 2936, 2840, 2250, 1608, 1511, 1258, 1185, 1030, 830, 633 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{19}H_{17}ClN_2O$ 324.1029; found 324.1050.



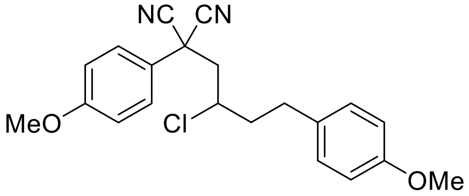
2-(2-Chloro-2-phenylethyl)-2-(4-methoxyphenyl)malononitrile **(3c)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (31.2 mg, 0.2 mmol), styrene (57.4 µL, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (6% EtOAc/hexanes) provided **3c** (50.2 mg) in 81% yield as a white amorphous solid.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48 (d, *J* = 9.0 Hz, 2H), 7.39-7.38 (m, 5H), 6.98 (d, *J* = 8.5 Hz, 2H), 5.02 (t, *J* = 7.0 Hz, 1H), 3.85 (s, 3H), 3.05 (dd, *J* = 14.7, 7.6 Hz, 1H), 2.86 (dd, *J* = 14.6, 6.8 Hz, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 160.9, 138.7, 129.7, 129.2, 127.4, 127.3, 123.2, 115.3, 114.6, 114.0, 58.0, 55.7, 50.6, 39.8.

IR (film) 2950, 2850, 2250, 1608, 1585, 1510, 1456, 1442, 1305, 1257, 1185, 1029 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{18}H_{15}ClN_2O$ 310.0873; found 310.0886.



2-(2-Chloro-4-(4-methoxyphenyl)butyl)-2-(4-methoxyphenyl)malononitrile **(3d)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (31.2 mg, 0.2 mmol), 1-(but-3-en-1-yl)-4-methoxybenzene (75.1 µL, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (6% EtOAc/hexanes) provided **3d** (60.2 mg) in 82% yield as a white crystalline solid.

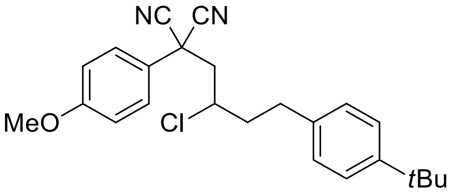
mp 73-75 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.92 – 3.88 (m, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 2.91 – 2.59 (m, 3H), 2.50 (dd, *J* = 14.9, 4.2 Hz, 1H), 2.06-2.00 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 158.3, 132.0, 129.5, 127.3, 123.2, 115.3, 115.1, 114.6, 114.2, 56.3, 55.6, 55.4, 49.5, 40.3, 39.8, 31.2.

IR (film) 2935, 2837, 2250, 1609, 1584, 1510, 1463, 1442, 1421, 1301, 1244, 1182, 1111, 1030 cm^{-1}.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{22}ClN_2O_2$ 369.1370; found 369.1363.



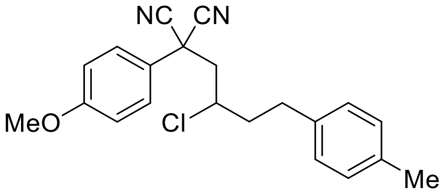
2-(4-(4-(tert-Butyl)phenyl)-2-chlorobutyl)-2-(4-methoxyphenyl)malononitrile **(3e)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), 1-(but-3-en-1-yl)-4-*tert*-butylbenzene (94.2 mg, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (7% EtOAc/hexanes) provided **3e** (55.3 mg) in 70% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 4.00-3.94 (m, 1H), 3.85 (s, 3H), 2.87-2.81 (m, 1H), 2.77-2.67 (m, 2H), 2.51 (dd, *J* = 14.5, 4.0 Hz, 1H), 2.10-2.05 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 149.4, 136.9, 128.2, 127.3, 125.6, 123.3, 115.3, 115.1, 114.6, 56.6, 55.7, 49.5, 40.1, 40.09, 34.5, 31.6, 31.5.

IR (film) 2960, 2867, 2249, 1608, 1511, 1258, 1185, 1030, 830, 796 cm^{-1}.

HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{24}H_{27}ClN_2O$ 394.1812; found 394.1826.



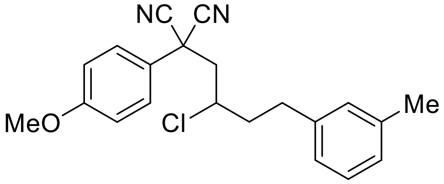
2-(2-Chloro-4-(p-tolyl)butyl)-2-(4-methoxyphenyl)malononitrile **(3f)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), 1-(but-3-en-1-yl)-4-methylbenzene (73.1 mg, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (7% EtOAc/hexanes) provided **3f** (44.5 mg) in 63% yield as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.98 – 3.88 (m, 1H), 3.85 (s, 3H), 2.83 (dt, *J* = 14.1, 7.1 Hz, 1H), 2.75 – 2.63 (m, 2H), 2.51 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.33 (s, 3H), 2.16 – 1.93 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 136.9, 136.0, 129.4, 128.4, 127.3, 123.2, 115.2, 115.1, 114.6, 56.4, 55.6, 49.5, 40.2, 39.8, 31.7, 21.1.

IR (film) 2935, 2840, 2249, 1608, 1511, 1258, 1185, 1031, 830, 809 cm^{-1}.

HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{21}H_{21}ClN_2O$ 352.1342; found 352.1349.



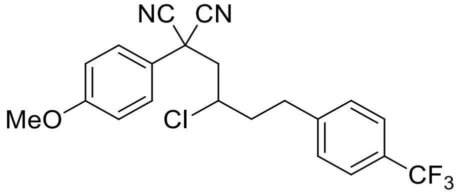
2-(2-Chloro-4-(m-tolyl)butyl)-2-(4-methoxyphenyl)malononitrile **(3g)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), 1-(but-3-en-1-yl)-3-methylbenzene (73.1 mg, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (7% EtOAc/hexanes) provided **3g** (59.9 mg) in 85% yield as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, *J* = 9.0 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.99-6.93 (m, 4H), 3.97-3.91 (m, 1H), 3.85 (s, 3H), 2.86-2.80 (m, 1H), 2.78-2.66 (m, 2H), 2.51 (dd, *J* = 15.0, 4.5 Hz, 1H), 2.32 (s, 3H), 2.09-2.03 (m, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 160.9, 139.9, 138.4, 129.4, 128.6, 127.3, 127.2, 125.6, 123.2, 115.3, 115.1, 114.6, 56.4, 55.7, 49.6, 40.1, 39.8, 32.1, 21.5.

IR (film) 2934, 2841, 2250, 1608, 1511, 1259, 1185, 1031, 830, 785 cm^{-1}.

HRMS (ESI-TOF) *m/z*: [M+ H]$^+$ calcd for $C_{21}H_{22}ClN_2O$ 353.1421; found 353.1422.



2-(2-Chloro-4-(4-(trifluoromethyl)phenyl)butyl)-2-(4-methoxyphenyl)malononitrile (3h) General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), 1-(but-3-en-1-yl)-4-trifluoromethylbenzene (100.1 mg, 0.5 mmol), and CuCl$_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (7% EtOAc/hexanes) provided **3h** (54.5 mg) in 67% yield as yellow oil.

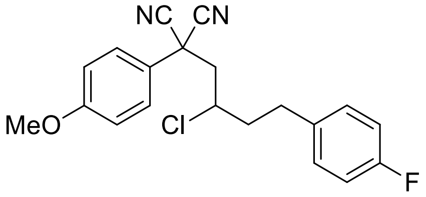
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.9 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.93-3.89 (m, 1H), 3.84 (s, 3H), 2.94 (ddd, *J* = 14.1, 8.3, 6.2 Hz, 1H), 2.86 – 2.70 (m, 2H), 2.53 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.25 – 2.01 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 161.0, 144.1, 129.25, 128.88 (q, $2J_{C\text{-}F}$ = 32.5 Hz), 128.92, 127.3, 125.6 (q, $3J_{C\text{-}F}$ = 3.8 Hz), 124.3 (q, $1J_{C\text{-}F}$ = 272.3 Hz), 123.0, 115.3, 115.0, 114.6, 56.1, 55.6, 49.5, 39.7, 39.6, 32.0.

^{19}F NMR (565 MHz, CDCl$_3$) δ –62.4.

IR (film) 2937, 2843, 2248, 1609, 1512, 1260, 1186, 1031, 830 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{21}H_{18}ClF_3N_2O$ 406.1060; found 406.1045.



2-(2-Chloro-4-(4-fluorophenyl)butyl)-2-(4-methoxyphenyl)malononitrile **(3i)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), 1-(but-3-en-1-yl)-4-fluorobenzene (75.1 mg, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (6% EtOAc/hexanes) provided **3i** (45.7 mg) in 64% yield as light yellow oil.

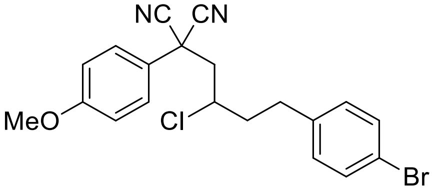
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 9.0 Hz, 2H), 7.09 (q, J = 5.5 Hz, 2H), 6.98-6.94 (m, 4H), 3.91-3.86 (m, 1H), 3.85 (s, 3H), 2.87-2.81 (m, 1H), 2.78-2.68 (m, 2H), 2.51 (dd, J = 14.5, 4.0 Hz, 1H), 2.07-2.02 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (d, $1J_{C\text{-}F}$ = 243.1 Hz), 160.7, 135.3 (d, $3J_{C\text{-}F}$ = 3.1 Hz), 129.7 (d, $2J_{C\text{-}F}$ = 7.9 Hz), 127.3, 123.1, 115.6, 115.5, 115.3, 114.5 (d, J = 54.0 Hz), 56.1, 55.7, 49.6, 40.1, 39.7, 31.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ –116.7.

IR (film) 2937, 2249, 1608, 1509, 1258, 1185, 1030, 829 cm^{-1}.

HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{20}H_{18}ClFN_2O$ 356.1092; found 356.1083.



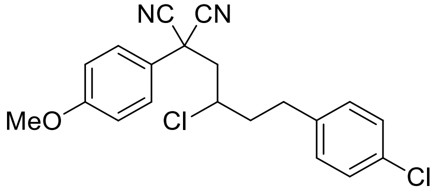
2-(4-(4-Bromophenyl)-2-chlorobutyl)-2-(4-methoxyphenyl)malononitrile **(3j)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), 1-(but-3-en-1-yl)-4-bromobenzene (105.5 mg, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (6% EtOAc/hexanes) provided **3j** (60.9 mg) in 73% yield as light yellow oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.91-3.86 (m, 1H), 3.85 (s, 3H), 2.86-2.79 (m, 1H), 2.78-2.66 (m, 2H), 2.51 (dd, *J* = 14.5, 4.5 Hz, 1H), 2.07-2.02 (m, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 161.0, 138.9, 131.8, 130.3, 127.3, 123.0, 120.3, 115.3, 115.0, 114.6, 56.1, 55.7, 49.6, 39.8, 39.7, 31.6.

IR (film) 2935, 2840, 2248, 1608, 1511, 1259, 1185, 1031, 830, 805 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{20}H_{18}BrClN_2O$ 416.0291; found 416.0285.



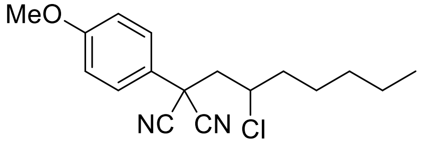
2-(2-Chloro-4-(4-chlorophenyl)butyl)-2-(4-methoxyphenyl)malononitrile **(3k)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), 1-(but-3-en-1-yl)-4-chlorobenzene (83.3 mg, 0.5 mmol), and CuCl$_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (6% EtOAc/hexanes) provided **3k** (56.0 mg) in 75% yield as a colorless oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.91 – 3.86 (m, 1H), 3.85 (s, 3H), 2.84 (dt, *J* = 13.9, 7.0 Hz, 1H), 2.78 – 2.65 (m, 2H), 2.51 (dd, *J* = 14.9, 4.3 Hz, 1H), 2.13 – 1.97 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 161.0, 138.4, 132.3, 129.9, 128.8, 127.3, 123.0, 115.3, 115.0, 114.6, 56.1 55.7, 49.5, 39.8, 39.7, 31.5.

IR (film) 2936, 2840, 2249, 1608, 1511, 1259, 1185, 1031, 830 cm^{-1}.

HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{20}H_{19}Cl_2N_2O$ 373.0874; found 373.0866.



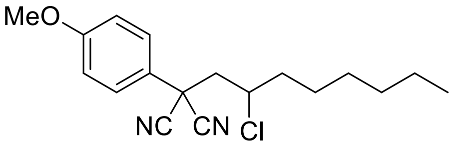
2-(2-Chloroheptyl)-2-(4-methoxyphenyl)malononitrile **(3l)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), hept-1-ene (70.1 µL, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (5% EtOAc/hexanes) provided **3l** (39.6 mg) in 65% yield as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 4.01-3.96 (m, 1H), 3.85 (s, 3H), 2.71 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.50 (dd, *J* = 15.0, 4.0 Hz, 1H), 1.79-1.73 (m, 2H), 1.57-1.36 (m, 2H), 1.33-1.20 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 127.3, 123.5, 115.3, 115.2, 114.7, 57.3, 55.7, 49.7, 39.9, 38.5, 31.1, 25.6, 22.5, 14.1.

IR (film) 2956, 2860, 2250, 1608, 1511, 1258, 1185, 1030, 829 cm^{-1}.

HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{17}H_{21}ClN_2O$ 304.1342; found 304.1357.



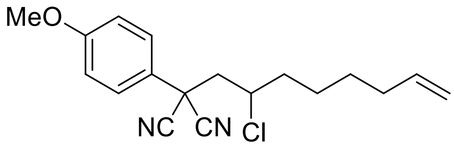
2-(2-Chlorooctyl)-2-(4-methoxyphenyl)malononitrile **(3m)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), oct-1-ene (77.9 µL, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (5% EtOAc/hexanes) provided **3m** (49.7 mg) in 78% yield as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 9.0 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 4.02-3.96 (m, 1H), 3.85 (s, 3H), 2.71 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.50 (dd, *J* = 15.0, 4.0 Hz, 1H), 1.79-1.73 (m, 2H), 1.51-1.37 (m, 2H), 1.33-1.22 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 127.4, 123.5, 115.3, 115.2, 114.7, 57.3, 55.7, 49.7, 39.9, 38.5, 31.7, 28.6, 25.9, 22.6, 14.1.

IR (film) 2930, 2858, 2250, 1608, 1511, 1258, 1185, 1031, 830 cm^{-1}.

HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{18}H_{23}ClN_2O$ 318.1499; found 318.1501.



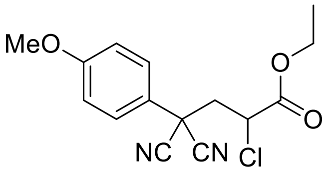
2-(2-Chlorooct-7-en-1-yl)-2-(4-methoxyphenyl)malononitrile **(3n)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), octa-1,7-diene (73.8 µL, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (4% EtOAc/hexanes) provided **3n** (38.0 mg) in 60% yield as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 5.82-5.73 (m, 1H), 5.03-4.94 (m, 2H), 4.02-3.96 (m, 1H), 3.85 (s, 3H), 2.71 (dd, J = 15.0, 9.0 Hz, 1H), 2.50 (dd, J = 15.0, 4.0 Hz, 1H), 2.05 (q, J = 7.0 Hz, 2H), 1.82-1.72 (m, 2H), 1.57-1.34 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 138.4, 127.3, 123.5, 115.3, 115.1, 115.0, 114.7, 57.2, 55.7, 49.6, 39.9, 38.3, 33.5, 28.2, 25.4.

IR (film) 2936, 2860, 2250, 1640, 1608, 1585, 1512, 1259, 1185, 1031, 830 cm^{-1}.

HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{18}H_{21}ClN_2O$ 316.1342; found 316.1337.



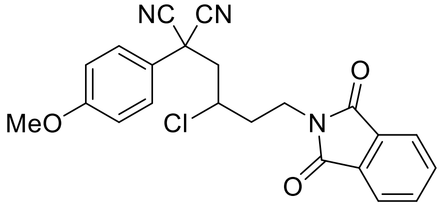
Ethyl 2-chloro-4,4-dicyano-4-(4-methoxyphenyl)butanoate **(3o)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), ethyl acrylate (53.2 µL, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (9% EtOAc/hexanes) provided **3o** (28.2 mg) in 46% yield as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 4.36 (t, J = 7.0 Hz, 1H), 4.25-4.18 (m, 2H), 3.85 (s, 3H), 3.04 (dd, J = 14.5, 6.5 Hz, 1H), 2.81 (dd, J = 15.0, 7.0 Hz, 1H), 1.31 (t, J = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 161.2, 127.5, 122.4, 115.4, 114.4, 114.0, 63.2, 55.7, 51.7, 45.7, 39.5, 14.0.

IR (film) 2983, 2842, 2250, 1744, 1609, 1512, 1260, 1186, 1028, 832 cm^{-1}.

HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{15}H_{15}ClN_2O_3$ 306.0771; found 306.0775.



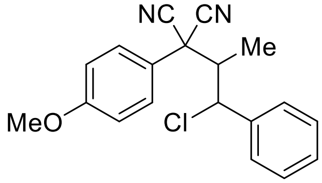
2*-(2-Chloro-4-(1,3-dioxoisoindolin-2-yl)butyl)-2-(4-methoxyphenyl)malononitrile* **(3p)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), 2-(but-3-en-1-yl)isoindoline-1,3-dione (50.3 mg, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (10% EtOAc/hexanes) provided **3p** (53.6 mg) in 66% yield as a yellow oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.01-3.96 (m, 1H), 3.91 – 3.69 (m, 5H), 2.75 (dd, *J* = 14.9, 9.3 Hz, 1H), 2.63 (dd, *J* = 14.9, 3.8 Hz, 1H), 2.24-2.07 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 168.2, 160.9, 134.3, 132.0, 127.4, 123.5, 123.1, 115.3, 115.0, 114.4, 55.6, 54.3, 48.9, 39.7, 36.9, 34.9.

IR (film) 3050, 2850, 2300, 1773, 1711, 1609, 1511, 1468, 1442, 1396, 1379, 1305, 1263, 1186, 1121, 1031 cm^{-1}.

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{22}H_{18}ClN_3O_3Na$ 430.0934; found 430.0963.



2-(1-Chloro-1-phenylpropan-2-yl)-2-(4-methoxyphenyl)malononitrile **(3q)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), β-methylstyrene (64.8 μL, 0.5 mmol), abd $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 80 °C for 24 h.

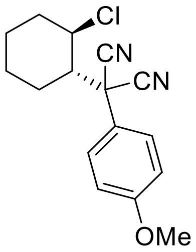
Chromatography (6% EtOAc/hexanes) provided **3q** (33.5 mg) in 51% yield (10:1 dr) as a colorless oil.

^{1}H NMR (600 MHz, CDCl$_3$) major diastereomer δ 7.60 (d, *J* = 8.9 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.24 (d, *J* = 6.9 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 4.95 (d, *J* = 2.5 Hz, 1H), 3.87 (s, 3H), 2.59 (qd, *J* = 6.7, 2.6 Hz, 1H), 1.34 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) major diastereomer δ 161.0, 138.6, 128.8, 128.7, 128.0, 127.1, 122.7, 115.3, 115.1, 113.8, 62.2, 55.7, 52.0, 46.4, 10.4; minor diastereomer δ 160.9, 136.4, 129.7, 128.8, 128.1,127.1, 122.9, 115.14,115.06, 114.8, 62.6, 56.1, 51.2, 45.5, 11.7

IR (film) 2950, 2850, 2250, 1608, 1585, 1511, 1451, 1386, 1304, 1257, 1185, 1084, 1030, 1003 cm^{-1}.

HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{19}H_{18}ClN_2O$ 325.1108; found 325.1106.



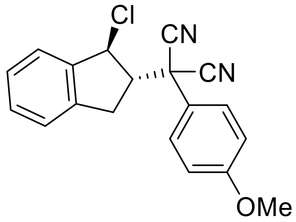
2-(2-Chlorocyclohexyl)-2-(4-methoxyphenyl)malononitrile **(3r)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), cyclohexene (50.6 µL, 0.5 mmol), and CuCl$_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 80 °C for 24 h. Chromatography (5% EtOAc/hexanes) provided **3r** (19.4 mg) in 34% yield (dr =10:3) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) major diastereomer δ 7.50 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.85 (m, 4H), 2.47 (t, *J* = 9.3 Hz, 1H), 2.30 (d, *J* = 13.0 Hz, 1H), 1.78 – 1.69 (m, 4H), 1.28 – 1.10 (m, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) major diastereomer δ 160.8, 128.3, 122.9, 116.0, 115.0, 114.3, 60.3, 55.6, 53.5, 45.5, 38.0, 28.8, 25.5, 24.9.

IR (film) 2940, 2863, 2250, 1608, 1511, 1449, 1301, 1257, 1220, 1185, 1030 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{16}H_{17}ClN_2O$ 288.1029; found 288.1014.



2-(1-Chloro-2,3-dihydro-1H-inden-2-yl)-2-(4-methoxyphenyl)malononitrile **(3s)** General procedure A was followed using 2-(4-methoxyphenyl)malononitrile (34.4 mg, 0.2 mmol), 1*H*-indene (34.4 µL, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 80 °C for 24 h. Chromatography (5% EtOAc/hexanes) followed by recrystallization (10% EtOAc/hexanes provided) **3s** (24.4 mg) in 38% (dr = 5:1) yield as a white crystalline solid.

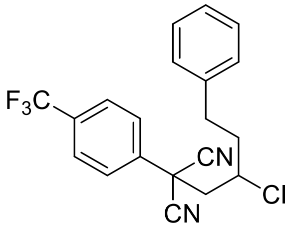
mp 108-110 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 4.7 Hz, 1H), 7.32 (dd, *J* = 5.7, 3.0 Hz, 2H), 7.21 (d, *J* = 4.7 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 2H), 5.42 (d, *J* = 6.1 Hz, 1H), 3.87 (s, 3H), 3.46 (q, *J* = 7.3, 6.1 Hz, 1H), 3.28 (dd, *J* = 16.4, 8.6 Hz, 1H), 3.09 (dd, *J* = 16.4, 7.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 140.7, 138.5, 129.8, 128.4, 127.9, 125.5, 124.7, 122.1, 115.3, 114.2, 113.9, 62.0, 59.3, 55.7, 44.6, 34.7.

IR (film) 2950, 2850, 2250, 1608, 1585, 1510, 1462, 1442, 1421, 1303, 1256, 1230, 1207, 1184, 1028, cm^{-1}.

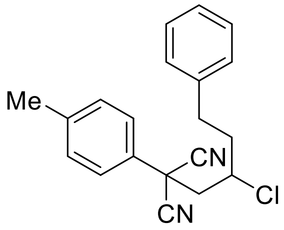
HRMS (EI-TOF) *m/z*: $[M]^+$ calcd for $C_{19}H_{15}ClN_2O$ 322.0873; found 322.0876.



2-(2-Chloro-4-phenylbutyl)-2-(4-(trifluoromethyl)phenyl)malononitrile **(3t)** General procedure A was followed using 2-(4-trifluoromethylphenyl)malononitrile (42.0 mg, 0.2 mmol), but-3-en-1-ylbenzene (75.1 µL, 0.5 mmol), and $CuCl_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (7% EtOAc/hexanes) provided **3t** (69.3 mg) in 92% yield as yellow oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 6.9 Hz, 2H), 3.91-3.89 (m, 1H), 2.19-2.86 (m, 1H), 2.82 – 2.69 (m, 2H), 2.54 (dd, *J* = 14.9, 3.8 Hz, 1H), 2.14-2.05 (m, 1H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 139.7, 135.4, 132.7 (q, $2J_{C\text{-}F}$ = 33.3 Hz), 128.8 (2C), 128.50, 127.1 (q, $1J_{C\text{-}F}$ = 3.7 Hz), 126.6, 123.4 (q, $3J_{C\text{-}F}$ = 272.6 Hz) 114.2, 113.8, 56.1, 49.2, 40.2, 40.0, 32.0.
^{19}F NMR (565 MHz, CDCl$_3$) δ –63.0.
IR (film) 3029, 2932, 2249, 1619, 1325, 1171, 1070, 839 cm^{-1}.

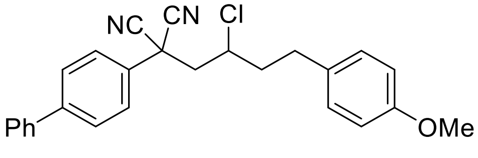
HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{20}H_{16}ClF_3N_2$ 376.0954; found 376.0967.



2-(2-Chloro-4-phenylbutyl)-2-(p-tolyl)malononitrile **(3u)** General procedure A was followed using 2-(4-methylphenyl)malononitrile (31.2 mg, 0.2 mmol), but-3-en-1-ylbenzene (75.1 µL, 0.5 mmol), and CuCl$_2$ (53.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (6% EtOAc/hexanes) provided **3u** (58.1 mg) in 90% yield as a yellow oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.07 – 3.85 (m, 1H), 2.87 (dt, *J* = 14.0, 7.1 Hz, 1H), 2.80 – 2.67 (m, 2H), 2.53 (d, *J* = 4.2 Hz, 1H), 2.40 (s, 3H), 2.07 (dt, *J* = 8.0, 6.6 Hz, 2H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 140.6, 140.0, 130.6, 128.7, 128.63, 128.55, 126.5, 125.8, 115.0, 114.5, 56.4, 49.5, 40.10, 40.05, 32.1, 21.2.
IR (film) 3028, 2925, 2250, 1603, 1511, 1236, 1194, 1031, 813, 750 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{20}H_{19}ClN_2$ 322.1237; found 322.1211.



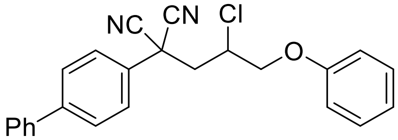
2-([1,1'-Biphenyl]-4-yl)-2-(2-chloro-4-(4-methoxyphenyl)butyl)malononitrile **(4a)** General procedure B was followed using 2-(2,3-dihydrobenzofuran-5-yl)malononitrile (36.8 mg, 0.2 mmol), 1-(but-3-en-1-yl)-4-methoxybenzene (75.1 μL, 0.5 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (10.7 mg, 0.04 mmol), and KCl (29.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C. Chromatography (5% EtOAc/hexanes) provided **4a** (56.3 mg) in 68% yield as an off white amorphous solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.64 – 7.56 (m, 4H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.35 – 3.84 (m, 1H), 3.74 (s, 3H), 2.85-2.79 (m, 2H), 2.74-2.69 (m, 1H), 2.58 (dd, *J* = 14.9, 4.1 Hz, 1H), 2.10 – 2.03 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 158.3, 143.3, 139.3, 131.9, 130.3, 129.5, 129.2, 128.6, 128.4, 127.3, 126.4, 114.9, 114.4, 114.1, 56.3, 55.3, 49.4, 40.2, 40.1, 31.2.

IR (film) 2930, 2250, 1611, 1464, 1409, 1300, 1076, 1007, 627, 559 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{26}H_{23}ClN_2O$ 414.1499; found 414.1491.

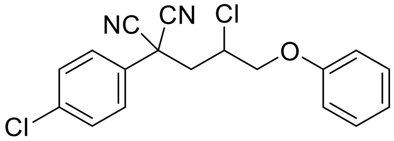


2-([1,1'-Biphenyl]-4-yl)-2-(2-chloro-3-phenoxypropyl)malononitrile **(4b)** General procedure B was followed using 2-([1,1'-biphenyl]-4-yl)malononitrile (43.6 mg, 0.2 mmol),(allyloxy)benzene (68.4 μL, 0.5 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (10.7 mg, 0.04 mmol), and KCl (29.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (5% EtOAc/hexanes) provided **4b** (43.2 mg) in 56% yield as a white amorphous solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.85 – 7.62 (m, 4H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.28 (dd, *J* = 17.0, 8.3 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 2H), 4.42 – 4.29 (m, 1H), 4.22 (dd, *J* = 10.0, 4.4 Hz, 1H), 4.08 (dd, *J* = 10.0, 7.3 Hz, 1H), 3.02 (dd, *J* = 15.0, 3.3 Hz, 1H), 2.85 (dd, *J* = 15.0, 9.3 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 157.6, 143.6, 139.4, 130.2, 129.8, 129.2, 128.7, 128.4, 127.3, 126.5, 122.1, 114.9, 114.8, 114.2, 70.6, 53.2, 46.2, 40.1.
IR (film) 3033, 2926, 2250, 1816, 1588, 1466, 1408, 1290, 1173, 1044, 1008, 884, 730 cm^{-1}.

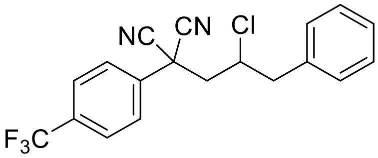
HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{24}H_{19}ClN_2O$ 386.1186; found 386.1194.



***2-(2-Chloro-3-phenoxypropyl)-2-(4-chlorophenyl)malononitrile* (4c)** General procedure B was followed using 2-(4-chlorophenyl)malononitrile (35.3 mg, 0.2 mmol), (allyloxy)benzene (68.4 μL, 0.5 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (10.7 mg, 0.04 mmol), and KCl (29.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C. Chromatography (5% EtOAc/hexanes) provided **4c** (37.2 mg) in 54% yield as white amorphous solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.58 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 2H), 4.30 – 4.23 (m, 1H), 4.22 (dd, *J* = 9.9, 4.3 Hz, 1H), 4.05 (dd, *J* = 10.0, 7.5 Hz, 1H), 2.95 (dd, *J* = 15.0, 3.1 Hz, 1H), 2.78 (dd, *J* = 15.0, 9.4 Hz, 1H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 157.5, 136.9, 130.3, 130.1, 129.9, 127.5, 122.2, 114.8, 114.5, 113.9, 70.5, 53.0, 46.2, 39.9.
IR (film) 3030, 2950, 2250, 1588, 1468, 1291, 1154, 1078, 720, 649 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{18}H_{14}Cl_2N_2O$ 344.0483; found 344.0482.

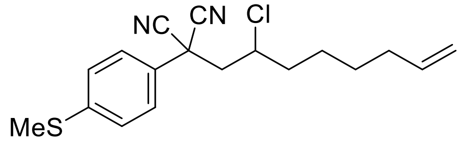


***2-(2-Chloro-3-phenylpropyl)-2-(4-(trifluoromethyl)phenyl)malononitrile* (4d)** General procedure B was followed using 2-(4-(trifluoromethyl)phenyl)malononitrile (42.0 mg, 0.2 mmol), allylbenzene (66.2 µL, 0.5 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (10.7 mg, 0.04 mmol), and KCl (29.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C. Chromatography (5% EtOAc/hexanes) provided **4d** (38.3 mg) in 53% yield as a yellow oil:

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.74 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 7.43 – 7.26 (m, 3H), 7.12 (d, J = 6.2 Hz, 2H), 4.33 – 4.04 (m, 1H), 3.17 (dd, J = 14.2, 6.7 Hz, 1H), 3.05 (dd, J = 14.2, 7.5 Hz, 1H), 2.72 (dd, J = 15.0, 9.8 Hz, 1H), 2.56 (dd, J = 15.0, 2.7 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 135.6, 135.5, 132.8 (q, $2J_{CF}$ = 33.3 Hz), 129.4, 129.1, 127.8, 127.1 (q, $3J_{CF}$ = 3.7 Hz), 126.7, 123.4 (q, $1J_{CF}$ = 272.7 Hz), 114.3, 113.6, 56.6, 48.0, 45.0, 40.3.
^{19}F NMR (565 MHz, CDCl$_3$) δ –63.02.
IR (film) 2910, 2250 1712, 1455, 1324, 1267, 1222, 1031, 910, 643, 569 cm^{-1}.

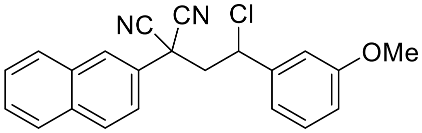
HRMS (ESI-TOF) *m/z*: [M -H]$^+$ calcd for $C_{19}H_{13}ClF_3N_2$ 361.0719; found 361.0722.



2-(2-Chlorooct-7-en-1-yl)-2-(4-(methylthio)phenyl)malononitrile **(4e)** General procedure B was followed using 2-(4-(methylthio)phenyl)malononitrile (37.6 mg, 0.2 mmol), octa-1,7-diene (73.8 µL, 0.5 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (10.7 mg, 0.04 mmol), and KCl (29.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C. Chromatography (5% EtOAc/hexanes) provided **4e** (37.8 mg) in 57% yield as a yellow oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.50 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 5.77 (m, 1H), 5.01 – 4.95 (m, 2H), 4.01-3.97 (m, 1H), δ 2.71 (dd, J = 14.8, 9.0 Hz, 1H), 2.52-2.48 (m, 4H), 2.05 (q, J = 7.1 Hz, 2H), 1.80-1.75 (m, 2H), 1.56-1.50 (m, 1H), 1.47 – 1.34 (m, 3H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 142.4, 138.4, 127.9, 127.0, 126.3, 115.0, 114.8, 114.4, 57.1, 49.5, 40.1, 38.3, 33.5, 28.2, 25.4, 15.3.
IR (film) 2923, 2854, 2250, 1639, 1596, 1461, 1405, 1266, 1233, 1014, 994, 719 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{18}H_{21}ClN_2S$ 332.1114; found 332.1105.



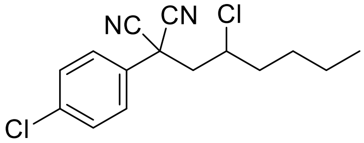
2-(2-Chloro-2-(3-methoxyphenyl)ethyl)-2-(naphthalen-2-yl)malononitrile **(4f)** General procedure B was followed using 2-(naphthalen-2-yl)malononitrile (38.4 mg, 0.2 mmol), 1-methoxy-3-vinylbenzene (69.2 μL, 0.5 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (10.7 mg, 0.04 mmol), and KCl (29.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C. Chromatography (5% EtOAc/hexanes) provided **4f** (46.8 mg) in 65% yield as a yellow oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.04 (d, *J* = 2.1 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 1H), 7.91-7.89 (m, 2H), 7.64 – 7.57 (m, 2H), 7.55 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 2.2 Hz, 1H), 6.83 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.01 (t, *J* = 7.1 Hz, 1H), 3.76 (s, 3H), 3.13 (dd, *J* = 14.7, 7.6 Hz, 1H), 2.95 (dd, *J* = 14.7, 6.7 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 160.1, 140.0, 133.5, 133.0, 130.4, 130.3, 128.5, 128.5, 128.1, 127.9, 127.8, 126.1, 122.1, 119.6, 115.1, 114.5, 113.9, 113.1, 58.0, 55.5, 50.3, 40.7.

IR (film) 2923, 2250, 1600, 1588, 1456, 1320, 1158, 894, 600 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{22}H_{17}ClN_2O$ 360.1029; found 360.1017.



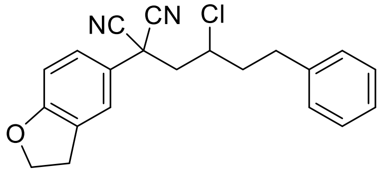
2-(2-Chlorohexyl)-2-(4-chlorophenyl)malononitrile **(4g)** General procedure B was followed using 2-(4-chlorophenyl)malononitrile (35.3 mg, 0.2 mmol), hex-1-ene (62.8 μL, 0.5 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (10.7 mg, 0.04 mmol), and KCl (29.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C. Chromatography (5% EtOAc/hexanes) provided **4g** (31.3 mg) in 53% yield as a yellow oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.56 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 4.02-3.98 (m, 1H), 2.71 (dd, *J* = 14.9, 9.3 Hz, 1H), 2.50 (dd, *J* = 14.8, 3.7 Hz, 1H), 1.80 – 1.76 (m, 2H), 1.53-1.46 (m, 1H), 1.42 – 1.29 (m, 3H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 136.8, 130.5, 130.3, 127.4, 114.5, 114.1, 57.2, 49.5, 40.1, 38.2, 28.0, 22.1, 13.9.

IR (film) 2958, 2930, 2863, 2250, 1595, 1466, 1434, 1380, 1322, 1232, 717, 683, 514 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{15}H_{16}Cl_2N_2$ 294.0691; found 294.0703.



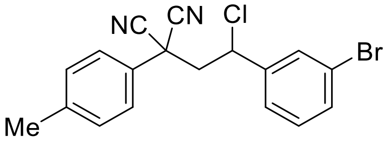
2-(2-Chloro-4-phenylbutyl)-2-(2,3-dihydrobenzofuran-5-yl)malononitrile **(4h)** General procedure B was followed using 2-(2,3-dihydrobenzofuran-5-yl)malononitrile (36.8 mg, 0.2 mmol), but-3-en-1-ylbenzene (75.1 µL, 0.5 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (10.7 mg, 0.04 mmol) and KCl (29.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C for 24 h. Chromatography (10% EtOAc/hexanes) provided **4h** (29.4 mg) in 42% yield as a yellow oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.34 (s, 1H), 7.30 – 7.24 (m, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 4.64 (t, *J* = 8.7 Hz, 2H), 4.13 – 3.79 (m, 1H), 3.24 (t, *J* = 8.7 Hz, 2H), 2.87 (dt, *J* = 14.0, 7.1 Hz, 1H), 2.79-2.65 (m, 2H), 2.50 (dd, *J* = 14.8, 4.1 Hz, 1H), 2.24 – 1.97 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 161.7, 140.0, 129.4, 128.7, 128.6, 126.5, 126.3, 123.1, 122.7, 115.2, 114.7, 110.4, 72.1, 56.4, 49.7, 40.1, 39.9, 32.1, 29.6.

IR (film) 2920, 2853, 2250, 1615, 1454, 1439, 1365, 1297, 1030, 884, 570 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{21}H_{19}ClN_2O$ 350.1186; found 350.1172.



2-(2-(3-Bromophenyl)-2-chloroethyl)-2-(p-tolyl)malononitrile **(4i)** General procedure B was followed using 2-(p-tolyl)malononitrile (31.2 mg, 0.2 mmol), 1-bromo-3-vinylbenzene (65.0 µL, 0.5 mmol), Cu(OTf)$_2$ (10.8 mg, 0.03 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (10.7 mg, 0.04 mmol), and KCl (29.8 mg, 0.4 mmol) in acetonitrile (1.0 mL) at 100 °C. Chromatography (5% EtOAc/hexanes) provided **4i** (52.2 mg) in 70% yield as a yellow oil

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.52 – 7.47 (m, 2H), 7.43 (d, J = 8.3 Hz, 2H), 7.35 – 7.21 (m, 4H), 4.95 (t, J = 7.6 Hz, 1H), 3.04 (dd, J = 14.7, 7.7 Hz, 1H), 2.83 (dd, J = 14.7, 6.6 Hz, 1H), 2.40 (s, 3H).

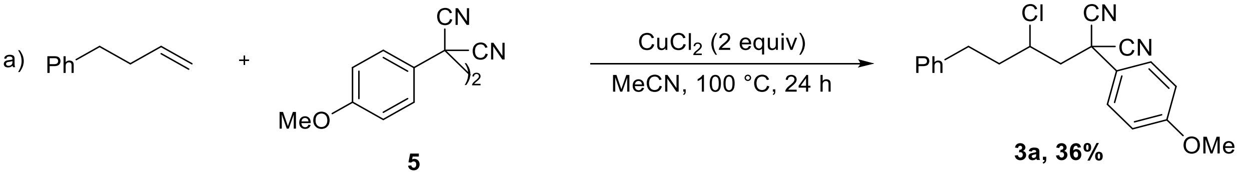
^{13}C NMR (151 MHz, CDCl$_3$) δ 140.8, 132.7, 130.74, 130.67, 130.4, 128.3, 126.1, 125.8, 123.2, 114.5, 113.8, 57.0, 50.3, 40.1, 21.2.

IR (film) 2924, 2250, 1687, 1571, 1511, 1476, 1195, 1043, 878, 756, 586 cm^{-1}.

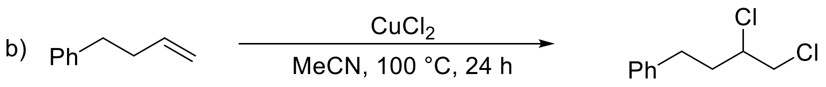
HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{18}H_{14}BrClN_2$ 372.0029; found 372.0033.

3. Mechanistic Study

General Procedure for the Control Experiments



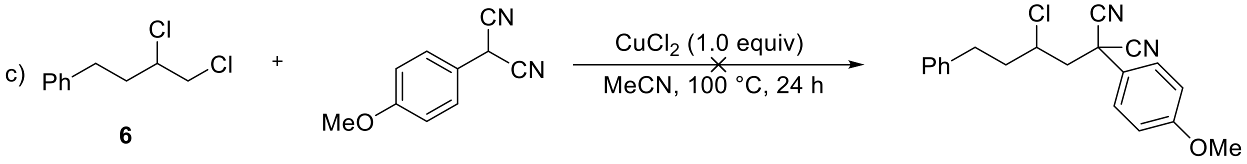
A flame dried 8 mL microwave vial equipped with a stirbar was charged with dimer **5** (17.1 mg, 0.05 mmol) and the vial was brought into a glovebox where CuCl$_2$ (26.8 mg, 0.2 mmol) was added. The vial was capped with a rubber septum and removed from the glovebox. Under an argon atmosphere, but-3-en-1-ylbenzene (37.5 µL, 0.25 mmol) and freshly distilled acetonitrile (0.5 ml, 0.2 M) were added to the vial. The vial was then carefully sealed with a Teflon cap using a crimper and placed in a heating block preheated at 100 °C with stirring. After 24 h, the reaction vial was removed from the heating block and allowed to cool to room temperature. The reaction mixture was diluted with EtOAc (3 mL) followed by water (2 mL). The layers were separated, and the organic layer was transferred to another flask. The aqueous layer was extracted with EtOAc (2x 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The resultant material was analyzed by ^{1}H-NMR spectroscopy with CH_2Br_2 (7µL) as internal standard.



6, 34%

A flame dried 8 mL microwave equipped with a stirbar was brought into a glovebox where $CuCl_2$ (53.6 mg, 0.4 mmol) was added. The vial was capped with a rubber septum and removed from the glovebox. Under an argon atmosphere, but-3-en-1-ylbenzene (75.1 µL, 0.5 mmol) and freshly distilled acetonitrile (1 mL, 0.2 M) were added to the vial. The vial was then carefully sealed with a Teflon cap using a crimper and placed in a heating block preheated at 100 °C with stirring. After 24 h, the reaction vial was removed from the heating block and allowed to cool to room temperature. The reaction mixture was diluted with EtOAc (5 mL) followed by water (3 mL). The layers were separated, and the organic layer was transferred to another flask. The aqueous layer was extracted with EtOAc (2x 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography with 5 % EtOAc/hexanes to obtain the product **6** (27.4 mg, 34% yield) as a yellow oil. The spectral data were in accordance with those in the literature.[6]

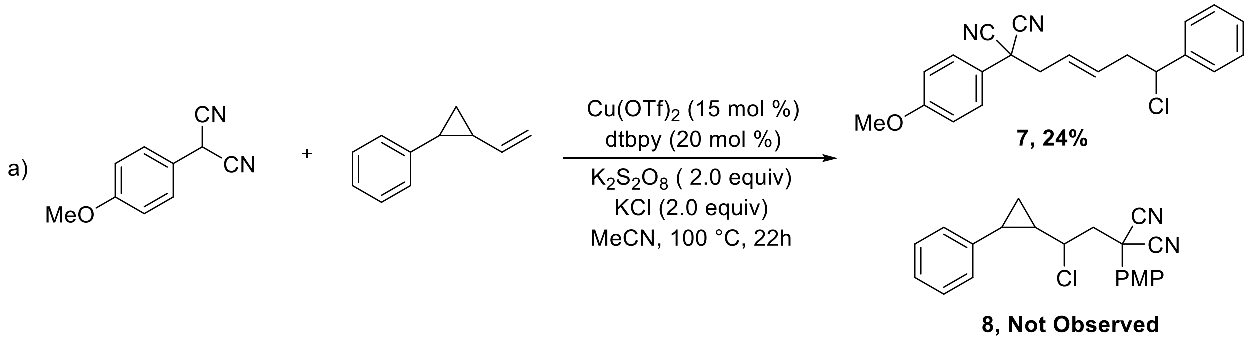
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.24-7.21 (m, 3H), 4.19 – 3.89 (m, 1H), 3.78 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.67 (dd, *J* = 11.3, 7.4 Hz, 1H), 2.95-2.90 (m, 1H), 2.78-2.74 (m, 1H), 2.50 – 2.20 (m, 1H), 2.07-2.00 (m, 1H).



6

A flame dried 8 mL microwave vial equipped with a stirbar was charged with 2-(4-methoxyphenyl) malononitrile (17.2 mg, 0.1 mmol) and the vial was brought into a glovebox where $CuCl_2$ (13.4 mg, 0.1 mmol) was added. The vial was capped with a rubber septum and removed from the glovebox. Under an argon atmosphere, compound **6** (20.2 mg, 0.1 mmol) and freshly distilled acetonitrile (0.5 mL, 0.2 M) were added into the vial. The vial was then carefully sealed with a Teflon cap with a crimper and placed in a heating block preheated at 100 °C with stirring. After 24 h, the reaction vial was removed from the heating block and allowed to cool to room temperature. The reaction mixture was diluted with EtOAc (3 mL) followed by water (2 mL). The layers were separated, and the organic layer was transferred to another flask. The aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The resultant material was analyzed by ^1H NMR spectroscopy with CH_2Br_2 (7μL) as internal standard.

