Supporting Information

Ag(I)-Catalyzed Diastereoselective Oxidative Cyclopropanation of Prochiral Alkyne-tethered 1,3-Dicarbonitriles

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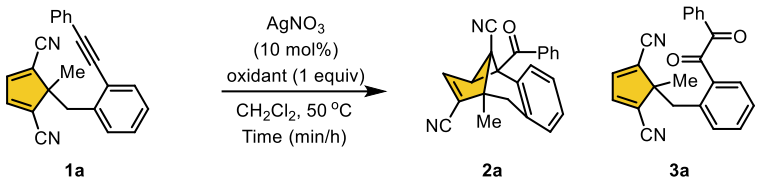
I. General details

***General information*:** Unless otherwise noted, all reagents were used as received from commercial suppliers. Silver-catalysts and $HClO_4$ were purchased from Sigma-Aldrich and used without further purification. All reactions were performed under inert atmosphere and in a flame-dried or oven-dried glassware with magnetic stirring. All solvents were dried before use following the standard procedures. Reactions were monitored using thin-layer chromatography (SiO_2). TLC plates were visualized with UV light (254 nm), iodine treatment or using *p*-anisaldehyde stain or *β*-napthol stain. Column chromatography was carried out using silica gel (100-200 mesh) packed in glass columns. NMR spectra were recorded at 300, 400, 500 MHz (H) and at 75, 100, 125 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.16 ppm) and DMSO (H: δ = 2.50, 3.33 and C: δ = 39.52 ppm) as internal standard, and coupling constants (*J*) are given in Hz. HRMS were recorded using ESI-TOF techniques.

II. Additional screening for oxidative cyclopropanation:

Table S1: Optimization of an oxidizing agent in presence of $AgNO_3$ catalyst[a,b]

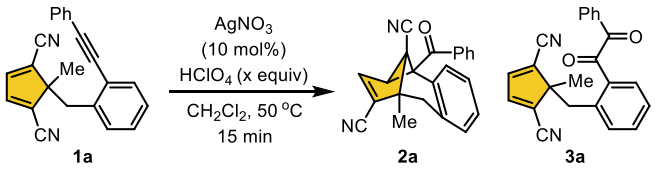


1a 2a 3a

Entry	oxidant	Time	Yield [**2a**%][c]	Yield [**3a**%][c]
1	$HClO_4$	15 min	72	7
2	$Mg(ClO_4)_2$	24 h	NR	-
3	MCPBA	24 h	NR	-
4	OXONE	24 h	NR	-
5	$LiClO_4$	24 h	NR	-
6	BAIB	24 h	NR	-
7	H_2O_2	24 h	NR	-
8	$NaClO_4$	24 h	NR	-
9	$K_2S_2O_8$	24 h	NR	-
10	$Mn(OAC)_2$	24 h	NR	-
11	TBHP	24 h	NR	-
12	CAN	24 h	NR	-
13	quinoline *N*-Oxide	24 h	NR	-
14	$NaIO_4$	24 h	NR	-
15	O_2	24 h	NR	-
16	3,4-dichloroisoquinoline 2-oxide	24 h	NR	-
17	DMSO	24 h	NR	-
18	DPSO	24 h	NR	-

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv) in CH_2Cl_2 (2 mL, 0.1 M) at 50 °C. [b] Used ~70% aqueous $HClO_4$ solution. [c] Isolated yields. DPSO = Diphenyl sulfoxide

Table S2: Optimization of $HClO_4$ loading[a,b]

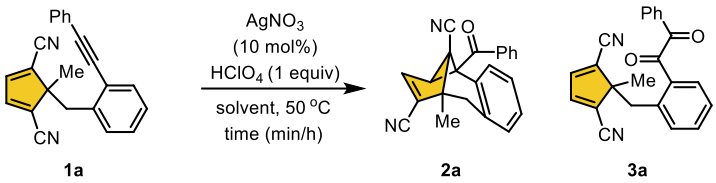


1a 2a 3a

Entry	$HClO_4$ (equiv)	Yield [**2a**%][c]	Yield [**3a**%][c]
1[d]	0.5	30	11
2	1.0	72	7
3	1.5	59	30
4	2.0	20	54

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv) in CH_2Cl_2 (2 mL, 0.1 M) at 50 °C. [b] Used ~70% aqueous $HClO_4$ solution. [c] Isolated yields. [d] More than 27% SM was recovered.

Table S3: Optimization of solvents[a,b]

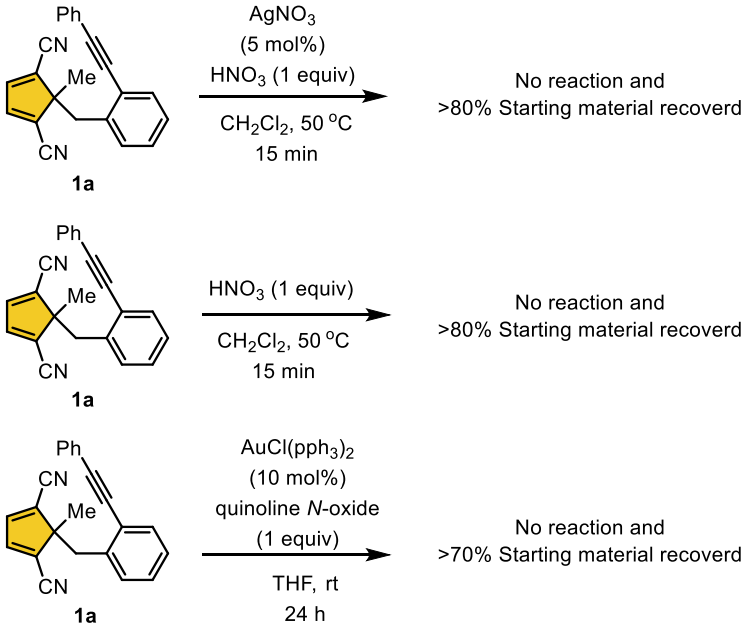


1a 2a 3a

entry	solvents	time	yield [**2a**%][c]	yield [**3a**%][c]
1	CH_2Cl_2	15 min	72	7
2	DCE	24 h	<5	-
3	THF	24 h	NR	-
4	DMF	24 h	NR	-
5	DMSO	24 h	NR	-
6	Et_2O	24 h	NR	-
7	MTBE	24 h	NR	-
8	ACN	24 h	NR	-
9	MeOH	24 h	NR	-
10	toluene	24 h	NR	-
11	^{t}BuOH	24 h	NR	-
12	Benzene	24 h	NR	-
13	MeTHF	24 h	NR	-
14	1,4-dioxane	24 h	NR	-
15	H_2O	24 h	NR	-

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv) in solvent (2 mL, 0.1 M) at 50 °C. [b] Used~70% aqueous $HClO_4$ solution. [c] Isolated yields.

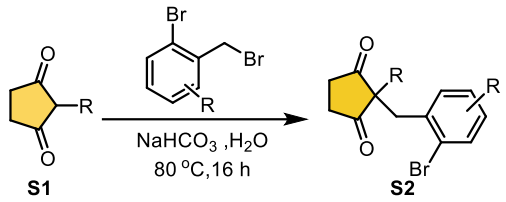
Miscellaneous reactions:



III. Experimental procedures and analytical data

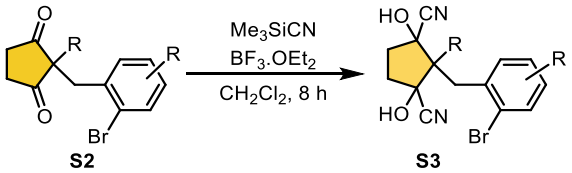
IIIA. Experimental procedures and analytical data of substrates

General procedure for the synthesis of 2,2-disubstituted-1,3-cyclopentanones:[1]



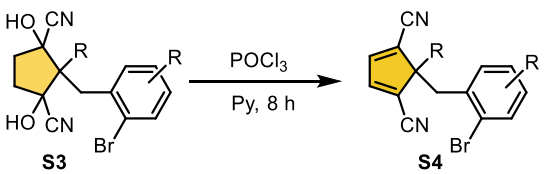
To a vigorously stirred suspension of 2-substituted l,3-cyclopentanedione **S1** (1 equiv) in water (1.0 M), was gradually added powdered $NaHCO_3$ (1 equiv) and stirred for additional 30 minutes. Then benzyl bromide (1.2 equiv) or substituted benzyl bromide was added to the reaction mixture and stirred at 80 ^oC in preheated oil bath for 16 h. Later, the reaction mixture was extracted with CH_2Cl_2 (2 times) and the combined organic solvent was washed with 5% NH_4Cl aqueous solution and dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The obtained crude residue was purified by flash column chromatography (hexane/EtOAc).

General procedure for the synthesis of cyclopentane-1,3-dihydroxy dicarbonitrile:[2]



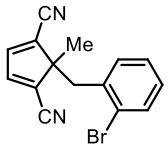
Me_3SiCN (2.1 equiv) and $BF_3.OEt_2$ (2 equiv) were added dropwise consecutively to a stirred solution of **S2** (1 equiv) in dry CH_2Cl_2 (0.3 M) under nitrogen atmosphere. The resulting mixture was heated at reflux using preheated oil bath for 8 h, the reaction was quenched at 0 ^oC by adding aqueous hydrochloric acid (1.0 M). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (two times). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was used for next step without further purification.

General procedure for the synthesis of cyclopentane-1,3 dicarbonitrile:[2]



Crude compounds **S3** (1 equiv) were dissolved in pyridine (0.5 M) followed by the addition of $POCl_3$ (5 equiv) under nitrogen atmosphere. After heating at 60 °C for 5 h, the reaction mixture was cooled to 0 °C and CH_2Cl_2 was added. Then, the mixture was poured into hydrochloric acid (2 M) slowly. After filtration through a pad of Celite, the filtration cake was washed with CH_2Cl_2 and the filtrate was moved into a separating funnel. The organic layer was collected, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with a saturated solution of sodium bicarbonate and brine, and dried over anhydrous Na_2SO_4. After removal of the organic solvent, the residue was purified by column chromatography on silica gel by using a mixture of hexanes and ethyl acetate as the mobile phase to yield **S4**.

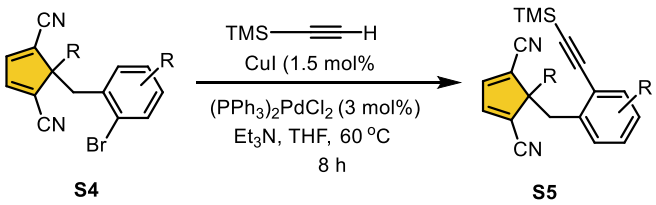
2-(2-Bromobenzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (S4):



Prepared according to the above-described procedure, overall yield 93% (2.3 g) over two steps. It was purified by flash chromatography (5% EtOAc/hexanes; R_f = 0.3) to afford a yellow solid; mp = 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.40 (m, 1H), 7.26 – 7.11 (m, 2H), 7.09 – 6.99 (m, 1H), 6.91 (s, 2H), 3.29 (s, 2H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 134.0, 133.4, 131.8, 130.7, 129.4, 127.2, 125.6, 114.4, 62.8, 40.6, 20.1; HRMS (ESI) calcd for $C_{15}H_{12}N_2Br$ $[M+H]^+$: 299.0180; found: 299.0178.

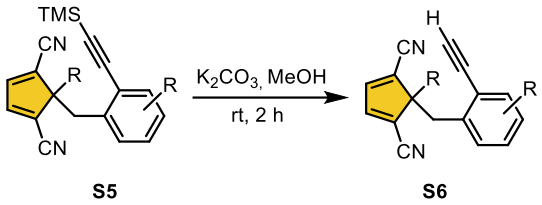
General procedure-A for the synthesis of substrate 1:

Sonogashira coupling for the synthesis of cyclopentane-1,3 dicarbonitrile alkynes S5:



To a solution of **S4** (1 equiv) in anhydrous THF (0.5 M), was added $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (5 mol%), Et_3N (1.7 equiv) and TMS acetylene (1.2 equiv). The mixture was stirred at 60 °C for 8 h. The reaction was cooled to room temperature, diluted with water, and the mixture was extracted with EtOAc. The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The obtained crude residue was purified by flash chromatography (hexane/EtOAc).

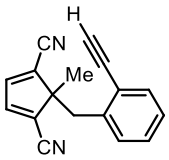
Synthesis of cyclopentane-1,3-dicarbonitrile alkynes S6:



S5 **S6**

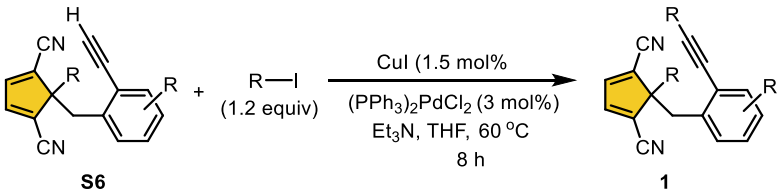
S5 (1.0 mmol, 1.0 equiv) was dissolved in 15 mL of dry methanol. After the addition of potassium carbonate (1.3 equiv), the mixture was stirred for 2 h at room temperature. The precipitated solid was filtered off and washed with EtOAC (20 mL). The mixture was concentrated in *vacuo*. and the residue was purified by flash column chromatography on silica gel to afford cyclopentane-1,3-dicarbonitrile alkynes **S6**.

2-(2-Ethynylbenzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (S6):



Prepared according to the described above in 85% yield (1.7 g). It was purified by flash chromatography (5% EtOAc/hexanes; R_f = 0.3) to afford a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.3 Hz, 1H), 7.30 – 7.17 (m, 3H), 6.93 (s, 2H), 3.41 (s, 2H), 3.35 (s, 1H), 1.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 136.6, 133.3, 130.8, 130.2, 128.5, 127.6, 122.9, 114.5, 83.5, 82.0, 63.2, 39.2, 20.1; HRMS (ESI) calcd for $C_{17}H_{13}N_2$ $[M+H]^+$: 245.1079; found: 245.1104.

Sonogashira coupling of S6 with aryl halides for the synthesis of substrate 1:[3]

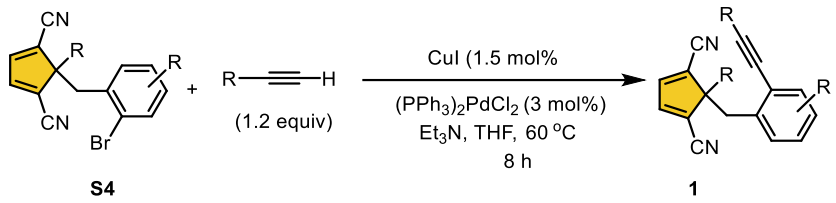


S6 **1**

To a solution of **S6** (4.0 mmol, 1 equiv) in anhydrous THF (0.5 M), was added $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (5 mol%), Et_3N (1.7 equiv) and aryl iodide (1.2 equiv). The mixture was stirred at 60 °C for 8h. The reaction was cooled to room temperature, diluted with water, and the mixture was extracted with EtOAc. The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The obtained crude residue was purified by flash chromatography (hexane/EtOAc) to afford **1**.

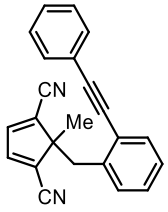
General procedure-B for the synthesis of substrate 1:

Sonogashira coupling of S4 with alkynes for the synthesis of substrate 1:



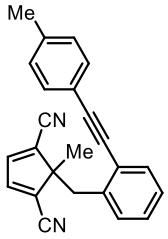
To a solution of **S4** (1 equiv) in anhydrous THF (0.5 M), was added $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (5 mol%), Et_3N (1.7 equiv) and substituted acetylene (1.3 equiv). The mixture was stirred at 60 °C for 8 h. The reaction was cooled to room temperature, diluted with water, and the mixture was extracted with EtOAc. The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The obtained crude residue was purified by flash chromatography (hexane/EtOAc) to give desired substrate **1**.

2-Methyl-2-(2-(phenylethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1a):



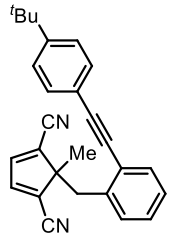
Prepared according to the general procedure-B as described above in 90% yield (96 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 149–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 3H), 7.36 – 7.27 (m, 3H), 7.23 – 7.12 (m, 3H), 6.88 (s, 2H), 3.34 (s, 2H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 135.8, 132.9, 131.7, 131.1, 130.3, 128.6, 128.5, 128.0, 127.8, 124.4, 123.2, 114.3, 94.9, 88.2, 63.1, 39.6, 19.7; HRMS (ESI) calcd for $C_{23}H_{17}N_2$ $[M+H]^+$: 321.1386; found: 321.1386.

2-Methyl-2-(2-(p-tolylethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1b):



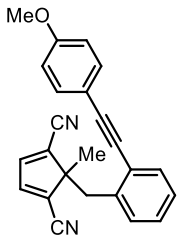
Prepared according to the general procedure-B as described above in 87% yield (98 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.4) to afford a colorless solid; mp = 156–158 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.25 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.97 (s, 2H), 3.43 (s, 2H), 2.40 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 135.7, 132.8, 131.6, 130.3, 129.3, 127.8, 127.8, 124.6, 120.2, 114.3, 95.1, 87.5, 63.1, 39.6, 21.7, 19.6.; HRMS (ESI) calcd for $C_{24}H_{19}N_2$ $[M+H]^+$: 335.1544; found: 335.1542.

2-(2-((4-(Tert-butyl)phenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1c):



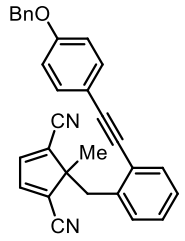
Prepared according to the general procedure-B as described above in 88% yield (111 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 153–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 1H), 7.51 – 7.48 (m, 2H), 7.43 – 7.37 (m, 2H), 7.31 – 7.21 (m, 3H), 6.96 (s, 2H), 3.41 (s, 2H), 1.56 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 141.4, 135.6, 132.8, 131.4, 131.1, 130.3, 127.8, 127.8, 125.5, 124.6, 120.2, 114.3, 95.0, 87.5, 63.0, 39.5, 34.9, 31.3, 19.5; HRMS (ESI) calcd for $C_{27}H_{25}N_2$ $[M+H]^+$: 377.2008; found: 377.2012.

2-(2-((4-Methoxyphenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1d):



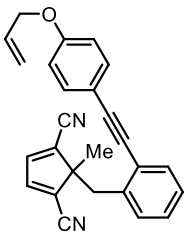
Prepared according to the general procedure-A as described above in 83% yield (119 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 145–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.37 (m, 3H), 7.25 – 7.13 (m, 3H), 6.87 (s, 2H), 6.85 – 6.79 (m, 2H), 3.76 (s, 3H), 3.33 (s, 2H), 1.48 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 141.3, 135.5, 133.2, 132.7, 131.2, 130.3, 127.8, 127.7, 124.7, 115.4, 114.4, 114.2, 95.0, 86.9, 63.2, 55.5, 39.6, 19.7; HRMS (ESI) calcd for $C_{24}H_{19}N_2O$ $[M+H]^+$: 351.1497; found: 351.1501.

2-(2-((4-(Benzyloxy)phenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1e):



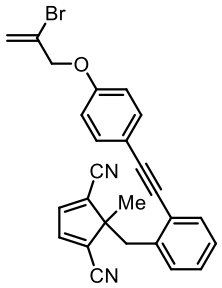
Prepared according to the general procedure-A as described above in 85% yield (148 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.4) to afford a colorless solid; mp = 137–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 1H), 7.40 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H), 7.22 – 7.14 (m, 4H), 7.12 (dd, *J* = 2.5, 1.3 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.91 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.85 (s, 2H), 5.02 (s, 2H), 3.32 (s, 2H), 1.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 141.4, 136.9, 135.8, 132.9, 131.1, 130.3, 129.6, 128.7, 128.1, 128.1, 127.8, 127.6, 124.6, 124.3, 117.4, 116.2, 114.3, 94.7, 88.0, 70.2, 63.1, 39.6, 19.6; HRMS (ESI) calcd for $C_{30}H_{23}N_2O$ $[M+H]^+$: 427.1799; found: 427.1804.

2-(2-((4-(Allyloxy)phenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1f):



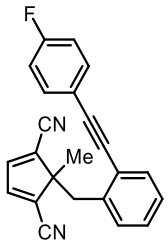
Prepared according to the general procedure-A as described above in 80% yield (123 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 3H), 7.29 – 7.24 (m, 3H), 6.97 (s, 2H), 6.95 – 6.91 (m, 2H), 6.08 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.45 (ddd, *J* = 17.3, 3.1, 1.6 Hz, 1H), 5.33 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.59 (dt, *J* = 5.3, 1.5 Hz, 2H), 3.42 (s, 2H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 141.3, 135.5, 133.2, 133.0, 132.7, 131.2, 130.3, 127.8, 127.7, 124.7, 118.1, 115.6, 114.9, 114.4, 95.0, 87.0, 69.0, 63.1, 39.6, 19.7; HRMS (ESI) calcd for $C_{26}H_{21}N_2O$ $[M+H]^+$: 377.1644; found: 377.1648.

2-(2-((4-((2-Bromoallyl)oxy)phenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1g):



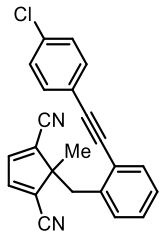
Prepared according to the general procedure-A as described above in 82% yield (153 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 151–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 3H), 7.20 – 7.13 (m, 3H), 6.87 (s, 2H), 6.86 – 6.81 (m, 2H), 5.93 (dd, *J* = 3.7, 1.7 Hz, 1H), 5.62 (dt, *J* = 2.3, 1.2 Hz, 1H), 4.59 (t, *J* = 1.4 Hz, 2H), 3.33 (s, 2H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 141.4, 135.6, 133.3, 132.8, 131.1, 130.3, 127.8, 126.7, 124.5, 118.1, 116.4, 115.1, 114.4, 94.6, 87.2, 71.7, 63.2, 39.6, 19.7; HRMS (ESI) calcd for $C_{26}H_{20}BrN_2O$ $[M+H]^+$: 455.0752; found: 455.0753.

2-(2-((4-Fluorophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1h):



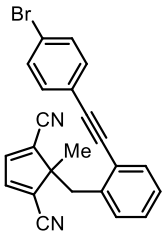
Prepared according to the general procedure-A as described above in 85% yield (118 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 123–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.48 (m, 3H), 7.40 – 7.22 (m, 3H), 7.15 – 7.04 (m, 2H), 6.97 (s, 2H), 3.44 (s, 2H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, J_{CF} = 249.9 Hz), 141.5, 135.7, 133.7 (d, J_{CF} = 8.4 Hz), 132.9, 131.1, 130.3, 128.1, 127.8, 124.1, 119.3 (d, J_{CF} = 3.7 Hz), 115.8 (d, J_{CF} = 22.2 Hz), 114.4, 93.8, 87.8, 63.2, 39.6, 19.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -118.58; HRMS (ESI) calcd for $C_{23}H_{14}N_2F$ $[M-H]^-$: 337.1137; found: 337.1135.

2-(2-((4-Chlorophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1i):



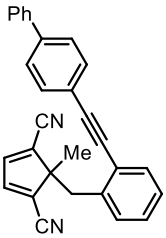
Prepared according to the general procedure-A as described above in 88% yield (128 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 131–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 3H), 7.37 – 7.31 (m, 2H), 7.28 – 7.18 (m, 3H), 6.93 (s, 2H), 3.40 (s, 2H), 1.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 135.8, 134.7, 133.0, 133.0, 131.0, 130.3, 128.9, 128.2, 127.8, 123.9, 121.7, 114.4, 93.7, 89.0, 63.2, 39.6, 19.8; HRMS (ESI) calcd for $C_{23}H_{16}ClN_2$ $[M+H]^+$: 355.0992; found: 355.1007.

2-(2-((4-Bromophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1j):



Prepared according to the general procedure-A as described above in 92% yield (150 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a yellow solid; mp = 124–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 3H), 7.49 – 7.42 (m, 2H), 7.35 – 7.14 (m, 3H), 6.97 (s, 2H), 3.44 (s, 2H), 1.58 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 135.7, 132.8, 131.1, 130.3, 130.0, 129.2, 127.9, 127.8, 125.5, 124.3, 122.3, 114.4, 90.1, 87.6, 63.2, 39.6, 19.8; HRMS (ESI) calcd for $C_{23}H_{14}BrN_2$ $[M-H]^-$: 397.0334; found: 397.0334.

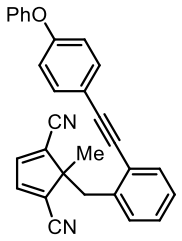
2-(2-([1,1'-Biphenyl]-4-ylethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1k):



Prepared according to the general procedure-A as described above in 95% yield (154 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.4) to afford a colorless solid; mp =

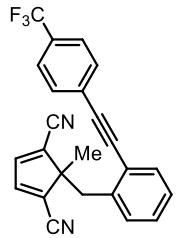
156–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 6H), 7.58 – 7.53 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.31 (m, 1H), 7.30 – 7.19 (m, 3H), 6.94 (s, 2H), 3.41 (s, 2H), 1.55 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 141.3, 140.5, 135.8, 132.9, 132.2, 131.2, 130.3, 129.0, 128.0, 127.9, 127.8, 127.2, 127.2, 124.4, 122.1, 114.4, 94.8, 88.9 63.2, 39.6, 19.7; HRMS (ESI) calcd for $C_{29}H_{21}N_2$ $[M+H]^+$: 397.1692; found: 397.1699.

2-Methyl-2-(2-((4-phenoxyphenyl)ethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1l):



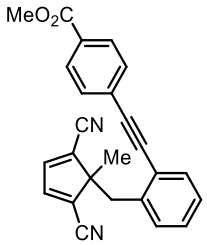
Prepared according to the general procedure-A as described above in 90% yield (152 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 151–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.4, 4.5 Hz, 3H), 7.34 – 7.21 (m, 2H), 7.20 – 7.11 (m, 3H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.87 (s, 2H), 3.33 (s, 2H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 156.4, 141.4, 135.6, 133.4, 132.8, 131.1, 130.3, 130.0, 127.9, 127.8, 124.4, 124.1, 119.7, 118.4, 117.7, 114.4, 94.5, 87.5, 63.1, 39.6, 19.7; HRMS (ESI) calcd for $C_{29}H_{21}N_2O$ $[M+H]^+$: 413.1634; found: 413.1648.

2-Methyl-2-(2-((4-(trifluoromethyl)phenyl)ethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1m):



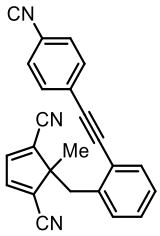
Prepared according to the general procedure-A as described above in 80% yield (127 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a orange solid; mp =172–174 °C; ^{1}H NMR (500 MHz, $CDCl_3$)δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.53 (m, 1H), 7.37 – 7.23 (m, 3H), 6.98 (s, 2H), 3.47 (s, 2H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 135.9, 133.2, 132.0, 131.0, 130.3, 130.2 (q, J_{CF} = 32.6 Hz),128.6, 127.9, 127.0, 125.4 (q, J_{CF} = 3.7 Hz), 124.1 (q, J_{CF} = 272.4 Hz), 123.5, 114.4, 93.3, 90.4, 63.2, 39.5, 19.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.81; HRMS (ESI) calcd for $C_{24}H_{16}F_3N_2$ $[M+H]^+$: 389.1249; found: 389.1260.

Methyl4-((2-((2,5-dicyano-1-methylcyclopenta-2,4-dien-1-yl)methyl)phenyl)ethynyl)benzoate (1n):



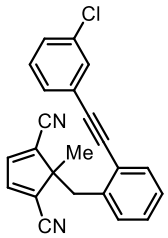
Prepared according to the general procedure-A as described above in 75% yield (116 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 176–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.35 – 7.24 (m, 3H), 6.97 (s, 2H), 3.94 (s, 3H), 3.44 (s, 2H), 1.58 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 141.5, 136.0, 133.1, 131.7, 131.0, 130.3, 129.8, 129.7, 128.5, 127.9, 123.7, 114.3, 94.0, 91.0, 63.1, 52.4, 39.5, 19.8; HRMS (ESI) calcd for $C_{25}H_{19}N_2O_2$ $[M+H]^+$: 379.1432; found: 379.1441.

2-(2-((4-Cyanophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1o):



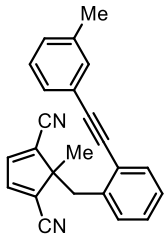
Prepared according to the general procedure-A as described above in 78% yield (110 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 163–165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 4H), 7.63 – 7.52 (m, 1H), 7.38 – 7.19 (m, 3H), 6.97 (s, 2H), 3.46 (s, 2H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 136.0, 133.2, 132.3, 132.2, 130.9, 130.3, 128.8, 128.1, 127.9, 123.2, 118.7, 114.4, 111.9, 93.0, 92.3, 63.2, 39.5, 20.1; HRMS (ESI) calcd for $C_{24}H_{14}N_3$ $[M-H]^-$: 344.1193 ; found : 344.1193.

2-(2-((3-Chlorophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1p):



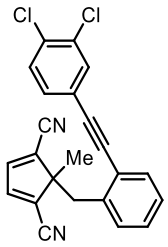
Prepared according to the general procedure-A as described above in 87% yield (131 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 143–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 3H), 7.32 – 7.24 (m, 2H), 7.19 – 7.15 (m, 3H), 6.87 (s, 2H), 3.34 (s, 2H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 135.7, 134.7, 133.0, 132.9, 131.0, 130.3, 128.9, 128.2, 127.8, 123.9, 121.7, 114.4, 93.7, 89.0, 63.1, 39.5, 19.8; HRMS (ESI) calcd for $C_{23}H_{16}ClN_2$ $[M+H]^+$: 355.0998; found: 355.0996.

2-Methyl-2-(2-(m-tolylethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1q):



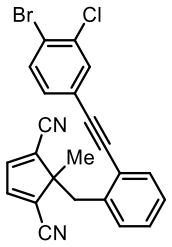
Prepared according to the general procedure-A as described above in 85% yield (116 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.4) to afford a brown solid; mp = 154–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.51 (m, 1H), 7.46 – 7.35 (m, 2H), 7.28 (d, *J* = 4.4 Hz, 4H), 7.19 (d, *J* = 6.6 Hz, 1H), 6.98 (s, 2H), 3.43 (s, 2H), 2.39 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 138.2, 135.7, 132.9, 132.3, 131.2, 130.3, 129.5, 128.8, 128.4, 127.9, 127.8, 124.5, 123.0, 114.3, 95.1, 87.8, 63.1, 39.6, 21.4, 19.6; HRMS (ESI) calcd for $C_{24}H_{19}N_2$ $[M+H]^+$: 335.1544; found: 335.1542.

2-(2-((3,4-Dichlorophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1r):



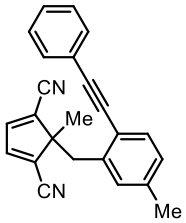
Prepared according to the general procedure-A as described above in 85% yield (135 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 146–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.7 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.36 – 7.28 (m, 2H), 7.20 – 7.15 (m, 3H), 6.87 (s, 2H), 3.34 (s, 2H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 135.9, 133.4, 133.1, 133.0, 132.7, 130.9, 130.6, 130.3, 128.5, 127.9, 123.5, 123.2, 114.4, 92.4, 90.0, 63.2, 39.5, 20.0; HRMS (ESI) calcd for $C_{23}H_{13}N_2Cl_2$ $[M-H]^-$: 387.0474; found: 387.0461.

2-(2-((4-Bromo-3-chlorophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1s):



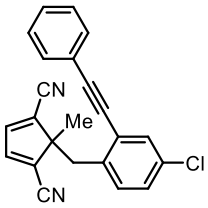
Prepared according to the general procedure-A as described above in 87% yield (154 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 173–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.9 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.25 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.20 – 7.15 (m, 3H), 6.87 (s, 2H), 3.34 (s, 2H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 135.9, 134.6, 133.8, 133.2, 133.0, 130.98, 131.0, 130.3, 128.5, 127.9, 123.9, 123.4, 123.0, 114.4, 92.5, 90.1, 63.2, 39.5, 19.9; HRMS (ESI) calcd for $C_{23}H_{13}BrClN_2$ $[M-H]^-$: 430.9969; found: 430.9956.

2-Methyl-2-(5-methyl-2-(phenylethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1t):



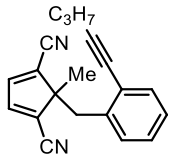
Prepared according to the general procedure-B as described above in 82% yield (92 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 142–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.15 – 7.01 (m, 2H), 6.97 (s, 2H), 3.34 (s, 2H), 2.36 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 138.2, 135.6, 132.7, 131.6, 131.3, 131.3, 128.7, 128.5, 128.4, 123.4, 121.4, 114.3, 94.1, 88.4, 63.0, 39.5, 21.6, 19.3; HRMS (ESI) calcd for $C_{24}H_{19}N_2$ $[M+H]^+$: 335.1545; found: 335.1543.

2-Methyl-2-(2-(p-tolylethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1u):



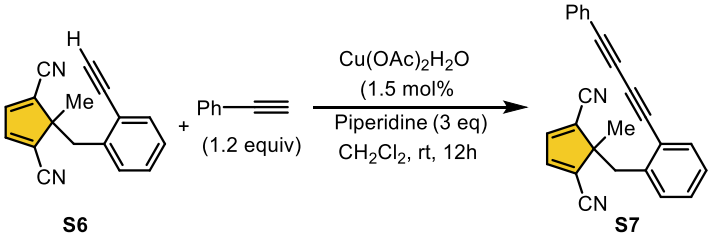
Prepared according to the general procedure-B as described above in 90% yield (107 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.4) to afford a yellow solid; mp = 137–139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.32 – 7.21 (m, 2H), 7.02 (s, 2H), 3.39 (s, 2H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 137.4, 133.9, 133.9, 131.7, 130.9, 130.3, 128.9, 128.6, 128.2, 122.9, 122.9, 114.1, 95.8, 87.11, 62.7, 39.2, 19.6; HRMS (ESI) calcd for $C_{23}H_{16}N_2Cl$ $[M+H]^+$: 355.0998; found: 355.0996.

2-(2-Bromobenzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1v):



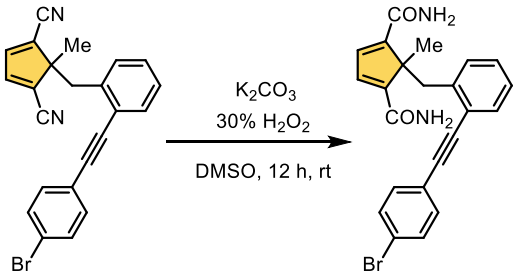
Prepared according to the general procedure-B as described above in 85% yield (82 mg). It was purified by flash chromatography (5% EtOAc/hexanes; R_f = 0.3) to afford a brown solid; mp = 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 1H), 7.15 – 7.04 (m, 3H), 6.83 (s, 2H), 3.31 (s, 2H), 2.39 (t, *J* = 7.1 Hz, 2H), 1.59 (ddd, *J* = 12.4, 8.3, 6.2 Hz, 2H), 1.48 (s, 3H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 135.6, 132.8, 131.0, 130.1, 127.5, 127.1, 124.9, 114.5, 96.4, 79.4, 63.3, 39.6, 22.1, 22.0, 20.1, 13.9; HRMS (ESI) calcd for $C_{20}H_{19}N_2$ $[M+H]^+$: 287.1544; found: 287.1543.

Procedure for the synthesis of 1,3-diynes S7:[3]



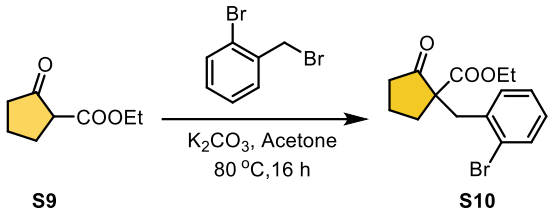
A mixture of cyclopentane-1,3-dicarbonitrile alkyne **S6** (0.8 mmol), phenylacetylene (1.6 mmol), piperidine (2.4 mmol), and $Cu(OAc)_2 \cdot H_2O$ (10 mol%) in CH_2Cl_2 (0.4 M, 2 mL) was stirred under open air atmosphere at 25 °C for 4 h. After completion of reaction (monitored by TLC), the mixture was concentrated in vacuo and the residue was purified by flash column chromatography (5% EtOAc/hexanes; R_f = 0.3) on silica gel to afford a brown solid 1,3-diyne **S7** in 88% yield (248 mg); mp = 125–127 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 3H), 7.35 – 7.25 (m, 3H), 7.23 – 7.13 (m, 3H), 6.89 (s, 2H), 3.30 (s, 2H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 137.3, 133.9, 132.7, 130.9, 130.5, 129.4, 128.9, 128.5, 127.9, 122.9, 121.8, 114.3, 83.3, 79.9, 79.6, 74.1, 63.0, 39.6, 19.9; HRMS (ESI) calcd for $C_{25}H_{17}N_2$ $[M+H]^+$: 345.1392; found: 345.1382.

Procedure for the synthesis of 1,3-diamide S8:[5]



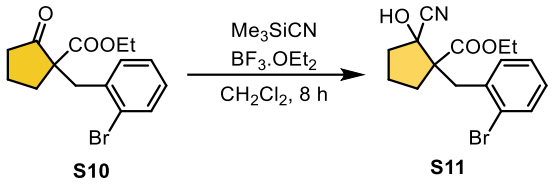
To a solution of compound **1j** (0.50 mmol, 1 equiv) in DMSO (3 mL) was addecd K_2CO_3 (139 mg, 2.0 equiv) and 30% H_2O_2 (0.5 mL, 10 equiv). The reaction mixture was allowed to stir at room temperature for 12 h and quenched with saturated aqueous $NaHCO_3$ (20 mL). The reaction mixture was extracted with of EtOAC (2 x 20 mL), dried combined organic layer over Na_2SO_4 and evaporated *in vacuo.* the residue was purified by flash column chromatography (60% EtOAc/hexanes; R_f = 0.4) on silica gel to afford a colorless solid 1,3-diamine **S8** in 85% yield (185 mg); mp = 200–203 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.70 – 7.65 (m, 2H), 7.63 – 7.59 (m, 2H), 7.43 (s, 2H), 7.35 – 7.32 (m, 1H), 7.11 – 7.08 (m, 2H), 6.97 – 6.96 (m, 1H), 6.95 (s, 2H), 6.83 (s, 2H), 3.73 (s, 2H), 1.63 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 165.3, 151.4, 140.2, 133.5, 132.0, 131.5, 128.7, 127.5, 126.0, 122.5, 122.2, 121.7, 91.5, 89.7, 58.8, 37.8, 23.0; HRMS (ESI) calcd for $C_{23}H_{20}O_2N_2Br$ $[M+H]^+$: 435.0694; found: 435.0702.

Procedure for the synthesis of Ethyl 1-(2-Bromobenzyl)-2-oxocyclopentane-1-carboxylate:[6]



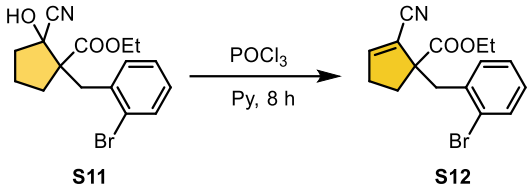
To a vigorously stirred suspension of ethyl 2-oxocyclopentane-1-carboxylate **S9** (1 equiv) in acetone (1.0 M), was gradually added K_2CO_3 (1 equiv) and stirred for additional 30 minutes. Then benzyl bromide (1.2 equiv) was added to the reaction mixture and stirred at 80 °C in preheated oil bath for 16 h. Later, the reaction mixture was concentrated and extracted with CH_2Cl_2 (2 times) and the combined organic solvent was washed with 5% NH_4Cl aqueous solution and dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The obtained crude residue was purified by flash column chromatography (hexane/EtOAc).

Procedure for the synthesis of Ethyl 1-(2-Bromobenzyl)-2-cyano-2-hydroxycyclopentane-1-carboxylate:[2]



Me_3SiCN (1.5 equiv) and $BF_3.OEt_2$ (1.5 equiv) were added dropwise consecutively to a stirred solution of **S11** (1 equiv) in dry CH_2Cl_2 (0.3 M) under nitrogen atmosphere. The resulting mixture was heated at reflux using preheated oil bath for 8 h, the reaction was quenched at 0 ^oC by adding aqueous hydrochloric acid (1.0 M). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (two times). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, Na_2SO_4 and concentrated in *vacuo*. The obtained crude residue was purified by flash column chromatography (20% EtOAc/hexanes; R_f = 0.4) on silica gel to afford a colorless oil S**12** in 85% yield (460 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.21 – 7.13 (m, 1H), 7.11 – 6.99 (m, 2H), 4.25 – 3.98 (m, 2H), 3.70 (s, 1H), 3.47 (d, *J* = 13.9 Hz, 1H), 2.99 (d, *J* = 13.9 Hz, 1H), 2.51 – 2.36 (m, 1H), 2.21 – 2.08 (m, 2H), 2.03 – 1.81 (m, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 135.9, 133.2, 131.5, 128.9, 127.5, 126.1, 119.7, 78.8, 63.0, 62.0, 39.0, 37.9, 28.3, 20.1, 13.9; HRMS (ESI) calcd for $C_{16}H_{19}O_3NBr$ $[M+H]^+$: 352.0535; found: 352.0542.

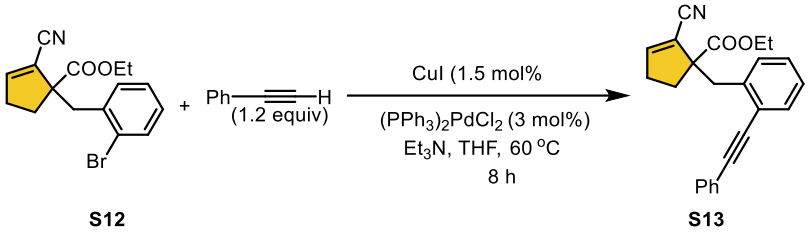
General procedure for the synthesis of Ethyl 1-(2-Bromobenzyl)-2-cyanocyclopent-2-ene-1-carboxylate:[2]



Compounds **S12** (1 equiv) were dissolved in pyridine (0.5 M) followed by the addition of $POCl_3$ (2.5 equiv) under nitrogen atmosphere. After heating at 60 ^oC for 3 h, the reaction mixture was cooled to 0 ^oC and CH_2Cl_2 was added. Then, the mixture was poured into hydrochloric acid (2 M) slowly. After filtration through a pad of Celite, the filtration cake was washed with CH_2Cl_2 and the filtrate was moved into a separating funnel. The organic layer was collected, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with a saturated solution of sodium bicarbonate and brine, and dried over anhydrous Na_2SO_4. After removal of the organic solvent, the

residue was purified by flash column chromatography (5% EtOAc/hexanes; R_f = 0.4) on silica gel to afford a colorless oil S**13** in 80% yield (348 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.07 – 7.02 (m, 1H), 6.67 (t, *J* = 2.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.55 (d, *J* = 14.2 Hz, 1H), 3.18 (d, *J* = 14.2 Hz, 1H), 2.54 – 2.29 (m, 2H), 2.19 – 1.99 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 152.2, 135.9, 133.3, 131.6, 128.9, 127.6, 126.3, 118.3, 115.7, 62.0, 39.8, 32.5, 31.7, 14.2; HRMS (ESI) calcd for $C_{16}H_{17}O_2NBr$ $[M+H]^+$: 334.0432; found: 334.0437.

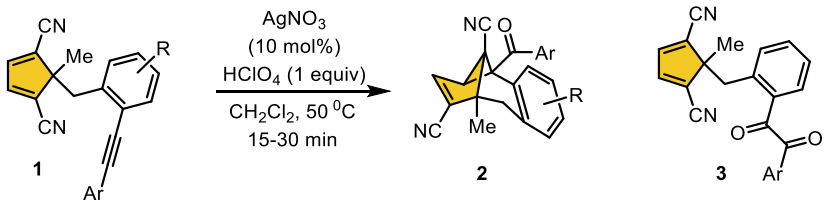
Sonogashira coupling of Ethyl 2-cyano-1-(2-(Phenylethynyl)benzyl)cyclopent-2-ene-1-carboxylate: [3]



To a solution of **S13** (1 equiv) in anhydrous THF (0.5 M), was added $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (5 mol%), Et_3N (1.7 equiv) and phenyl acetylene (1.3 equiv). The mixture was stirred at 60 °C for 8 h. The reaction was cooled to room temperature, diluted with water, and the mixture was extracted with EtOAc. The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The obtained crude residue was purified by flash chromatography flash column chromatography (5% EtOAc/hexanes; R_f = 0.5) on silica gel to afford a colorless oil **S14** in 88% yield (280 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 3H), 7.34 – 7.26 (m, 3H), 7.22 – 7.14 (m, 3H), 6.63 (t, *J* = 1.9 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.73 (d, *J* = 13.7 Hz, 1H), 3.18 (d, *J* = 13.7 Hz, 1H), 2.41 – 2.25 (m, 3H), 2.09 – 1.91 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 151.9, 137.9, 132.5, 131.6, 130.4, 128.6, 128.5, 127.2, 124.6, 123.2, 118.3, 116.0, 93.8, 88.5, 62.5, 61.9, 38.8, 32.5, 31.6, 14.2; HRMS (ESI) calcd for $C_{24}H_{22}NO_2$ $[M+H]^+$: 356.1640; found: 356.1645.

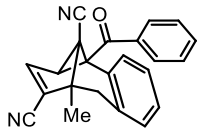
IIIB. Experimental procedure & analytical data of products:

General procedure for Ag(I)-catalyzed stereoselective cyclopropanation:



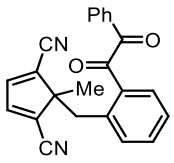
A dried screw-cap vial was charged with cyclopentene dinitrile alkynes **1** (0.2 mmol, 1.0 equiv), and $AgNO_3$ (3.4 mg, 10.0 mol%) in CH_2Cl_2 (2 mL, 0.1 M) was added $HClO_4$ (18 µL, ~70% aqueous solution, 1.0 equiv). The reaction mixture was stirred at 50 °C in oil bath for 15-30 minutes (monitored by TLC). Then, it was cooled to room temperature and quenched with aqueous $NaHCO_3$ (5 mL) solution. The mixture was extracted with CH_2Cl_2 (3 x 5 mL) and combined organic solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate) to afford the desired product **2** along with trace amount of uncyclized 1,3-dicarbonyl product **3**. [Note: For small scale reaction, we didn't observe any problem with aq. $HClO_4$. However, for large scale, it recommends to perform the reaction in the presence of laboratory protective shield].

7*b*-Benzoyl-2a1-isocyano-2a-methyl-2*a*,2*a*1,7*b*,7*c*-tetrahydro-3*H* benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2a):



Prepared according to the general procedure as described above in 72% yield (48 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 218–220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.59 (m, 2H), 7.48-7.45 (m, 1H), 7.34-7.31 (m, 2H), 7.24-7.19 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.34 (d, *J* = 2.6 Hz, 1H), 3.99 (d, *J* = 2.6 Hz, 1H), 3.41 (d, *J* = 16.2 Hz, 1H), 2.93 (d, *J* = 16.2 Hz, 1H), 1.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 142.2, 134.7, 133.8, 133.8, 129.5, 129.4, 129.1, 129.1, 128.8, 128.3, 128.0, 124.3, 115.2, 113.3, 52.4, 47.3, 43.5, 37.5, 33.4, 23.3; HRMS (ESI) calcd for $C_{23}H_{17}N_2O$ $[M+H]^+$: 337.1341; found: 337.1294.

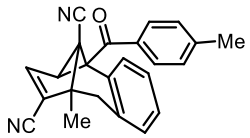
2-Methyl-2-(2-(2-oxo-2-phenylacetyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (3a):



Prepared according to the general procedure as described above in 7% yield (5 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.5) to afford a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 7.89 (m, 1H), 7.75 – 7.64 (m, 2H), 7.59 – 7.47 (m, 3H), 7.43 – 7.34 (m, 2H), 7.27 – 7.06 (m, 1H), 7.01 (s, 2H), 3.75 (s, 2H), 1.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 194.2,

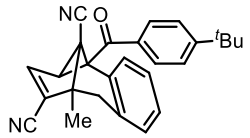
141.6, 137.2, 135.0, 133.7, 133.6, 133.4, 133.3, 133.0, 131.0, 130.2, 129.2, 128.1, 114.4, 62.7, 37.2, 20.1; HRMS (ESI) calcd for $C_{23}H_{17}N_2O_2$ $[M+H]^+$: 353.1278; found: 353.1284.

2a^1-Isocyano-2a-methyl-7b-(4-methylbenzoyl)-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2b):



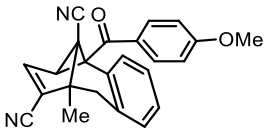
Prepared according to the general procedure as described above in 64% yield (47 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 211–213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.16 – 7.03 (m, 3H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.33 (d, *J* = 2.6 Hz, 1H), 3.96 (d, *J* = 2.6 Hz, 1H), 3.40 (d, *J* = 16.2 Hz, 1H), 2.92 (d, *J* = 16.2 Hz, 1H), 2.32 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 192.6, 144.9, 142.3, 133.8, 132.0, 129.7, 129.5, 129.1, 129.0, 128.3, 128.2, 124.2, 115.3, 113.3, 52.4, 47.4, 43.5, 37.6, 33.3, 23.4, 21.9; HRMS (ESI) calcd for $C_{24}H_{19}N_2O$ $[M+H]^+$: 351.1497; found: 351.1504.

4-(*tert*-Butyl)benzoyl)-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2c):



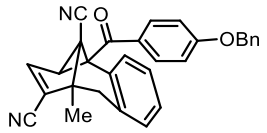
Prepared according to the general procedure as described above in 75% yield (61 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 202–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.17 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 2.5 Hz, 1H), 3.96 (d, *J* = 2.5 Hz, 1H), 3.41 (d, *J* = 16.1 Hz, 1H), 2.92 (d, *J* = 16.1 Hz, 1H), 1.73 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 157.7, 142.3, 133.8, 131.8, 129.6, 129.4, 129.1, 129.0, 128.3, 128.2, 125.8, 124.2, 115.3, 113.3, 52.4, 47.4, 43.5, 37.6, 35.3, 33.2, 31.1, 23.3; HRMS (ESI) calcd for $C_{27}H_{25}N_2O$ $[M+H]^+$: 393.1967; found: 393.1970.

2a^1-Isocyano-7b-(4-methoxybenzoyl)-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3*H*-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2d):



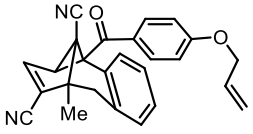
Prepared according to the general procedure as described above in 74% yield (56 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 230–232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.56 (m, 2H), 7.25 – 7.18 (m, 2H), 7.11 – 7.07 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.84 – 6.75 (m, 2H), 6.34 (d, *J* = 2.6 Hz, 1H), 3.95 (d, *J* = 2.6 Hz, 1H), 3.80 (s, 3H), 3.38 (d, *J* = 16.2 Hz, 1H), 2.92 (d, *J* = 16.2 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3, 164.0, 142.4, 133.7, 132.1, 129.4, 129.1, 129.0, 128.4, 128.3, 127.3, 124.1, 115.3, 114.1, 113.4, 55.6, 52.4, 47.3, 43.6, 37.6, 33.1, 23.4; HRMS (ESI) calcd for $C_{24}H_{19}N_2O_2$ $[M+H]^+$: 367.1447; found: 367.1445.

4-(Benzyloxy)benzoyl)-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2e):



Prepared according to the general procedure as described above in 81% yield (74 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 238–240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.9 Hz, 2H), 7.38 – 7.21 (m, 4H), 7.19 – 7.07 (m, 3H), 7.02 – 6.95 (m, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.22 (d, *J* = 2.6 Hz, 1H), 4.94 (s, 2H), 3.84 (d, *J* = 2.6 Hz, 1H), 3.28 (d, *J* = 16.2 Hz, 1H), 2.81 (d, *J* = 16.2 Hz, 1H), 1.62 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 163.2, 142.4, 136.0, 133.7, 132.1, 129.4, 129.1, 129.0, 128.8, 128.5, 128.3, 127.6, 127.5, 124.1, 115.3, 114.9, 113.4, 70.3, 52.4, 47.3, 43.6, 37.6, 33.1, 23.4; HRMS (ESI) calcd for $C_{30}H_{23}N_2O_2$ $[M+H]^+$: 443.1760; found: 443.1755.

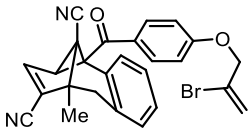
4-(Allyloxy)benzoyl)-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2f):



Prepared according to the general procedure as described above in 79% yield (58 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 234–236

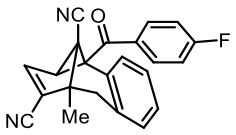
°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.9 Hz, 2H), 7.29 – 7.17 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.33 (d, *J* = 2.5 Hz, 1H), 5.99 (ddd, *J* = 22.5, 10.6, 5.3 Hz, 1H), 5.49 – 5.08 (m, 2H), 4.52 (d, *J* = 5.3 Hz, 2H), 3.95 (d, *J* = 2.5 Hz, 1H), 3.38 (d, *J* = 16.2 Hz, 1H), 2.92 (d, *J* = 16.2 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 163.0, 142.4, 133.7, 132.3, 132.1, 129.4, 129.1, 128.0, 128.3, 127.4, 125.5, 125.5, 124.1, 118.5, 115.3, 114.8, 113.4, 69.1, 52.4, 47.3, 43.6, 37.6, 33.1, 23.4; HRMS (ESI) calcd for $C_{26}H_{21}N_2O_2$ $[M+H]^+$: 393.1603; found: 393.1595.

4-((2-Bromoallyl)oxy)benzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2g):



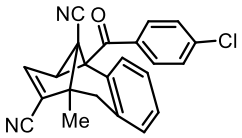
Prepared according to the general procedure as described above in 67% yield (66 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 214–216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.9 Hz, 2H), 7.31 – 7.17 (m, 2H), 7.13 – 7.06 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.33 (d, *J* = 2.6 Hz, 1H), 5.92 (d, *J* = 2.0 Hz, 1H), 5.68 – 5.65 (m, 1H), 4.62 (s, 2H), 3.95 (d, *J* = 2.6 Hz, 1H), 3.38 (d, *J* = 16.2 Hz, 1H), 2.92 (d, *J* = 16.2 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 162.0, 142.3, 133.7, 132.1, 129.3, 129.2, 129.0, 128.3, 128.2, 128.1, 125.8, 124.1, 118.5, 115.3, 114.9, 113.3, 71.6, 52.4, 47.3, 43.5, 37.5, 33.2, 23.3; HRMS (ESI) calcd for $C_{26}H_{20}BrO_2N_2$ $[M+H]^+$: 471.0708; found: 471.0698.

4-Fluorobenzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2h):



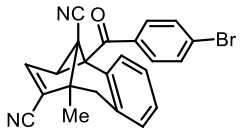
Prepared according to the general procedure as described above in 63% yield (46 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 234–236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H), 7.25 – 7.10 (m, 2H), 7.04 – 6.99 (m, 1H), 6.97 – 6.85 (m, 3H), 6.26 (d, *J* = 2.5 Hz, 1H), 3.91 (d, *J* = 2.5 Hz, 1H), 3.31 (d, *J* = 16.2 Hz, 1H), 2.86 (d, *J* = 16.3 Hz, 1H), 1.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 165.9 (d, J_{CF} = 256.8 Hz), 142.1, 133.8, 132.3 (d, J_{CF} = 9.6 Hz), 131.0 (d, J_{CF} = 2.9 Hz), 129.4, 129.3, 128.4, 127.8, 124.3, 116.1 (d, J_{CF} = 22.3 Hz), 115.1, 113.2, 52.4, 47.2, 43.6, 37.5, 33.3, 23.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.00; HRMS (ESI) calcd for $C_{23}H_{16}FN_2O$ $[M+H]^+$: 355.1247; found: 355.1287.

4-Chlorobenzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2i):



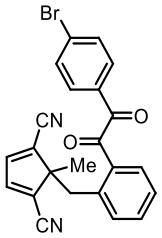
Prepared according to the general procedure as described above in 67% yield (52 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 247–249 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.57 (m, 2H), 7.42 – 7.21 (m, 4H), 7.17 – 7.07 (m, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.36 (d, *J* = 2.6 Hz, 1H), 4.01 (d, *J* = 2.6 Hz, 1H), 3.40 (d, *J* = 16.2 Hz, 1H), 2.96 (d, *J* = 16.3 Hz, 1H), 1.75 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 142.0, 140.3, 133.8, 133.0, 130.9, 129.4, 129.3, 129.2, 128.4, 127.6, 124.3, 115.0, 113.2, 52.4, 47.2, 43.5, 37.5, 33.4, 23.3; HRMS (ESI) calcd for $C_{23}H_{16}ClN_2O$ $[M+H]^+$: 371.0951; found: 371.1016.

4-Bromobenzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3*H*-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2j):



Prepared according to the general procedure as described above in 65% yield (54 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 239–241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.39 (m, 4H), 7.28 – 7.20 (m, 2H), 7.12 – 7.04 (m, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 2.6 Hz, 1H), 3.99 (d, *J* = 2.6 Hz, 1H), 3.37 (d, *J* = 16.3 Hz, 1H), 2.93 (d, *J* = 16.3 Hz, 1H), 1.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 142.0, 133.8, 133.4, 132.2, 130.9, 129.4, 129.3, 129.3, 129.2, 128.5, 127.6, 124.3, 115.0, 113.2, 52.4, 47.2, 43.5, 37.5, 33.4, 23.3; HRMS (ESI) calcd for $C_{23}H_{16}BrN_2O$ $[M+H]^+$: 415.0446; found: 415.0453.

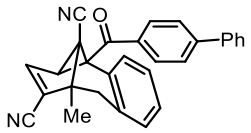
2-(2-(2-(4-Bromophenyl)-2-oxoacetyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (3j):



Prepared according to the general procedure as described above in 8% yield (86 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.5) to afford a yellow liquid; ^{1}H NMR (300

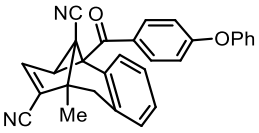
MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 2H), 7.72 – 7.65 (m, 2H), 7.60 – 7.47 (m, 2H), 7.45 – 7.33 (m, 2H), 7.01 (s, 2H), 3.74 (s, 2H), 1.56 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.7, 193.1, 141.7, 137.2, 133.7, 133.6, 132.8, 132.6, 132.0, 131.6, 131.0, 130.7, 128.1, 114.4, 62.7, 37.2, 20.1; HRMS (ESI) calcd for $C_{23}H_{16}BrN_2O_2$ $[M+H]^+$: 431.0393; found: 431.0389.

[1,1'-Biphenyl]-4-carbonyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2k):



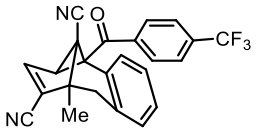
Prepared according to the general procedure as described above in 80% yield (67 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 218–220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.68 (m, 2H), 7.57 – 7.52 (m, 4H), 7.46 – 7.34 (m, 3H), 7.31 – 7.19 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.35 (d, *J* = 2.6 Hz, 1H), 4.01 (d, *J* = 2.6 Hz, 1H), 3.44 (d, *J* = 16.2 Hz, 1H), 2.95 (d, *J* = 16.2 Hz, 1H), 1.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 146.4, 142.2, 139.5, 133.8, 133.2, 130.2, 129.4, 129.2, 129.1, 129.0, 128.5, 128.4, 128.0, 127.4, 127.3, 124.2, 115.2, 113.3, 52.4, 47.4, 43.5, 37.6, 33.4, 23.3; HRMS (ESI) calcd for $C_{29}H_{21}N_2O$ $[M+H]^+$: 413.1654; found: 413.1660.

