Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

Benzylic C-H Arylation with Dicyanoarenes via Convergent Paired-Electrolysis

Shanyu Tang and Guillaume Vincent*

Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO)
Université Paris-Saclay, CNRS
91405 Orsay, France
E-mail: guillaume.vincent@universite-paris-saclay.fr

Contents

A. General Information..... 3

B. Optimization Study and control experiments 4

C. Cyclic voltammetry (CV) 9

D. Experimental procedures and characterization data of products..... 11

Scope of the benzylic C-H Arylation 11

Competitive experiment between 1a and 1a-d_2 25

Synthesis of substituted 1,4-dicyanoarenes 3b-d 26

E. NMR Spectra of products 30

F. References..... 90

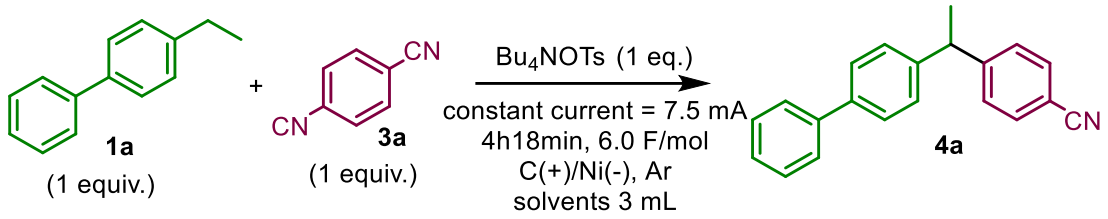
A. General Information

Unless otherwise noted, all reagent-grade chemicals and other solvents were obtained from commercial suppliers and used as received. Reactions were visualized under UV (254 nm) and/or by staining with Phospho Molybdic Acid or $KMnO_4$ solution followed by heating. Solvents were dried by distillation under argon from the following: tetrahydrofuran (sodium/benzophenone), acetonitrile and *N,N*-dimethylformamide (calcium hydride). Flash chromatography was performed on silica gel (Chromagel Si60ACC [70-200 μm]) as a stationary phase. Preparative thin-layer chromatography was performed on silica gel 60 F254 plates. ^{1}H NMR spectra were recorded on Bruker DRX300 (300 MHz), Bruker AM360 (360 MHz) and Bruker DRX400 (400 MHz) instruments, chemical shifts (δ) are given in parts per million with respect to the residual protonated solvent (δ = 7.26 ppm for $CDCl_3$), which served as an internal standard. ^{13}C NMR spectra were recorded on DRX400 (100 MHz), DRX300 (75 MHz) and AM360 (90 MHz) and chemical shifts are expressed with respect to the deuterated solvent (δ = 77.16 ppm for $CDCl_3$). Coupling constant(s) in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: s (singlet), d (doublet), t (triplet), q (quadruplet), hept (heptet), m (multiplet). Structural assignments were made with additional information from gCOSY, gHSQC gHMBC and NOESY experiments. High resolution mass spectra (HRMS) were recorded using Electrospray Ionization (ESI) method with a Bruker Daltonics MicrOTOF-Q instrument. Electrosynthesis experiments were performed with the ElectraSyn 2.0 (IKA) device. Cyclic voltammograms were obtained on Metrohm Autolab PGSTAT101 potentiostat.

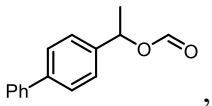
B. Optimization Study and control experiments

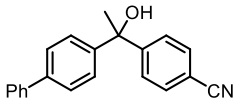
Undivided cell, electrodes are 1.5 cm x 0.8 cm x 0.2 cm submerged, **3a** (0.2 mmol), electrolyte (0.2 mmol), 3 mL of solvent, room temperature, argon.

Table S1. *Solvent Optimization.*



Entry	Solvents	Yield (%) 4a	Yield (%) 1a
1	DMF	39	44
2[a]	DMF/HFIP = 2/1	traces	20
3	CH_3CN	27	47
4	CH_3CN/HFIP = 5/1	not detected	traces
5	DCE/CH_3CN = 4/1	20	50
6	THF/DMF = 1/1	30	44
7	EtOAc/CH_3CN	30	57
8	THF/CH_3CN = 4/1	37	33
9	THF/CH_3CN = 2/1	44	27
10	THF/CH_3CN = 1/2	46	27
11	THF/CH_3CN = 1/1	48	22
12	THF	8	85
13[b]	2Me-THF/CH_3CN = 1/1	26	44
14	DMA	not detected	major product
15	NMP	not detected	major product
16	DMSO	not detected	major product

[a] 23% 

, 19% 

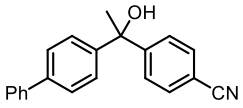
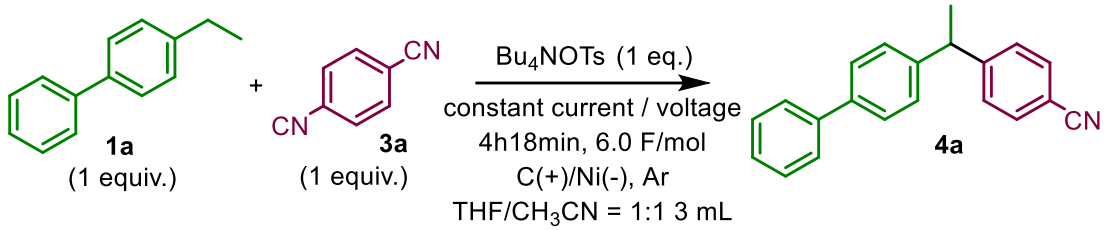
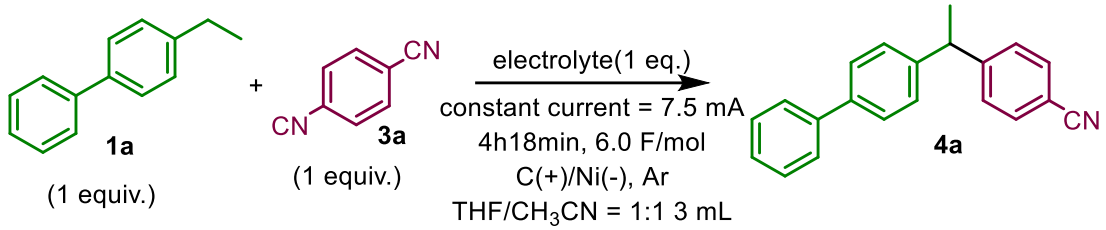
[b] 13% 