General Procedure for the Radical Probe experiment



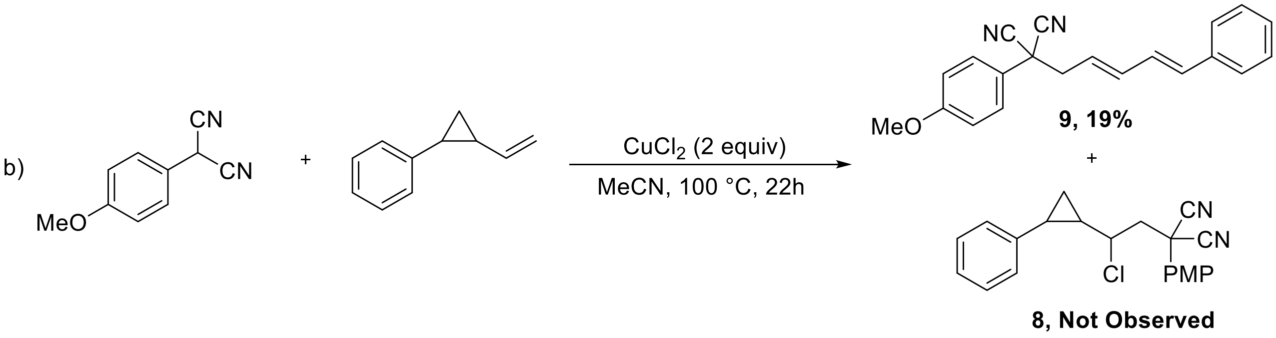
A flame dried 8 mL microwave vial equipped with a stirbar was charged with 2-(4-methoxyphenyl) malononitrile (34.4 mg, 0.2 mmol) and $K_2S_2O_8$ (0.4 mmol, 108 mg) and the vial was brought into a glovebox where $Cu(OTf)_2$ (10.8 mg, 0.03 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (10.7 mg, 0.04 mmol), and KCl (29.8 mg, 0.4 mmol) were added. The vial was capped with a rubber septum and removed from the glovebox. Under an argon atmosphere, (2-vinylcyclopropyl)benzene (36 mg, 0.5 mmol) and freshly distilled acetonitrile (1 mL, 0.2 M) were added to the vial. The vial was then carefully sealed with a Teflon cap using a crimper and placed in a heating block preheated at 100 °C with stirring. After 24 h, the reaction vial was removed from the heating block and allowed to cool to room temperature. The reaction mixture was diluted with EtOAc (5 mL) followed by water (3 mL). The layers were separated and the organic layer was transferred to another flask. The aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The resultant matereial was purified by silica gel column chromatography (5% EtOAc/hexanes) to obtain **7** (17 mg, 24%) which was contaminated with **9** (~10%) as yellow oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40 (d, *J* = 8.9 Hz, 2H), 7.38 – 7.30 (m, 5H), 6.96 (d, *J* = 8.6 Hz, 2H), 5.70 (dt, *J* = 14.6, 7.0 Hz, 1H), 5.51 (dt, *J* = 15.3, 7.4 Hz, 1H), 4.84 (t, *J* = 7.1 Hz, 1H), 3.84 (s, 3H), 3.07 – 2.77 (m, 4H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 160.8, 140.9, 135.1, 128.9, 128.6, 127.4, 127.2, 124.0, 123.3, 115.1, 115.0, 114.9, 62.3, 55.7, 45.7, 43.0, 42.1.

IR (film) 2935, 2250, 1608, 1585, 1455, 1442, 1421, 1306, 972, 795, 761, 605 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{21}H_{19}ClN_2O$ 350.1186; found 350.1172.



A flame dried 8 mL microwave vial equipped with a stir-bar was charged with 2-(4-methoxyphenyl) malononitrile (34.4 mg, 0.2 mmol) and the vial was brought into a glovebox where $CuCl_2$ (53.6 mg, 0.4 mmol) was added. The vial was capped with a rubber septum and removed from the glovebox. Under an argon atmosphere, (2-vinylcyclopropyl) benzene (36 mg, 0.5 mmol) and freshly distilled acetonitrile (1 mL, 0.2 M) were added to the vial. The vial was then carefully sealed with a Teflon cap using a crimper and placed in a heating block preheated at 100 °C with stirring. After 24 h, the reaction vial was removed from the heating block and allowed to cool to room temperature. The mixture was diluted with EtOAc (5 mL) followed by water (3 mL). The layers were separated, and the organic layer was transferred to another flask. The aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The resultant residue was purified by silica gel column chromatography (5% EtOAc/hexanes) to yield **9** (12 mg, 19%) as off white amorphous solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, J = 8.9 Hz, 2H), 7.40 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.7 Hz, 2H), 7.28 – 7.13 (m, 1H), 6.99 (d, J = 8.9 Hz, 2H), 6.75 (ddd, J = 15.6, 10.4, 0.8 Hz, 1H), 6.59 (d, J = 15.7 Hz, 1H), 6.42 (ddd, J = 15.0, 10.5, 0.9 Hz, 1H), 5.88 – 5.61 (m, 1H), 3.85 (s, 3H), 3.01 (d, J = 7.6 Hz, 2H).

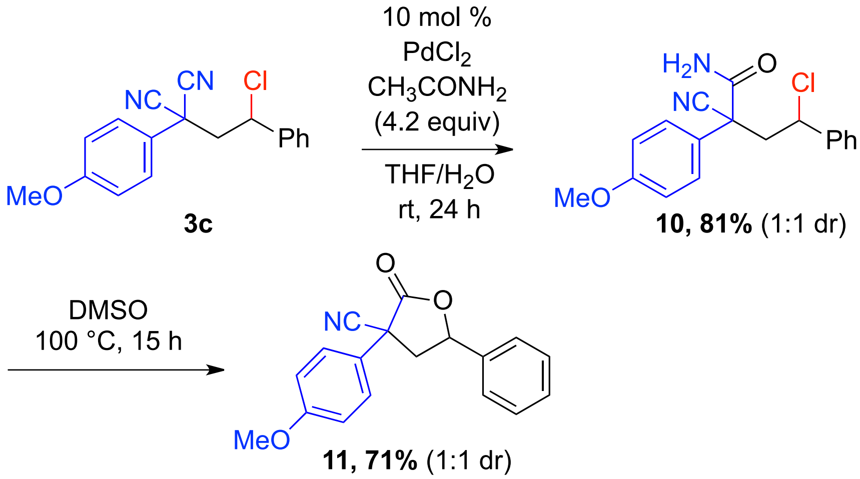
^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 138.4, 136.8, 134.7, 128.8, 128.2, 127.4, 127.4, 126.7, 123.3, 122.7, 115.09, 115.05, 55.6, 46.2, 42.3.

IR (film) 3025, 2250, 1607, 1584, 1463, 1421, 810, 795, 605, 530 cm^{-1}.

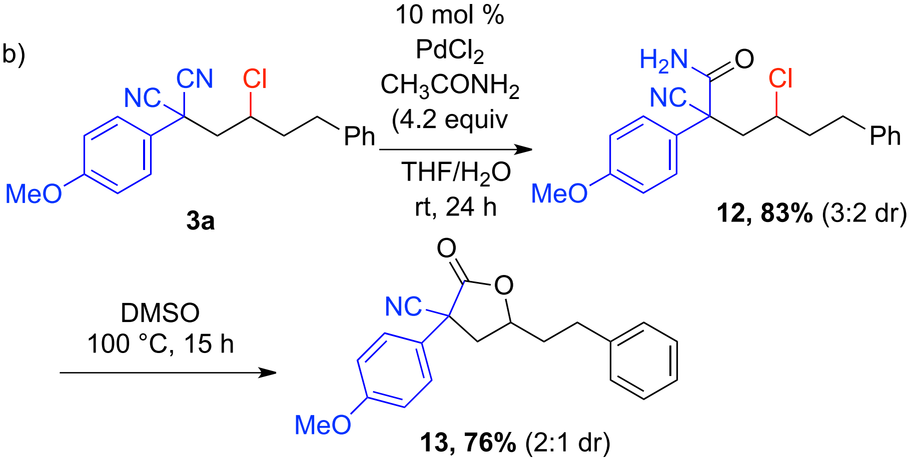
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{19}N_2O$ 315.1497; found 315.1501.

General procedure for the post-modification of alkene carbo-halogenation product

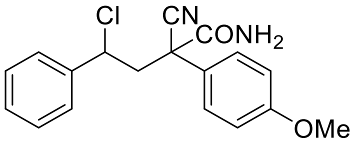
a)



b)



An oven dried 8 mL microwave vial equipped with a stir-bar was charged with $PdCl_2$ (6.8 mg, 0.04 mmol), **3a** or **3c** (0.2 mmol), and acetamide (49.6 mg, 0.84 mmol) followed by addition of 3:1 THF/H_2O (0.8 mL). Under argon, the vial was capped with a rubber septum and stirred at room temperature. After 24 h, the reaction mixture was diluted with water (3 mL) and extracted with EtOAc (3 x 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The resultant material was purified by silica-gel column chromatography (20% EtOAc/Hexanes).



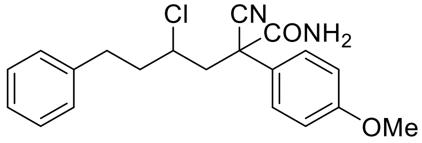
4-Chloro-2-cyano-2-(4-methoxyphenyl)-4-phenylbutanamide (10) Obtained as a white amorphous solid as a 1:1 mixture of diastereomers in 81% yield (53.1 mg).

^{1}H NMR (600 MHz, DMSO) δ 7.66 (s, 0.5H), 7.64 (s, 0.5H), 7.61 (s, 0.5H), 7.56 (s, 0.5H), 7.43 – 7.27 (m, 7H), 7.02 (d, *J* = 8.9 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 1H), 5.31 – 4.63 (m, 1H), 3.78 (s, 1.5H), 3.76 (s, 1.5H), 3.27 (dd, *J* = 14.9, 8.8 Hz, 0.5H), 3.17 – 3.01 (m, 1H), 2.87 (dd, *J* = 14.9, 5.4 Hz, 0.5H).

^{13}C NMR (151 MHz, DMSO) diastereomer 1 δ 167.6, 159.2, 140.5, 128.6, 128.6, 127.4, 127.3, 127.2, 119.1, 114.4, 60.2, 55.3, 51.6, 44.2 **diastereomer 2** δ 167.4, 159.3, 140.4, 128.8, 128.6, 127.5, 127.4, 127.3, 118.8, 114.3, 59.9, 55.3, 51.4, 44.6.

IR (film) 3300, 3250, 2900, 2850, 2250, 1702, 1613, 1456, 1344, 1265, 825, 684 cm^{-1}.

HRMS (ESI-TOF) *m/z*: [M + Na]$^{+}$ calcd for $C_{18}H_{17}ClN_{2}NaO_{2}$ 351.0876; found 351.0878.



4-chloro-2-cyano-2-(4-methoxyphenyl)-6-phenylhexanamide (12) Obtained as a white amorphous solid as a 3:2 mixture of diastereomers in 83% yield (59.1 mg).

^{1}H NMR (600 MHz, DMSO) δ 7.68 (s, 0.4H), 7.65 (s, 0.4H), 7.59 (s, 0.6H), 7.57 (s, 0.6H), 7.38 (m, 2H), 7.30 – 7.09 (m, 5H), 6.98 (d, *J* = 8.9 Hz, 2H), 4.00-3.96 (m, 0.40H), 3.84-3.80 (m, 0.60H), 3.77 (s, 3H), 2.90 – 2.59 (m, 4H), 2.24 – 1.89 (m, 2H).

^{13}C NMR (151 MHz, DMSO) δ Major diastereomer 167.8, 159.2, 140.5, 128.3, 128.3, 127.4, 127.3, 126.0, 119.6, 114.3, 59.4, 55.3, 51.5, 44.1, 43.1, 31.5. Minor diastereomer δ 167.6, 159.2, 140.5, 128.4, 128.3, 127.6, 127.3, 126.0, 119.6, 114.3, 59.3, 55.3, 51.5, 44.1, 43.1, 31.5.

IR (film) 3250, 3200, 2950, 2850, 2250, 1701, 1607, 1510, 1453, 1293, 1121, 615 cm^{-1}.

HRMS (ESI-TOF) *m/z*: [M - HCl]$^{+}$ calcd for $C_{20}H_{20}N_{2}O_{2}$ 320.1525; found 320.1536.

The purified hydrolyzed product was then dissolved in DMSO (1 mL) in a 8 mL microwave vial, sealed with Teflon cap with a crimper, and heated at 100 °C. After 15 h, the reaction mixture was allowed to cool to room temperature, diluted with water (10 mL) and extracted with EtOAc (2 x 3 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated.

3-(4-Methoxyphenyl)-2-oxo-5-phenyltetrahydrofuran-3-carbonitrile **11)** Obtained as a white amorphous solid (41.6 mg, 71% yield) that is a 1:1 mixture of diastereomers.

Diastereomer 1

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.62 – 7.33 (m, 7H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.82 (dd, *J* = 10.7, 5.3 Hz, 1H), 3.83 (s, 3H), 3.37 (dd, *J* = 13.5, 5.3 Hz, 1H), 2.72 (dd, *J* = 13.5, 10.7 Hz, 1H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 169.1, 160.4, 136.4, 129.6, 129.3, 128.2, 125.8, 124.6, 116.8, 114.9, 79.2, 55.6, 49.3, 46.4.

Diastereomer 2

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.47 (d, *J* = 7.1 Hz, 2H), 7.44 – 7.37 (m, 3H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 5.41 (dd, *J* = 10.5, 5.4 Hz, 1H), 3.85 (s, 3H), 3.19 (ddd, *J* = 13.4, 5.5, 1.5 Hz, 1H), 3.01 (ddd, *J* = 12.6, 10.6, 1.5 Hz, 1H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 169.6, 160.7, 136.3, 129.7, 129.3, 127.8, 125.9, 123.8, 117.9, 115.4, 79.5, 55.7, 49.0, 45.0.
IR (film) 2950, 2850, 2250, 1777, 1607, 1329, 1214, 940, 796, 742, 573 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{18}H_{15}NO_3$ 293.1052; found two components 293.1057 and 293.1033.

3-(4-Methoxyphenyl)-2-oxo-5-phenethyltetrahydrofuran-3-carbonitrile **(13)** Obtained as light-yellow oil (48.8 mg, 76%) that is a 1:2 mixture of diastereomers.

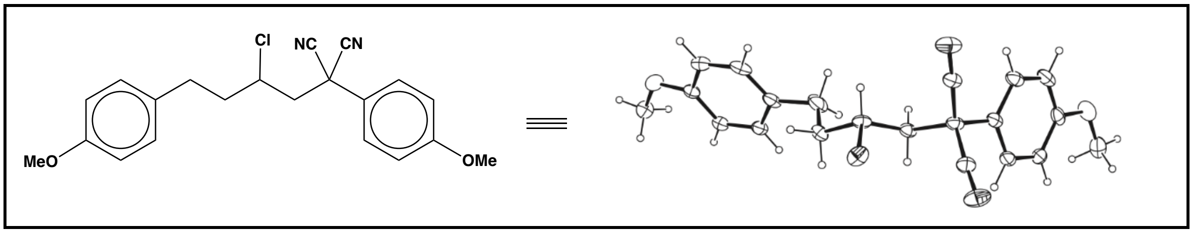
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40 (d, *J* = 8.8 Hz, 0.60H), 7.37 (d, *J* = 8.8 Hz, 1.40H), 7.34-7.30 (m, 2H), 7.28 – 7.15 (m, 3H), 6.96 (d, *J* = 8.4 Hz, 0.60H), 6.95 (d, *J* = 8.4 Hz, 1.40H), 4.80-4.76 (m, 0.30H), 4.49 – 4.45 (m, 0.60H), 3.82 (s, 0.90H), 3.82 (s, 2.10H), 3.06 (dd, *J* = 13.4, 5.3 Hz, 0.30H), 2.98 – 2.82 (m, 1.70H), 2.82– 2.72 (m, 1H), 2.69 (dd, *J* = 13.3, 9.7 Hz, 0.70H), 2.40 (dd, *J* = 13.4, 10.0 Hz, 0.30H), 2.25 – 2.10 (m, 1H), 2.09 – 1.95 (m, 1H).
^{13}C NMR (151 MHz, CDCl$_3$) Major diastereomer δ 169.8, 160.5, 140.1, 128.8, 128.5, 127.6, 126.6,124.1, 118.2, 115.2, 78.0, 55.5, 48.4, 42.4, 36.6, 31.6. Minor diastereomer δ 169.4, 160.3, 140.1, 128.8, 128.4, 128.03, 126.6, 125.0, 116.9,114.8, 77.8, 55.5, 48.8, 44.0, 36.5, 31.6.
IR (film) 2950, 2850, 2250, 1775, 1608, 1496, 1347, 1123, 918, 796 cm^{-1}.

HRMS (EI-TOF) *m/z*: [M]$^+$ calcd for $C_{20}H_{19}NO_3$ 321.1365; found 321.1378.

4. X-ray Structure Determination of Compound 3d

General Procedure

In a 20 mL 4-dram vial, compound **3d** or **3s** were dissolved in a limited amount of 10 % EtOAc/Hexanes solution. The vial was sealed with a white screw cap and placed in a freezer (-30 °C). After 24 h, crystals of the compounds were observed which was then analyzed by X-ray Crystallography.



Compound 3d, $C_{21}H_{21}ClN_2O_2$, crystallizes in the monoclinic space group $P2_1/n$ (systematic absences 0k0: k=odd and h0l: h+l=odd) with a=15.2765(7)Å, b=5.9467(3)Å, c=21.5897(9)Å, β=108.640(2)°, V=1858.43(15)Å^3, Z=4, and d_{calc}=1.318 g/cm$_3$. X-ray intensity data were collected on a Bruker D8QUEST [1] CMOS area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of twenty-four 0.5° rotation frames with exposures of 10 seconds. A total of 912 frames were collected with a crystal to detector distance of 33.0 mm, rotation widths of 0.5° and exposures of 20 seconds:

scan type	2θ	ω	φ	χ	Frames
ω	3.18	196.87	144.00	54.72	304
ω	3.18	196.87	216.00	54.72	304
ω	3.18	196.87	72.00	54.72	304

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and σ(F^2) values. A total of 28465 reflections were measured over the ranges $5.732 \leq 2\theta \leq 50.812°$, $-18 \leq h \leq 18$, $-7 \leq k \leq 7$, $-26 \leq l \leq 26$ yielding 3419 unique reflections (R_{int} = 0.0507). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.6737, 0.7452). The structure was solved by direct methods - ShelXT [4]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2018 [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2) + (0.0332P)^2 + 1.2712P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0465 and wR2=0.0978 for 3007 observed reflections for which $F > 4\sigma(F)$ and R1=0.0557 and wR2=0.1018 and GOF =1.148 for all 3419 unique, non-zero reflections and 264 variables. The maximum Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.22 and -0.28 e/Å^3.

Figure S1 illustrates the ORTEP at 50% thermal ellipsoids. Table S1 lists cell information, data collection parameters, and refinement data.

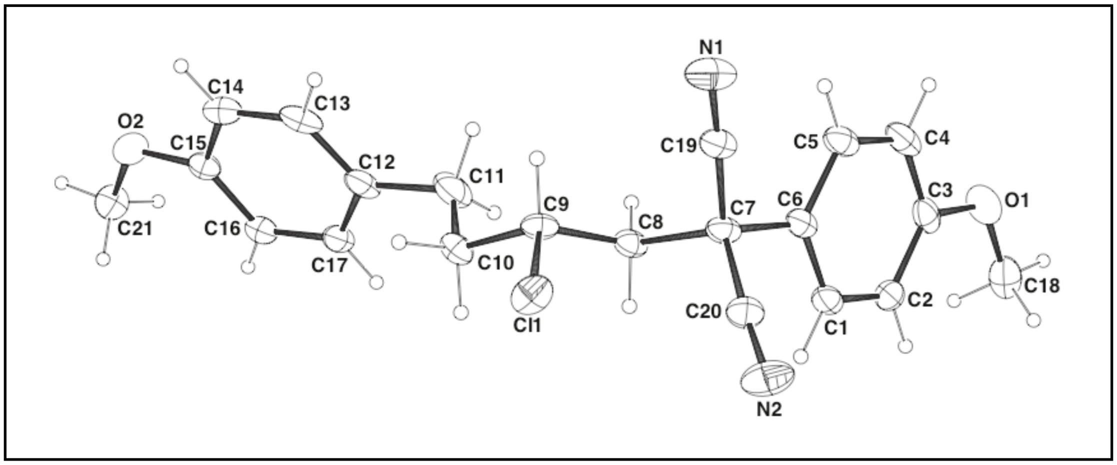


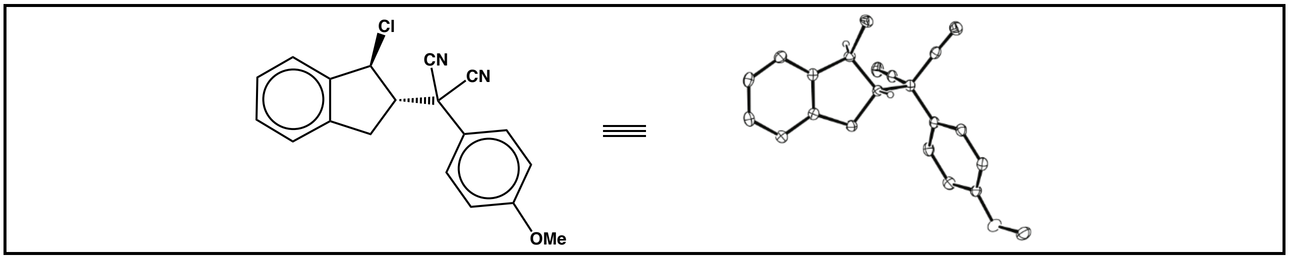
Figure S1. ORTEP drawing of the title compound with 50% thermal ellipsoids.

Table S1. Summary of Structure Determination of Compound 3d

Empirical formula	$C_{21}H_{21}ClN_2O_2$
Formula weight	368.85
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a	15.2765(7)Å
b	5.9467(3)Å
c	21.5897(9)Å
β	108.640(2)°
Volume	1858.43(15)Å^3
Z	4
d_{calc}	1.318 g/cm^3
μ	0.223 mm^{-1}
F(000)	776.0
Crystal size, mm	0.19 × 0.11 × 0.09
2θ range for data collection	5.732 - 50.812°
Index ranges	$-18 \leq h \leq 18$, $-7 \leq k \leq 7$, $-26 \leq l \leq 26$
Reflections collected	28465
Independent reflections	3419[R(int) = 0.0507]
Data/restraints/parameters	3419/12/264
Goodness-of-fit on F^2	1.148
Final R indexes [I>=2σ (I)]	$R_1 = 0.0465$, $wR_2 = 0.0978$
Final R indexes [all data]	$R_1 = 0.0557$, $wR_2 = 0.1018$
Largest diff. peak/hole	0.22/-0.28 eÅ^{-3}

This report has been created with Olex2 [6], compiled on 2018.05.29 svn.r3508 for OlexSys.

5. X-ray Structure Determination of Compound 3s



Compound **3s**, $C_{19}H_{15}ClN_2O$, crystallizes in the triclinic space group PT with a=7.7845(4)Å, b=8.6499(4)Å, c=12.8267(6)Å, α=94.616(2)°, β=105.960(2)°, γ=103.582(2)°, V=797.39(7)Å^3, Z=2, and d_{calc}=1.344 g/cm$_3$. X-ray intensity data were collected on a Bruker APEXII [1] CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 2670 frames were collected with a crystal to detector distance of 37.8 mm, rotation widths of 0.5° and exposures of 3 seconds:

scan type	2θ	ω	φ	χ	Frames
ω	19.34	15.47	306.00	-54.74	225
ω	19.34	15.47	204.00	-54.74	225
ω	19.34	15.47	102.00	-54.74	225
ω	19.34	15.47	0.00	-54.74	225
ω	19.34	15.47	255.00	-54.74	225
ω	19.34	15.47	51.00	-54.74	225
ω	19.34	15.47	153.00	-54.74	225
ϕ	19.34	10.15	0.00	-24.00	720
ϕ	19.34	15.45	360.00	-57.50	375

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 24019 reflections were measured over the ranges $3.344 \leq 2\theta \leq 55.06°$, $-10 \leq h \leq 9$, $-9 \leq k \leq 11$, $-16 \leq l \leq 15$ yielding 3665 unique reflections ($R_{int} = 0.0333$). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.7201, 0.7456). The structure was solved by direct methods - ShelXT [4]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2018 [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+(0.0364P)^2+0.4271P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0345 and wR2=0.0812 for 3094 observed reflections for which $F > 4\sigma(F)$ and R1=0.0439 and wR2=0.0858 and GOF =1.024 for all 3665 unique, non-zero reflections and 209 variables. The maximum Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.38 and -0.25 e/Å^3. Figure S2 shows the ORTEP at 50% thermal ellipsoids and Table S2 lists cell information, data collection parameters, and refinement data.

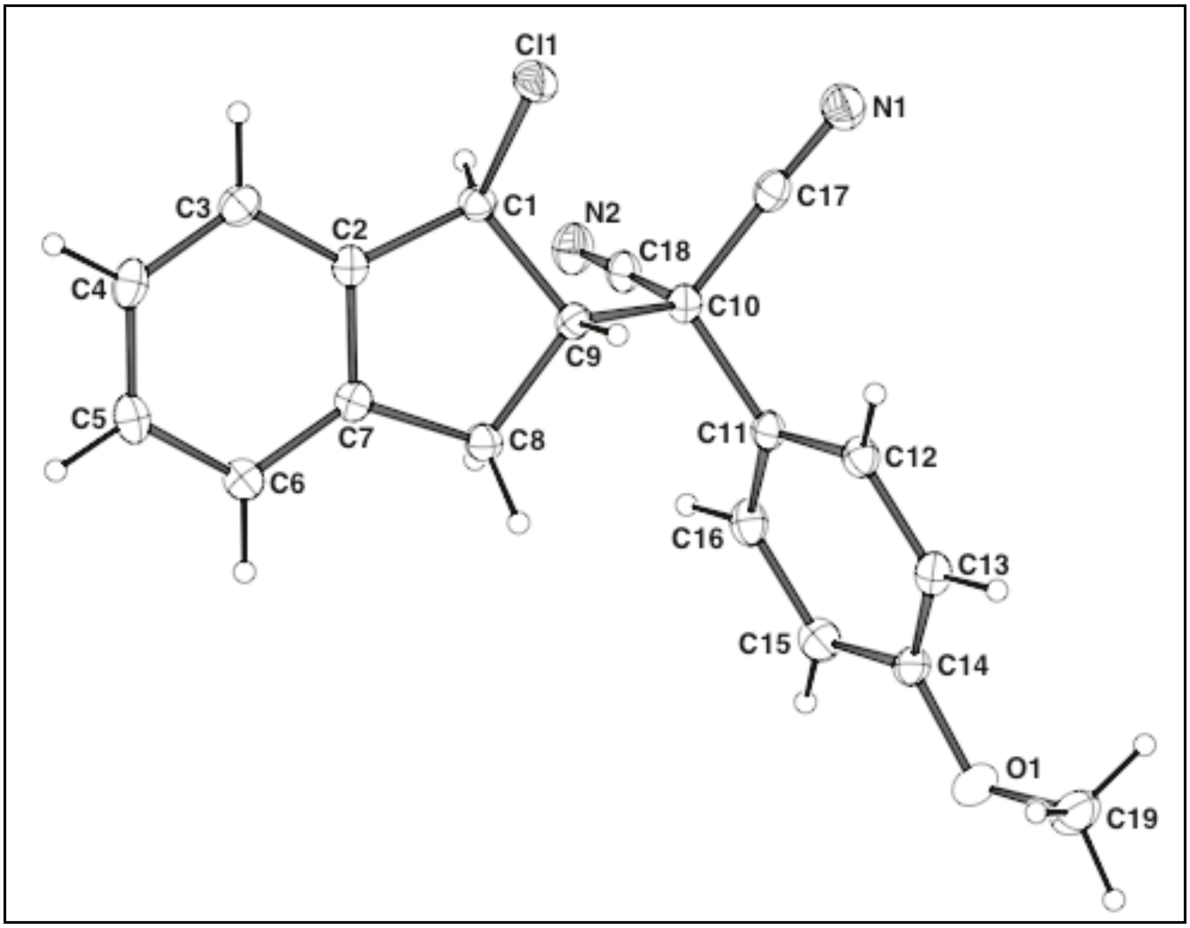


Figure S2. ORTEP drawing of the title compound with 50% thermal ellipsoids.

Table S2. Summary of Structure Determination of Compound 3s

Empirical formula	$C_{19}H_{15}ClN_2O$
Formula weight	322.78
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	7.7845(4)A
b	8.6499(4)A
c	12.8267(6)A
α	94.616(2)°
β	105.960(2)°
γ	103.582(2)°
Volume	797.39(7)A^3
Z	2
d_{calc}	1.344 g/cm^3
μ	0.245 mm^{-1}
F(000)	336.0
Crystal size, mm	0.22 × 0.12 × 0.06
2θ range for data collection	3.344 - 55.06°
Index ranges	$-10 \leq h \leq 9$, $-9 \leq k \leq 11$, $-16 \leq l \leq 15$
Reflections collected	24019
Independent reflections	3665[R(int) = 0.0333]
Data/restraints/parameters	3665/0/209
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	$R_1 = 0.0345$, $wR_2 = 0.0812$
Final R indexes [all data]	$R_1 = 0.0439$, $wR_2 = 0.0858$
Largest diff. peak/hole	0.38/-0.25 eA^{-3}

6. References

(1) Kohler, D. G.; Gockel, S. N.; Kennemur, J. L.; Waller, P. J.; Hull, K. L. Palladium-Catalysed Anti-Markovnikov Selective Oxidative Amination. *Nat. Chem.* **2018**, *10* (3), 333–340. https://doi.org/10.1038/nchem.2904.

(2) Peterson, J. P.; Winter, A. H. Solvent Effects on the Stability and Delocalization of Aryl Dicyanomethyl Radicals: The Captodative Effect Revisited. *J. Am. Chem. Soc.* **2019**, *141* (32), 12901–12906. https://doi.org/10.1021/jacs.9b06576.

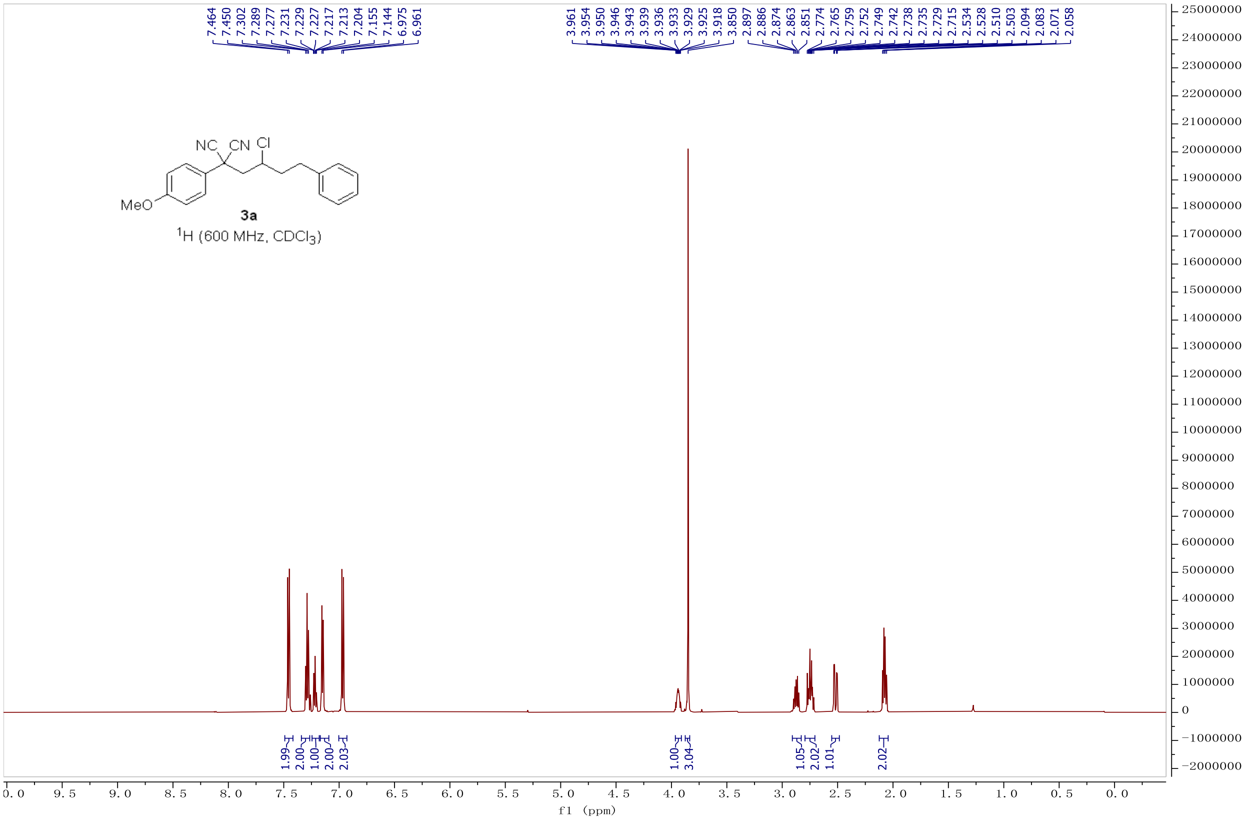
(3) Peterson, J. P.; Geraskina, M. R.; Zhang, R.; Winter, A. H. Effect of Substituents on the Bond Strength of Air-Stable Dicyanomethyl Radical Thermochromes. *J. Org. Chem.* **2017**, *82* (12), 6497–6501. https://doi.org/10.1021/acs.joc.7b01188.

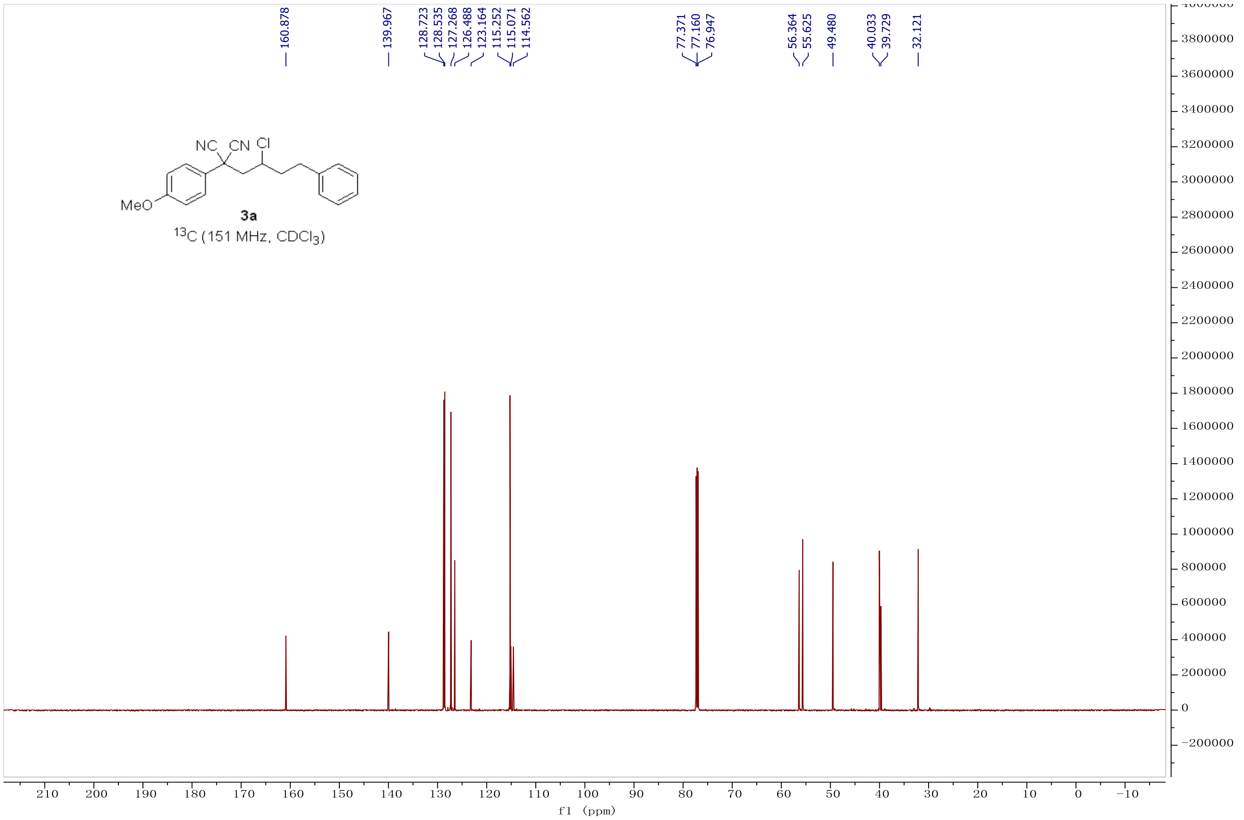
(4) Peterson, J. P.; Ellern, A.; Winter, A. H. Spin Delocalization, Polarization, and London Dispersion Forces Govern the Formation of Diradical Pimers. *J. Am. Chem. Soc.* **2020**, *142* (11), 5304–5313. https://doi.org/10.1021/jacs.0c00190.

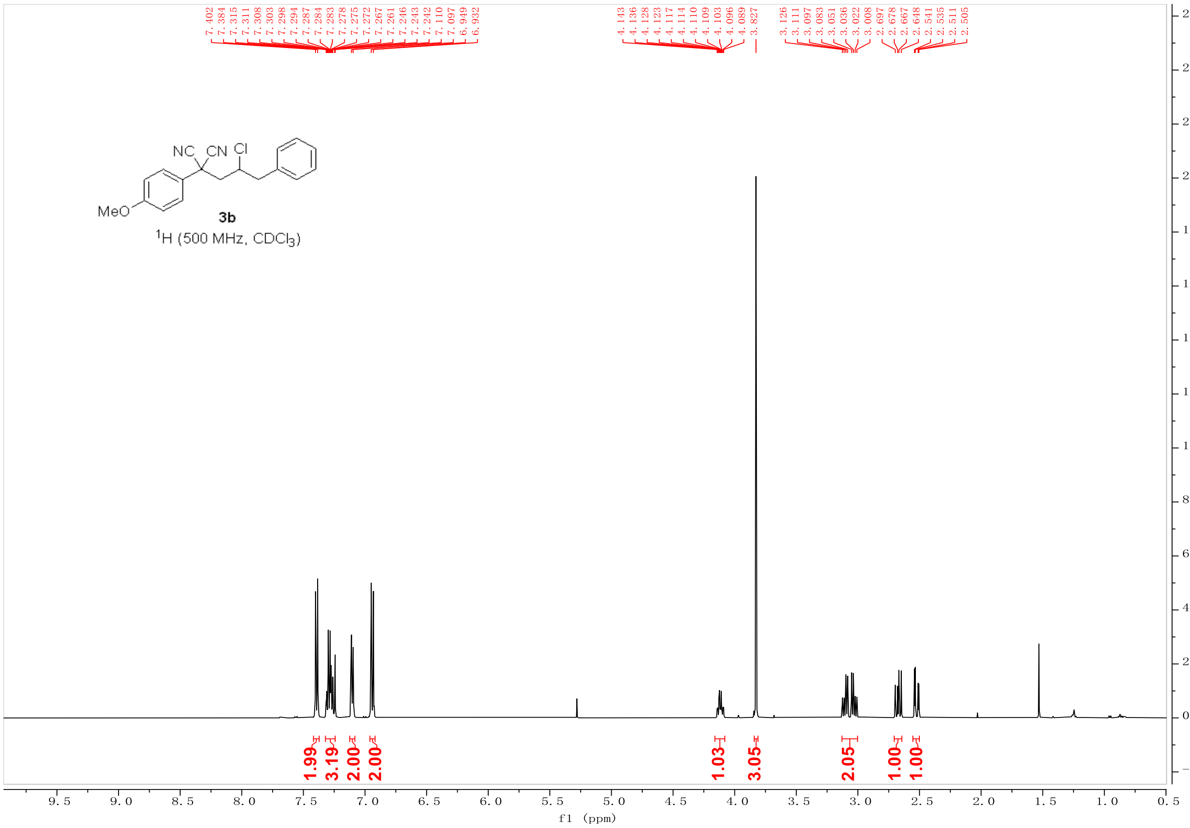
(5) Chen, X. M.; Ning, X. S.; Kang, Y. B. Aerobic Acetoxyhydroxylation of Alkenes Co-Catalyzed by Organic Nitrite and Palladium. *Org. Lett.* **2016**, *18* (20), 5368–5371. https://doi.org/10.1021/acs.orglett.6b02743.

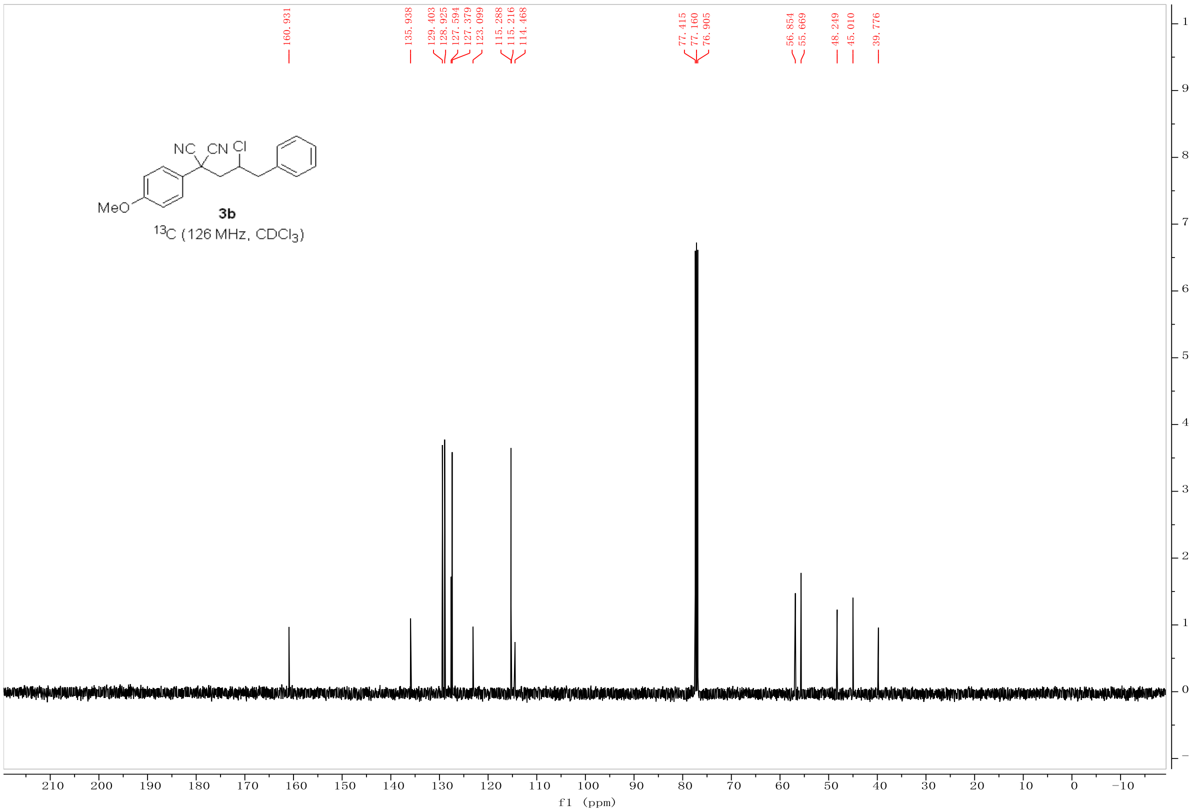
(6) Egami, H.; Yoneda, T.; Uku, M.; Ide, T.; Kawato, Y.; Hamashima, Y. Difunctionalization of Alkenes Using 1-Chloro-1,2-Benziodoxol-3-(1H)-One. *J. Org. Chem.* **2016**, *81* (10), 4020–4030. https://doi.org/10.1021/acs.joc.6b00295.