2a^1-Isocyano-2a-methyl-7b-(4-phenoxybenzoyl)-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2l):



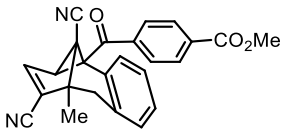
Prepared according to the general procedure as described above in 84% yield (73 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 244–246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 2H), 7.46 – 7.31 (m, 2H), 7.30 – 7.18 (m, 3H), 7.17 – 7.08 (m, 1H), 7.03-7.01 (m, 3H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.33 (d, *J* = 2.6 Hz, 1H), 3.96 (d, *J* = 2.6 Hz, 1H), 3.35 (d, *J* = 16.2 Hz, 1H), 2.90 (d, *J* = 16.2 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 162.7, 154.9, 142.3, 133.7, 132.0, 130.2, 129.3, 129.2, 129.0, 128.7, 128.4, 128.1, 125.1, 124.1, 120.8, 117.0, 115.3, 113.3, 52.4, 47.3, 43.5, 37.5, 33.2, 23.3; HRMS (ESI) calcd for $C_{29}H_{21}N_2O_2$ $[M+H]^+$: 429.1603; found: 429.1612.

2a^1-Isocyano-2a-methyl-7b-(4-(trifluoromethyl)benzoyl)-2a,2a^1,7b,7c-tetrahydro-3*H*-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2m):



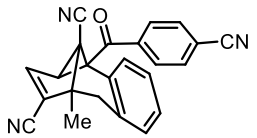
Prepared according to the general procedure as described above in 60% yield (50 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a brown solid ; mp = 244–246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.13 (m, 2H), 7.05 – 6.93 (m, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.27 (d, *J* = 2.6 Hz, 1H), 3.96 (d, *J* = 2.6 Hz, 1H), 3.32 (d, *J* = 16.3 Hz, 1H), 2.88 (d, *J* = 16.3 Hz, 1H), 1.67 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.5, 141.9, 137.5, 134.8 (q, J_{CF} = 33.1 Hz), 133.9, 129.8, 129.5, 129.4, 129.4, 128.5, 127.3, 125.9 (q, J_{CF} = 3.4 Hz), 124.5, 123.4 (q, J_{CF} = 273.5 Hz), 115.0, 113.1, 52.5, 47.2, 43.5, 37.5, 33.6, 23.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.36; HRMS (ESI) calcd for $C_{24}H_{16}N_2F_3O$ $[M+H]^+$: 405.1203; found: 405.1209.

Methyl 2-cyano-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3*H*-benzo[*f*]cyclopropa[*cd*]indene-7b-carbonyl) benzoate (2n):



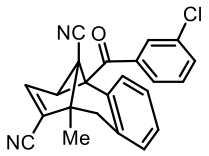
Prepared according to the general procedure as described above in 53% yield (43 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 255–257 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.16 (m, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.34 (d, *J* = 2.5 Hz, 1H), 4.02 (d, *J* = 2.5 Hz, 1H), 3.89 (s, 3H), 3.40 (d, *J* = 16.2 Hz, 1H), 2.94 (d, *J* = 16.3 Hz, 1H), 1.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 165.8, 141.9, 138.0, 134.2, 133.8, 129.8, 129.4, 129.2, 129.2, 129.2, 128.3, 127.3, 124.3, 114.9, 113.1, 52.5, 52.4, 47.2, 43.4, 37.4, 33.6, 23.2; HRMS (ESI) calcd for $C_{25}H_{19}N_2O_3$ $[M+H]^+$: 395.1396; found: 395.1432.

4-Cyanobenzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3*H*-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2o):



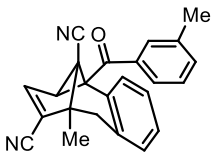
Prepared according to the general procedure as described above in 56% yield (41 mg). It was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 241–243 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.52 (m, 4H), 7.35 – 7.22 (m, 2H), 7.11 (t, *J* = 6.9 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.37 (d, *J* = 2.2 Hz, 1H), 4.06 (d, *J* = 2.2 Hz, 1H), 3.40 (d, *J* = 16.4 Hz, 1H), 2.98 (d, *J* = 16.4 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 141.7, 138.0, 134.0, 132.6, 129.7, 129.6, 129.5, 129.4, 128.6, 127.0, 124.6, 117.6, 116.9, 114.9, 113.0, 52.6, 47.1, 43.6, 37.5, 33.8, 23.3; HRMS (ESI) calcd for $C_{24}H_{16}N_3O$ $[M+H]^+$: 362.1290; found: 362.1287.

3-Chlorobenzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3*H*-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2p):



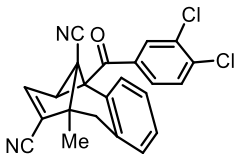
Prepared according to the general procedure as described above in 76% yield (57 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 231–233 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.6 Hz, 2H), 7.25 – 7.12 (m, 4H), 7.04 – 6.97 (m, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.26 (d, *J* = 2.6 Hz, 1H), 3.91 (d, *J* = 2.6 Hz, 1H), 3.30 (d, *J* = 16.3 Hz, 1H), 2.86 (d, *J* = 16.3 Hz, 1H), 1.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 142.0, 140.3, 133.8, 132.9, 130.8, 129.3, 129.2, 129.2, 128.4, 127.6, 124.3, 115.0, 113.2, 52.4, 47.1, 43.5, 37.4, 33.4, 23.3; HRMS (ESI) calcd for $C_{23}H_{16}ON_2Cl$ $[M+H]^+$: 371.0945; found: 371.0945.

2a^1-Isocyano-2a-methyl-7b-(3-methylbenzoyl)-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2q):



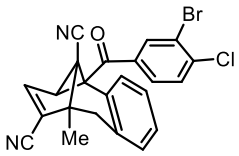
Prepared according to the general procedure as described above in 73% yield (54 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 218–220 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.16 (m, 4H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 6.33 (d, *J* = 2.6 Hz, 1H), 3.98 (d, *J* = 2.6 Hz, 1H), 3.40 (d, *J* = 16.2 Hz, 1H), 2.93 (d, *J* = 16.2 Hz, 1H), 2.30 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 142.3, 138.6, 134.6, 134.6, 133.8, 130.1, 129.3, 129.0, 129.0, 128.5, 128.2, 128.1, 126.7, 124.1, 115.2, 113.3, 52.4, 47.3, 43.5, 37.5, 33.4, 23.3, 21.4; HRMS (ESI) calcd for $C_{24}H_{19}ON_2$ $[M+H]^+$: 351.1495; found: 351.1491.

3,4-Dichlorobenzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2r):



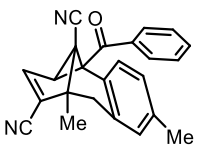
Prepared according to the general procedure as described above in 74% yield (62mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 250–252 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.24 – 7.13 (m, 2H), 7.04 (dd, *J* = 10.2, 3.9 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 3.92 (d, *J* = 2.4 Hz, 1H), 3.29 (d, *J* = 16.3 Hz, 1H), 2.88 (d, *J* = 16.3 Hz, 1H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 141.8, 138.6, 134.1, 133.8, 133.7, 131.6, 130.9, 129.6, 129.4, 129.4, 128.6, 128.3, 127.2, 124.4, 114.9, 113.1, 52.5, 47.0, 43.5, 37.4, 33.5, 23.3; HRMS (ESI) calcd for $C_{23}H_{15}N_2Cl_2O$ $[M+H]^+$: 405.0561; found: 405.0587.

3-Bromo-4-chlorobenzoyl-2a^1-isocyano-2a,5-dimethyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2s):



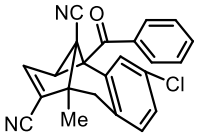
Prepared according to the general procedure as described above in 71% yield (65 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 242–244°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.1 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.22 (m, 3H), 7.21 – 7.10 (m, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.36 (d, *J* = 2.6 Hz, 1H), 4.02 (d, *J* = 2.6 Hz, 1H), 3.38 (d, *J* = 16.3 Hz, 1H), 2.97 (d, *J* = 16.3 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 141.8, 135.7, 134.8, 134.2, 133.8, 131.2, 129.6, 129.4, 129.4, 129.2, 128.6, 128.2, 127.2, 124.4, 114.9, 113.1, 52.5, 47.0, 43.5, 37.4, 33.5, 23.3; HRMS (ESI) calcd for $C_{23}H_{14}ON_2BrCl$ $[M]^+$: 447.9975; found: 447.9972.

7b-Benzoyl-2a^1-isocyano-2a,5-dimethyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2t):



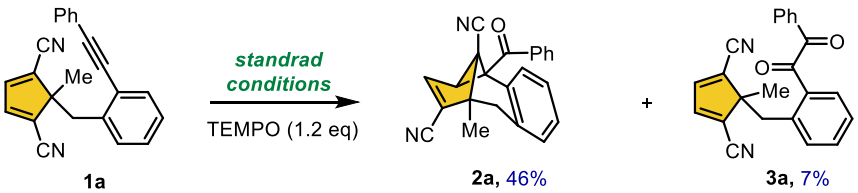
Prepared according to the general procedure as described above in 55% yield (40 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 242–244 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.55 – 7.42 (m, 1H), .37 – 7.29 (m, 2H), 7.04 (s, 1H), 6.85 (d, *J* = 1.9 Hz, 2H), 6.33 (d, *J* = 2.6 Hz, 1H), 3.96 (d, *J* = 2.6 Hz, 1H), 3.36 (d, *J* = 16.2 Hz, 1H), 2.87 (d, *J* = 16.2 Hz, 1H), 2.26 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.4, 142.3, 139.1, 134.7, 133.7, 133.6, 129.7, 129.7, 129.2, 129.1, 128.8, 124.8, 124.3, 115.3, 113.4, 52.4, 47.3, 43.4, 37.6, 33.3, 23.4, 21.3; HRMS (ESI) calcd for $C_{24}H_{19}N_2O$ $[M+H]^+$: 351.1497; found: 351.1494.

7b-Benzoyl-6-chloro-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2u):



Prepared according to the general procedure as described above in 58% yield (45 mg). It was purified by flash chromatography (10% EtOAc/hexanes; R_f = 0.3) to afford a colorless solid; mp = 261–263 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59– 7.56 (m, 2H), 7.47 – 7.37 (m, 1H), 7.31 – 7.26 (m, 2H), 7.22 – 7.15 (m, 1H), 6.98 (ddd, *J* = 8.3, 2.2, 0.7 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.28 (d, *J* = 2.6 Hz, 1H), 3.93 (d, *J* = 2.6 Hz, 1H), 3.32 (d, *J* = 16.3 Hz, 1H), 2.83 (d, *J* = 16.3 Hz, 1H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 142.2, 135.8, 134.8, 134.5, 134.0, 130.7, 129.5, 129.1, 128.9, 128.7, 126.6, 124.2, 114.9, 113.1, 52.4, 46.9, 43.5, 37.4, 33.5, 23.2; HRMS (ESI) calcd for $C_{23}H_{16}ClN_2O$ $[M+H]^+$: 371.0940; found: 371.0945.

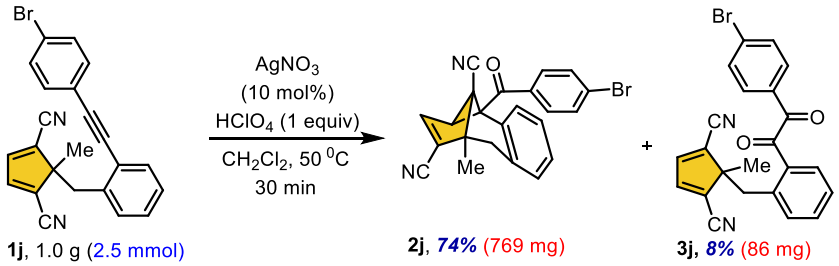
Control experiment on 1a:



A dried screw-cap vial was charged with dinitrile alkyne **1a** (0.2 mmol, 1.0 equiv), and $AgNO_3$ (3.4 mg, 10.0 mol%) in CH_2Cl_2 (2 mL, 0.1 M) then added $HClO_4$ (18 µL, ~70% aqueous solution, 1.0 equiv) and TEMPO (37 mg, 1.2 equiv). The reaction mixture was stirred at 50 °C in oil bath for 30 min (monitored by TLC). Then, it was cooled to room temperature and quenched with aqueous $NaHCO_3$ (5 mL) solution. The mixture was extracted with CH_2Cl_2 (3 x 5 mL), combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified

by flash column chromatography on silica gel (hexanes/ethyl acetate) to afford product **2a** in 46% yield and by-product **3a** in 7% yield.

IIIC. Gram-scale reaction of 1j:

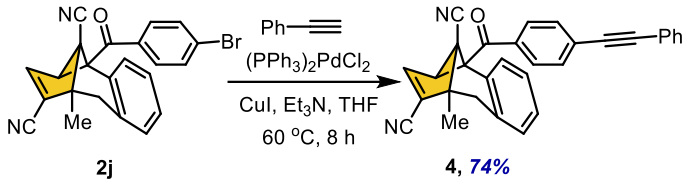


1j, 1.0 g (2.5 mmol) **2j**, *74%* (769 mg) **3j**, *8%* (86 mg)

A dried screw-cap vial was charged with alkyne **1j** (2.5 mmol, 1.0 equiv), and $AgNO_3$ (42.2 mg, 10.0 mol%) in CH_2Cl_2 (17 mL, 0.1 M) then added $HClO_4$ (0.2 mL, ~70% aqueous solution, 1.0 equiv). The reaction mixture was stirred at 50 °C in oil bath for 1 hour (monitored by TLC). Then, it was cooled to room temperature and quenched with aqueous $NaHCO_3$ (15 mL) solution. The mixture was extracted with CH_2Cl_2 (3 x 20 mL), combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by to flash column chromatography on silica gel (10% EtOAc/hexanes; R_f = 0.3) to afford the desired product **2j** (74%, 769 mg) and by-product **3j** (8%, 86 mg). [Note: For small scale reaction, we didn't observe any problem with aq. $HClO_4$. However, for large scale, it recommends to perform the reaction in the presence of laboratory protective shield]

Synthetic utility:

2a[1]-Isocyano-2a-methyl-7b-(4-(phenylethynyl)benzoyl)-2a,2a[1],7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (4):[4]

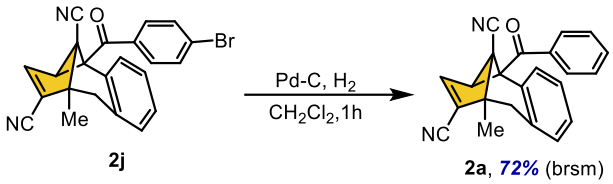


2j **4**, *74%*

To a solution of **2j** (0.14 mmol, 1 equiv) in anhydrous THF (0.5 M), was added $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (5 mol%), Et_3N (1.7 equiv) and phenyl acetylene (1.2 equiv). The mixture was stirred at 60 °C for 8h. The reaction was cooled to room temperature, diluted with water (5 mL), and extracted with EtOAc (3 x 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated in *vacuo.* The obtained crude residue was purified by flash chromatography (20% EtOAc/hexanes; R_f = 0.3) to afford desired product **4** as a colorless solid in 74% yield (47 mg); mp = 255–257 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.33 (m, 5H), 7.31 – 7.02 (m, 6H), 6.45 (d, *J* = 2.2 Hz, 1H), 5.92 (d, *J* = 2.2 Hz, 1H), 2.88 (d, *J* = 14.9 Hz, 1H), 2.78 (d, *J* = 14.9 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 139.4, 135.3, 131.8, 131.7, 130.1, 128.7, 128.5, 128.5,

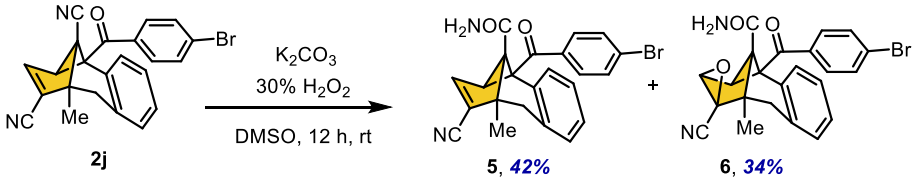
127.7, 127.5, 126.6, 125.1, 122.9, 118.1, 113.8, 107.5, 91.6, 89.1, 88.9, 59.7, 57.6, 41.7, 26.0; HRMS (ESI) calcd for $C_{31}H_{21}N_2O$ $[M+H]^+$: 437.1654; found: 437.1632.

7b-Benzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3*H*-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2a):[4]



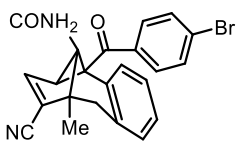
To a stirred solution of compound **2j** (0.15 mmol, 1 equiv) in CH_2Cl_2 (2 mL,0.1 M) added 10% Pd/C (0.1 equiv) and continued the reaction under hydrogen atmosphere for 1 h. Then, the reaction mixture was filtered through celite, concentrated under reduced pressure. The crude product was purified using flash column chromatography (10% EtOAc/hexane R_f = 0.5) to obtain **2a** in 72% yield (18 mg) based on recovered starting material **2j**.

Oxidation on 2j :[5]



To a solution of compound **2j** (0.14 mmol, 1 equiv) in DMSO (4 mL) was addecd K_2CO_3 (39 mg, 2.0 equiv) and 30% H_2O_2 (0.2 mL, 10 equiv). The reaction mixture was allowed to stir at room temperature for 12 h and quenched with saturated aqueous $NaHCO_3$ (10 mL). The reaction mixture was extracted with of EtOAC (2 x 15 mL), dried combined organic layer over Na_2SO_4 and evaporated *in vacuo.* The residue was purified by chromatography on silica gel (30% EtOAc/hexanes;) to provide compound **5** (R_f = 0.3) in 42% yield (26 mg) and compound **6** (R_f = 0.5) in 34% yield (22 mg).

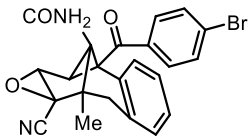
4-Bromobenzoyl-2a-methyl-2a^1-((oxo-l3-methyl)-l4-azaneyl)-2a,2a^1,7b,7c-tetrahydro-3*H*-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (5):



Colour: colorless solid; mp = 257–259 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.47 – 7.42 (m, 2H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.22 (td, *J* = 7.5, 1.3 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.97

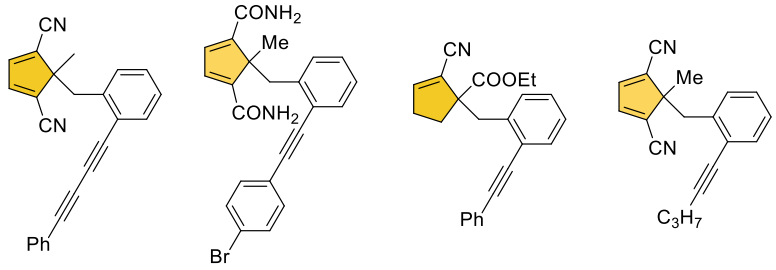
(dd, *J* = 7.7, 1.0 Hz, 1H), 6.03 (s, 1H), 5.16 (s, 1H), 3.77 (d, *J* = 15.8 Hz, 1H), 3.72 (d, *J* = 0.5 Hz, 1H), 3.48 (d, *J* = 0.5 Hz, 1H), 3.20 (d, *J* = 15.8 Hz, 1H), 1.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 165.1, 145.0, 135.9, 133.9, 132.1, 131.4, 131.0, 129.3, 129.1, 128.9, 128.7, 128.3, 127.7, 116.0, 52.2, 46.9, 41.8, 38.0, 35.2, 23.1; HRMS (ESI) calcd for $C_{23}H_{18}BrN_2O_2$ $[M+H]^+$: 433.0551; found: 433.0541.

6b-(4-Bromobenzoyl)-1b-methyl-1b^1-((oxo-l^3-methyl)-l4-azaneyl)-1b,1b1,2,6b,6c,6d-hexahydro-1aH-benzo[5,6]cyclopropa[3,4]indeno[1,2-b]oxirene-1a-carbonitrile (6):



Colour: colorless solid; mp = 261–263 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.50 – 7.40 (m, 2H), 7.16 (ddd, *J* = 10.6, 8.8, 4.2 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.02 (d, *J* = 2.5 Hz, 1H), 5.29 (s, 2H), 3.89 (d, *J* = 2.5 Hz, 1H), 3.46 (d, *J* = 15.7 Hz, 1H), 3.23 (d, *J* = 15.7 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 166.9, 134.8, 133.5, 132.1, 131.1, 130.8, 129.0, 128.8, 128.3, 128.0, 127.9, 116.2, 64.2, 64.1, 46.8, 46.1, 40.1, 38.1, 21.0; HRMS (ESI) calcd for $C_{23}H_{18}BrN_2O_3$ $[M+H]^+$: 449.0486; found: 449.0495.

Failure exemples :

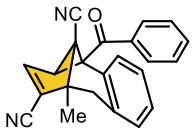


S7 **S8** **S14** **1v**

S7 and **1v** were failed to give the desired product under standard reaction conditions and in both cases >80% of starting material was recovered, while in the case of **S8** and **S14** starting material decomposed over the course of the reaction.

IV. X-Ray crystallographic data:

X-ray crystallographic data for compound 2a:



2a, CCDC - 2370423

The purified compound **2a** was dissolved in a mixed solvent of CH_2Cl_2/n-hexane (1:5), and placed in a dark cabinet for slowly evaporation. White crystals were collected after few days for X-ray analysis

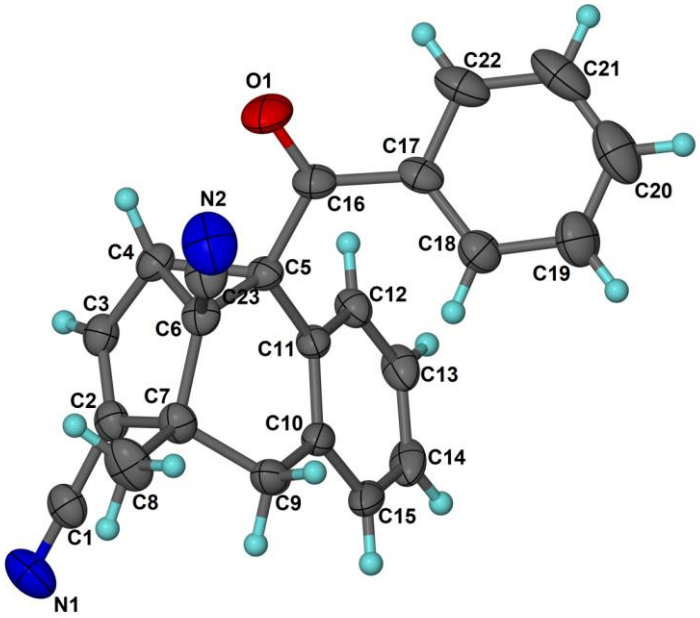


Figure caption: ORTEP diagram of KB1011 compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal data for compound 2a (KB1011): $C_{23}H_{16}N_2O$, M = 336.38, Orthorhombic, Space group *Pbca* (No.61), a = 9.5854(7)Å, b = 17.6825(13)Å, c = 21.0981(14)Å, α = 90°, β = 90°, γ = 90°, V = 3576.0(4)Å^3, Z = 8, D_c = 1.250 g/cm^3, F_{000} = 1408, Bruker D8 QUEST PHOTON III C7 HPAD detector, Mo-Kα radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 55°, μ = 0.077 mm^{-1}, 30918 reflections collected, 4088 unique (R_{int} = 0.0475), 237 parameters, *R1* = 0.0491, *wR2* = 0.1273, *R* indices based on 2403 reflections with I > 2σ(I) (refinement on F^2), Final *GooF* = 1.019, largest difference hole and peak = -0.178 and 0.132 e.Å^{-3}. The **CCDC deposition number 2370423** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

Data collection and Structure solution details:

X-ray data for the compound were collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 Å) and a PHOTON-III C7 HPAD detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs[7]. The structure was solved using intrinsic phasing method[7] and further refined with the SHELXL[8-10] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms]. **CCDC deposition number 2370423** contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

V. References :

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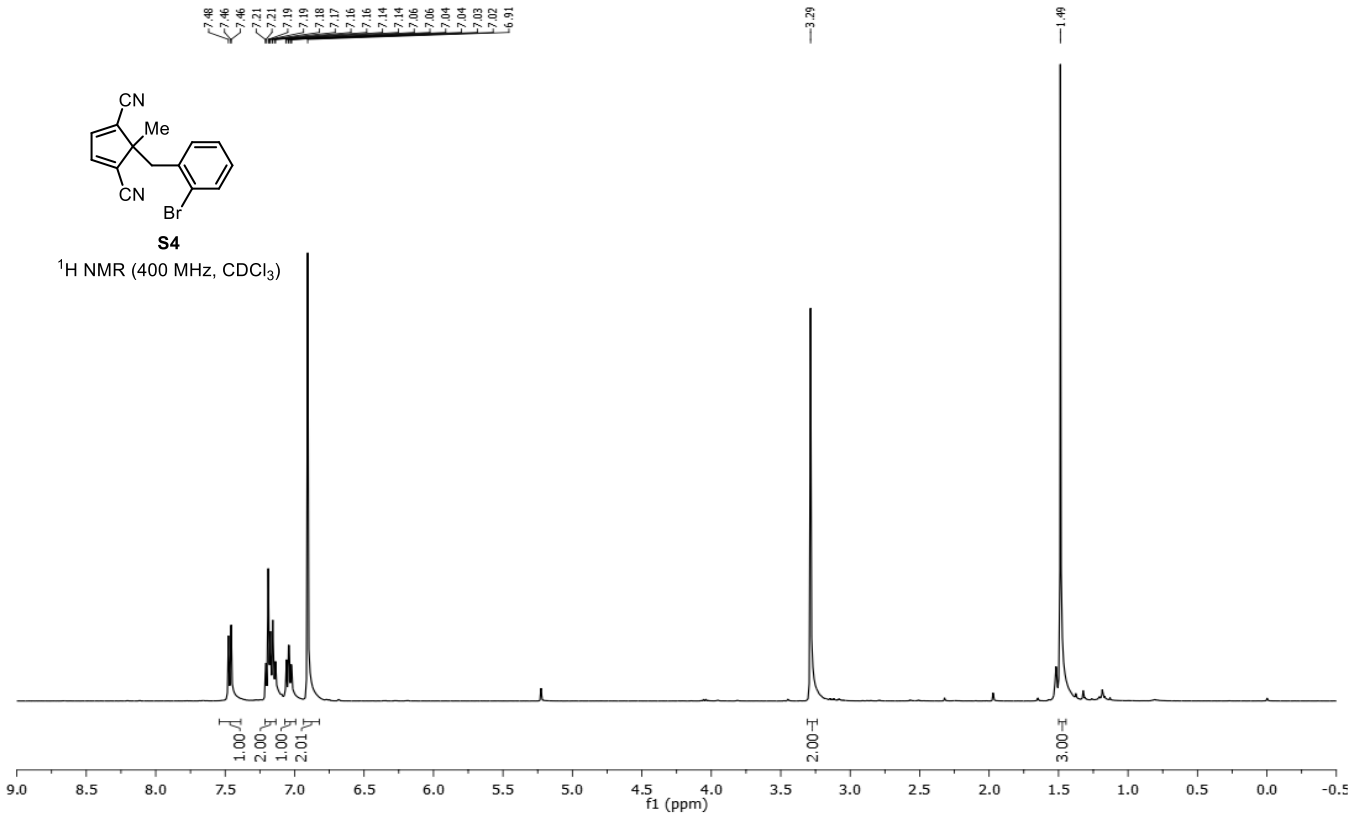
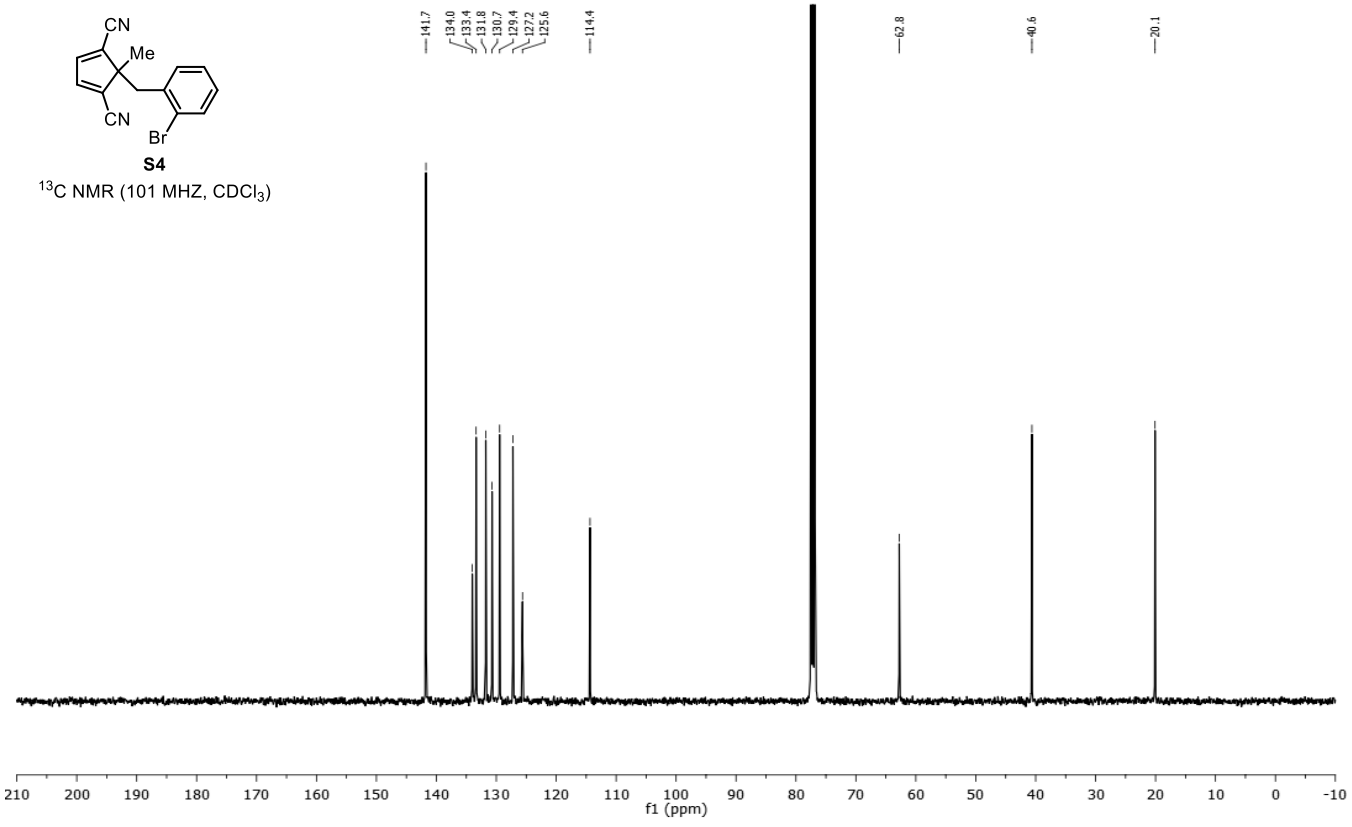
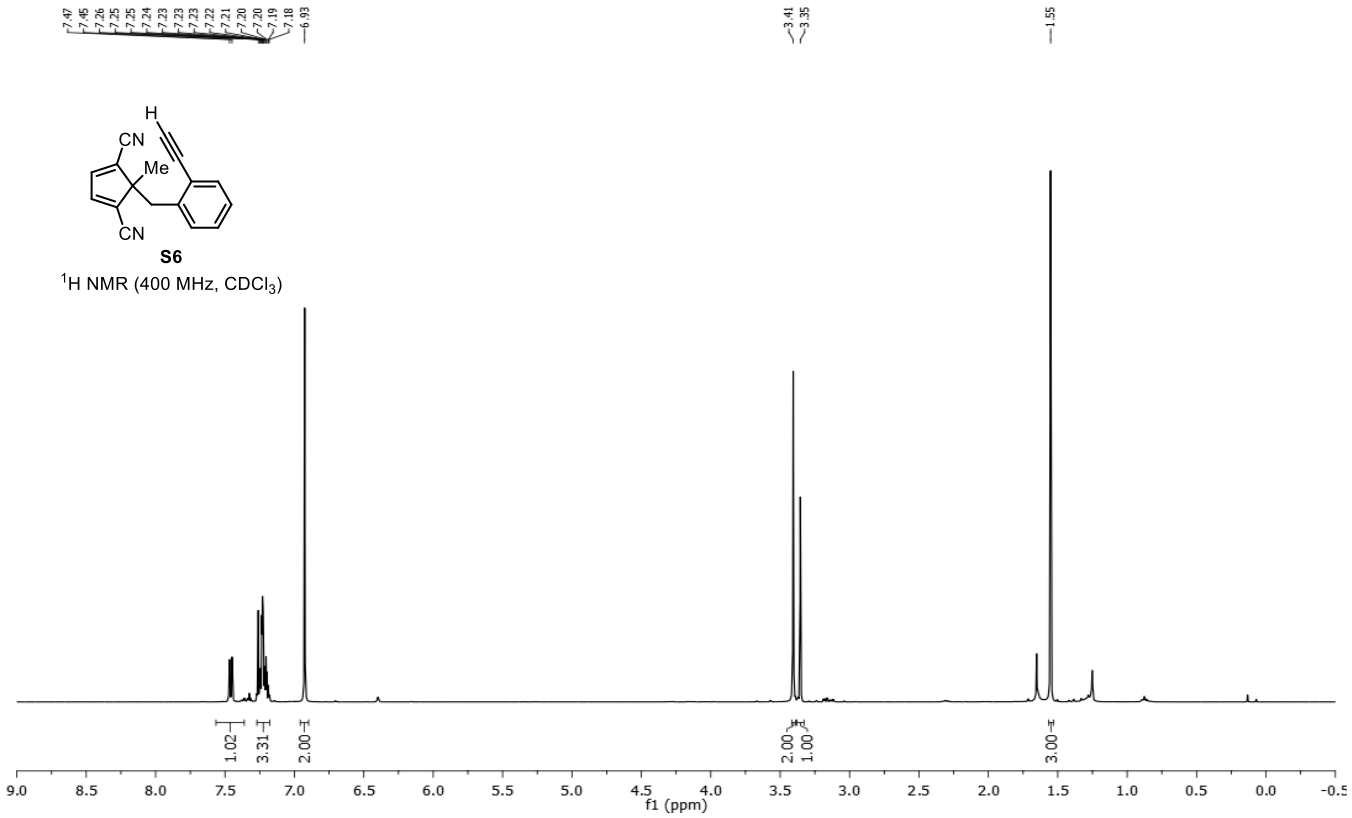
VII. ^{1}H&^{13}C NMR Spectra

2-(2-Bromobenzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (S4):



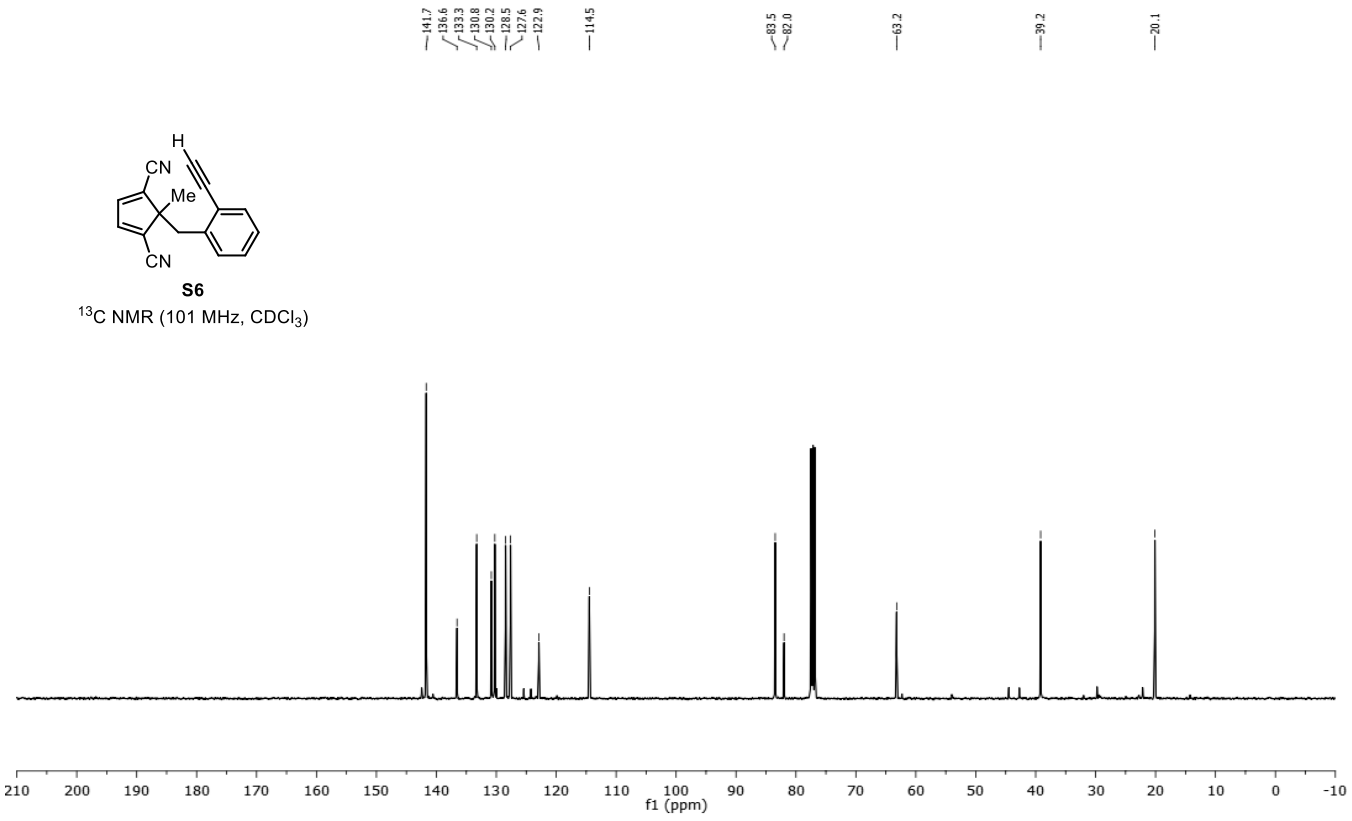


2-(2-Ethynylbenzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (S6):



S6

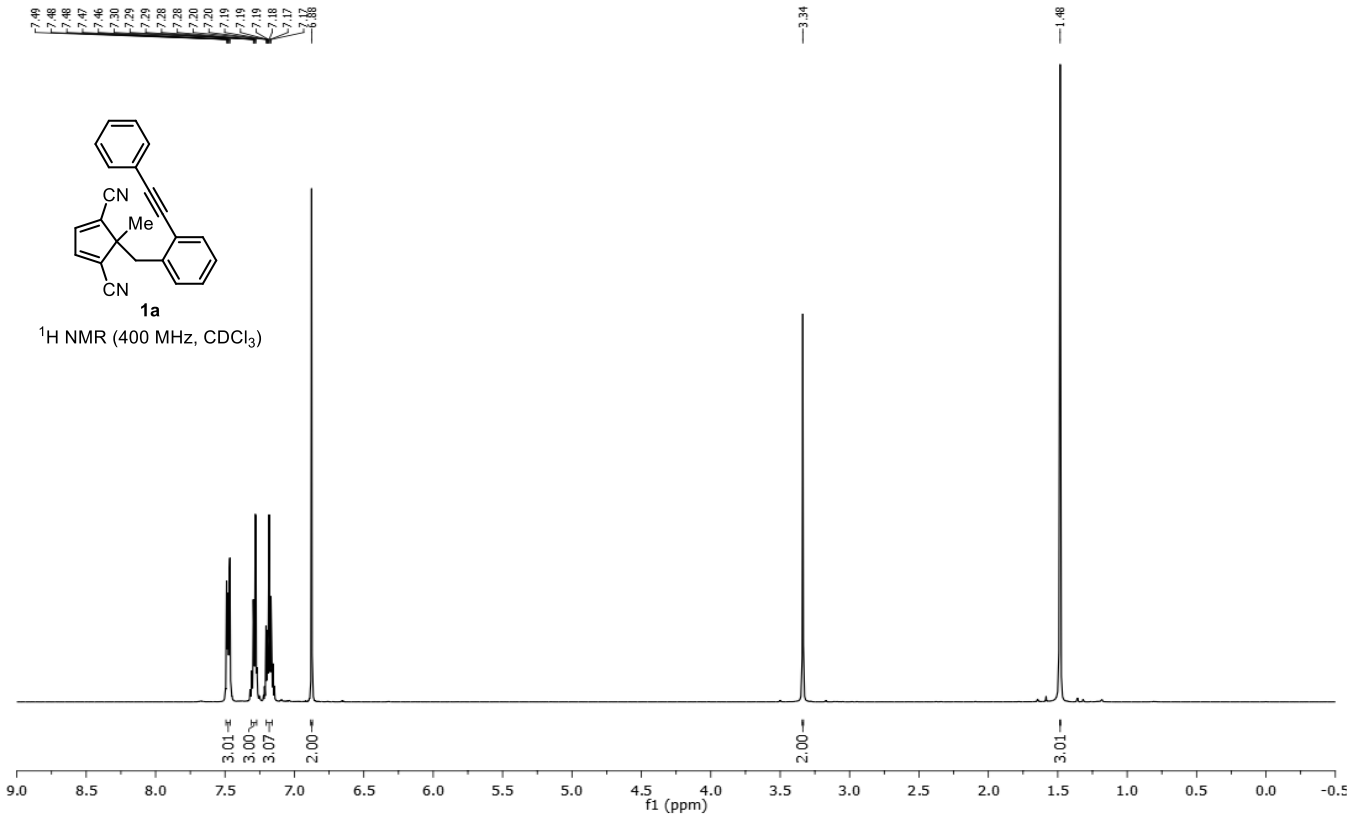
^{1}H NMR (400 MHz, $CDCl_3$)

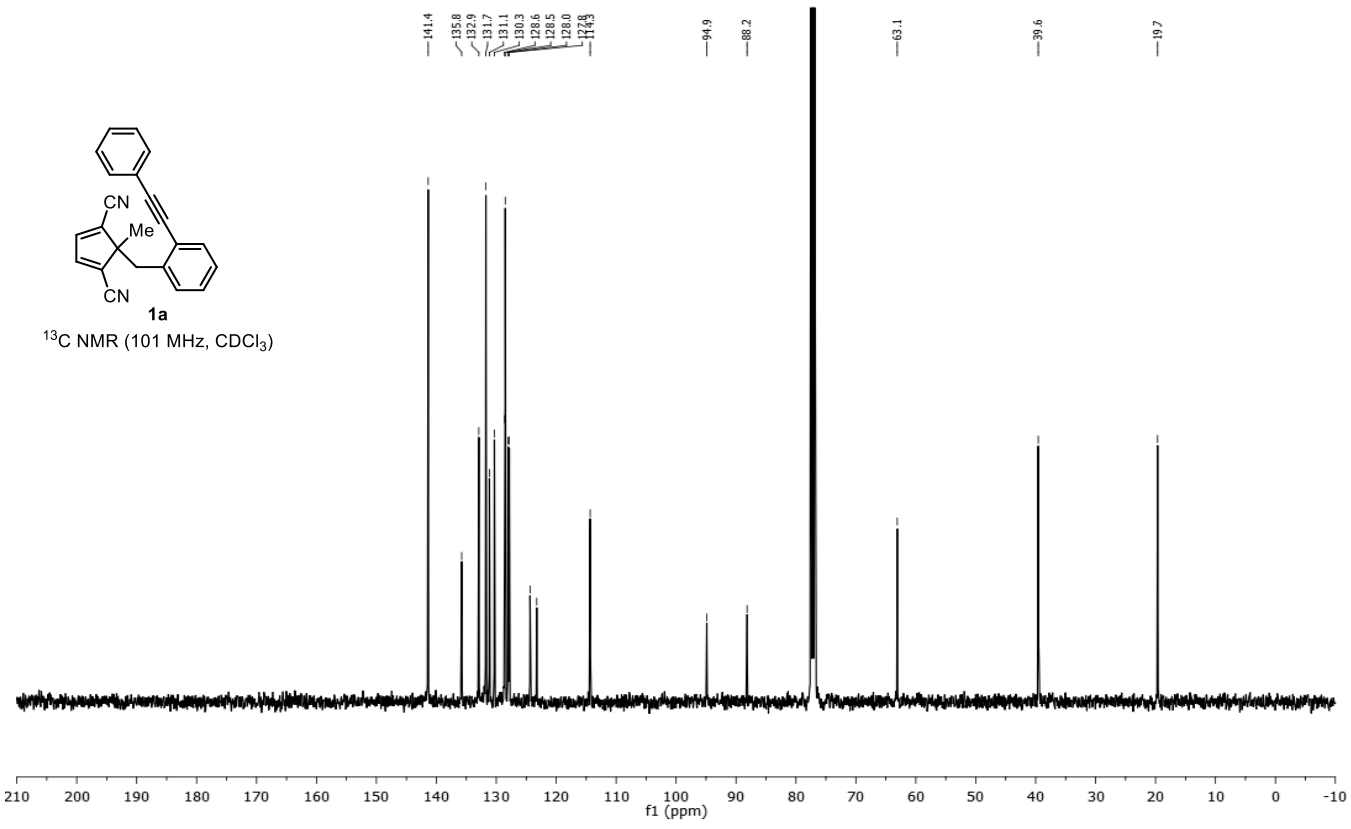


S6

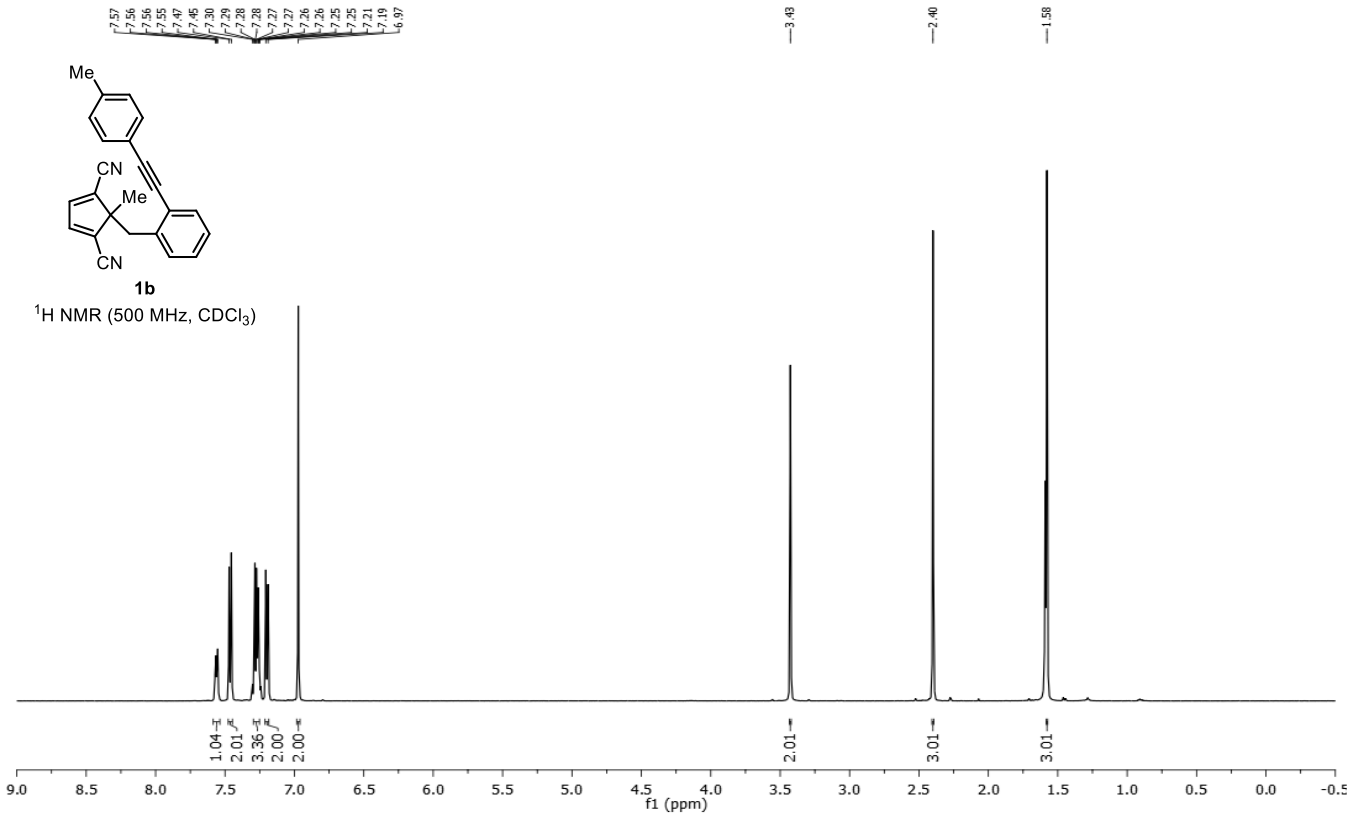
^{13}C NMR (101 MHz, $CDCl_3$)

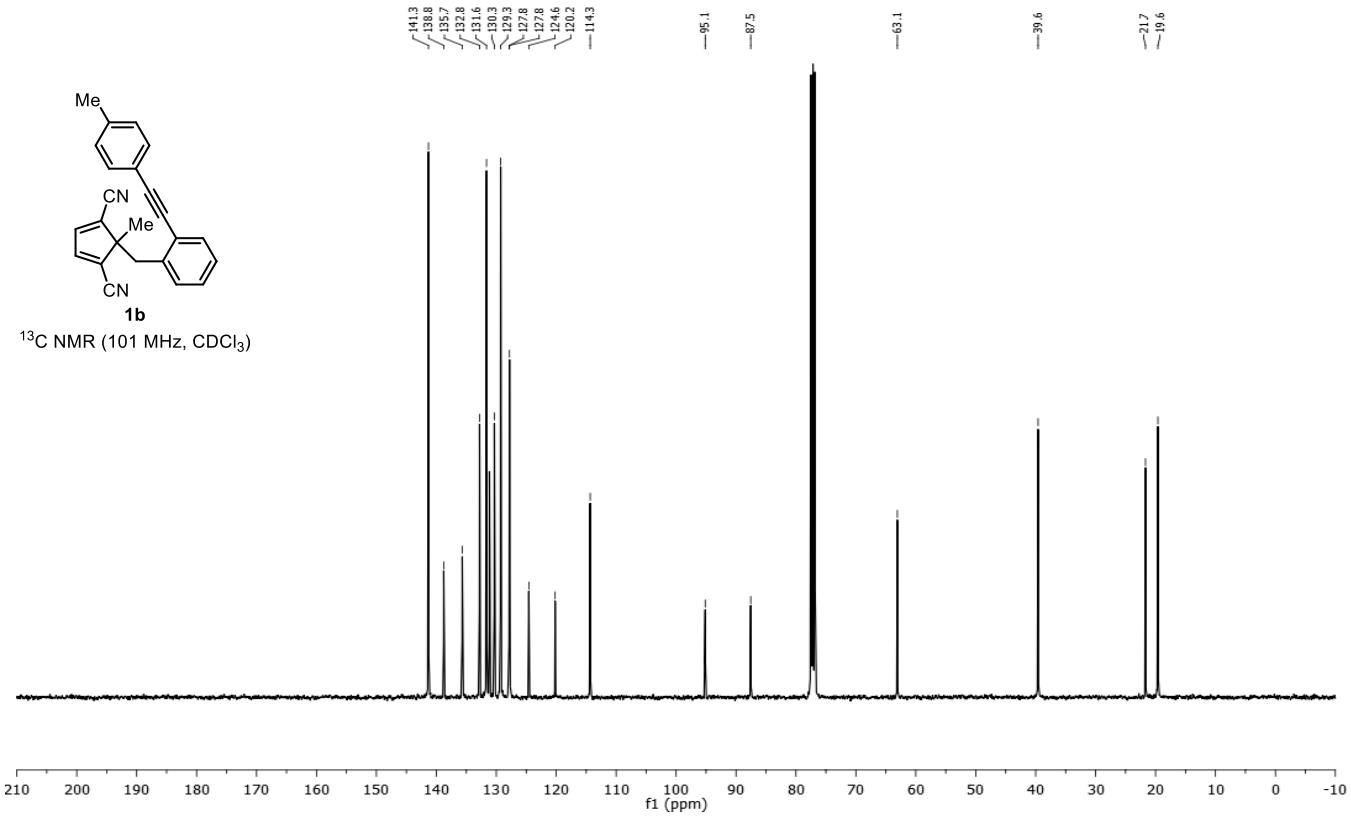
2-Methyl-2-(2-(phenylethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1a):



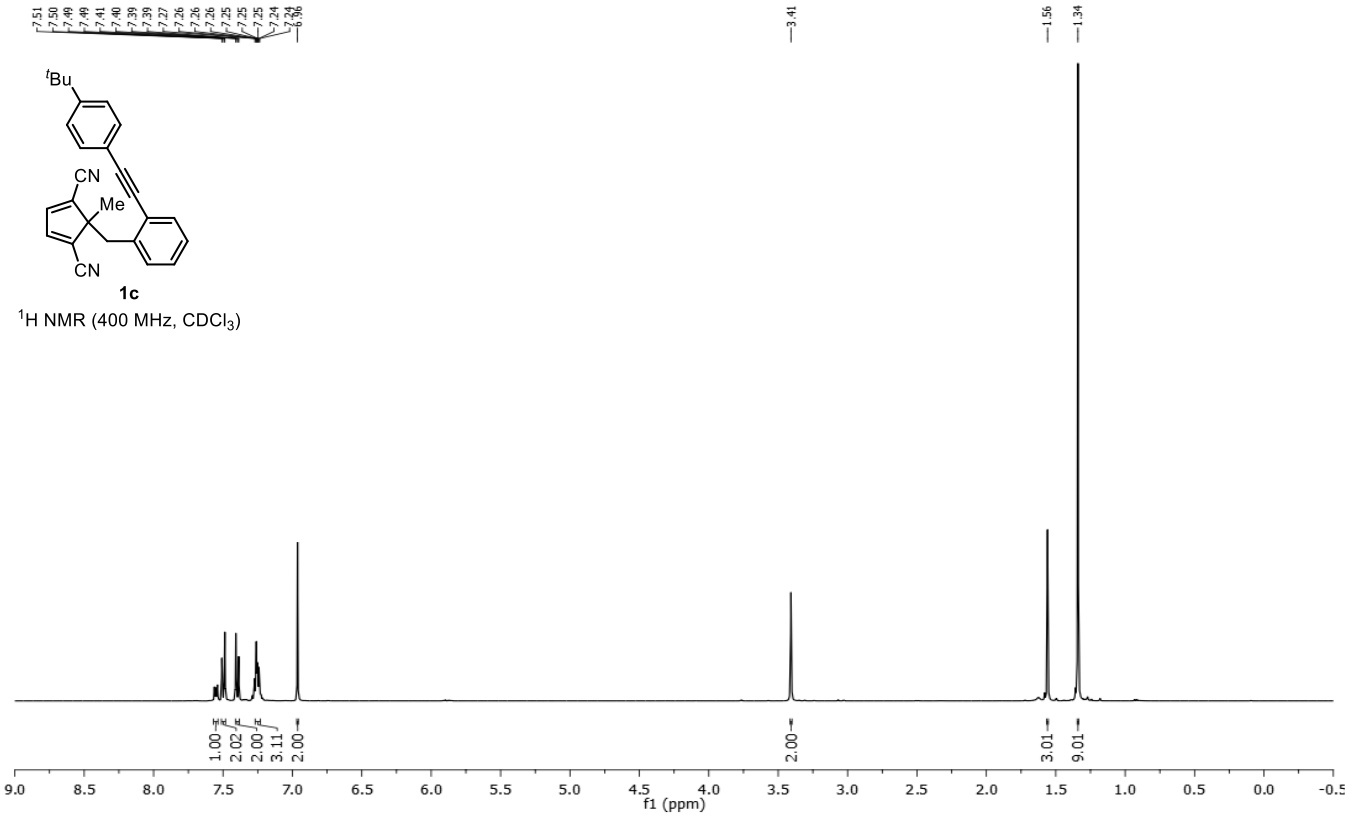


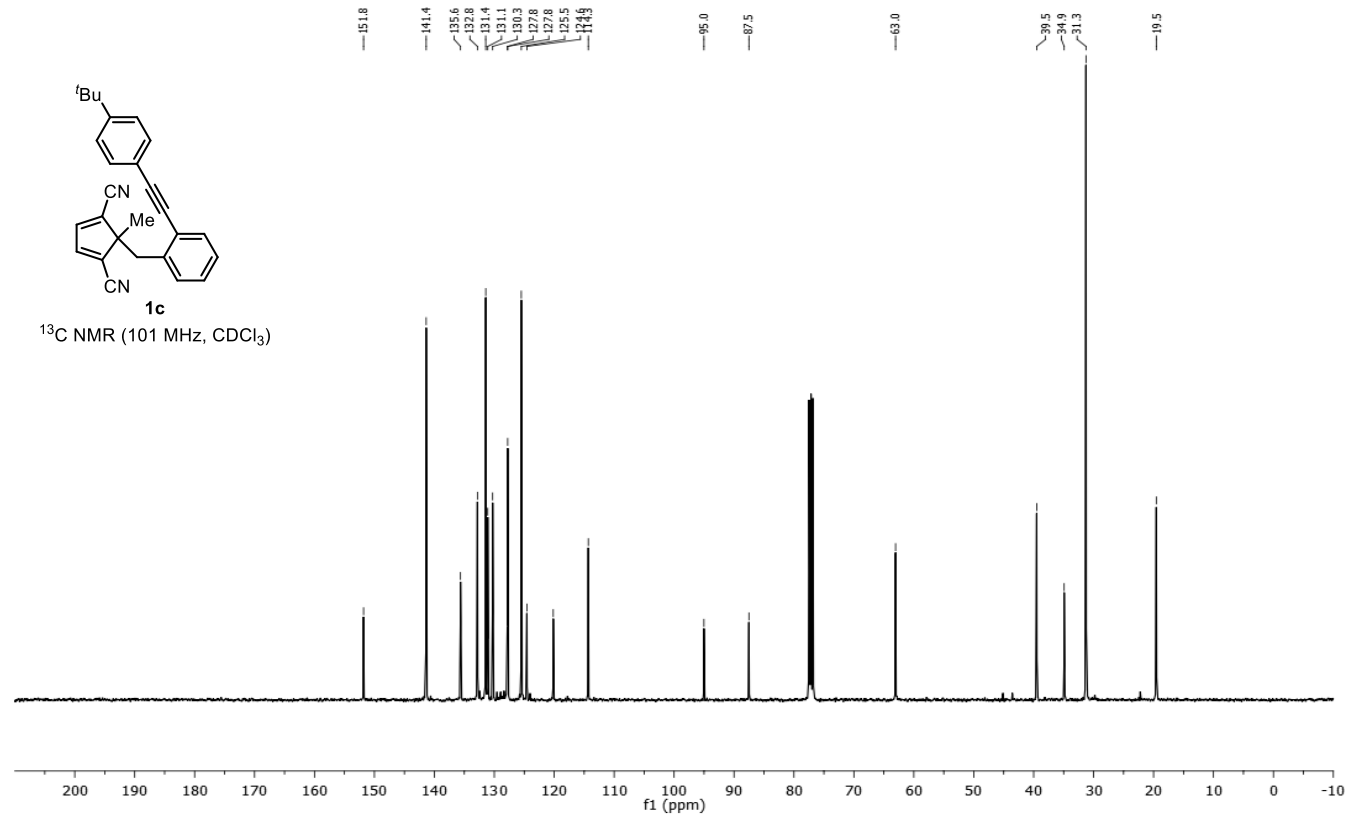
2-Methyl-2-(2-(p-tolylethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1b):