Table S2. *Current and concentration optimization.*



Entry	Current/voltage	Concentration (mol/L)	Yield (%) 4a	Yield (%) 1a
1	7.5 mA	0.067	48	22
2	4 mA	0.033	46	38
3	15 mA	0.133	39	38
4	5 mA	0.067	42	25
5	10 mA	0.067	34	33
6	4 V	0.067	37	8

Table S3. *Electrolyte optimization.*



Entry	electrolyte	Yield (%) 4a	Yield (%) 1a
1	Bu_4NClO_4	traces	>90%
2	Bu_4NBF_4	traces	>90%
3	Bu_4NOTf	not detected	>90%
4	Bu_4NOAc	not detected	>90%
5[a]	$LiN(Tf)_2$	not detected	traces
6	Bu_4NNO_3	13	50
7	Bu_4NPF_6	traces	>90%
8	Et_4NOTs	37	40
9	Bu_4NOTs	48	22

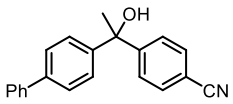
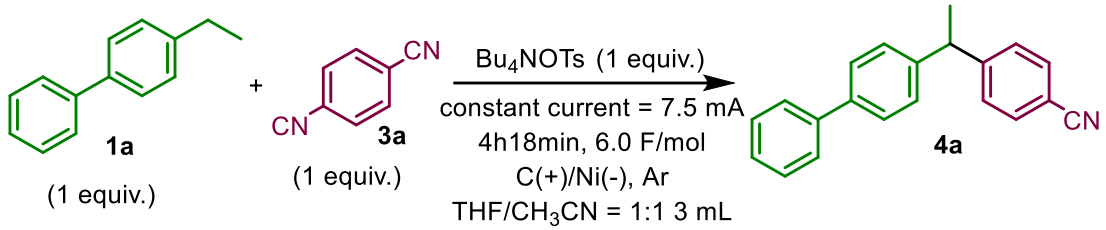
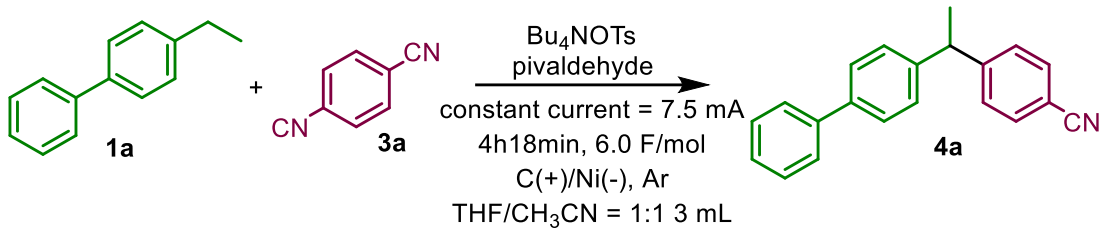
[a] 37% 

Table S4. *Aldehyde optimization.*



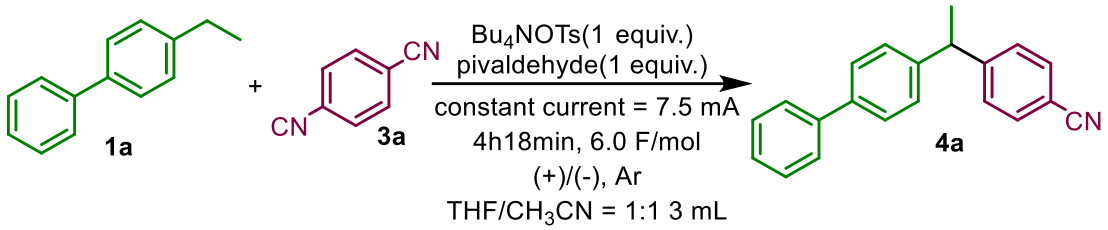
Entry	Aldehyde (1 eq.)	Yield (%) 4a	Yield (%) 1a
1	/	48	22
2	pivaldehyde	58	19
3	octanal	12	52
4	benzaldehyde	21	25
5	cyclohexanal	51	17
6	valeraldehyde	12	44

Table S5. *Ratio of substrates and quantity of electricity optimization.*



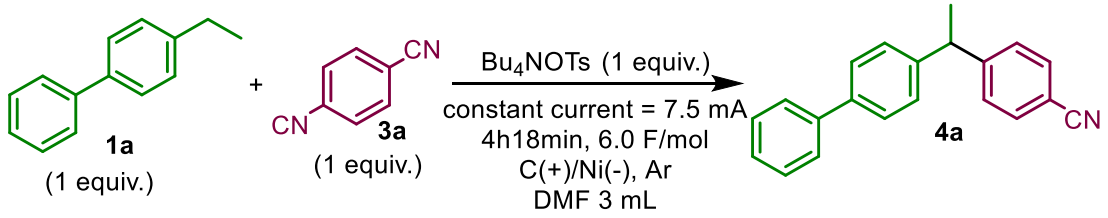
Entry	Eq. of 3a and pivaldehyde	Charge (F/mol)	Yield (%) 4a	Yield (%) 1a
1	1	6	58	19
2	2	6	58	5
3	1.5	6	58	19
4	1.5	8	60	8
5	1.5	4.5	25	48
6	0.5	6	60	60

Table S6. *Electrodes optimization.*

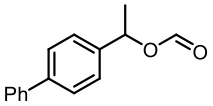


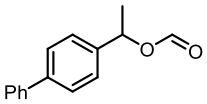
Entry	Electrodes	Yield (%) 4a	Yield (%) 1a
1	C(+)/Ni(-)	58	19
2	Pt(+)/Ni(-)	traces	>90
3	C(+)/C(-)	37	8
4	C(+)/Pt(-)	53	16