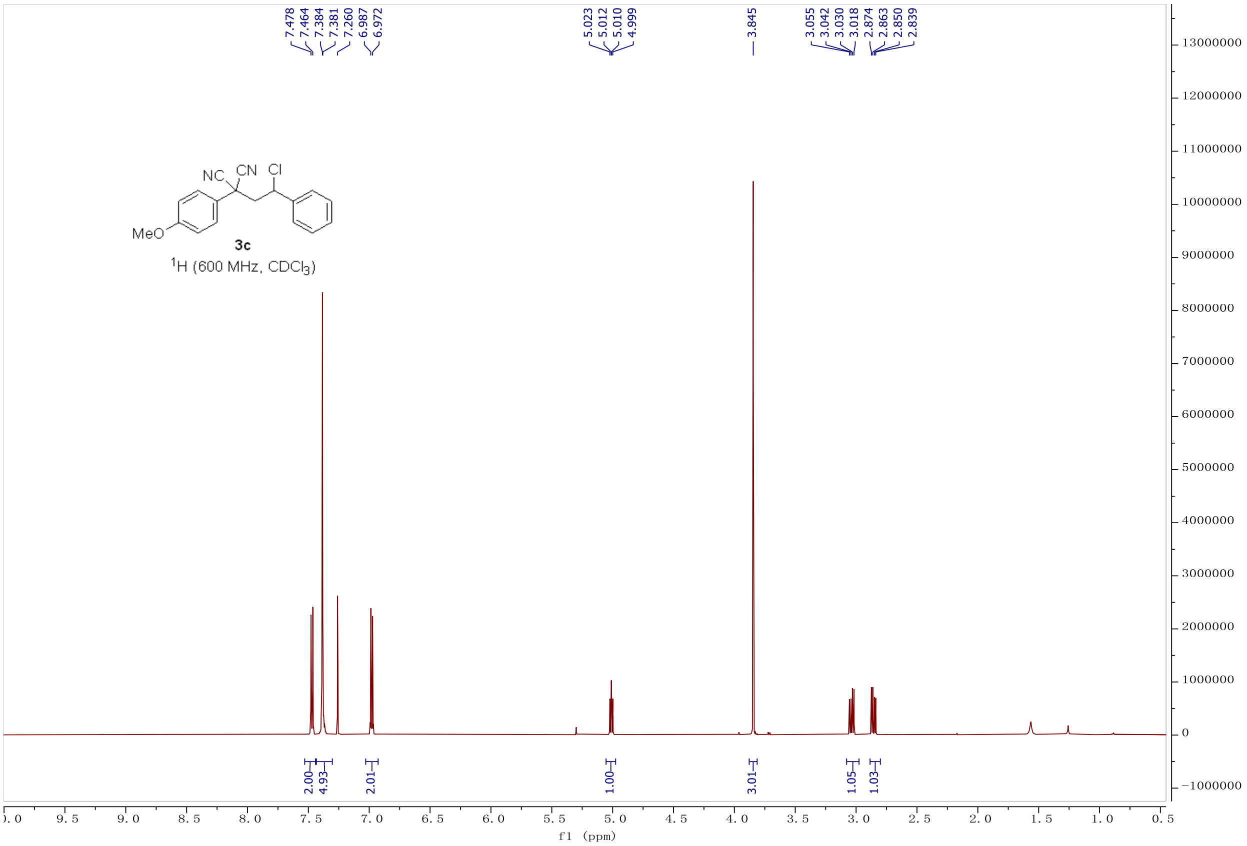
7. NMR Spectra

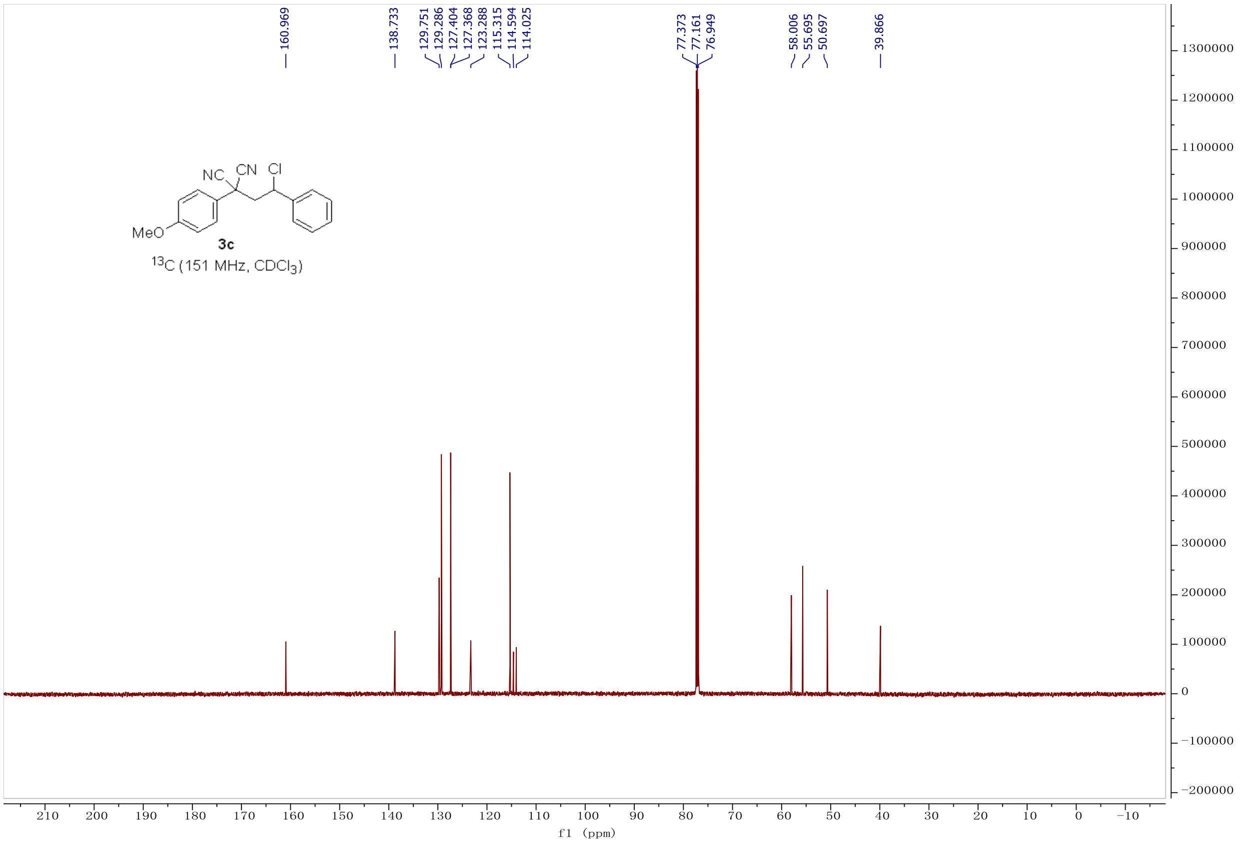


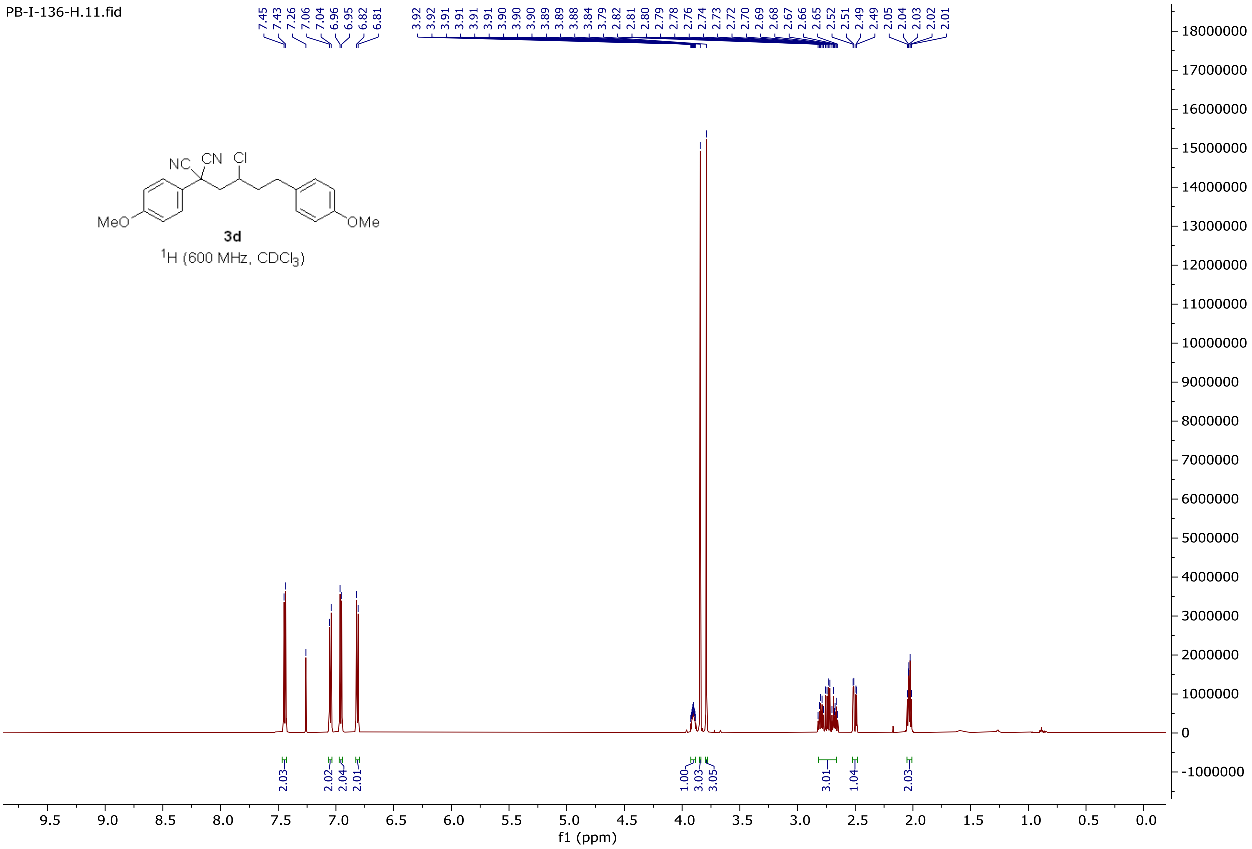


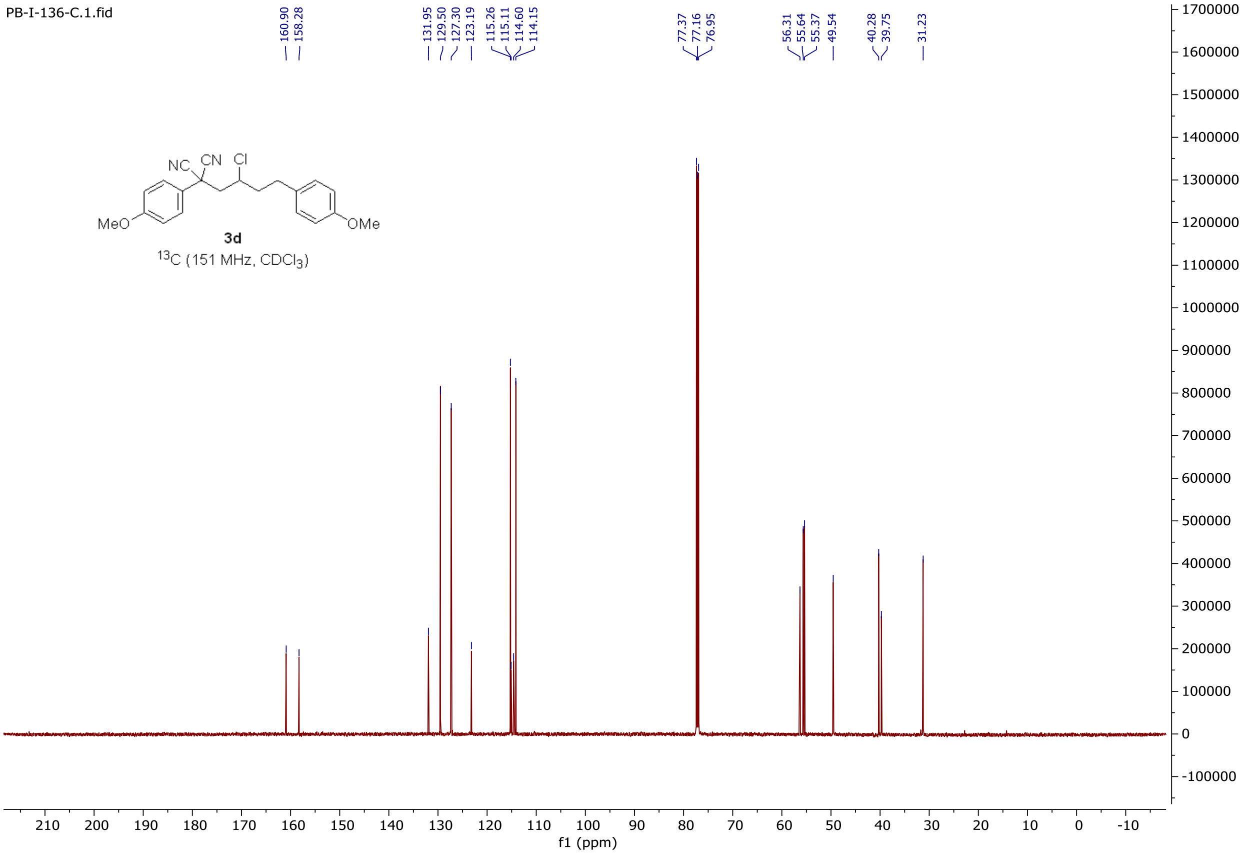

7.402
7.384
7.315
7.311
7.308
7.303
7.298
7.294
7.287
7.284
7.283
7.278
7.275
7.272
7.267
7.261
7.246
7.243
7.242
7.110
7.097
6.949
6.932
4.143
4.136
4.128
4.123
4.117
4.114
4.110
4.109
4.103
4.096
4.089
3.827
3.126
3.111
3.097
3.083
3.051
3.036
3.022
3.008
2.697
2.678
2.667
2.648
2.541
2.535
2.511
2.505
NC
CN
Cl
MeO
3b
^{1}H (500 MHz, CDCl$_3$)
1.99
3.19
2.00
2.00
1.03
3.05
2.05
1.00
1.00
f1 (ppm)

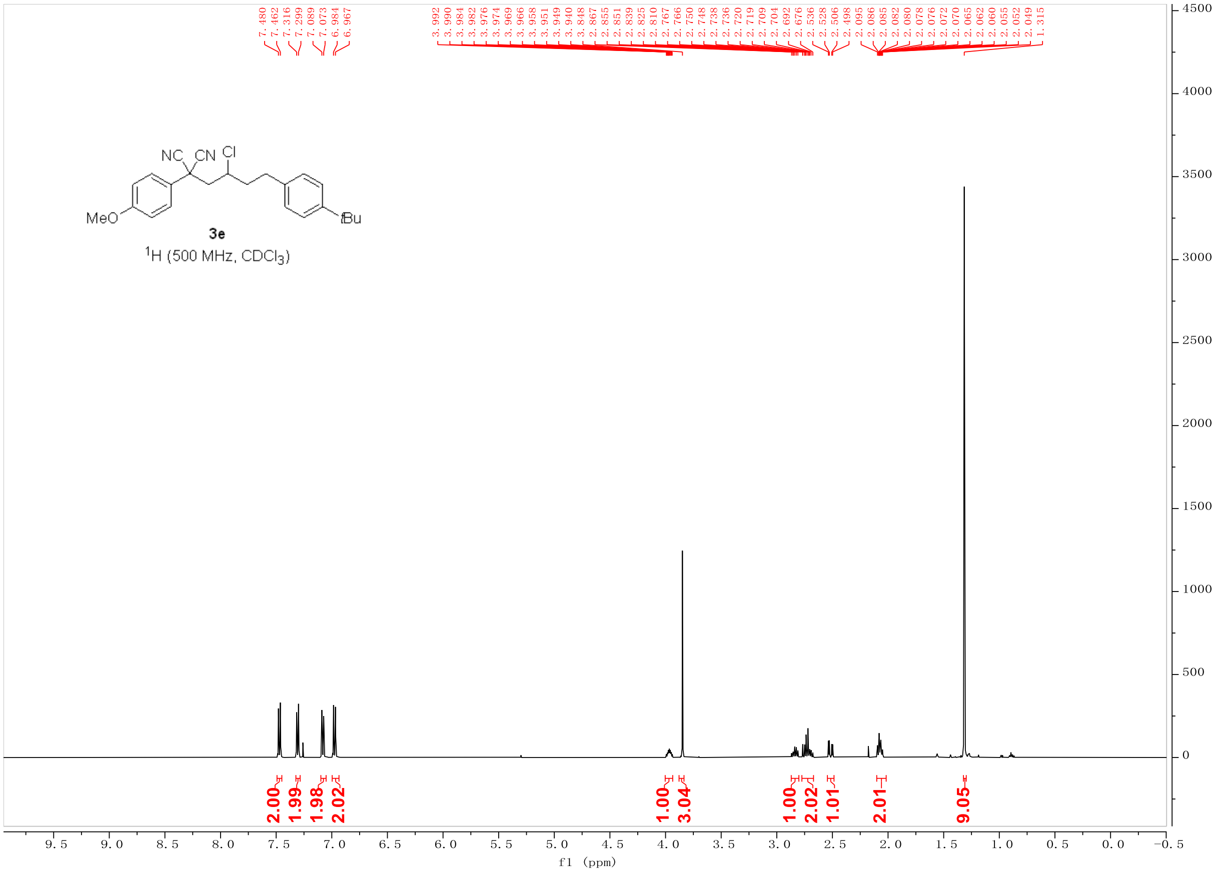

160.931
135.938
129.403
128.925
127.594
127.379
123.099
115.288
115.216
114.468
77.415
77.160
76.905
56.854
55.669
48.249
45.010
39.776
NC
CN
Cl
MeO
3b
^{13}C (126 MHz, CDCl$_3$)
f1 (ppm)


7.478
7.464
7.384
7.381
7.260
6.987
6.972
5.023
5.012
5.010
4.999
3.845
3.055
3.042
3.030
3.018
2.874
2.863
2.850
2.839
NC
CN
Cl
MeO
3c
^{1}H (600 MHz, CDCl$_3$)
2.00
4.93
2.01
1.00
3.01
1.05
1.03
f1 (ppm)


160.969
138.733
129.751
129.286
127.404
127.368
123.288
115.315
114.594
114.025
77.373
77.161
76.949
58.006
55.695
50.697
39.866
NC
CN
Cl
MeO
3c
^{13}C (151 MHz, CDCl$_3$)
f1 (ppm)

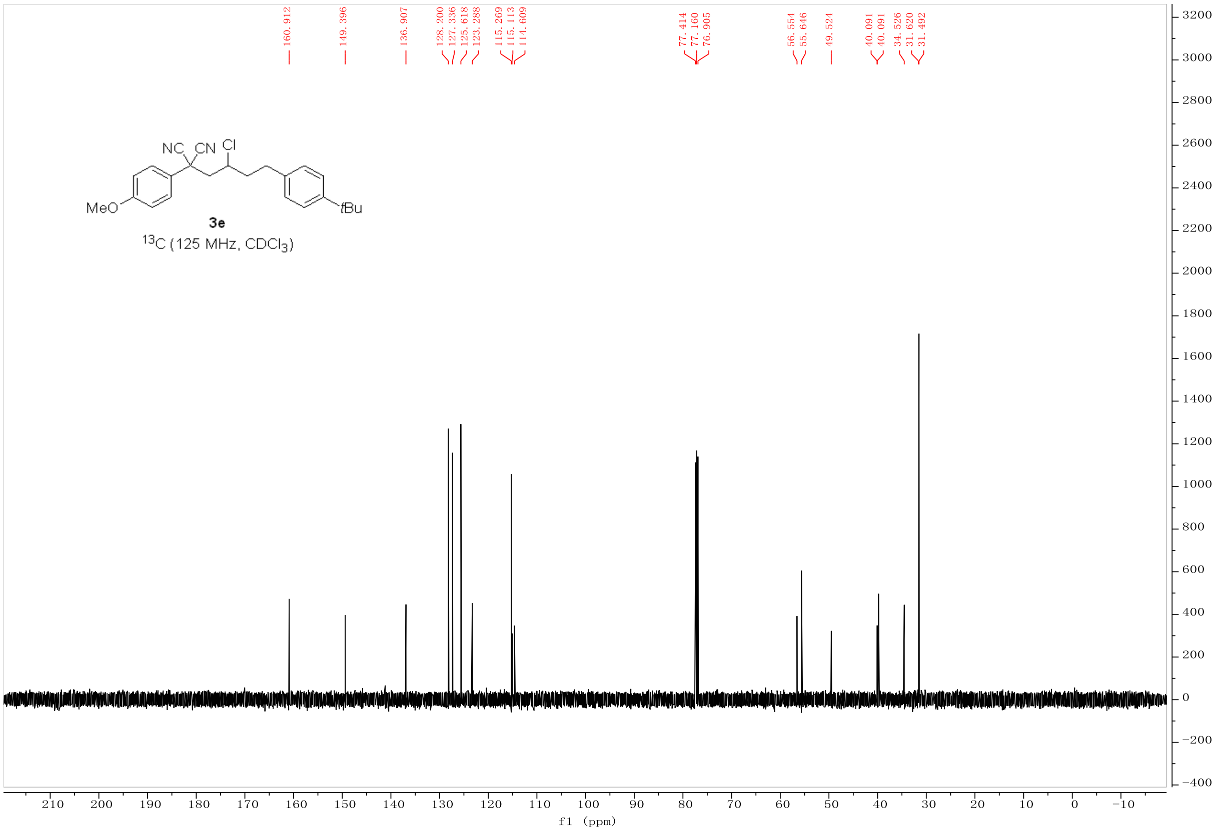

PB-I-136-H.11.fid
7.45 7.43 7.26 7.06 7.04 6.96 6.95 6.82 6.81
3.92 3.92 3.91 3.91 3.91 3.91 3.90 3.90 3.90 3.89 3.89 3.88 3.84 3.79 2.82 2.81 2.80 2.79 2.78 2.76 2.74 2.73 2.72 2.70 2.69 2.68 2.67 2.66 2.65 2.52 2.51 2.49 2.49 2.05 2.04 2.03 2.02 2.01
NC CN Cl
MeO OMe
3d
^{1}H (600 MHz, CDCl$_3$)
2.03 2.02 2.04 2.01 1.00 3.03 3.05 3.01 1.04 2.03
f1 (ppm)


PB-I-136-C.1.fid
160.90 158.28 131.95 129.50 127.30 123.19 115.26 115.11 114.60 114.15 77.37 77.16 76.95 56.31 55.64 55.37 49.54 40.28 39.75 31.23
NC CN Cl
MeO OMe
3d
^{13}C (151 MHz, CDCl$_3$)
f1 (ppm)



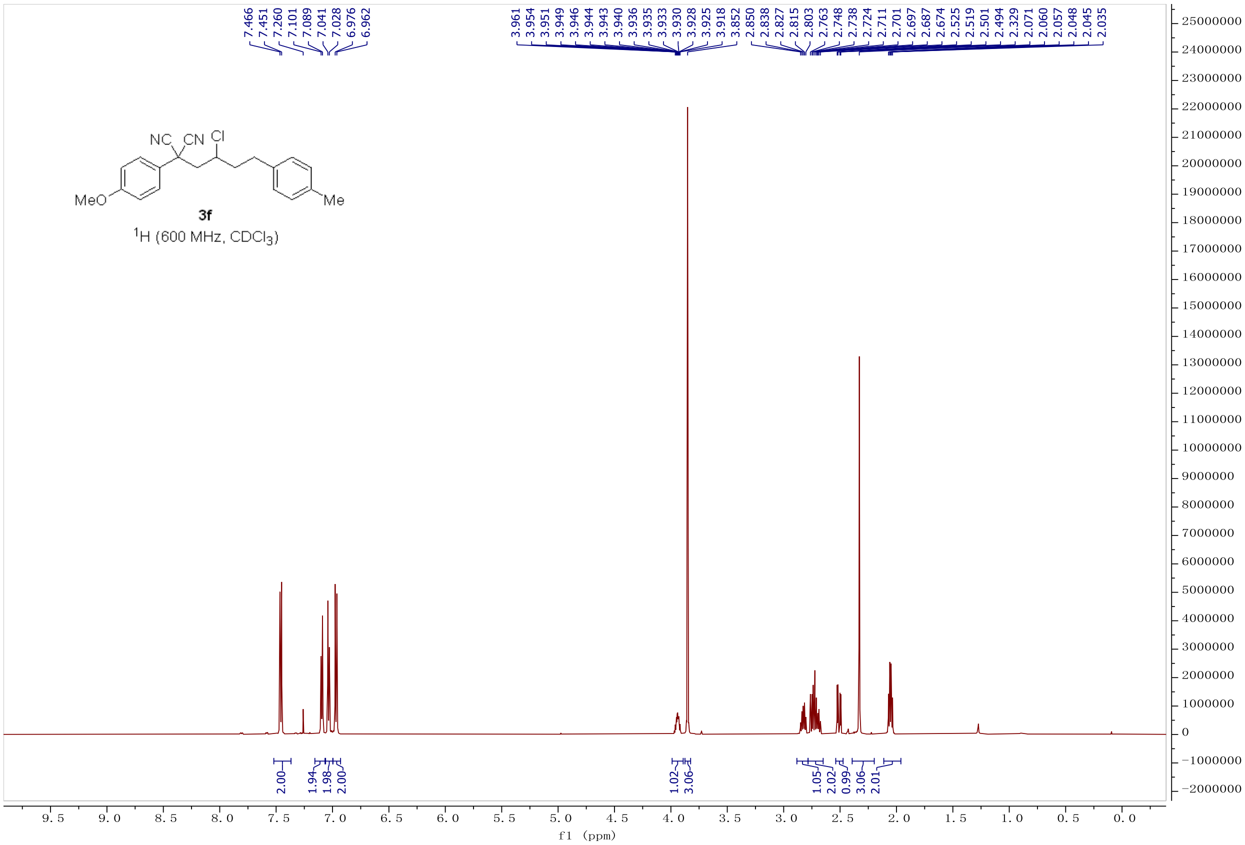
3e

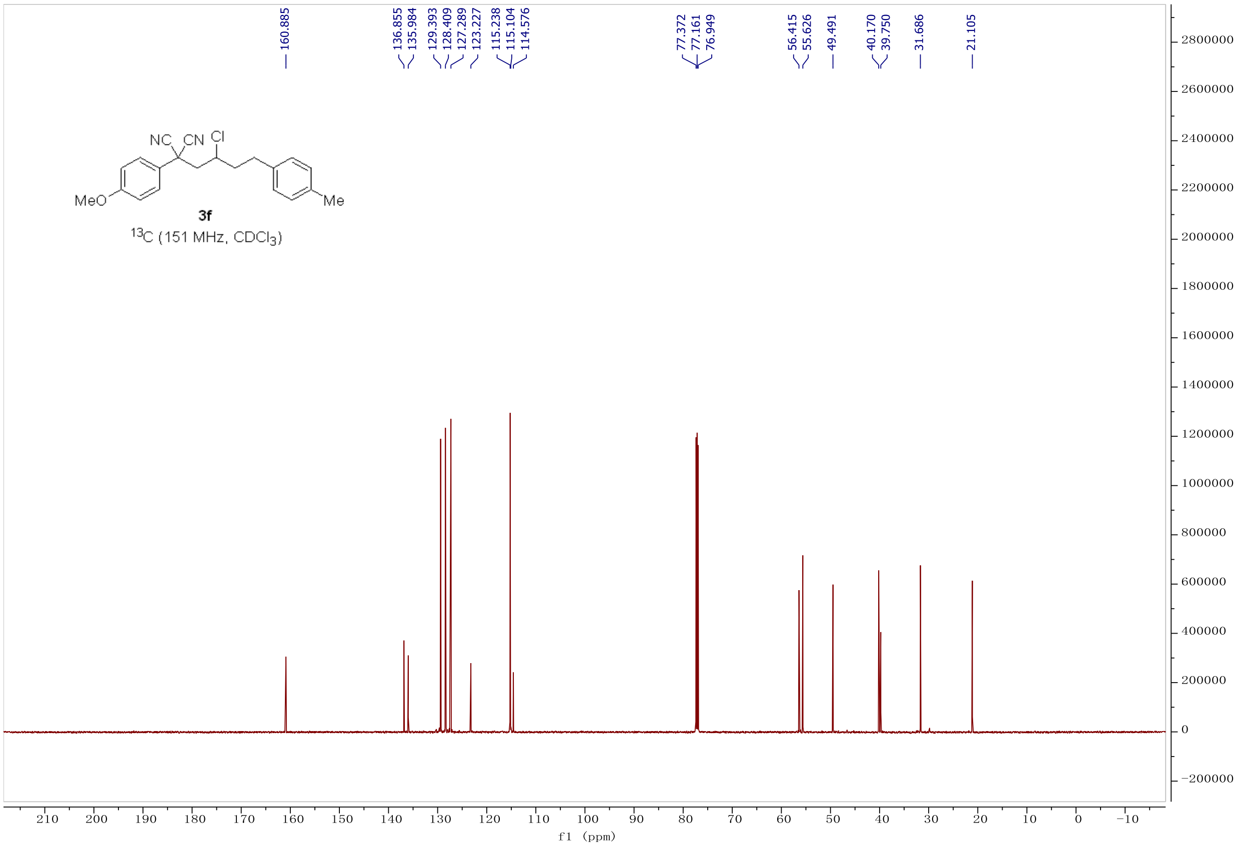
^{1}H (500 MHz, $CDCl_3$)

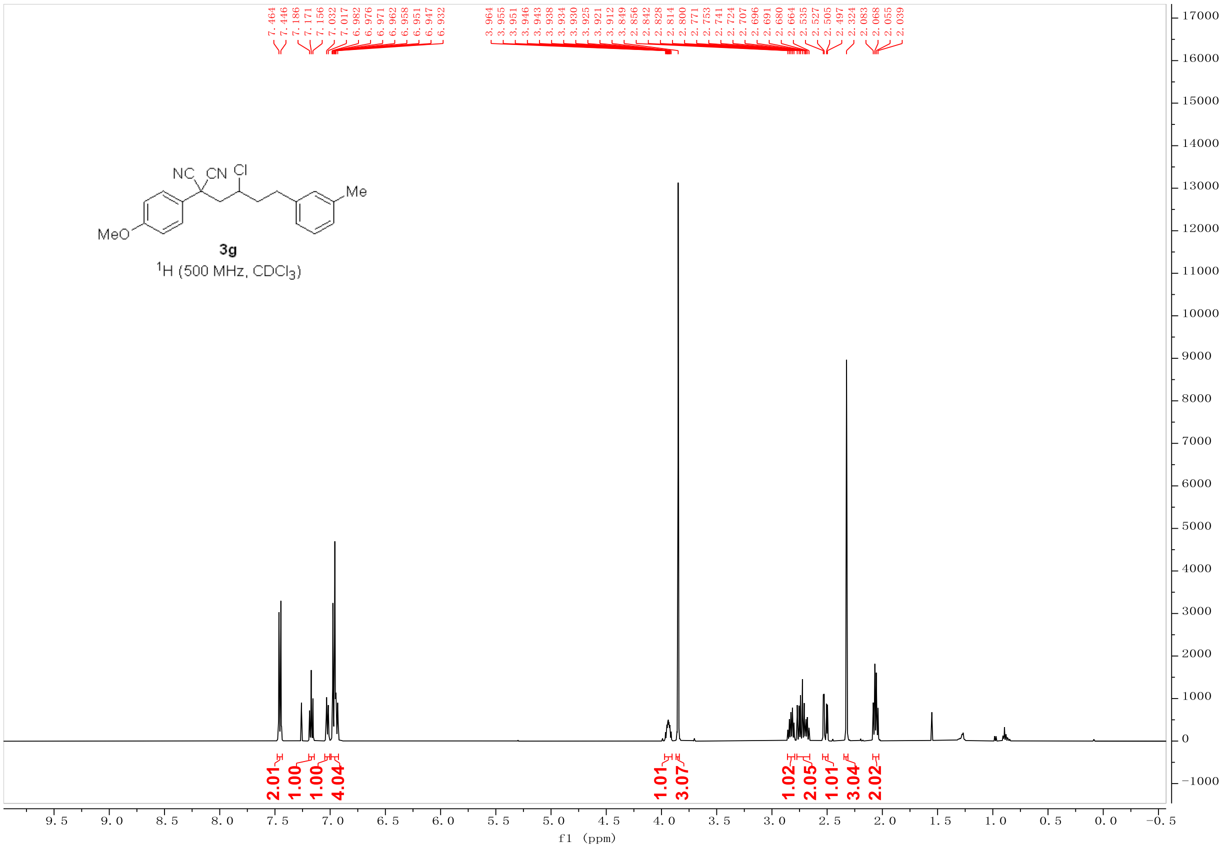


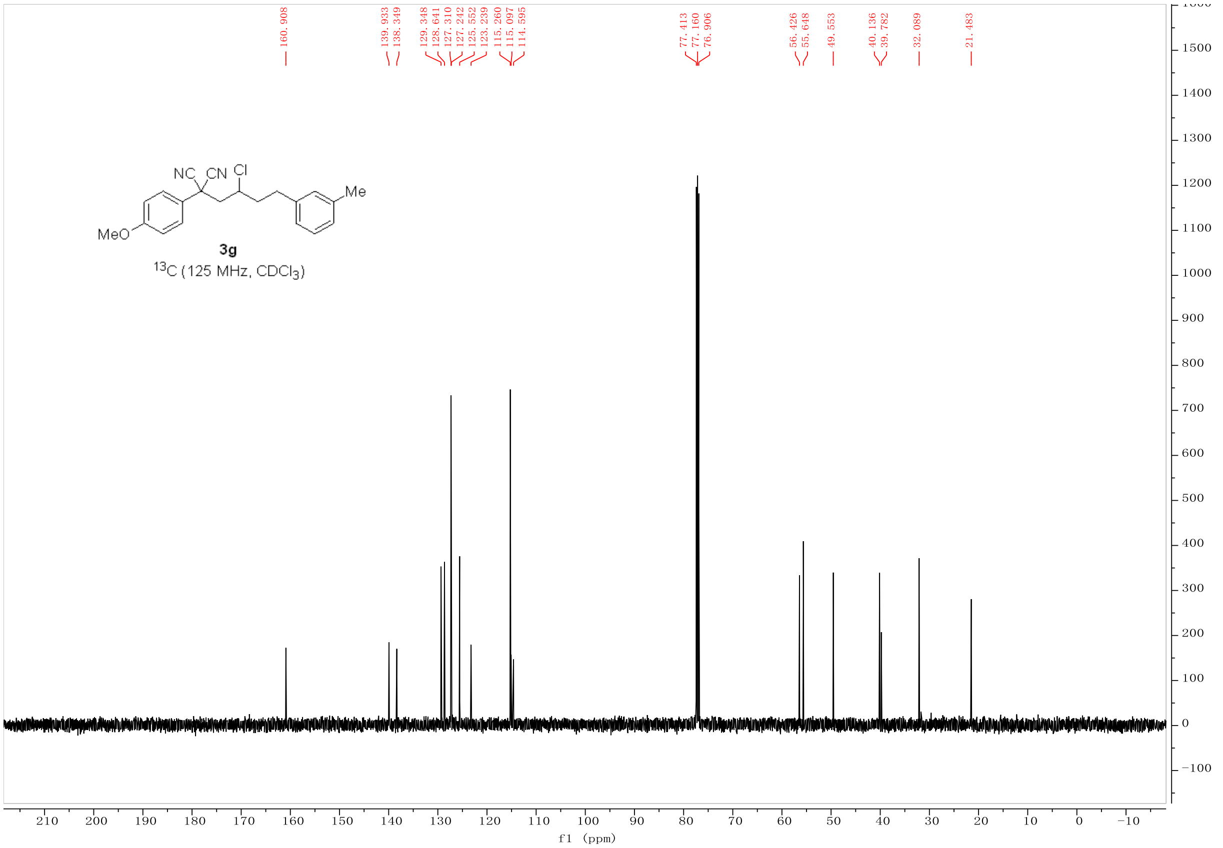
3e

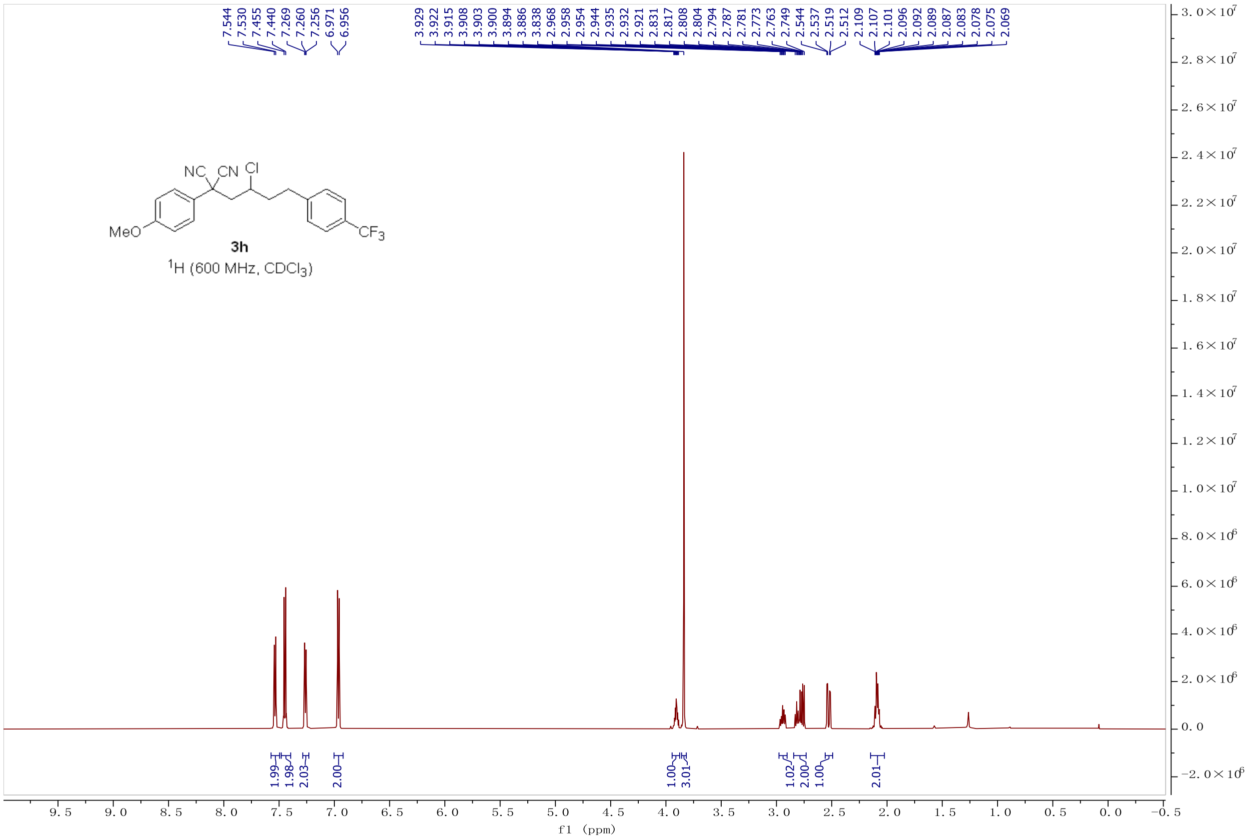
^{13}C (125 MHz, $CDCl_3$)


7.466
7.451
7.260
7.101
7.089
7.041
7.028
6.976
6.962
3.961
3.954
3.951
3.949
3.946
3.944
3.943
3.940
3.936
3.935
3.933
3.930
3.928
3.925
3.918
3.852
2.850
2.838
2.827
2.815
2.803
2.763
2.748
2.738
2.724
2.711
2.701
2.697
2.687
2.674
2.525
2.519
2.501
2.494
2.329
2.071
2.060
2.057
2.048
2.045
2.035
NC
CN
Cl
MeO
Me
3f
^{1}H (600 MHz, CDCl$_3$)
2.00
1.94
1.98
2.00
1.02
3.06
1.05
2.02
0.99
3.06
2.01
f1 (ppm)

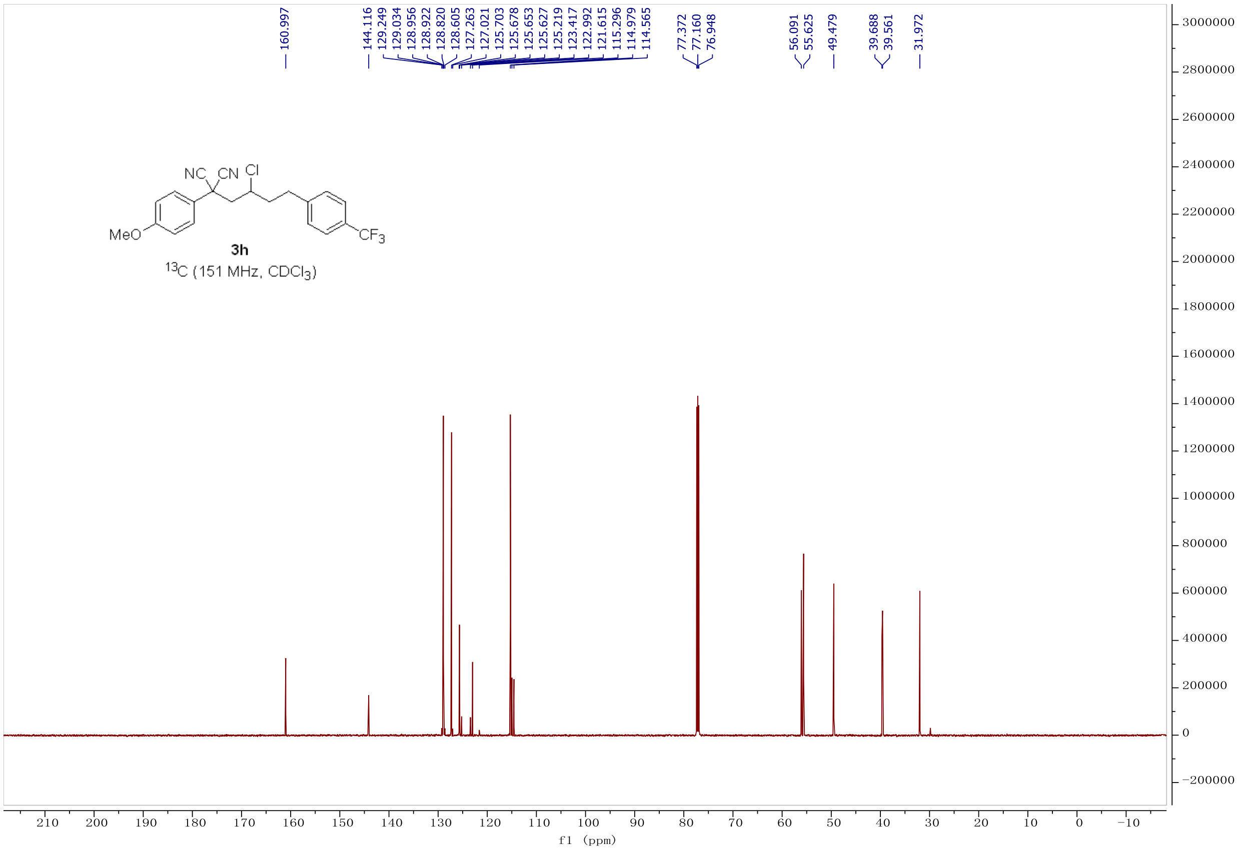

160.885
136.855
135.984
129.393
128.409
127.289
123.227
115.238
115.104
114.576
77.372
77.161
76.949
56.415
55.626
49.491
40.170
39.750
31.686
21.105
NC
CN
Cl
MeO
Me
3f
^{13}C (151 MHz, CDCl$_3$)
f1 (ppm)


7.464
7.446
7.186
7.171
7.156
7.032
7.017
6.982
6.976
6.971
6.962
6.958
6.951
6.947
6.932
3.964
3.955
3.951
3.946
3.943
3.938
3.934
3.930
3.925
3.921
3.912
3.849
2.856
2.842
2.828
2.814
2.800
2.771
2.753
2.741
2.724
2.707
2.696
2.691
2.680
2.664
2.535
2.527
2.506
2.497
2.324
2.083
2.068
2.055
2.039
NC
CN
Cl
Me
MeO
3g
^{1}H (500 MHz, CDCl$_3$)
2.01
1.00
1.00
4.04
1.01
3.07
1.02
2.05
1.01
3.04
2.02
f1 (ppm)

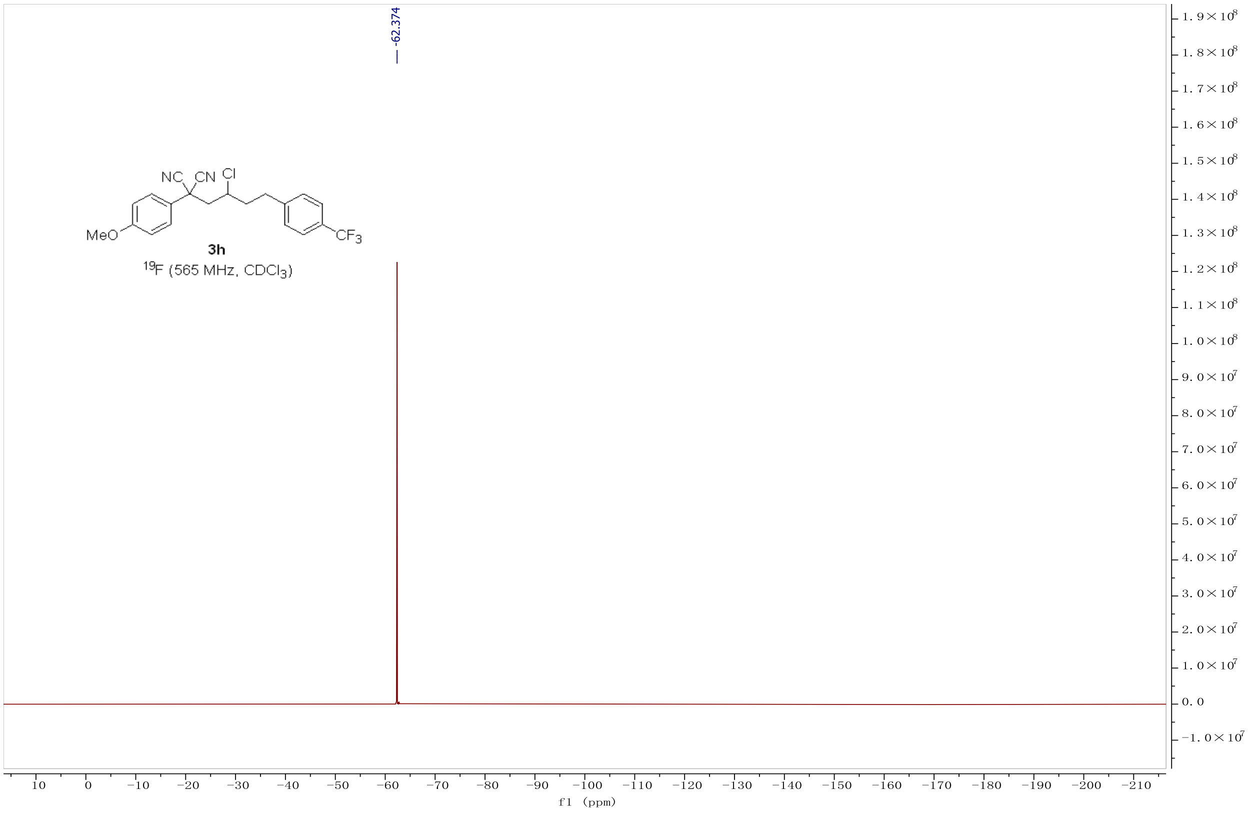

160.908
139.933
138.349
129.348
128.641
127.310
127.232
125.552
123.239
115.260
115.097
114.595
77.413
77.160
76.906
56.426
55.648
49.553
40.136
39.782
32.089
21.483
NC
CN
Cl
Me
MeO
3g
^{13}C (125 MHz, CDCl$_3$)
f1 (ppm)