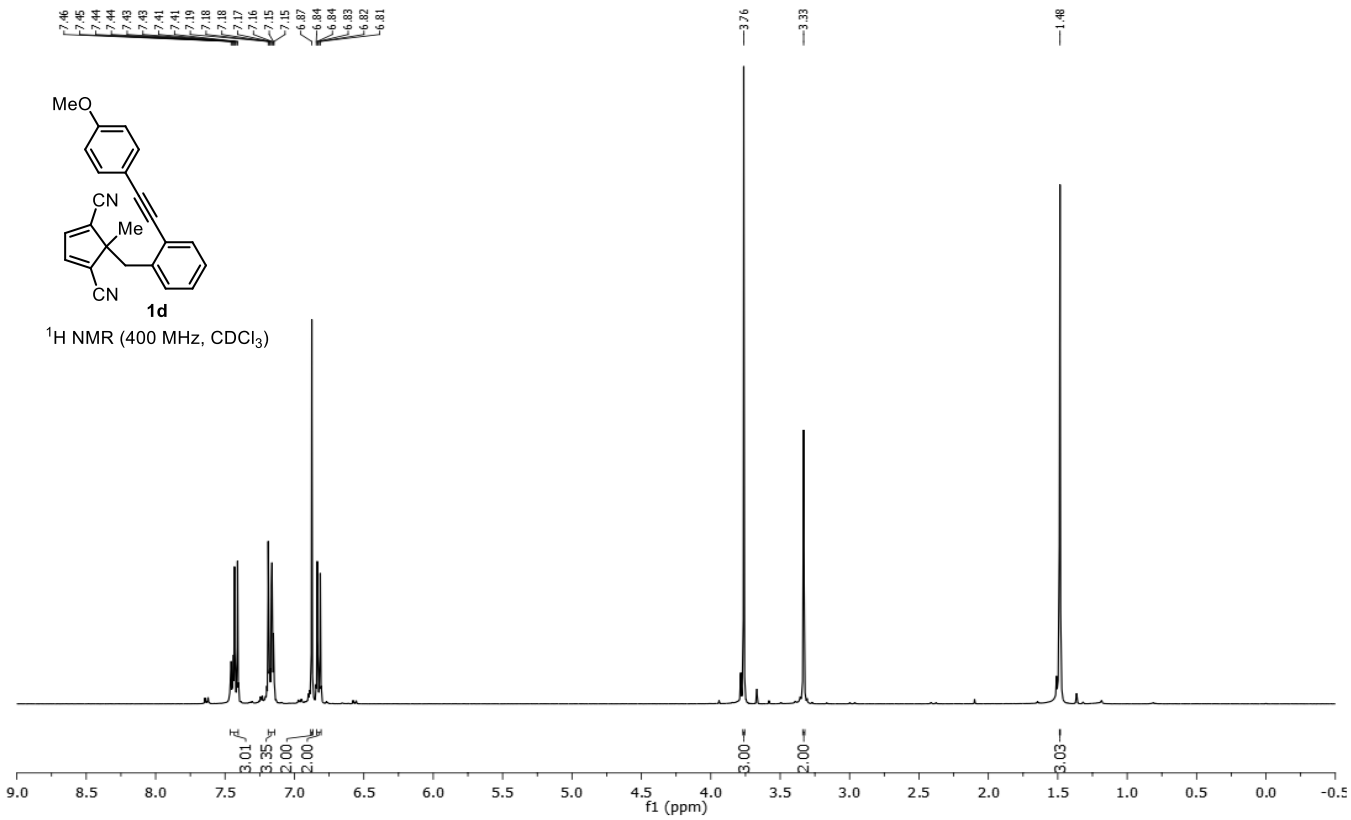


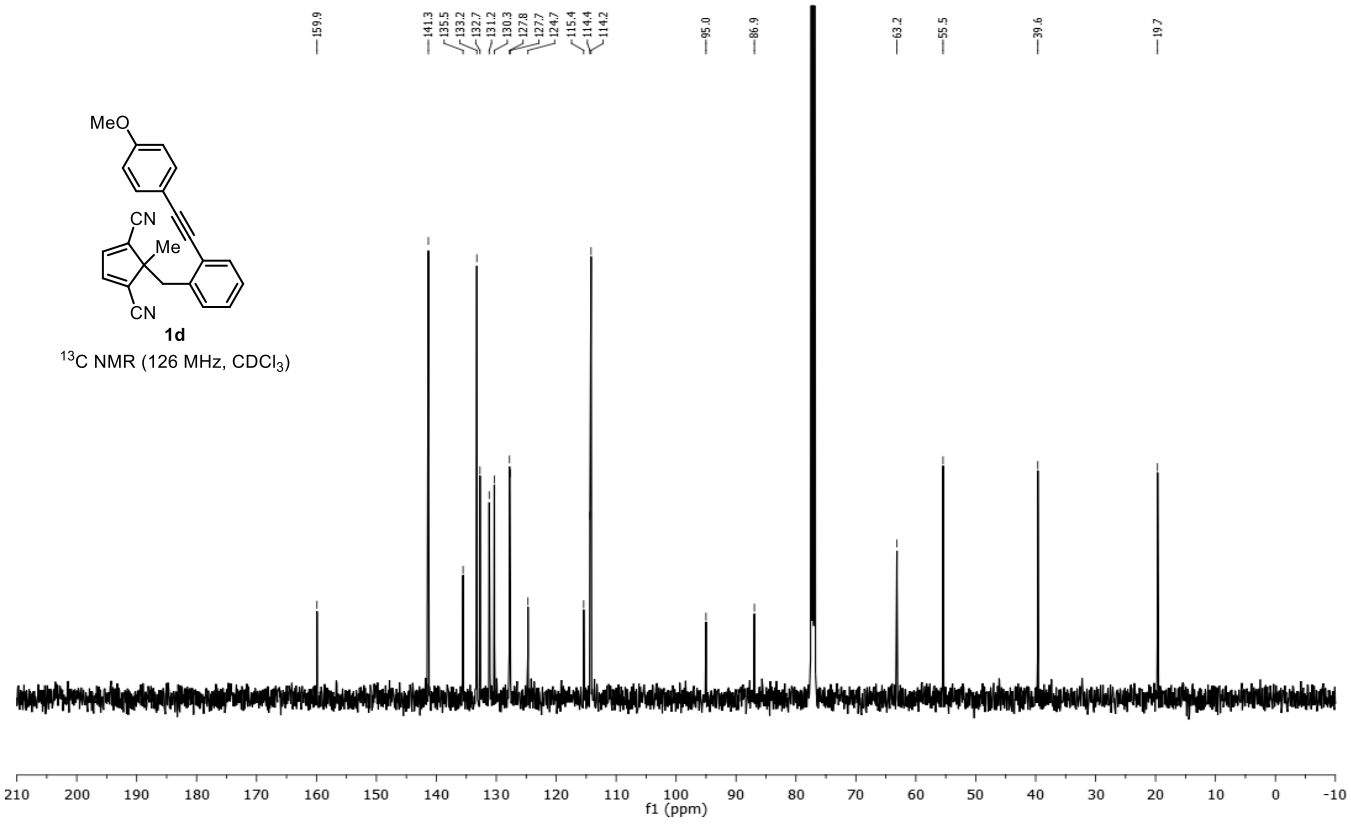
2-(2-((4-(Tert-butyl)phenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1c):



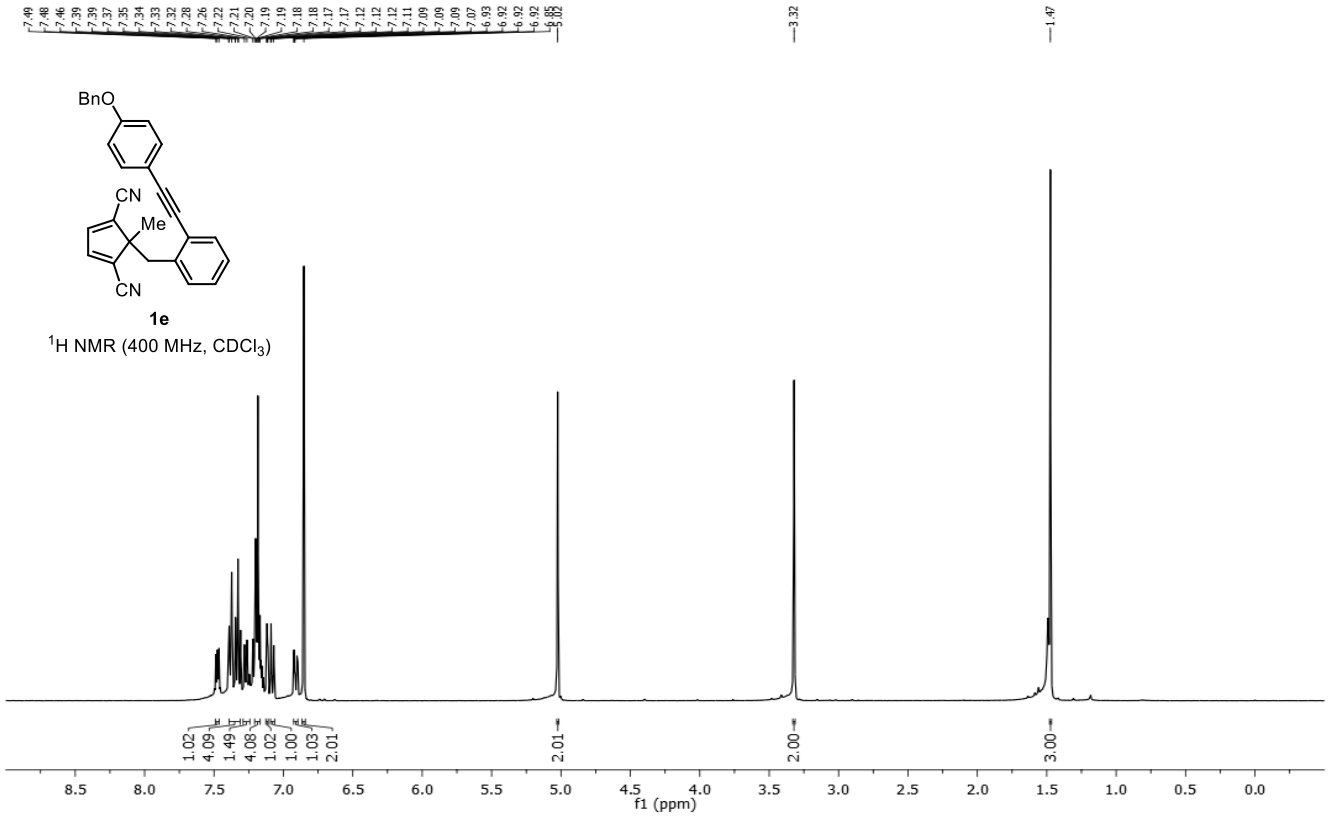


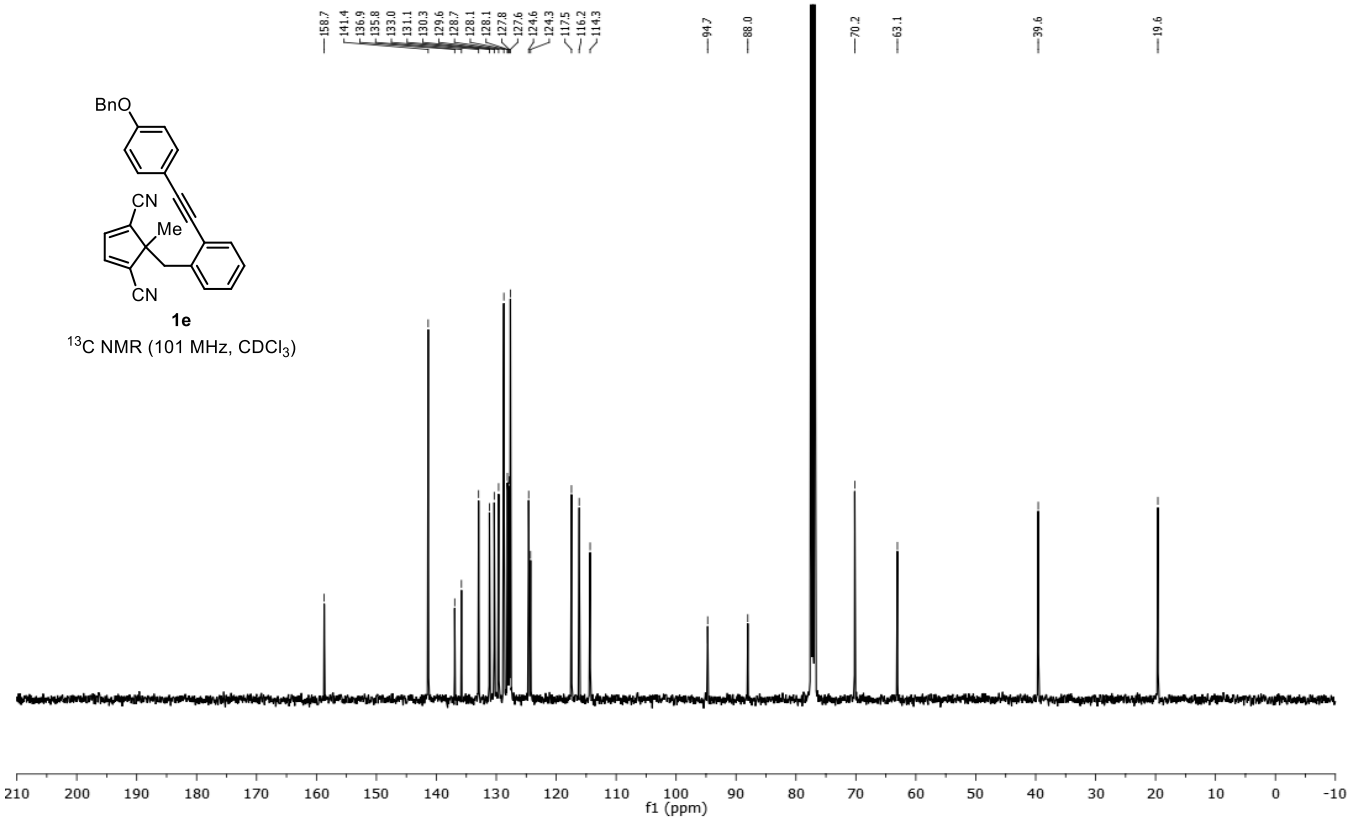
2-(2-((4-Methoxyphenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1d):



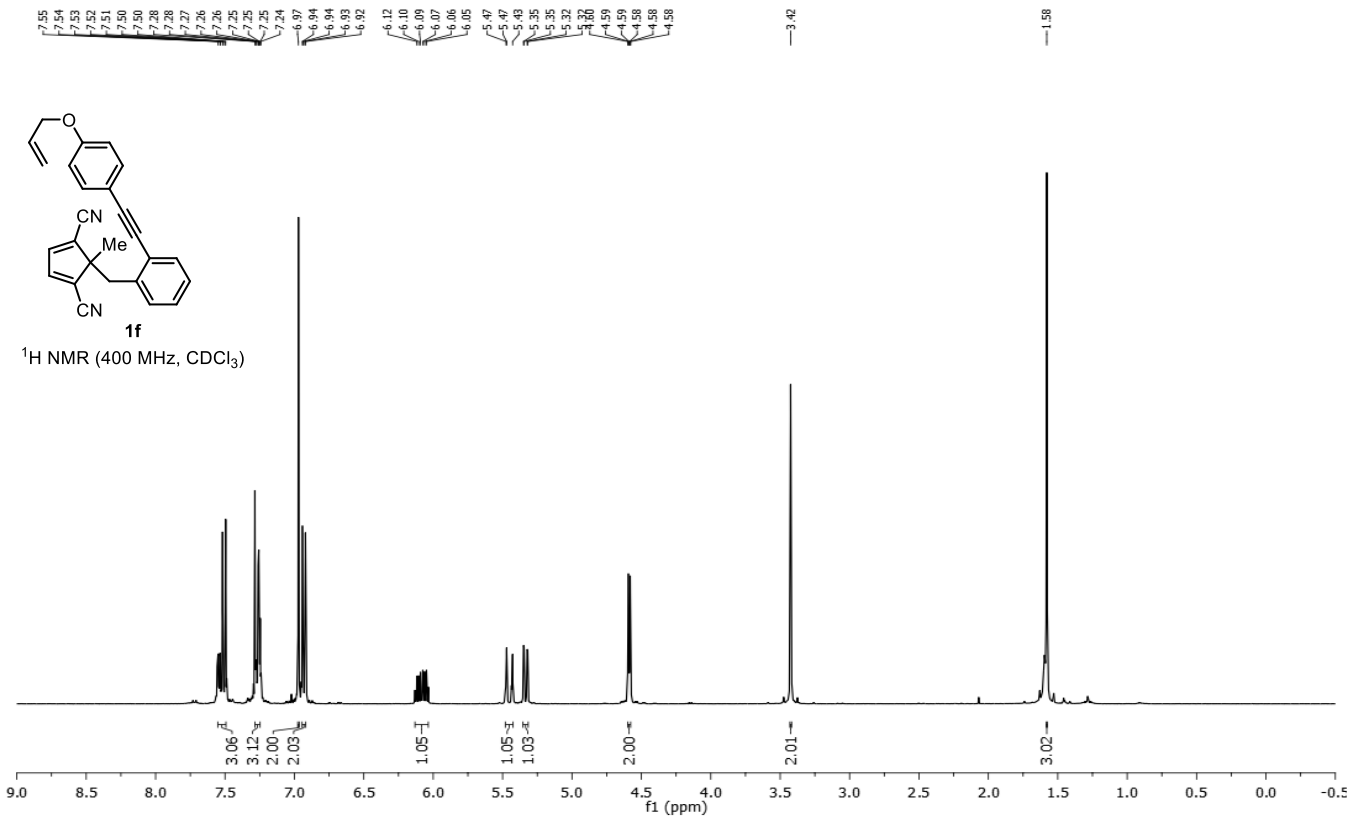


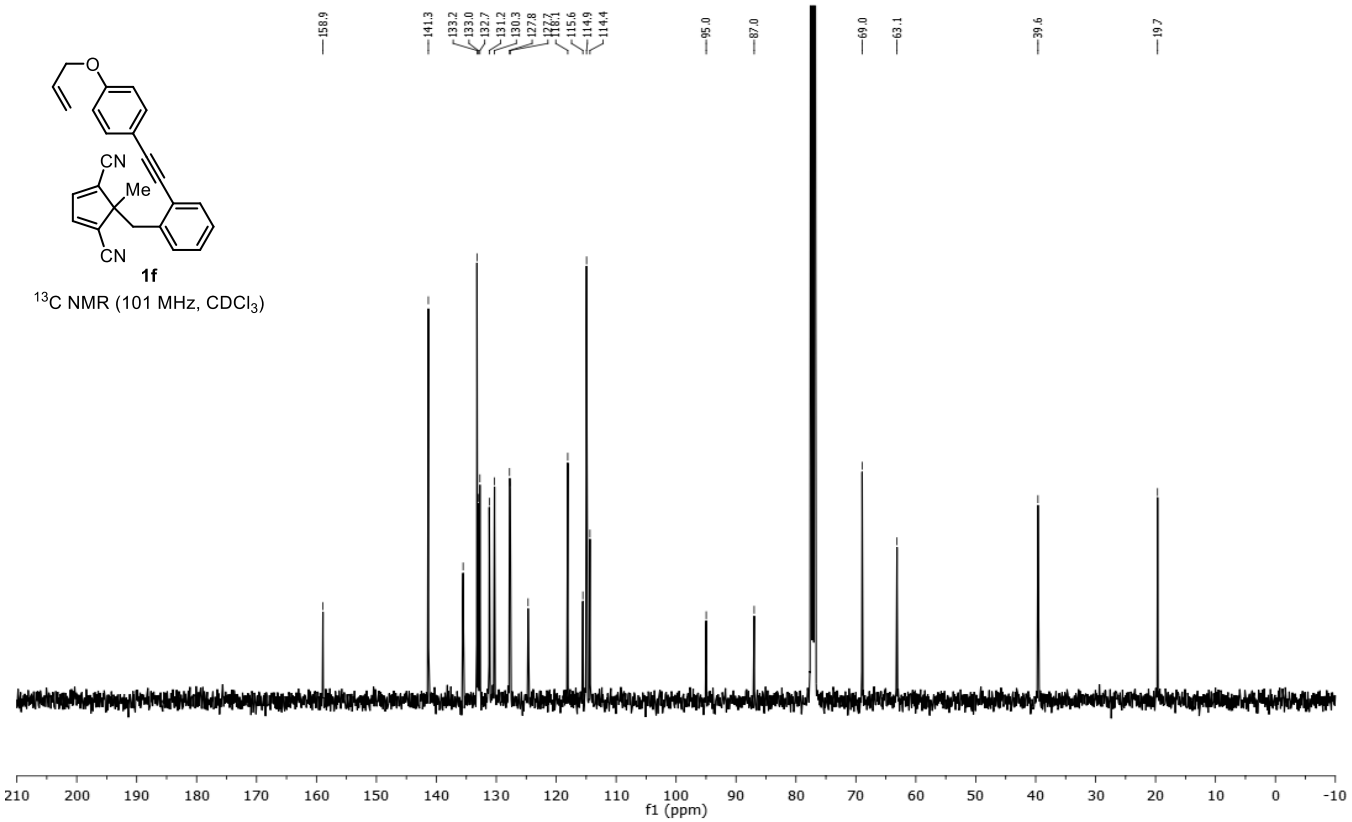
2-(2-((4-(Benzyloxy)phenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1e):



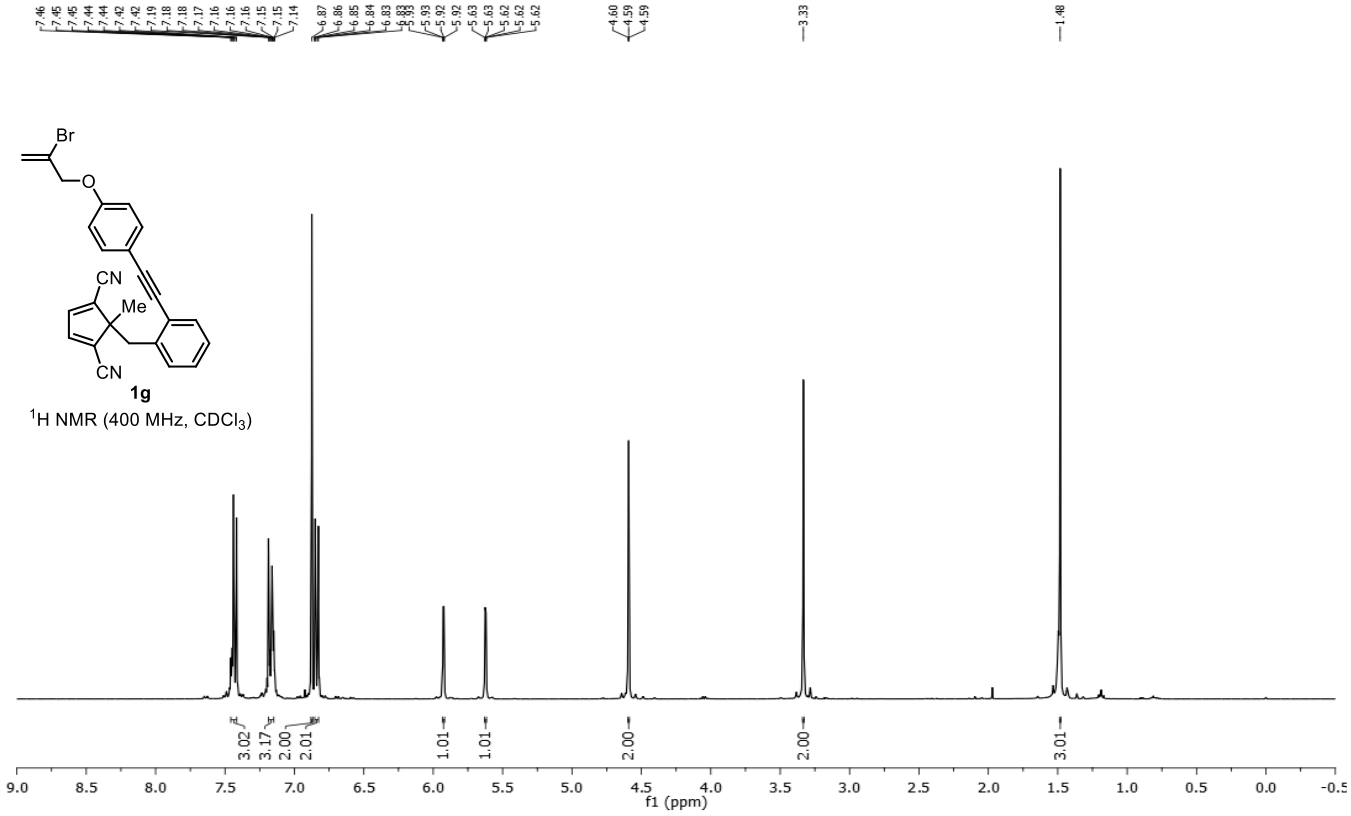


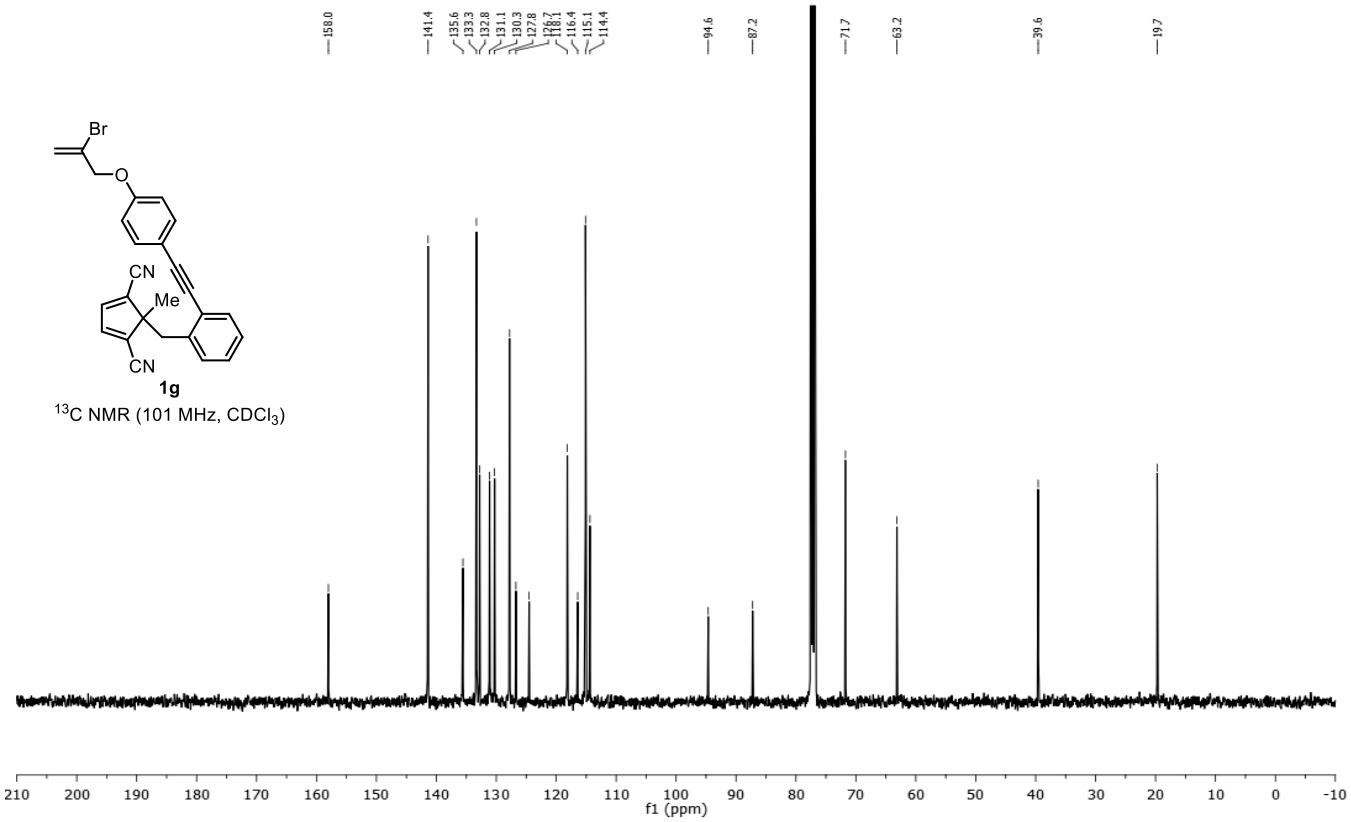
2-(2-((4-(Allyloxy)phenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1f):



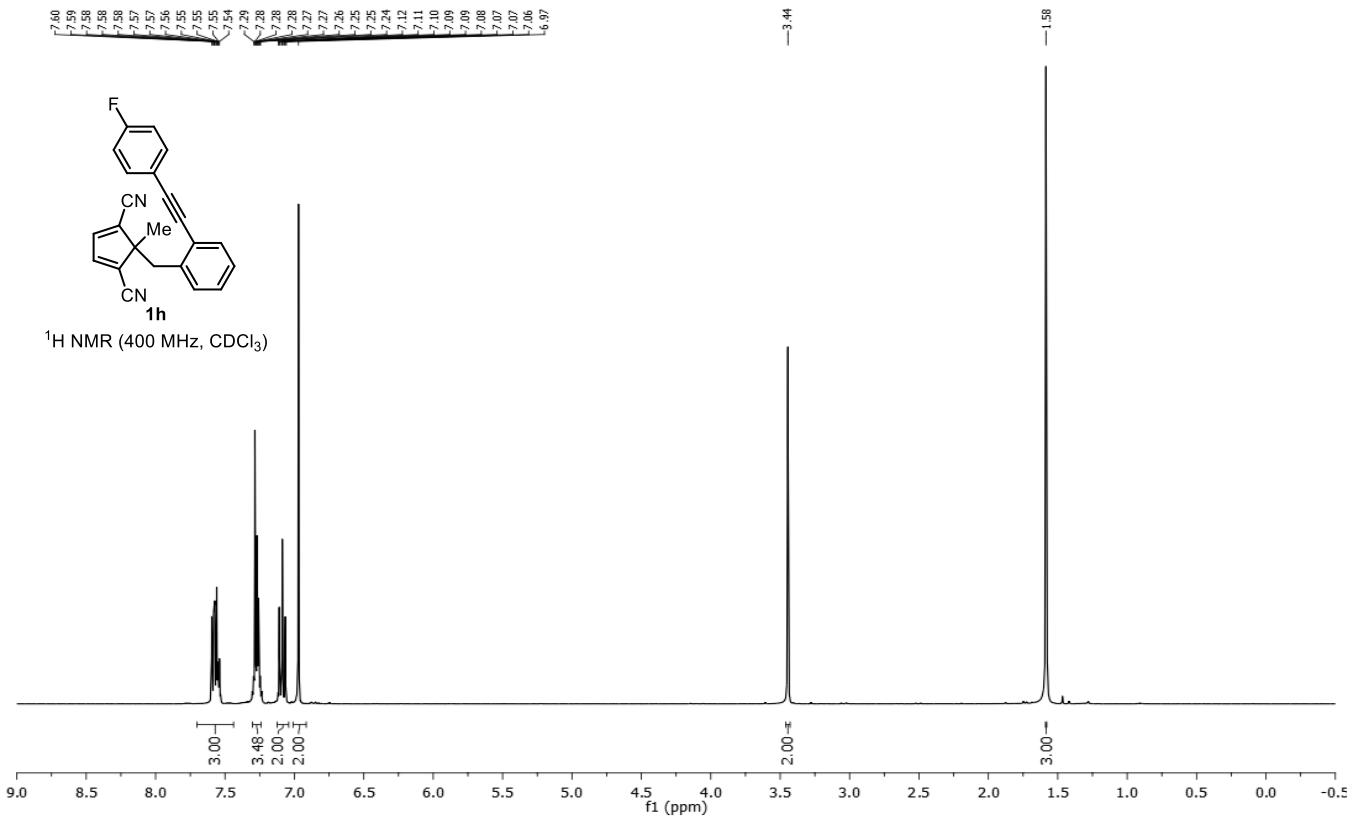


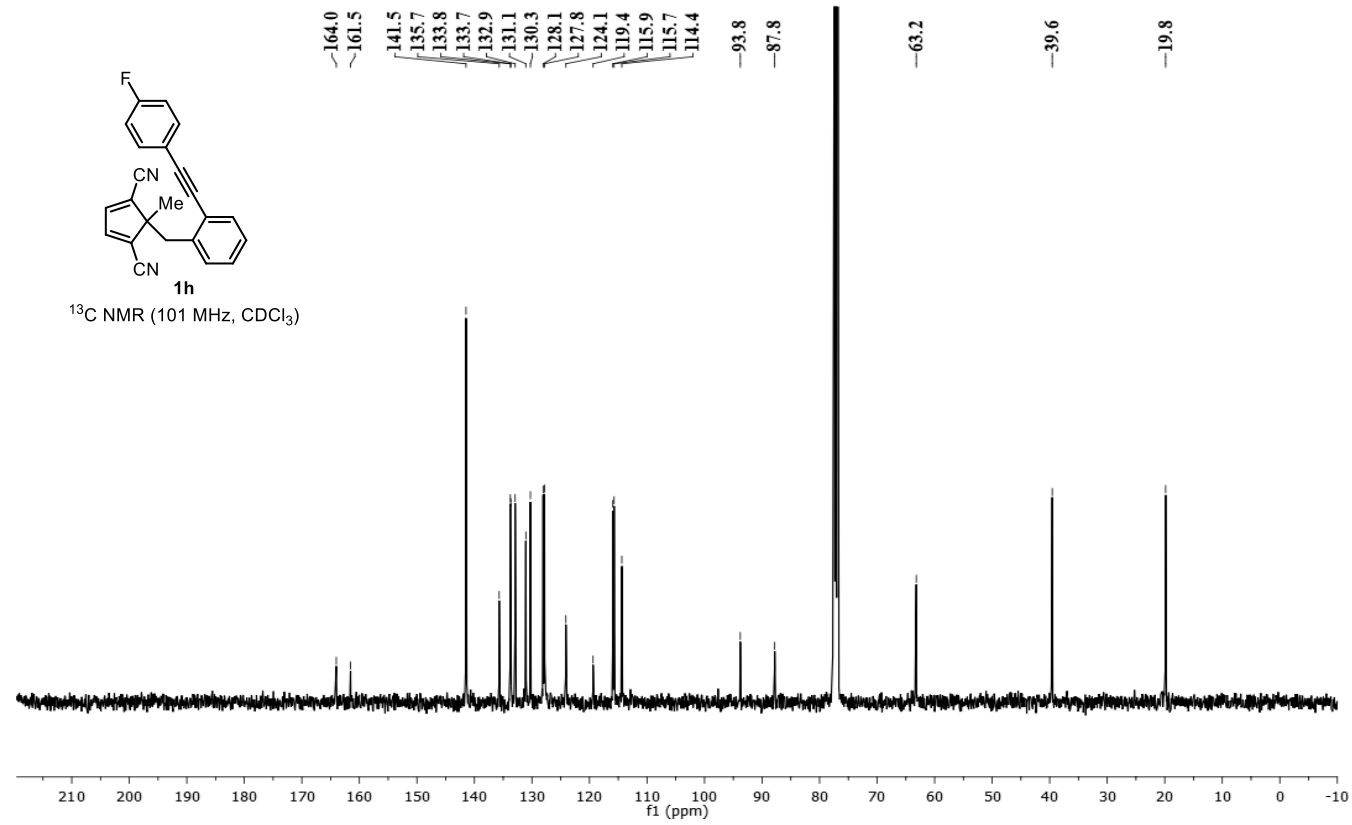
2-(2-((4-((2-Bromoallyl)oxy)phenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1g):

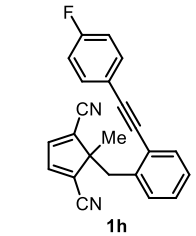




2-(2-((4-Fluorophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1h):



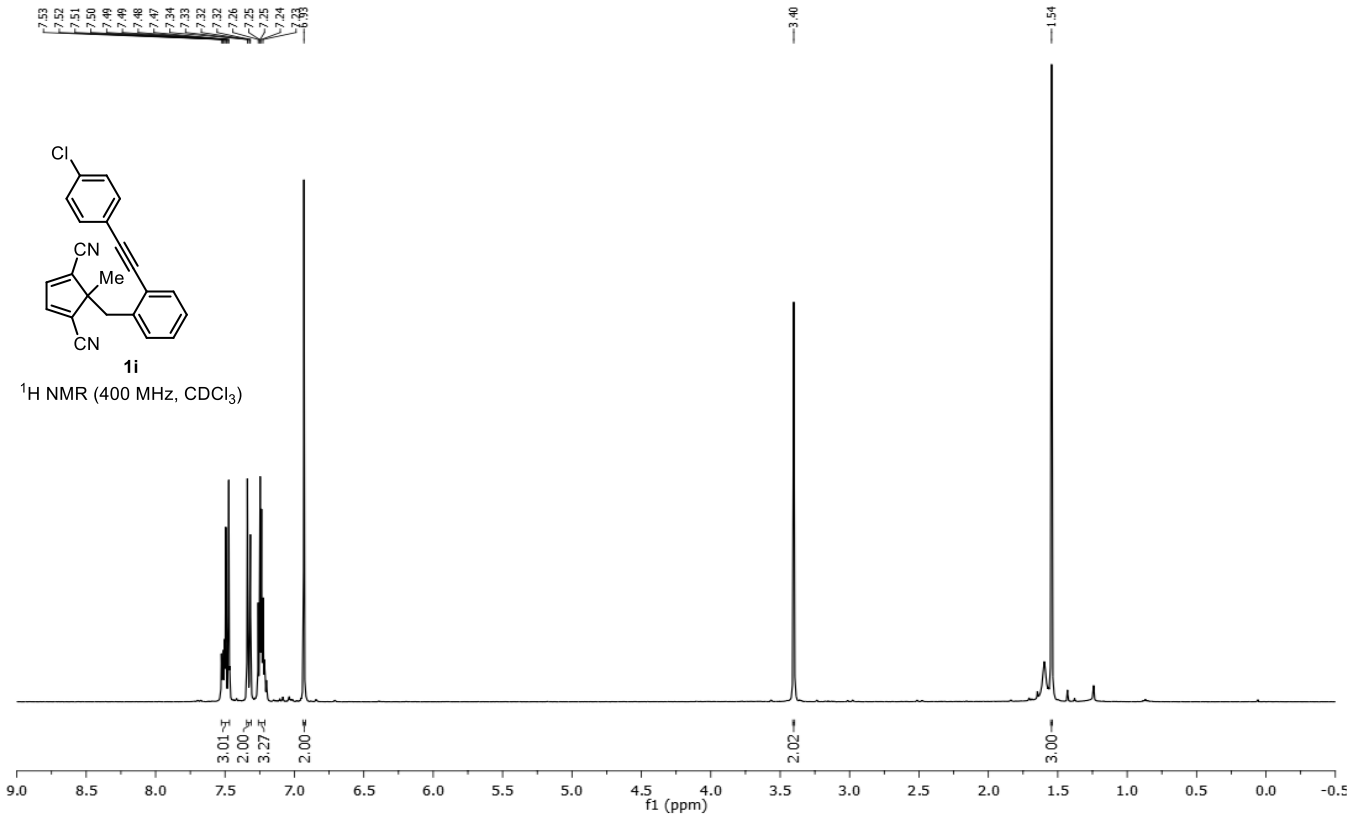


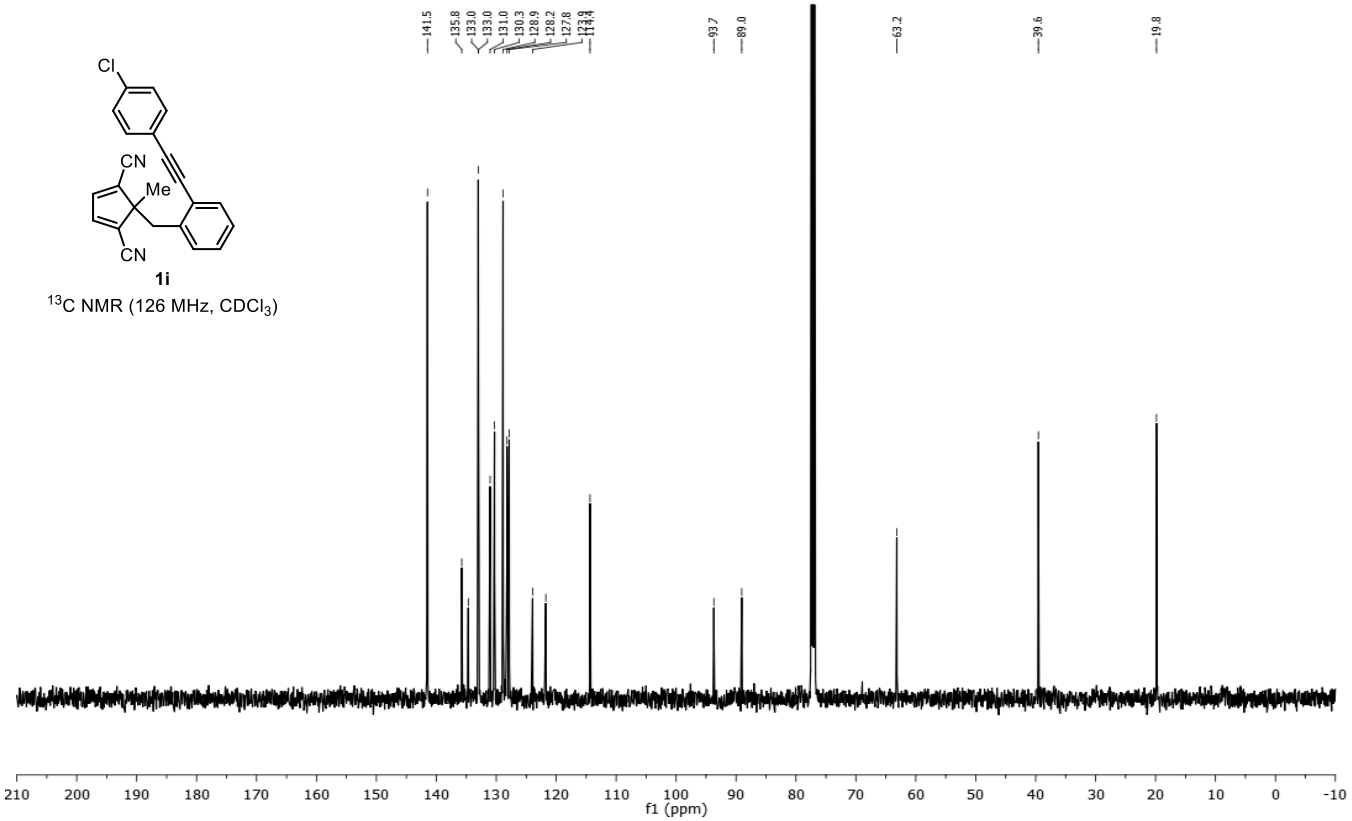


1h

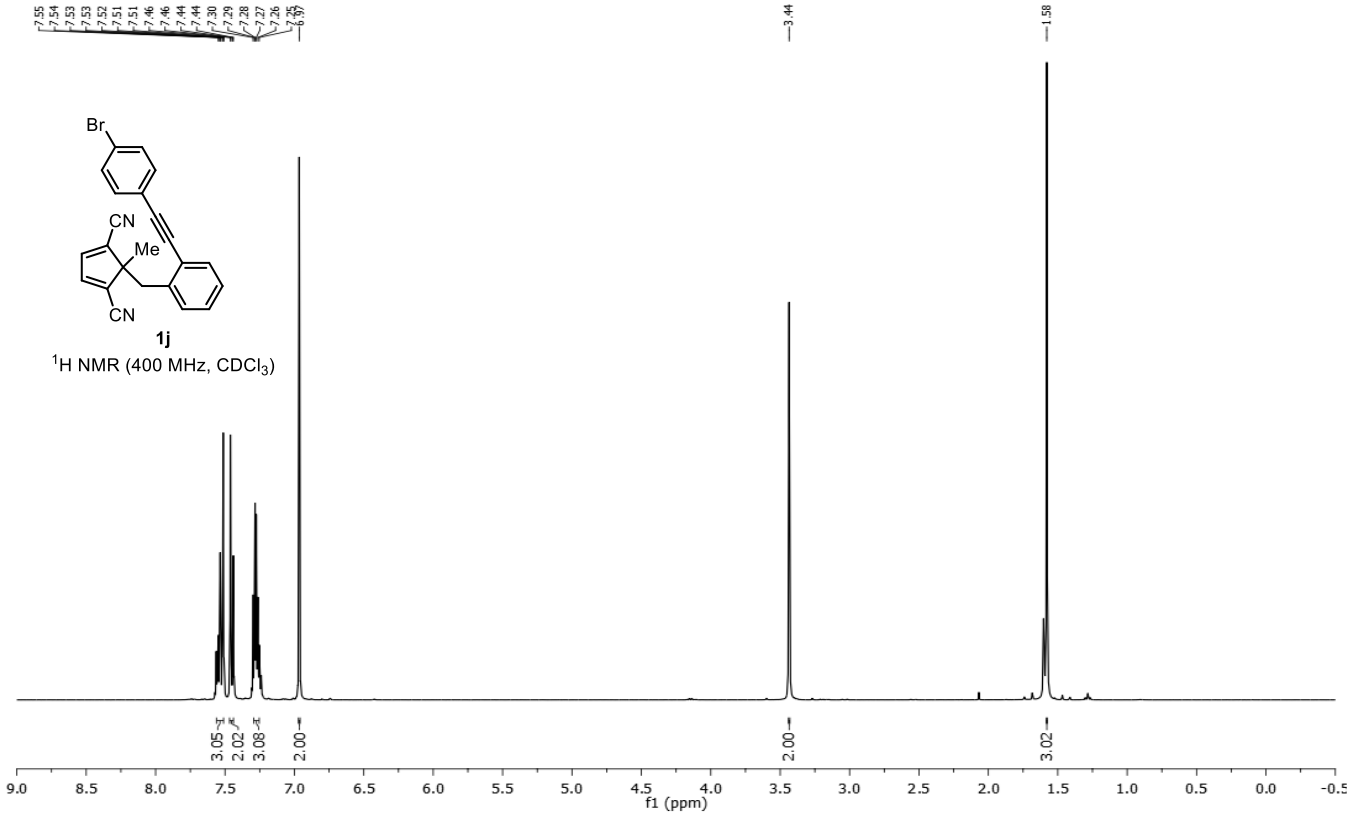
^{19}F NMR (377 MHz, $CDCl_3$)

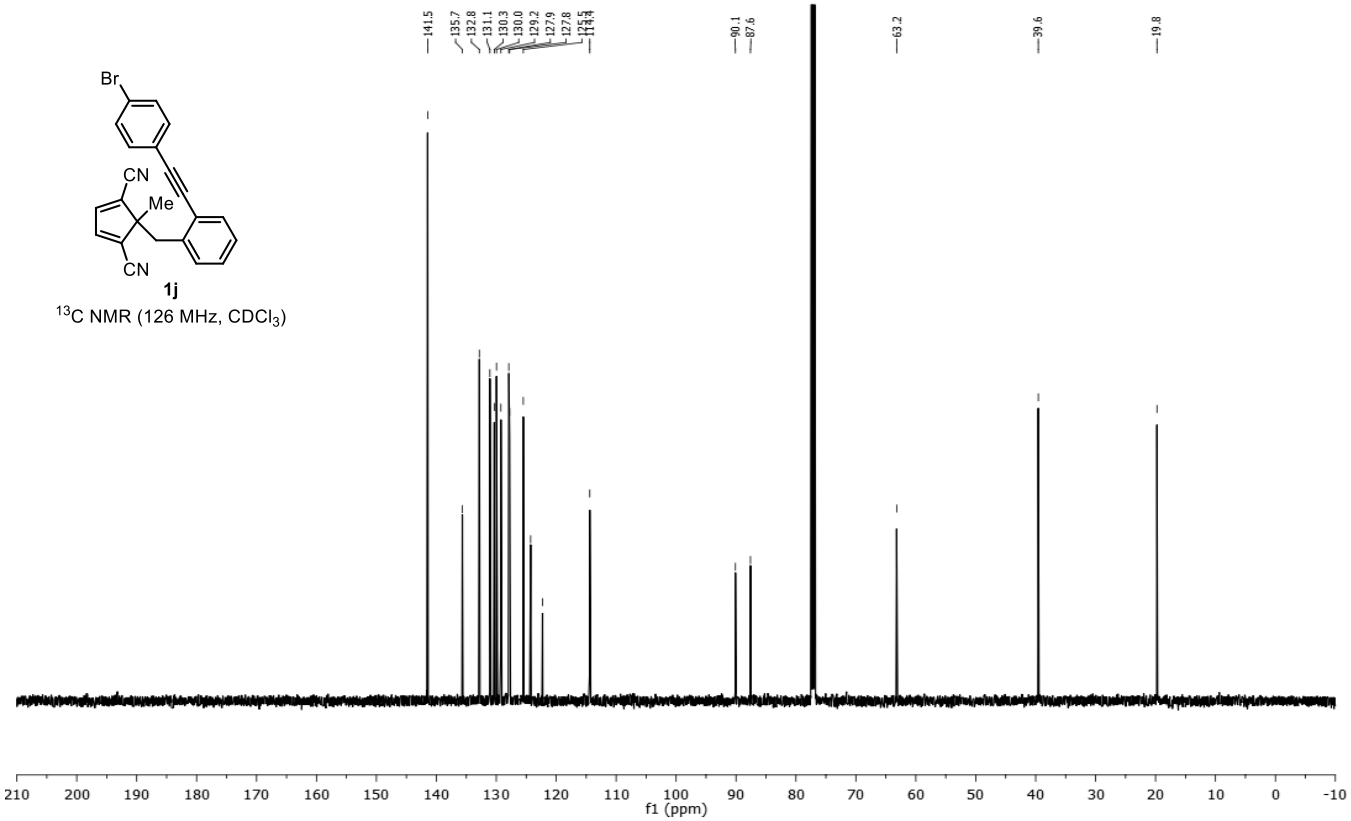
2-(2-((4-Chlorophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1i):



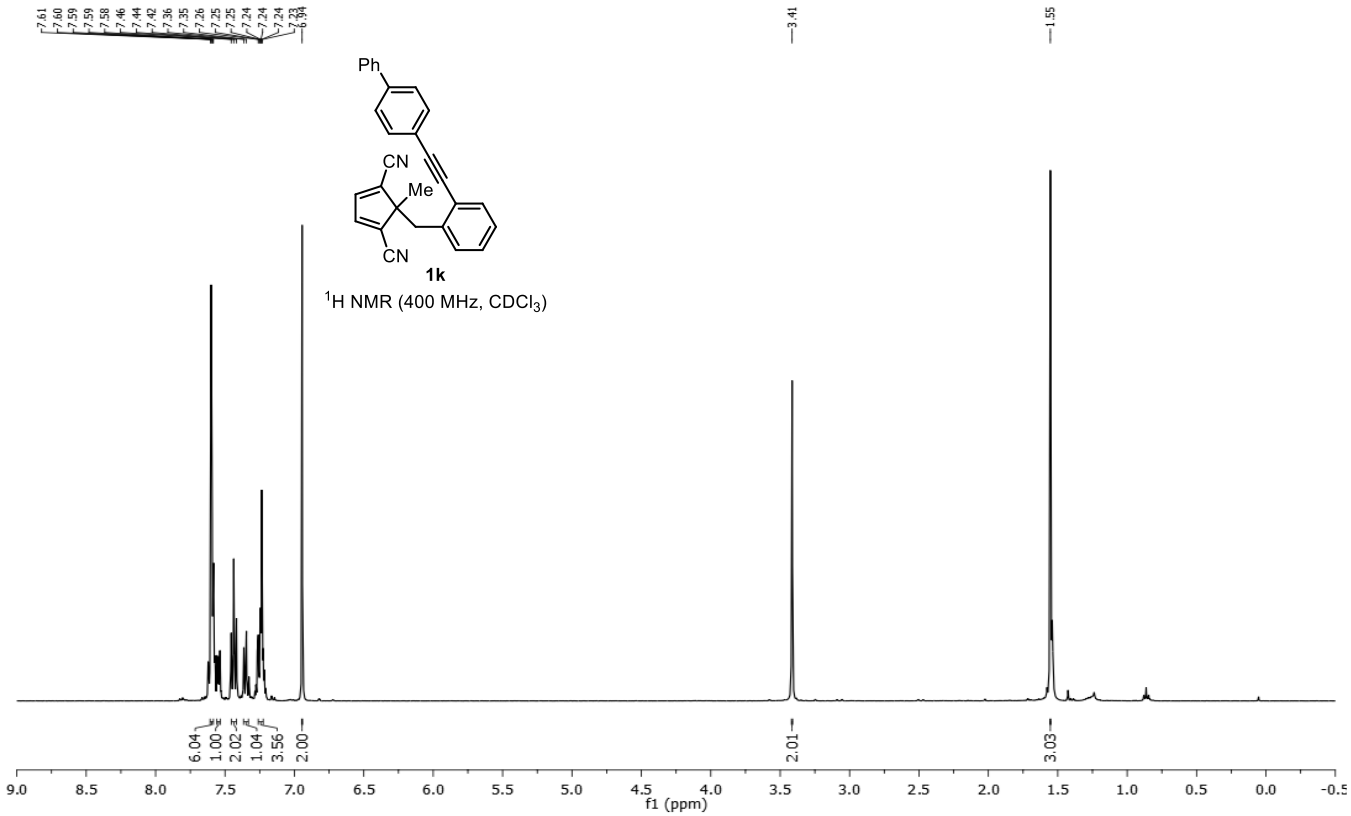


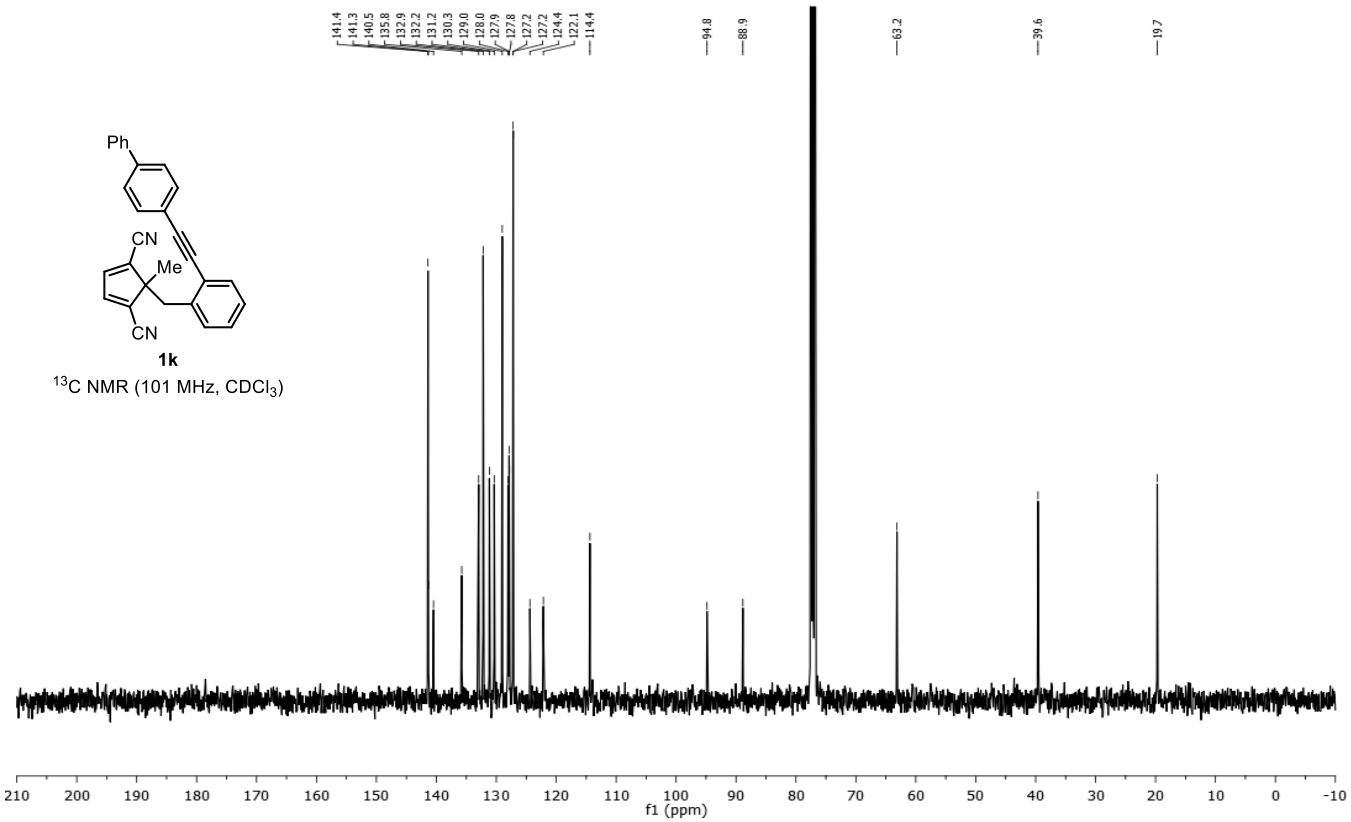
2-(2-((4-Bromophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1j):