Table S7. *Additive optimization (DMF as solvent).*

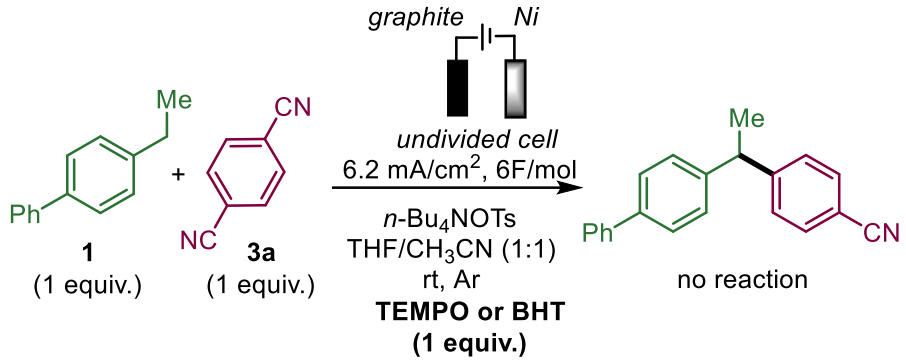


Entry	Additive	Yield (%) 4a	Yield (%) 1a
1	2,6-lutidine (1 eq.)	19	44
2	K_2CO_3 (1 eq.)	5	82
3	DABCO (3 eq.)	not detected	>90
4	Tempo (5%)	14	60
5	DDQ (5%)	14	63
6	N-hydroxyphtalimide (20%)	14	63
7	Tri(4-bromophenyl)amine	traces	>90
8[a]	MsOH (1 eq.)	traces	22
9	Triphenylsilanethiol (20%)	traces	71
10	Dibenzenesulfonamide (10%)	32	47
11	Dibenzenesulfonamide (10%) + K_2CO_3 (10%)	traces	>90
12	Ferrocene (20%)	traces	>90
13	FePc (10%)	traces	>90
14	Salcomine (10%)	traces	65
15	$MnCl_2$ (10%) + 1,10-phenanthroline (20%)	traces	>90
16[b]	$NiBr_2$ (10%)+ bbbpy (20%)	7	60

[a] 40% 

[b] 26% 

Scheme S1. *Control experiments in presence of TEMPO or BHT.*



C. Cyclic voltammetry (CV)

Cyclic voltammetry experiments (CV) were performed with a Metrohm Autolab PGSTAT101 potentiostat connected to a Nova software interface in a three-electrode cell connected to a Schlenk line under argon at 20 °C with a scan rate of 0.05 $V \cdot s^{-1}$ using a glassy carbon disk (d = 3 mm) as working electrode, a platinum wire as counter electrode and a Ag/AgCl electrode as reference in 5 mL of a 0.1 M solution of *n*-$Bu_4N.BF_4$ in the solvent.

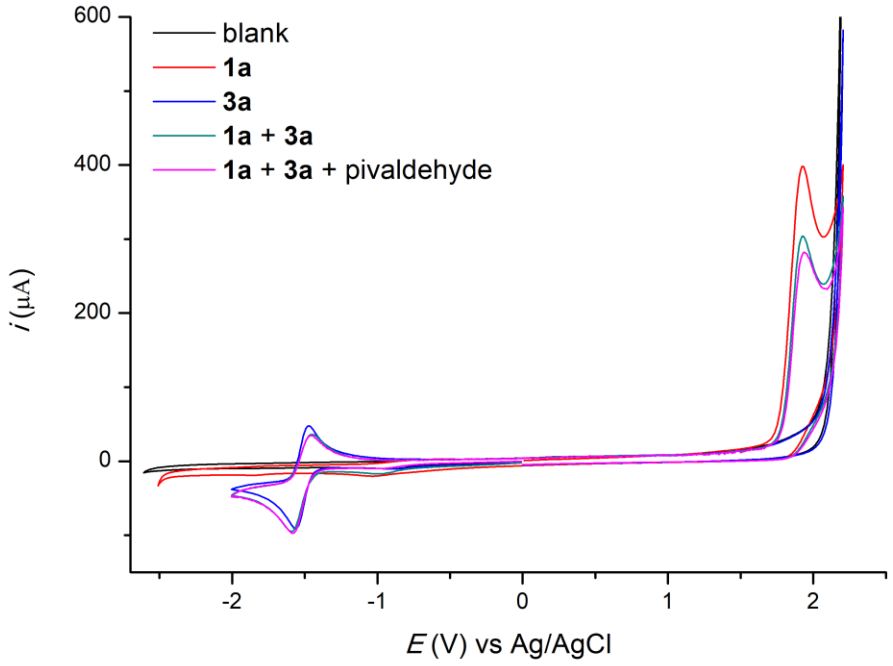


Figure S1. *Cyclic voltammetry of the reactants* ***1a***, ***3a*** *and pivaldehyde.*
(2 mM of each compounds in a 1:1 solution of THF and acetonitrile).