3h

^1H (600 MHz, $CDCl_3$)

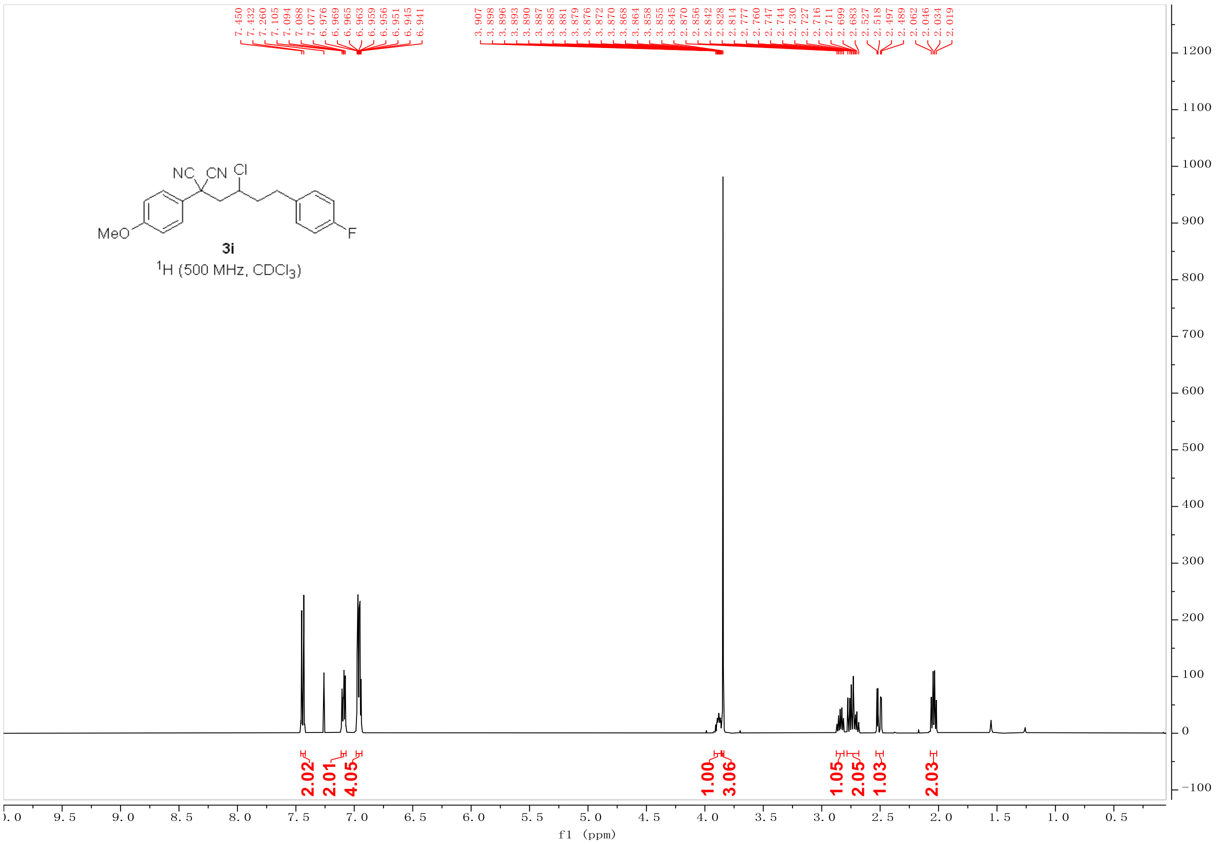

3h

^{13}C (151 MHz, $CDCl_3$)



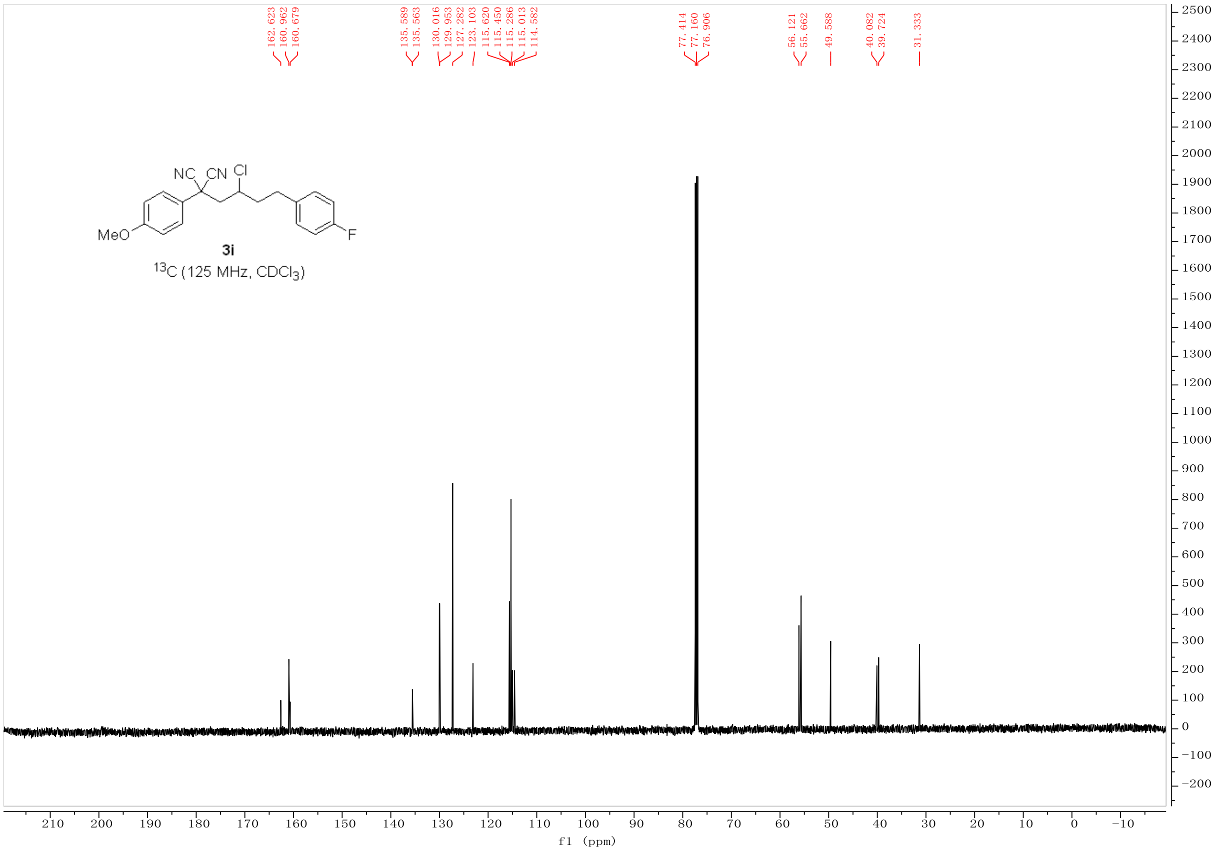
3h

^{19}F (565 MHz, CDCl$_3$)



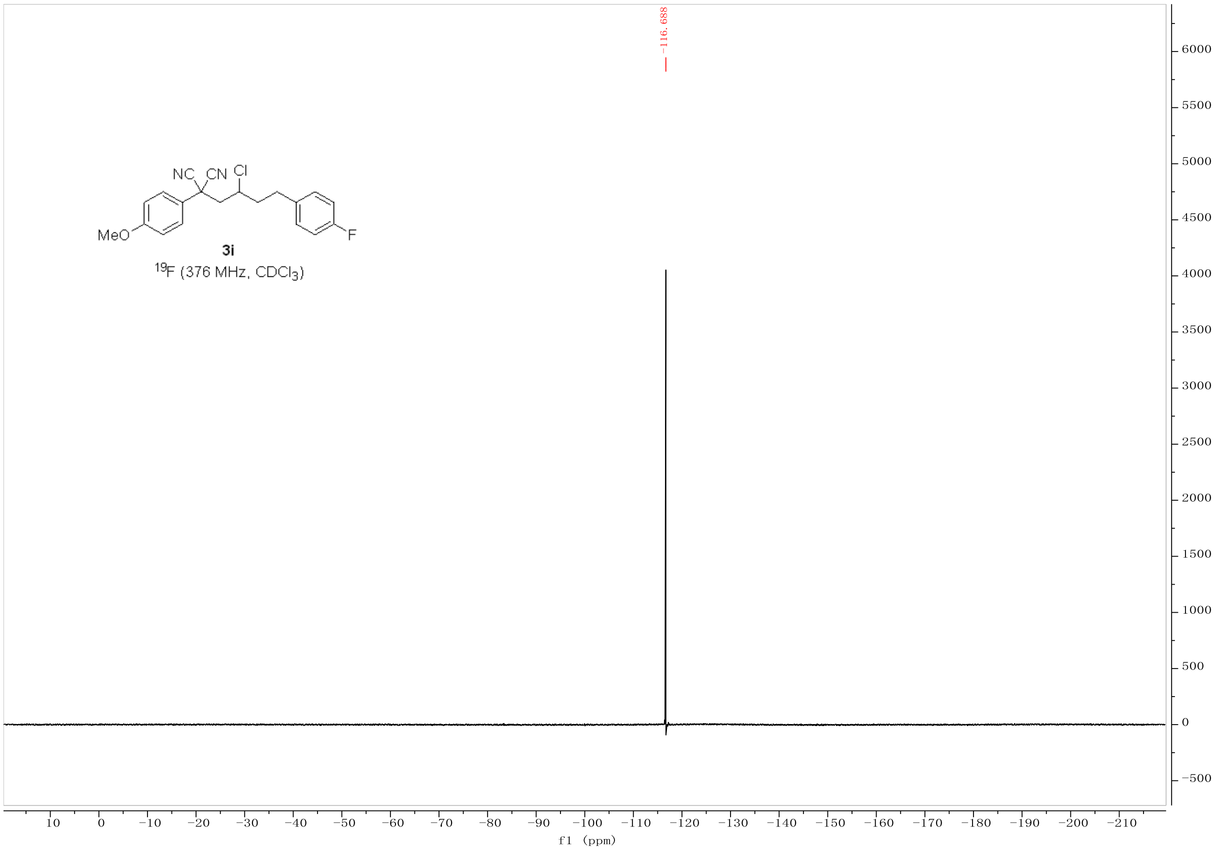
3i

^{1}H (500 MHz, CDCl$_3$)



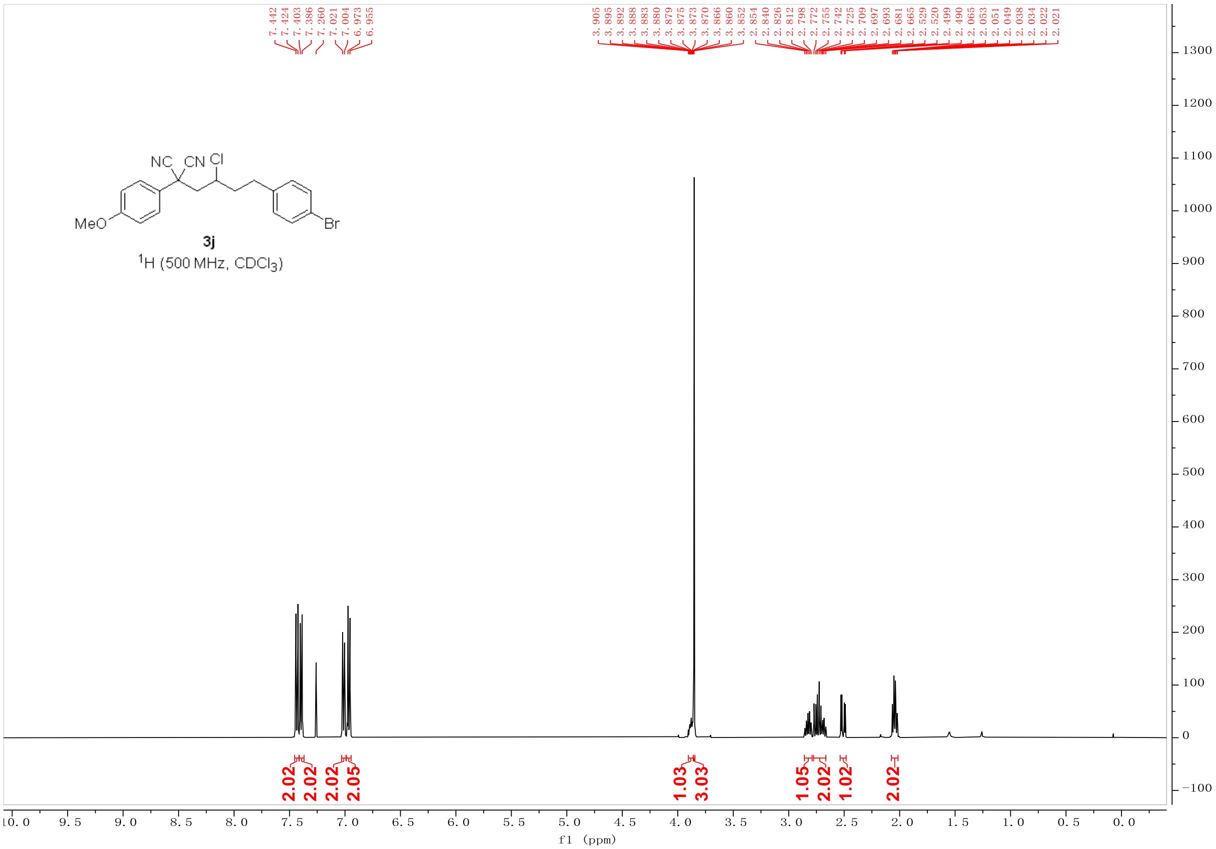
3i

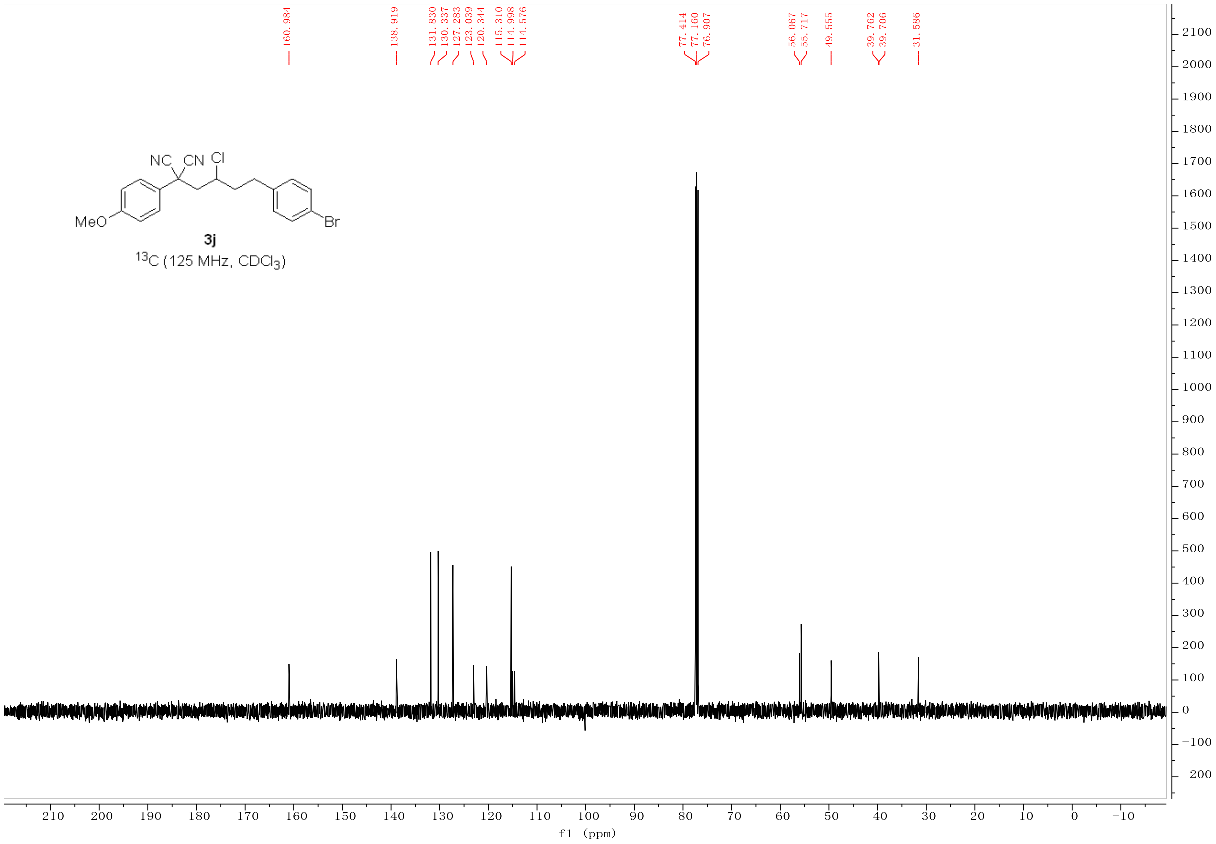
^{13}C (125 MHz, $CDCl_3$)

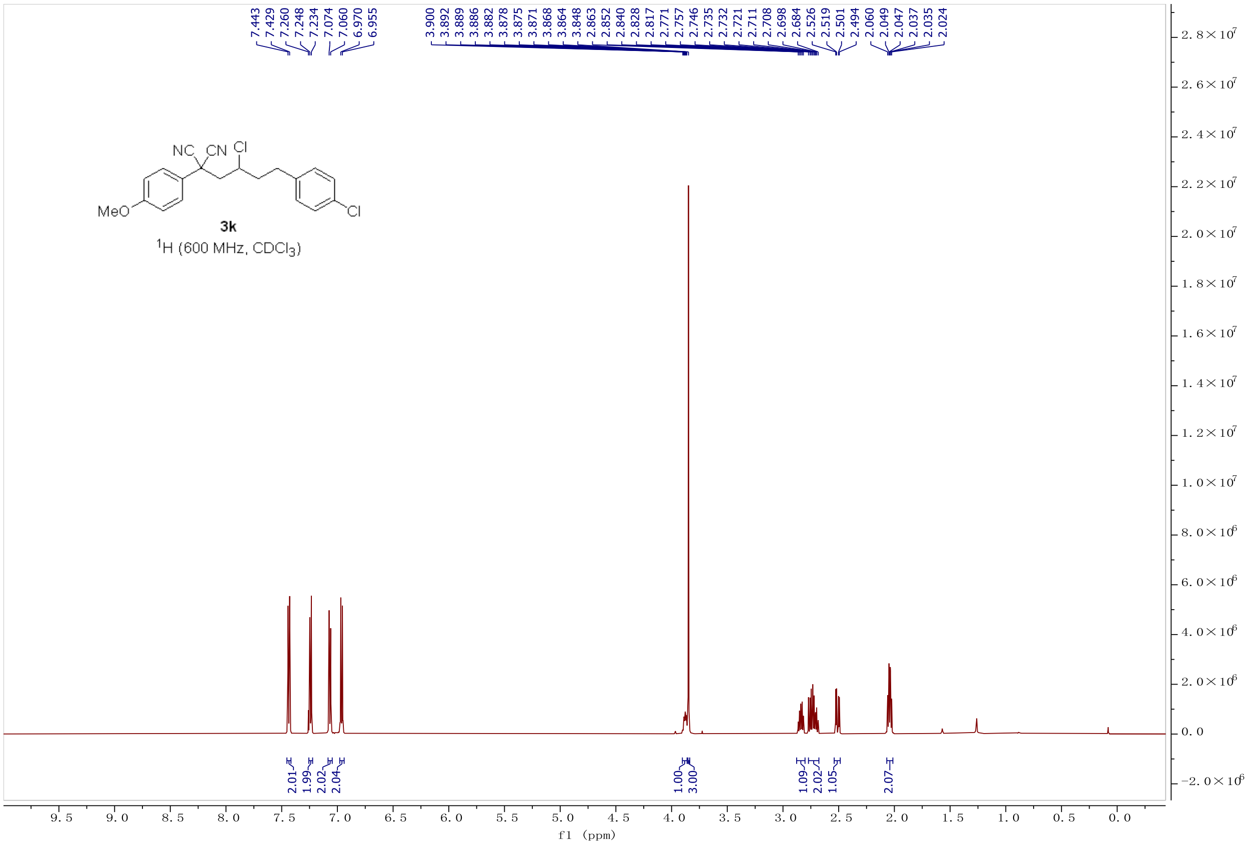


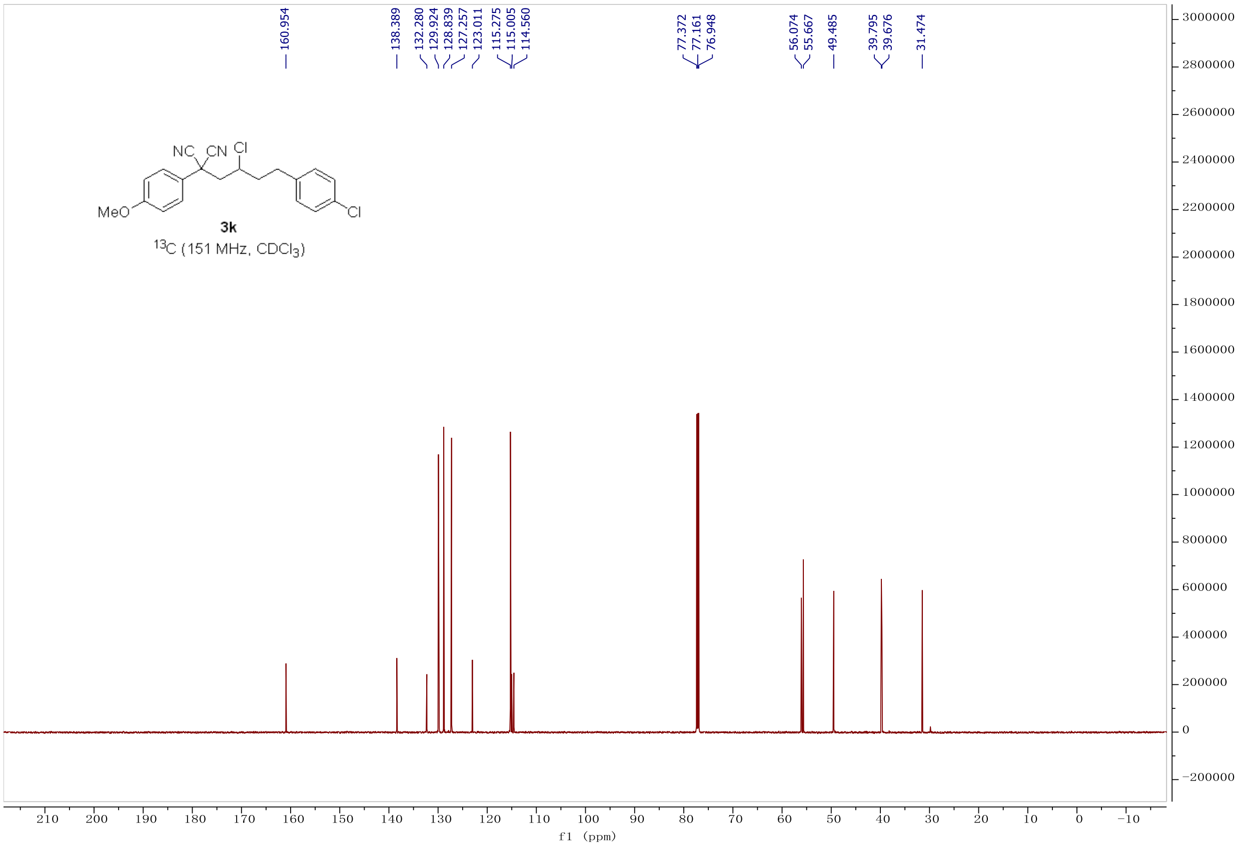
3i

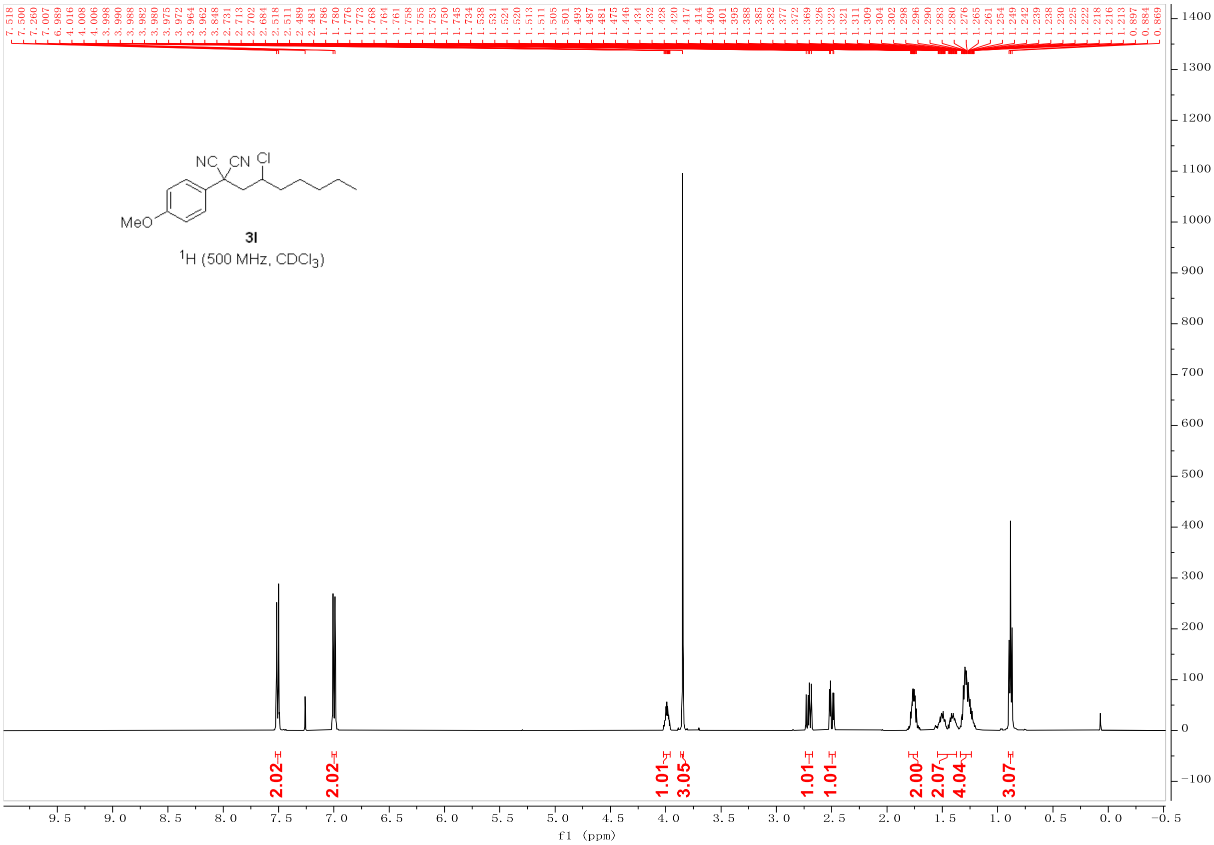
^{19}F (376 MHz, $CDCl_3$)

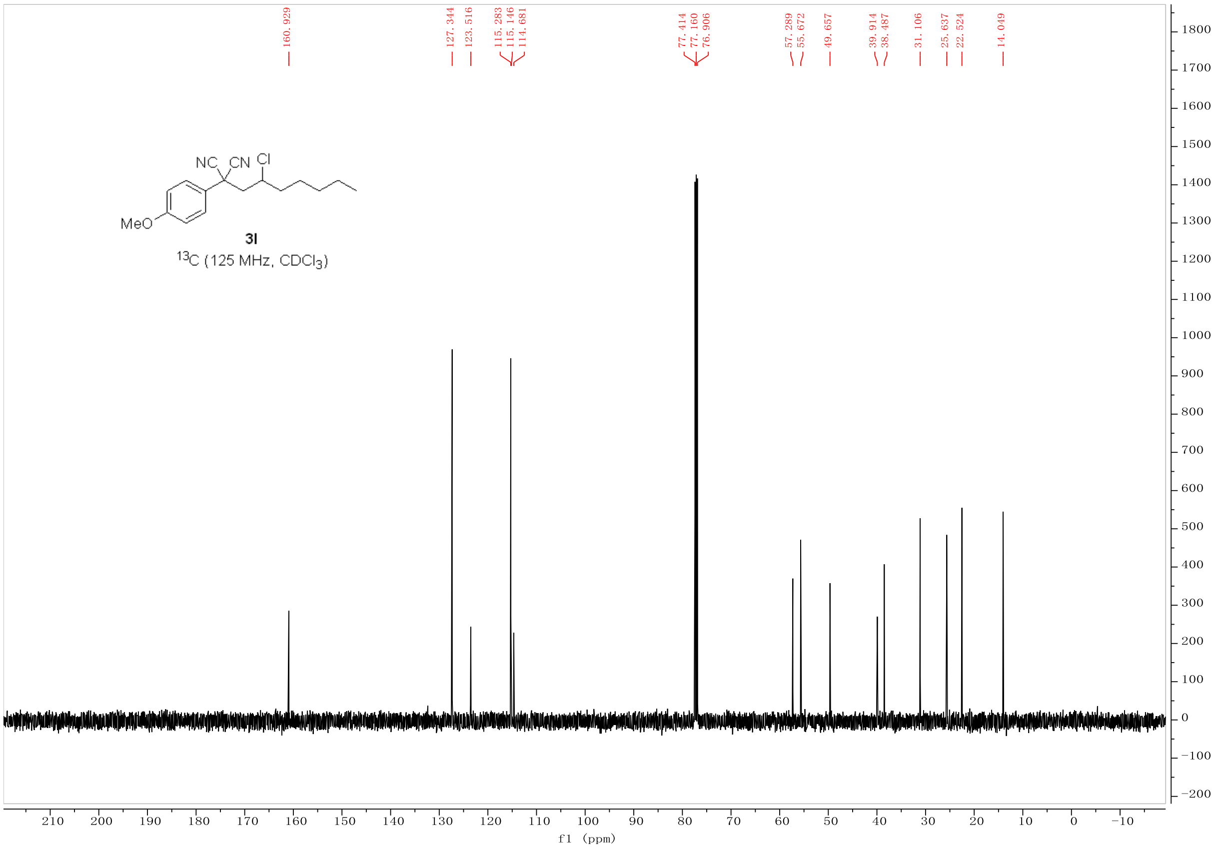

7.442
7.424
7.403
7.386
7.260
7.021
7.004
6.973
6.955
3.905
3.895
3.892
3.888
3.883
3.880
3.879
3.875
3.873
3.870
3.866
3.860
3.852
2.854
2.840
2.826
2.812
2.798
2.772
2.755
2.742
2.725
2.709
2.697
2.693
2.681
2.665
2.529
2.520
2.499
2.490
2.065
2.053
2.051
2.049
2.038
2.034
2.022
2.021
NC
CN
Cl
MeO
Br
3j
^{1}H (500 MHz, CDCl$_3$)
2.02
2.02
2.02
2.05
1.03
3.03
1.05
2.02
1.02
2.02
f1 (ppm)

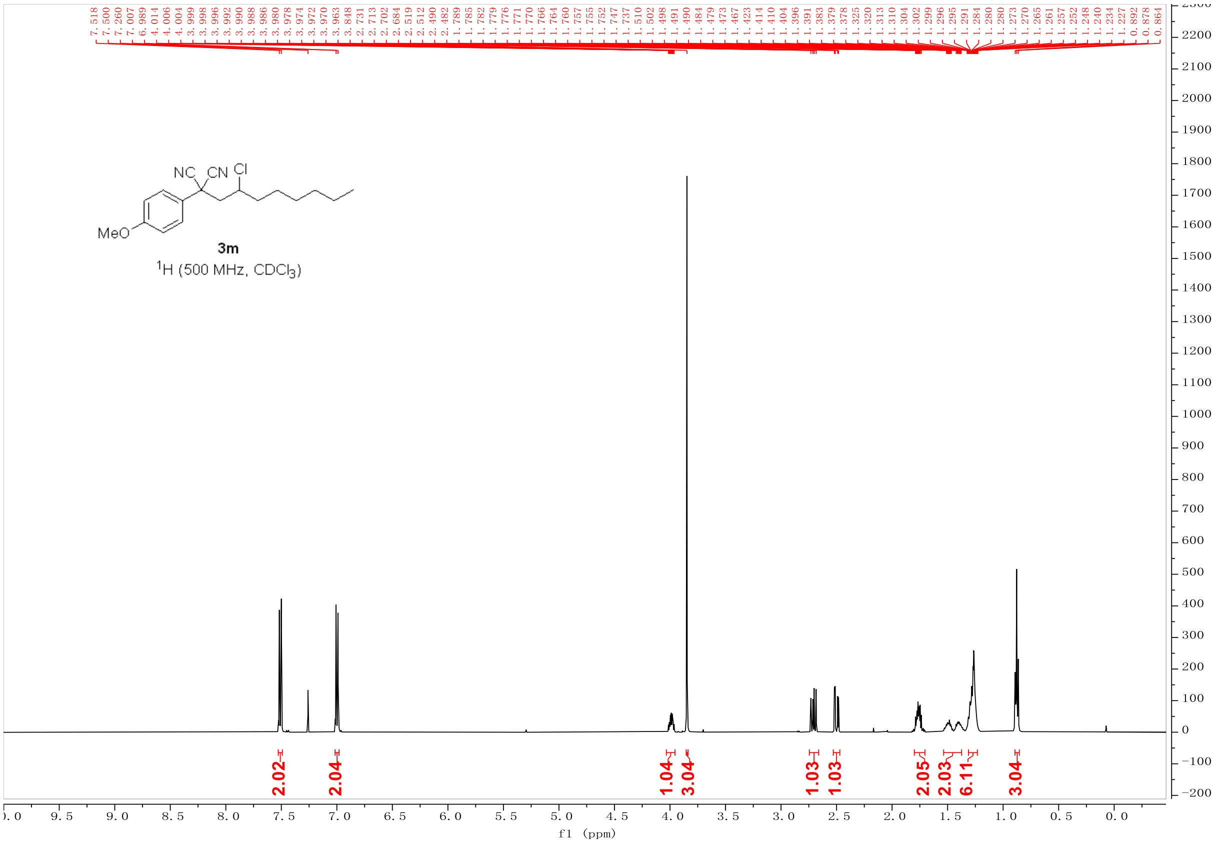

160.984
138.919
131.830
130.337
127.283
123.039
120.344
115.310
114.998
114.576
77.414
77.160
76.907
56.067
55.717
49.555
39.762
39.706
31.586
NC
CN
Cl
MeO
Br
3j
^{13}C (125 MHz, CDCl$_3$)
f1 (ppm)

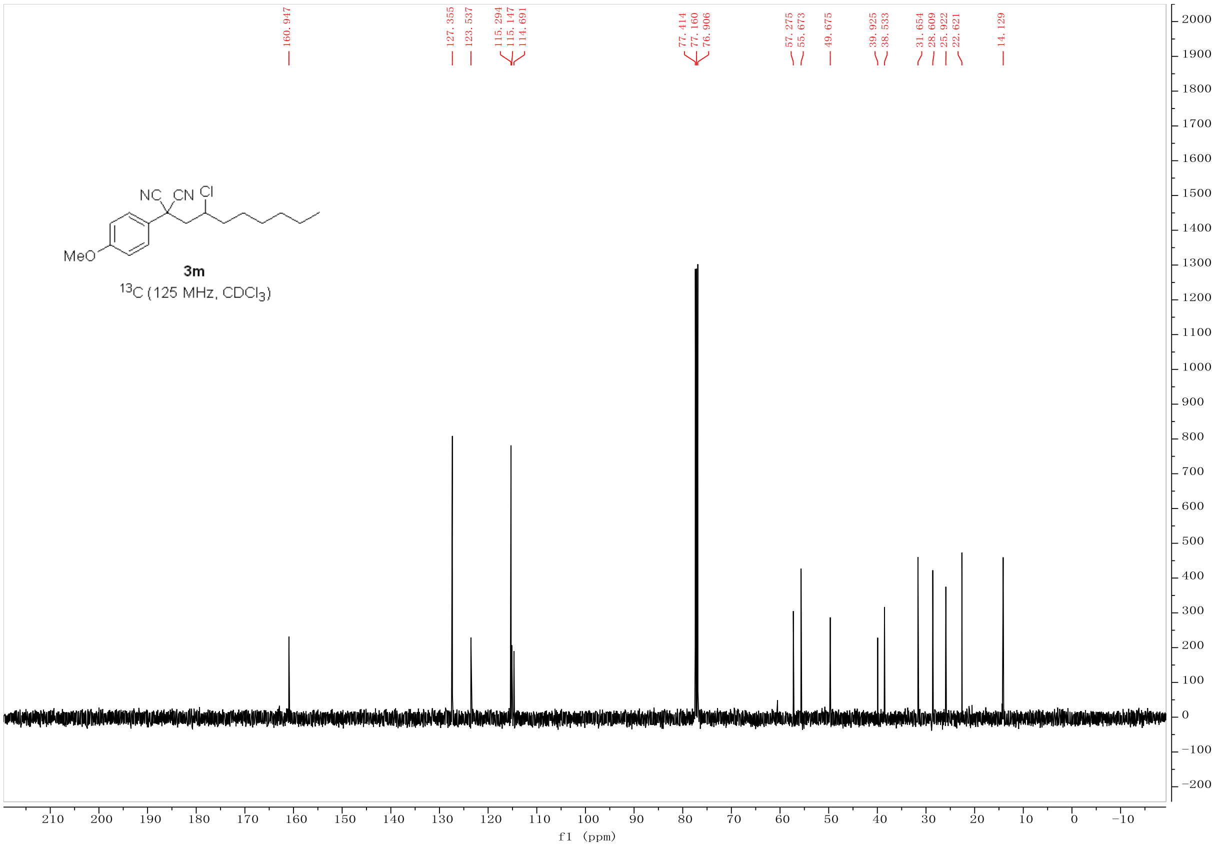

7.443
7.429
7.260
7.248
7.234
7.074
7.060
6.970
6.955
3.900
3.892
3.889
3.886
3.882
3.878
3.875
3.871
3.868
3.864
3.848
2.863
2.852
2.840
2.828
2.817
2.771
2.757
2.746
2.735
2.732
2.721
2.711
2.708
2.698
2.684
2.526
2.519
2.501
2.494
2.060
2.049
2.047
2.037
2.035
2.024
NC
CN
Cl
MeO
Cl
3k
^{1}H (600 MHz, CDCl$_3$)
2.01
1.99
2.02
2.04
1.00
3.00
1.09
2.02
1.05
2.07
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)
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
−2.0×10^6

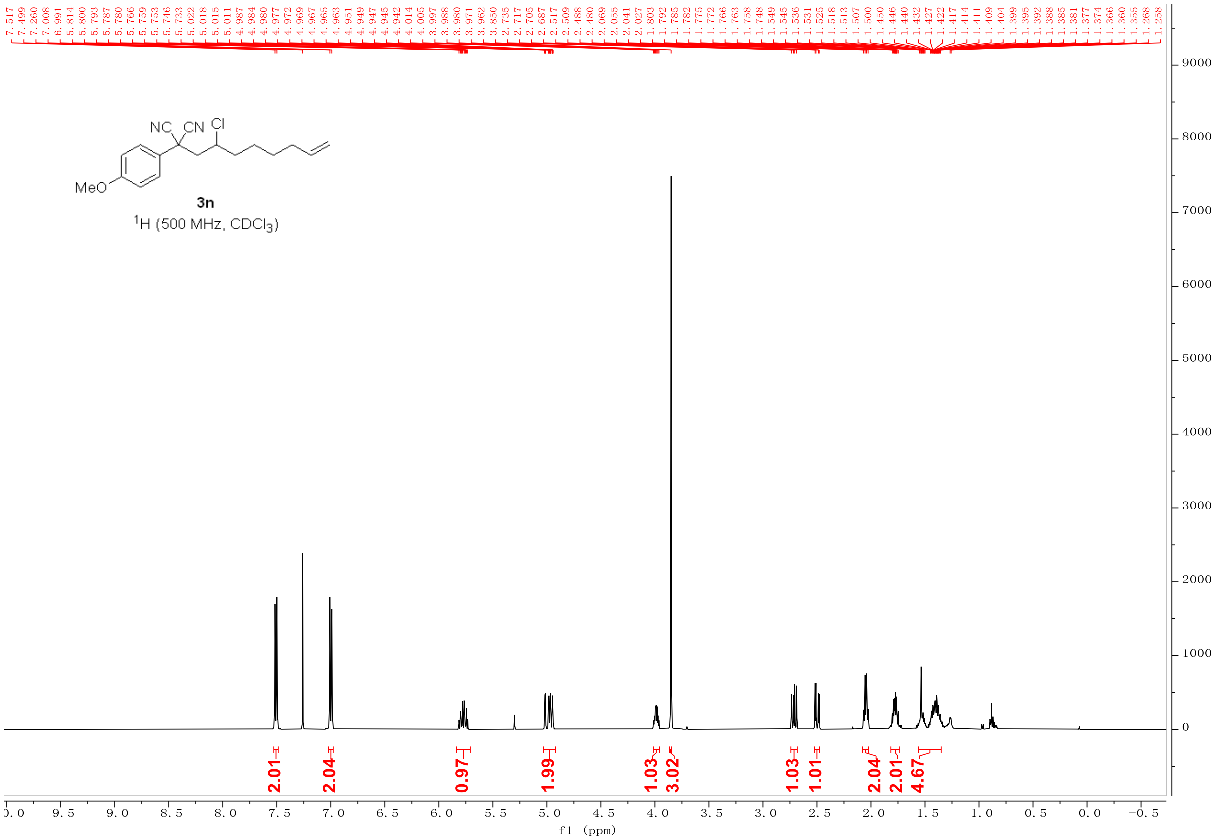

160.954
138.389
132.280
129.924
128.839
127.257
123.011
115.275
115.005
114.560
77.372
77.161
76.948
56.074
55.667
49.485
39.795
39.676
31.474
NC
CN
Cl
MeO
Cl
3k
^{13}C (151 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
−200000

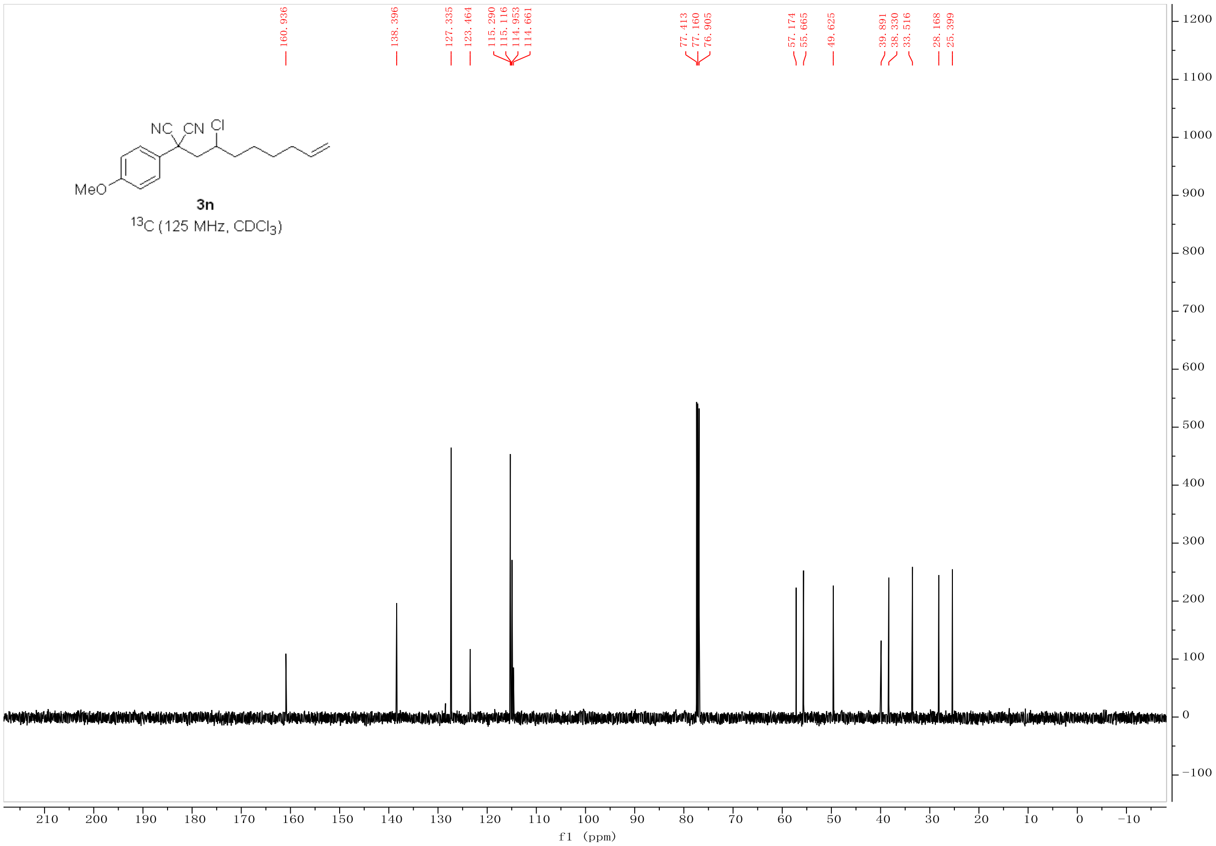

7.518
7.500
7.260
7.007
6.989
4.016
4.008
4.006
3.998
3.990
3.988
3.982
3.980
3.975
3.972
3.964
3.962
3.848
2.731
2.713
2.702
2.684
2.518
2.511
2.489
2.481
1.786
1.780
1.776
1.773
1.768
1.764
1.761
1.758
1.755
1.753
1.750
1.745
1.734
1.538
1.531
1.524
1.520
1.513
1.511
1.505
1.501
1.493
1.487
1.481
1.475
1.446
1.434
1.432
1.428
1.420
1.417
1.414
1.409
1.401
1.395
1.388
1.385
1.382
1.377
1.372
1.369
1.326
1.323
1.321
1.311
1.309
1.304
1.302
1.298
1.296
1.290
1.283
1.280
1.276
1.265
1.261
1.254
1.249
1.242
1.239
1.238
1.230
1.225
1.222
1.218
1.216
1.213
0.897
0.884
0.869
NC
CN
Cl
MeO
3l
^{1}H (500 MHz, CDCl$_3$)
2.02
2.02
1.01
3.05
1.01
1.01
2.00
2.07
4.04
3.07
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)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