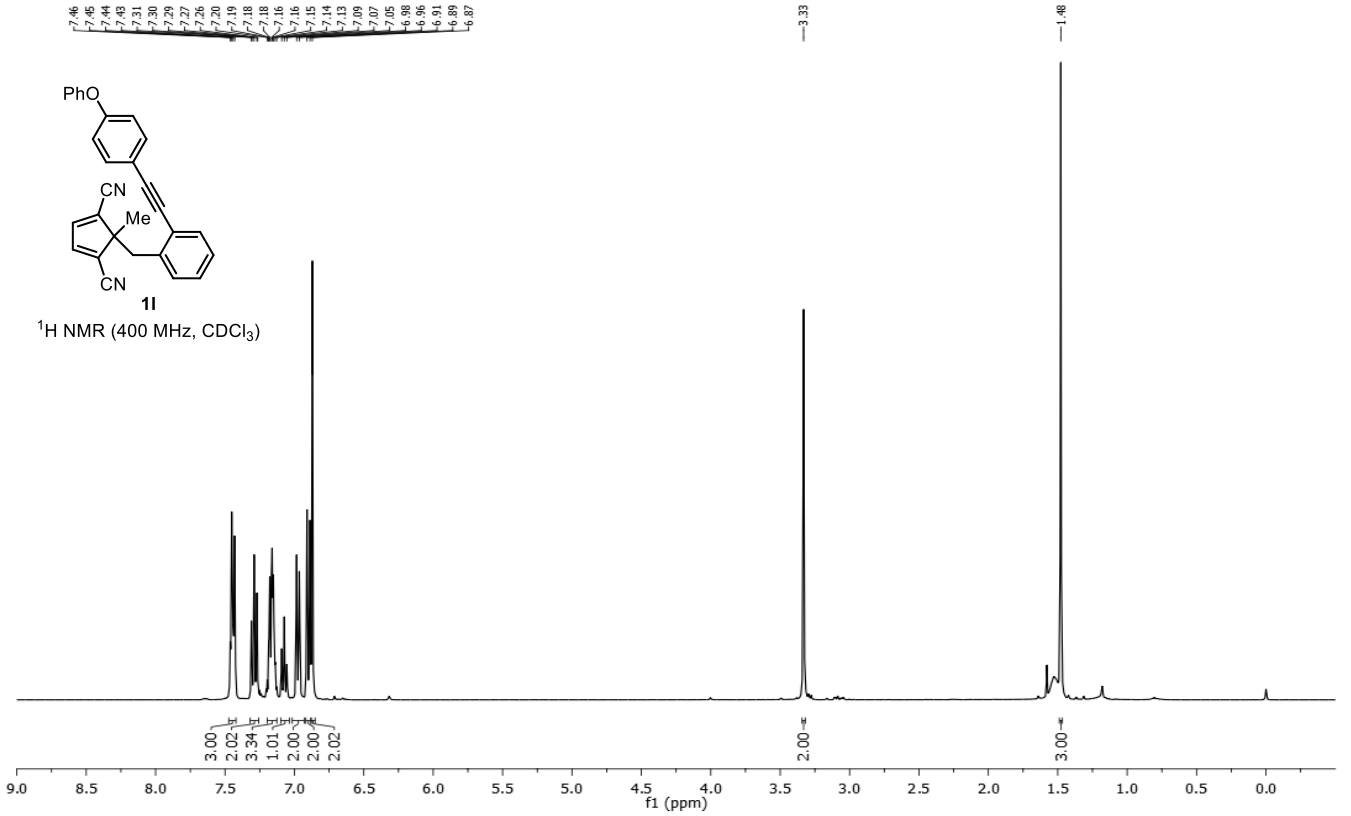


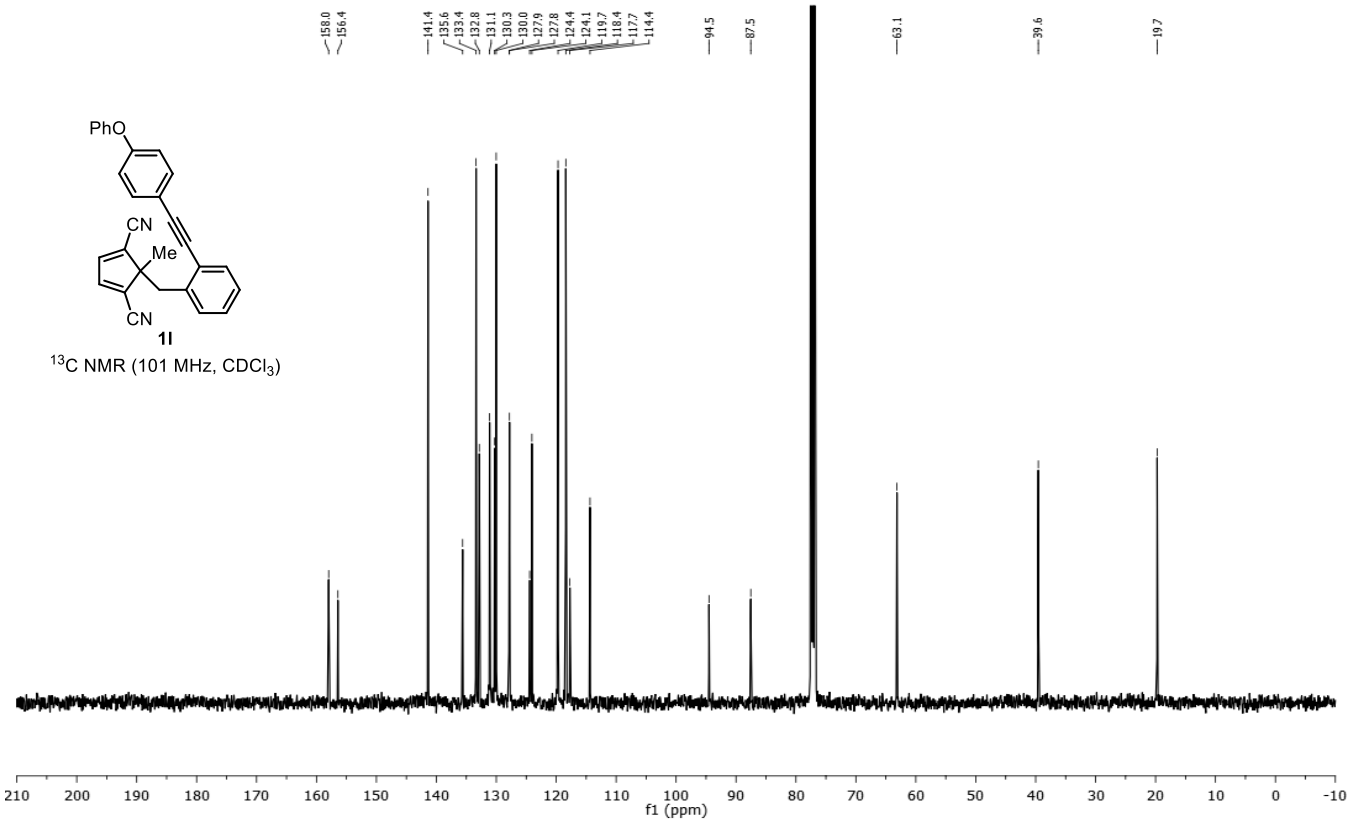
2-(2-([1,1'-Biphenyl]-4-ylethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1k):



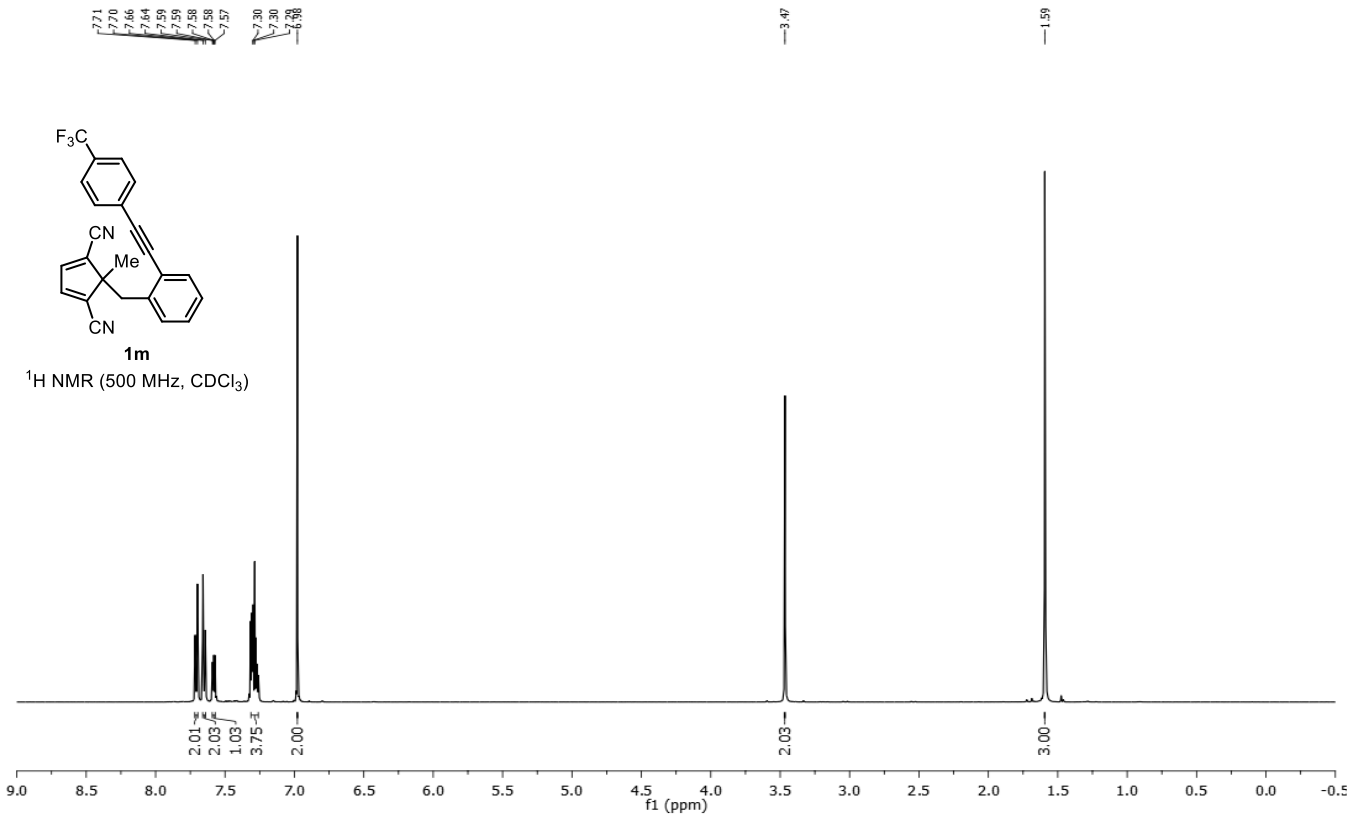


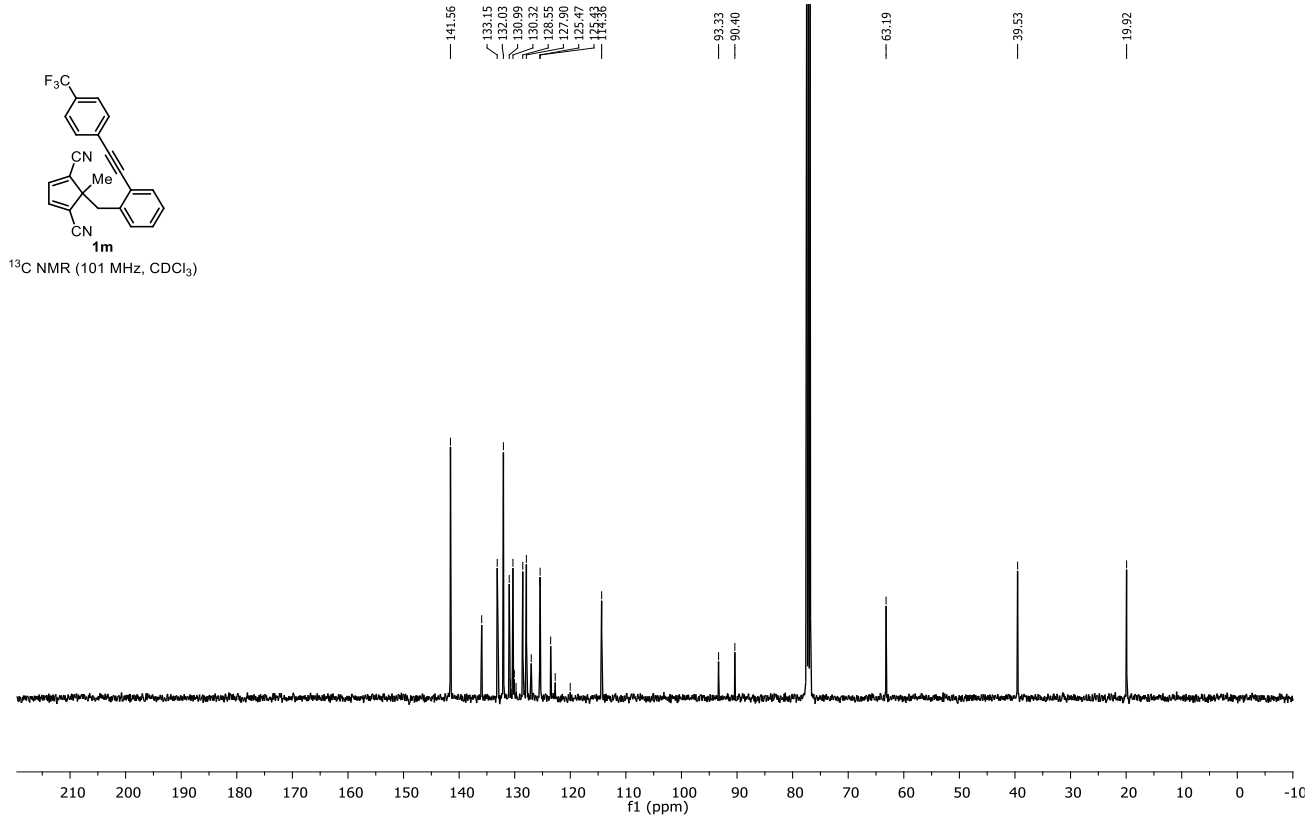
2-Methyl-2-(2-((4-phenoxyphenyl)ethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1l):

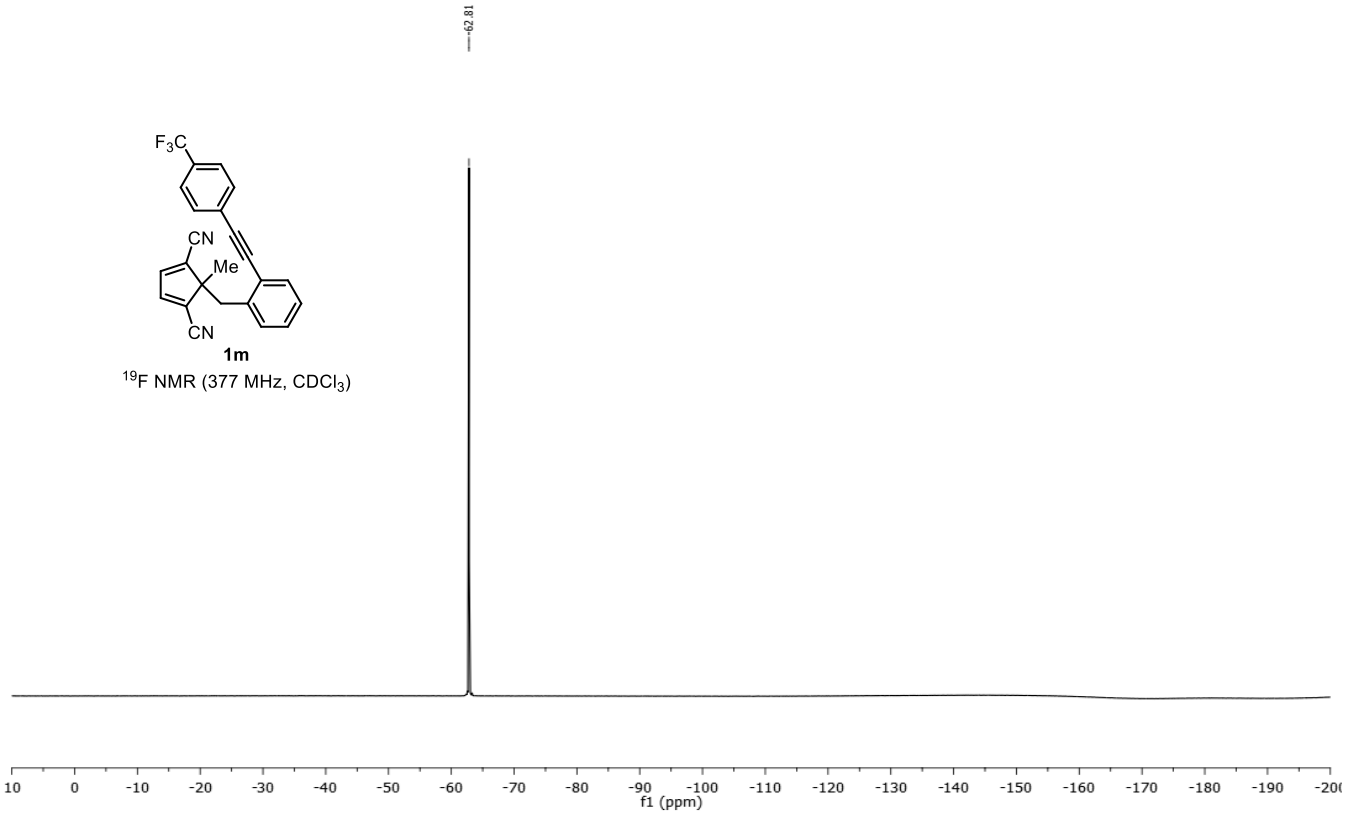




2-Methyl-2-(2-((4-(trifluoromethyl)phenyl)ethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1m):



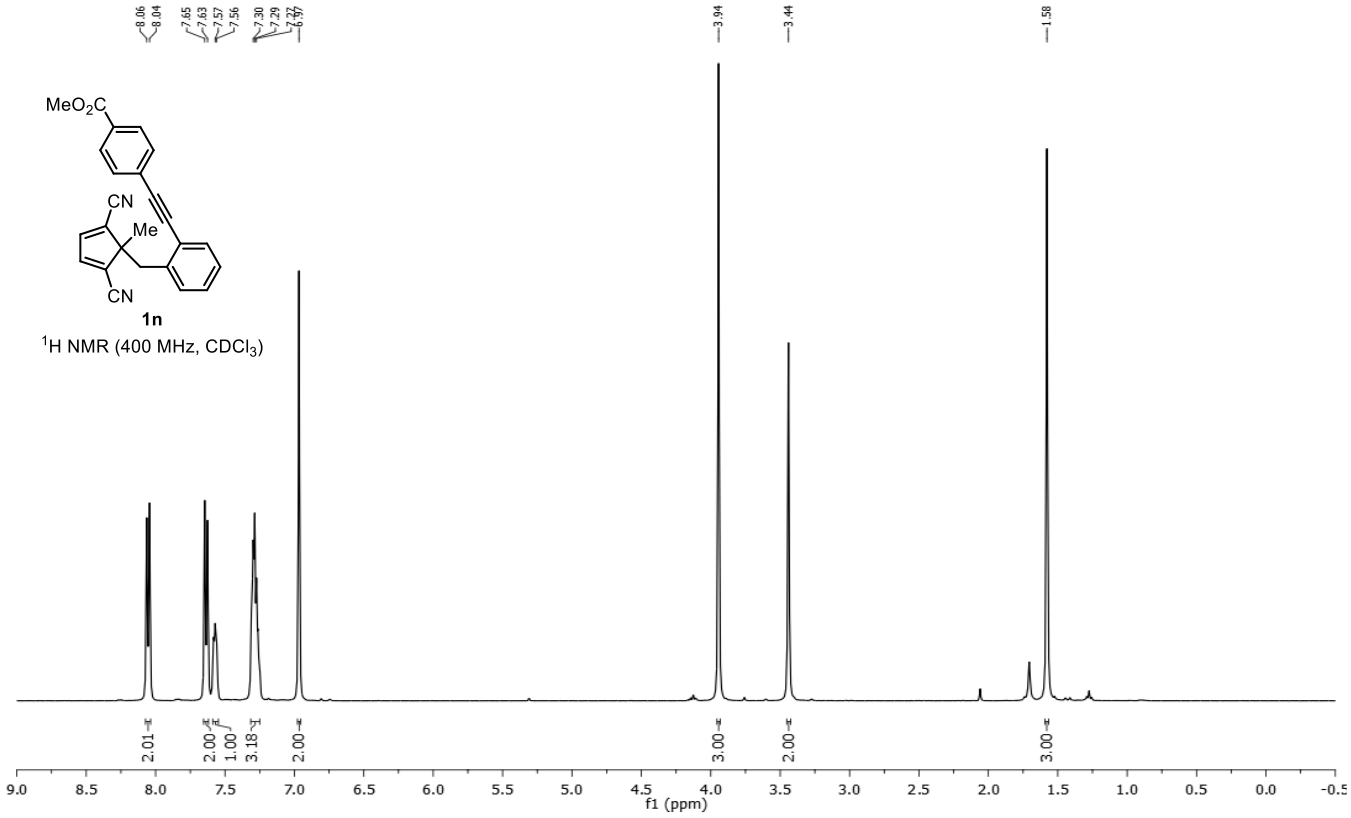


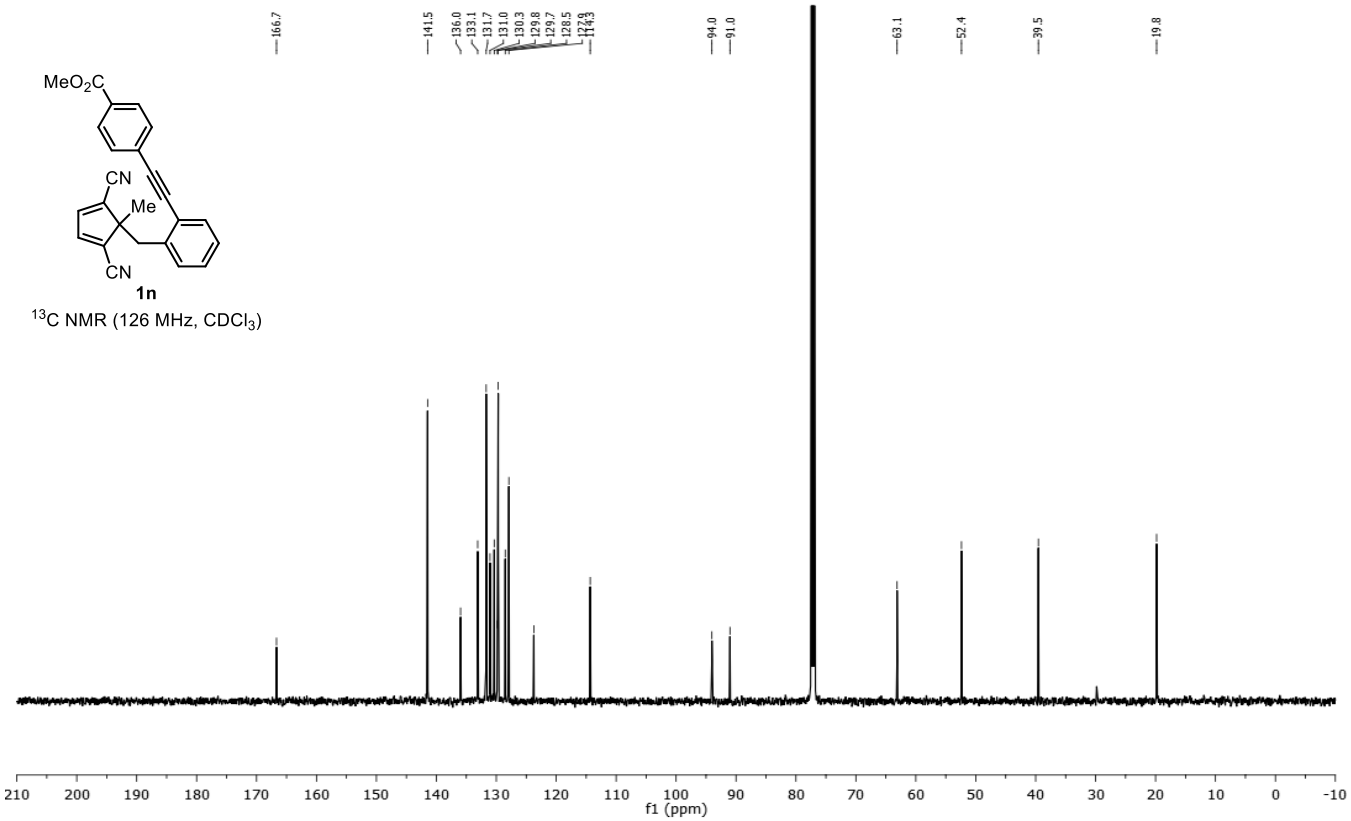


1m

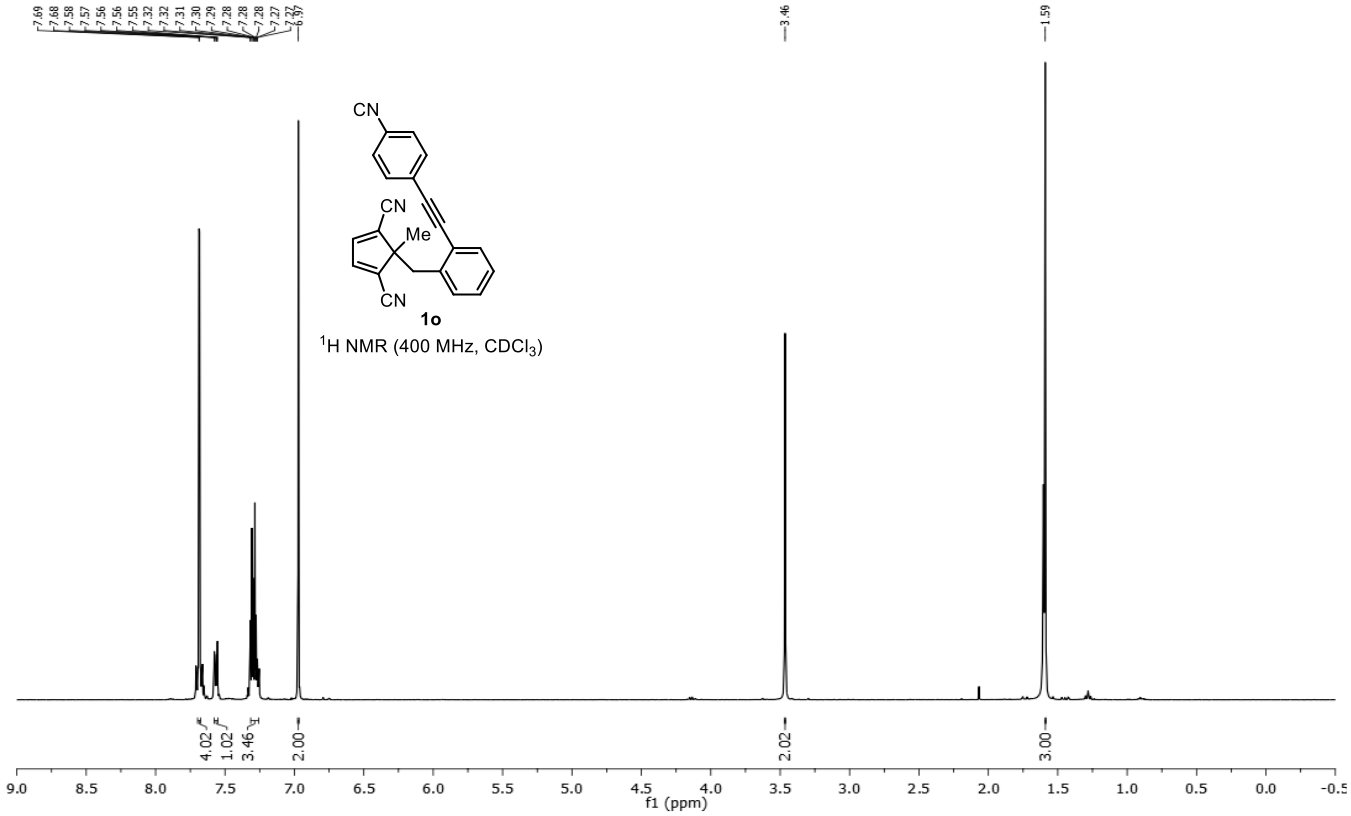
^{19}F NMR (377 MHz, $CDCl_3$)

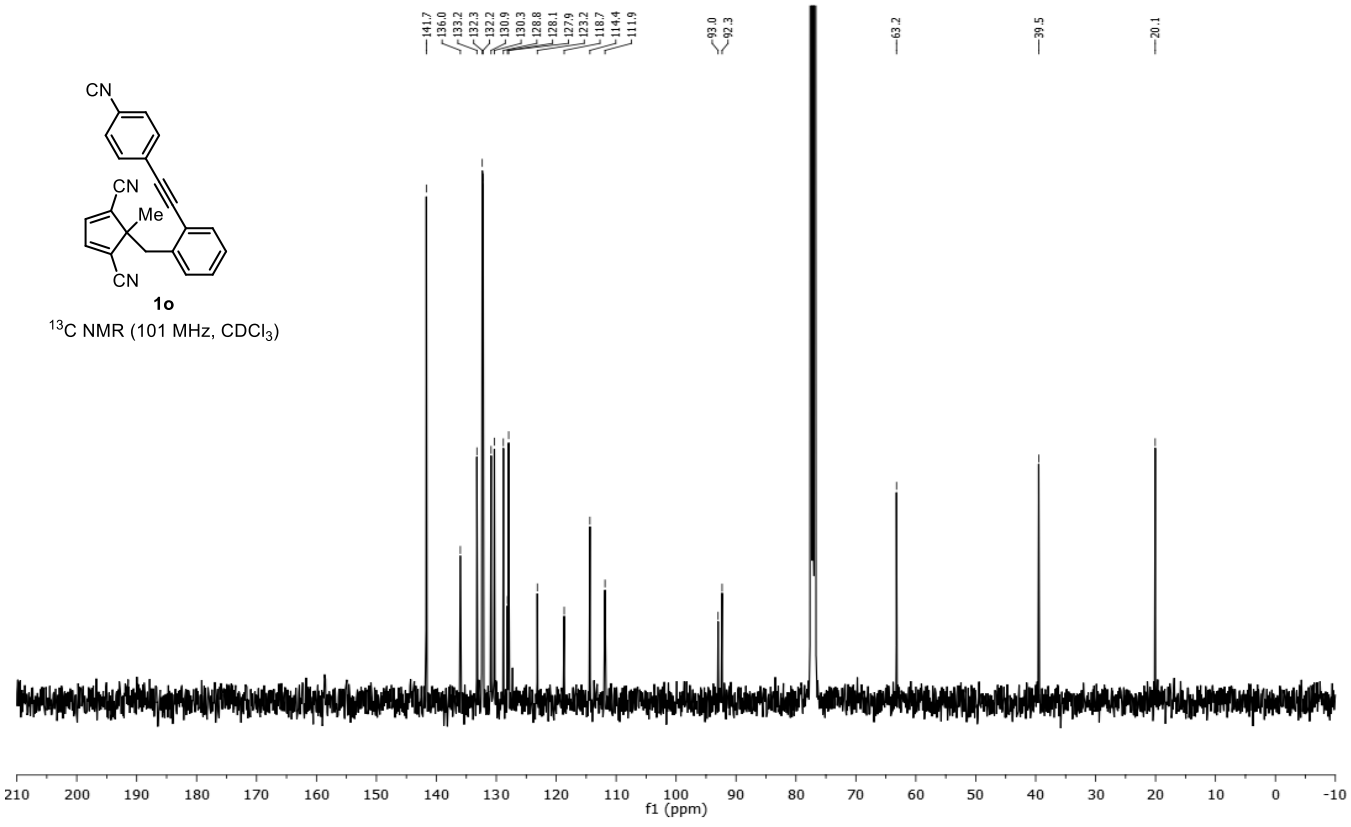
Methyl 4-((2-((2,5-dicyano-1-methylcyclopenta-2,4-dien-1-yl)methyl)phenyl)ethynyl)benzoate (1n):



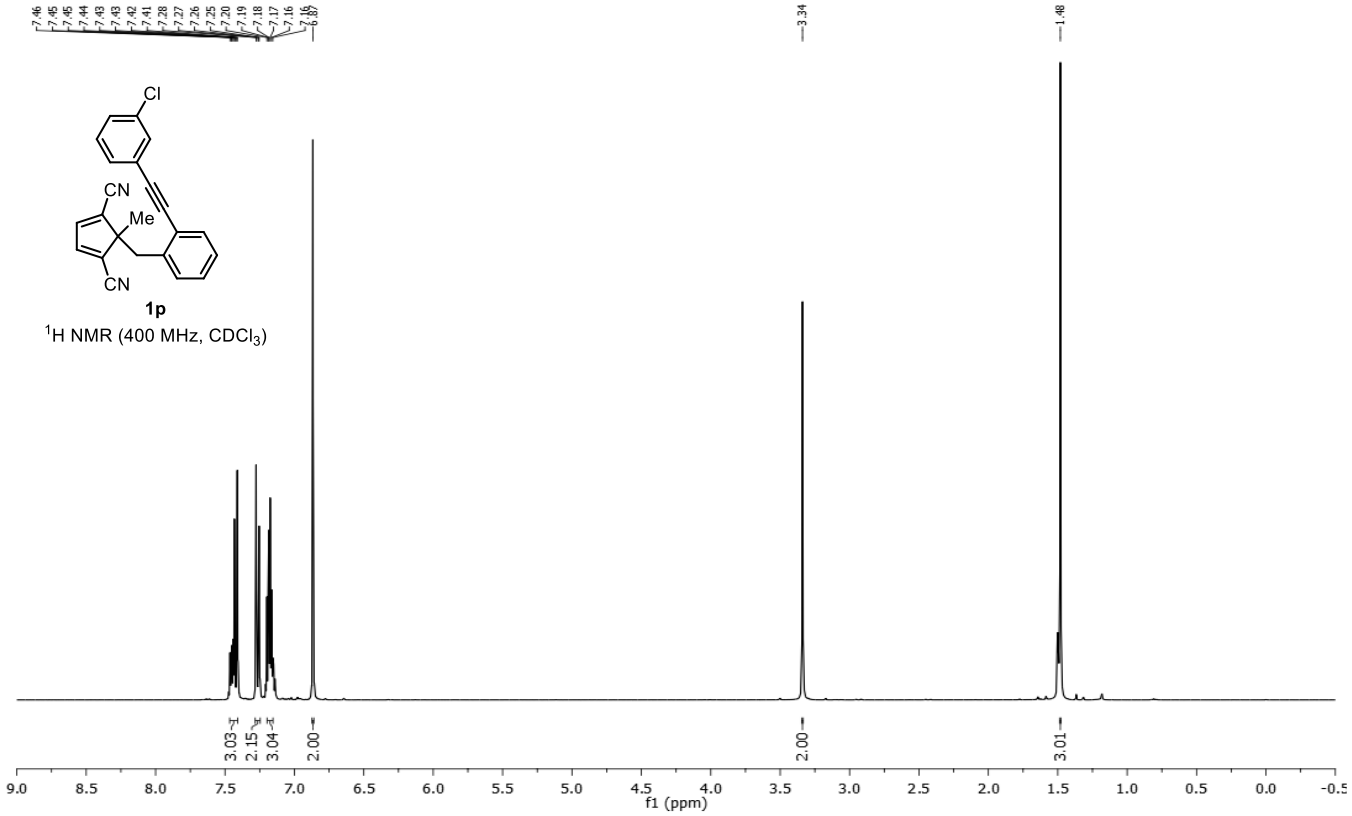


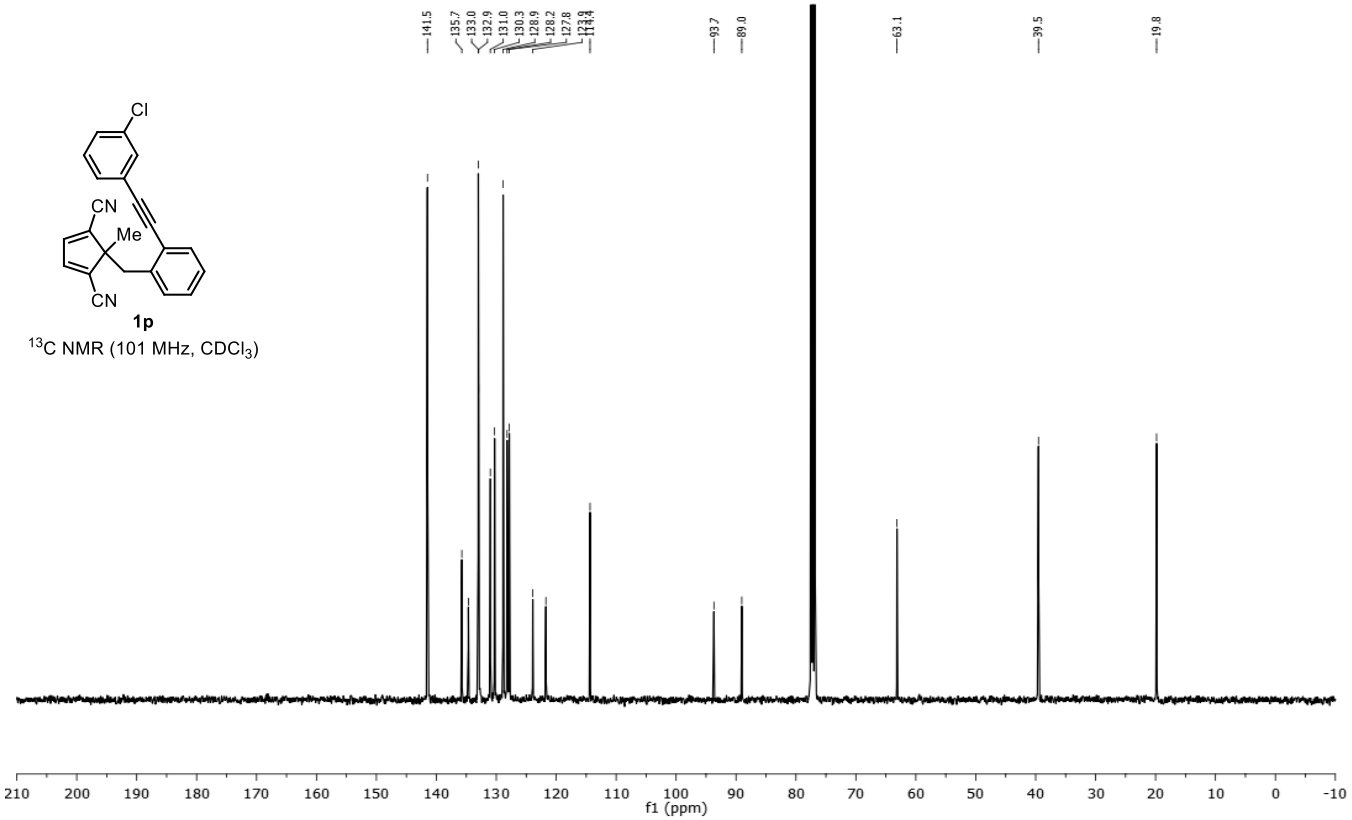
2-(2-((4-Cyanophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1o):



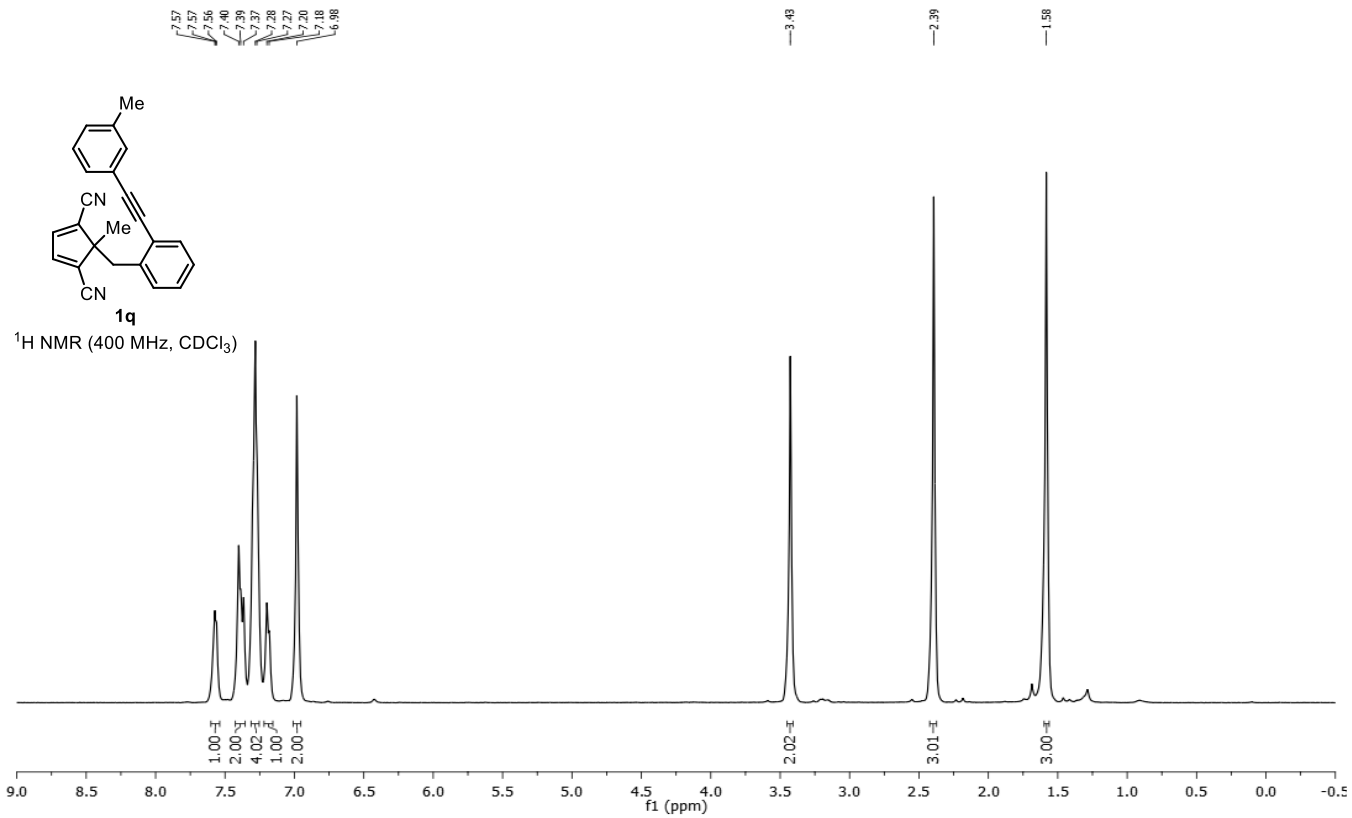


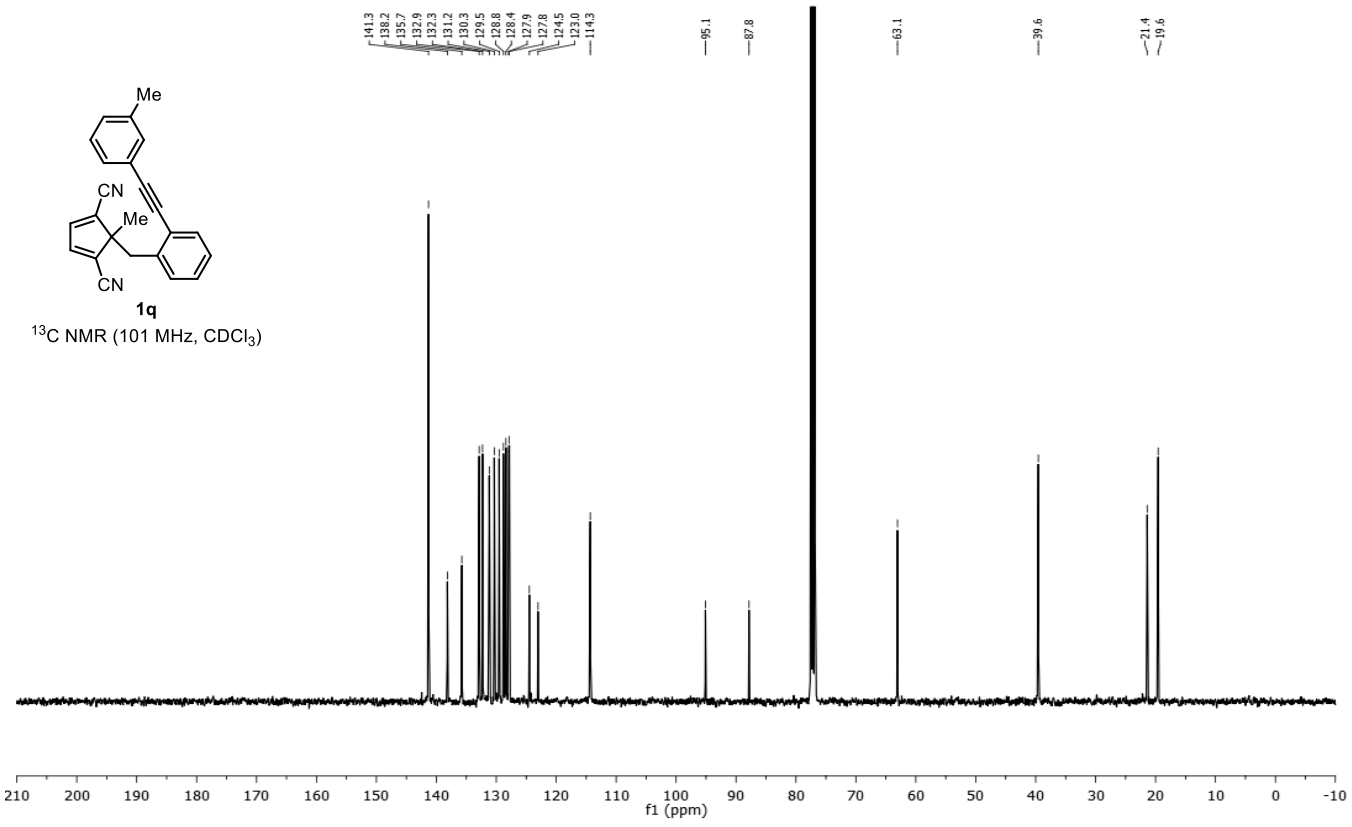
2-(2-((3-Chlorophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1p):



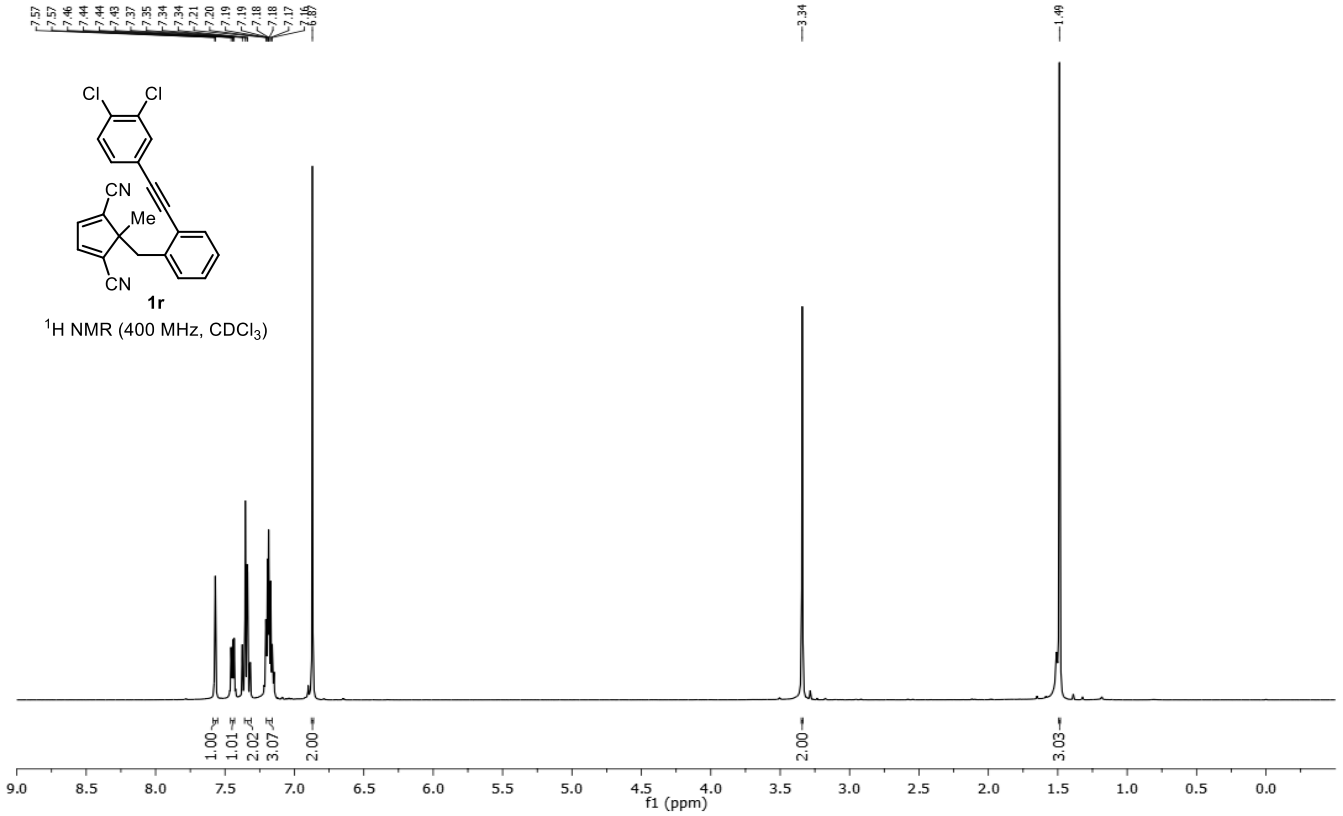


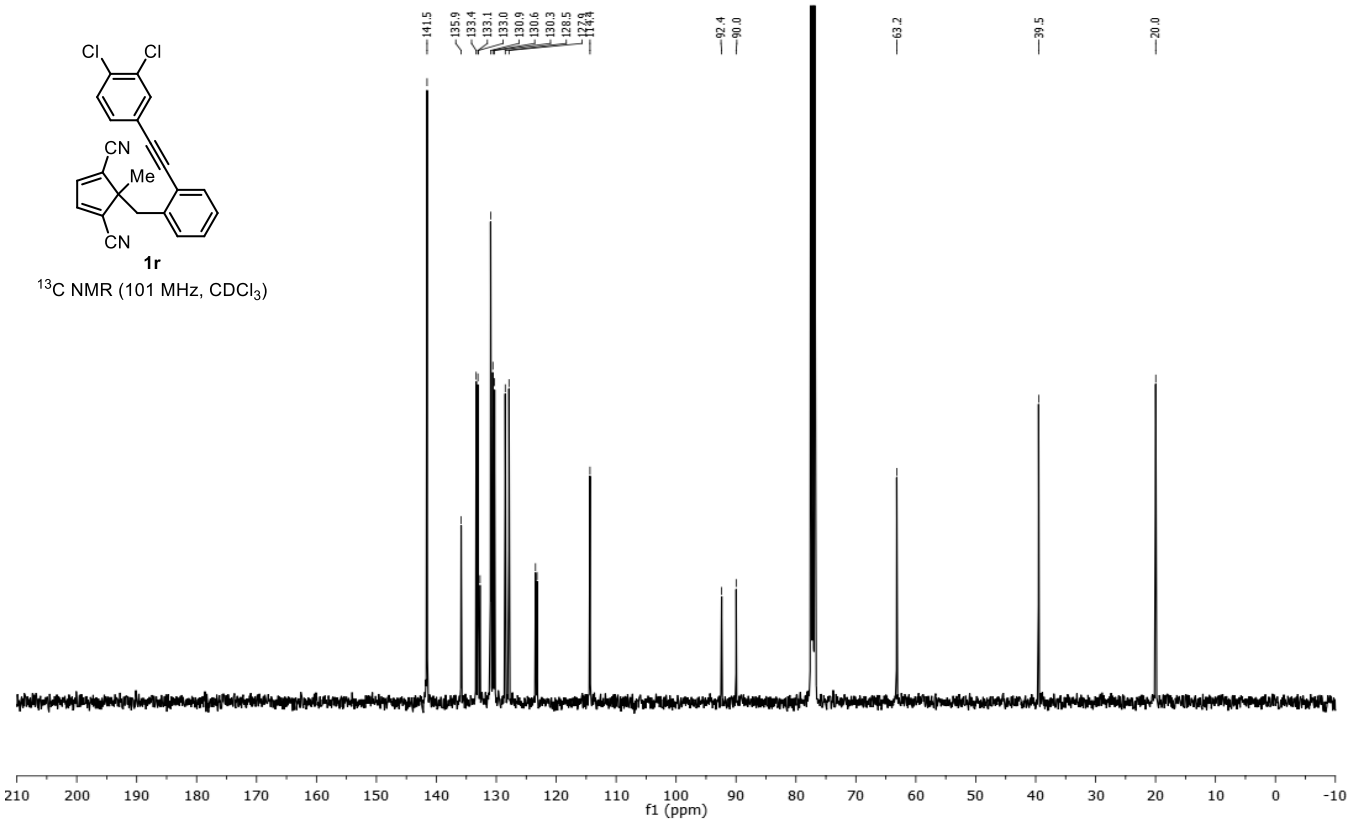
2-Methyl-2-(2-(m-tolylethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1q):



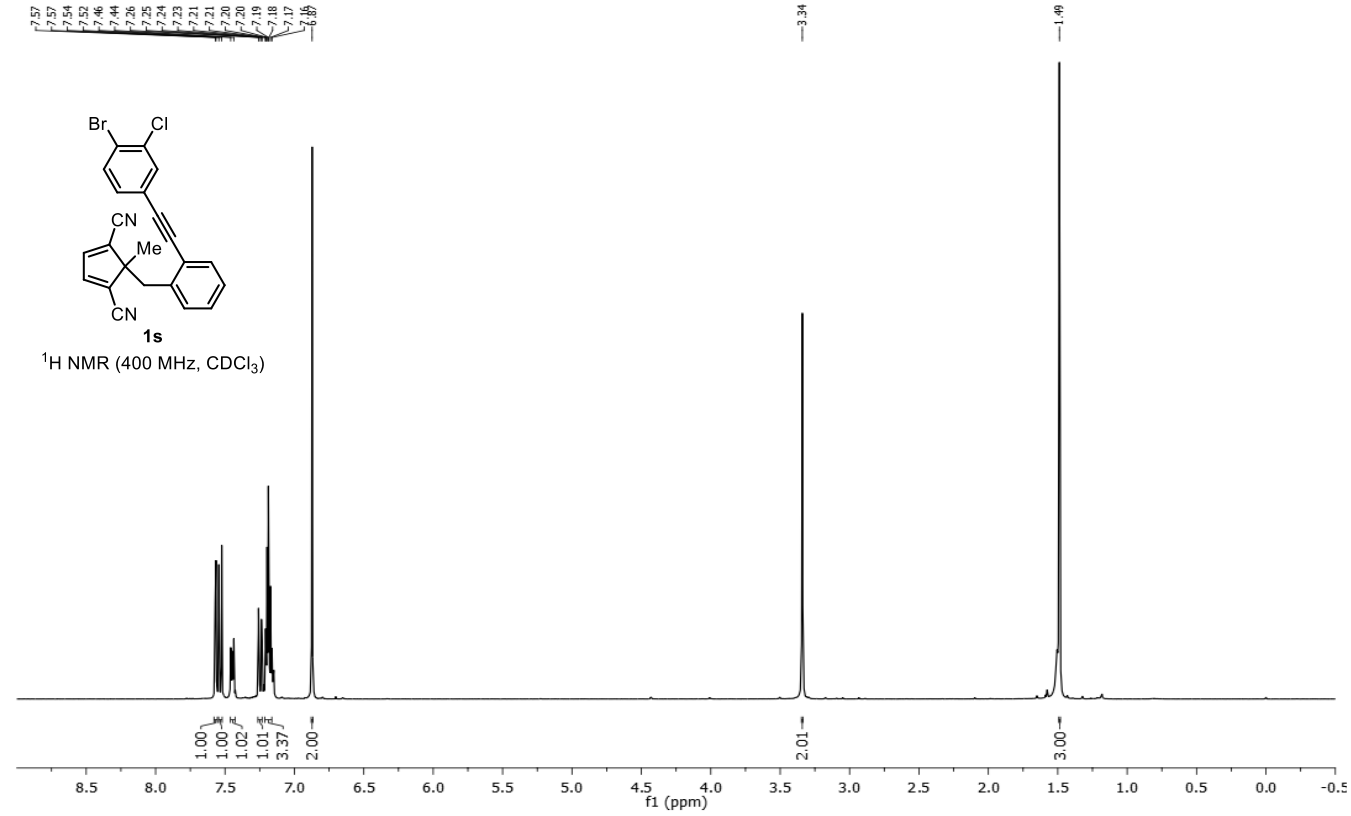


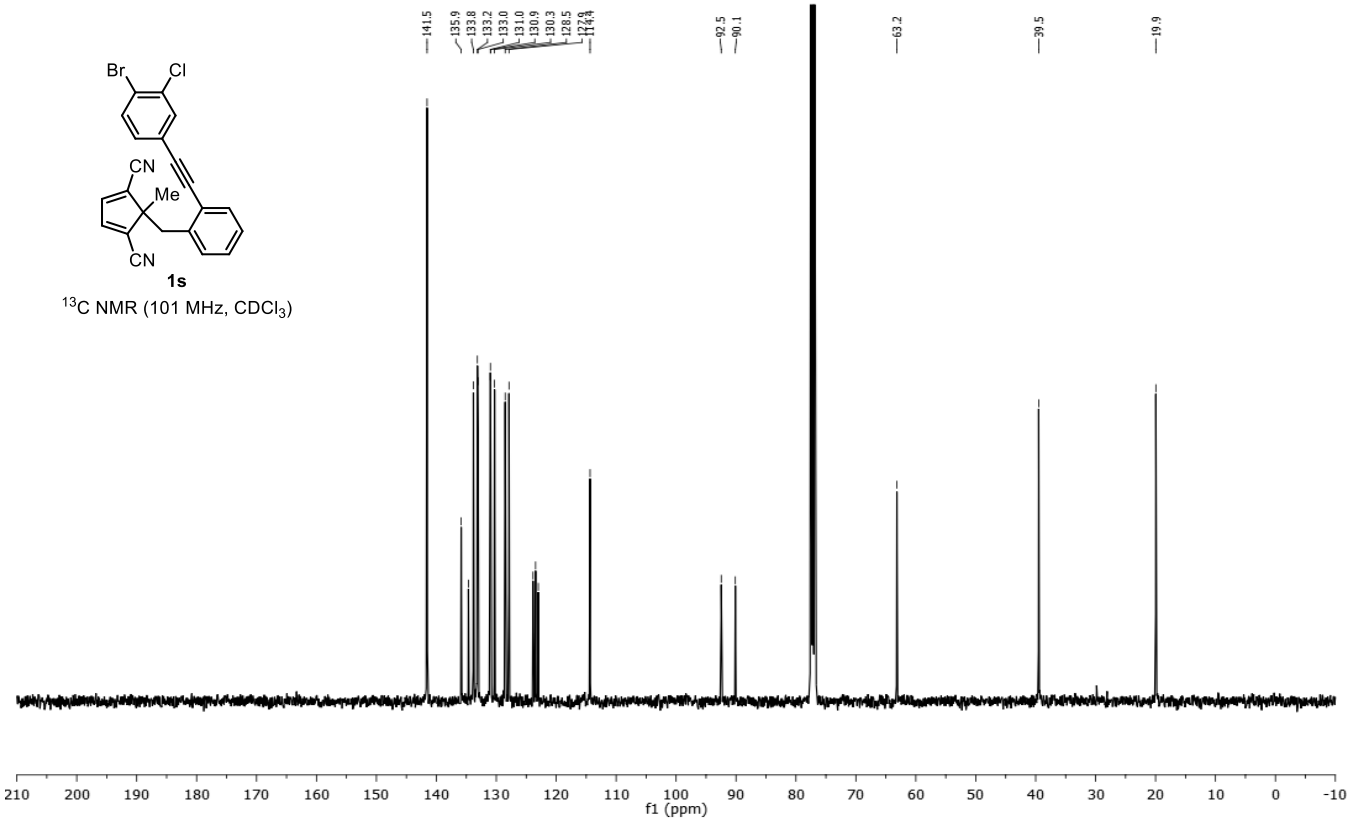
2-(2-((3,4-Dichlorophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1r):