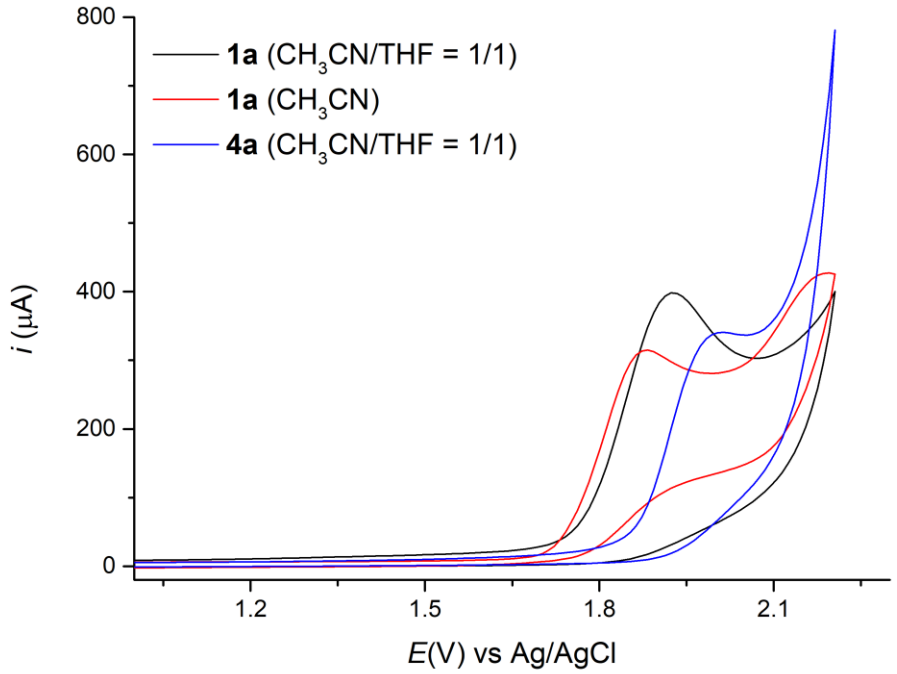


Figure S2. *Cyclic voltammetry of benzylic substrate* ***1a*** *and bisbenzylic product* ***4a*****.**
(2 mM of each compounds in a 1:1 solution of THF and acetonitrile or pure acetonitrile).

D. Experimental procedures and characterization data of products

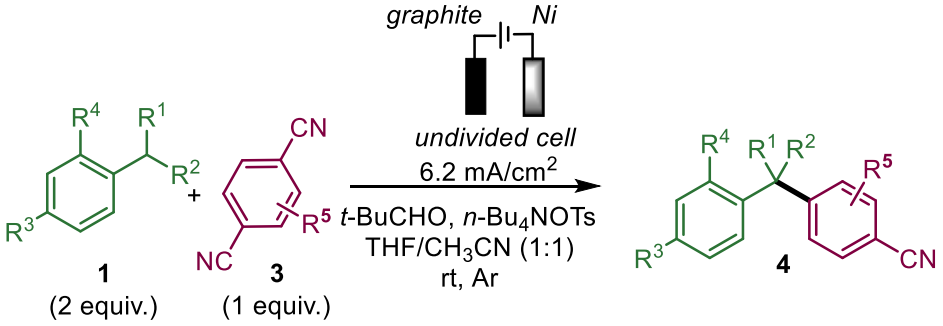
Electrolysis general information

Electrochemical reactions were performed with the ElectraSyn 2.0 package (IKA) using the constant current mode. The reactions were conducted in a 5 mL vial with a stir bar and a graphite-SK-50 (5.0 x 0.8 x 0.2 cm) working electrode (anode) and a nickel-plated (5.0 x 0.8 x 0.2 cm) counter-electrode (cathode) with a distance of 0.6 cm between the two electrodes (**Figure S3**).

Figure S3. *Experimental electrochemical set-up with ElectraSyn 2.0*

Scope of the benzylic C-H Arylation

- *General procedure **A** for the synthesis of compounds **4***

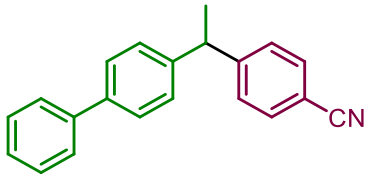


To the 5 mL vial with a stir bar were successively added benzylic substrate **1** (0.4 mmol), dicyanoarene **3** (0.2 mmol), *n*-Bu_4NOTs (0.2 mmol, 82.6 mg, 1.0 equiv.), pivaldehyde (0.2 mmol, 17.2 mg, 1.0 equiv.) 1.5 mL of CH_3CN and 1.5 mL of THF. The cell was then equipped with a graphite anode and a nickel-plated cathode, and then evacuated and backfilled with an argon balloon. This cycle was repeated three times. The reaction mixture was electrolyzed under a constant current of 7.5 mA (~ 6.25 mA/cm^2, 1.5 cm x 0.8 cm x 0.2 cm submerged) for 4 hours 18 mins (6.0 F/mol) at room temperature.

The reaction solution was concentrated under a vacuum and then purified by preparative TLC.

- Compound **4a** was prepared from 4-ethyl-1,1'-biphenyl **1a** (72.8 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1) to afford nitrile **4a** as a white solid (34 mg, yield: 60 %).
  1 mmol scale experiment: To the 20 mL vial with a stir bar were successively added the benzylic substrate **1a** (2 mmol, 364 mg), 1,4-dicyanobenzene **3a** (1 mmol, 128 mg), *n*-Bu_4NOTs (1 mmol, 413 mg, 1.0 equiv.), pivaldehyde (1 mmol, 86 mg, 1.0 equiv.), 7.5 mL of CH_3CN and 7.5 mL of THF. The cell was then equipped with a graphite anode and a nickel cathode, and then evacuated and backfilled with an argon balloon. This cycle was repeated three times. The reaction mixture was electrolyzed under a constant current of 15 mA (~ 6.25 mA/cm^2, 3.0 cm x 0.8 cm x 0.2 cm submerged) for 13.5 hours (7.5 F/mol) at room temperature. The reaction solution was concentrated under a vacuum and then purified by flash chromatography (PE/Et_2O = 5/1) to afford nitrile **4a** as a white solid (155 mg, yield: 55%).
  5 mmol scale experiment: To the 20 mL vial with a stir bar were successively added the benzylic substrate **1a** (10 mmol, 1820 mg, 2 equiv.), 1,4-dicyanobenzene **3a** (5 mmol, 640 mg, 1 equiv.), *n*-Bu_4NOTs (5 mmol, 2115 mg, 1.0 equiv.), pivaldehyde (5 mmol, 430 mg, 1.0 equiv.), 6 mL of CH_3CN and 6 mL of THF. The cell was then equipped with a graphite anode and a nickel cathode, and then evacuated and backfilled with an argon balloon. This cycle was repeated three times. The reaction mixture was electrolyzed under a constant current of 37.5 mA (~ 15.6 mA/cm^2, 3.0 cm x 0.8 cm x 0.2 cm submerged) for 21.5 hours (6 F/mol) at room temperature. The reaction solution was concentrated under a vacuum and then purified by flash chromatography (PE/Et_2O = 5/1) to afford nitrile **4a** as a white solid (950 mg, yield: 67%).