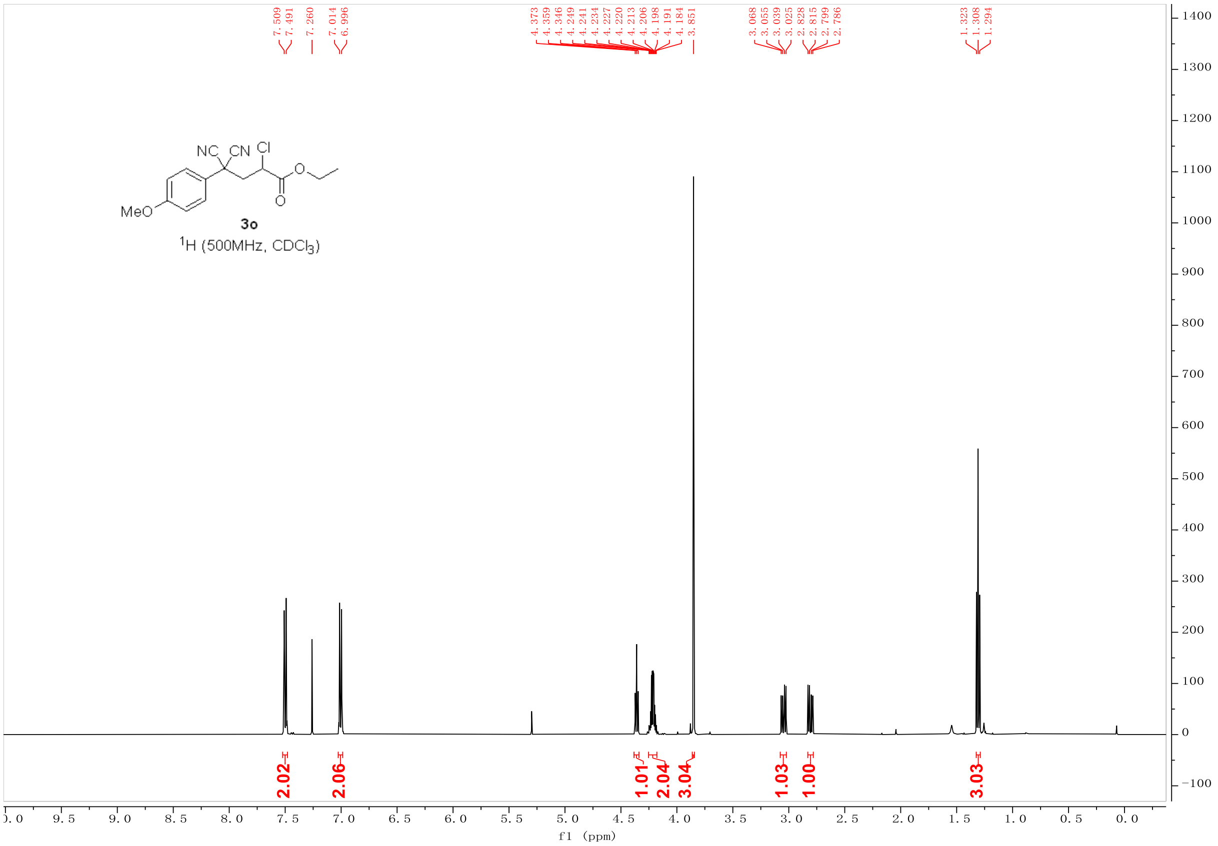

160.929
127.344
123.516
115.283
115.146
114.681
77.414
77.160
76.906
57.289
55.672
49.657
39.914
38.487
31.106
25.637
22.524
14.049
NC
CN
Cl
MeO
3l
^{13}C (125 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

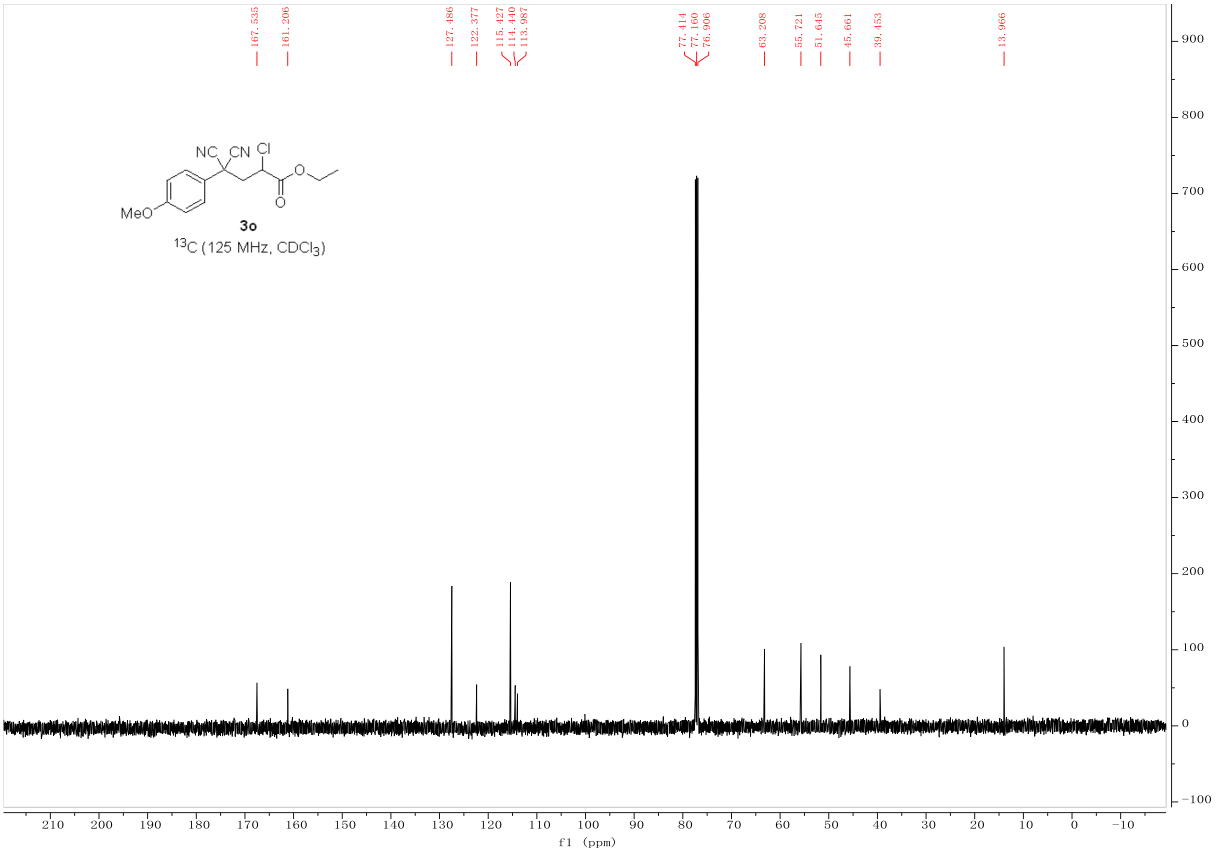

7.518
7.500
7.260
7.007
6.989
4.014
4.006
4.004
3.999
3.998
3.996
3.992
3.990
3.988
3.986
3.980
3.978
3.974
3.972
3.970
3.963
3.848
2.731
2.713
2.702
2.684
2.519
2.512
2.490
2.482
1.789
1.785
1.782
1.779
1.776
1.771
1.770
1.766
1.764
1.760
1.757
1.755
1.752
1.747
1.737
1.510
1.502
1.498
1.491
1.490
1.484
1.479
1.473
1.467
1.423
1.414
1.410
1.404
1.396
1.391
1.383
1.379
1.378
1.325
1.320
1.313
1.310
1.304
1.302
1.299
1.296
1.295
1.291
1.284
1.280
1.280
1.273
1.270
1.265
1.261
1.257
1.252
1.248
1.240
1.234
1.227
0.892
0.878
0.864
NC
CN
Cl
MeO
3m
^{1}H (500 MHz, CDCl$_3$)
2.02
2.04
1.04
3.04
1.03
1.03
2.05
2.03
6.11
3.04
f1 (ppm)

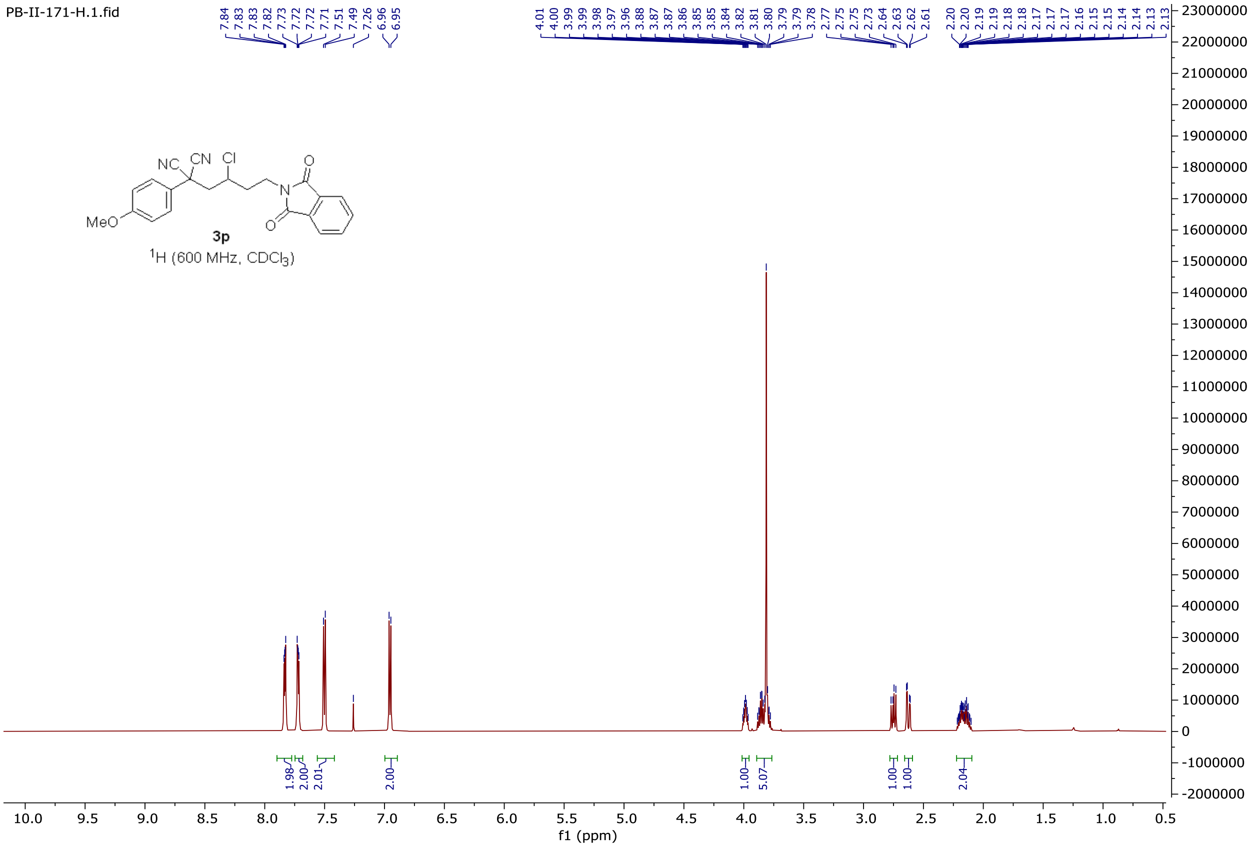

160.947
127.355
123.537
115.294
115.147
114.691
77.414
77.160
76.906
57.275
55.673
49.675
39.925
38.533
31.654
28.609
25.922
22.621
14.129
NC
CN
Cl
MeO
3m
^{13}C (125 MHz, CDCl$_3$)
f1 (ppm)


7.517
7.499
7.260
7.008
6.991
5.814
5.800
5.793
5.787
5.780
5.766
5.759
5.753
5.746
5.733
5.022
5.018
5.015
5.011
4.987
4.984
4.980
4.977
4.972
4.969
4.967
4.965
4.963
4.951
4.949
4.947
4.945
4.942
4.014
4.005
3.997
3.988
3.980
3.971
3.962
3.850
2.735
2.717
2.705
2.687
2.517
2.509
2.488
2.480
2.069
2.055
2.041
2.027
1.803
1.792
1.785
1.782
1.775
1.772
1.766
1.763
1.758
1.748
1.549
1.545
1.536
1.531
1.525
1.518
1.513
1.507
1.500
1.450
1.446
1.440
1.432
1.427
1.422
1.417
1.414
1.411
1.409
1.404
1.399
1.395
1.392
1.388
1.385
1.381
1.377
1.374
1.366
1.360
1.355
1.268
1.258
NC
CN
Cl
MeO
3n
^{1}H (500 MHz, CDCl$_3$)
2.01
2.04
0.97
1.99
1.03
3.02
1.03
1.01
2.04
2.01
4.67
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0.0
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)


160.936
138.396
127.335
123.464
115.290
115.116
114.953
114.661
77.413
77.160
76.905
57.174
55.665
49.625
39.891
38.330
33.516
28.168
25.399
NC
CN
Cl
MeO
3n
^{13}C (125 MHz, CDCl$_3$)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
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)

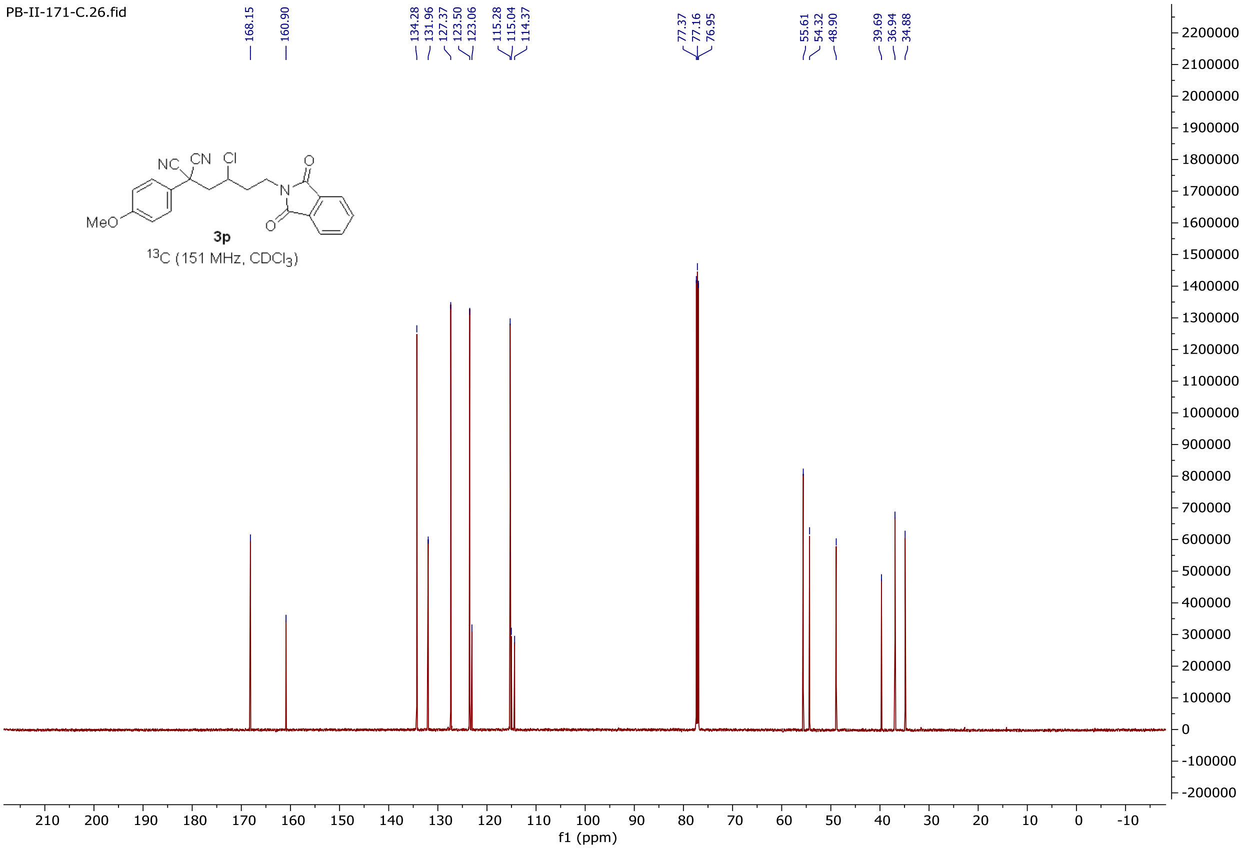

7.509
7.491
7.260
7.014
6.996
4.373
4.359
4.346
4.249
4.241
4.234
4.227
4.220
4.213
4.206
4.198
4.191
4.184
3.851
3.068
3.055
3.039
3.025
2.828
2.815
2.799
2.786
1.323
1.308
1.294
NC
CN
Cl
O
O
MeO
3o
^{1}H (500MHz, CDCl$_3$)
2.02
2.06
1.01
2.04
3.04
1.03
1.00
3.03
f1 (ppm)


167.535
161.206
127.486
122.377
115.427
114.440
113.987
77.414
77.160
76.906
63.208
55.721
51.645
45.661
39.453
13.966
NC
CN
Cl
O
O
MeO
3o
^{13}C (125 MHz, CDCl$_3$)
f1 (ppm)



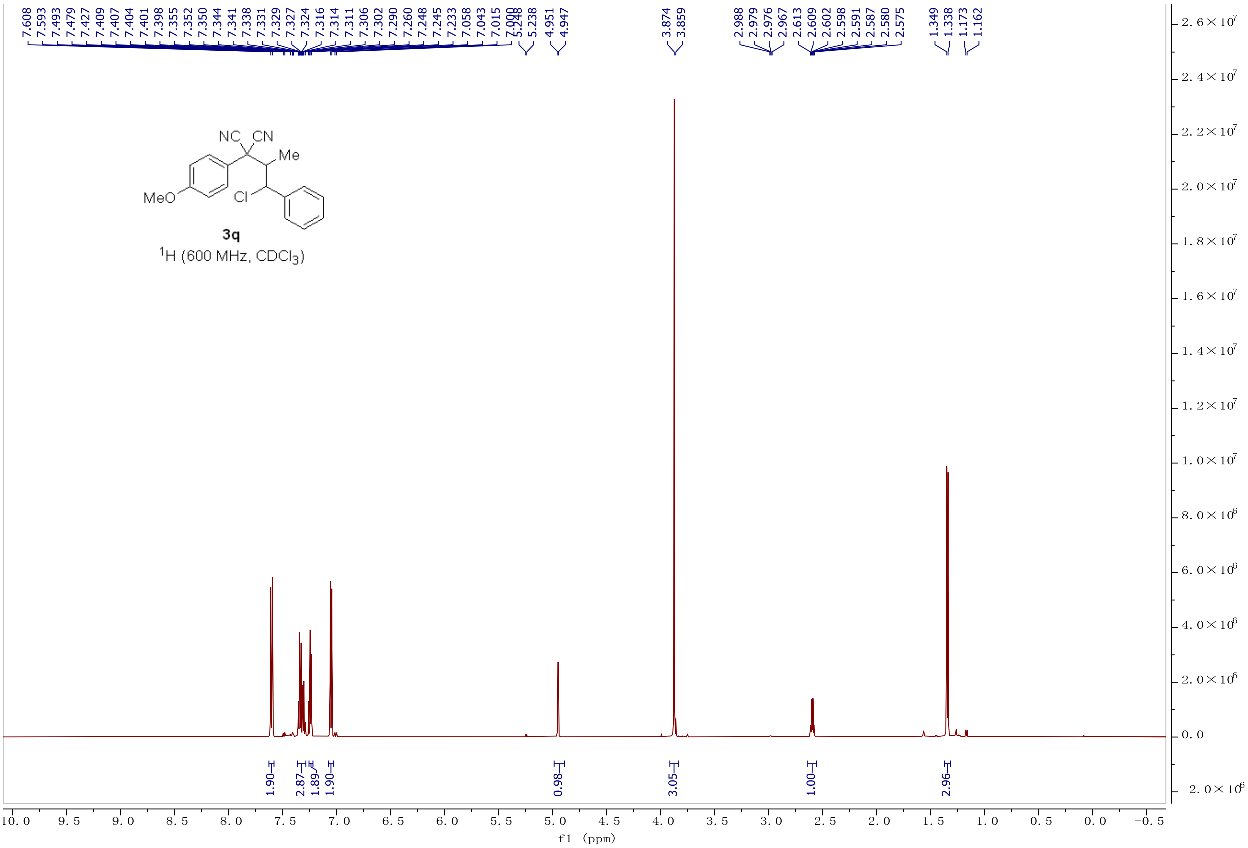
3p

^{1}H (600 MHz, CDCl$_3$)



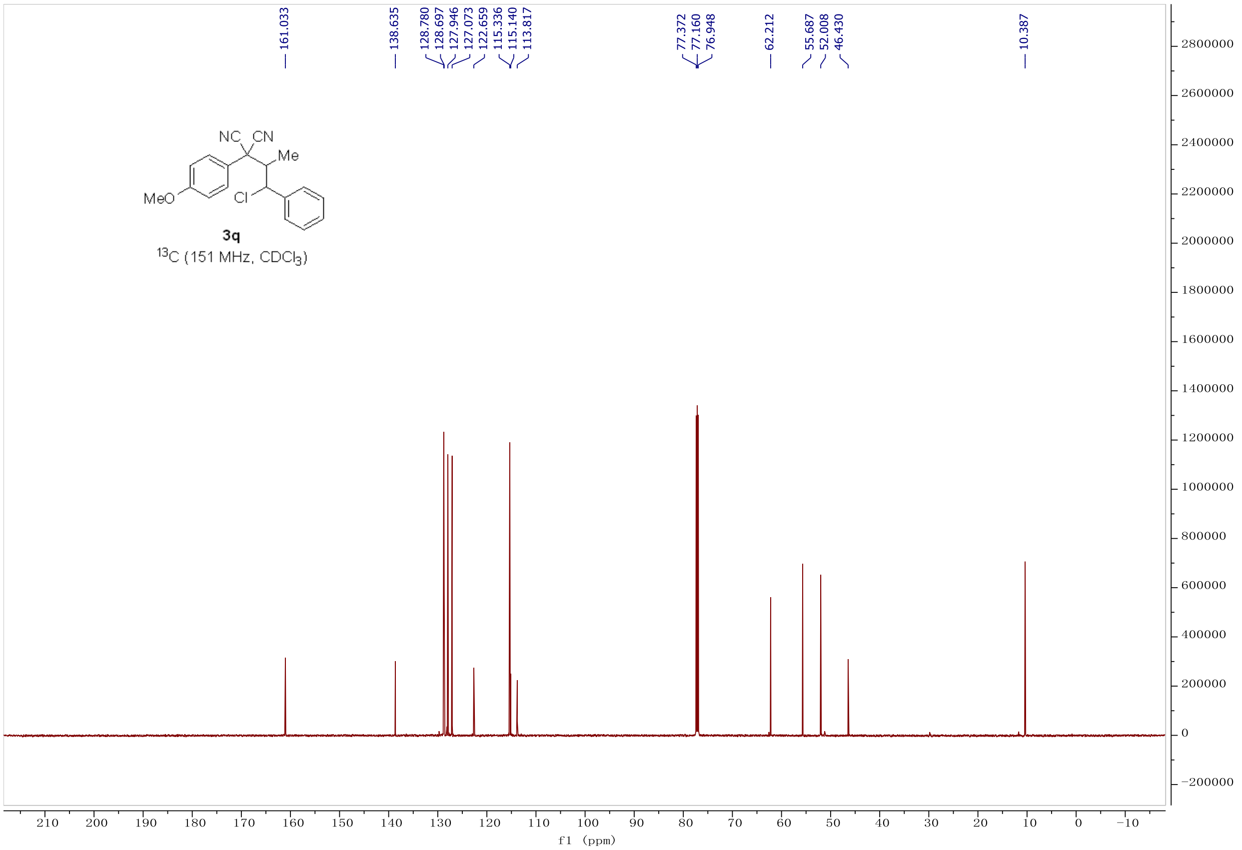
3p

^{13}C (151 MHz, CDCl$_3$)



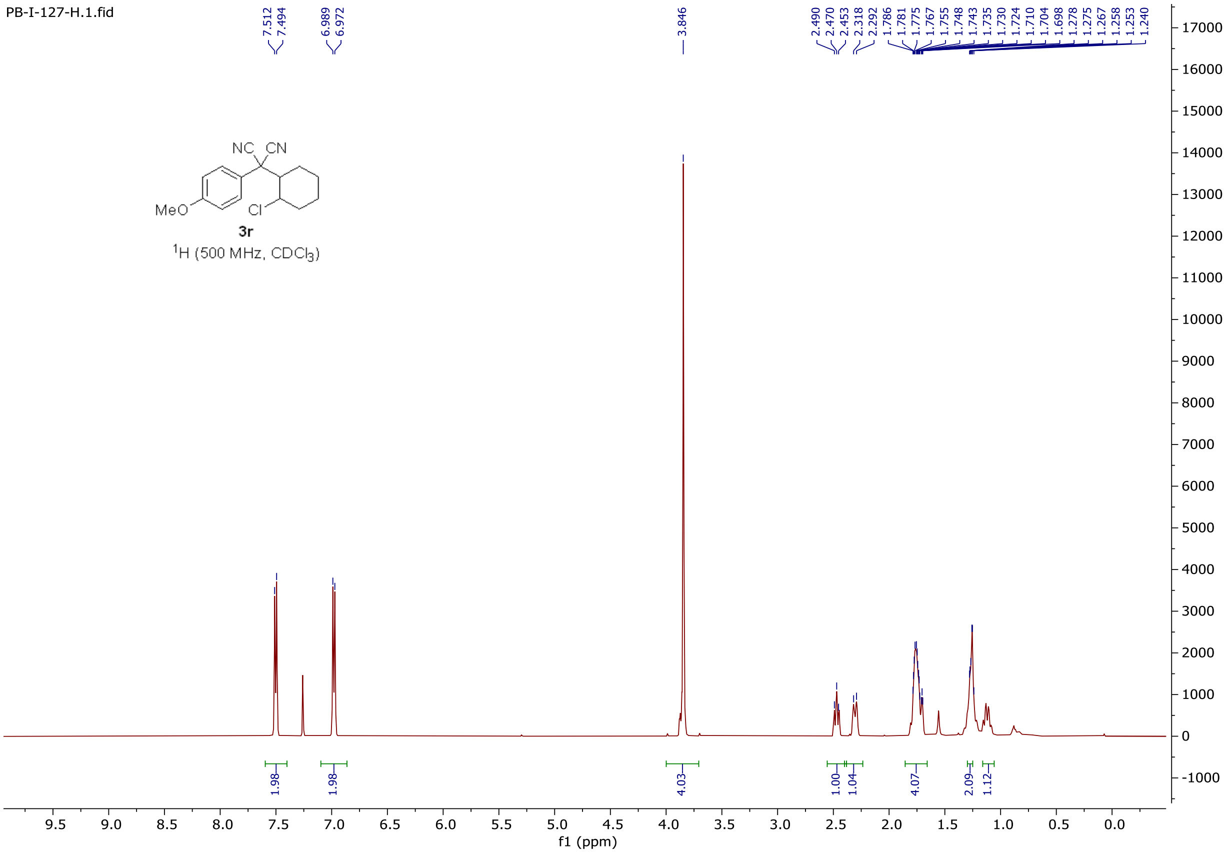
3q

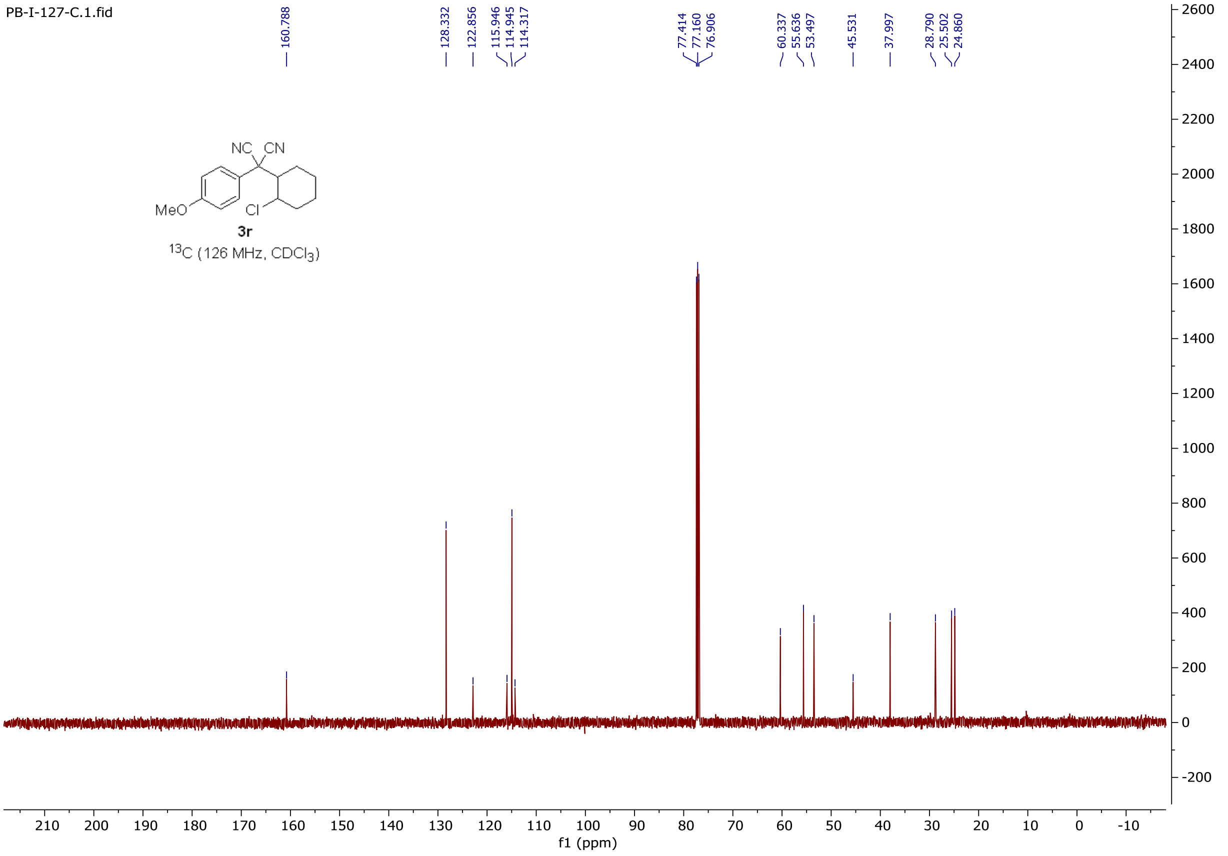
^1H (600 MHz, $CDCl_3$)

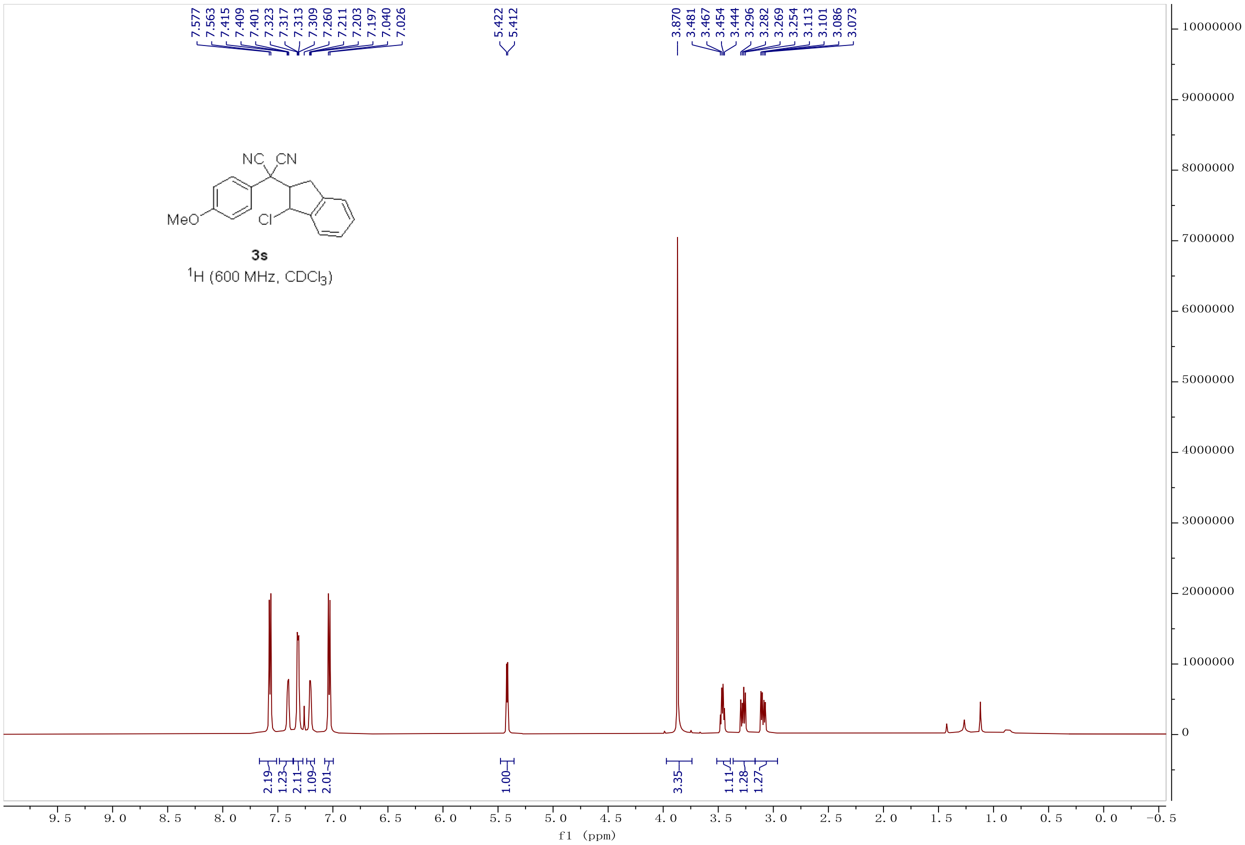


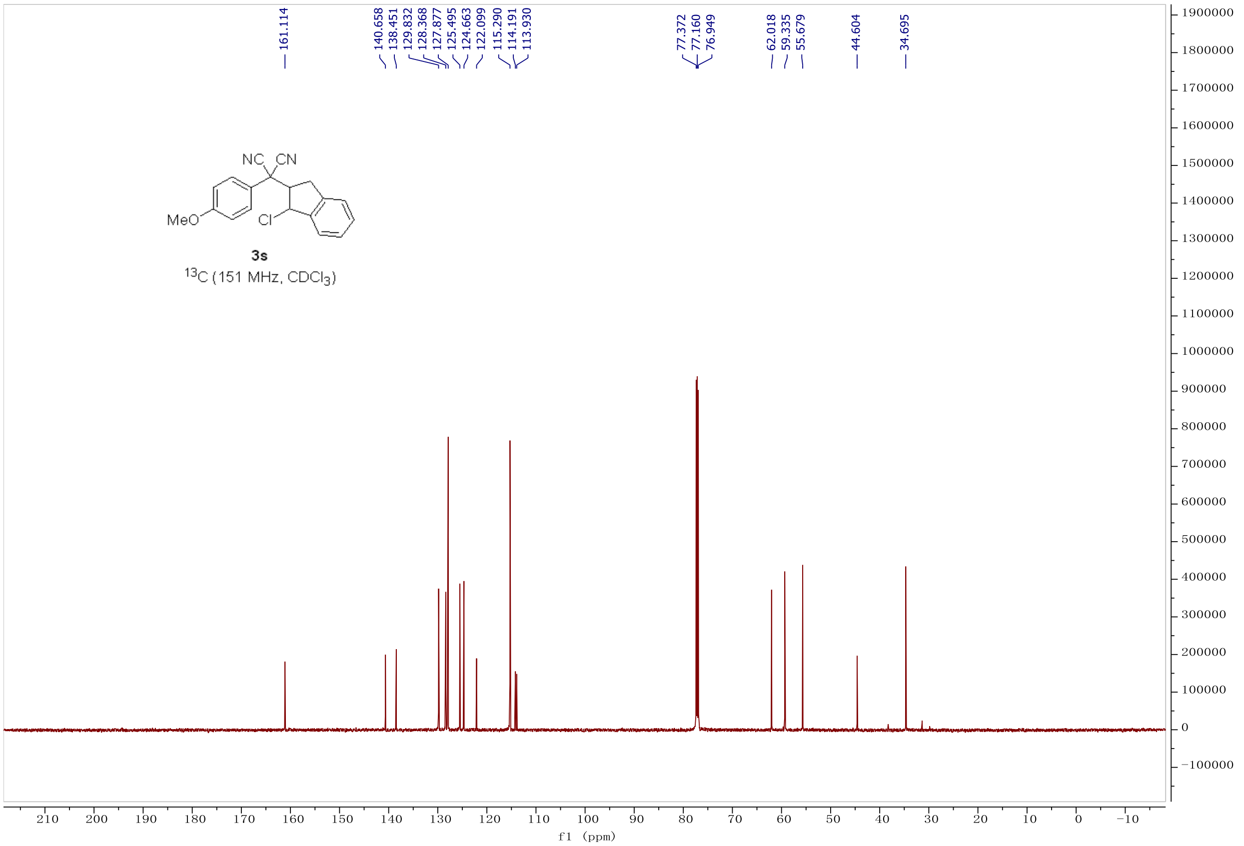
3q

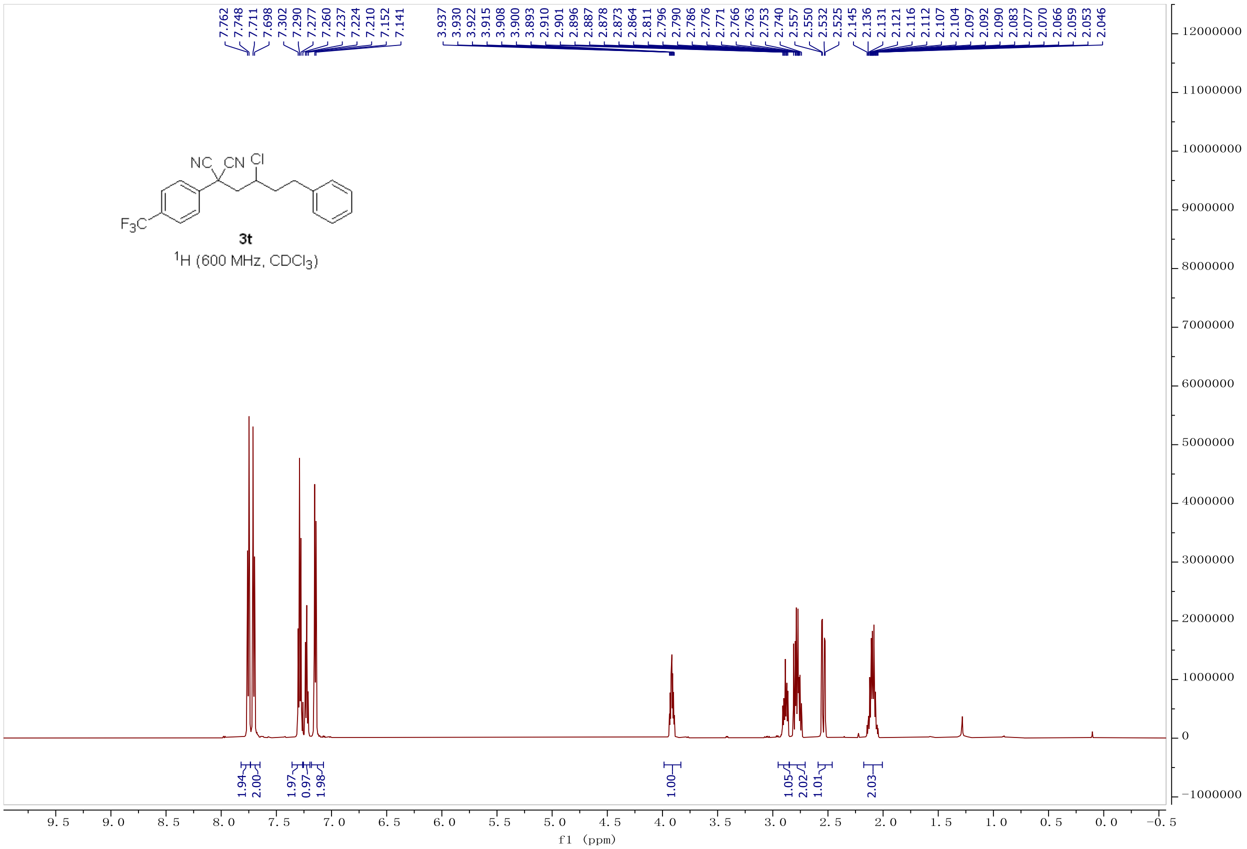
^{13}C (151 MHz, $CDCl_3$)

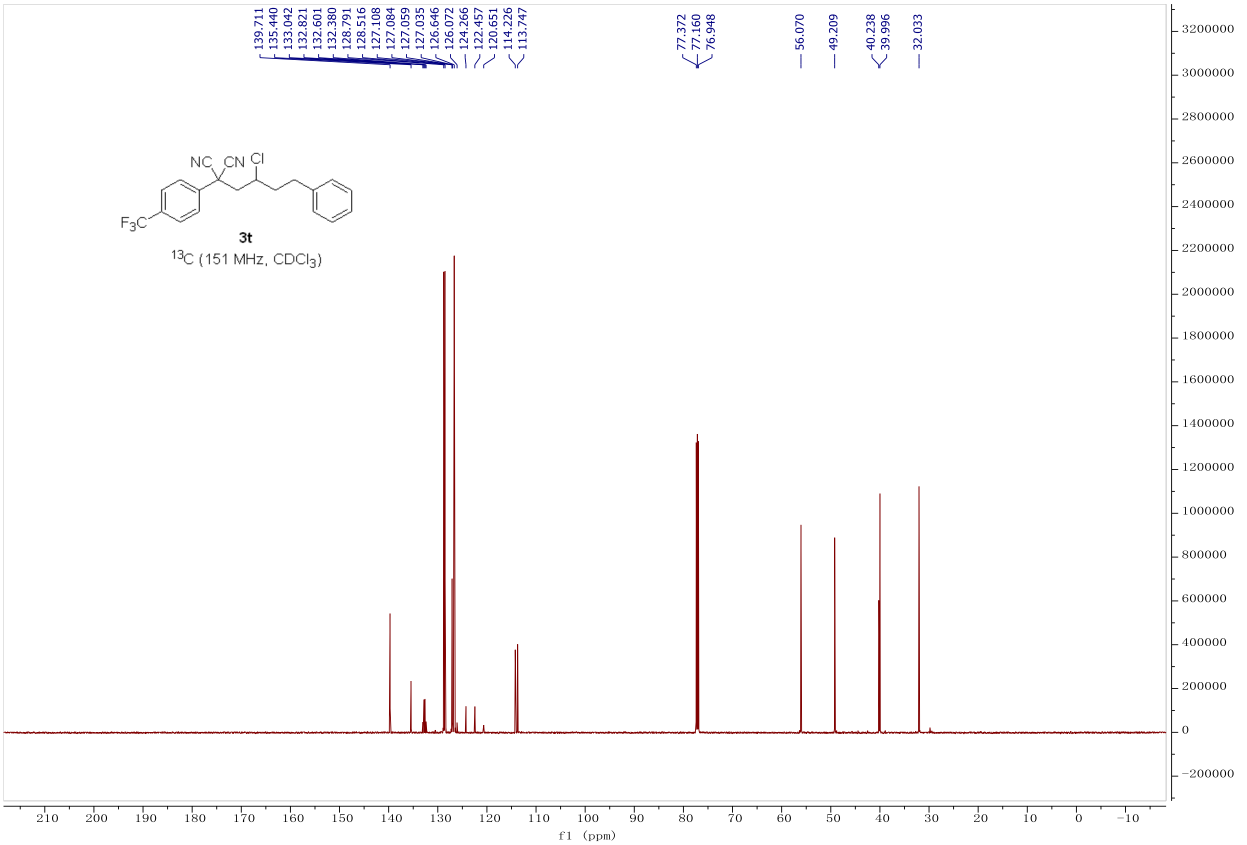

PB-I-127-H.1.fid
7.512
7.494
6.989
6.972
3.846
2.490
2.470
2.453
2.318
2.292
1.786
1.781
1.775
1.767
1.755
1.748
1.743
1.735
1.730
1.724
1.710
1.704
1.698
1.278
1.275
1.267
1.258
1.253
1.240
NC CN
MeO
Cl
3r
^{1}H (500 MHz, CDCl$_3$)
1.98
1.98
4.03
1.00
1.04
4.07
2.09
1.12
f1 (ppm)