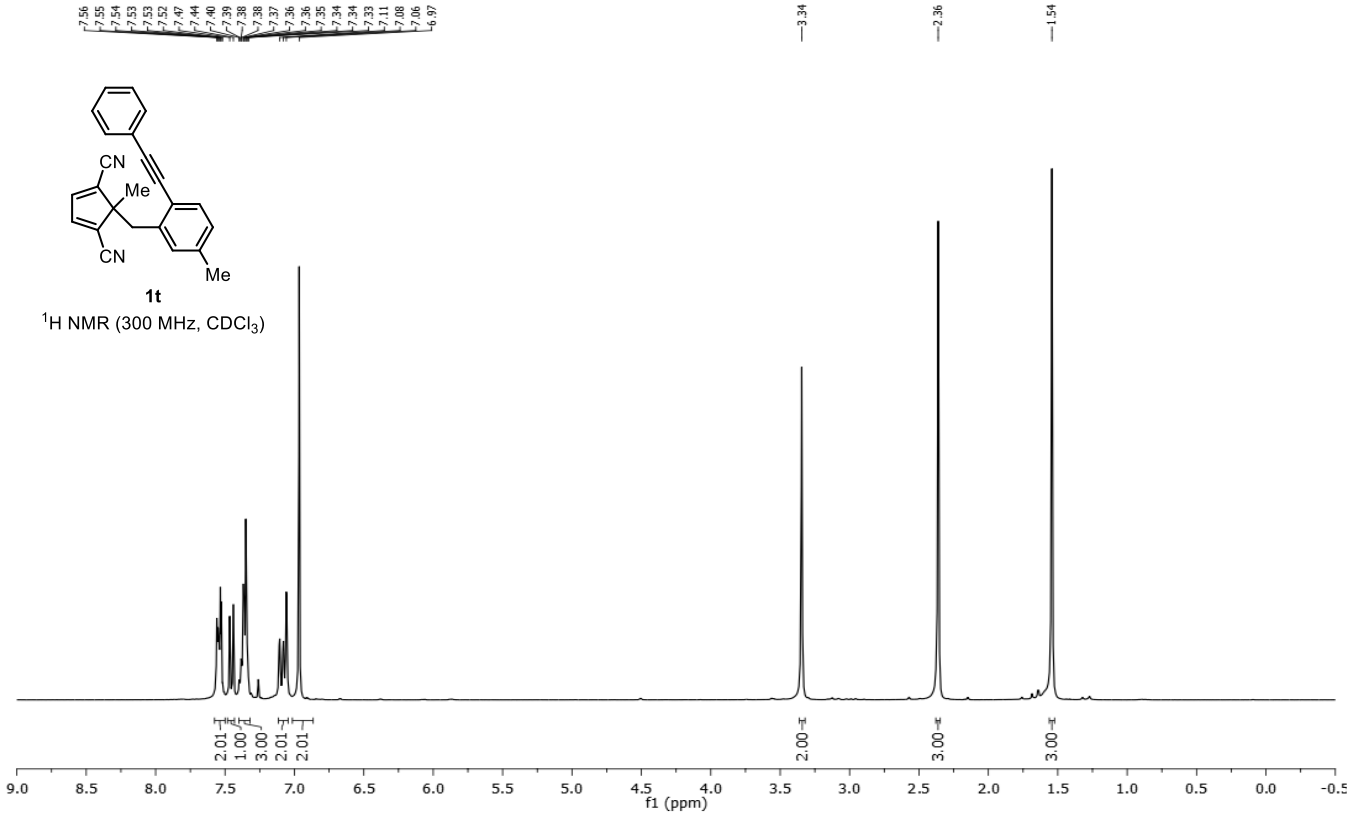


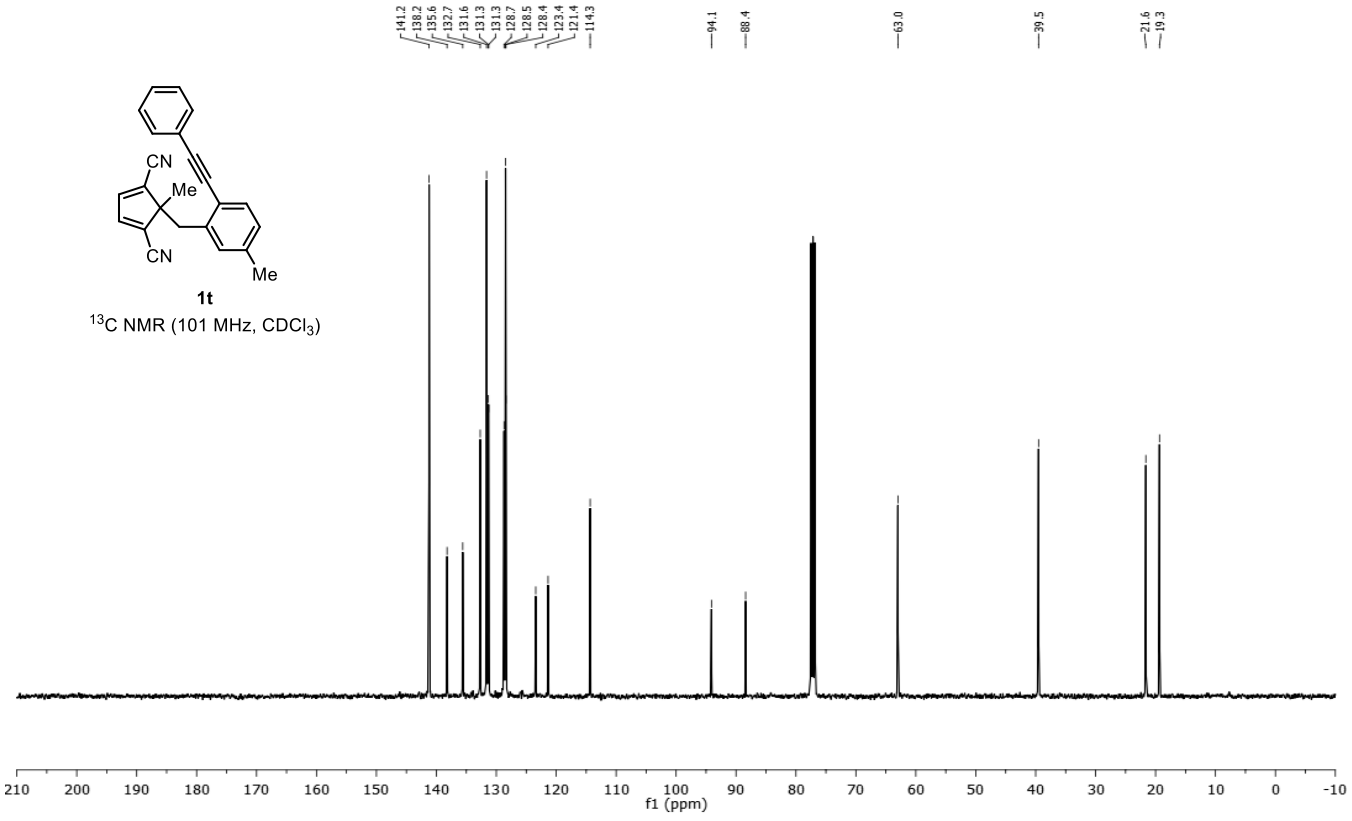
2-(2-((4-Bromo-3-chlorophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1s):



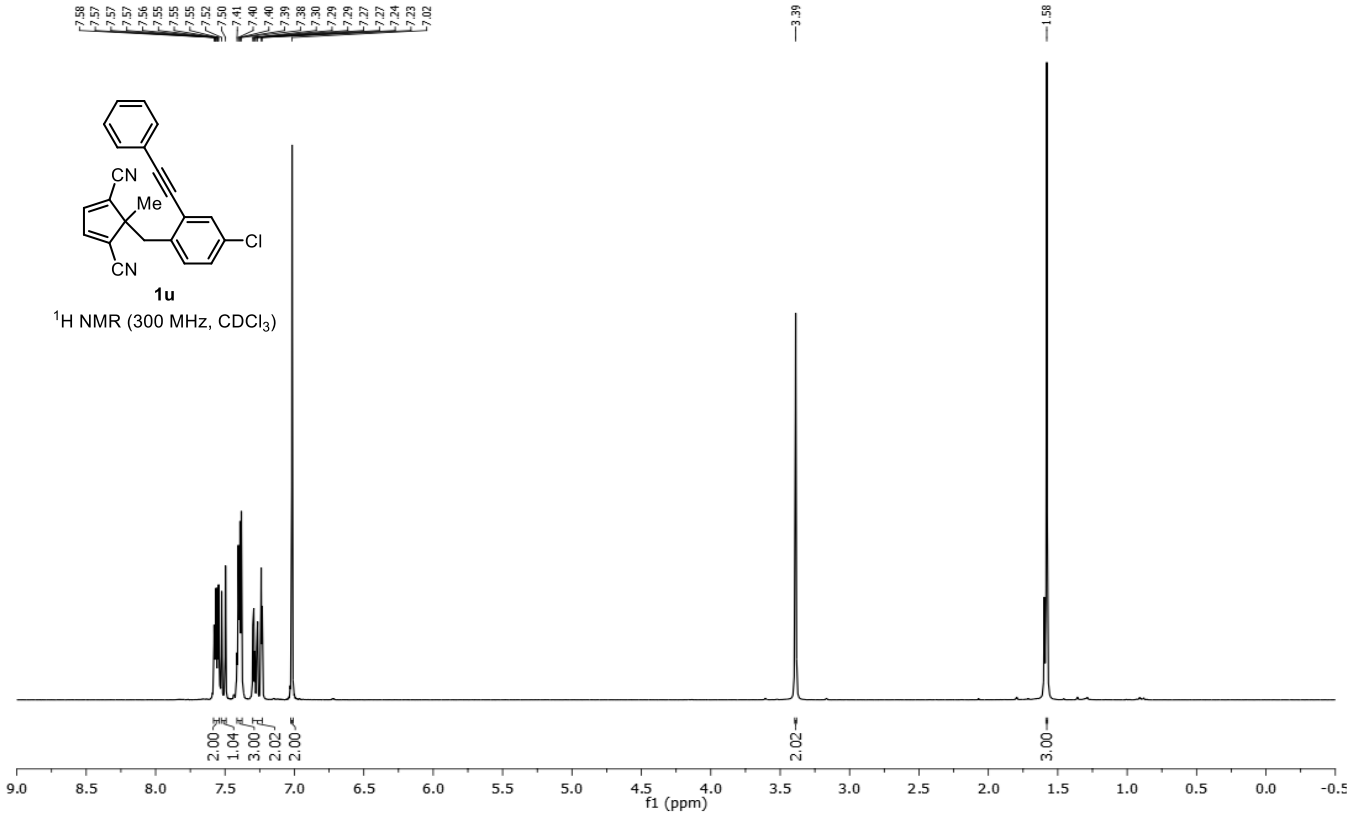


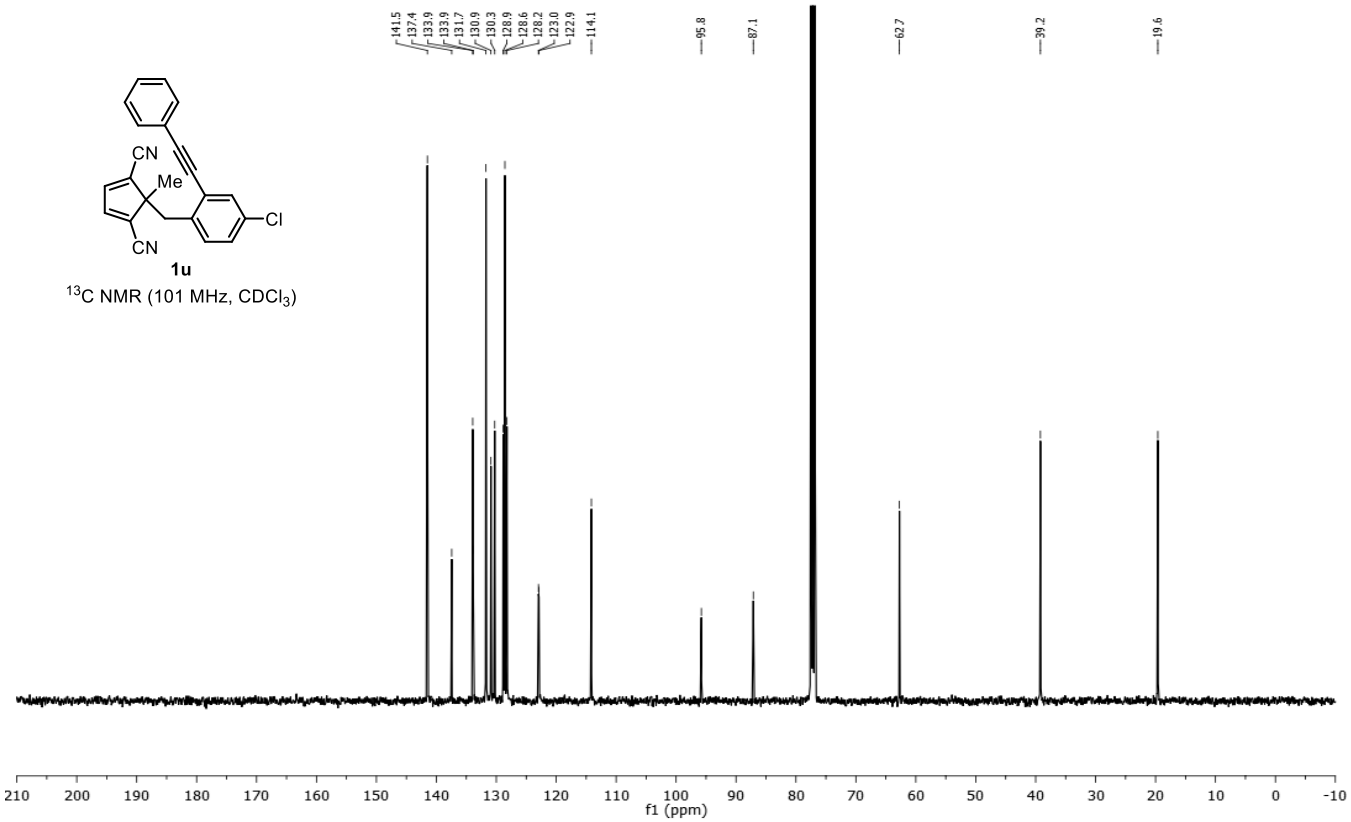
2-Methyl-2-(5-methyl-2-(phenylethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1t):



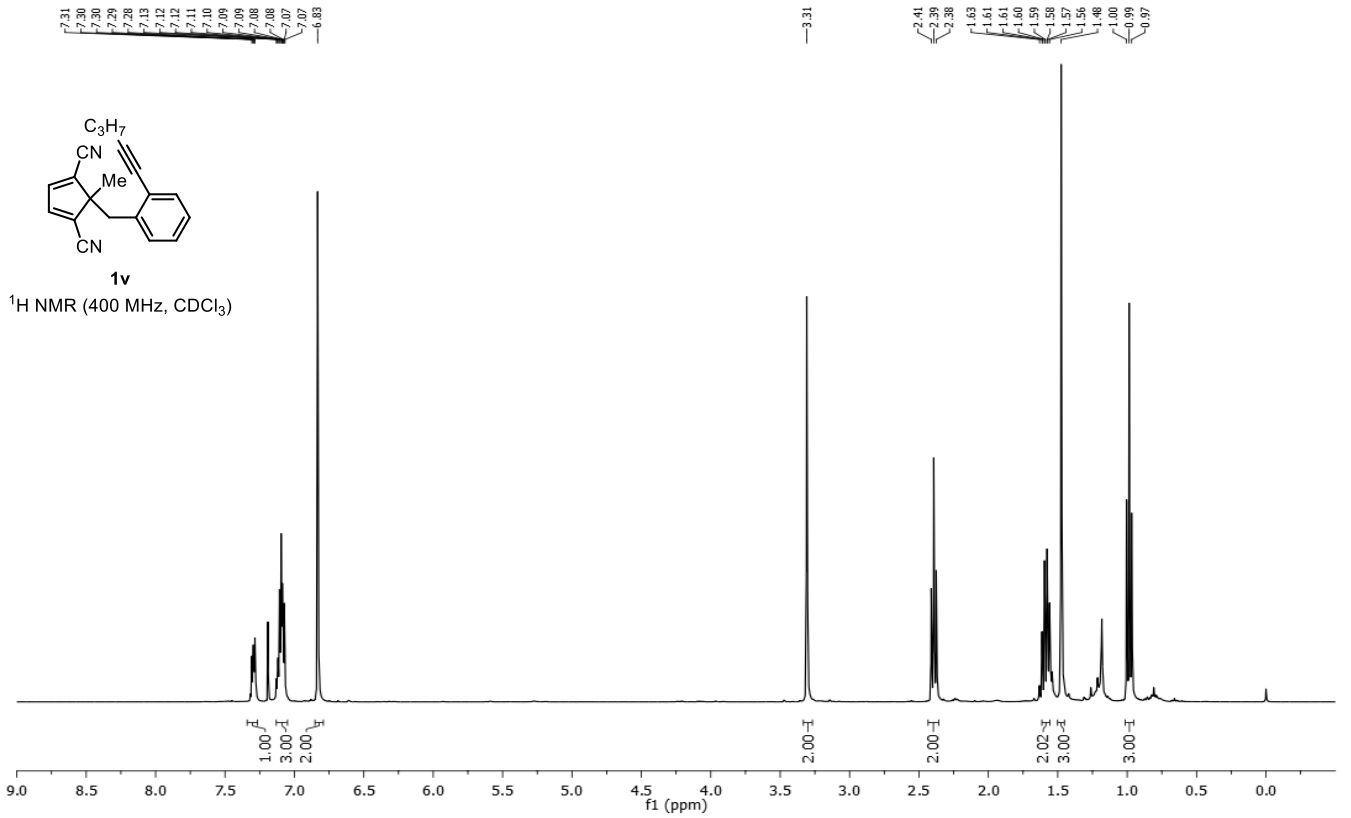


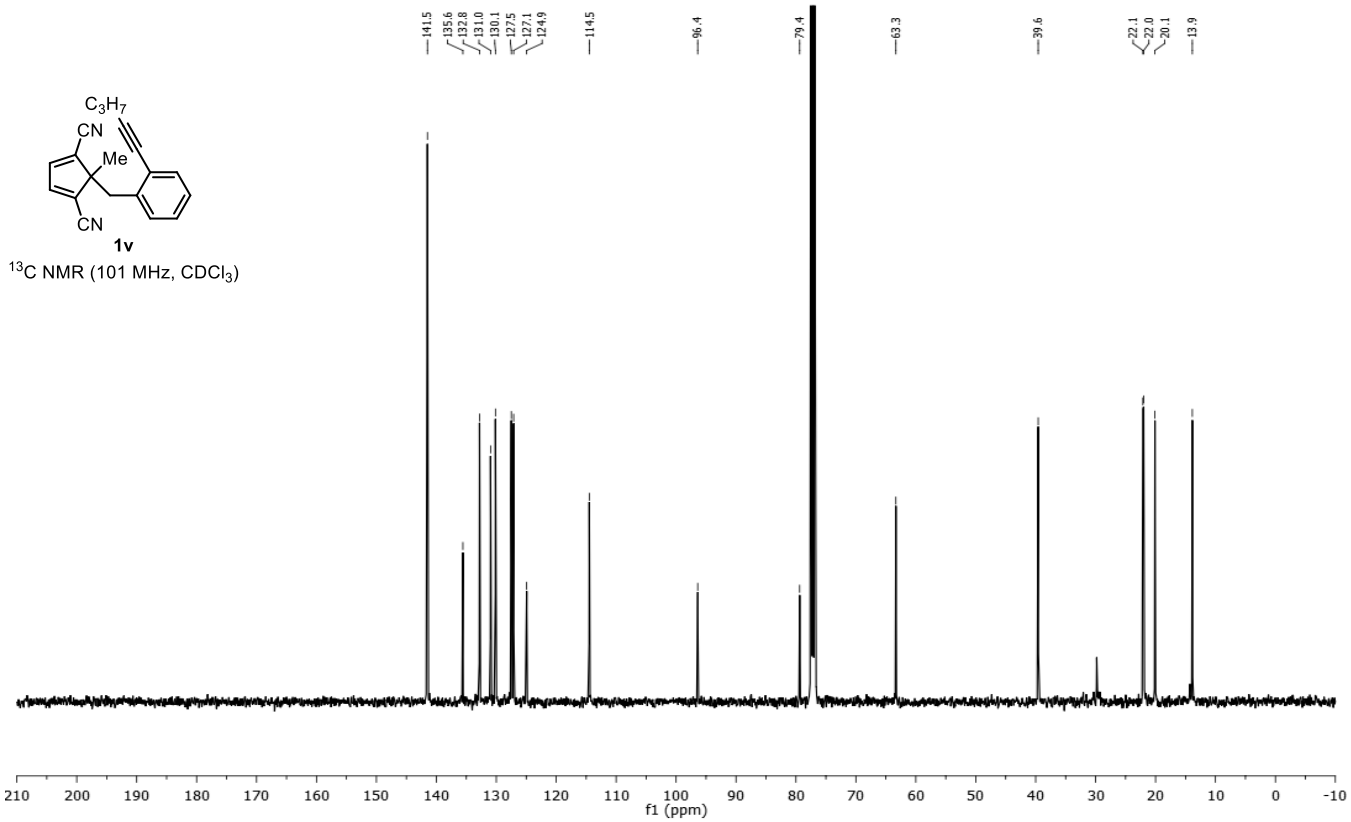
2-Methyl-2-(2-(p-tolylethynyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (1u):



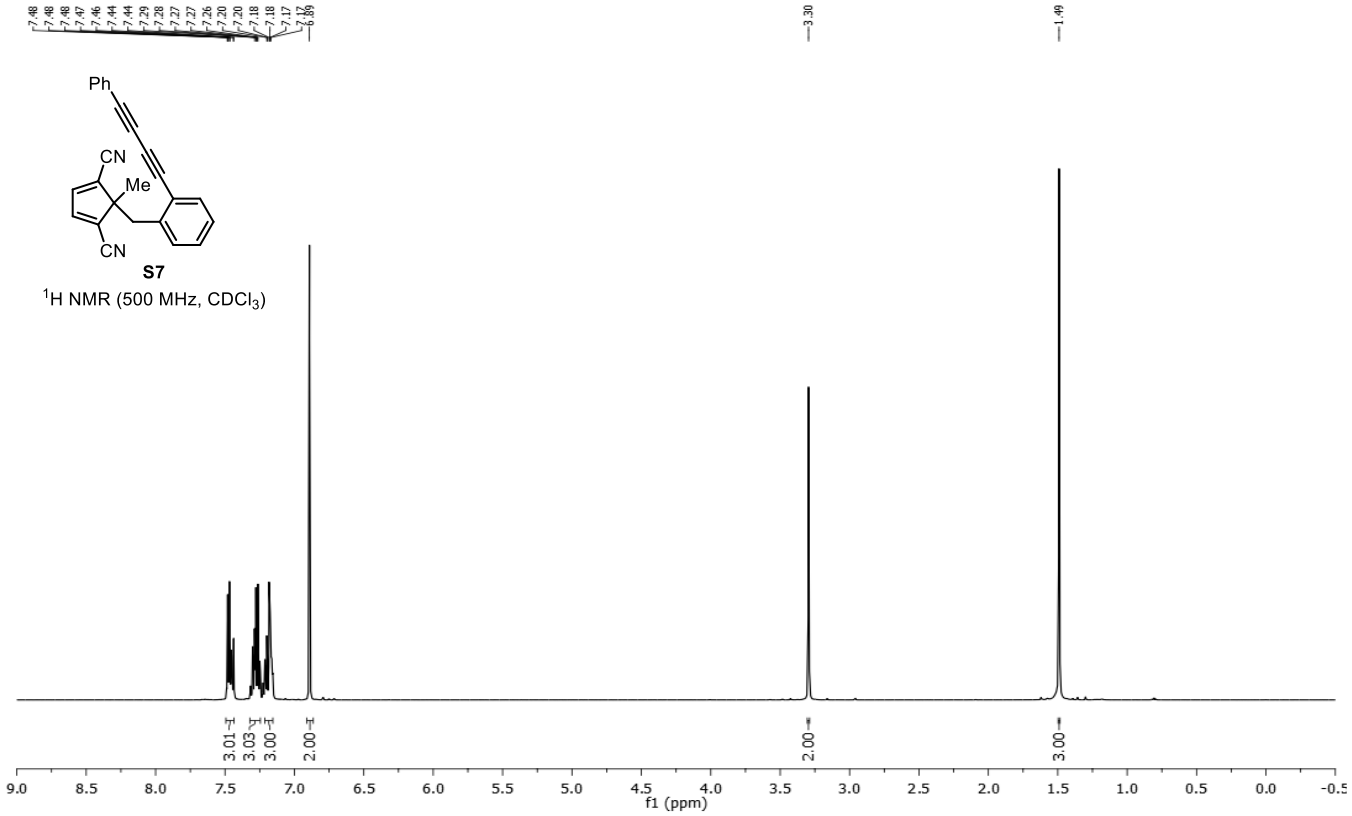


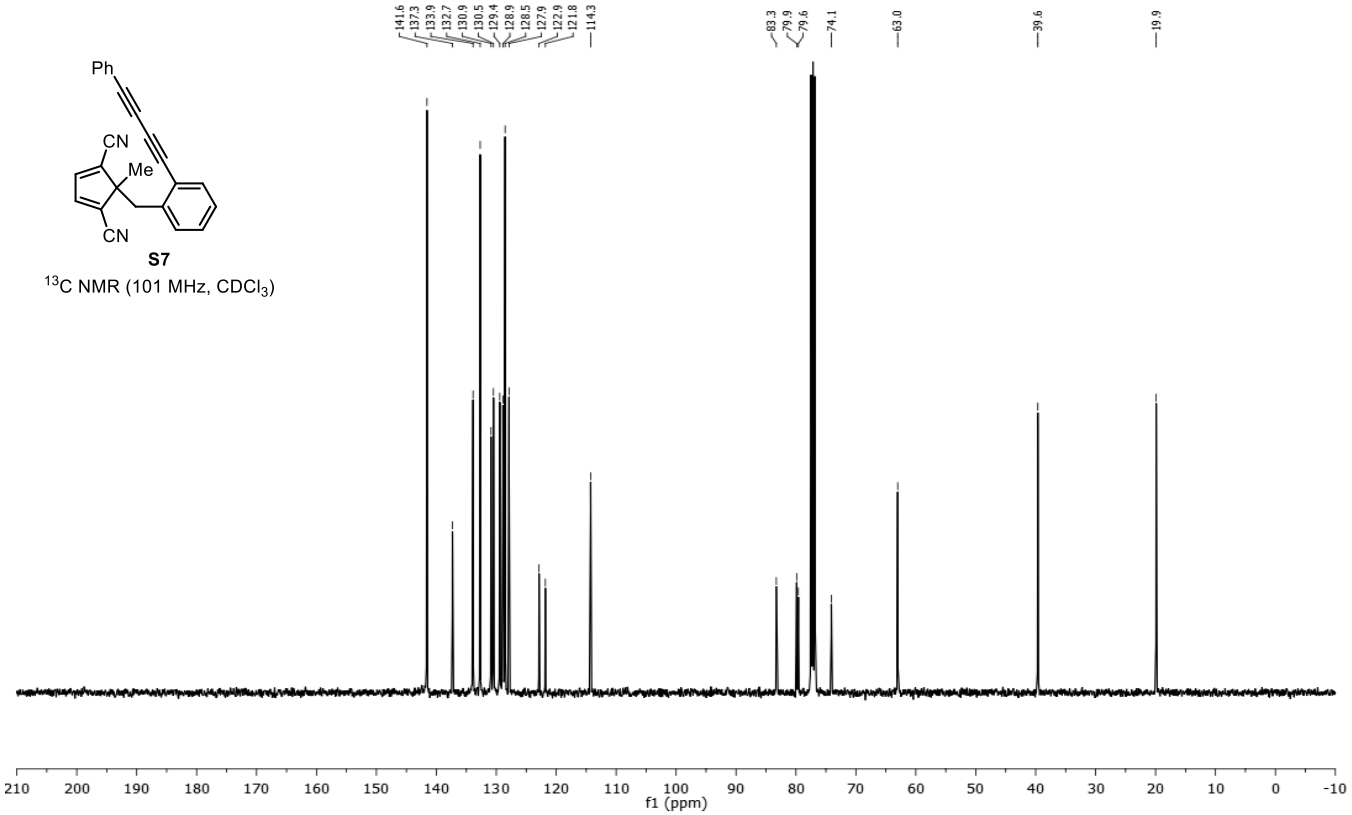
2-(2-Bromobenzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (1v):



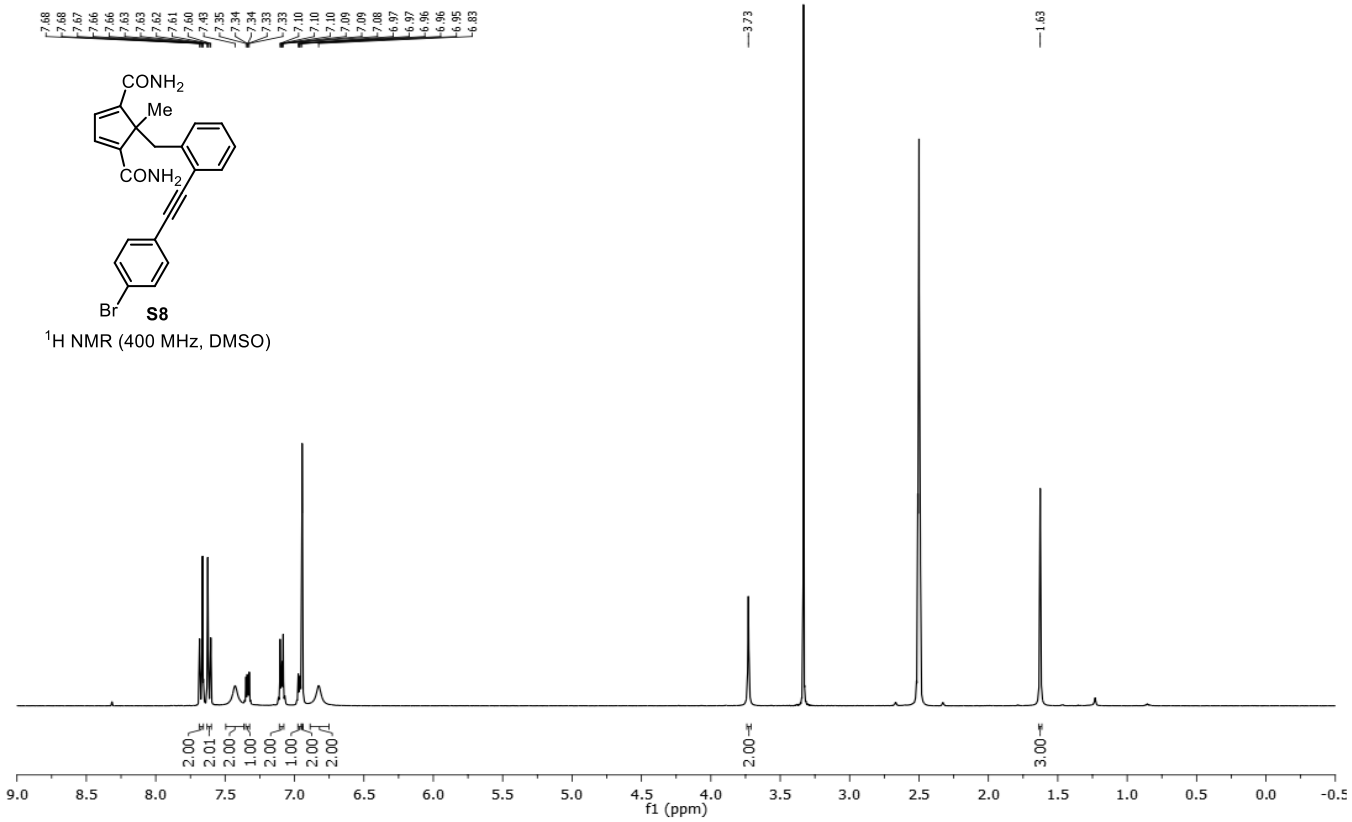


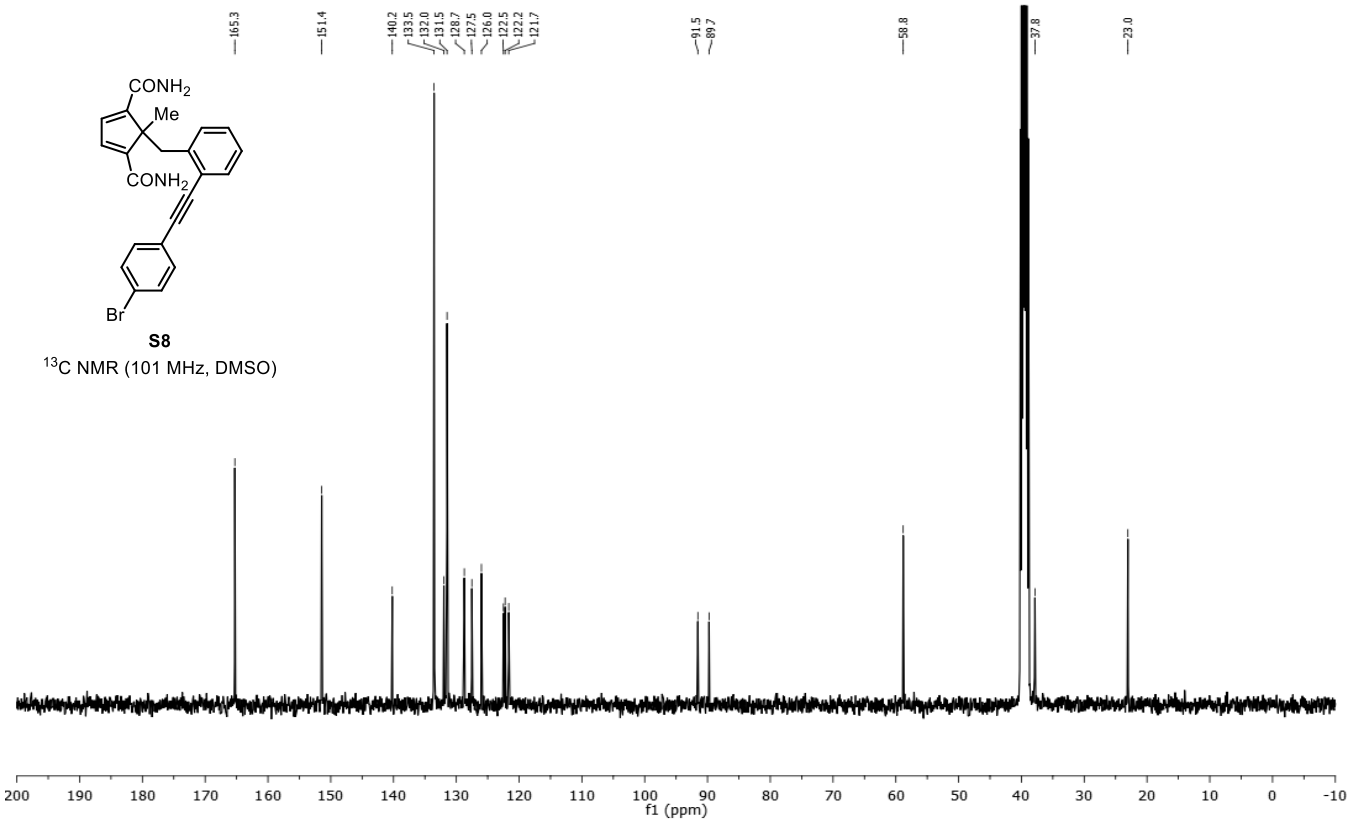
2-(2-Bromobenzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (S7):



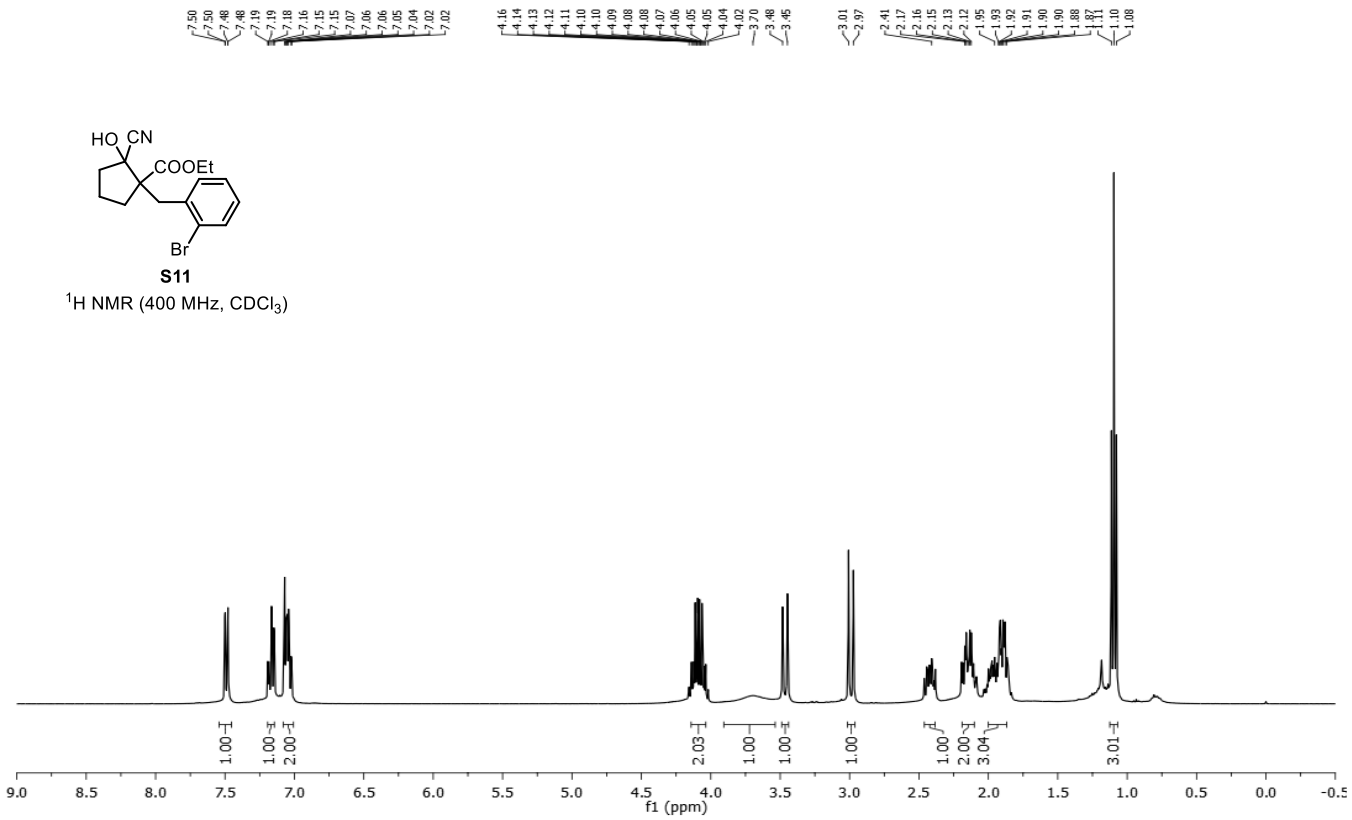


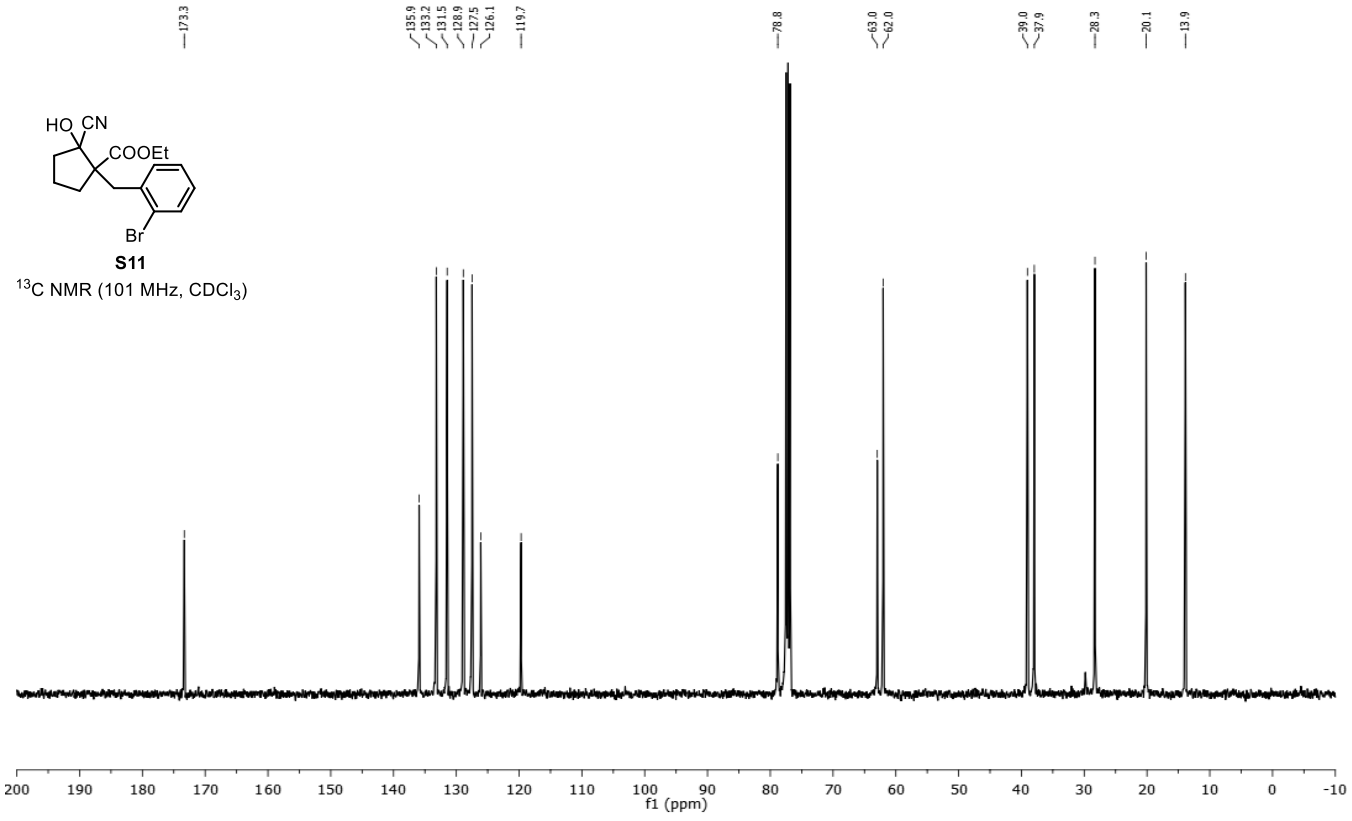
2-(2-((4-bromophenyl)ethynyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarboxamide (S8):



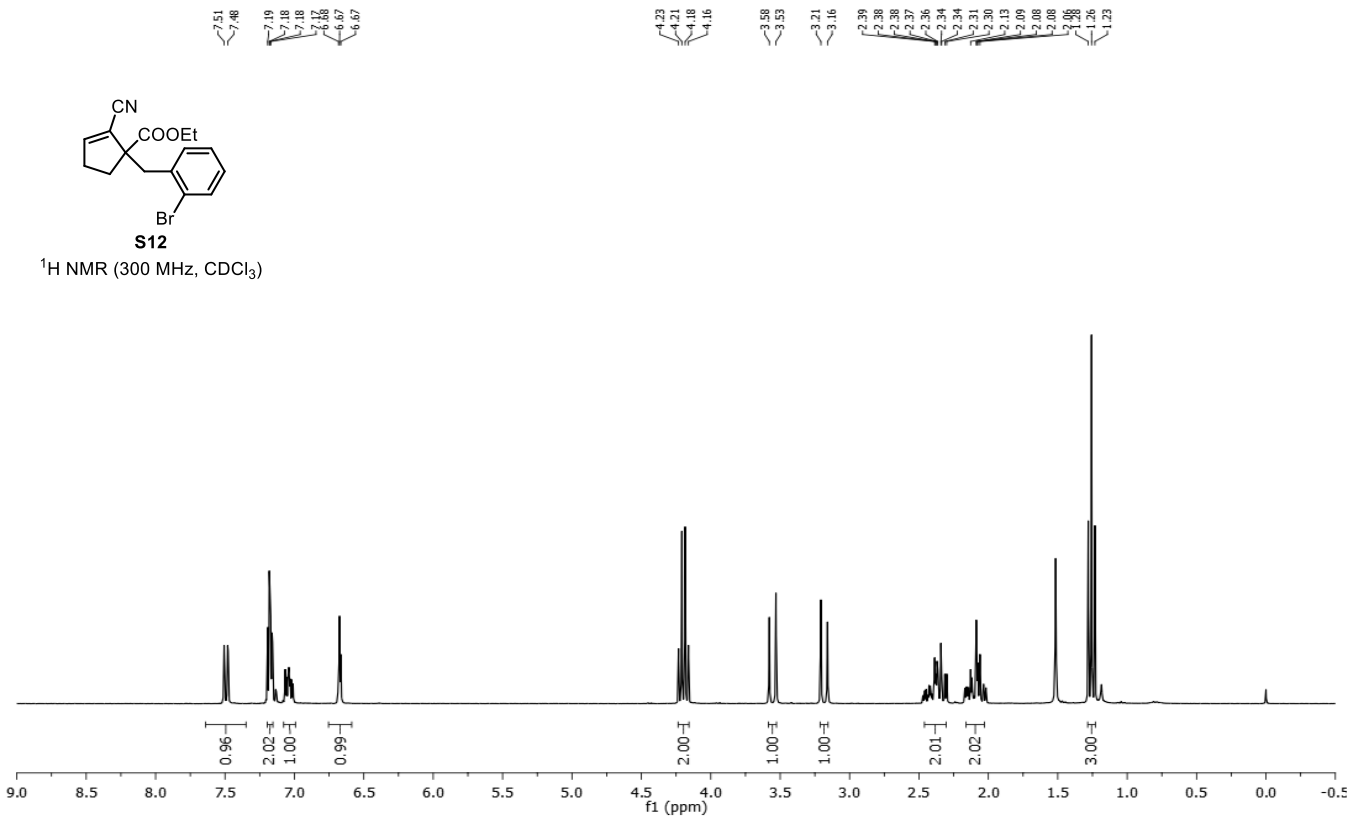


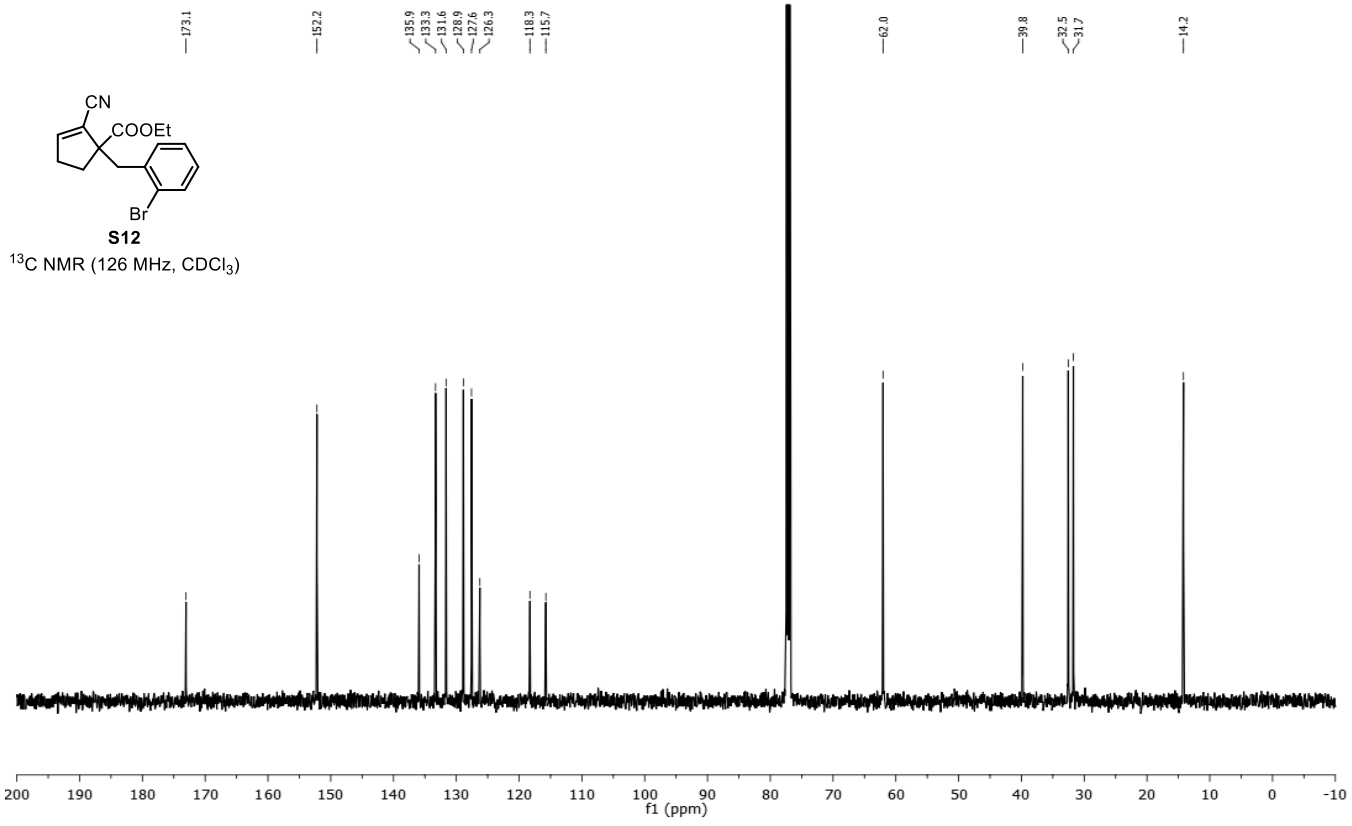
Ethyl 1-(2-Bromobenzyl)-2-cyano-2-hydroxycyclopentane-1-carboxylate (S11):



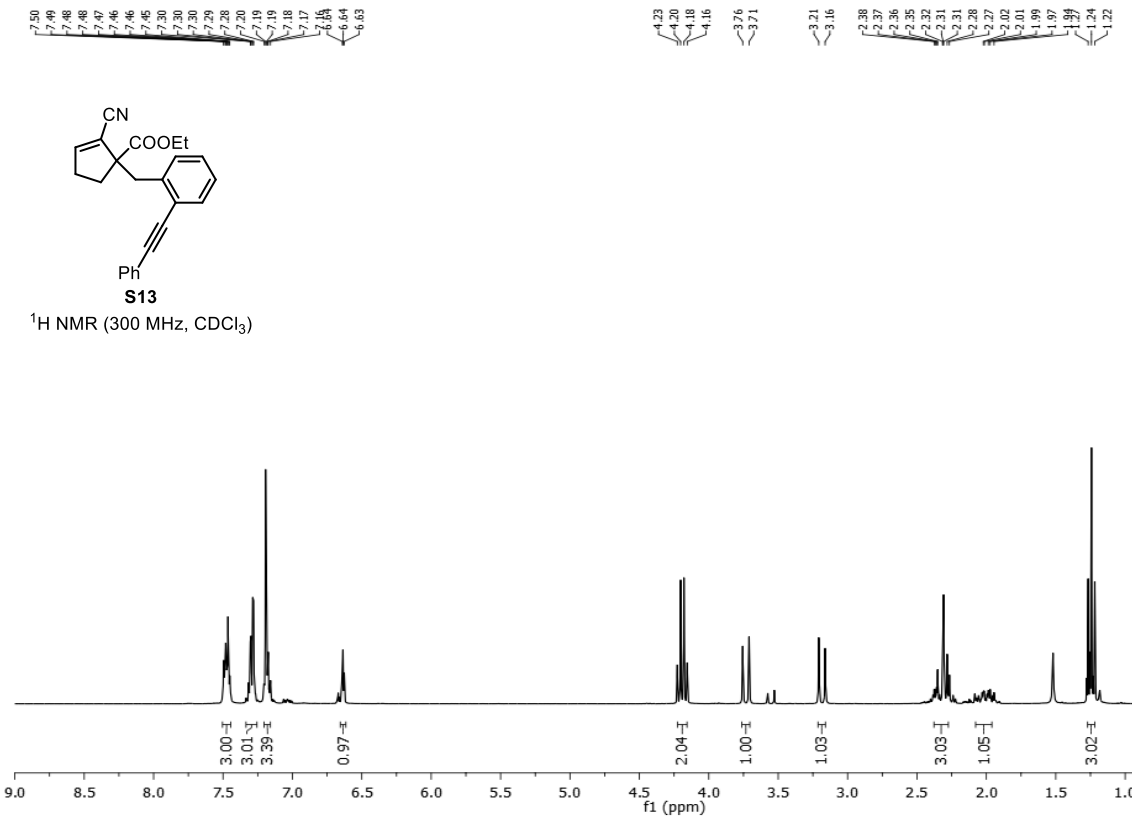


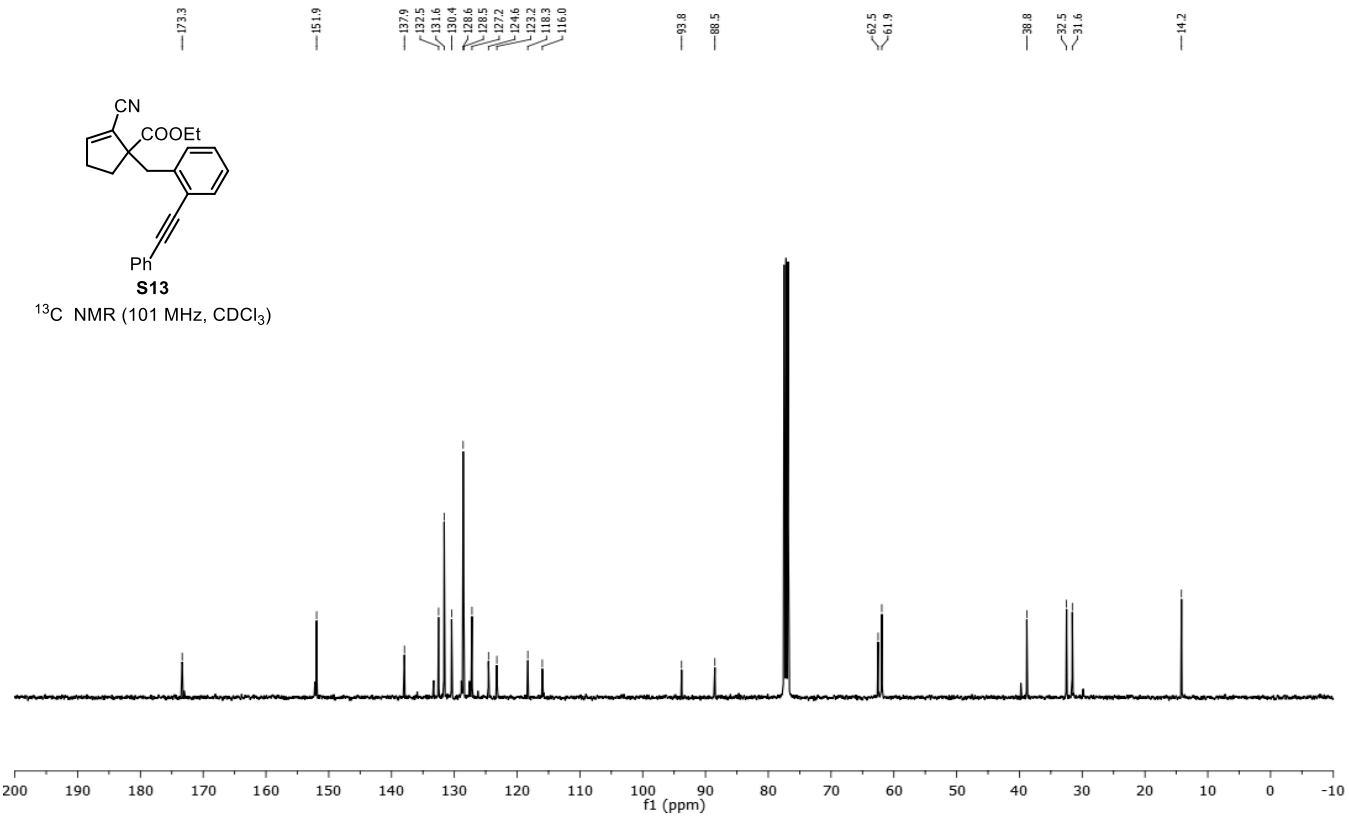
Ethyl 1-(2-Bromobenzyl)-2-cyanocyclopent-2-ene-1-carboxylate (S12):