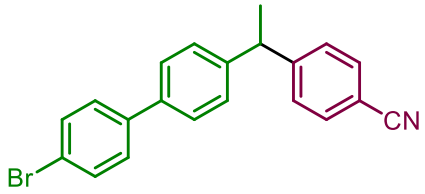
4-(1-([1,1'-biphenyl]-4-yl)ethyl)benzonitrile (4a):



Rf: 0.62 (PE/Et_2O = 3/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.56 (m, 6H), 7.51-7.44 (m, 2H), 7.41-7.34 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 1H), 1.72 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 143.8, 140.7, 139.6, 132.3, 128.8, 128.5, 128.0, 127.4, 127.3, 127.0, 119.0, 110.1, 44.6, 21.5.
HRMS-ESI: *m/z* 306.1239 ($[M+Na]^+$, $C_{21}H_{17}NNa^+$ calcd. 306.1253).
The spectral data are consistent with those reported in the literature.

- Compounds **4b** was prepared from 4-bromo-4'-ethyl-1,1'-biphenyl **1b** (104 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1) to afford nitrile **4b** as a white solid (16 mg, yield: 22 %).

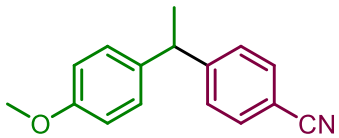
4-(1-(4'-bromo-[1,1'-biphenyl]-4-yl)ethyl)benzonitrile (4b):



Rf: 0.44 (PE/Et_2O = 3/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 144.4, 139.7, 138.5, 132.5, 132.0, 128.7, 128.6, 128.3, 127.3, 121.7, 119.1, 110.2, 44.7, 21.6.
HRMS-ESI: *m/z* 384.0368 ($[M+Na]^+$, $C_{21}H_{16}BrNNa^+$ calcd. 384.0358).

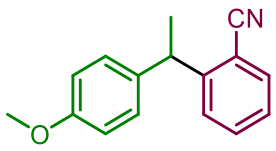
- Compounds **4c-*p*** and **4c-*o*** were prepared from 1-ethyl-4-methoxybenzene **1c** (54.4 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1, **Rf** = 0.44) to afford a 85:15 mixture of nitriles **4c-*p*** and **4c-*o*** as a colorless liquid (33 mg, yield: 70 %). **4c-*p*** and **4c-*o*** can be separated by preparative TLC (PE/Et_2O = 20/1).

4-(1-(4-methoxyphenyl)ethyl)benzonitrile (4c-*p*):



Rf: 0.10 (PE/Et_2O = 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 152.5, 136.9, 132.3, 128.6, 128.4, 119.1, 114.1, 109.9, 55.4, 44.2, 21.7.
HRMS-ESI: *m/z* 260.1034 ($[M+Na]^+$, $C_{16}H_{15}NNaO^+$ calcd. 260.1046).
The spectral data are consistent with those reported in the literature.[2]

2-(1-(4-methoxyphenyl)ethyl)benzonitrile (4c-*o*):

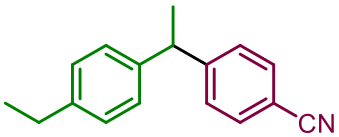


Rf: 0.12 (PE/Et_2O = 20/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.58 (q, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 150.9, 136.2, 133.2, 133.1, 128.8, 127.7, 126.7, 118.3, 114.1, 112.4, 55.4, 42.3, 21.7.
HRMS-ESI: *m/z* 260.1046 ($[M+Na]^+$, $C_{16}H_{15}NNaO^+$ calcd. 260.1046).

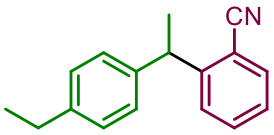
- Compounds **4d-*p*** and **4d-*o*** were prepared from 1,4-diethylbenzene **1d** (53.6 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1, **Rf** = 0.69) to afford a 85:15 mixture of nitriles **4d-*p*** and **4d-*o*** as a colorless liquid (34 mg, yield: 72 %). **4d-*p*** and **4d-*o*** can be separated by preparative TLC (PE/Et_2O = 20/1).

4-(1-(4-ethylphenyl)ethyl)benzonitrile (4d-*p*):



Rf: 0.24 (PE/Et_2O = 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.15 (q, *J* = 8.3 Hz, 2H), 7.10 (q, *J* = 8.3 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.64 (d, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 142.7, 142.0, 132.3, 128.5, 128.2, 127.6, 119.2, 110.0, 44.7, 28.5, 21.6, 15.6.
HRMS-ESI: *m/z* 258.1246 ($[M+Na]^+$, $C_{17}H_{17}NNa^+$ calcd. 258.1253).

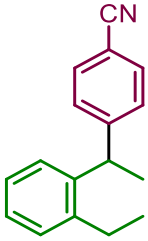
2-(1-(4-ethylphenyl)ethyl)benzonitrile (4d-*o*):



Rf: 0.26 (PE/Et_2O = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 4.60 (q, *J* = 7.2 Hz, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.68 (d, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 142.7, 141.2, 133.1, 133.1, 128.2, 127.8, 127.7, 126.7, 118.3, 112.4, 42.7, 28.5, 21.6, 15.6.
HRMS-ESI: *m/z* 258.1249 ($[M+Na]^+$, $C_{17}H_{17}NNa^+$ calcd. 258.1253).

- Compound **4e** was prepared from 1,2-diethylbenzene **1e** (53.6 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 5/1) to afford nitrile **4e** as a colorless liquid (19 mg, yield: 40 %).

4-(1-(2-ethylphenyl)ethyl)benzonitrile (4e):



Rf: 0.46 (PE/Et_2O = 5/1).

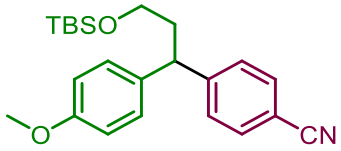
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.23-7.15 (m, 4H), 4.45 (q, *J* = 7.2 Hz, 1H), 2.72-2.45 (m, 2H), 1.63 (d, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 142.0, 141.9, 132.3, 129.0, 128.6, 127.2, 127.0, 126.4, 119.2, 109.9, 40.4, 25.7, 22.2, 15.4.