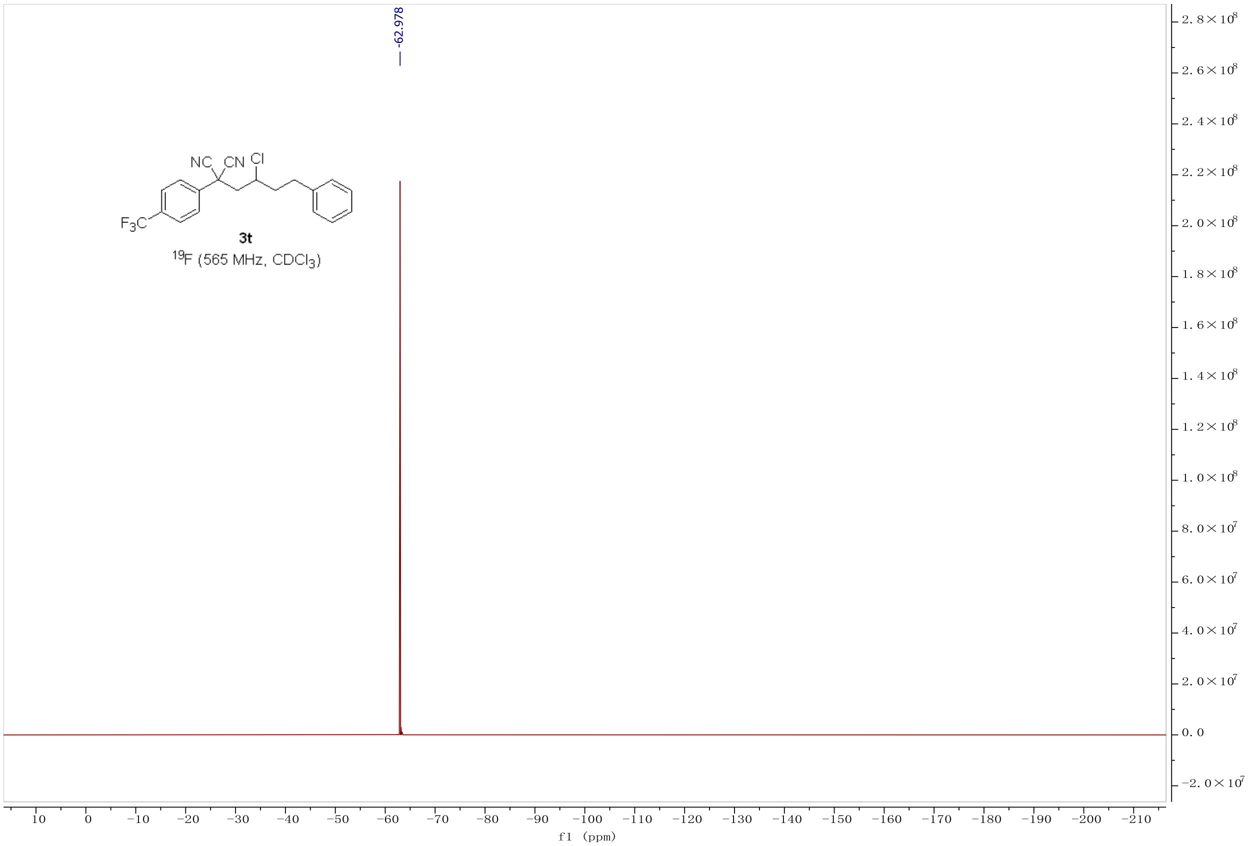

PB-I-127-C.1.fid
160.788
128.332
122.856
115.946
114.945
114.317
77.414
77.160
76.906
60.337
55.636
53.497
45.531
37.997
28.790
25.502
24.860
NC CN
MeO
Cl
3r
^{13}C (126 MHz, CDCl$_3$)
f1 (ppm)


7.577
7.563
7.415
7.409
7.401
7.323
7.317
7.313
7.309
7.260
7.211
7.203
7.197
7.040
7.026
5.422
5.412
3.870
3.481
3.467
3.454
3.444
3.296
3.282
3.269
3.254
3.113
3.101
3.086
3.073
NC
CN
MeO
Cl
3s
1H (600 MHz, CDCl3)
2.19
1.23
2.11
1.09
2.01
1.00
3.35
1.11
1.28
1.27
f1 (ppm)


161.114
140.658
138.451
129.832
128.368
127.877
125.495
124.663
122.099
115.290
114.191
113.930
77.372
77.160
76.949
62.018
59.335
55.679
44.604
34.695
NC
CN
MeO
Cl
3s
13C (151 MHz, CDCl3)
f1 (ppm)

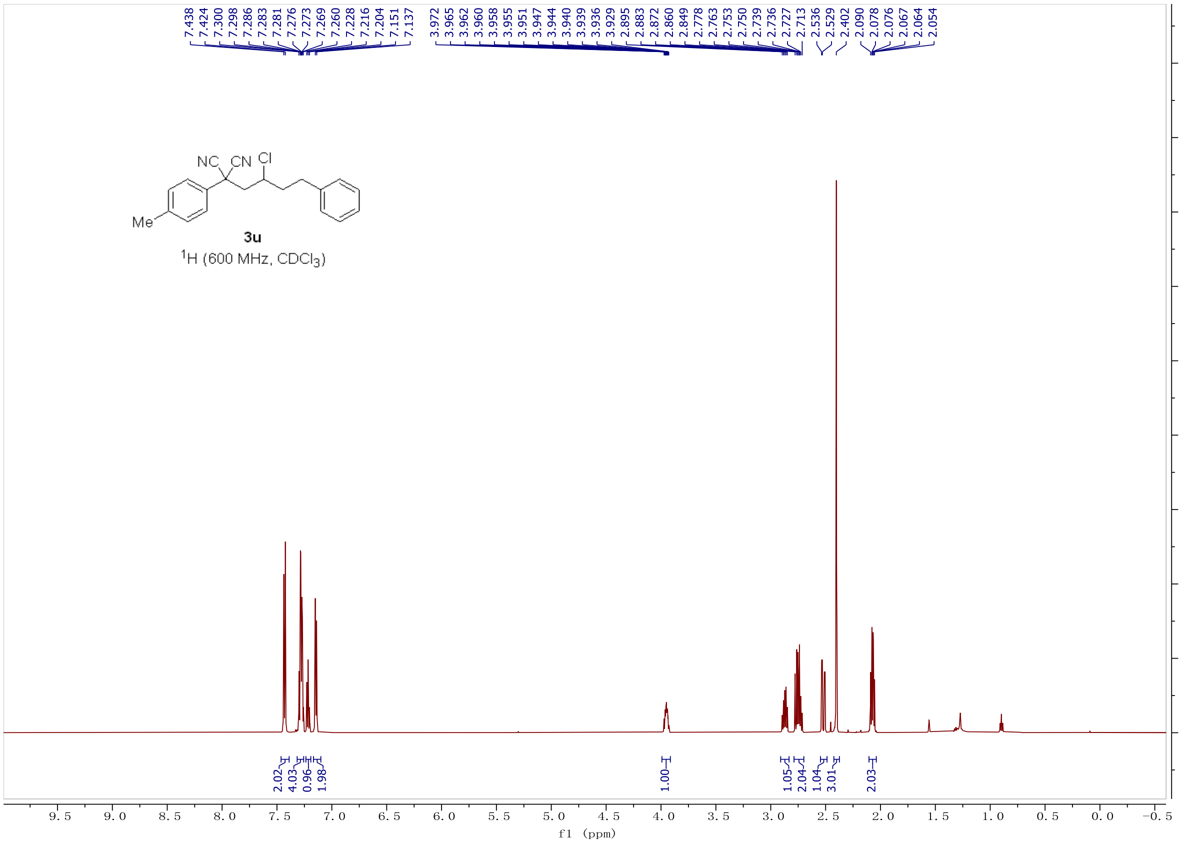

7.762
7.748
7.711
7.698
7.302
7.290
7.277
7.260
7.237
7.224
7.210
7.152
7.141
3.937
3.930
3.922
3.915
3.908
3.900
3.893
2.910
2.901
2.896
2.887
2.878
2.873
2.864
2.811
2.796
2.790
2.786
2.776
2.771
2.766
2.763
2.753
2.740
2.557
2.550
2.532
2.525
2.145
2.136
2.131
2.121
2.116
2.112
2.107
2.104
2.097
2.092
2.090
2.083
2.077
2.070
2.066
2.059
2.053
2.046
NC
CN
Cl
F3C
3t
1H (600 MHz, CDCl3)
1.94
2.00
1.97
0.97
1.98
1.00
1.05
2.02
1.01
2.03
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)
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000


139.711
135.440
133.042
132.821
132.601
132.380
128.791
128.516
127.108
127.084
127.059
127.035
126.646
126.072
124.266
122.457
120.651
114.226
113.747
77.372
77.160
76.948
56.070
49.209
40.238
39.996
32.033
NC
CN
Cl
F3C
3t
13C (151 MHz, CDCl3)
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)
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000



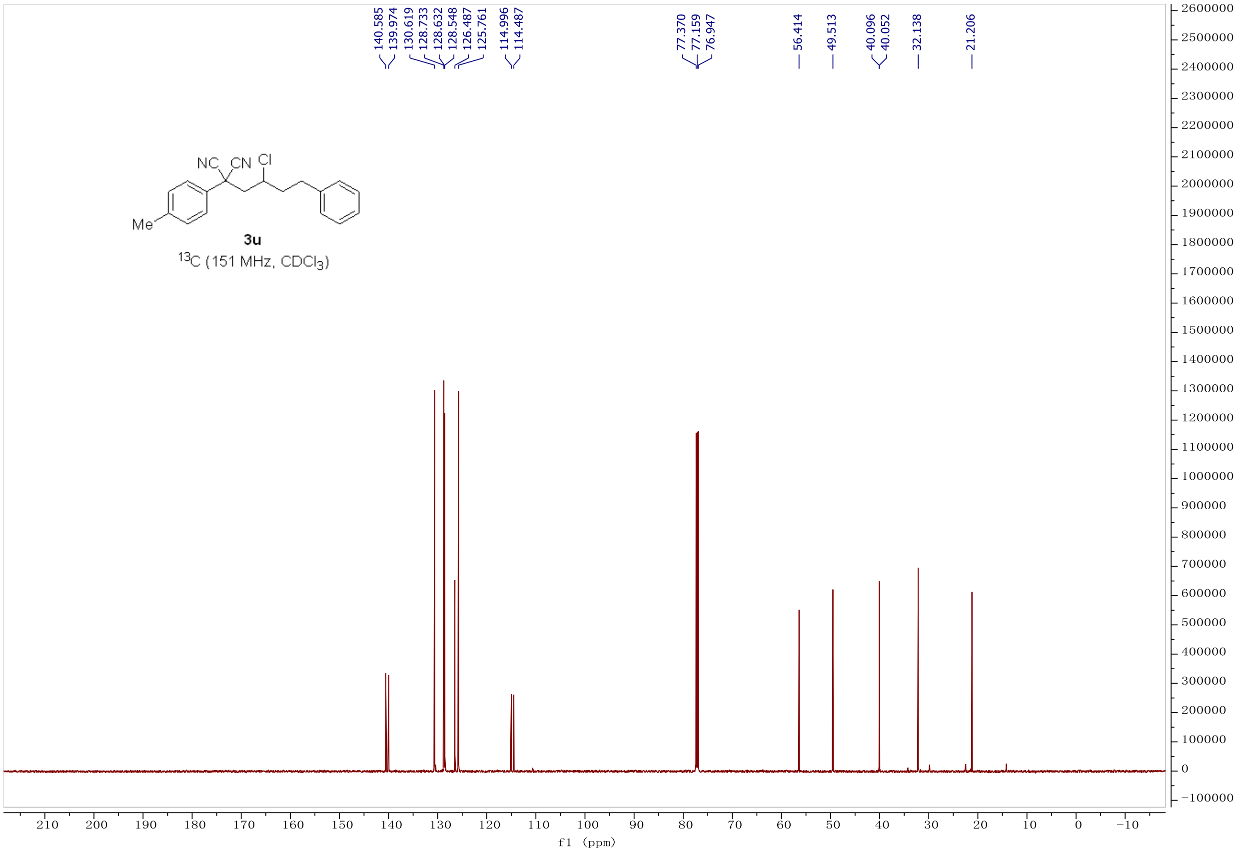
3t

^{19}F (565 MHz, CDCl$_3$)

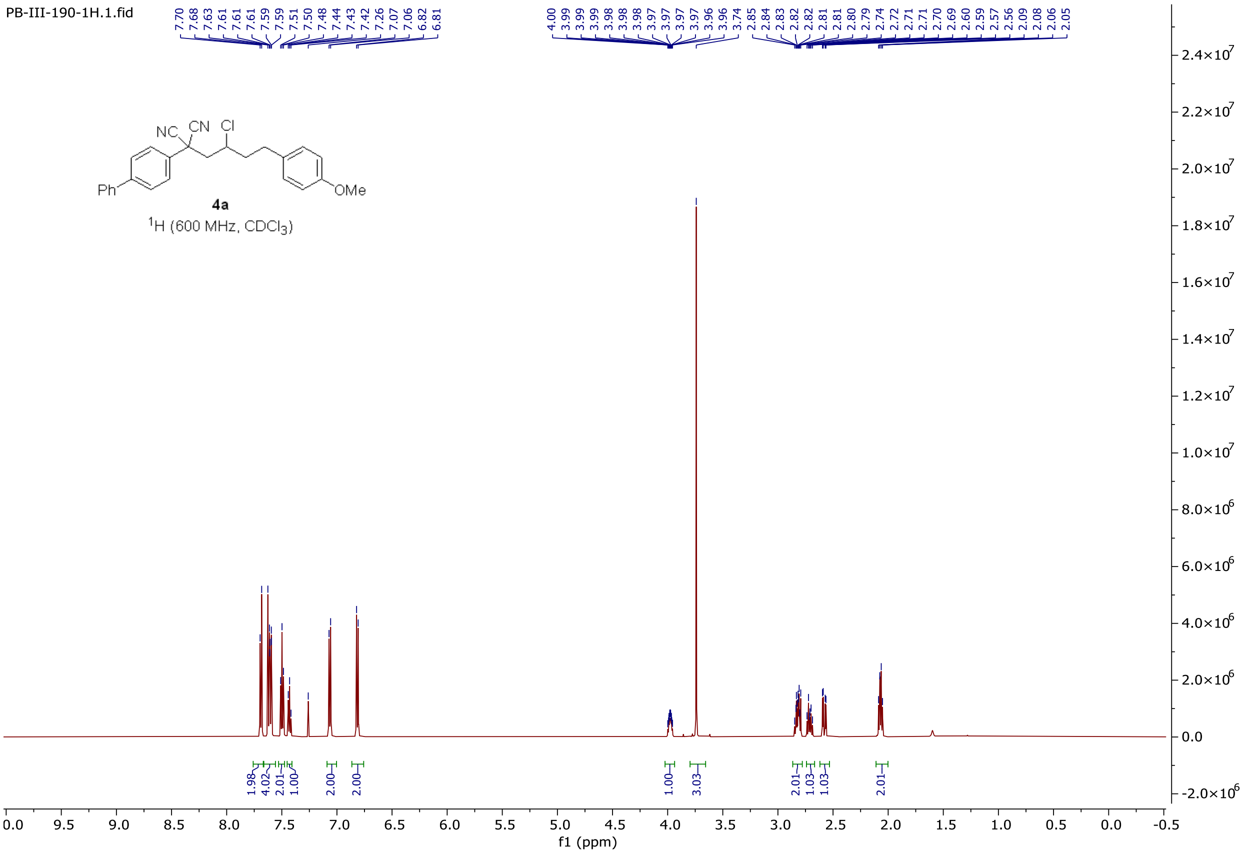


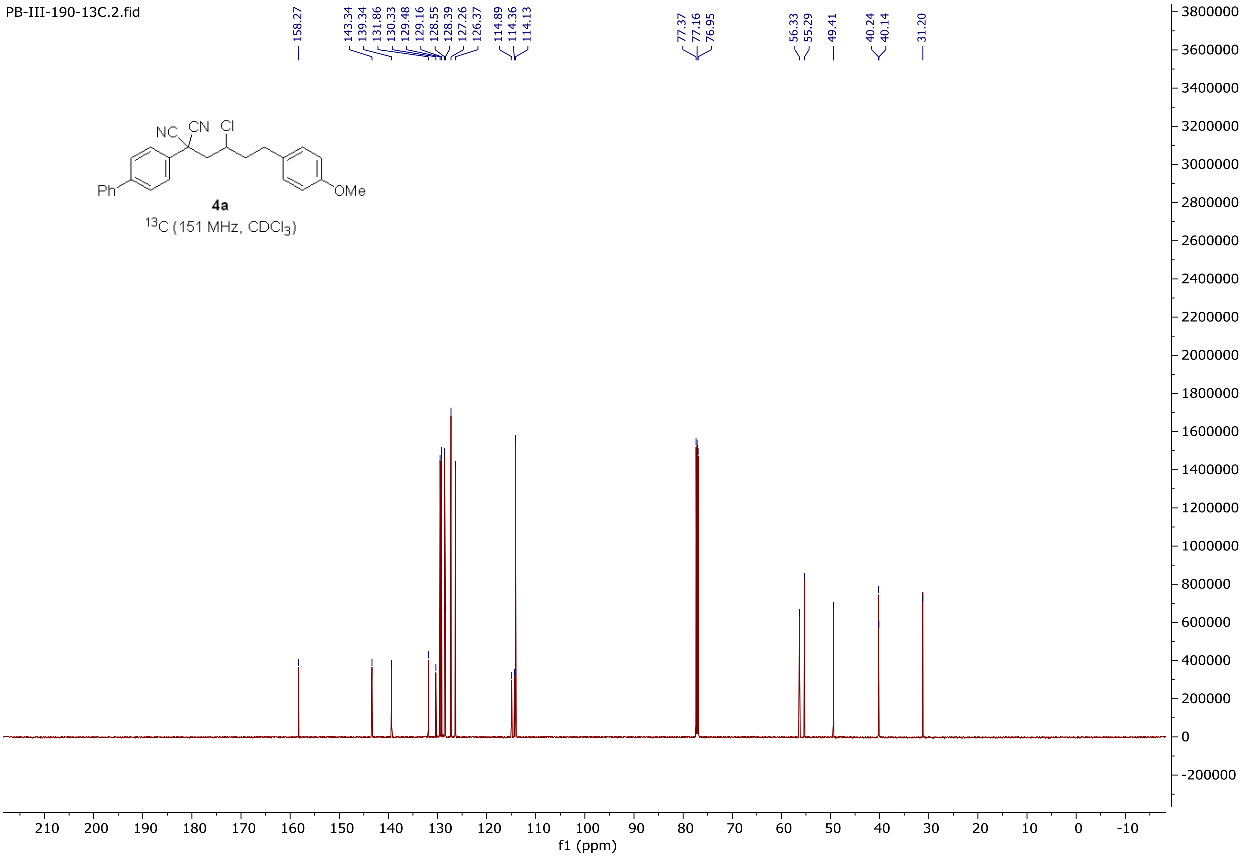
3u

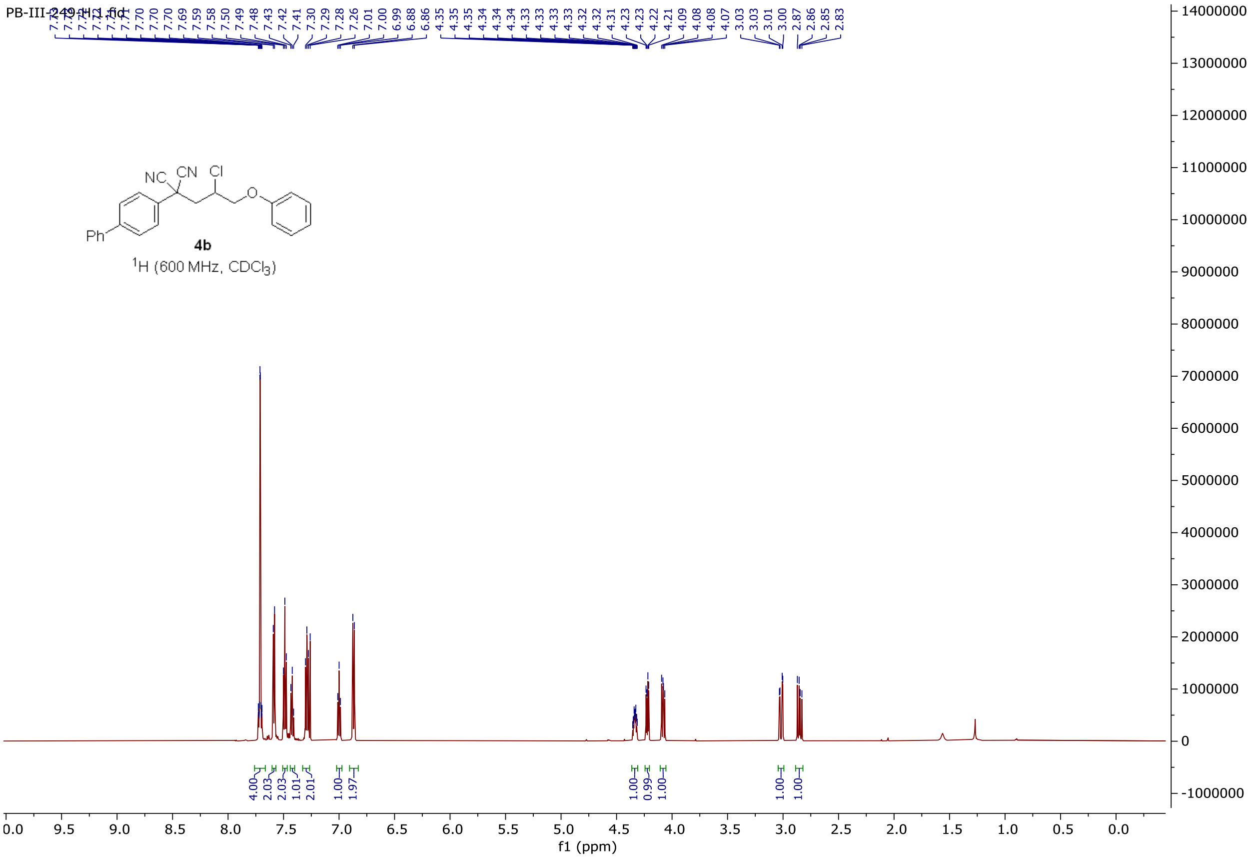
^{1}H (600 MHz, CDCl$_3$)

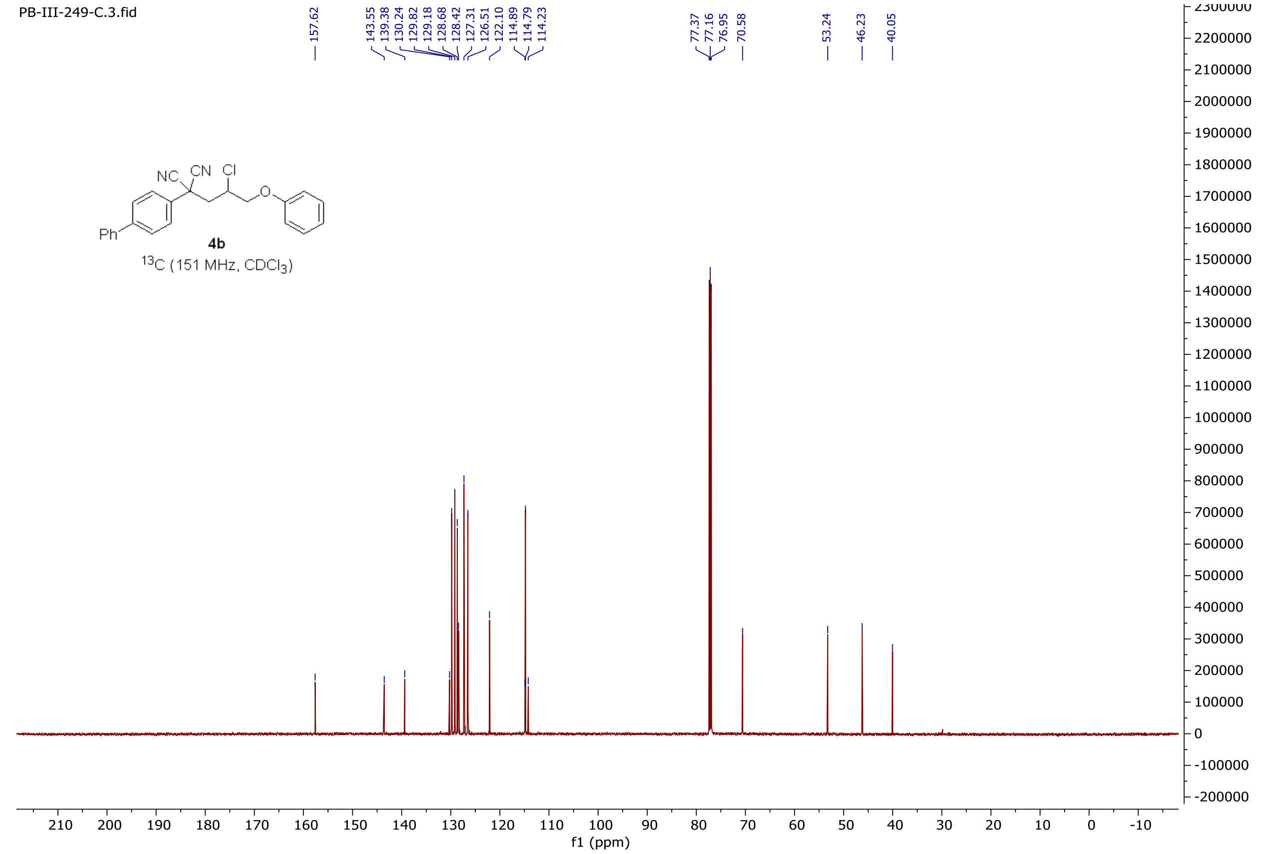


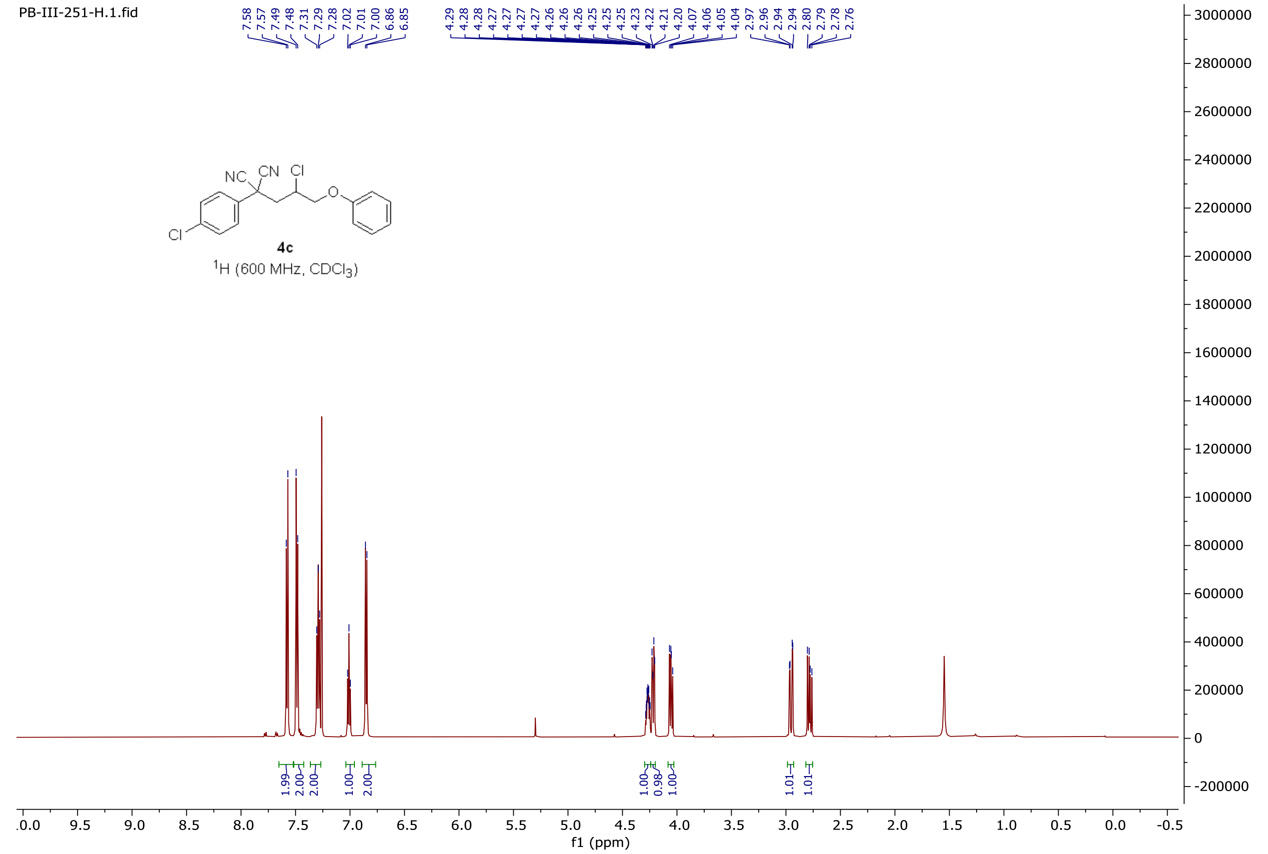
PB-III-190-1H.1.fid

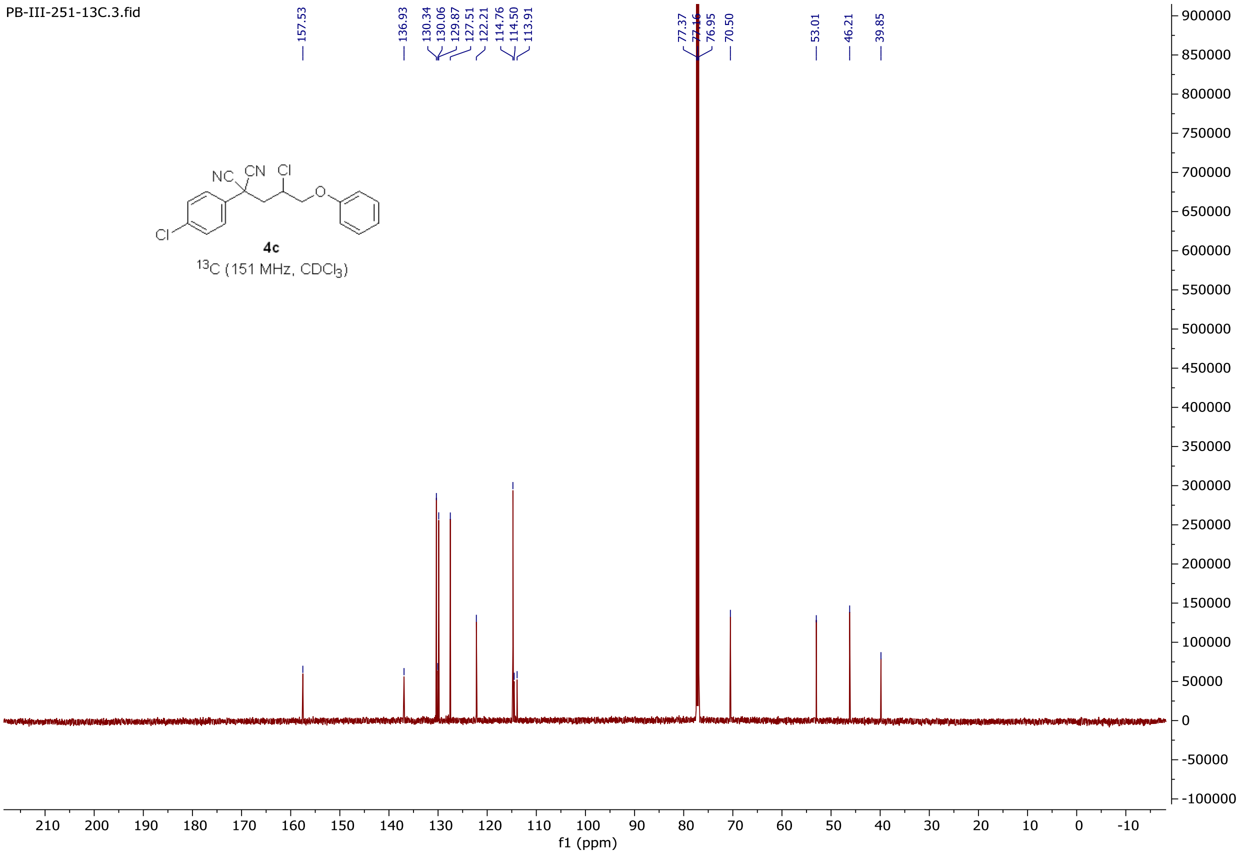


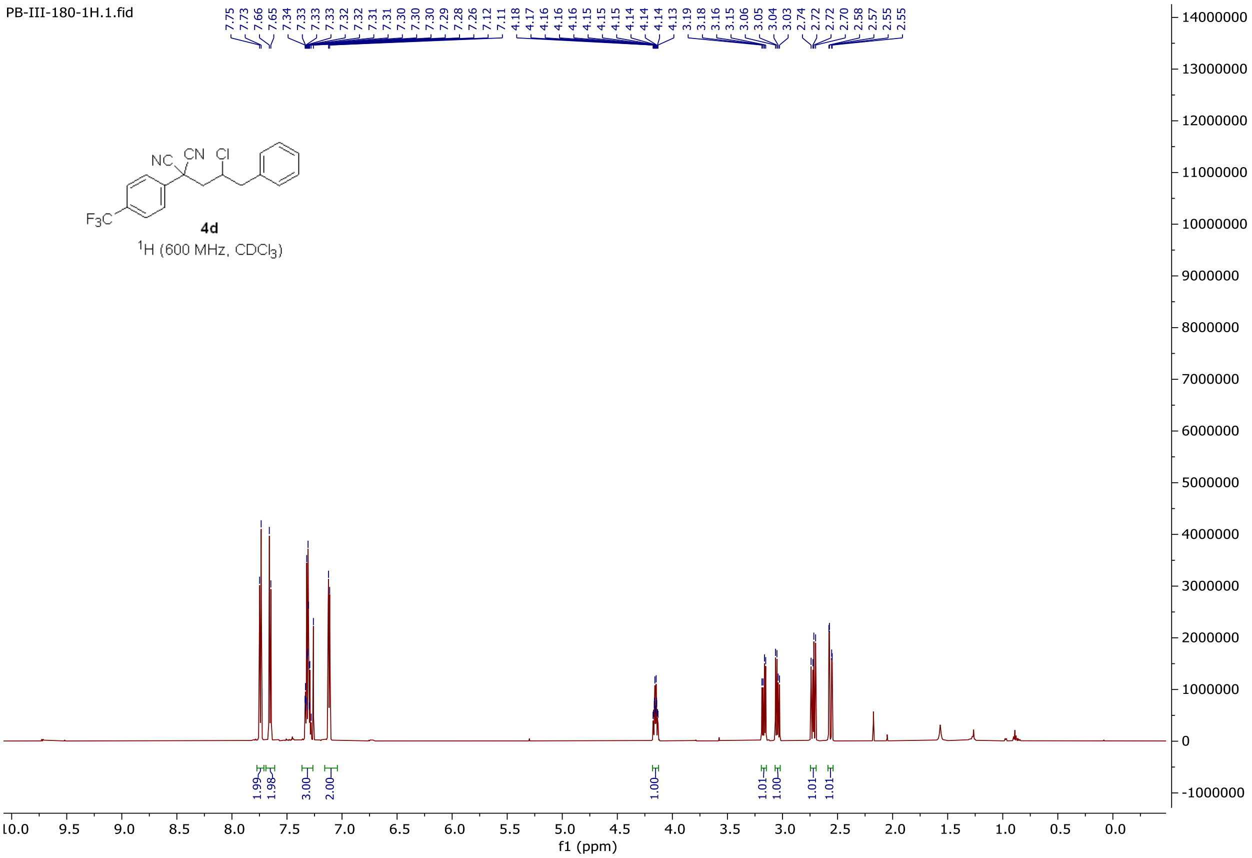

PB-III-190-13C.2.fid
158.27
143.34
139.34
131.86
130.33
129.48
129.16
128.55
128.39
127.26
126.37
114.89
114.36
114.13
77.37
77.16
76.95
56.33
55.29
49.41
40.24
40.14
31.20
NC
CN
Cl
Ph
OMe
4a
13C (151 MHz, CDCl3)
3800000
3600000
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
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)

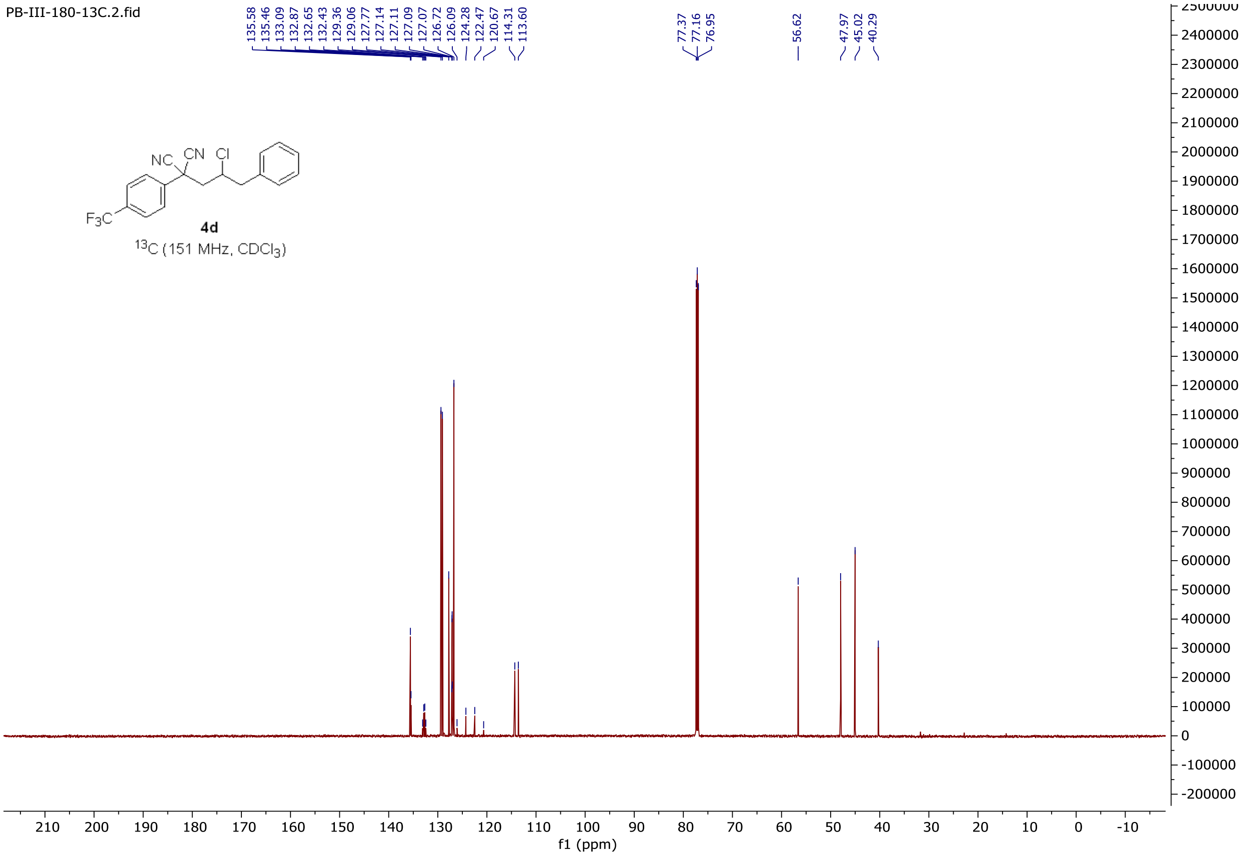

PB-III-249-H.1.fid
7.72
7.70
7.70
7.70
7.69
7.59
7.58
7.50
7.49
7.48
7.43
7.42
7.41
7.30
7.29
7.28
7.26
7.01
7.00
6.99
6.88
6.86
4.35
4.35
4.35
4.34
4.34
4.34
4.33
4.33
4.33
4.33
4.32
4.32
4.31
4.23
4.23
4.22
4.21
4.09
4.08
4.08
4.07
3.03
3.03
3.01
3.00
2.87
2.86
2.85
2.83
NC
CN
Cl
O
Ph
4b
1H (600 MHz, CDCl3)
4.00
2.03
2.03
1.01
2.01
1.00
1.97
1.00
0.99
1.00
1.00
1.00
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
0.0
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)

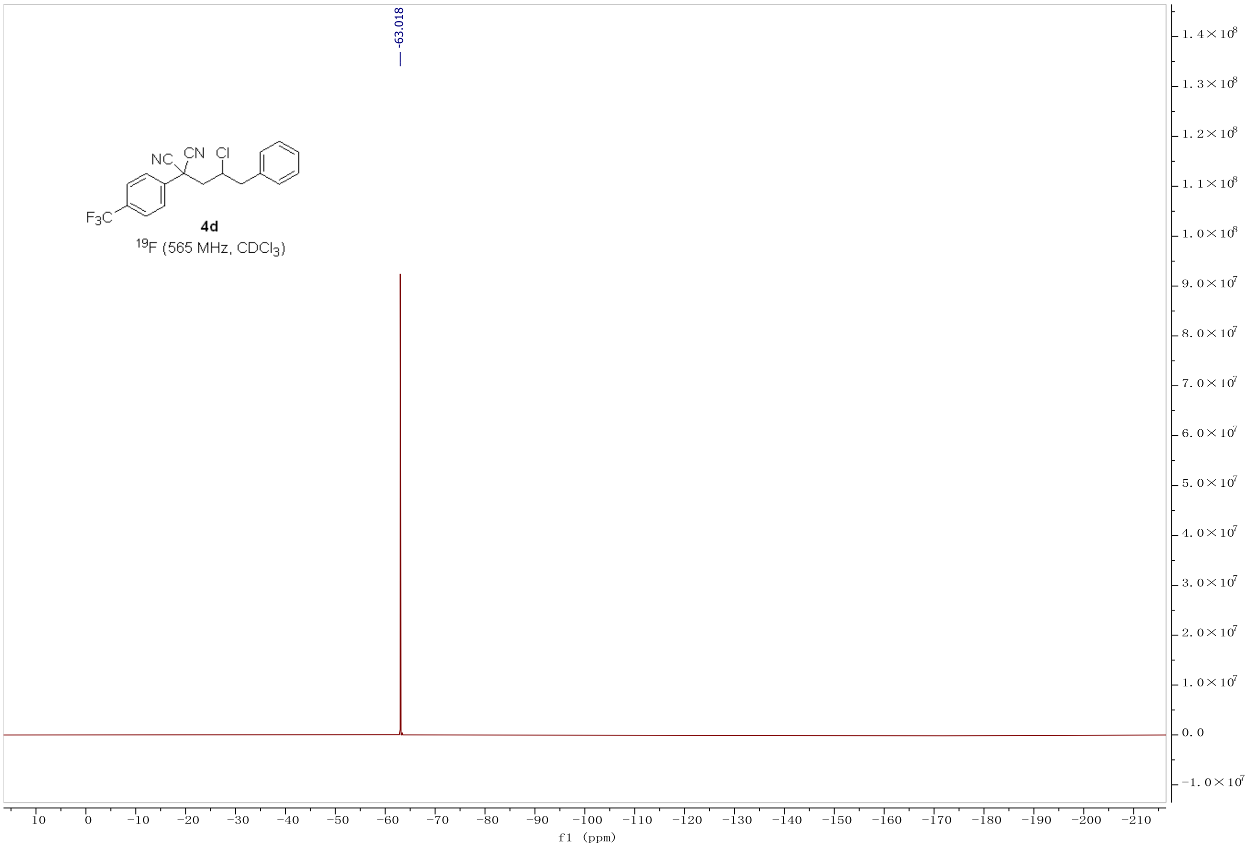

PB-III-249-C.3.fid
157.62
143.55
139.38
130.24
129.82
129.18
128.68
128.42
127.31
126.51
122.10
114.89
114.79
114.23
77.37
77.16
76.95
70.58
53.24
46.23
40.05
NC
CN
Cl
O
Ph
4b
^{13}C (151 MHz, CDCl$_3$)
f1 (ppm)

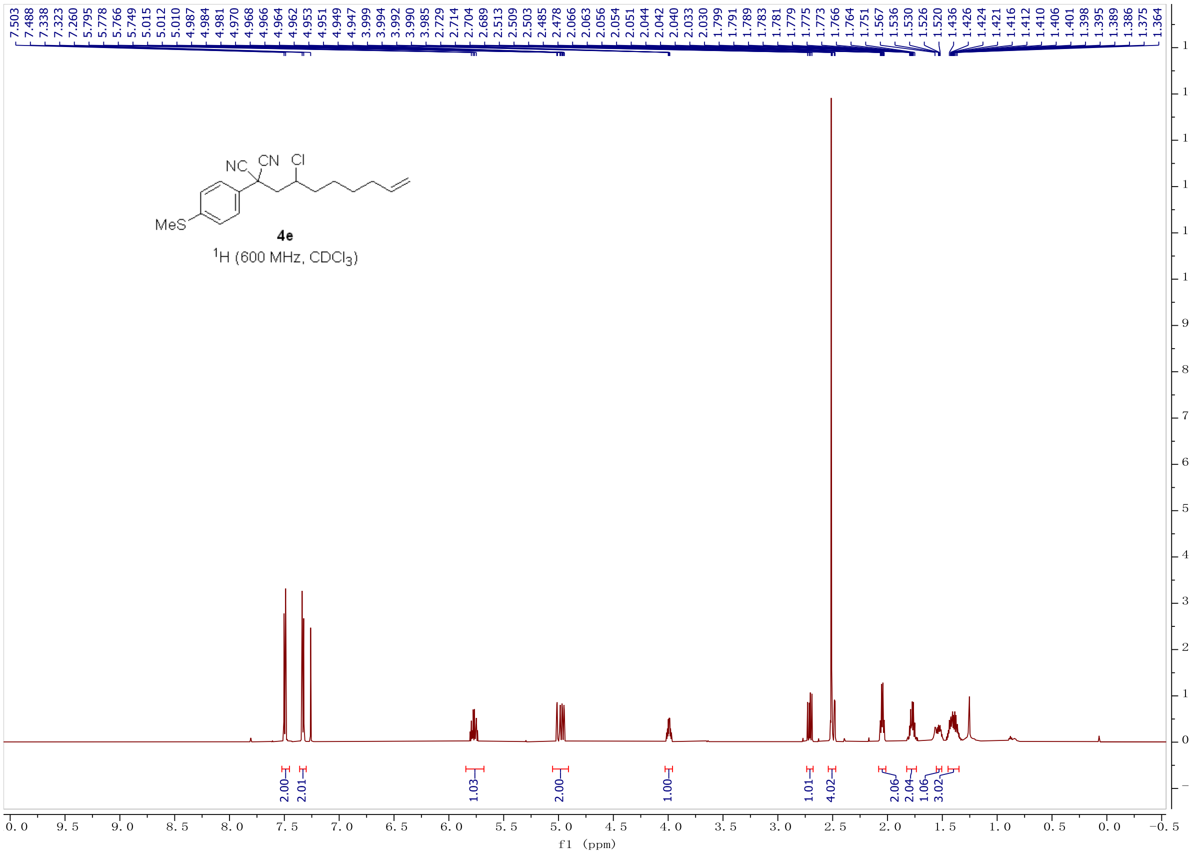

PB-III-251-H.1.fid
7.58
7.57
7.49
7.48
7.31
7.29
7.28
7.02
7.01
7.00
6.86
6.85
4.29
4.28
4.28
4.27
4.27
4.27
4.27
4.26
4.26
4.25
4.25
4.25
4.23
4.22
4.21
4.20
4.07
4.06
4.05
4.04
2.97
2.96
2.94
2.94
2.80
2.79
2.78
2.76
NC
CN
Cl
O
Cl
4c
^{1}H (600 MHz, CDCl$_3$)
1.99
2.00
2.00
1.00
2.00
1.00
0.98
1.00
1.01
1.01
f1 (ppm)