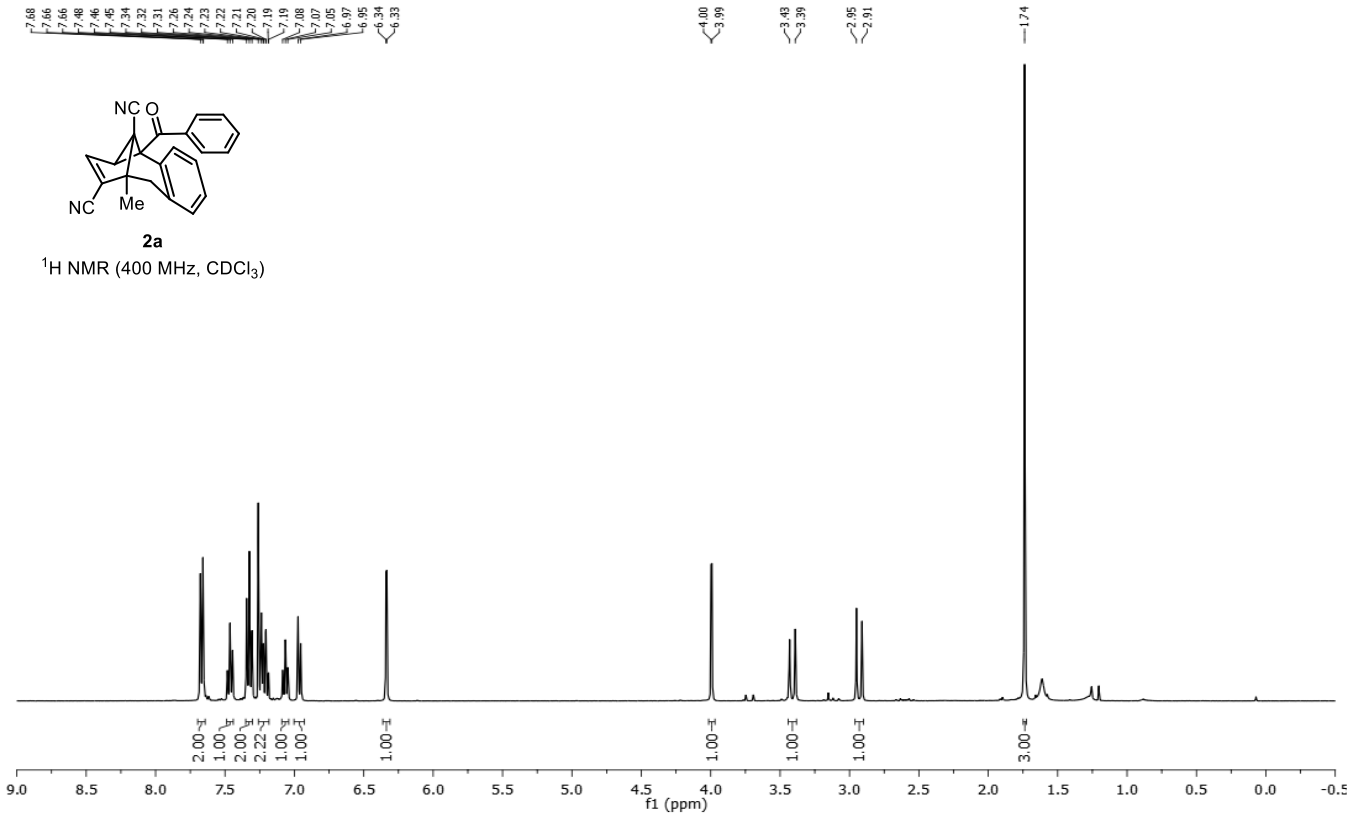


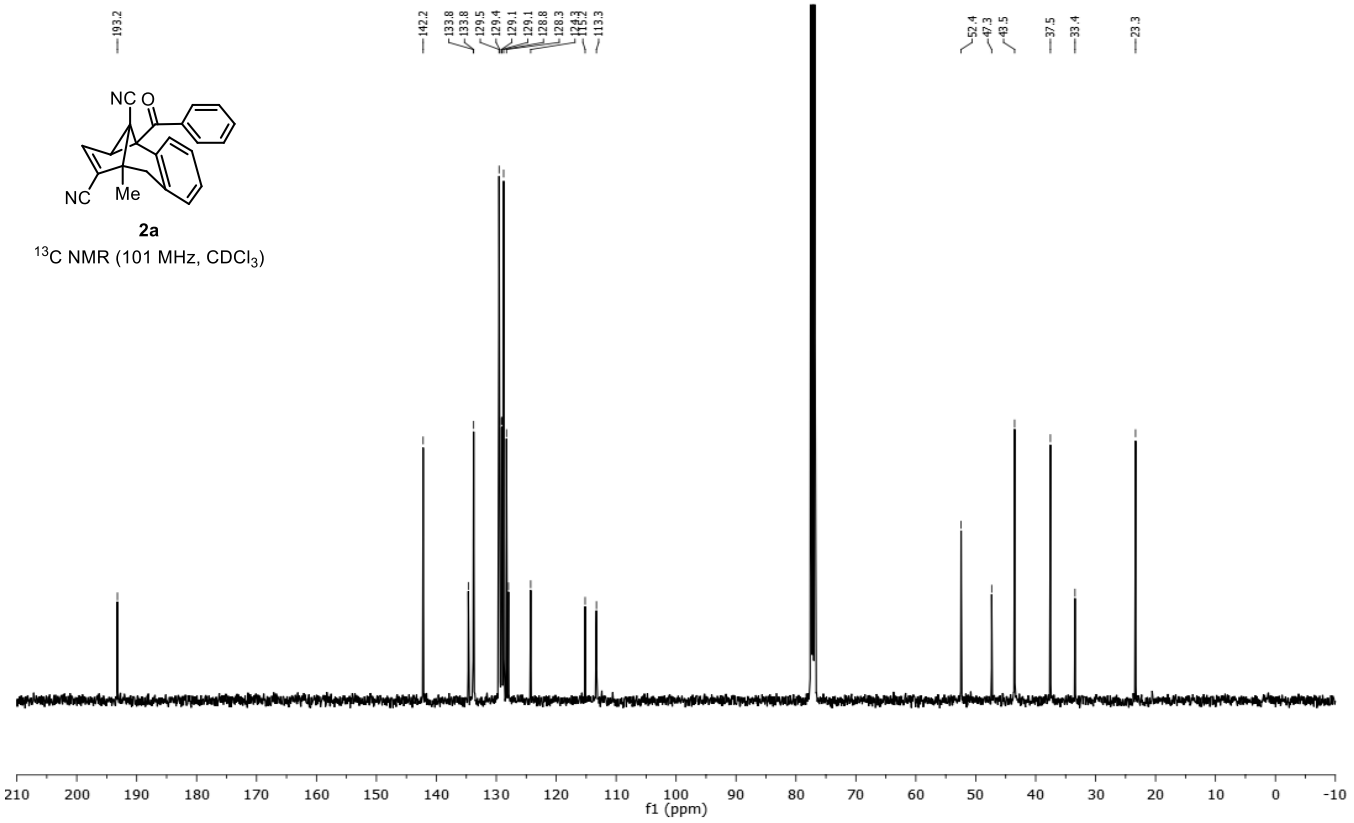
Ethyl 2-cyano-1-(2-(phenylethynyl)benzyl)cyclopent-2-ene-1-carboxylate (S13):



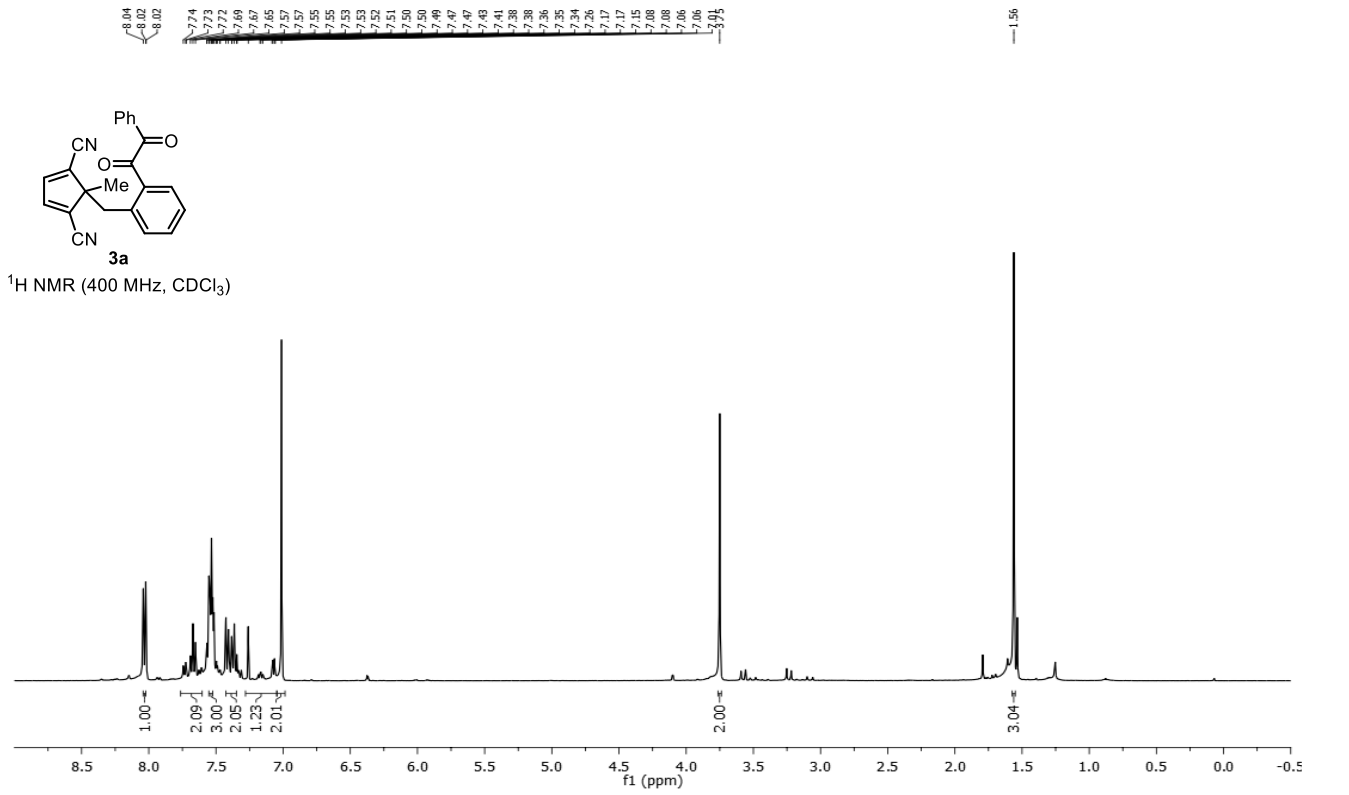


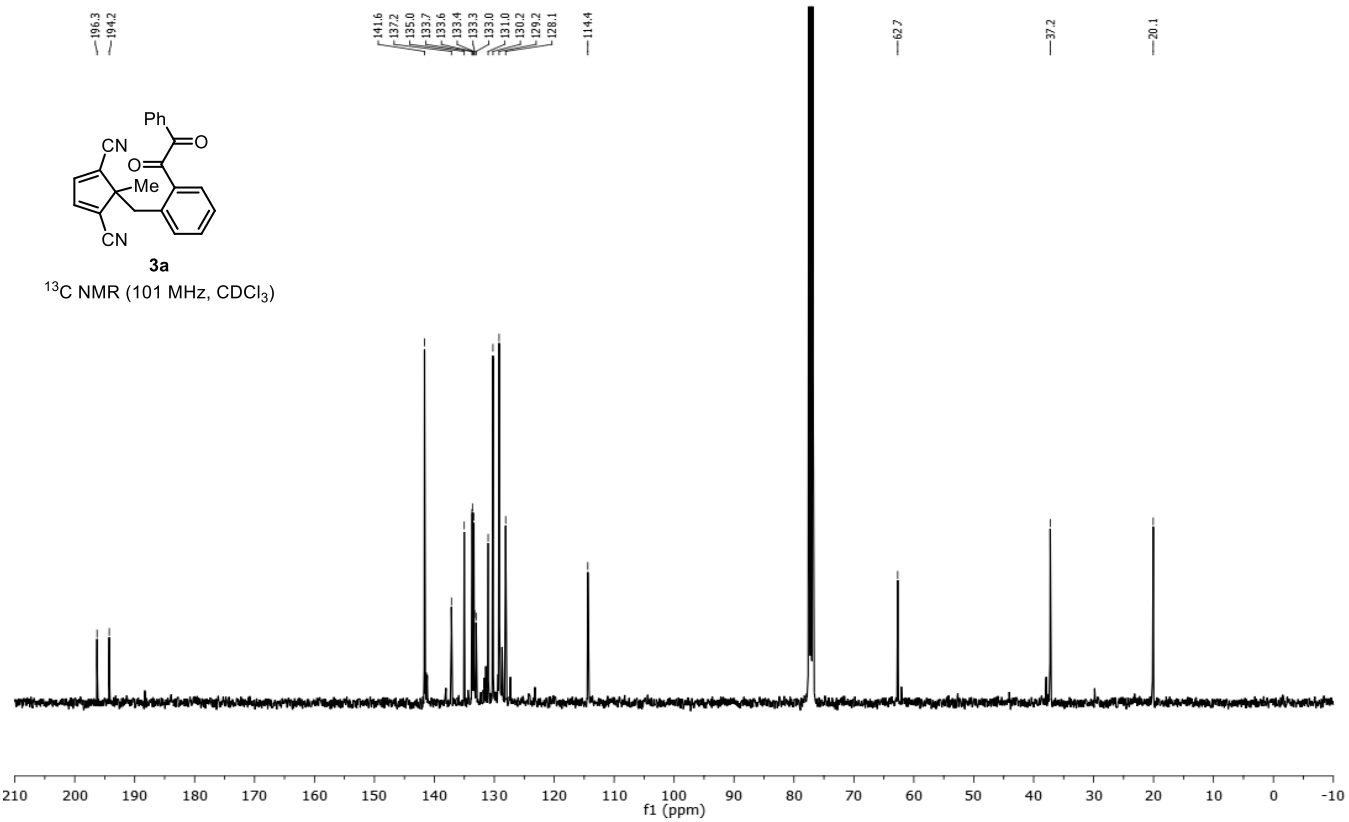
7b-Benzoyl-2a1-isocyano-2a-methyl-2a,2a1,7b,7c-tetrahydro-3*H* benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2a):



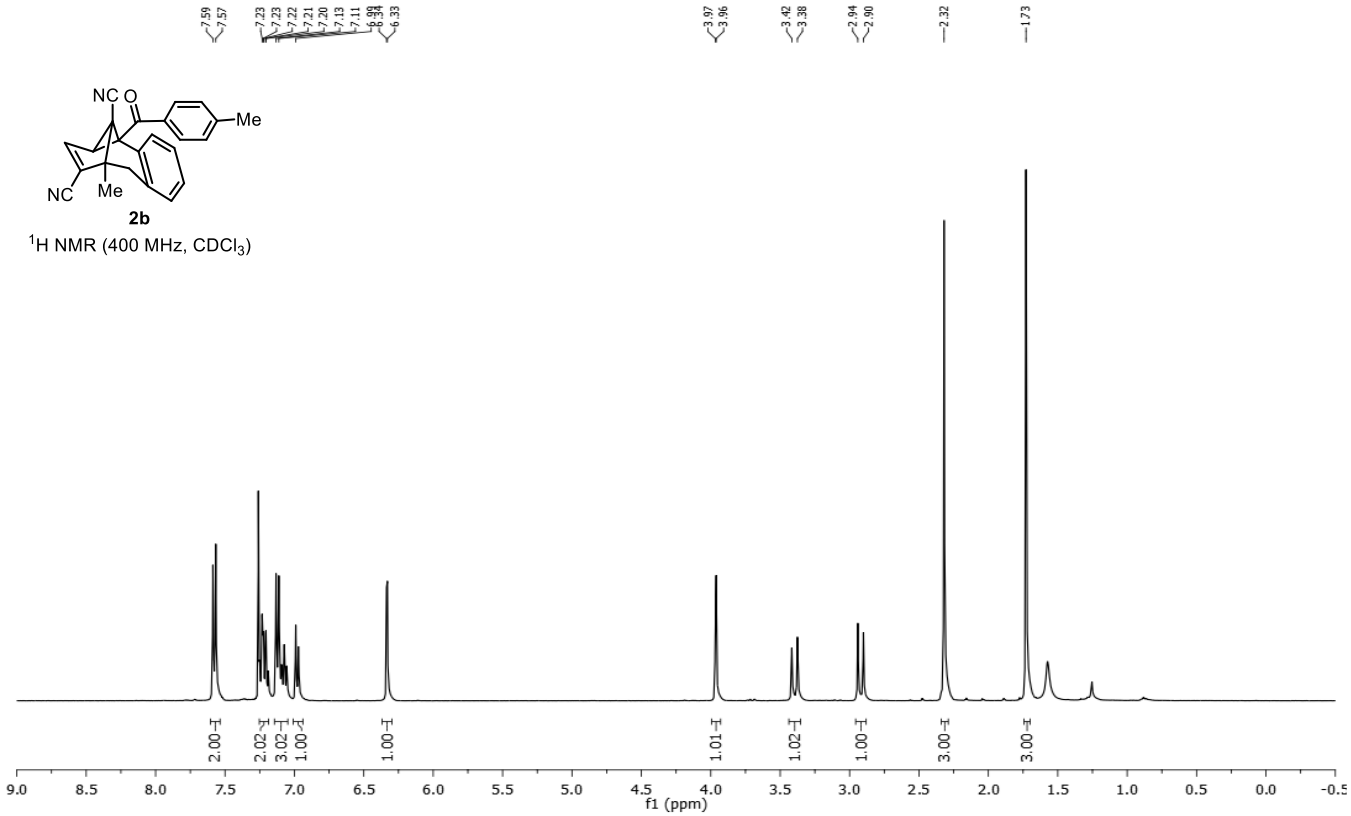


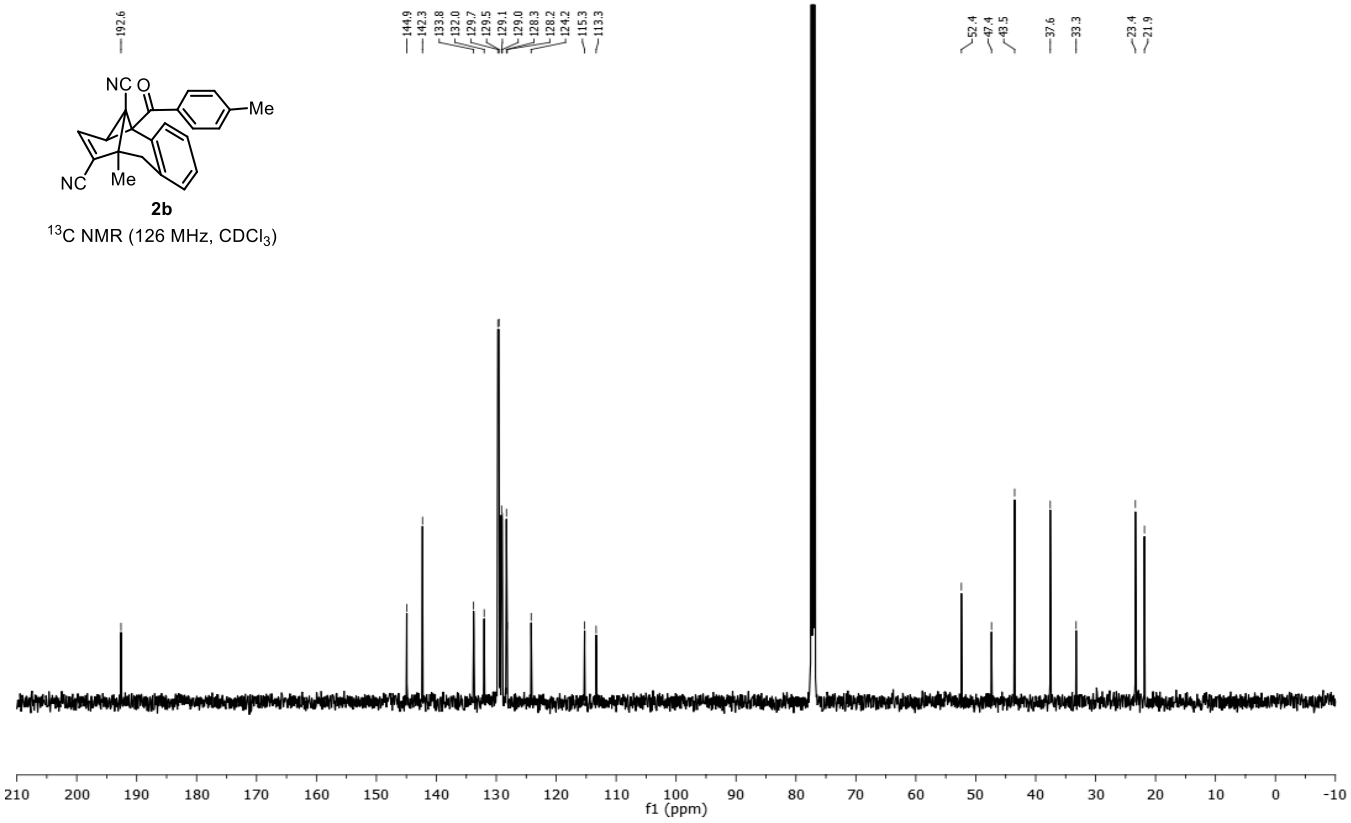
2-Methyl-2-(2-(2-oxo-2-phenylacetyl)benzyl)cyclopenta-3,5-diene-1,3-dicarbonitrile (3a):



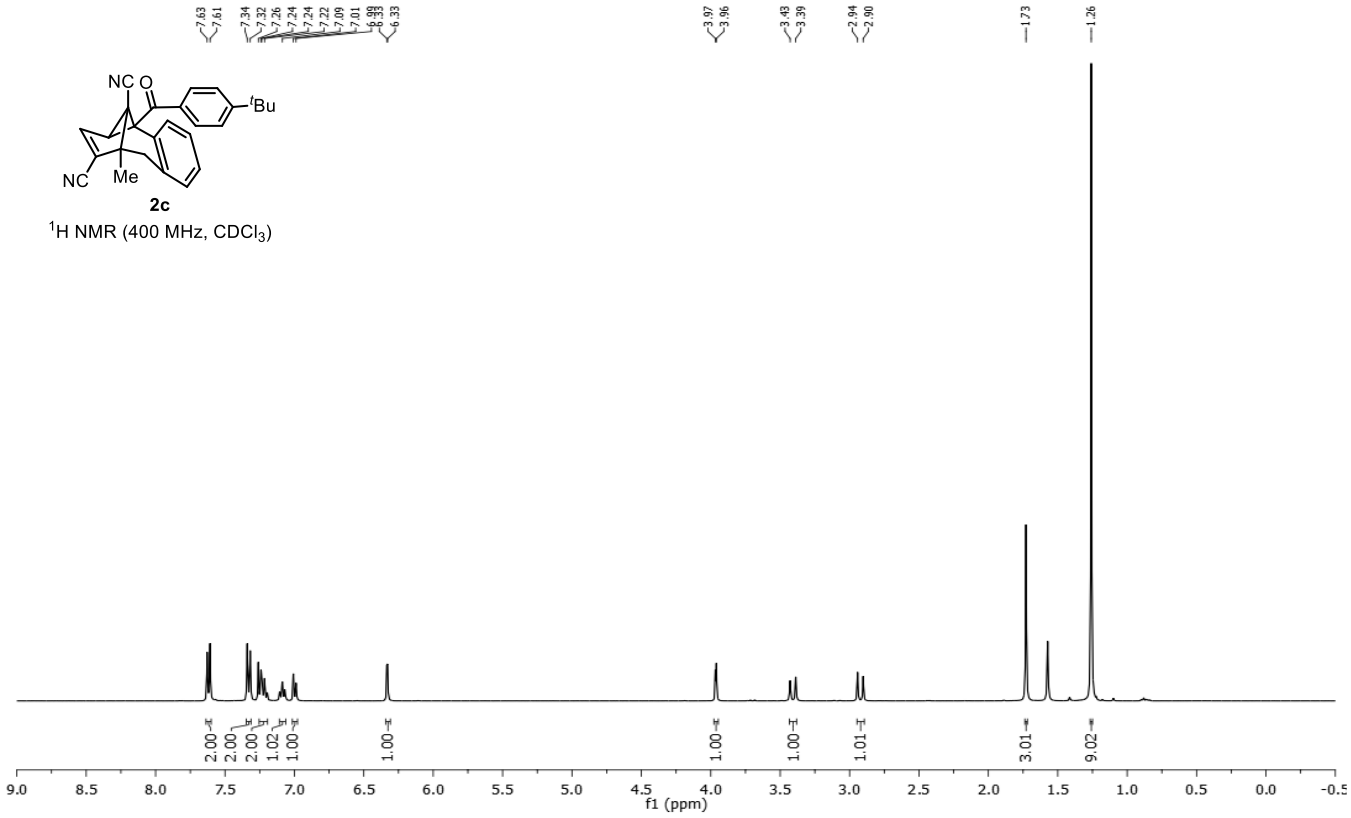


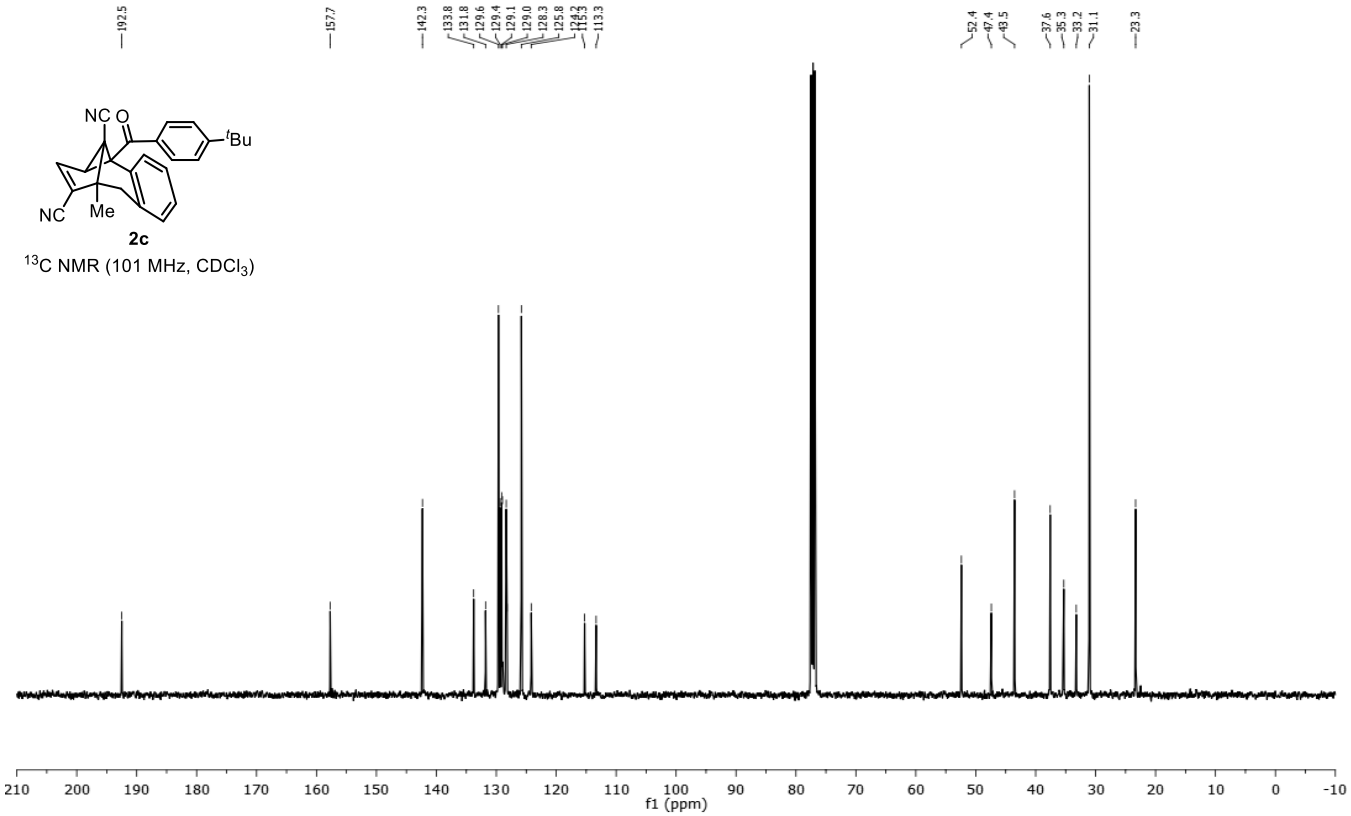
2a^1-Isocyano-2a-methyl-7b-(4-methylbenzoyl)-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile(2b):



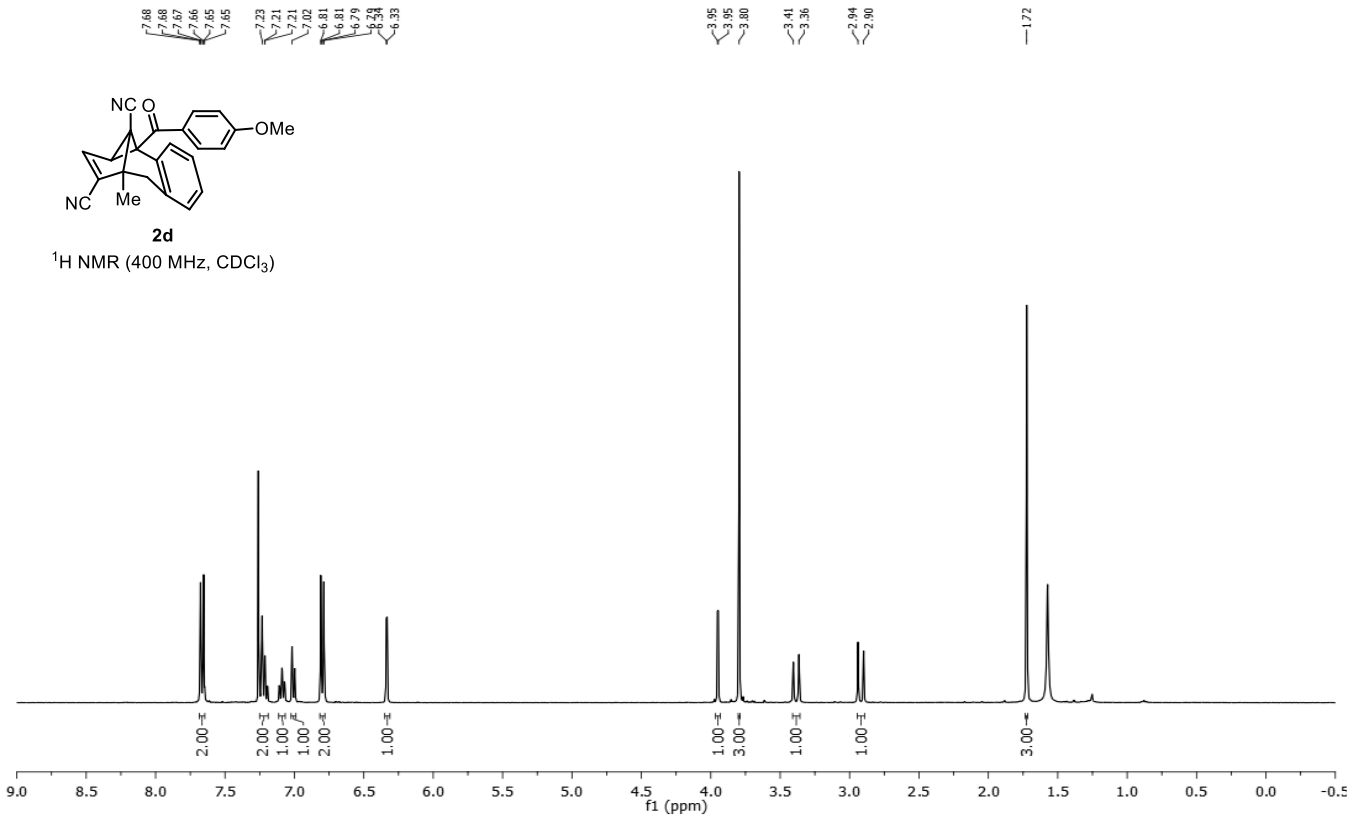


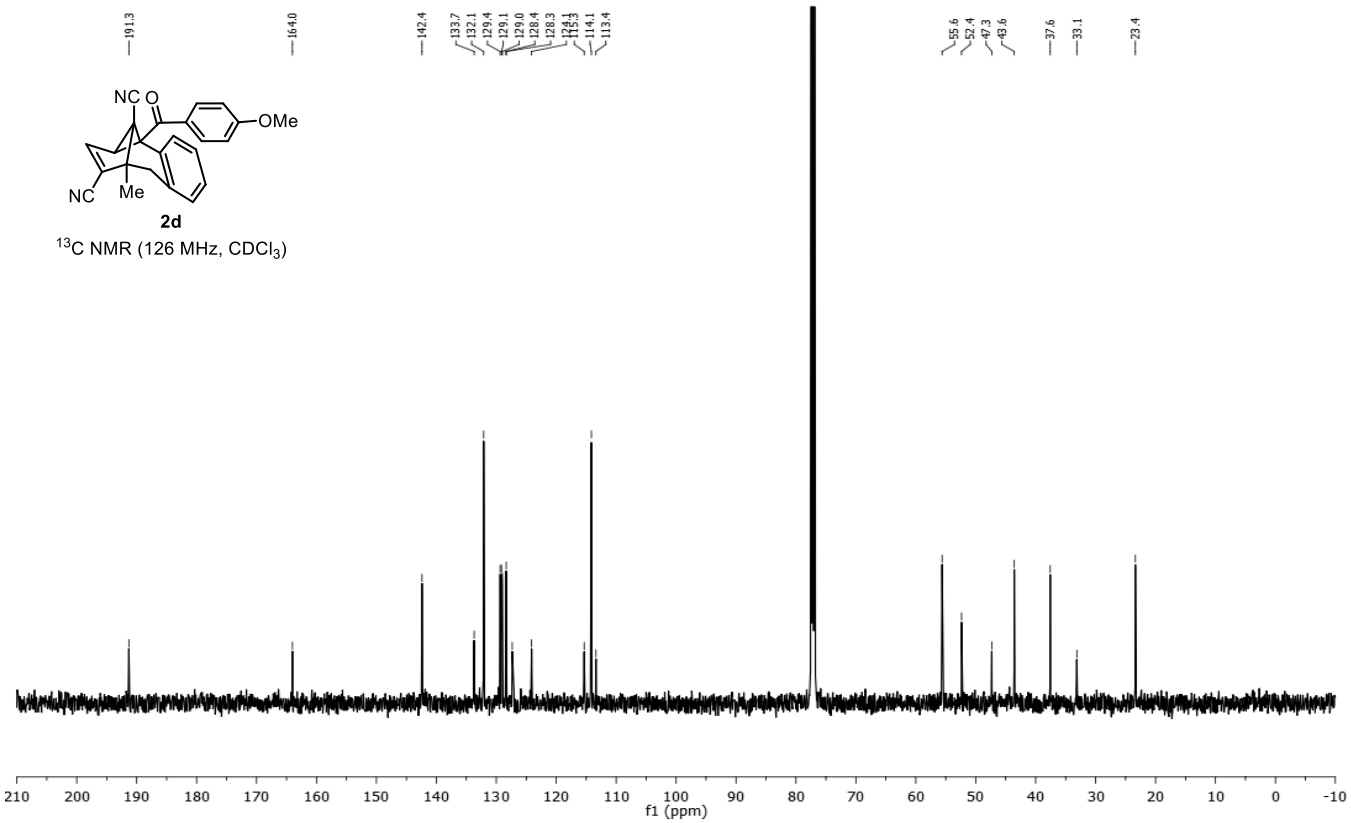
4-(Tert-butyl)benzoyl)-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2c):



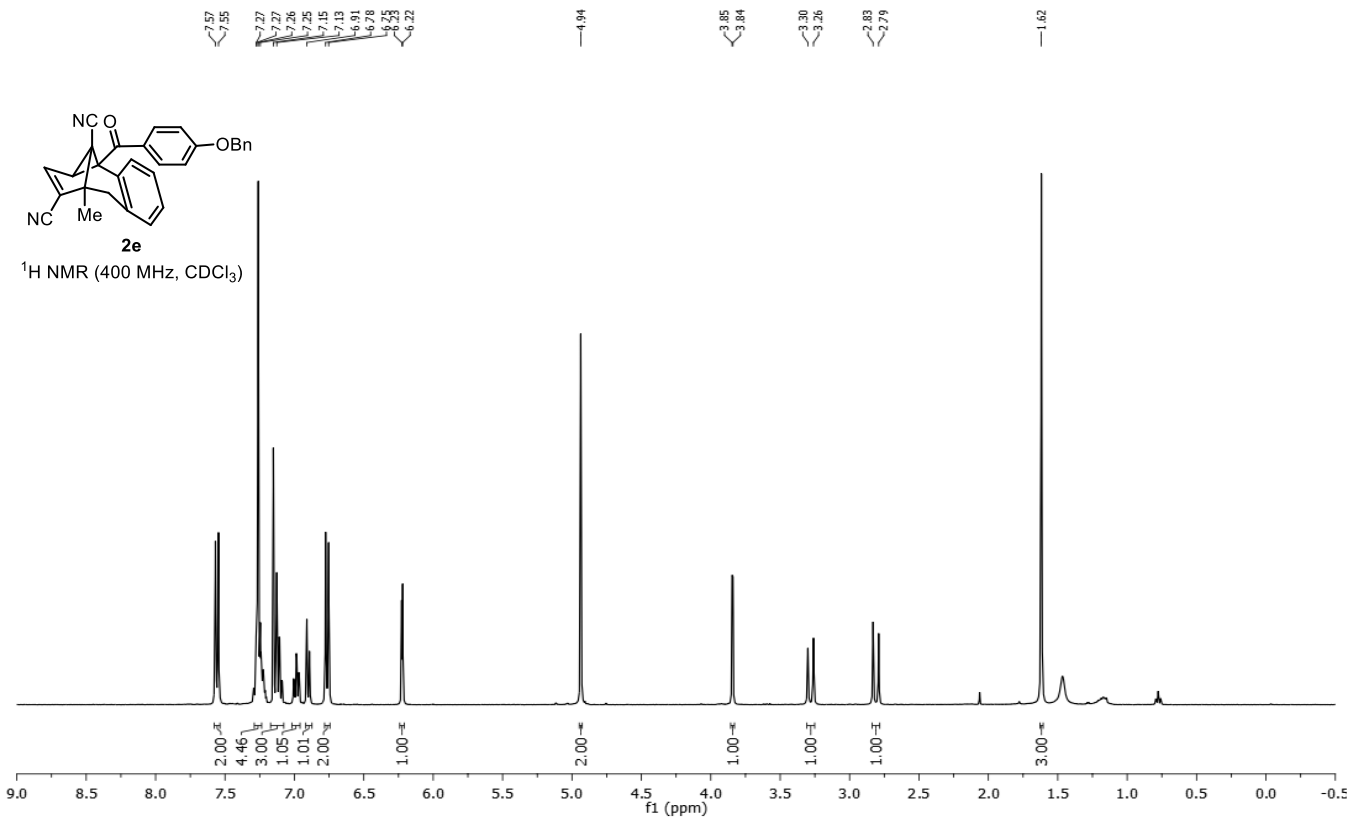


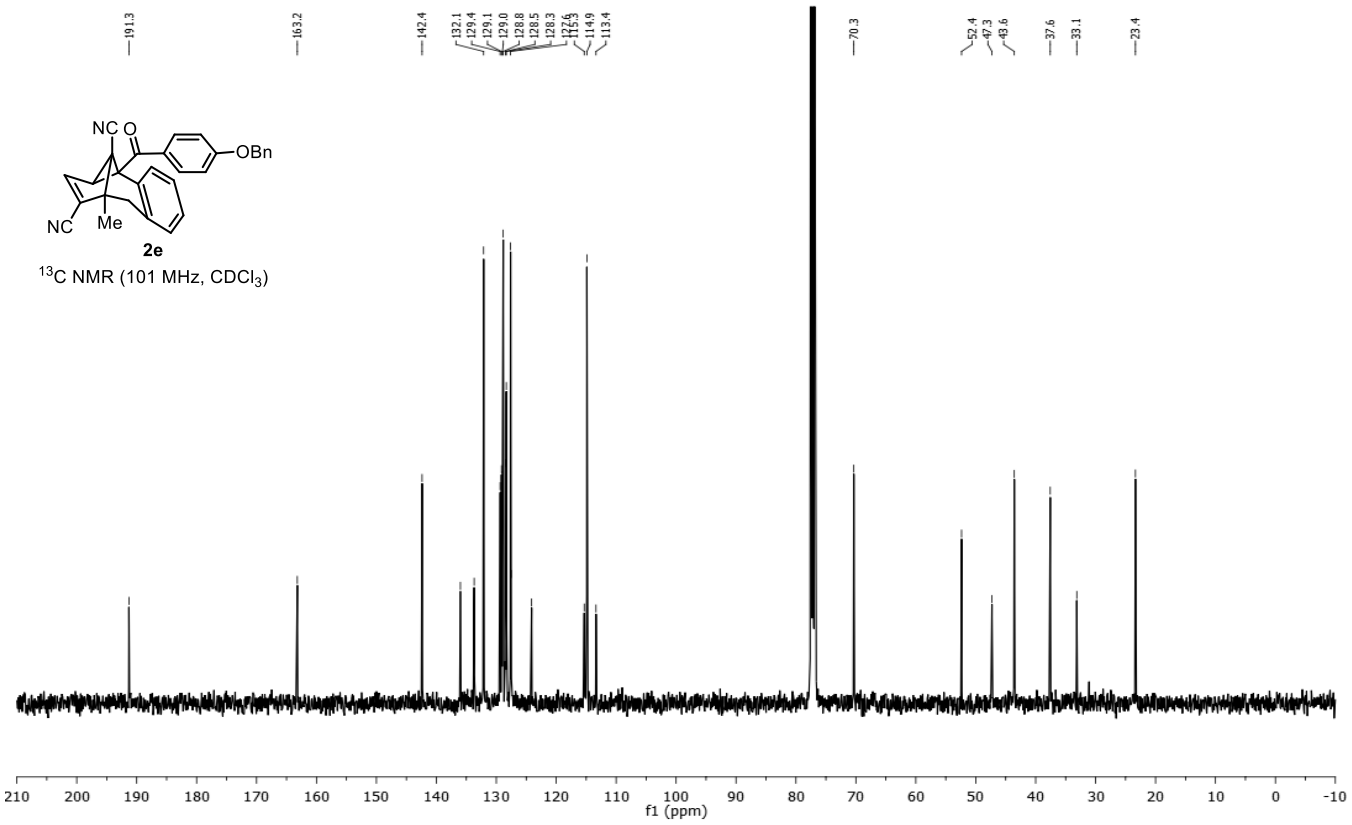
2a^1-Isocyano-7b-(4-methoxybenzoyl)-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2d):



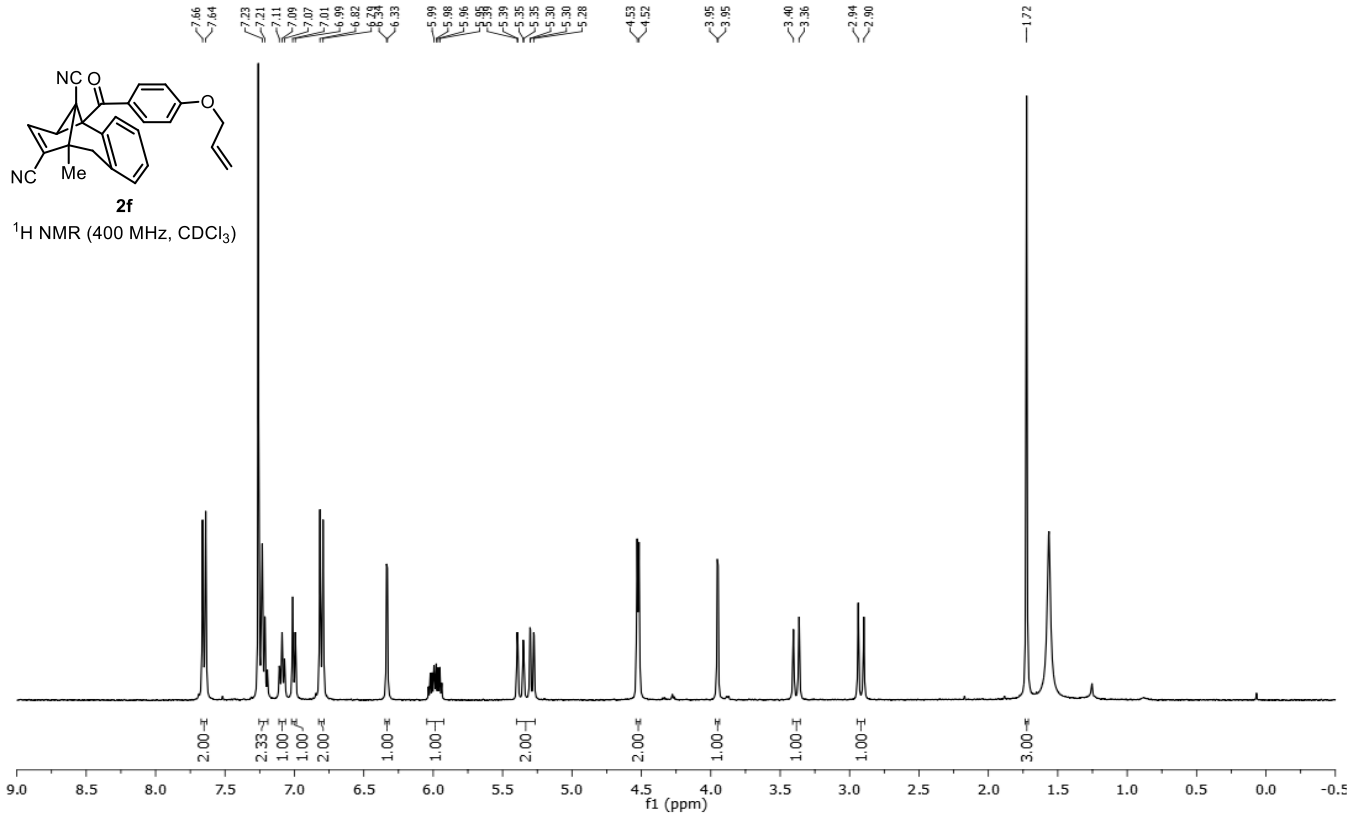


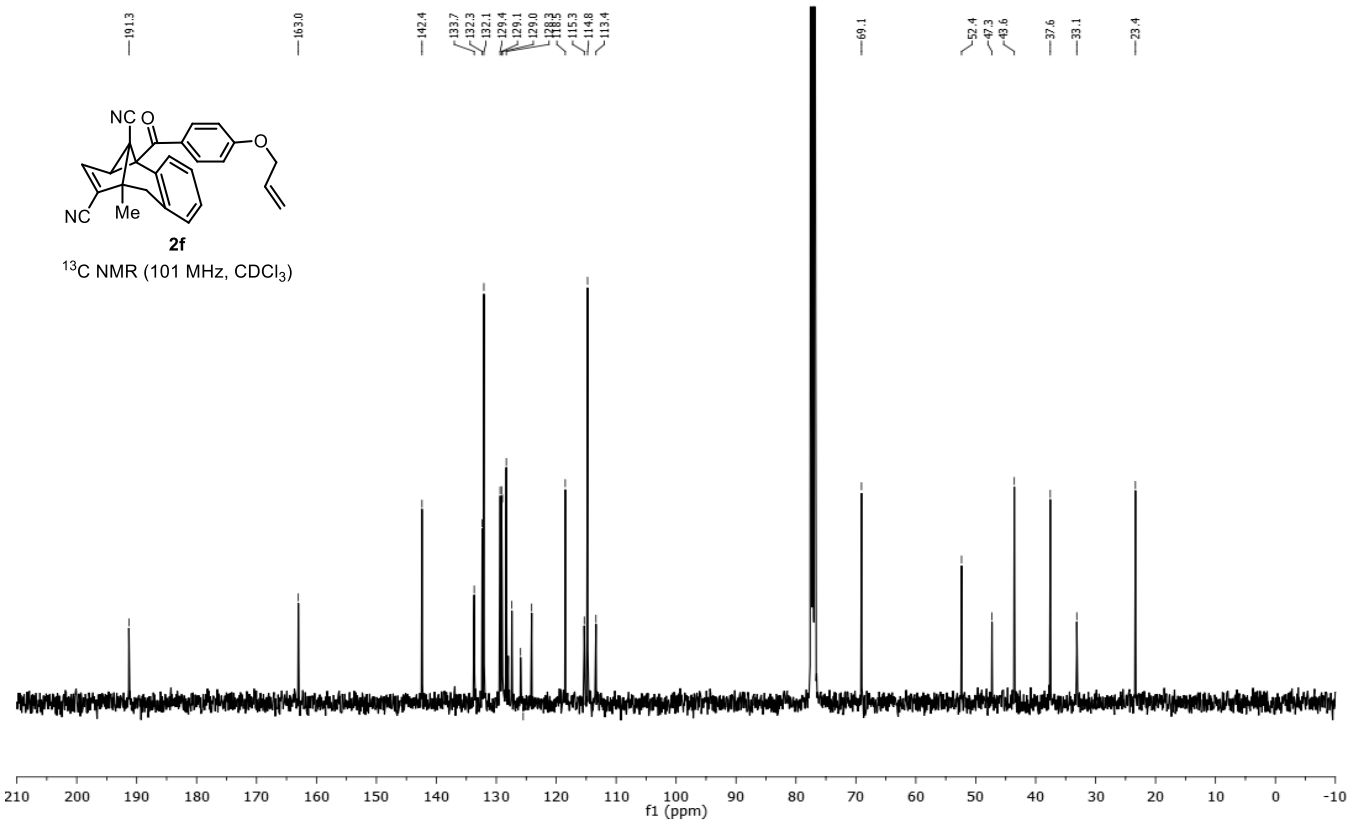
4-(Benzyloxy)benzoyl)-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2e):



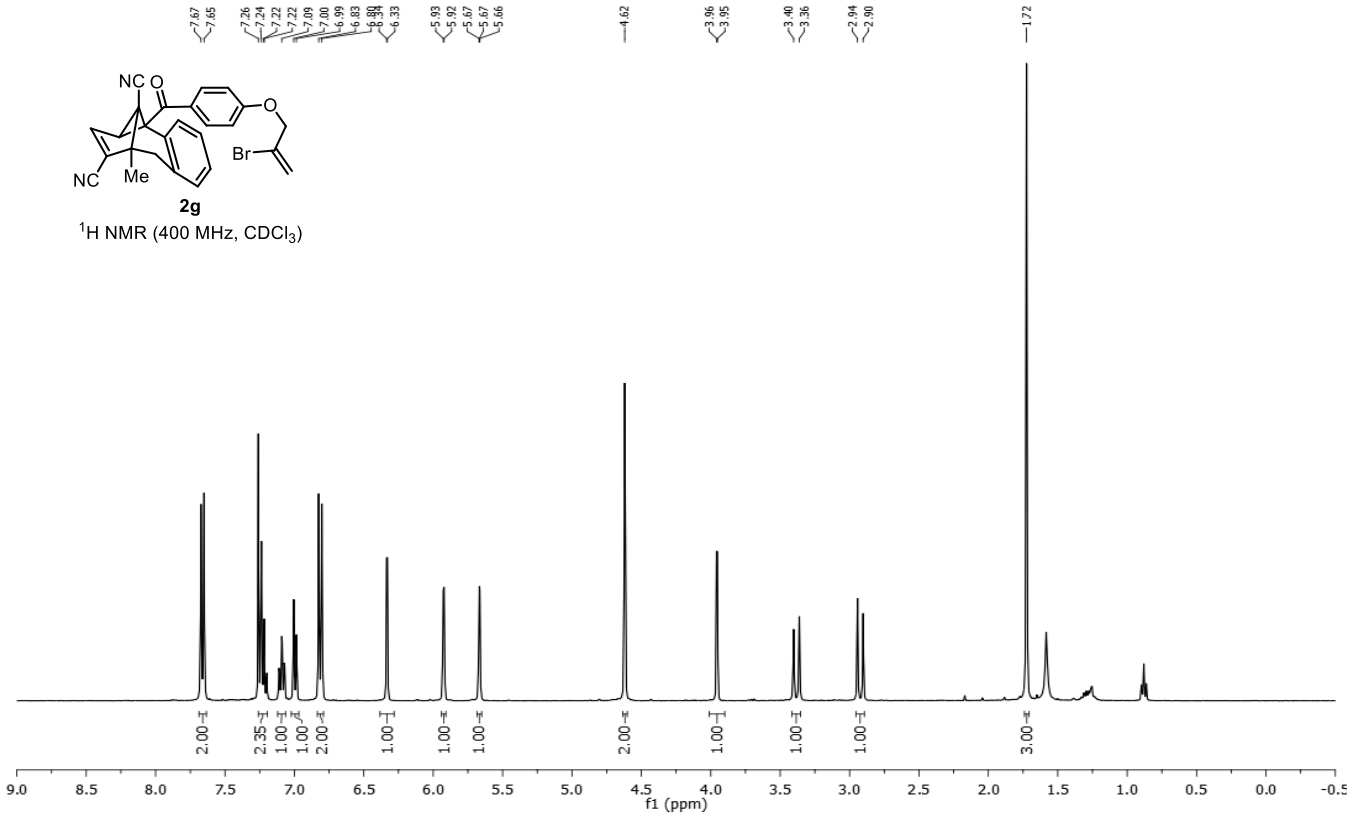


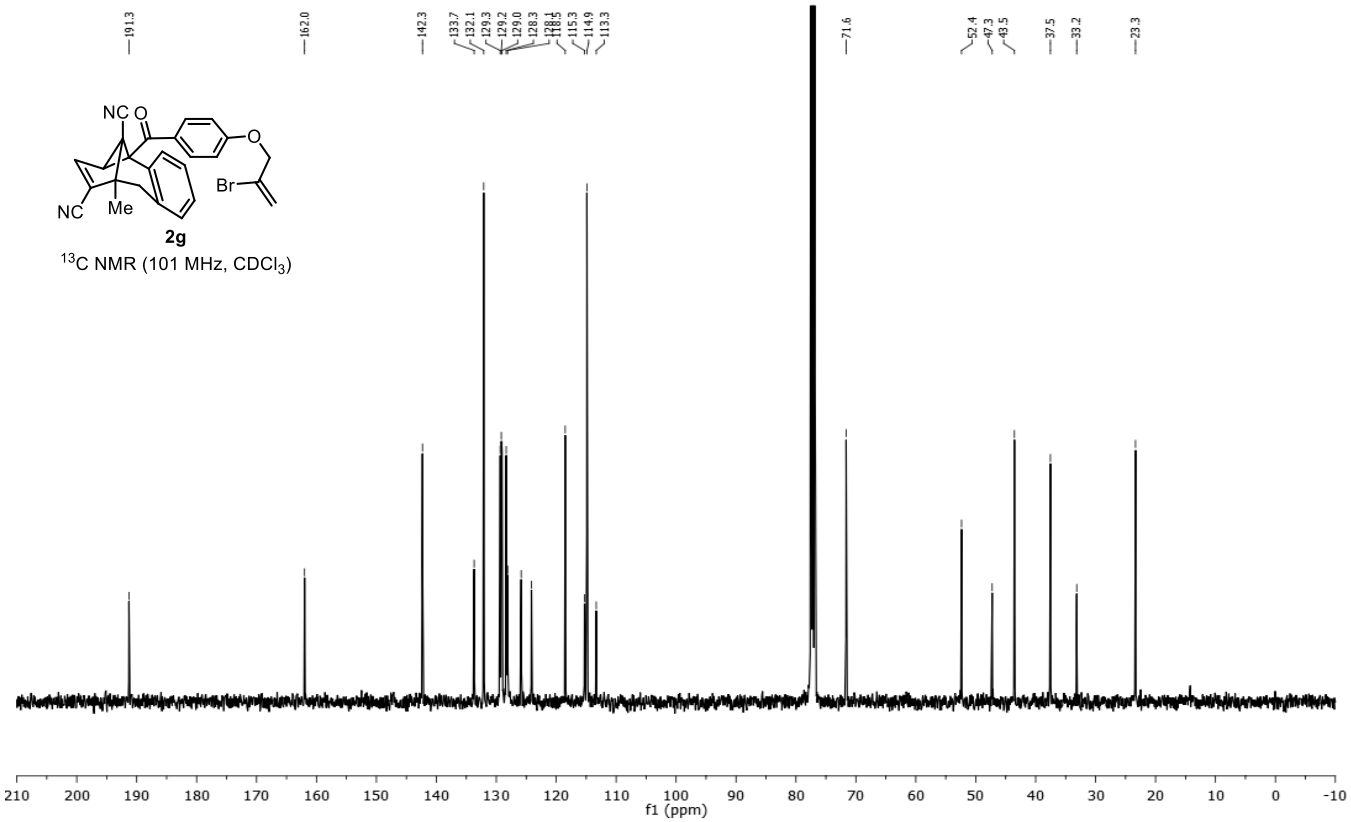
4-(Allyloxy)benzoyl)-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2f):



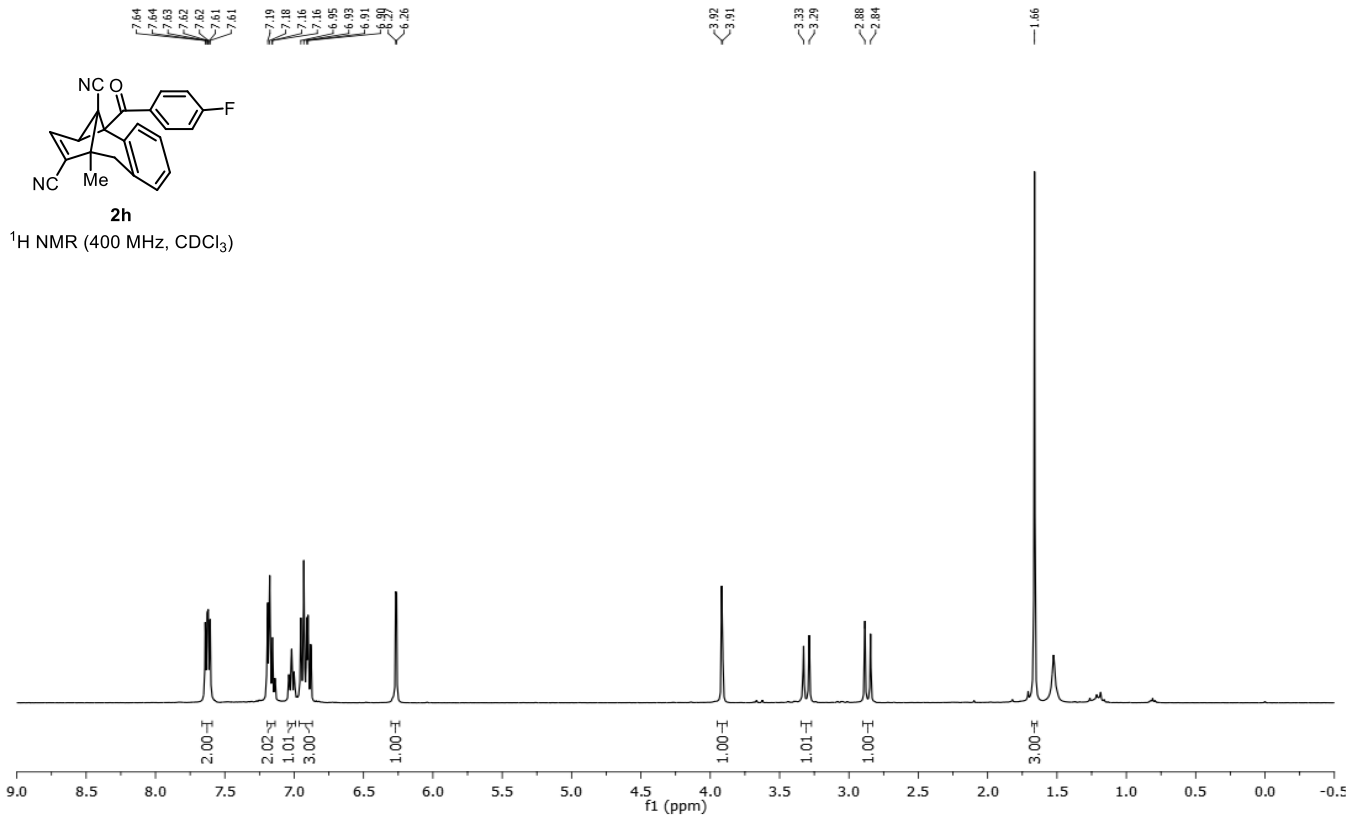


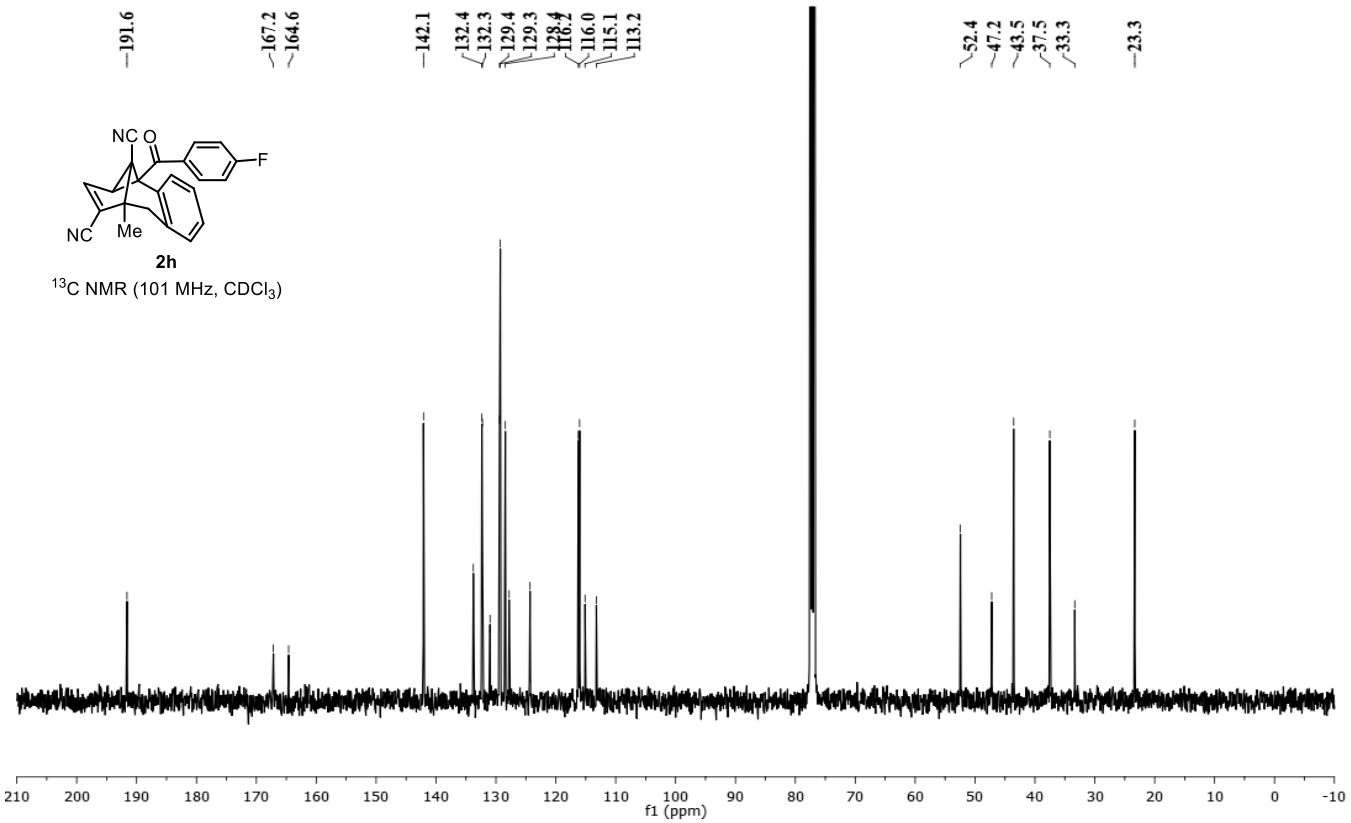
4-((2-Bromoallyl)oxy)benzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2g):