HRMS-ESI: *m/z* 258.1242 ($[M+Na]^+$, $C_{17}H_{17}NNa^+$ calcd. 258.1253).

- Compound **4f** was prepared from tert-butyl(3-(4-methoxyphenyl)propoxy)dimethylsilane **1f** (112 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1) to afford nitrile **4f** as a colorless liquid (39 mg, yield: 51 %).

4-(3-((tert-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)propyl)benzonitrile (4f):



Rf: 0.57 (PE/Et_2O = 3/1).

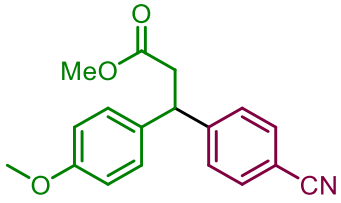
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.18 (t, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.51 (t, *J* = 6.2 Hz, 2H), 2.26-2.15 (m, 2H), 0.88 (s, 9H), -0.02 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 151.1, 135.3, 132.4, 129.0, 128.8, 119.1, 114.2, 110.0, 60.5, 55.4, 46.3, 38.2, 26.0, 18.4, -5.3.

HRMS-ESI: *m/z* 404.2000 ($[M+Na]^+$, $C_{23}H_{31}NNaO_2Si^+$ calcd. 404.2016).

- Compound **4g** was prepared from methyl 3-(4-methoxyphenyl)propanoate **1g** (77.6 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/EA = 3/1) to afford nitrile **4g** as a colorless liquid (31 mg, yield: 53 %).

methyl 3-(4-cyanophenyl)-3-(4-methoxyphenyl)propanoate (4g):

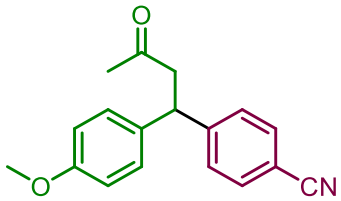


Rf: 0.44 (PE/EA = 3/1).

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.55 (t, *J* = 7.9 Hz, 1H), 3.77 (s, 3H), 3.59 (s, 3H), 3.03 (d, *J* = 7.9 Hz, 2H).
^{13}C NMR (90 MHz, $CDCl_3$) δ 171.9, 158.7, 149.4, 134.2, 132.6, 128.7, 128.5, 118.9, 114.4, 110.5, 55.4, 52.0, 46.3, 40.3.
HRMS-ESI: *m/z* 318.1094 ($[M+Na]^+$, $C_{18}H_{17}NNaO_3^+$ calcd. 318.1101).
The spectral data are consistent with those reported in the literature.[3]

- Compound **4h** was prepared from 4-(4-methoxyphenyl)butan-2-one **1h** (71.2 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1) to afford nitrile **4h** as a colorless liquid (37 mg, yield: 66 %).

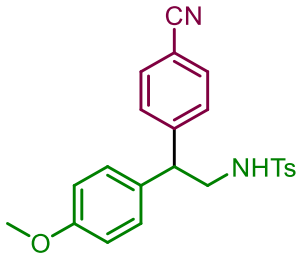
4-(1-(4-methoxyphenyl)-3-oxobutyl)benzonitrile (4h):



Rf: 0.55 (PE/Et_2O = 3/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.59 (t, *J* = 7.3 Hz, 1H), 3.76 (s, 3H), 3.16 (d, *J* = 7.3 Hz, 2H), 2.10 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 158.6, 150.0, 134.6, 132.5, 128.8, 128.6, 118.9, 114.4, 110.4, 55.4, 49.4, 45.2, 30.7.
HRMS-ESI: *m/z* 280.1337 ($[M+H]^+$, $C_{18}H_{18}NO_2^+$ calcd. 280.1332).
The spectral data are consistent with those reported in the literature.[3]

- Compound **4i** was prepared from *N*-(4-methoxyphenethyl)-4-methylbenzenesulfonamide **1i** (122 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (DCM/CH_3OH = 50/1) to afford nitrile **4i** as a white solid (10 mg, yield: 12 %).

***N*-(2-(4-cyanophenyl)-2-(4-methoxyphenyl)ethyl)-4-methylbenzenesulfonamide (4i):**

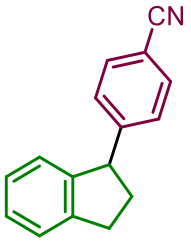


Rf: 0.44 (DCM/CH_3OH = 50/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7

Hz, 2H), 4.27 (t, *J* = 6.2 Hz, 1H), 4.10 (t, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.61-3.41 (m, 2H), 2.45 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 147.0, 143.9, 136.8, 132.6, 131.3, 130.0, 129.1, 128.8, 127.2, 118.7, 114.7, 111.0, 55.4, 50.1, 47.1, 21.7.
HRMS-ESI: *m/z* 429.1225 ($[M+Na]^+$, $C_{23}H_{22}N_2NaO_3S^+$ calcd. 429.1243).

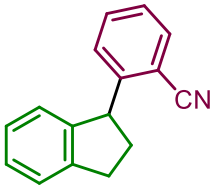
- Compounds **4j-*p*** and **4j-*o*** were prepared from 1-(tert-butyl)-4-methylbenzene **1j** (59.2 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1, **Rf** = 0.64) to afford a 82:18 mixture of nitriles **4j-*p*** and **4j-*o*** (*ortho*-nitrile) as a colorless liquid (27 mg, yield: 62 %). **4j-*p*** and **4j-*o*** can be separated by preparative TLC (PE/Et_2O = 20/1).

4-(2,3-dihydro-1H-inden-1-yl)benzonitrile (4j-*p*):



Rf: 0.19 (PE/Et_2O = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.3Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 4.41 (t, *J* = 8.2 Hz, 1H), 3.13-2.94 (m, 2H), 2.69-2.56 (m, 1H), 2.08-1.97 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 145.5, 144.4, 132.5, 129.0, 127.2, 126.8, 124.9, 124.7, 119.2, 110.3, 51.8, 36.5, 31.9.
HRMS-ESI: *m/z* 242.0931 ($[M+Na]^+$, $C_{16}H_{13}NNa^+$ calcd. 242.0940).