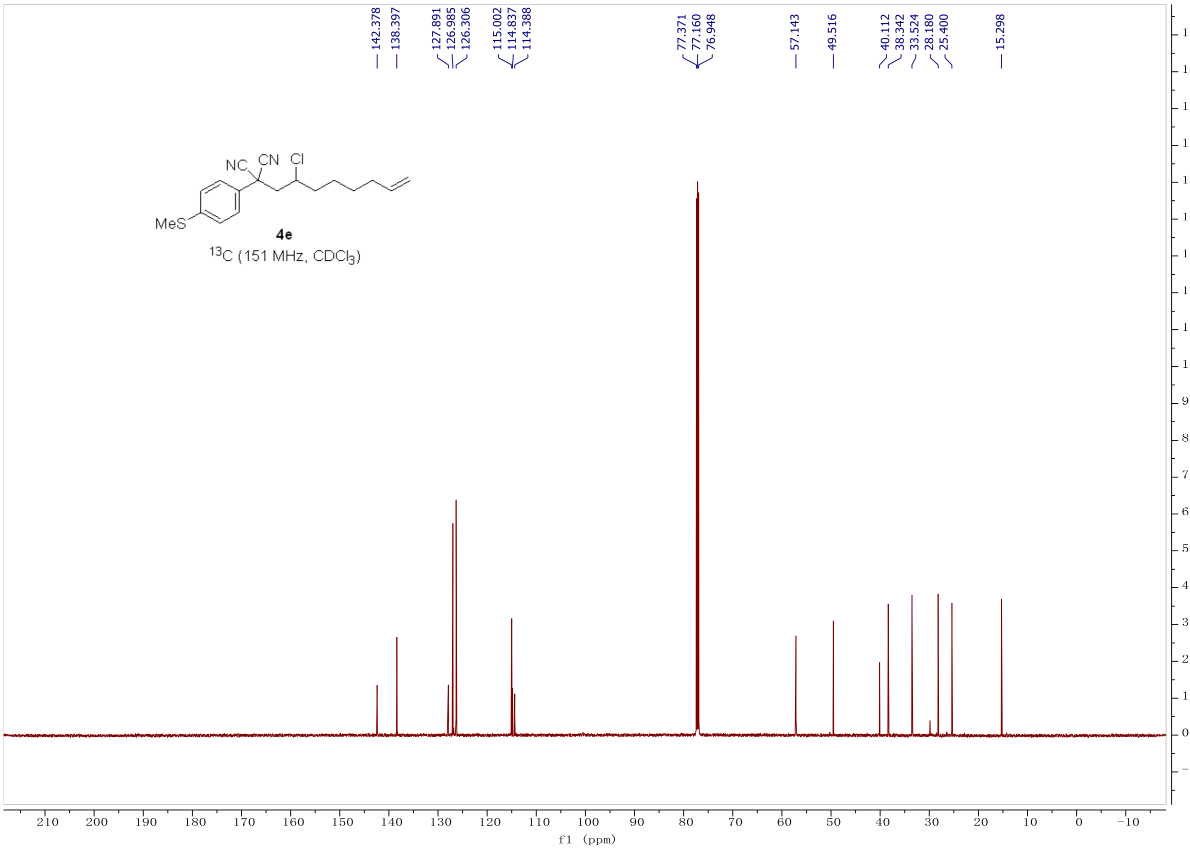

PB-III-251-13C.3.fid
157.53
136.93
130.34
130.06
129.87
127.51
122.21
114.76
114.50
113.91
77.37
77.16
76.95
70.50
53.01
46.21
39.85
NC
CN
Cl
O
Cl
4c
^{13}C (151 MHz, CDCl$_3$)
900000
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
-100000
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)

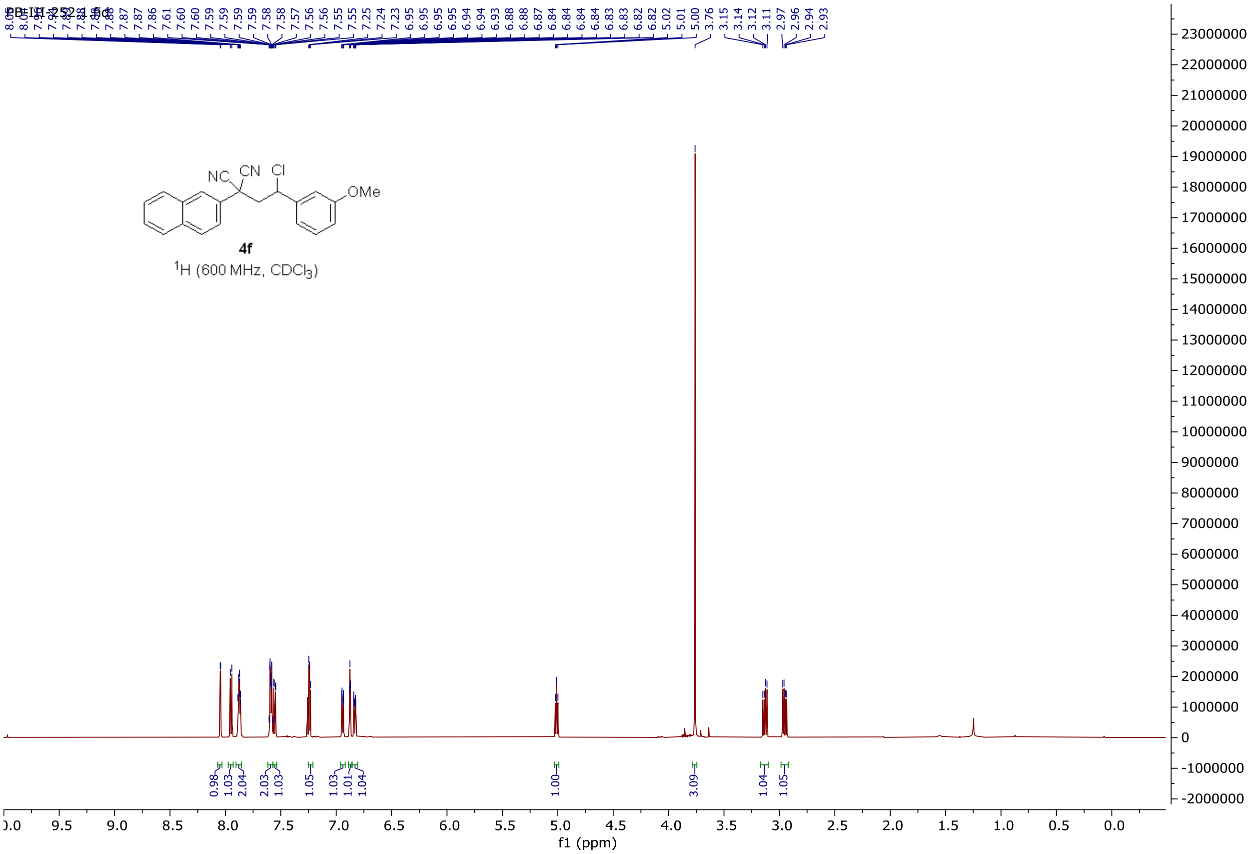

PB-III-180-1H.1.fid
7.75
7.73
7.66
7.65
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.28
7.26
7.12
7.11
4.18
4.17
4.16
4.16
4.16
4.15
4.15
4.15
4.14
4.14
4.14
4.13
3.19
3.18
3.16
3.15
3.06
3.05
3.04
3.03
2.74
2.72
2.72
2.70
2.58
2.57
2.55
2.55
NC
CN
Cl
F$_3$C
4d
^{1}H (600 MHz, CDCl$_3$)
1.99
1.98
3.00
2.00
1.00
1.01
1.00
1.01
1.01
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
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)


PB-III-180-13C.2.fid
135.58
135.46
133.09
132.87
132.65
132.43
129.36
129.06
127.77
127.14
127.11
127.09
127.07
126.72
126.09
124.28
122.47
120.67
114.31
113.60
77.37
77.16
76.95
56.62
47.97
45.02
40.29
NC
CN
Cl
F3C
4d
13C (151 MHz, CDCl3)
2500000
2400000
2300000
2200000
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
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)


-63.018
NC
CN
Cl
F3C
4d
19F (565 MHz, CDCl3)
1.4×10^8
1.3×10^8
1.2×10^8
1.1×10^8
1.0×10^8
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
-1.0×10^7
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

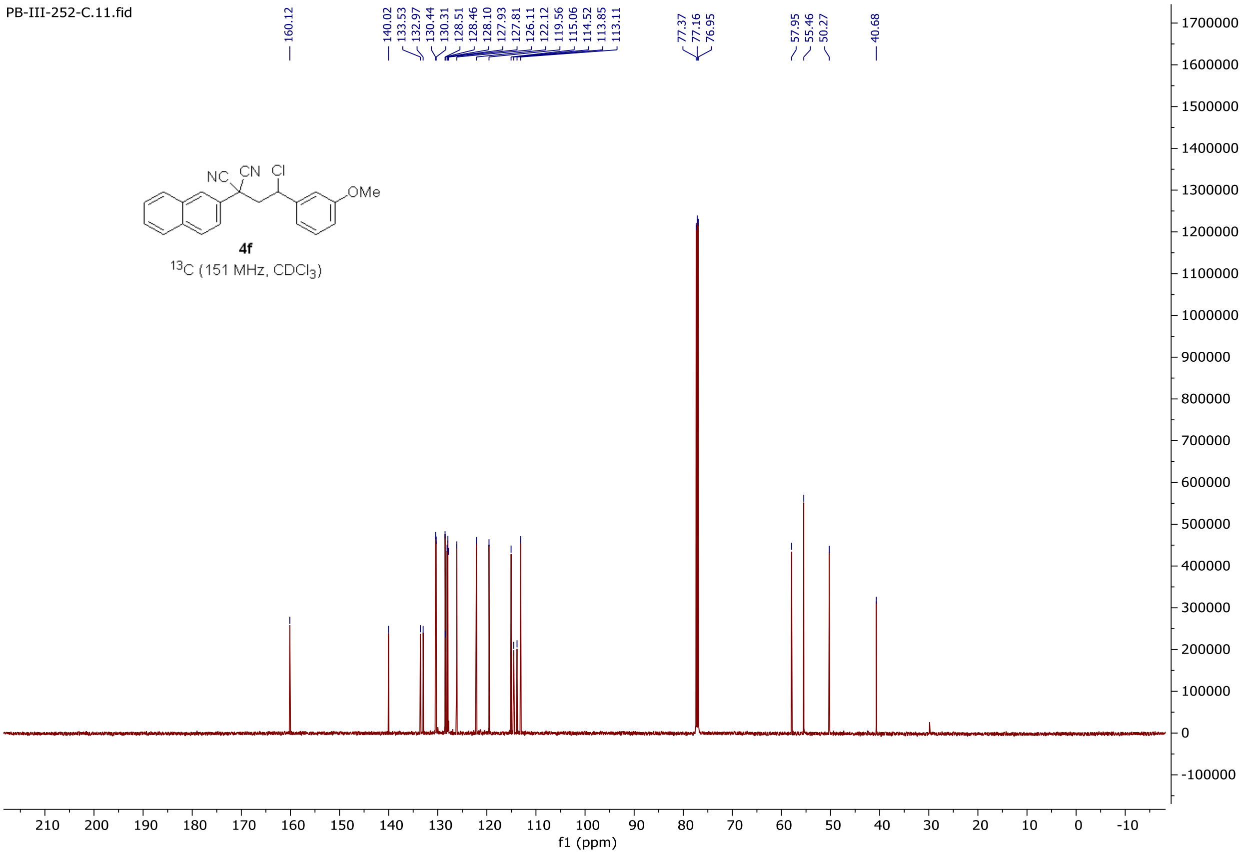

7.503
7.488
7.338
7.323
7.260
5.795
5.778
5.766
5.749
5.015
5.012
5.010
4.987
4.984
4.981
4.970
4.968
4.966
4.964
4.962
4.953
4.951
4.949
4.947
3.999
3.994
3.992
3.990
3.985
2.729
2.714
2.704
2.689
2.513
2.509
2.503
2.485
2.478
2.066
2.063
2.056
2.054
2.051
2.044
2.042
2.040
2.033
2.030
1.799
1.791
1.789
1.783
1.781
1.779
1.775
1.773
1.766
1.764
1.751
1.567
1.536
1.530
1.526
1.520
1.436
1.426
1.424
1.421
1.416
1.412
1.410
1.406
1.401
1.398
1.395
1.389
1.386
1.375
1.364
NC
CN
Cl
MeS
4e
^{1}H (600 MHz, CDCl$_3$)
2.00
2.01
1.03
2.00
1.00
1.01
4.02
2.06
2.04
1.06
3.02
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
0.0
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)


142.378
138.397
127.891
126.985
126.306
115.002
114.837
114.388
77.371
77.160
76.948
57.143
49.516
40.112
38.342
33.524
28.180
25.400
15.298
NC
CN
Cl
MeS
4e
^{13}C (151 MHz, CDCl$_3$)
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
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)



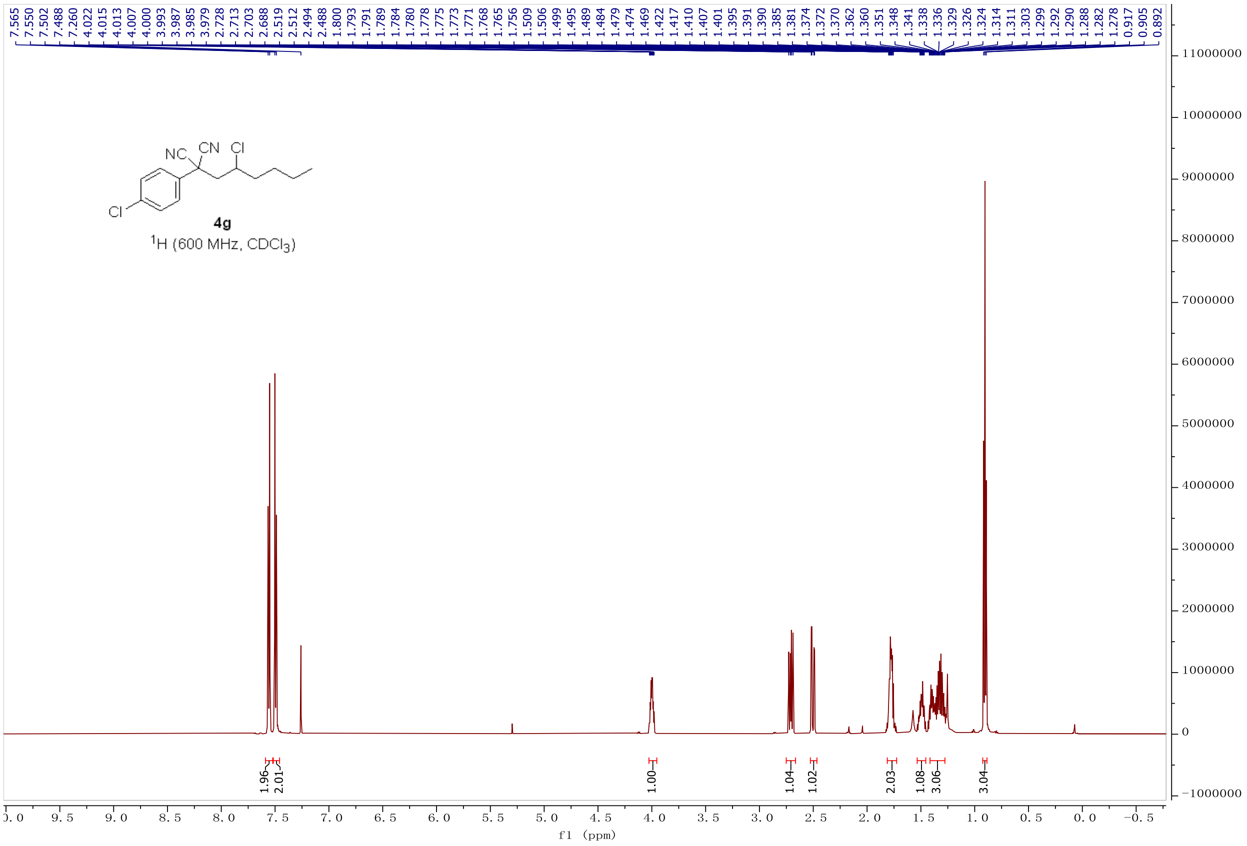
4f

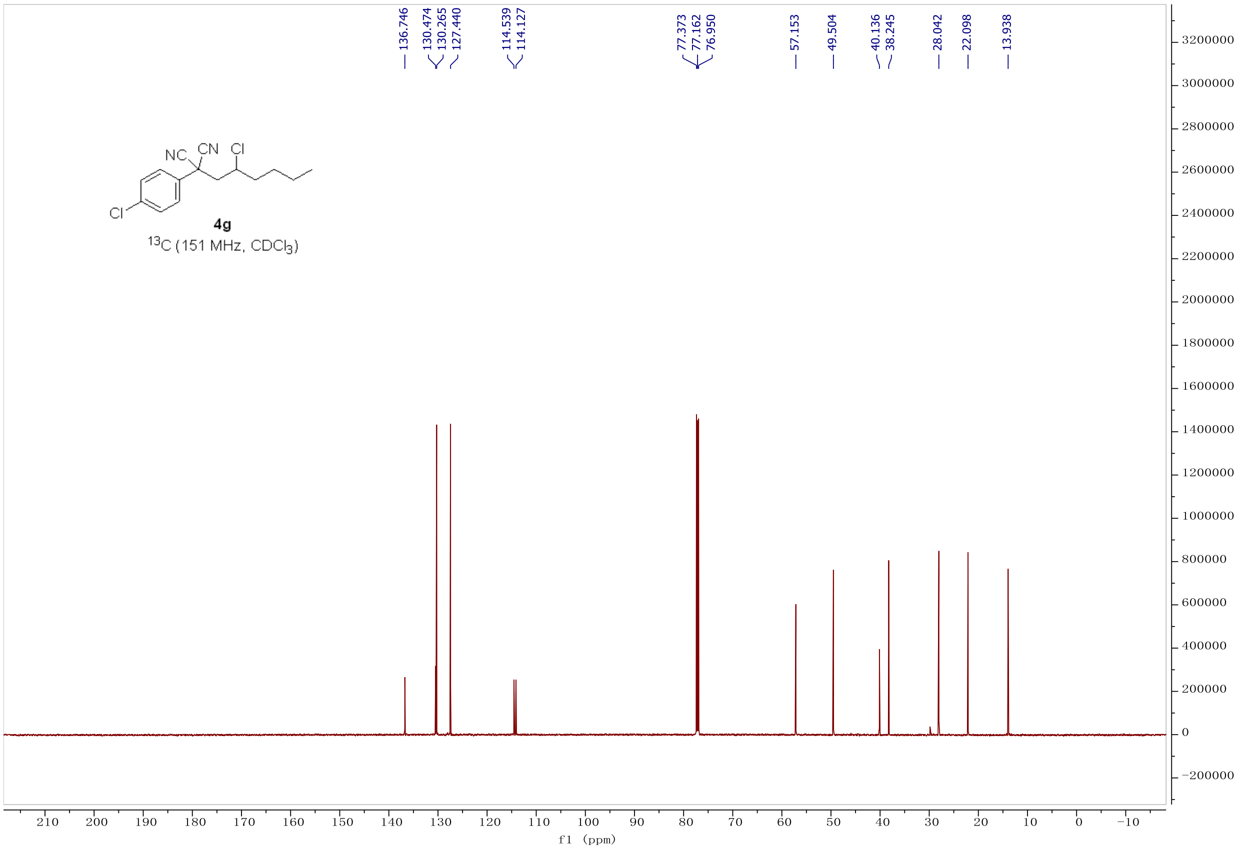
^{1}H (600 MHz, CDCl$_3$)

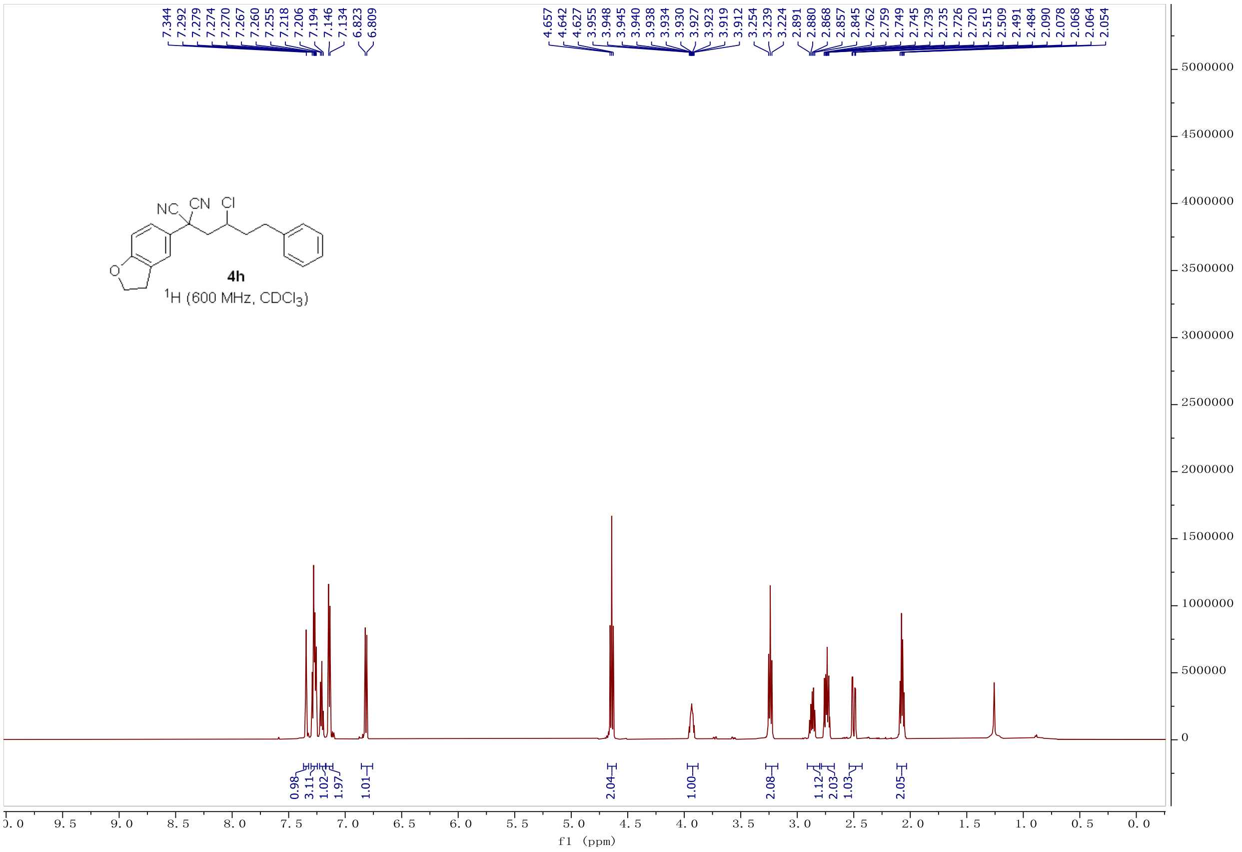


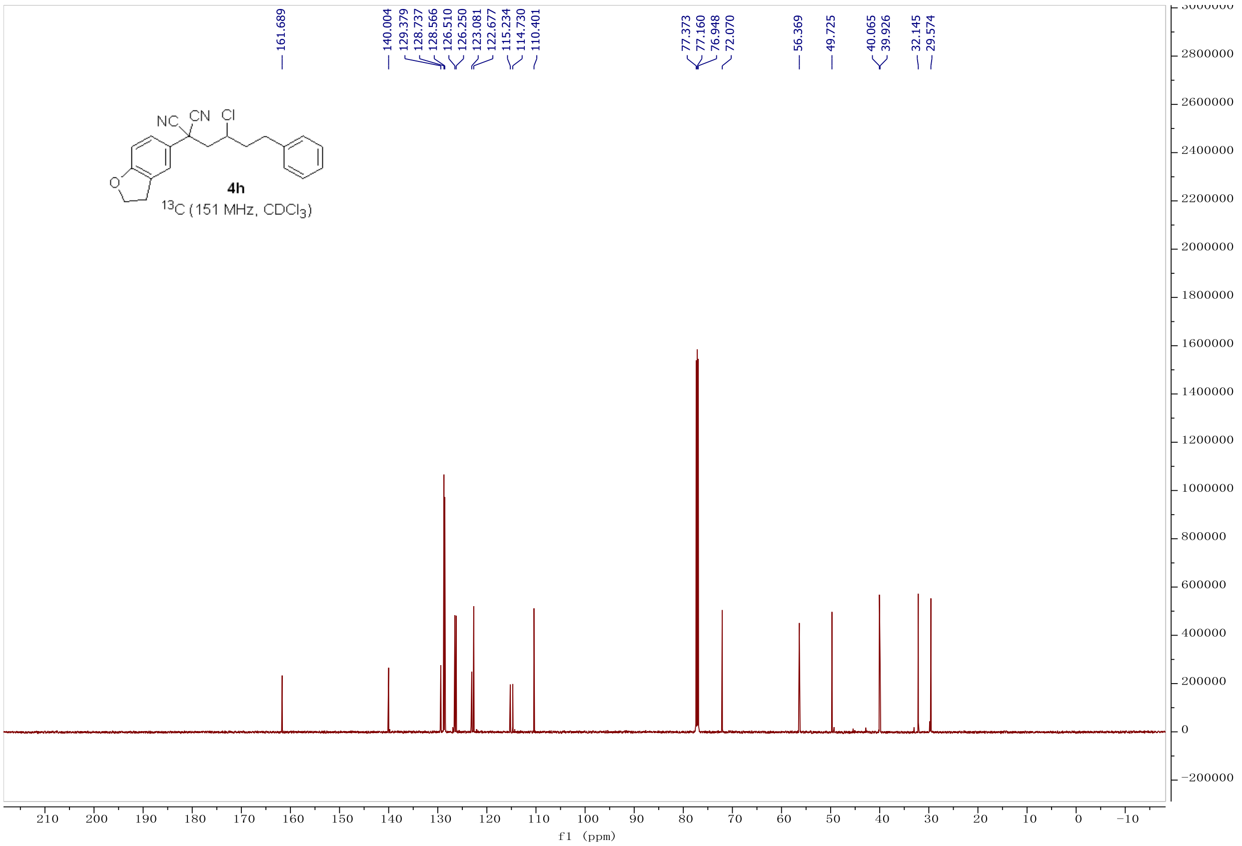
4f

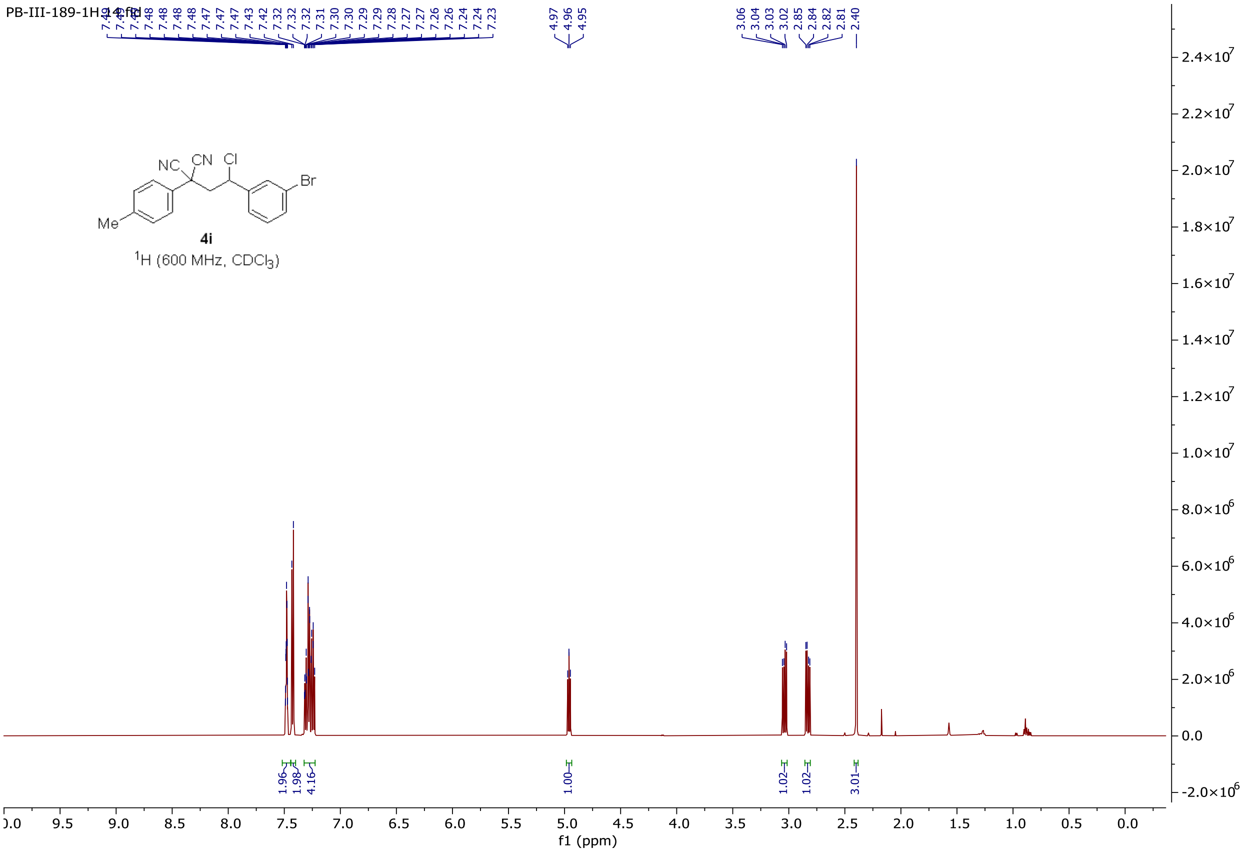
^{13}C (151 MHz, CDCl$_3$)

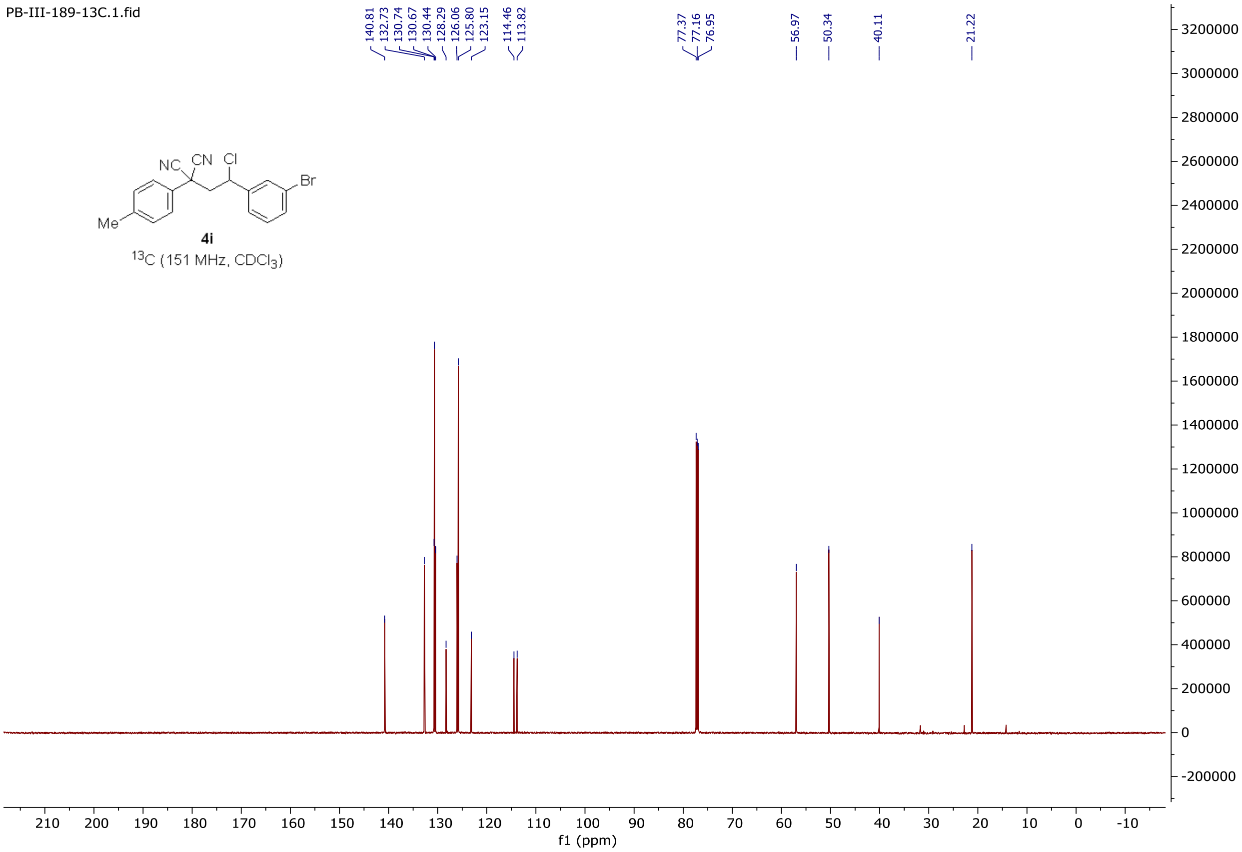

7.565
7.550
7.502
7.488
7.260
4.022
4.015
4.013
4.007
4.000
3.993
3.987
3.985
3.979
2.728
2.713
2.703
2.688
2.519
2.512
2.494
2.488
1.800
1.793
1.791
1.789
1.784
1.780
1.778
1.775
1.773
1.771
1.768
1.765
1.756
1.509
1.506
1.499
1.495
1.489
1.484
1.479
1.474
1.469
1.422
1.417
1.410
1.407
1.401
1.395
1.391
1.390
1.385
1.381
1.374
1.372
1.370
1.362
1.360
1.351
1.348
1.341
1.338
1.336
1.329
1.326
1.324
1.314
1.311
1.303
1.299
1.292
1.290
1.288
1.282
1.278
0.917
0.905
0.892
NC
CN
Cl
Cl
4g
^{1}H (600 MHz, CDCl$_3$)
1.96
2.01
1.00
1.04
1.02
2.03
1.08
3.06
3.04
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
−1000000
0.0
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)

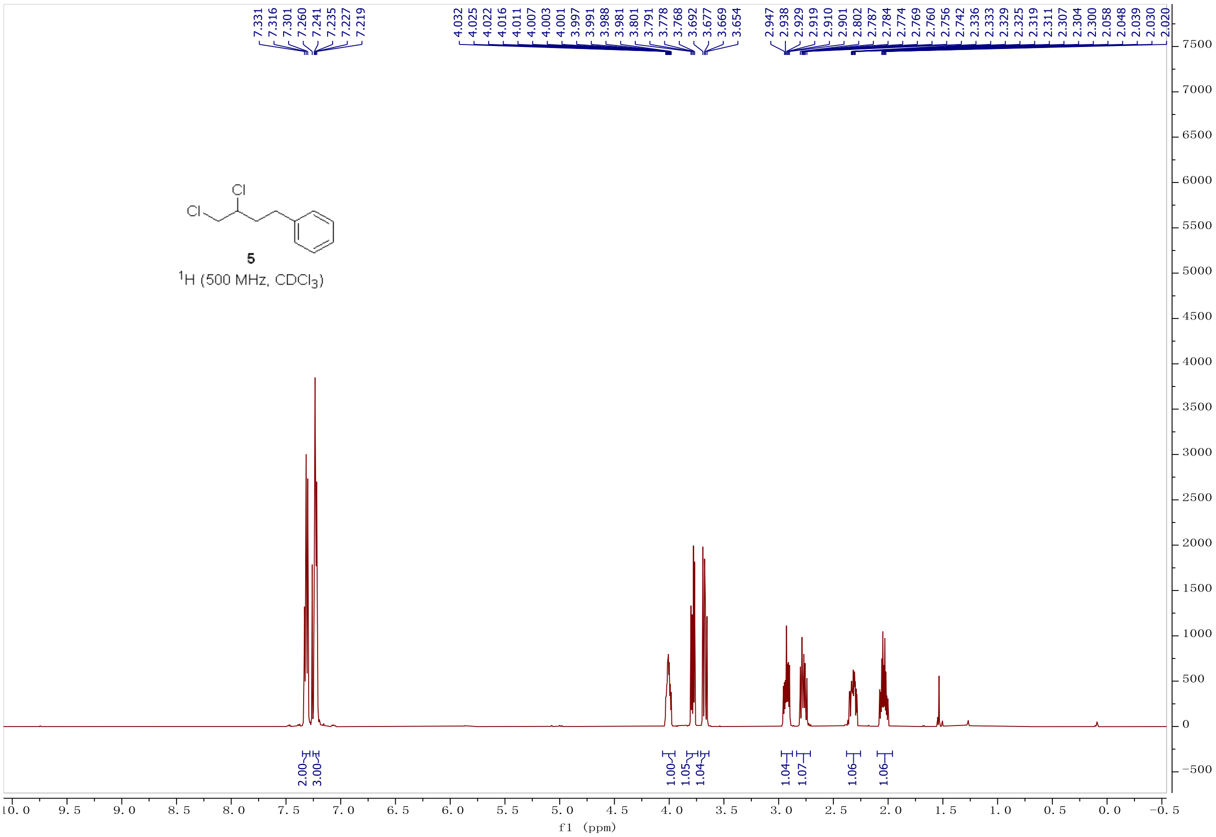

136.746
130.474
130.265
127.440
114.539
114.127
77.373
77.162
76.950
57.153
49.504
40.136
38.245
28.042
22.098
13.938
NC
CN
Cl
Cl
4g
^{13}C (151 MHz, CDCl$_3$)
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
−200000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.344
7.292
7.279
7.274
7.270
7.267
7.260
7.255
7.218
7.206
7.194
7.146
7.134
6.823
6.809
4.657
4.642
4.627
3.955
3.948
3.945
3.940
3.938
3.934
3.930
3.927
3.923
3.919
3.912
3.254
3.239
3.224
2.891
2.880
2.868
2.857
2.845
2.762
2.759
2.749
2.745
2.739
2.735
2.726
2.720
2.515
2.509
2.491
2.484
2.090
2.078
2.068
2.064
2.054
NC
CN
Cl
O
4h
^{1}H (600 MHz, CDCl$_3$)
0.98
3.11
1.02
1.97
1.01
2.04
1.00
2.08
1.12
2.03
1.03
2.05
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
0.0
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)


161.689
140.004
129.379
128.737
128.566
126.510
126.250
123.081
122.677
115.234
114.730
110.401
77.373
77.160
76.948
72.070
56.369
49.725
40.065
39.926
32.145
29.574
NC
CN
Cl
O
4h
^{13}C (151 MHz, CDCl$_3$)
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
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)

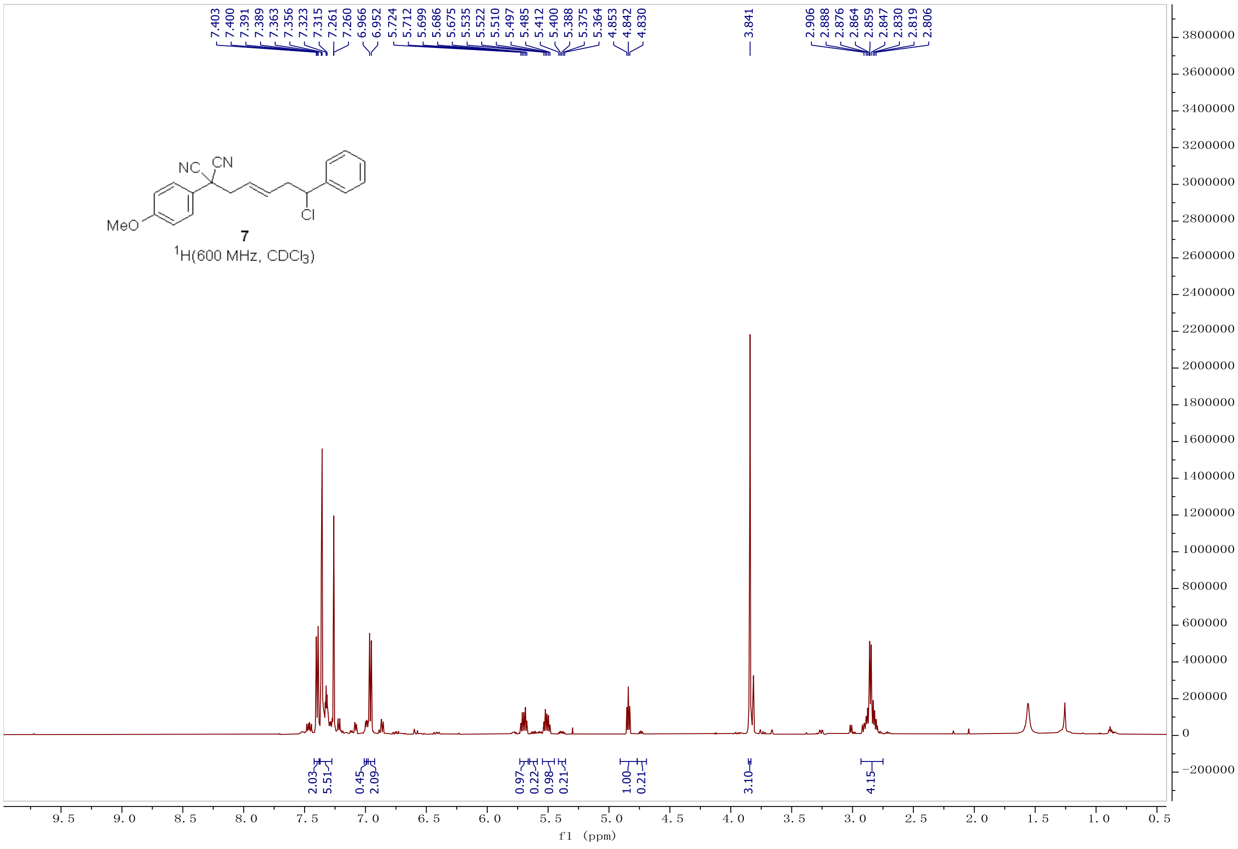

PB-III-189-1H.14.fid
7.49 7.49 7.4 7.48 7.48 7.48 7.48 7.47 7.47 7.47 7.43 7.42 7.32 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.24 7.24 7.23
4.97 4.96 4.95
3.06 3.04 3.03 3.02 2.85 2.84 2.82 2.81 2.40
NC CN Cl
Br
Me
4i
¹H (600 MHz, CDCl₃)
1.96 1.98 4.16
1.00
1.02 1.02
3.01
2.4×10⁷
2.2×10⁷
2.0×10⁷
1.8×10⁷
1.6×10⁷
1.4×10⁷
1.2×10⁷
1.0×10⁷
8.0×10⁶
6.0×10⁶
4.0×10⁶
2.0×10⁶
0.0
-2.0×10⁶
0.0 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)


PB-III-189-13C.1.fid
140.81 132.73 130.74 130.67 130.44 128.29 126.06 125.80 123.15 114.46 113.82
77.37 77.16 76.95
56.97
50.34
40.11
21.22
NC CN Cl
Br
Me
4i
¹³C (151 MHz, CDCl₃)
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
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)