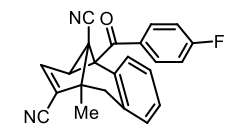




4-Fluorobenzoyl-2a[1]-isocyano-2a-methyl-2a,2a[1],7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2h):



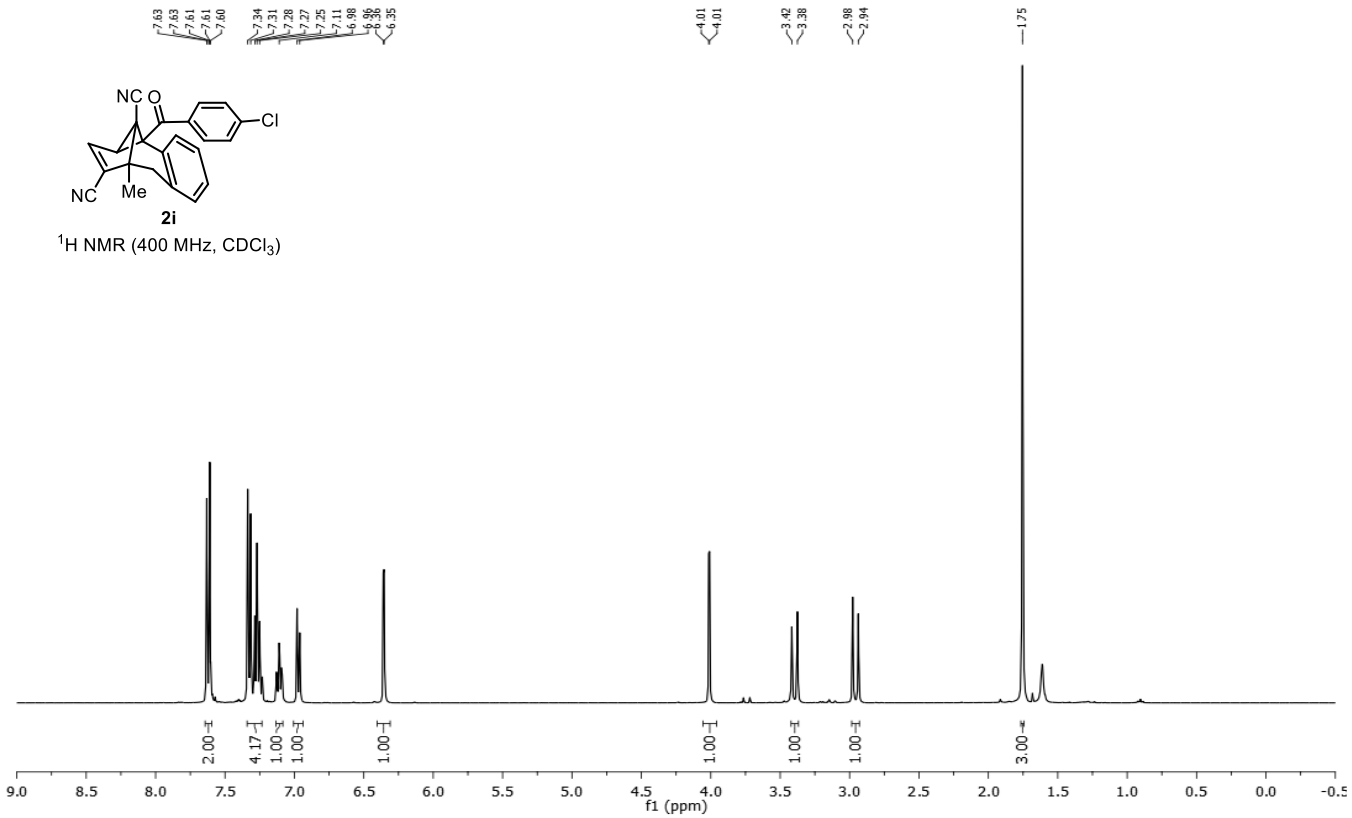


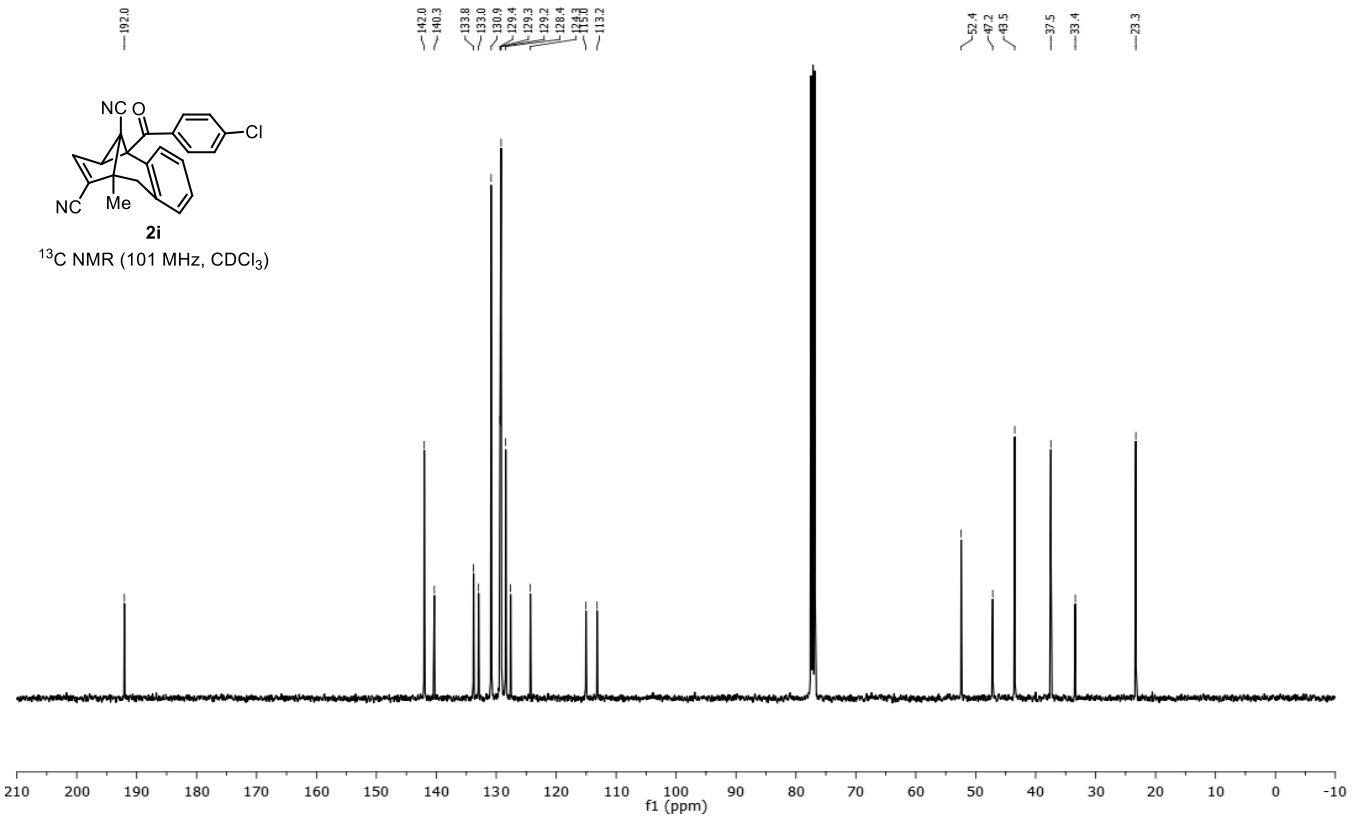


2h

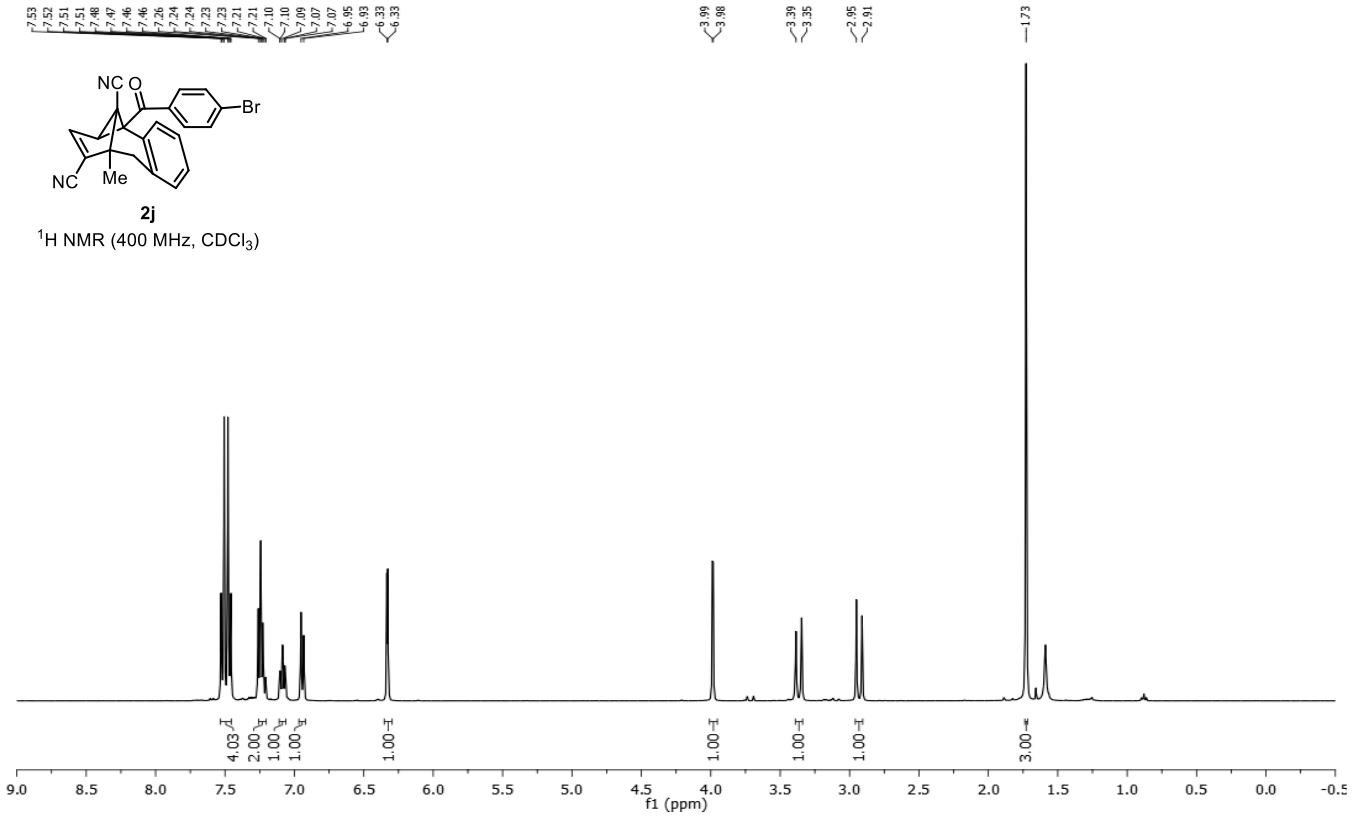
^{19}F NMR (376 MHz, $CDCl_3$)

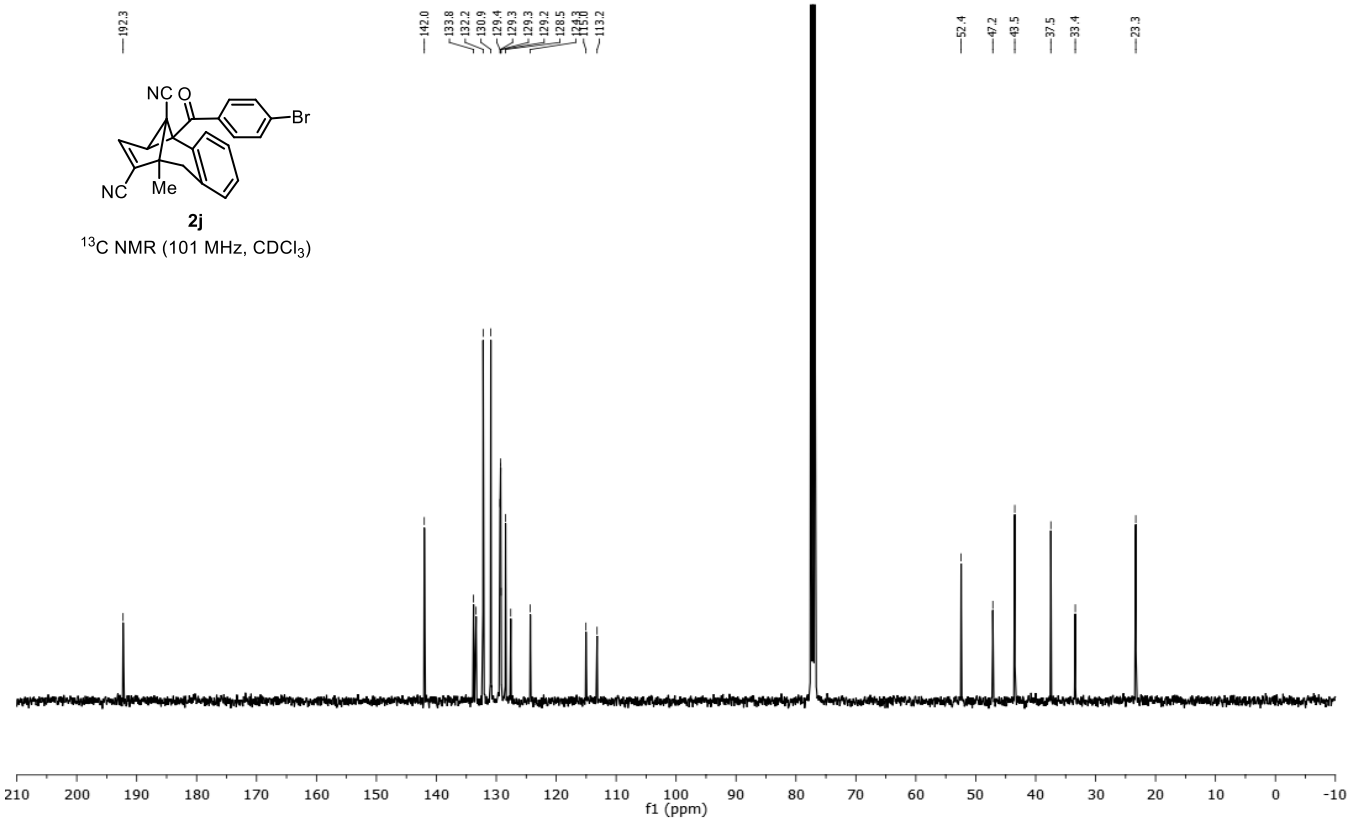
4-Chlorobenzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2i):



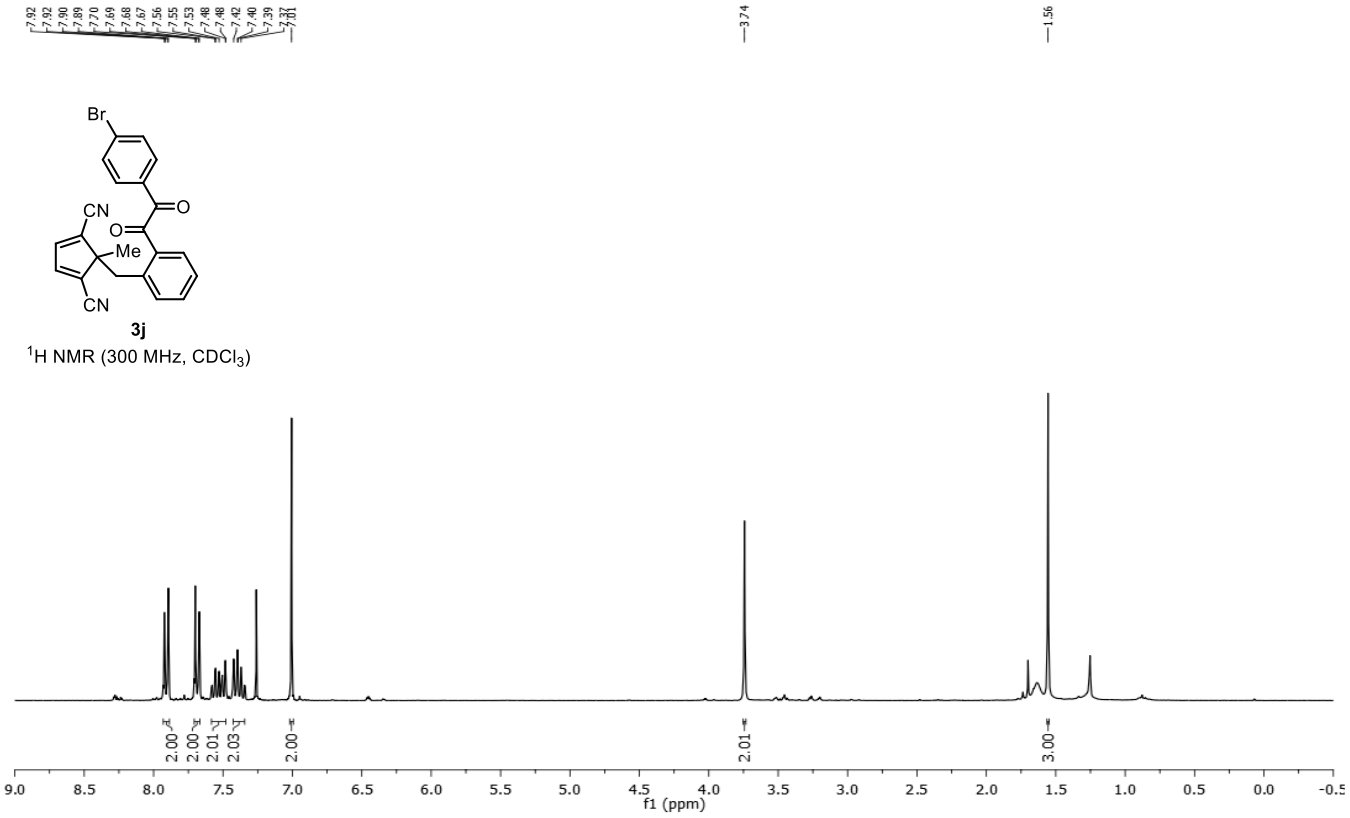


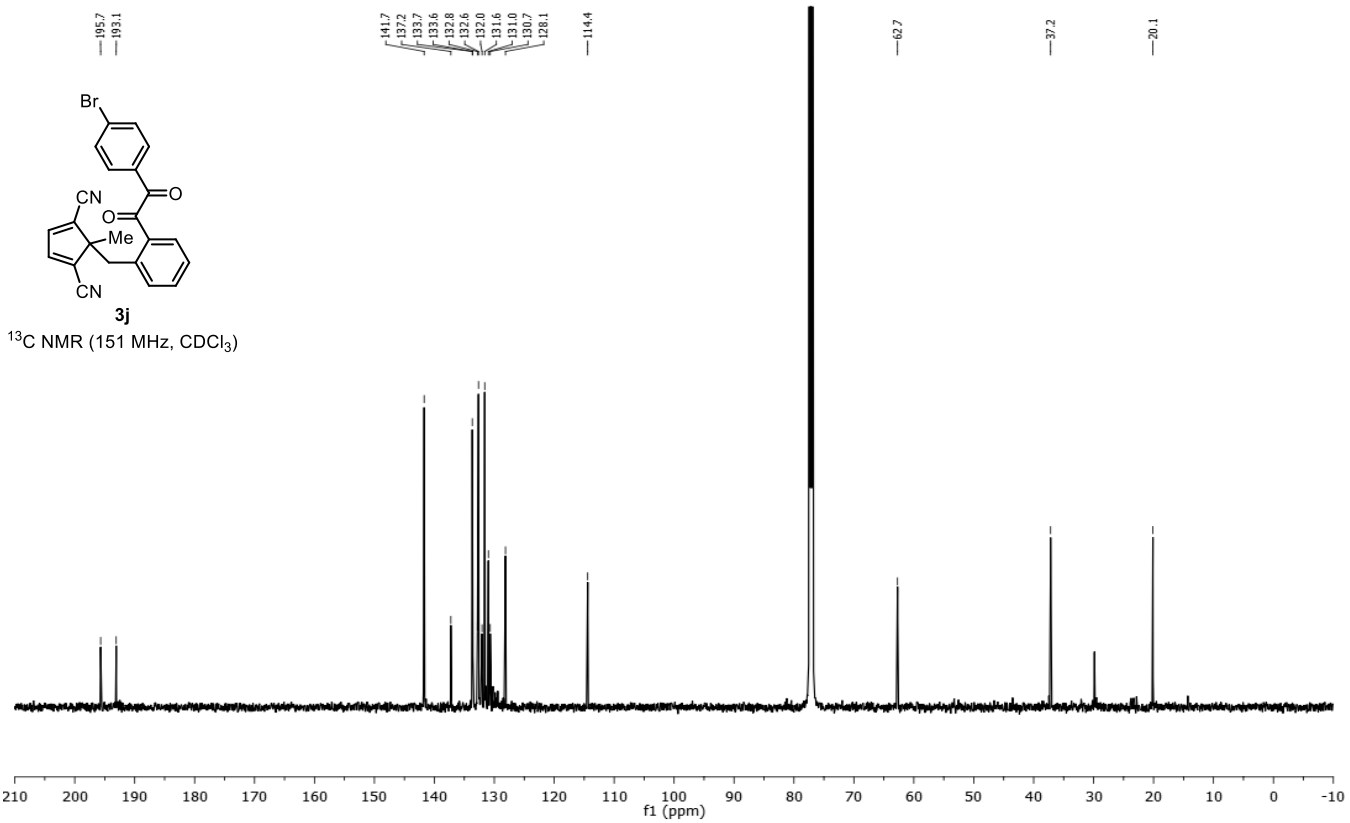
4-Bromobenzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2j):



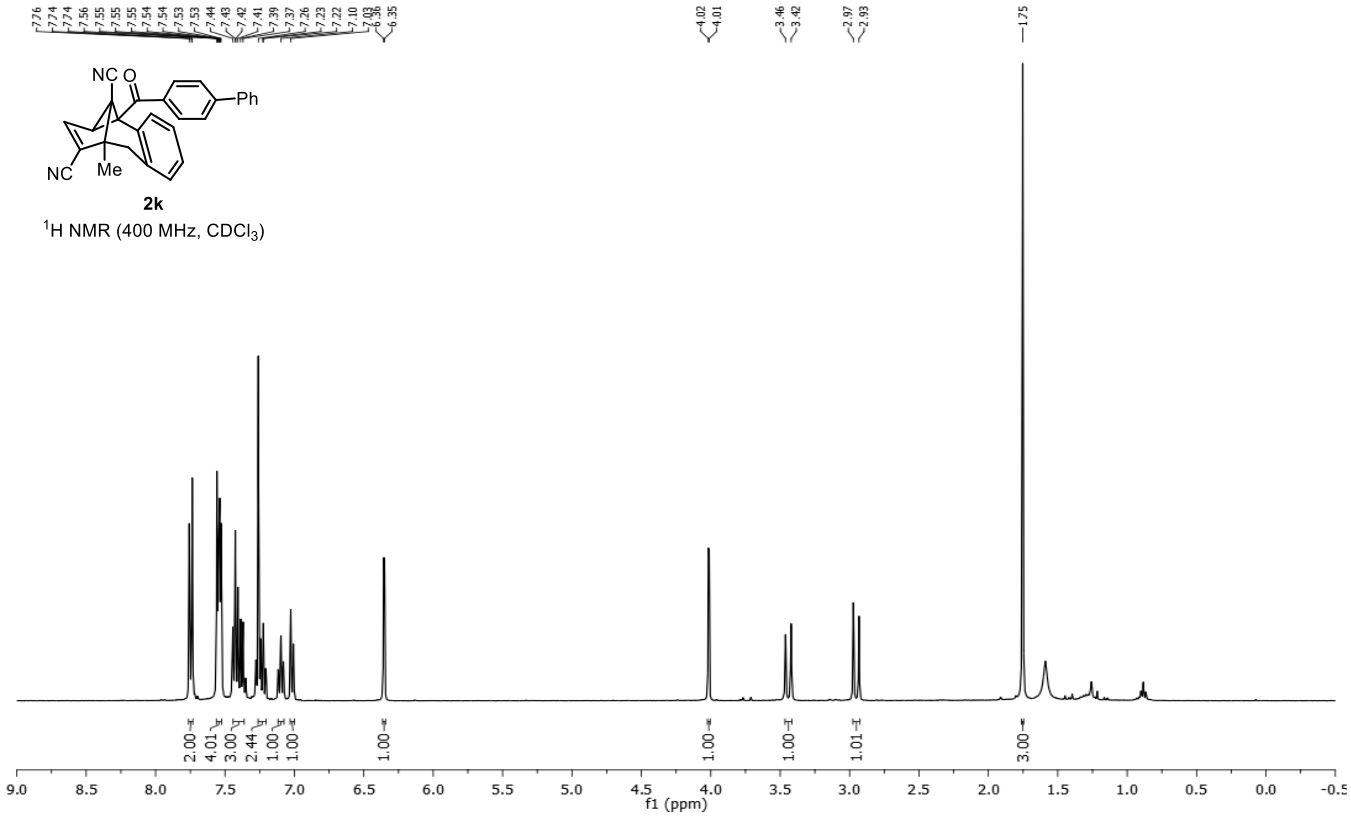


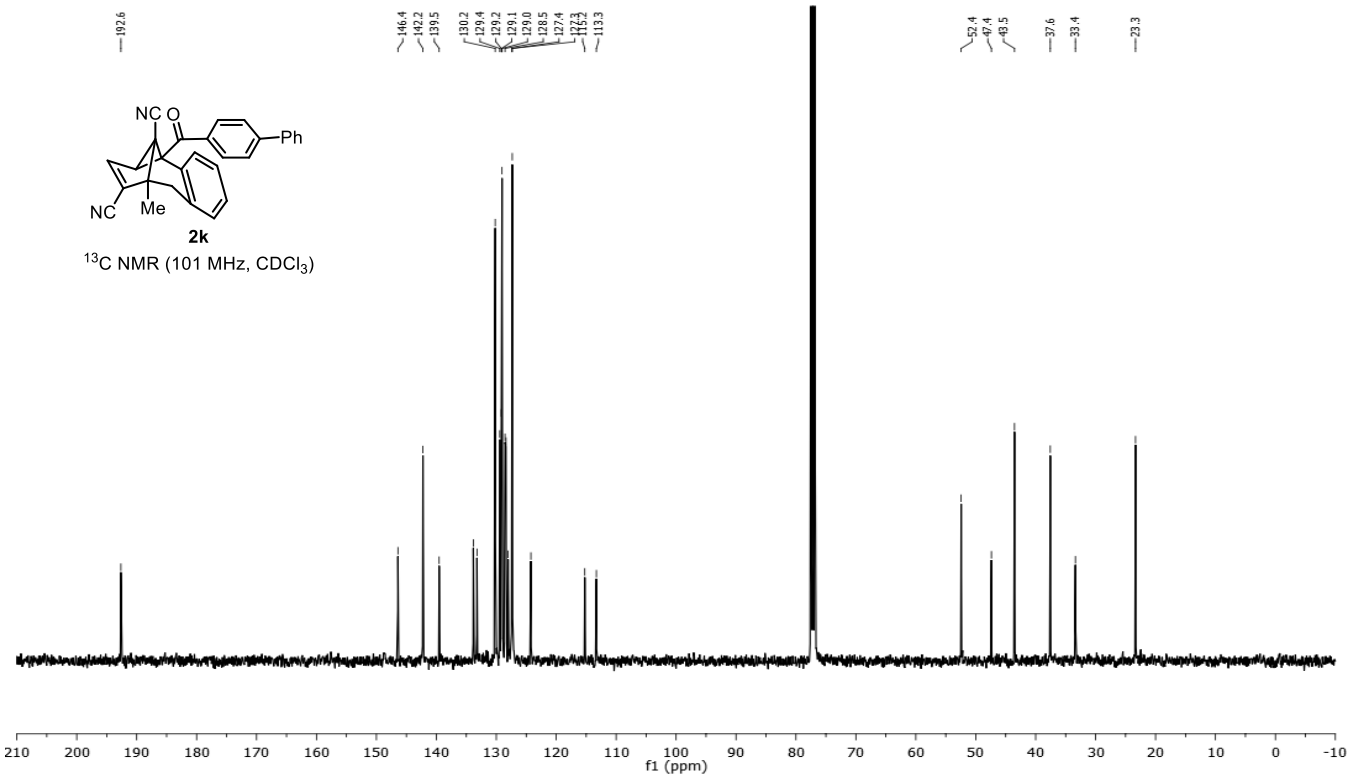
2-(2-(2-(4-Bromophenyl)-2-oxoacetyl)benzyl)-2-methylcyclopenta-3,5-diene-1,3-dicarbonitrile (3j):



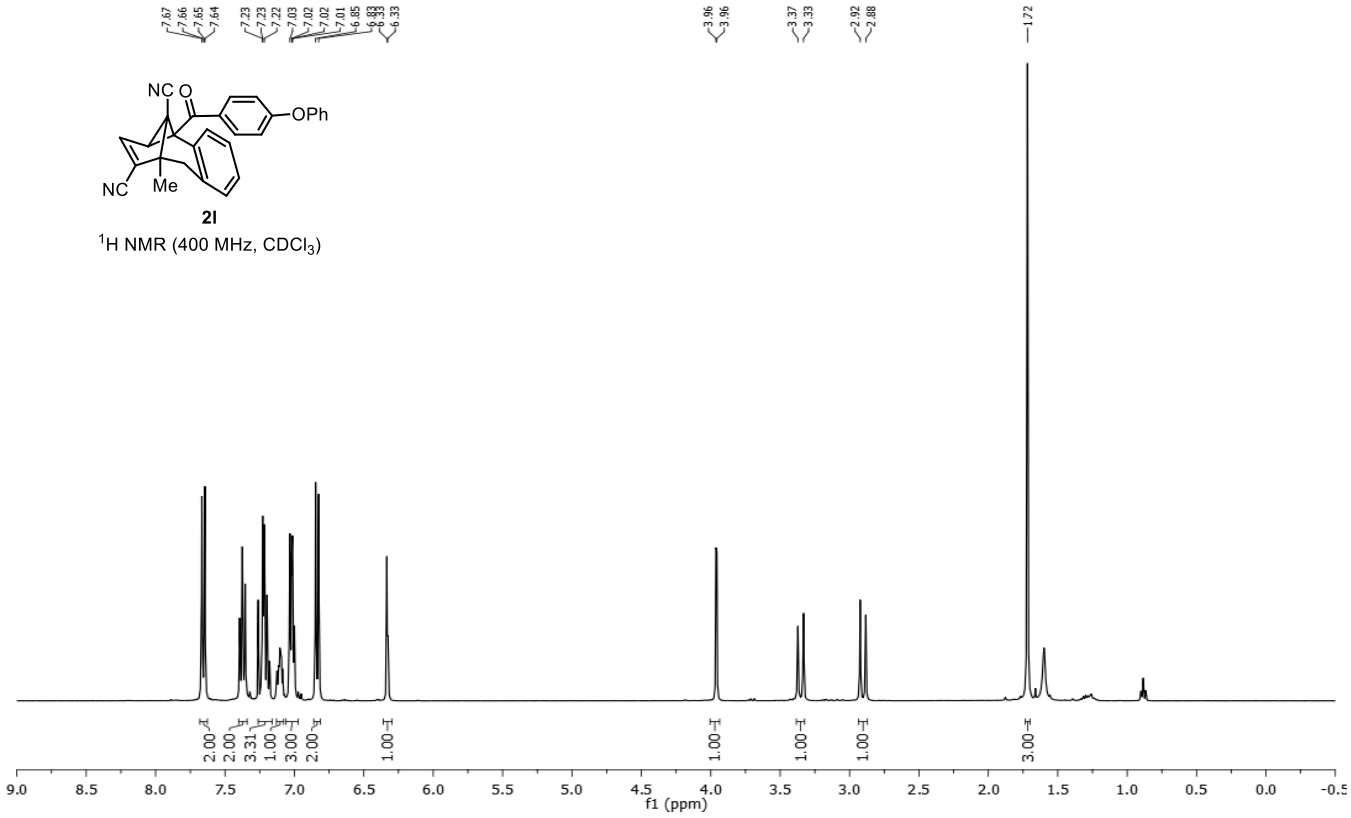


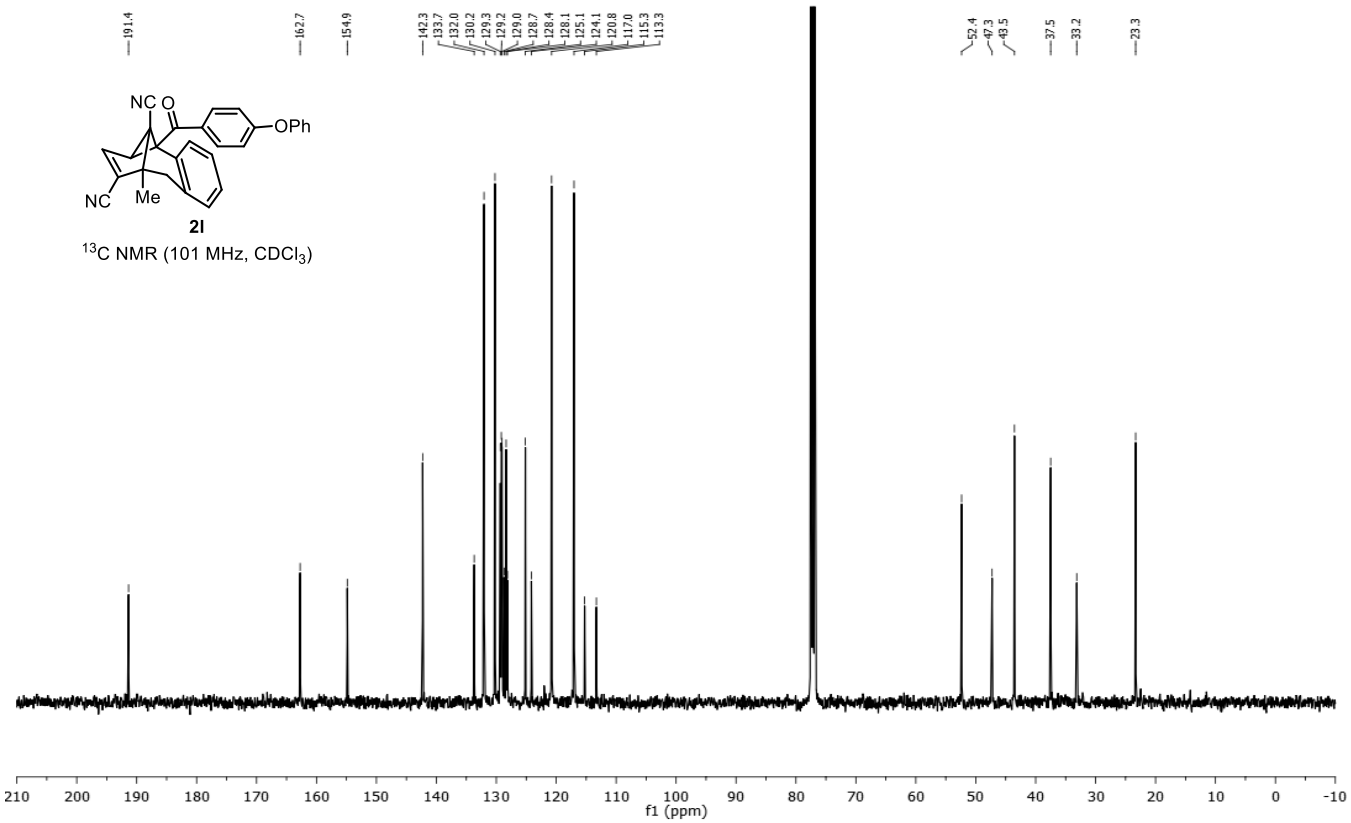
[1,1'-Biphenyl]-4-carbonyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2k):



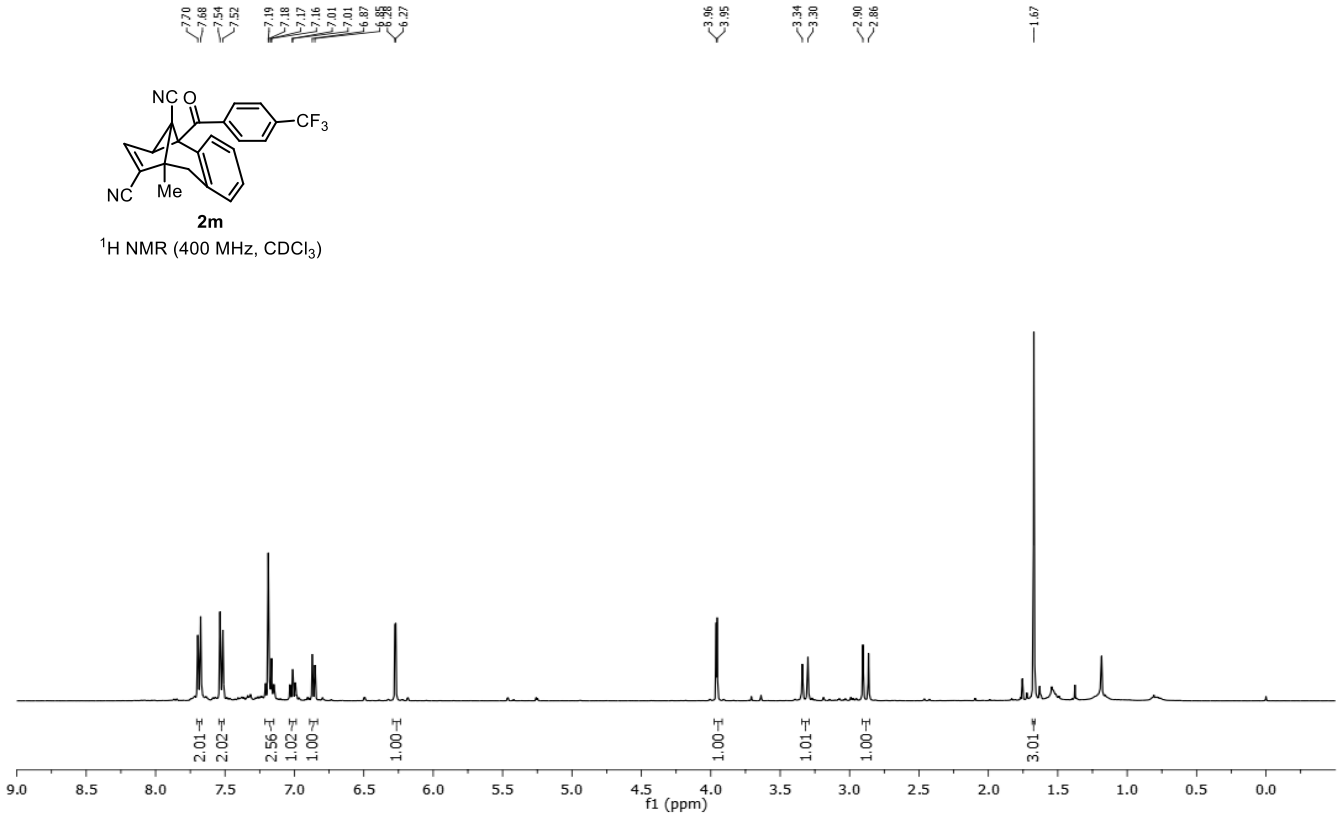


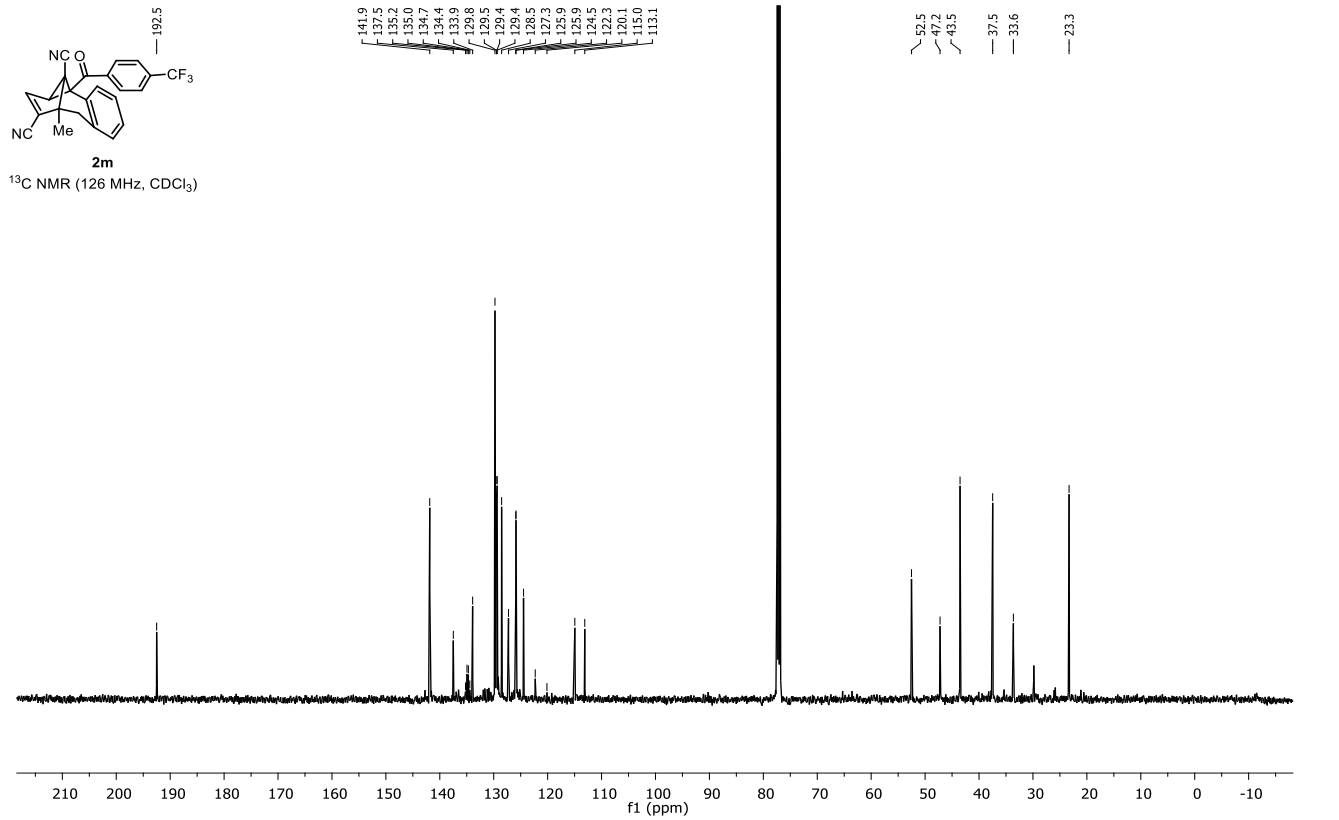
2a[1]-Isocyano-2a-methyl-7b-(4-phenoxybenzoyl)-2a,2a[1],7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2l):

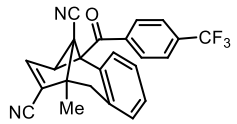




2a[1]-Isocyano-2a-methyl-7b-(4-(trifluoromethyl)benzoyl)-2a,2a[1],7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2m):



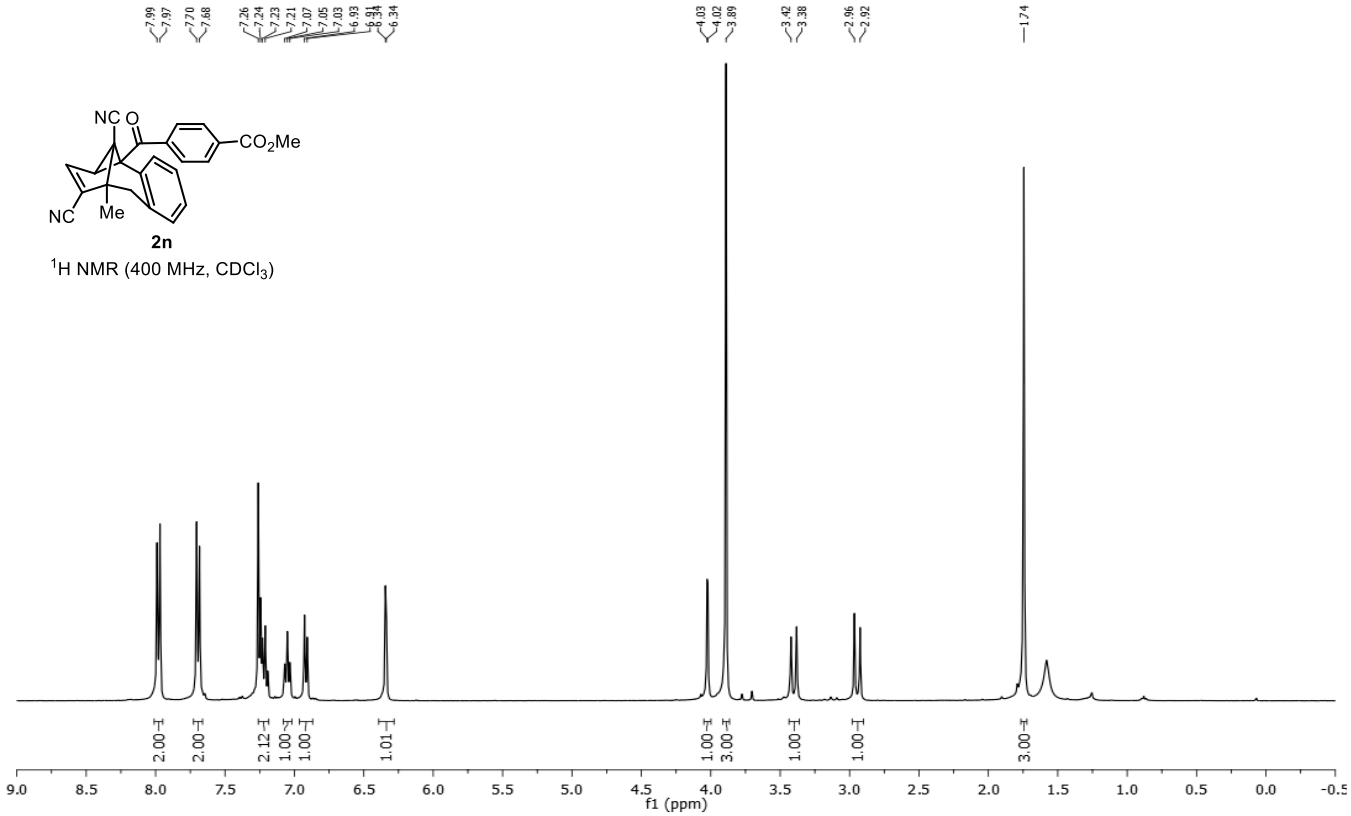


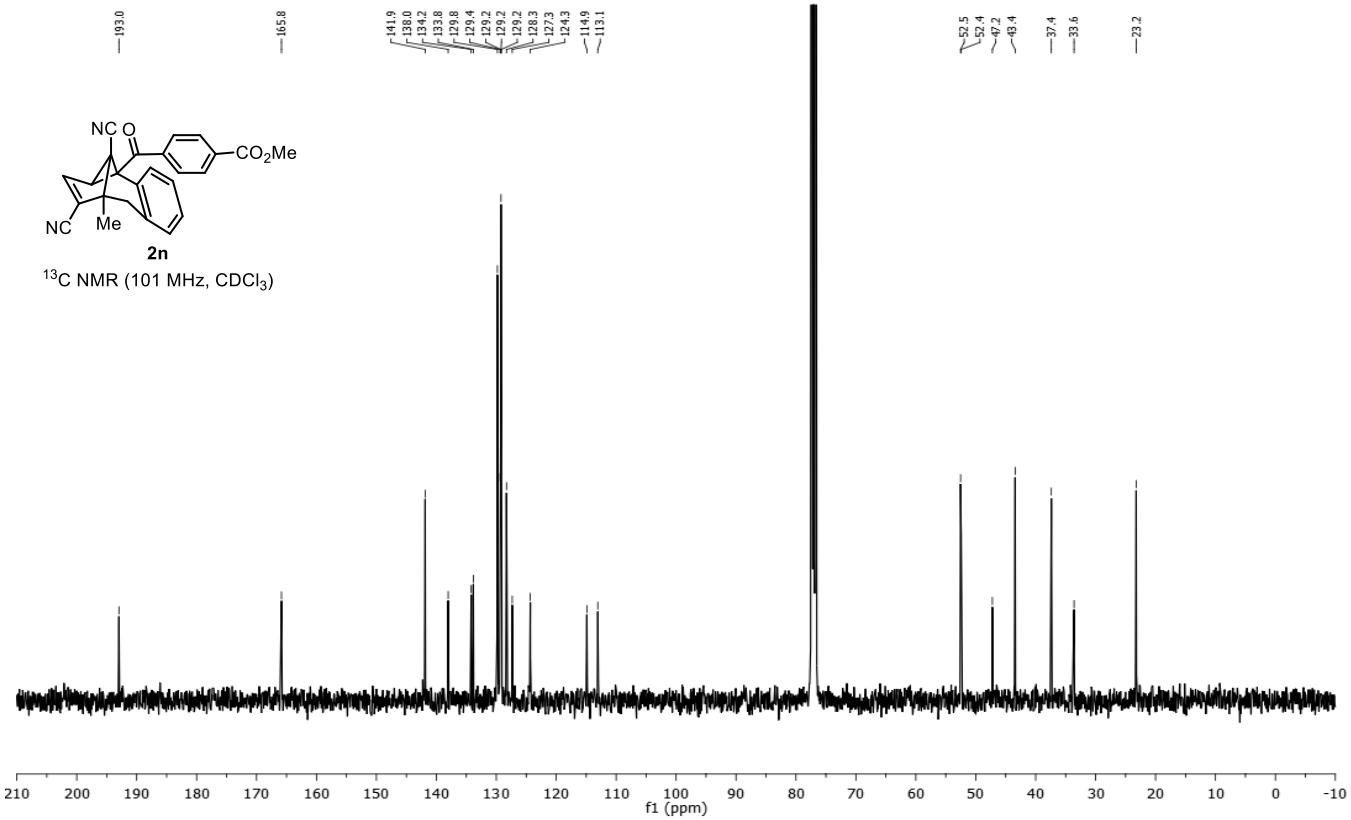


2m

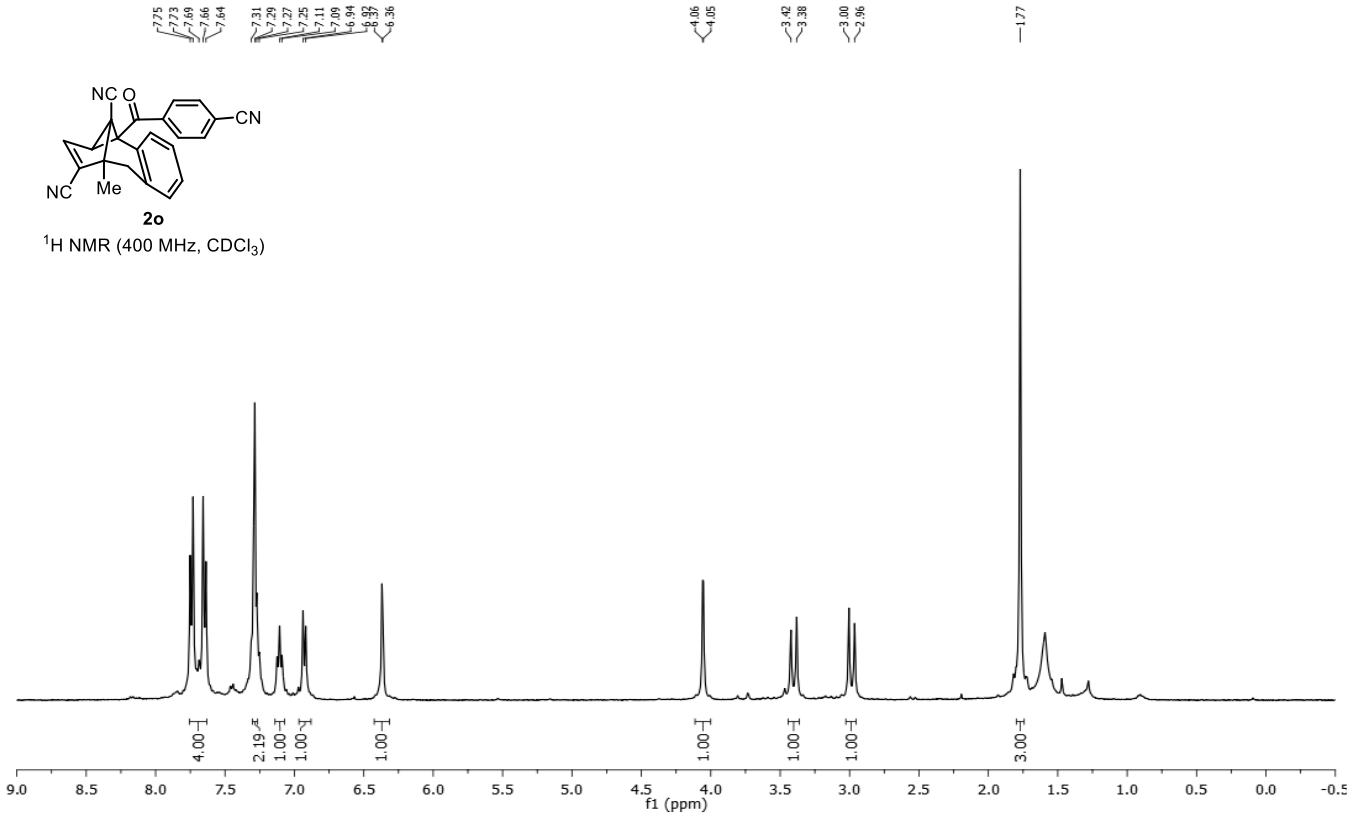
^{19}F NMR (377 MHz, $CDCl_3$)

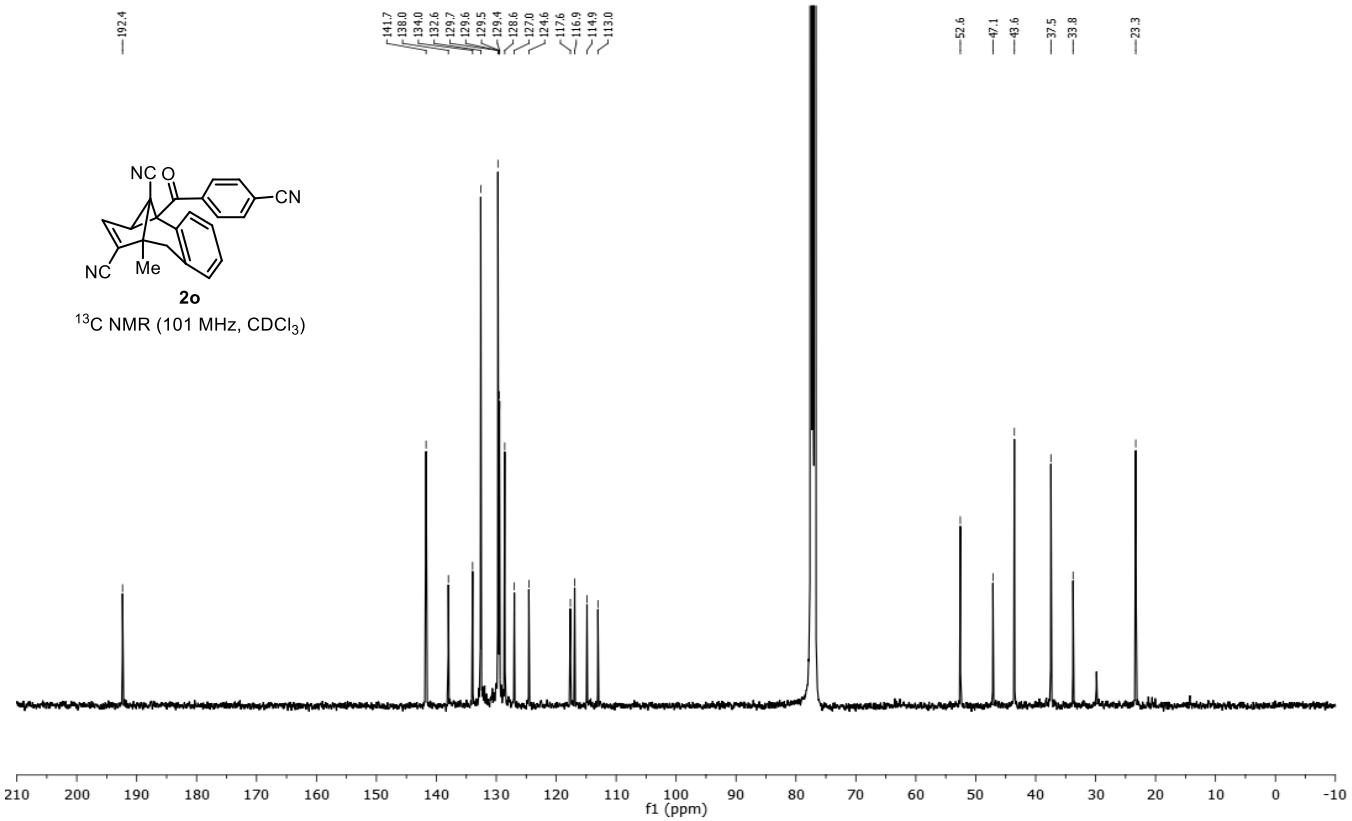
Methyl 2-cyano-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-7b-carbonyl) benzoate (2n):