2-(2,3-dihydro-1H-inden-1-yl)benzonitrile (4j-*o*):

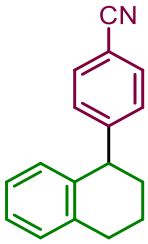


Rf: 0.22 (PE/Et_2O = 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.35-7.28 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 4.85 (t, *J* = 8.1 Hz, 1H), 3.13-2.95 (m, 2H), 2.80-2.69 (m, 1H), 2.10-1.96 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 144.9, 144.7, 133.2, 133.0, 128.3, 127.3, 127.0, 126.8, 125.0, 124.8, 118.3, 112.8, 49.7, 36.0, 31.9.
HRMS-ESI: *m/z* 242.0933 ($[M+Na]^+$, $C_{16}H_{13}NNa^+$ calcd. 242.0940).

- Compounds **4k-*p*** and **4k-*o*** were prepared from 1,2,3,4-tetrahydronaphthalene **1k** (52.8 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol),

following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1, **Rf** = 0.64) to afford a 81:19 mixture of nitriles **4k-*p*** and **4k-*o*** as a colorless liquid (27 mg, yield: 58 %). **4k-*p*** and **4k-*o*** can be separated by preparative TLC (PE/Et_2O = 20/1).

4-(1,2,3,4-tetrahydronaphthalen-1-yl)benzonitrile (4k-*p*):



Rf: 0.20 (PE/Et_2O = 20/1).

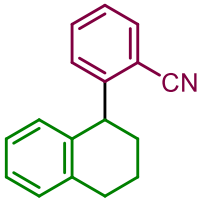
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.18-7.15 (m, 2H), 7.09-7.02 (m, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 4.20 (t, *J* = 6.4 Hz, 1H), 2.97-2.81 (m, 2H), 2.24-2.13 (m, 1H), 1.91-1.73 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 137.8, 137.8, 132.3, 130.1, 129.7, 129.4, 126.6, 126.1, 119.2, 110.0, 45.8, 33.1, 29.7, 20.8.

HRMS-ESI: *m/z* 256.1087 ([M+Na]$^+$, $C_{17}H_{15}NNa^+$ calcd. 256.1097).

The spectral data are consistent with those reported in the literature.[1]

2-(1,2,3,4-tetrahydronaphthalen-1-yl)benzonitrile (4k-*o*):



Rf: 0.23 (PE/Et_2O = 20/1).

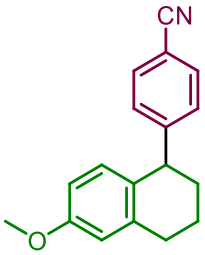
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.19-7.11 (m, 2H), 7.09-7.01 (m, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 4.61 (t, *J* = 6.7 Hz, 1H), 2.99-2.83 (m, 2H), 2.31-2.22 (m, 1H), 1.95-1.77(m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 138.1, 137.6, 133.1, 132.7, 130.1,130.1, 129.4, 126.7, 126.7, 126.2, 118.3, 112.7, 44.0, 32.4, 29.8, 20.9.

HRMS-ESI: *m/z* 256.1087 ([M+Na]$^+$, $C_{17}H_{15}NNa^+$ calcd. 256.1097).

- Compound **4l** was prepared from 6-methoxy-1,2,3,4-tetrahydronaphthalene **1l** (64.8 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1) to afford nitrile **4l** as a colorless liquid (21 mg, yield: 40 %).

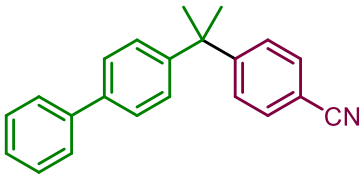
4-(6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)benzonitrile (4l):



Rf: 0.67(PE/Et_2O = 3/1).
^{1}H NMR (360 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.70-6.59 (m, 3H), 4.13 (t, *J* = 6.3 Hz, 1H), 3.79 (s, 3H), 2.95-2.77 (m, 2H), 2.21-2.10 (m, 1H), 1.87-1.69 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 153.6, 139.0, 132.2, 131.1, 130.0, 129.6, 119.3, 113.6, 112.5, 109.9, 55.3, 45.1, 33.3, 30.1, 20.7.
HRMS-ESI: *m/z* 264.1375 ($[M+H]^+$, $C_{18}H_{18}NNO^+$ calcd. 264.1383).

- Compound **4m** was prepared from 4-isopropyl-1,1'-biphenyl **1m** (78.4 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1) to afford nitrile **4m** as a white solid (19 mg, yield: 32 %).

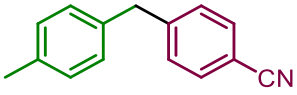
4-(2-([1,1'-biphenyl]-4-yl)propan-2-yl)benzonitrile (4m):



Rf: 0.62 (PE/Et_2O = 3/1).
^{1}H NMR (360 MHz, $CDCl_3$) δ 7.60-7.55 (m, 4H), 7.54-7.49 (m, 2H), 7.46-7.40 (m, 2H), 7.39-7.30 (m, 3H), 7.28-7.22 (m, 2H), 1.72 (s, 6H).
^{13}C NMR (90 MHz, $CDCl_3$) δ 156.3, 148.3, 140.7, 139.2, 132.1, 128.9, 127.8, 127.4, 127.3, 127.1, 119.2, 109.8, 43.5, 30.5.
HRMS-ESI: *m/z* 320.1421 ($[M+Na]^+$, $C_{22}H_{19}NNa^+$ calcd. 320.1410).

- Compounds **4n-*p*** and **4n-*o*** were prepared from *p*-xylene **1n** (42.4 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1, **Rf** = 0.50) to afford a 86:14 mixture of nitriles **4n-*p*** and **4n-*o*** as a colorless liquid (28 mg, yield: 68 %). **4n-*p*** and **4n-*o*** can be separated by preparative TLC (PE/Et_2O = 20/1).