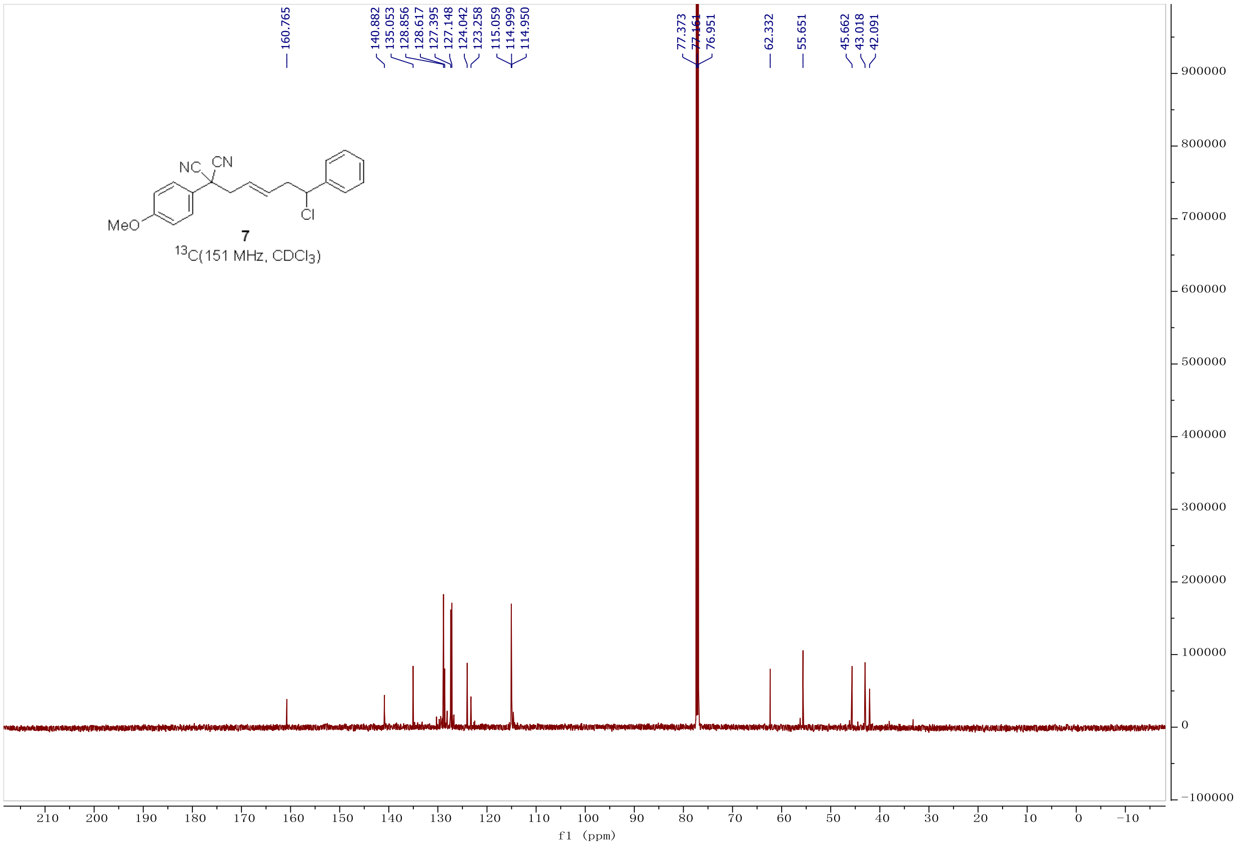
5

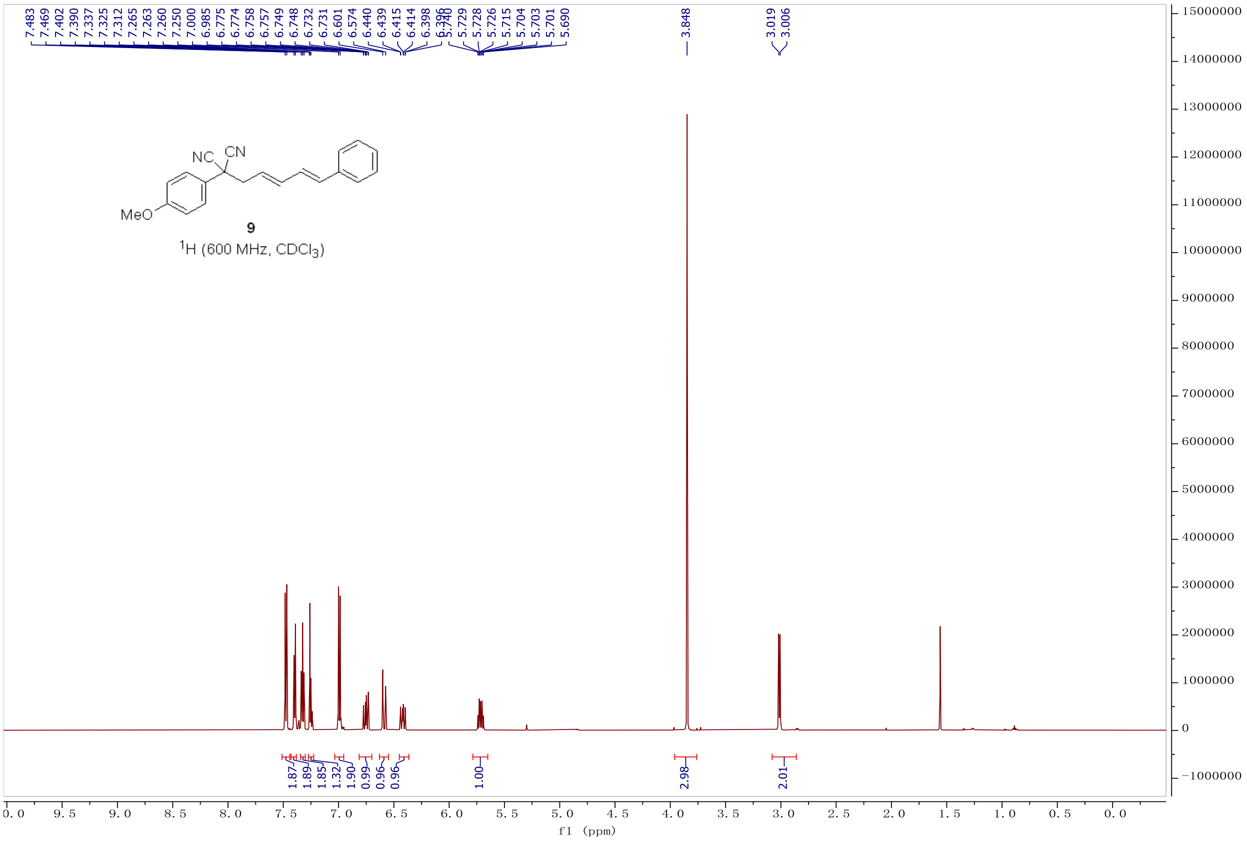
^{1}H (500 MHz, $CDCl_3$)

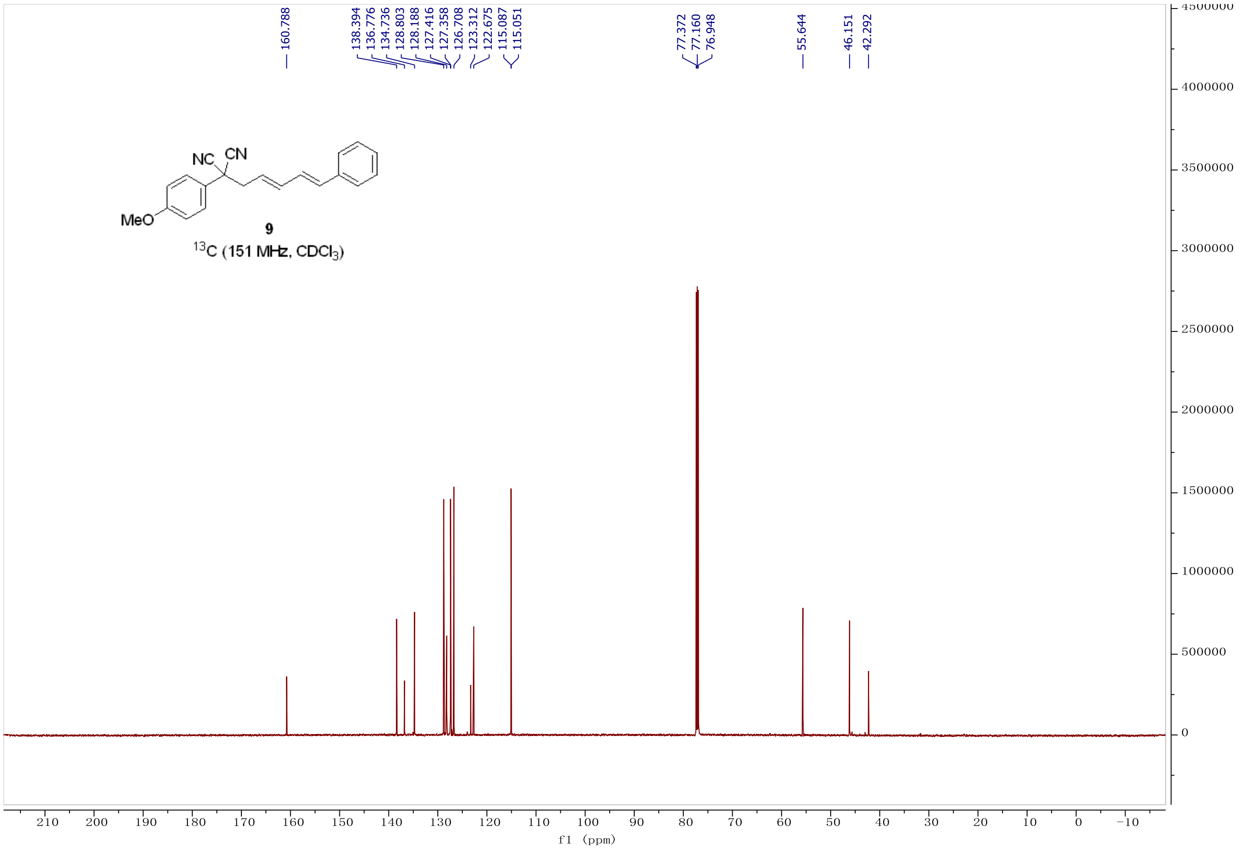


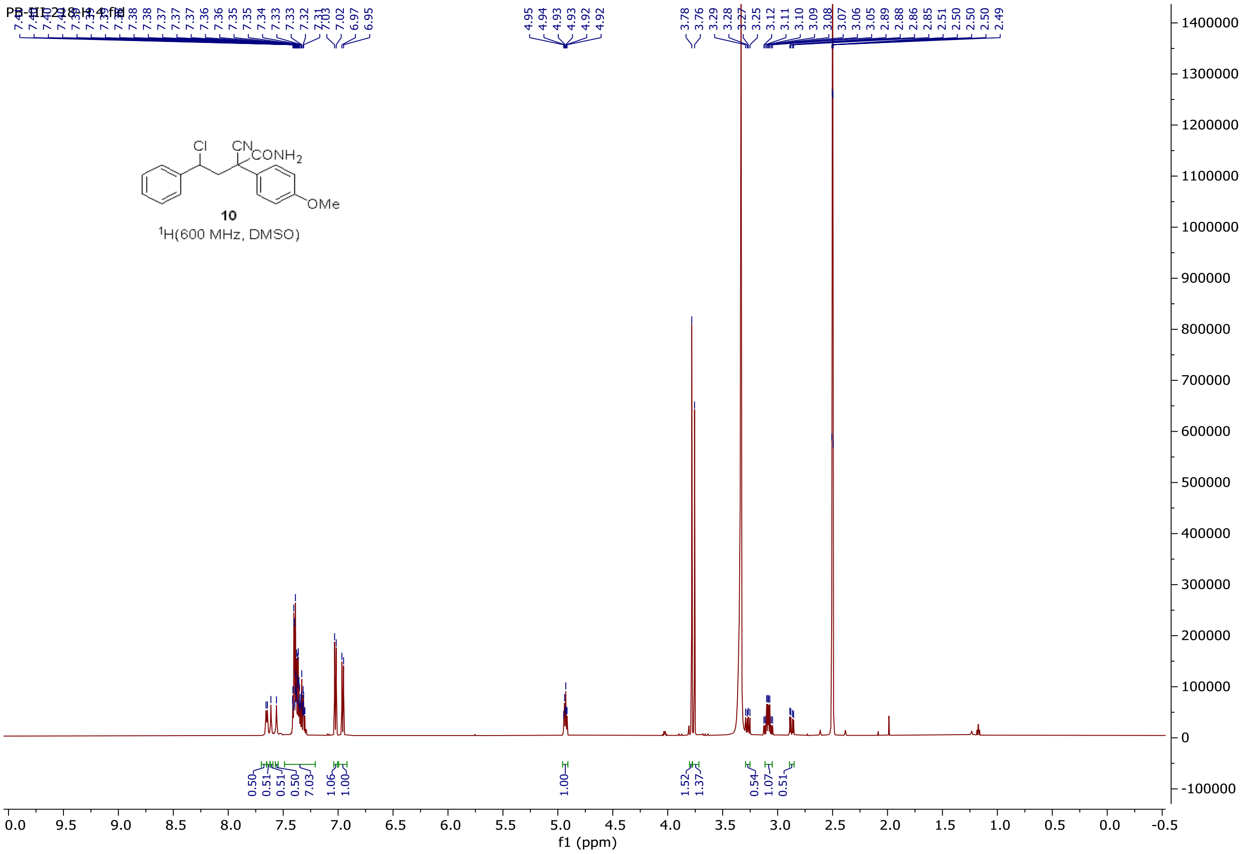
7

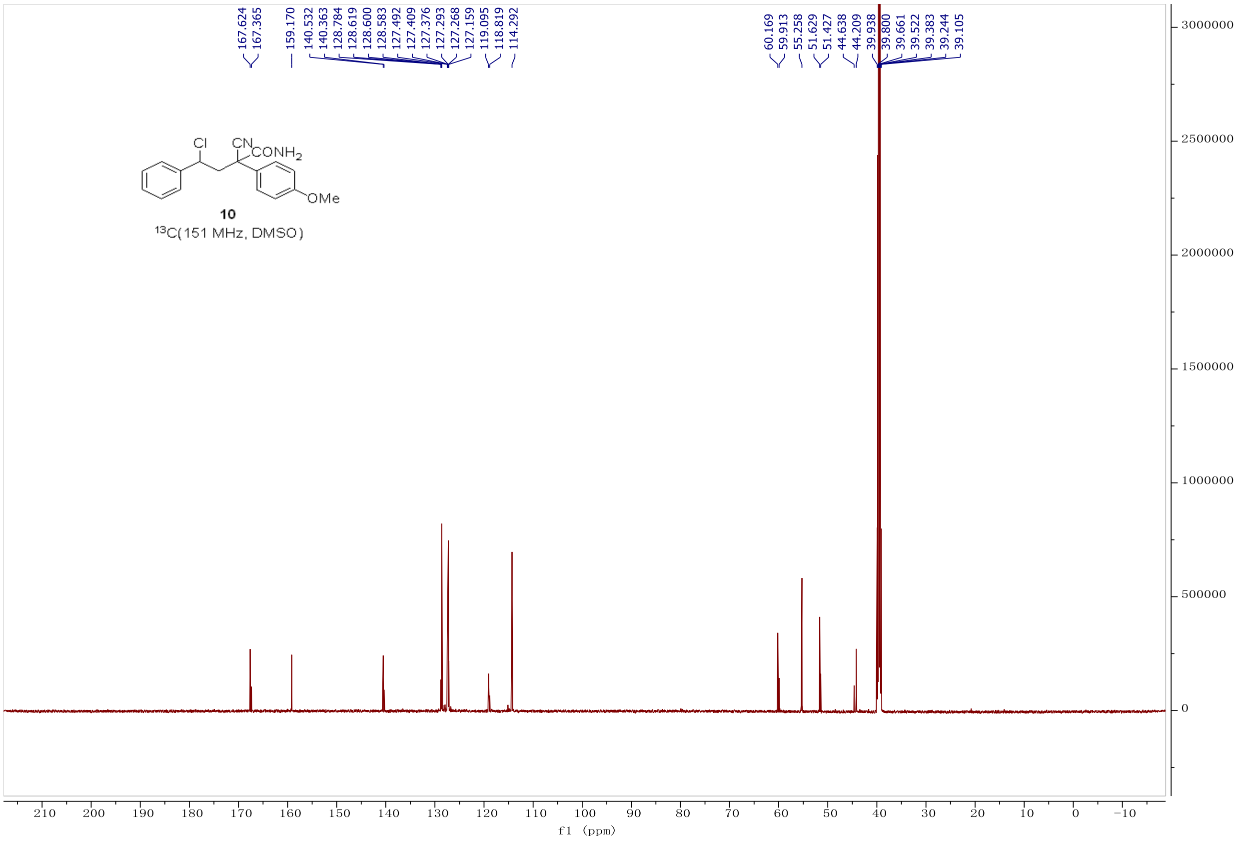
^{1}H(600 MHz, $CDCl_3$)


160.765
140.882
135.053
128.856
128.617
127.395
127.148
124.042
123.258
115.059
114.999
114.950
77.373
77.161
76.951
62.332
55.651
45.662
43.018
42.091
NC
CN
MeO
Cl
7
^{13}C(151 MHz, CDCl$_3$)
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
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)


7.483
7.469
7.402
7.390
7.337
7.325
7.312
7.265
7.263
7.260
7.250
7.000
6.985
6.775
6.774
6.758
6.757
6.749
6.748
6.732
6.731
6.601
6.574
6.440
6.439
6.415
6.414
6.398
6.396
5.740
5.729
5.728
5.726
5.715
5.704
5.703
5.701
5.690
3.848
3.019
3.006
NC
CN
MeO
9
^{1}H (600 MHz, CDCl$_3$)
1.87
1.89
1.85
1.32
1.90
0.99
0.96
0.96
1.00
2.98
2.01
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
−1000000
0.0
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)

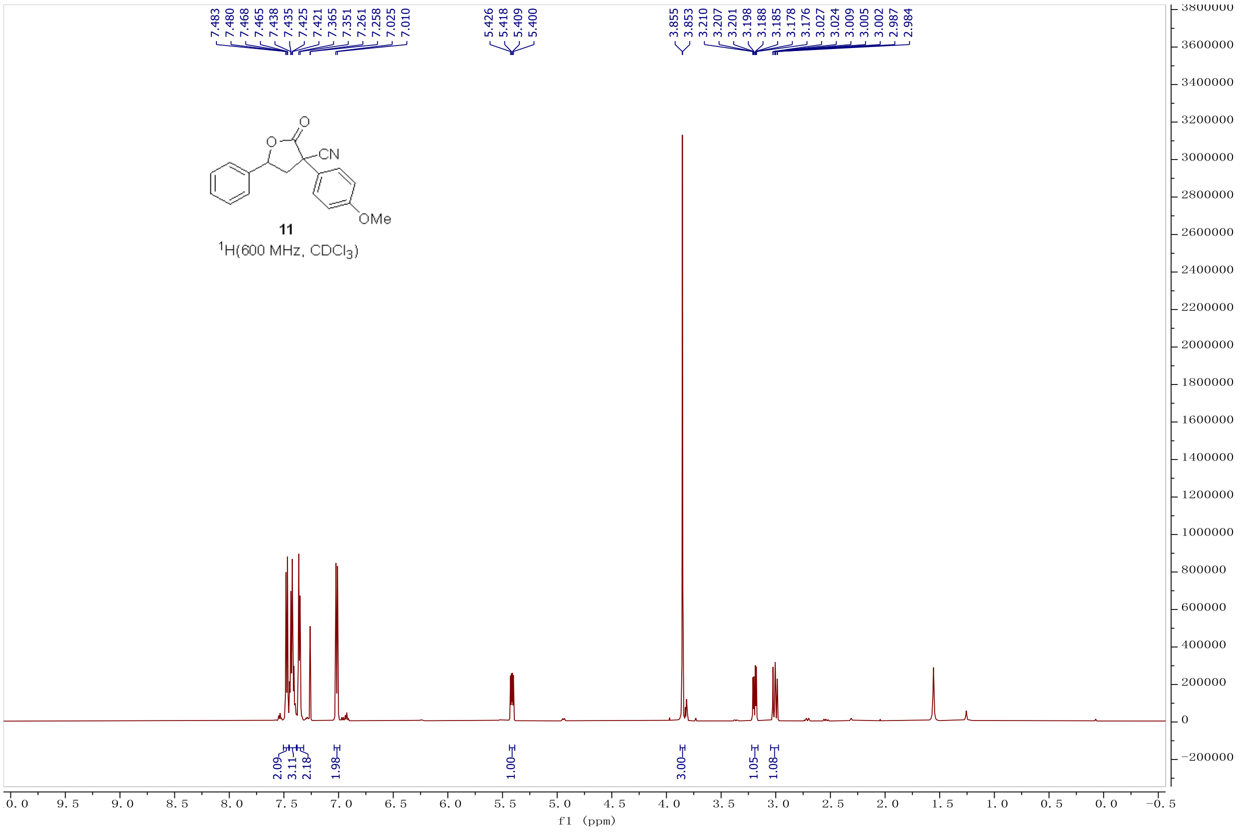

160.788
138.394
136.776
134.736
128.803
128.188
127.416
127.358
126.708
123.312
122.675
115.087
115.051
77.372
77.160
76.948
55.644
46.151
42.292
NC
CN
MeO
9
^{13}C (151 MHz, CDCl$_3$)
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


PB-III-218-H.4.fid
7.41
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.03
7.02
6.97
6.95
4.95
4.94
4.93
4.93
4.92
4.92
3.78
3.76
3.29
3.28
3.27
3.25
3.12
3.11
3.10
3.09
3.08
3.07
3.06
3.05
2.89
2.88
2.86
2.85
2.51
2.50
2.50
2.50
2.49
Cl
CN
CONH$_2$
OMe
10
^{1}H(600 MHz, DMSO)
0.50
0.51
0.50
7.03
1.06
1.00
1.00
1.52
1.37
0.54
1.07
0.51
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
0.0
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)



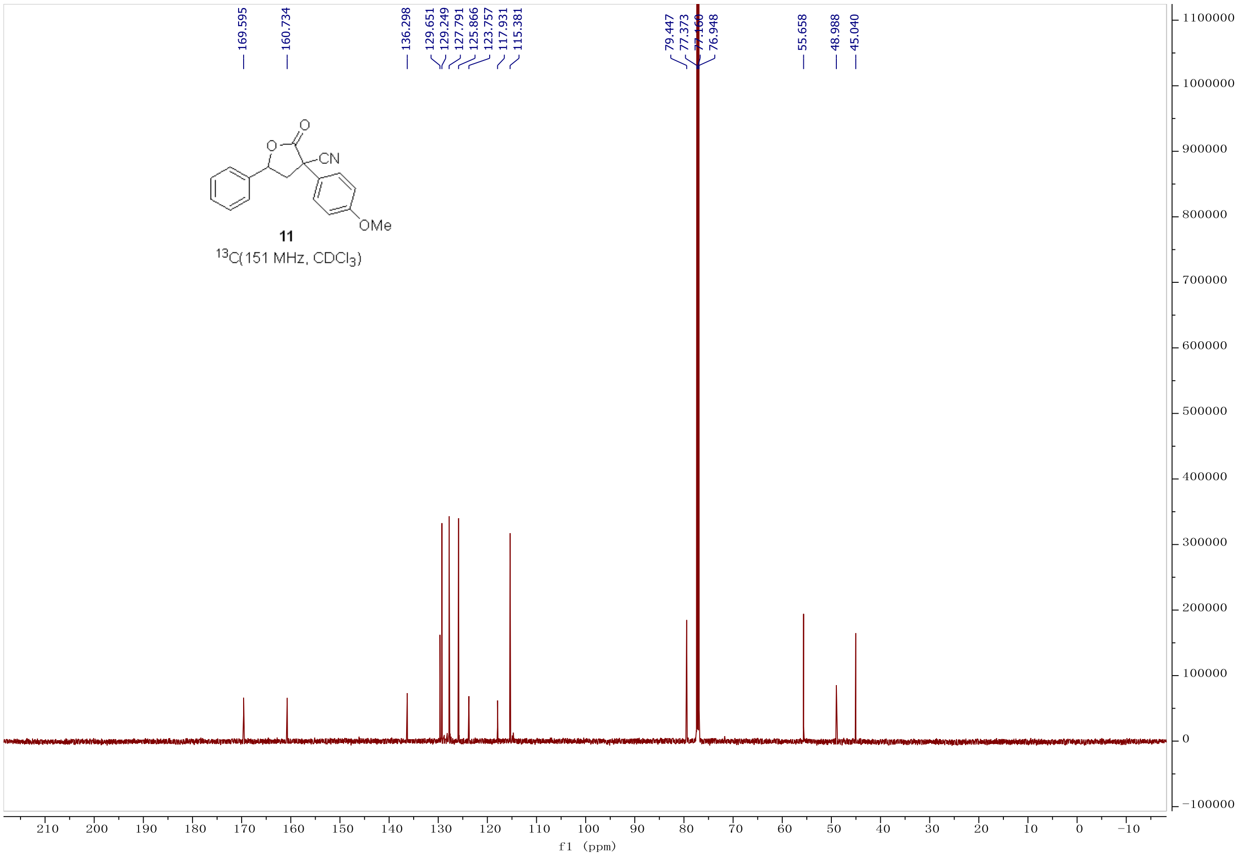
10

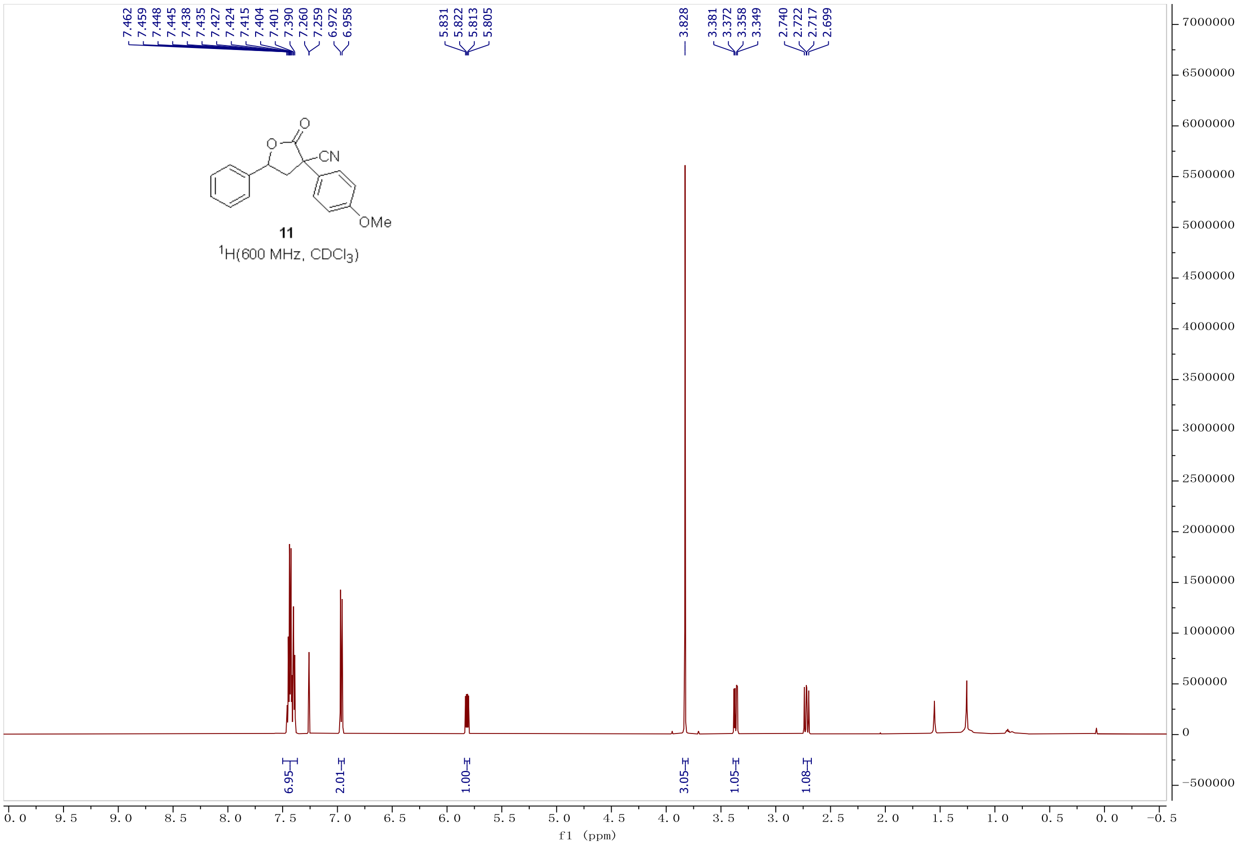
^{13}C(151 MHz, DMSO)

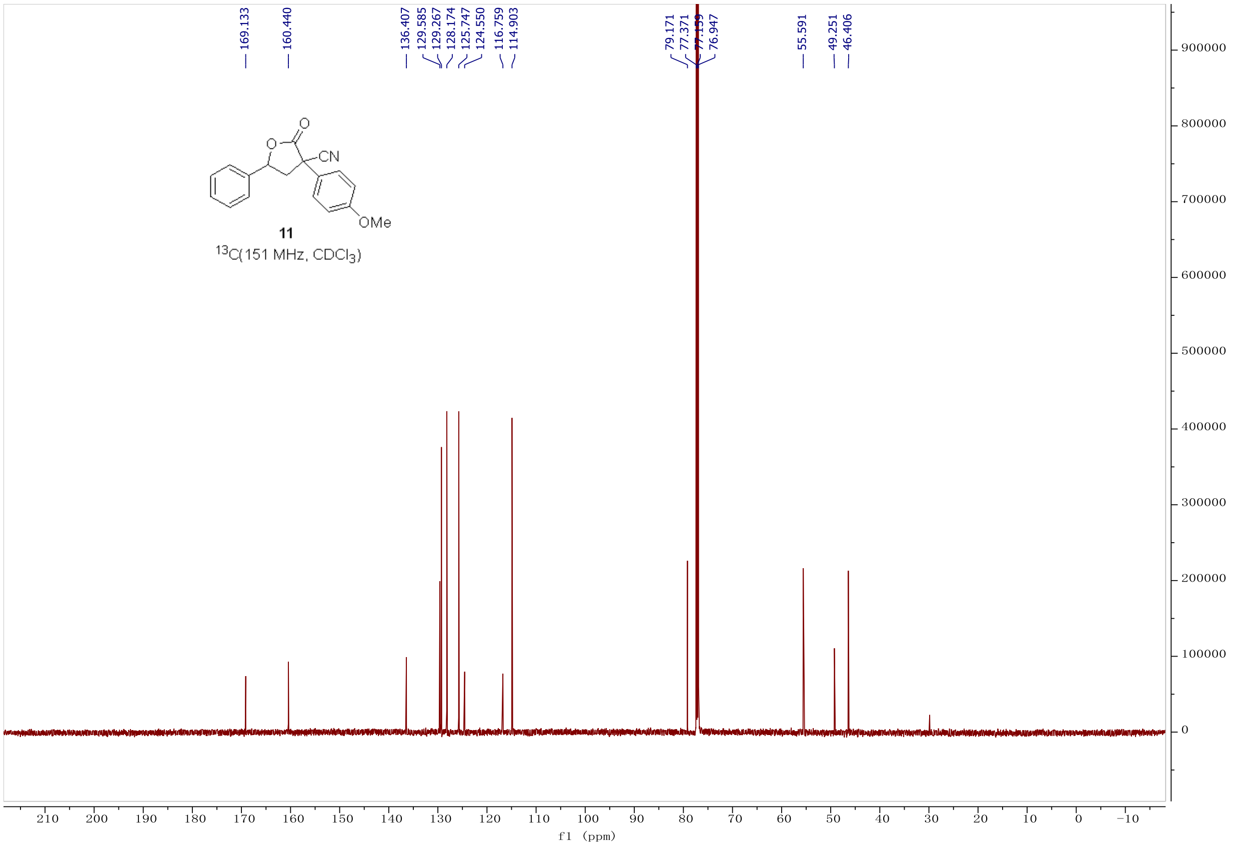


11

^{1}H(600 MHz, CDCl$_3$)

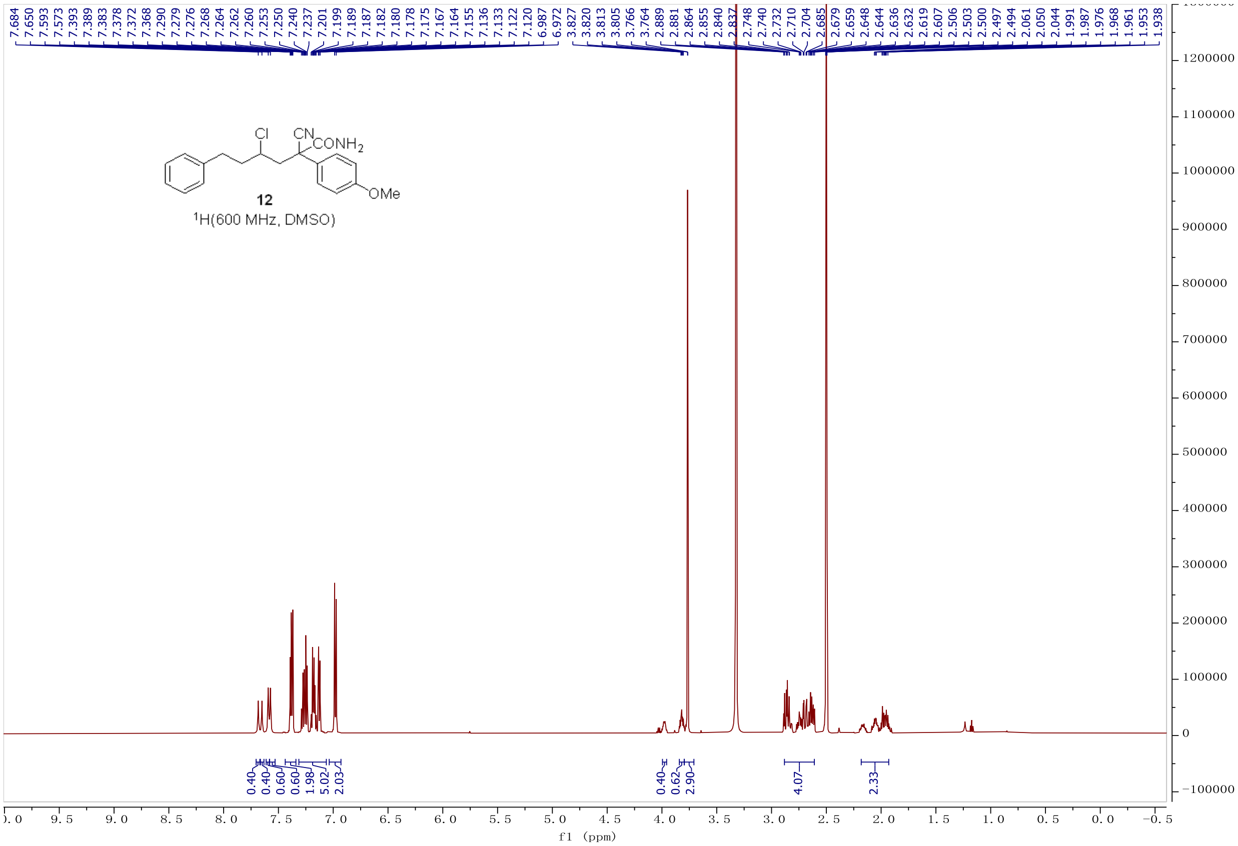

169.595
160.734
136.298
129.651
129.249
127.791
125.866
123.757
117.931
115.381
79.447
77.373
77.160
76.948
55.658
48.988
45.040
O
O
CN
OMe
11
^{13}C(151 MHz, CDCl$_3$)
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.462
7.459
7.448
7.445
7.438
7.435
7.427
7.424
7.415
7.404
7.401
7.390
7.260
7.259
6.972
6.958
5.831
5.822
5.813
5.805
3.828
3.381
3.372
3.358
3.349
2.740
2.722
2.717
2.699
O
O
CN
OMe
11
^{1}H(600 MHz, CDCl$_3$)
6.95
2.01
1.00
3.05
1.05
1.08
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
−500000
0.0 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)



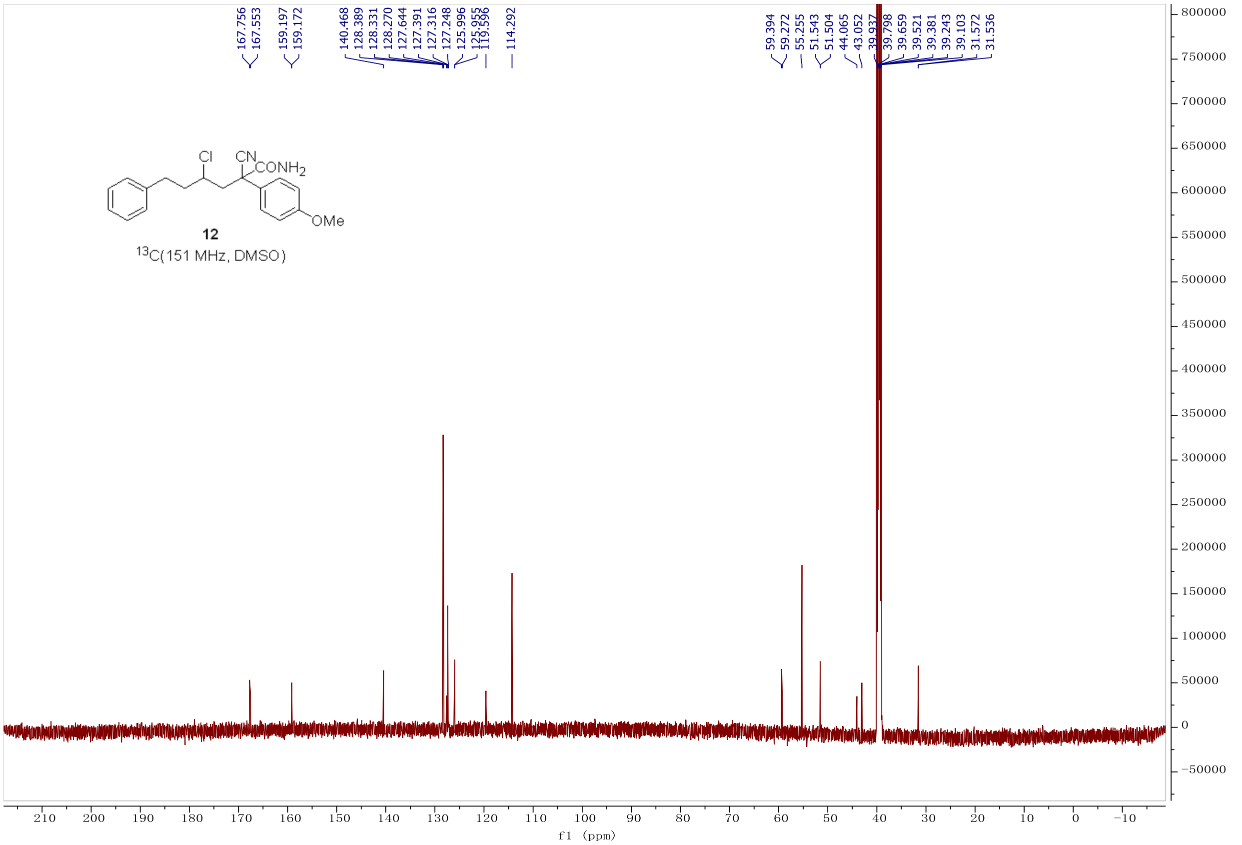
11

^{13}C(151 MHz, CDCl$_3$)

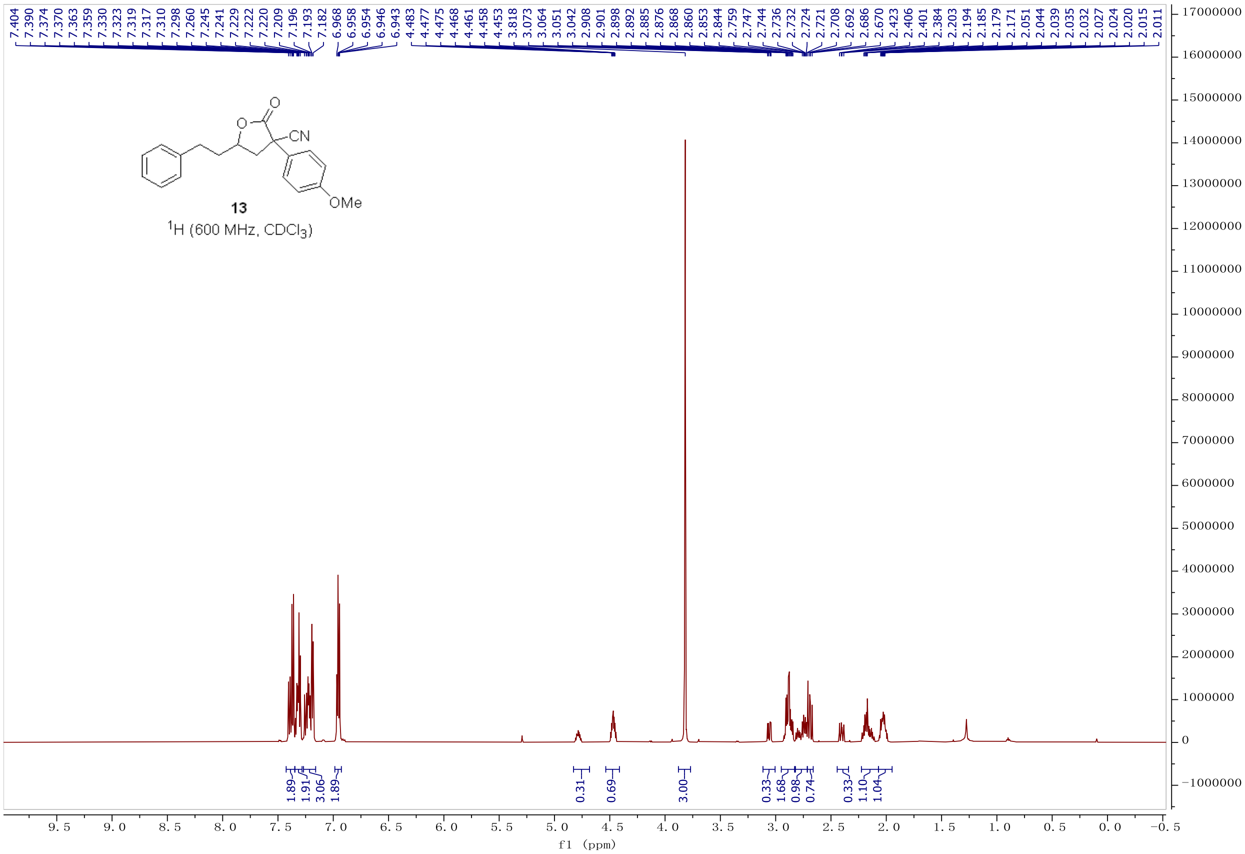


12

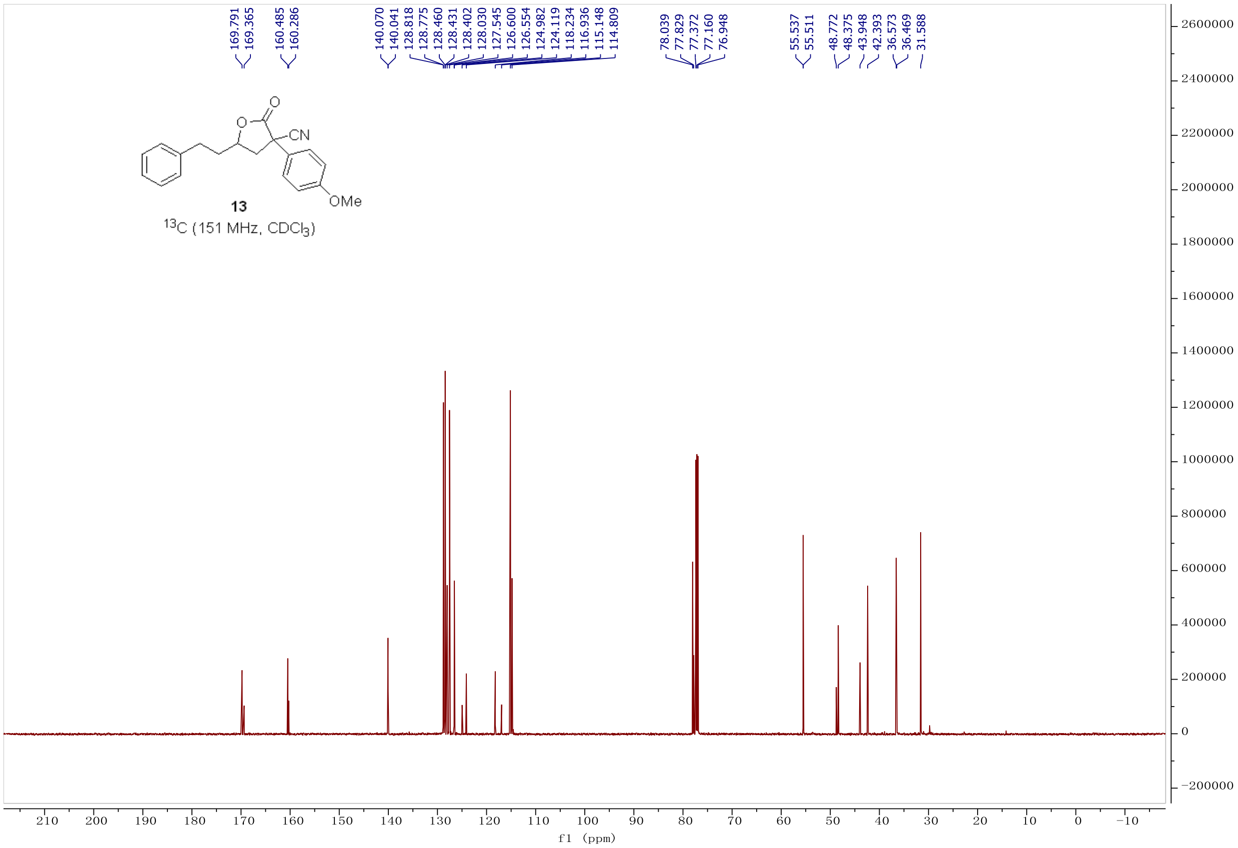
^{1}H(600 MHz, DMSO)


12

^{13}C(151 MHz, DMSO)


13

^{1}H (600 MHz, CDCl$_3$)


169.791
169.365
160.485
160.286
140.070
140.041
128.818
128.775
128.460
128.431
128.402
128.030
127.545
126.600
126.554
124.982
124.119
118.234
116.936
115.148
114.809
78.039
77.829
77.372
77.160
76.948
55.537
55.511
48.772
48.375
43.948
42.393
36.573
36.469
31.588
O
O
CN
OMe
13
^{13}C (151 MHz, CDCl$_3$)
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
−200000
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)