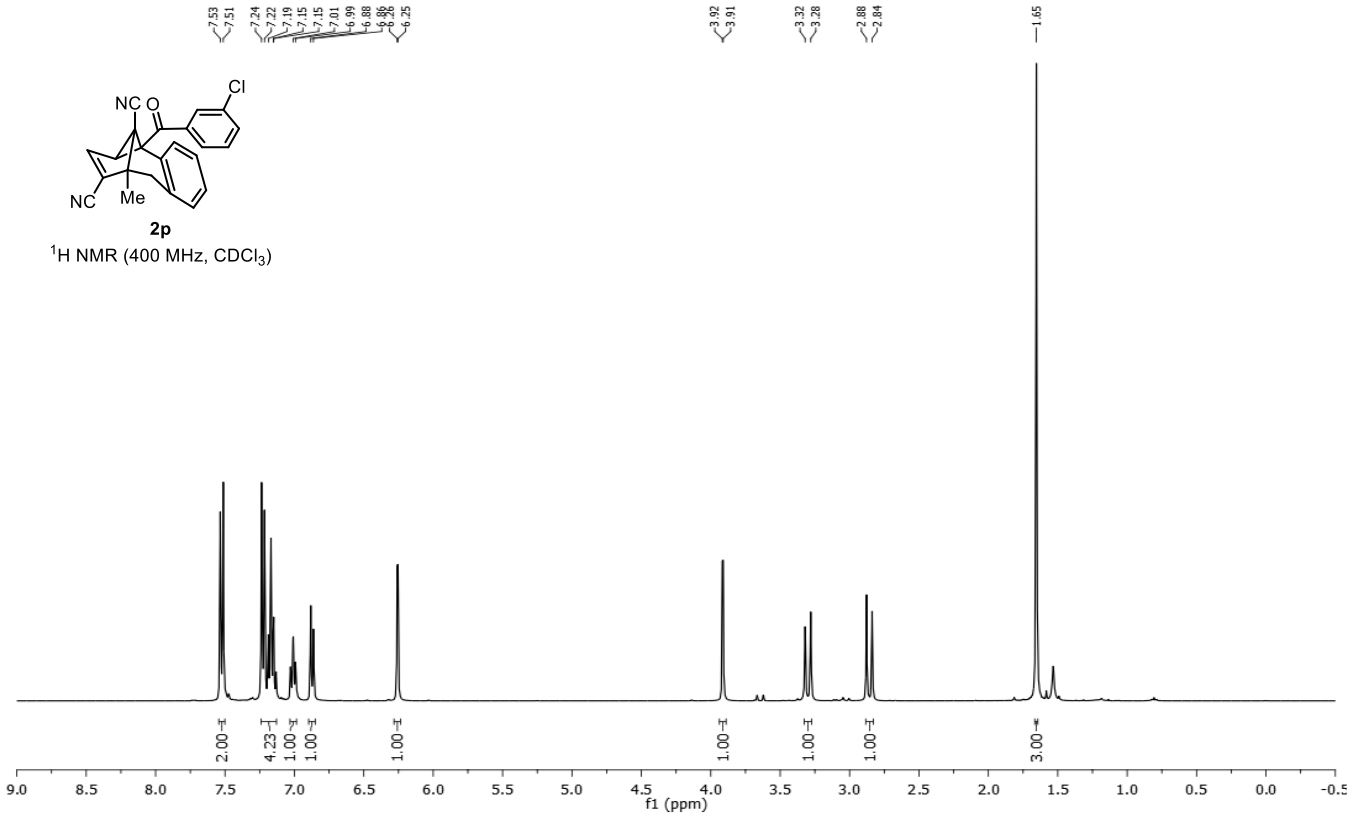


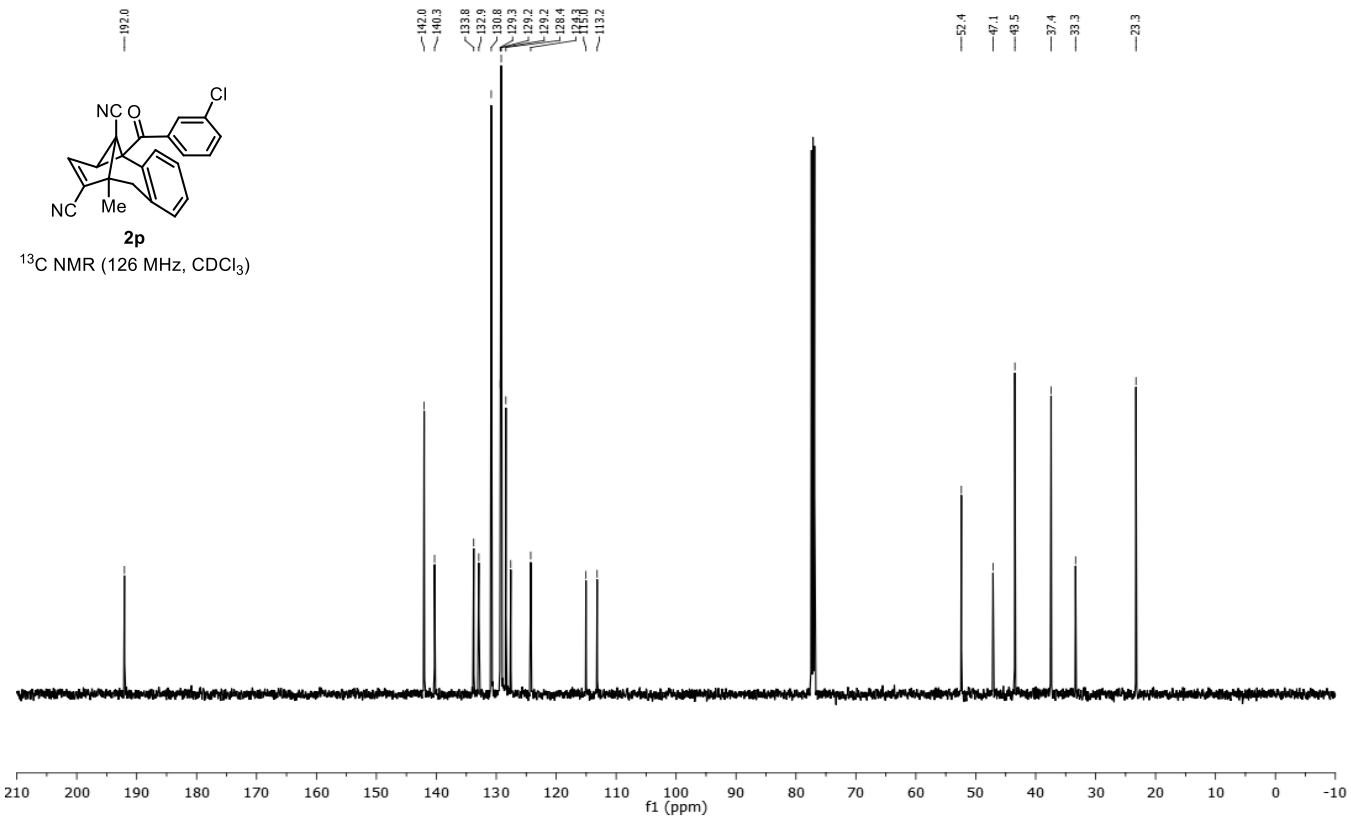
4-Cyanobenzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2o):



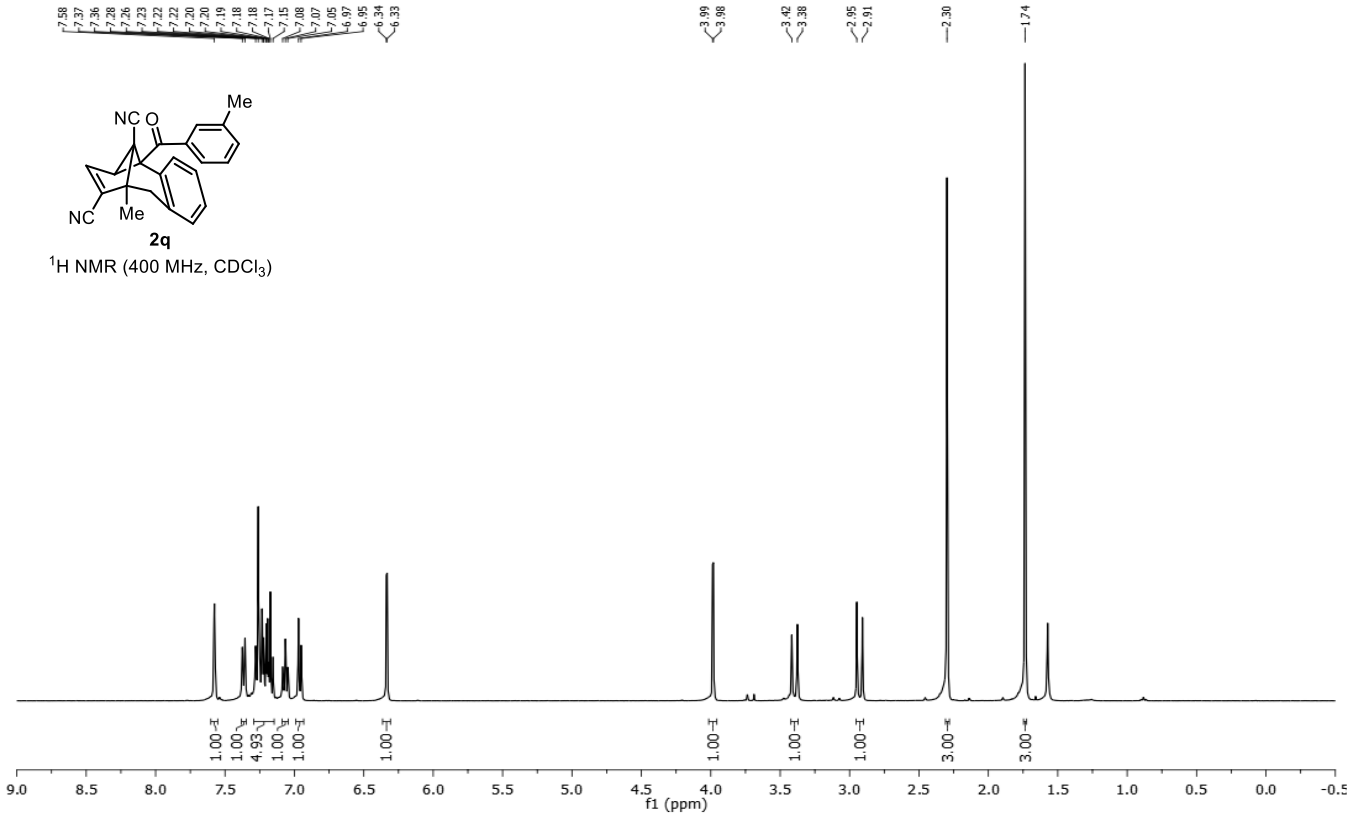


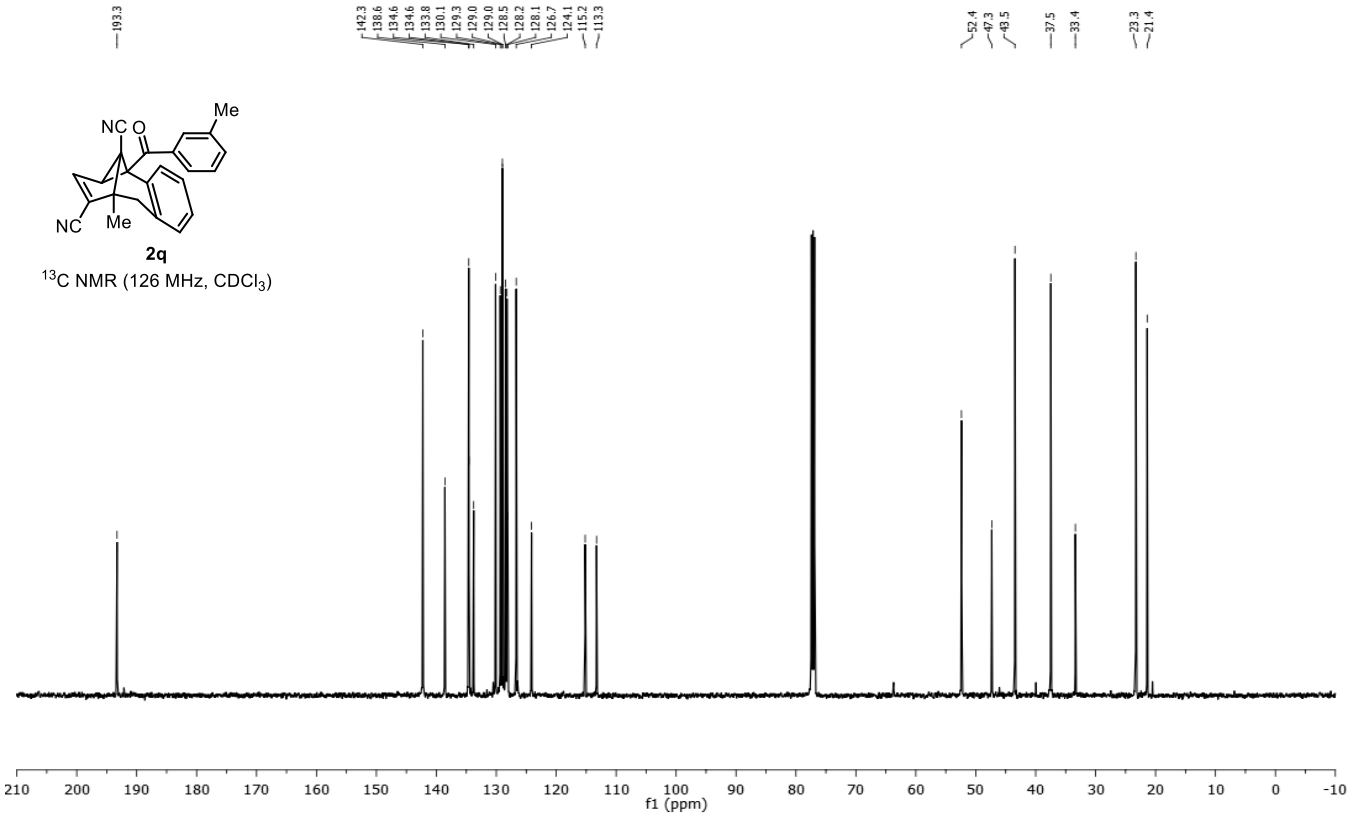
3-Chlorobenzoyl-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2p):



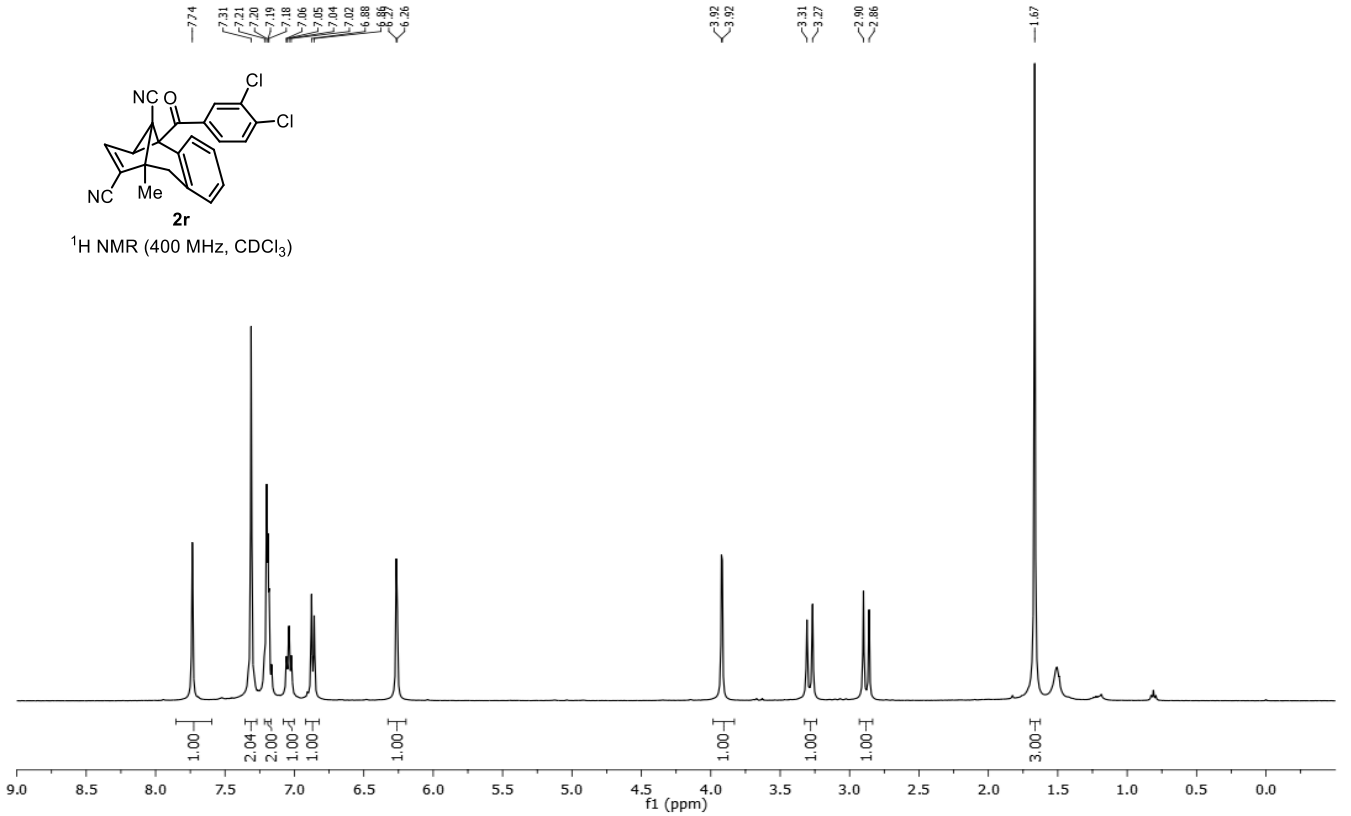


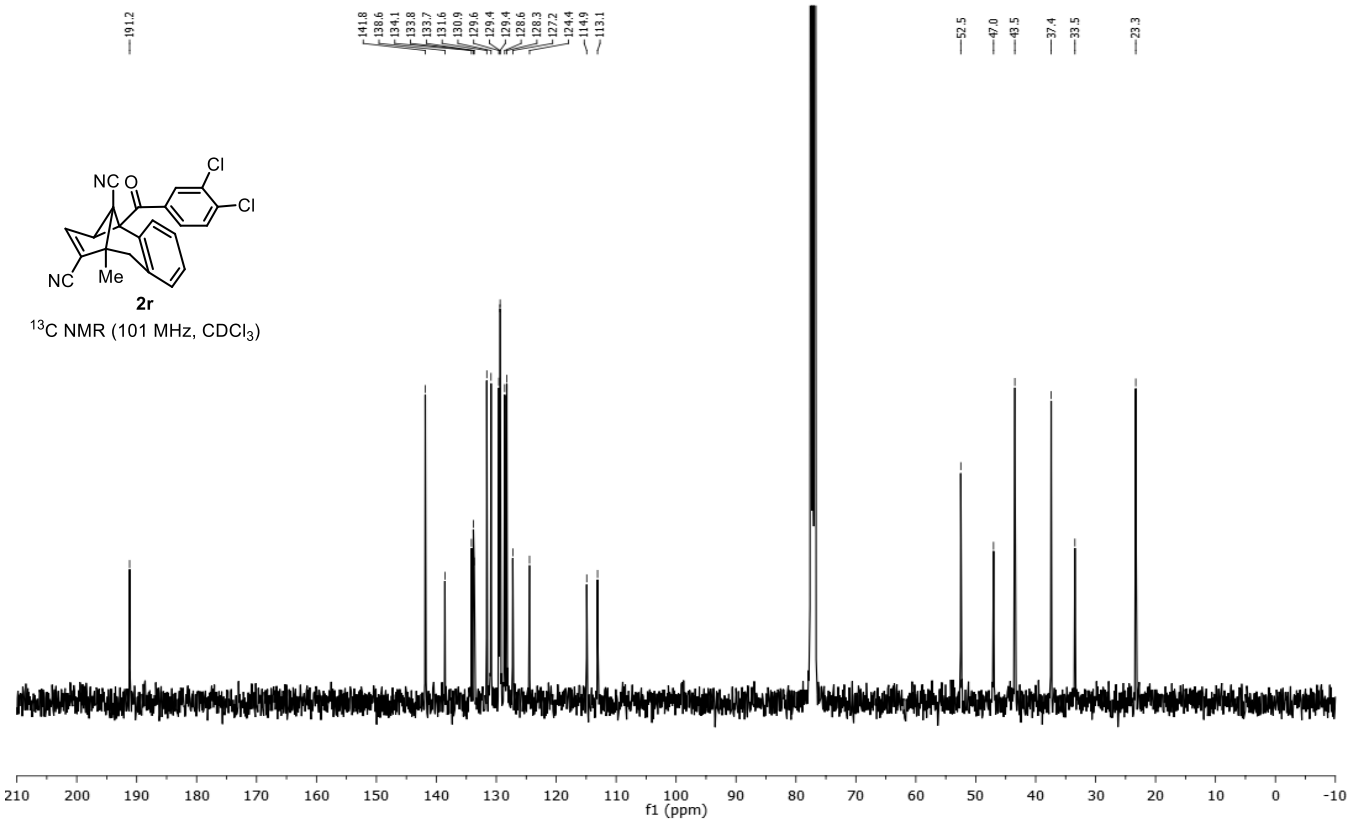
2a^1-Isocyano-2a-methyl-7b-(3-methylbenzoyl)-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2q):



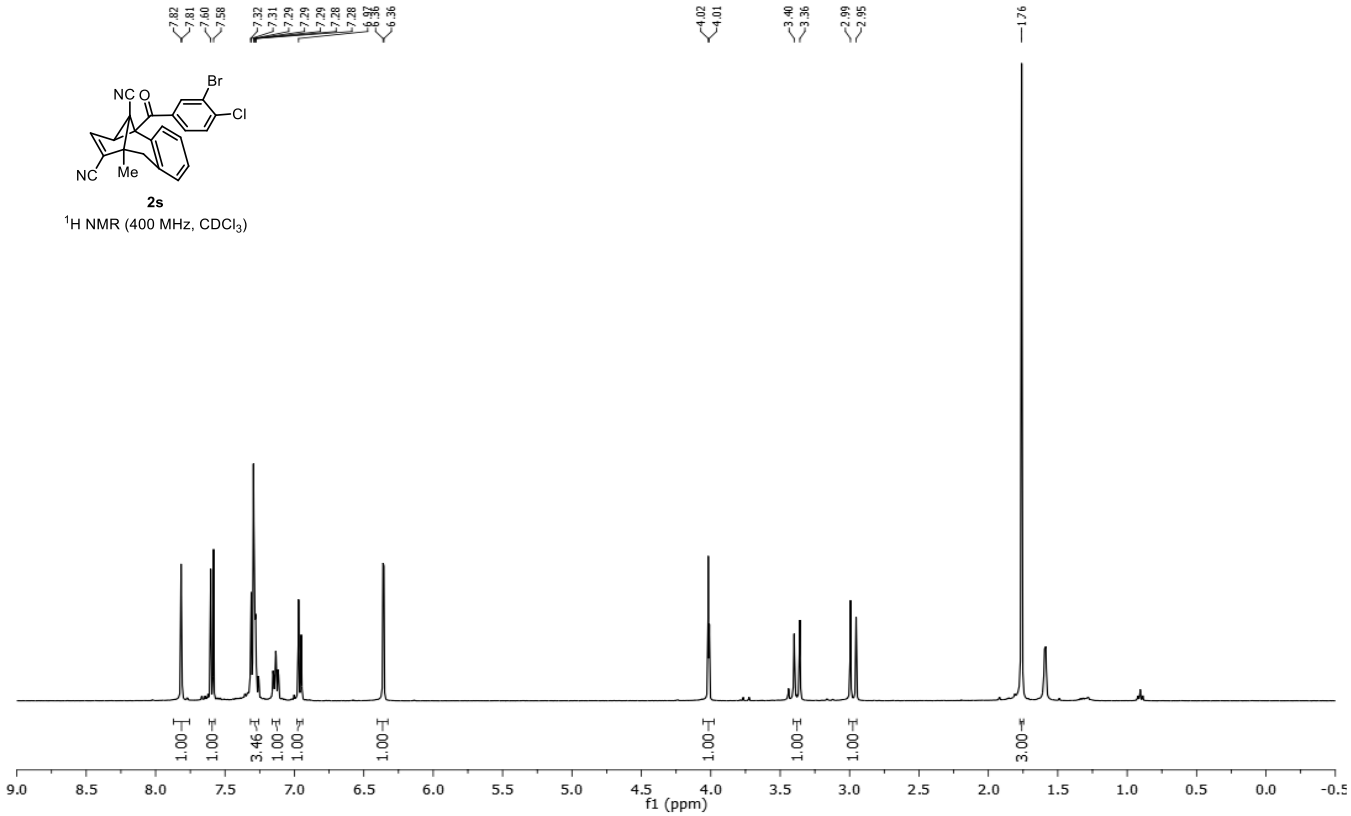


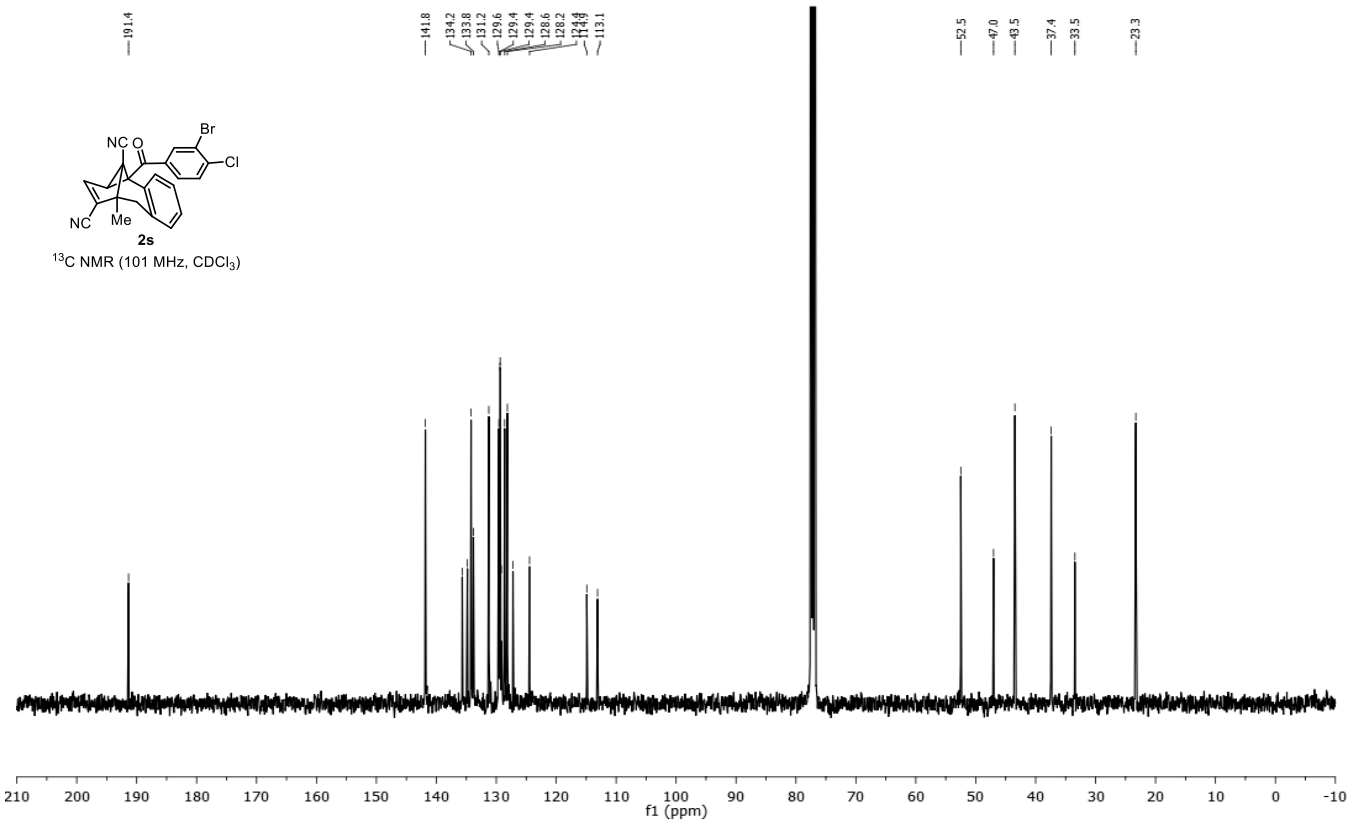
3,4-Dichlorobenzoyl-2a[1]-isocyano-2a-methyl-2a,2a[1],7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2r):



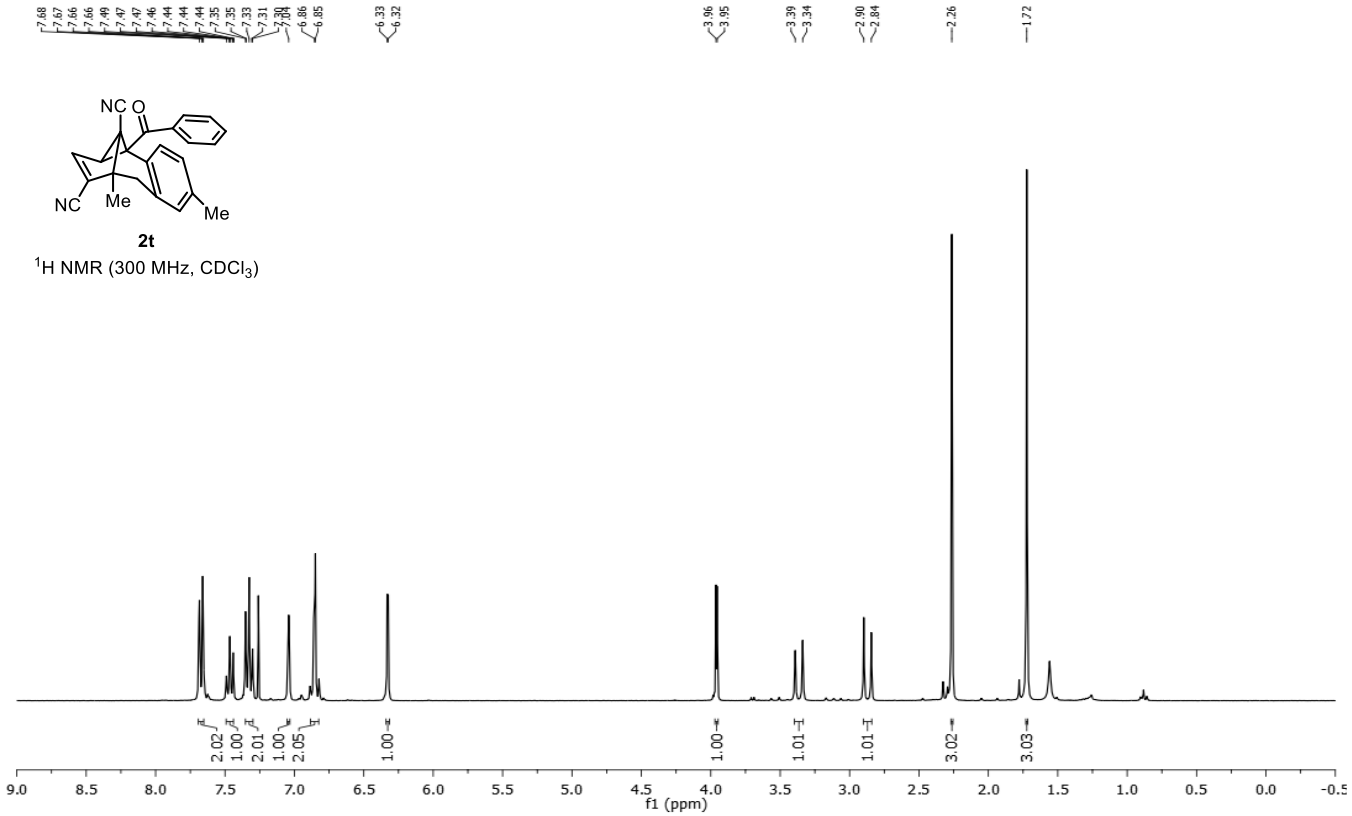


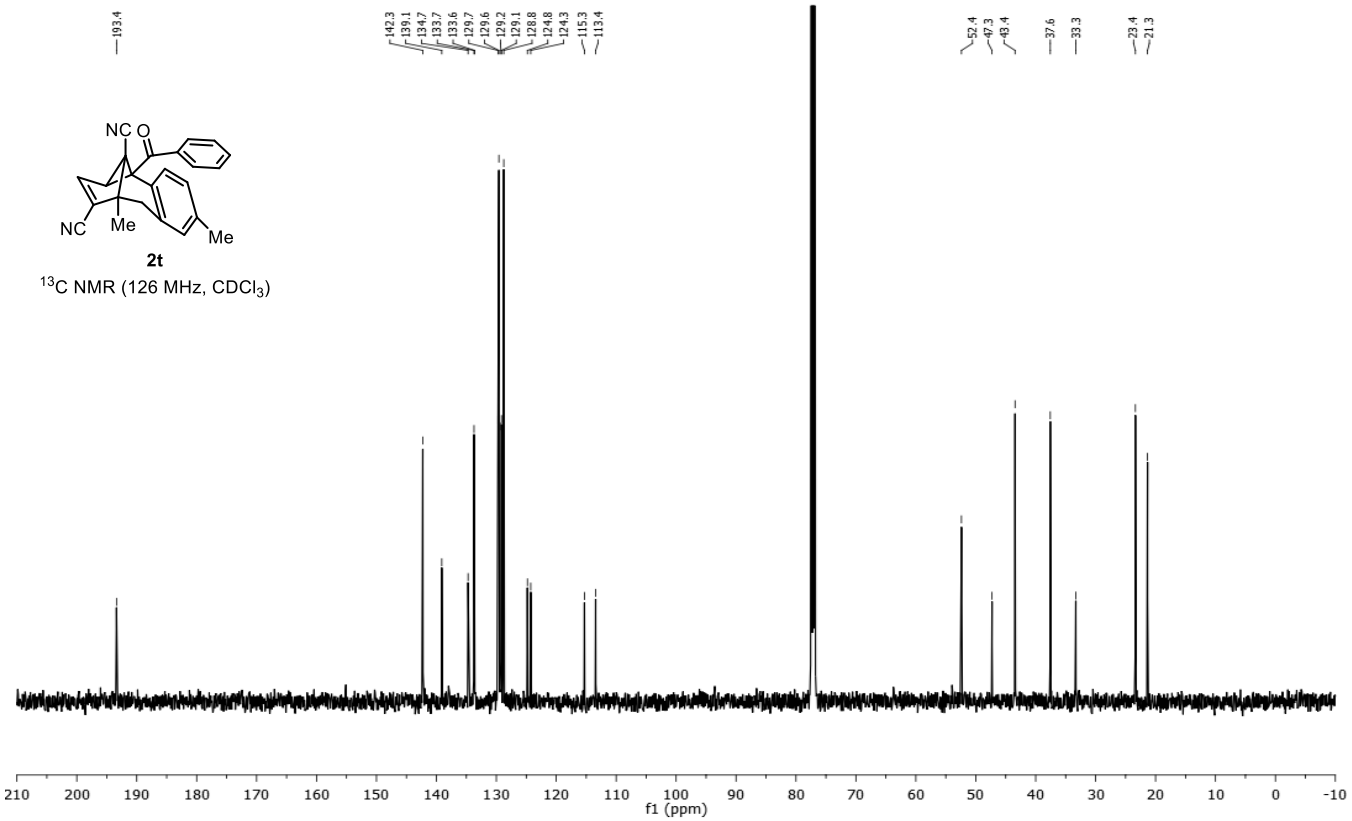
3-Bromo-4-chlorobenzoyl-2a[1]-isocyano-2a,5-dimethyl-2a,2a[1],7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2s):



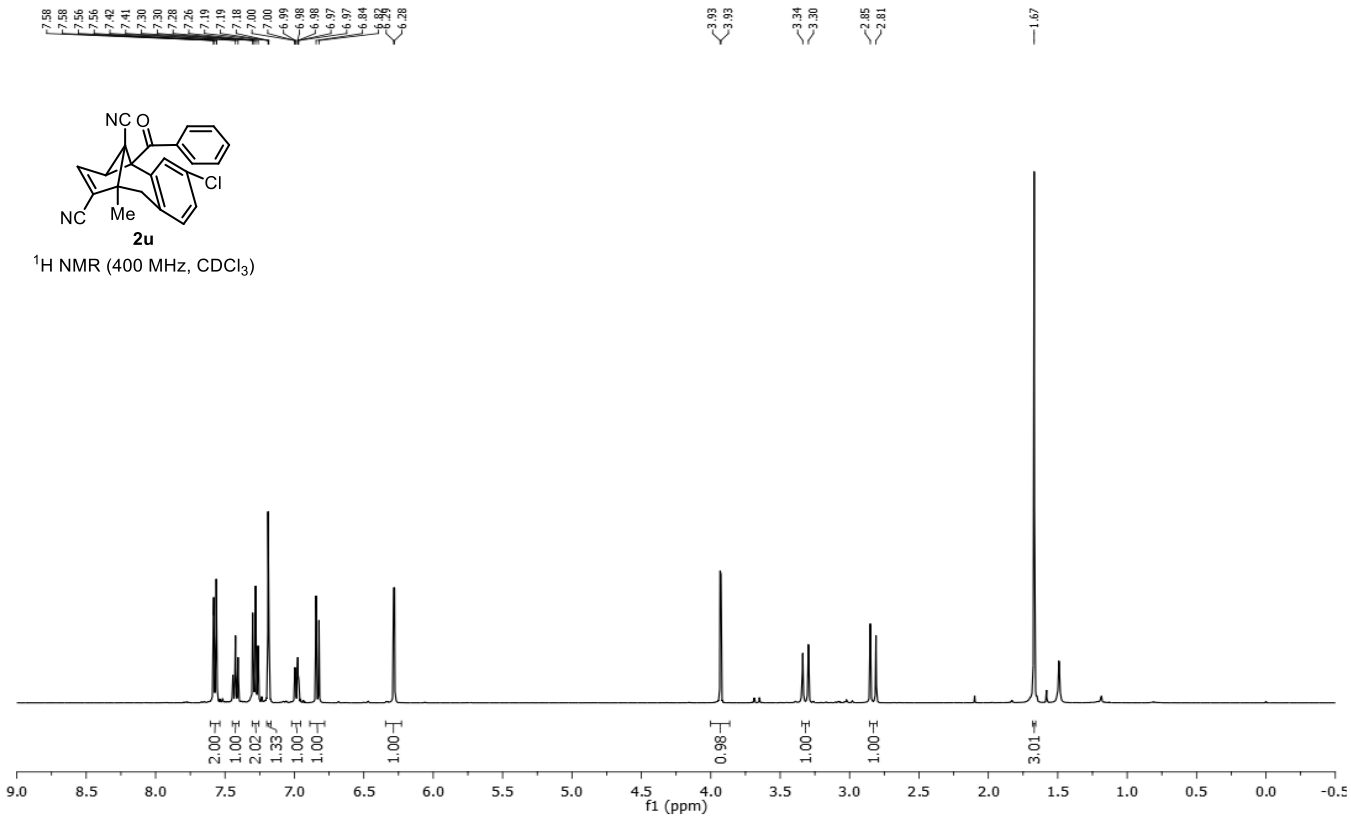


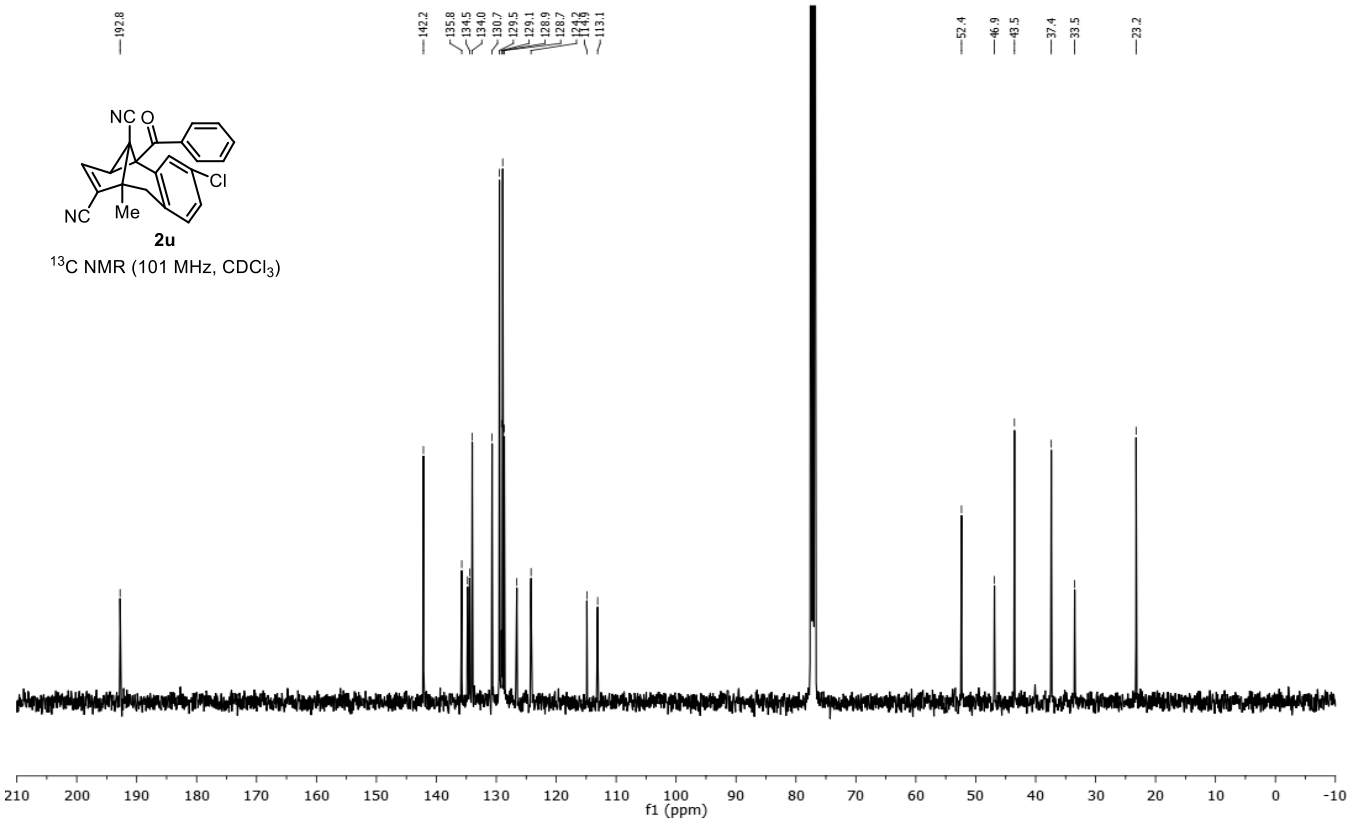
7b-Benzoyl-2a^1-isocyano-2a,5-dimethyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2t):



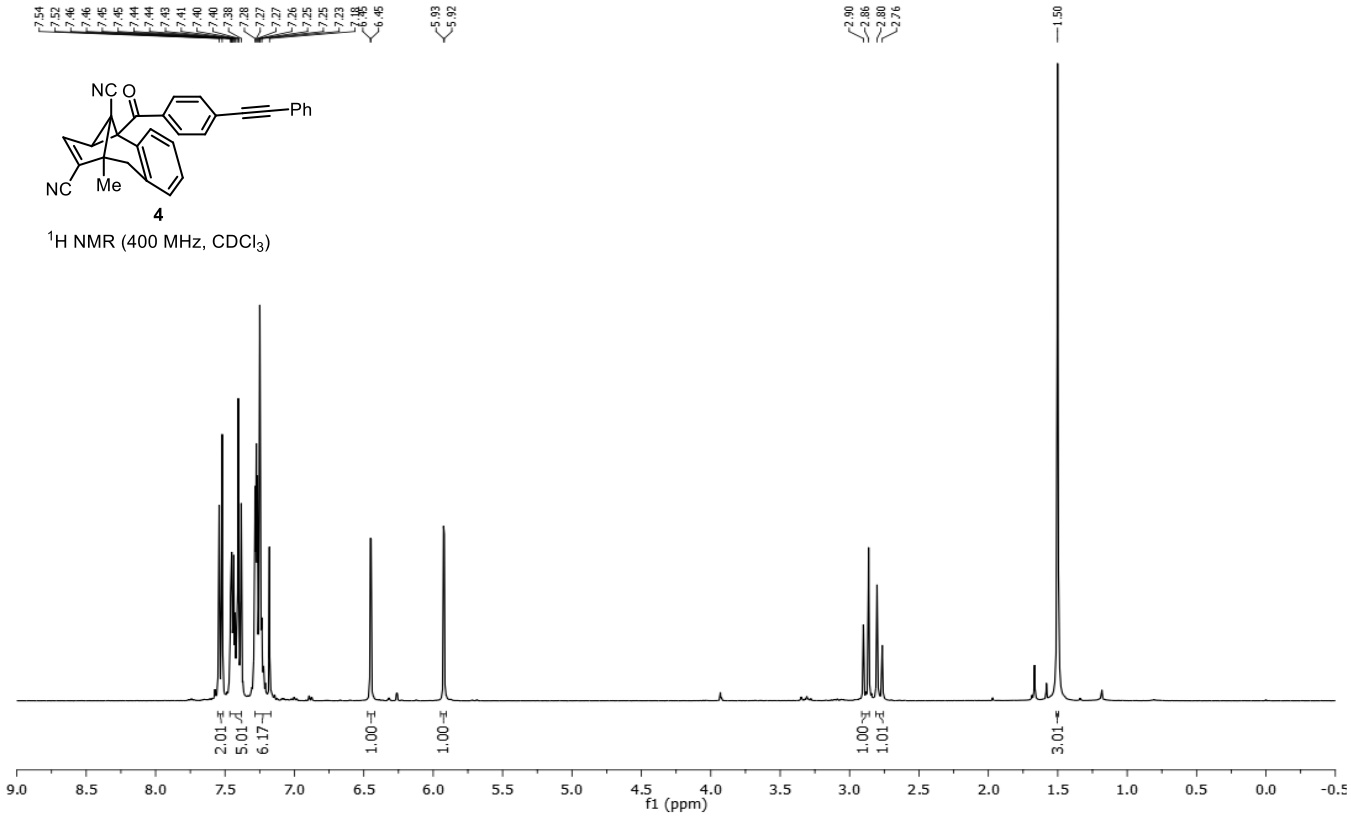


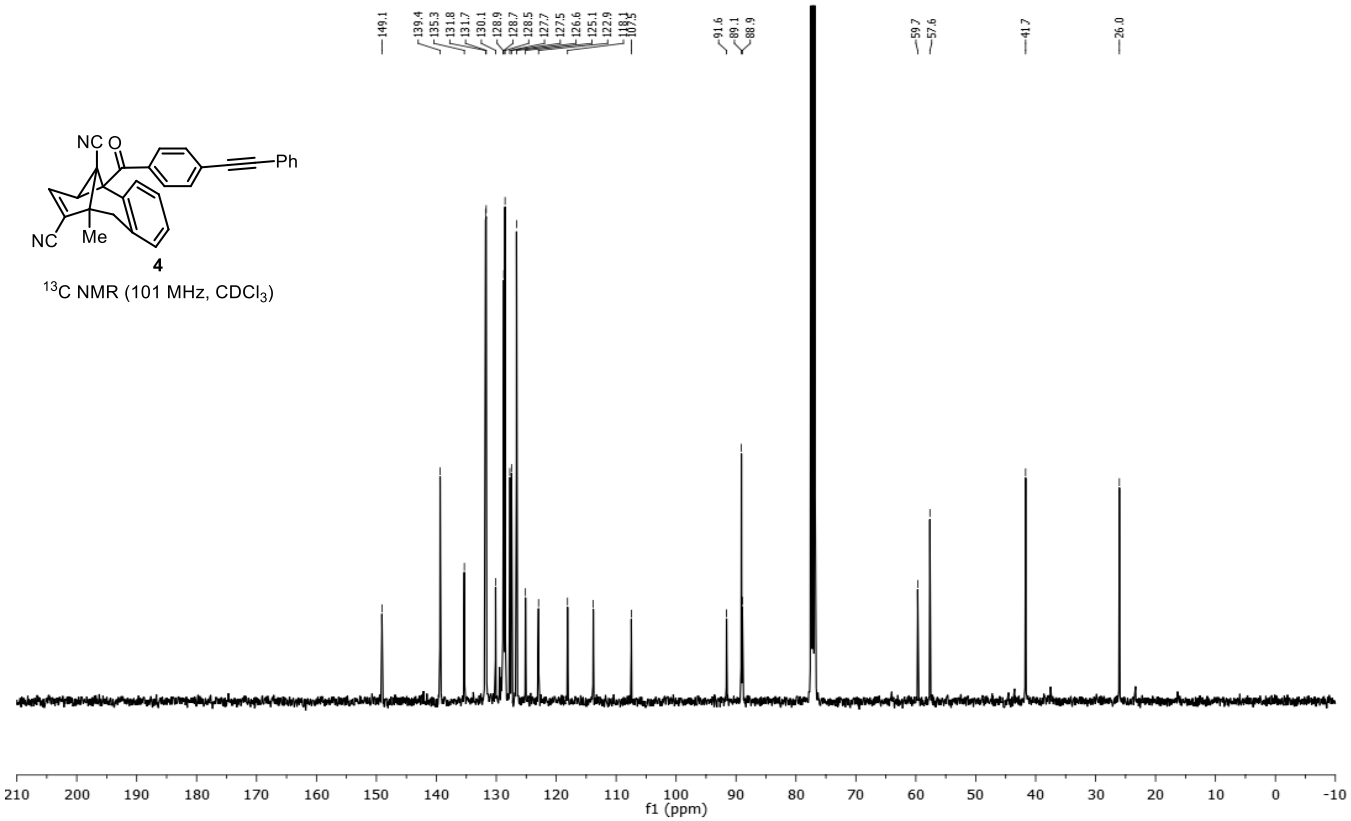
7b-Benzoyl-6-chloro-2a^1-isocyano-2a-methyl-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (2u):



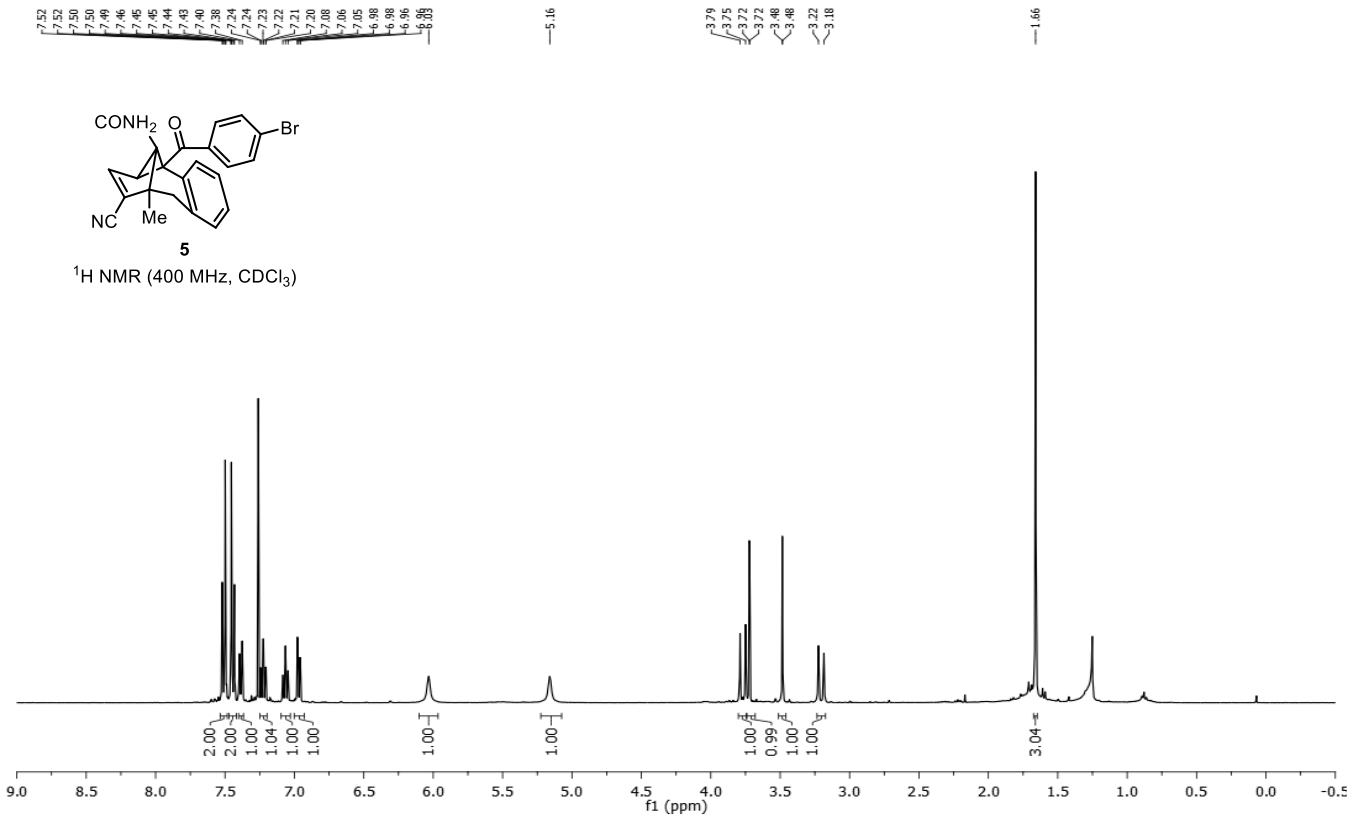


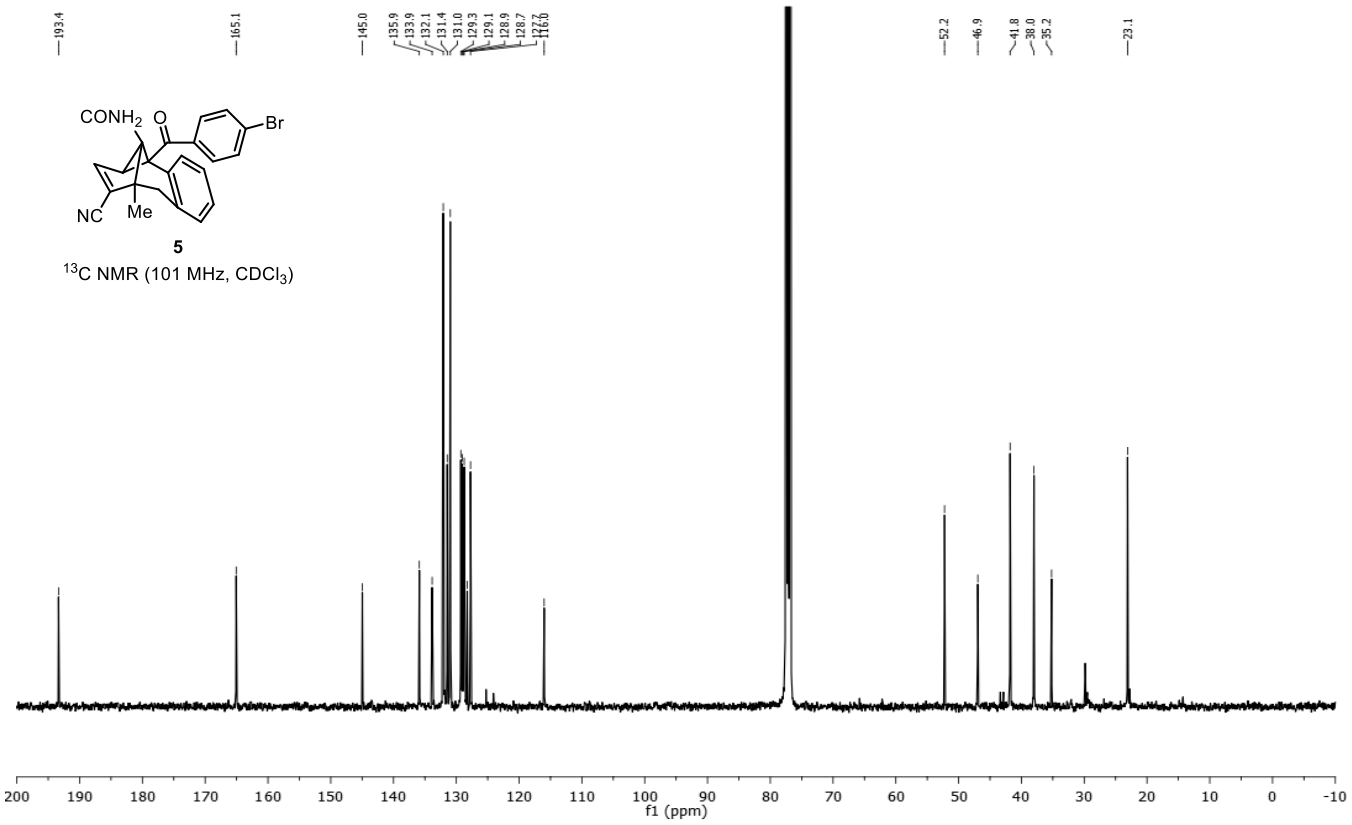
2a[1]-Isocyano-2a-methyl-7b-(4-(phenylethynyl)benzoyl)-2a,2a[1],7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (4):





4-Bromobenzoyl-2a-methyl-2a^1-((oxo-l3-methyl)-l4-azaneyl)-2a,2a^1,7b,7c-tetrahydro-3H-benzo[*f*]cyclopropa[*cd*]indene-2-carbonitrile (5):





6b-(4-Bromobenzoyl)-1b-methyl-1b^{1}-((oxo-l^{3}-methyl)-l4-azaneyl)-1b,1b1,2,6b,6c,6d-hexahydro-1aH-benzo[5,6]cyclopropa[3,4]indeno[1,2-b]oxirene-1a-carbonitrile (6):