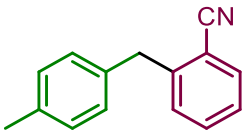
4-(4-methylbenzyl)benzonitrile (4n-*p*):



Rf: 0.18 (PE/Et_2O = 20/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.99 (s, 2H), 2.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 136.4, 132.4, 129.7, 129.6, 129.0, 119.1, 110.2, 41.7, 21.1.
HRMS-ESI: *m/z* 230.0935 ($[M+Na]^+$, $C_{15}H_{13}NNa^+$ calcd. 230.0940).
The spectral data are consistent with those reported in the literature.[4]

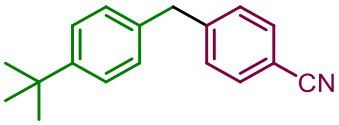
2-(4-methylbenzyl)benzonitrile (4n-*o*):



Rf: 0.21 (PE/Et_2O = 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.32-7.25 (m, 2H), 7.12 (s, 4H), 4.17 (s, 2H), 2.32 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 136.5, 135.9, 133.0, 133.0, 130.2, 129.6, 129.0, 126.8, 118.3, 112.7, 40.0, 21.2.
HRMS-ESI: *m/z* 230.0937 ($[M+Na]^+$, $C_{15}H_{13}NNa^+$ calcd. 230.0940).
The spectral data are consistent with those reported in the literature.[5]

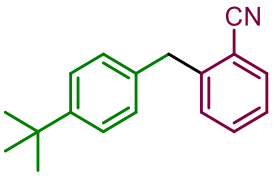
- Compounds **4o-*p*** and **4o-*o*** were prepared from 1-(tert-butyl)-4-methylbenzene **1o** (59.2 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1, **Rf** = 0.64) to afford a 84:16 mixture of nitriles **4o-*p*** and **4o-*o*** as a colorless liquid (28 mg, yield: 56 %). **4o-*p*** and **4o-*o*** can be separated by preparative TLC (PE/Et_2O = 20/1).

4-(4-(tert-butyl)benzyl)benzonitrile (4o-*p*):



Rf: 0.20 (PE/Et_2O = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 4.00 (s, 2H), 1.31 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 147.1, 136.4, 132.4, 129.8, 128.7, 125.8, 119.1, 110.2, 41.7, 34.6, 31.5.
HRMS-ESI: *m/z* 272.1399 ($[M+Na]^+$, $C_{18}H_{19}NNa^+$ calcd. 272.1410).
The spectral data are consistent with those reported in the literature.[4]

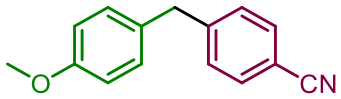
2-(4-(tert-butyl)benzyl)benzonitrile (4o-*o*):



Rf: 0.22 (PE/Et_2O = 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.30-7.27 (m, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 4.18 (s, 2H), 1.30 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 145.4, 135.9, 133.0, 133.0, 130.3, 128.8, 126.8, 125.8, 118.4, 112.8, 39.9, 34.6, 31.5.
HRMS-ESI: *m/z* 272.1405 ($[M+Na]^+$, $C_{18}H_{19}NNa^+$ calcd. 272.1410).
The spectral data are consistent with those reported in the literature.[5]

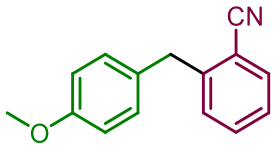
- Compounds **4p-*p*** and **4p-*o*** were prepared from 1-methoxy-4-methylbenzene **1p** (48.8 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1, **Rf** = 0.38) to afford a 76:24 mixture of nitriles **4p-*p*** and **4p-*o*** as a colorless liquid (32 mg, yield: 72 %). **4p-*p*** and **4p-*o*** can be separated by preparative TLC (PE/Et_2O = 20/1).

4-(4-methoxybenzyl)benzonitrile (4p-*p*):



Rf: 0.09 (PE/Et_2O = 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 2H), 3.78 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 147.4, 132.4, 131.5, 130.1, 129.6, 119.1, 114.3, 110.0, 55.4, 41.2.
HRMS-ESI: *m/z* 246.0883 ($[M+Na]^+$, $C_{15}H_{13}NNaO^+$ calcd. 246.0889).
The spectral data are consistent with those reported in the literature.[4]

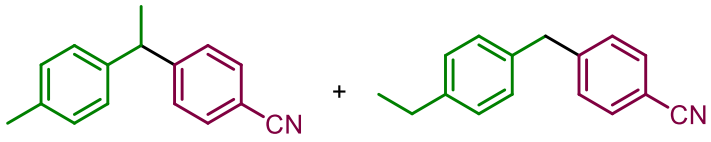
2-(4-methoxybenzyl)benzonitrile (4p-*o*):



Rf: 0.11 (PE/Et_2O = 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.32-7.23 (m, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.15 (s, 2H), 3.79 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 145.6, 133.1, 133.0, 131.0, 130.1, 130.1, 126.8, 118.4, 114.3, 112.6, 55.4, 39.5.
HRMS-ESI: *m/z* 246.0885 ($[M+Na]^+$, $C_{15}H_{13}NNaO^+$ calcd. 246.0889).
The spectral data are consistent with those reported in the literature.[5]

- Compounds **4q** and **4r** were prepared from 1-ethyl-4-methylbenzene **1q** (48 mg, 0.4 mmol) and 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1) to afford a 77:23 mixture of nitriles **4q** and **4r** as a colorless liquid (12 mg, yield: 27 %).

4-(1-(p-tolyl)ethyl)benzonitrile (4q) and 4-(4-ethylbenzyl)benzonitrile (4r):



4q **4r**

Rf: 0.58 (PE/Et_2O = 3/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.52 (m, 2H), 7.34-7.26 (m, 2H), 7.18-7.04 (m, 4H), 4.17 (q, *J* = 7.2 Hz, 0.77H$_{4p}$), 4.00 (s, 0.46H$_{4q}$), 2.63 (q, *J* = 7.6 Hz, 0.46H$_{4q}$), 2.32 (s, 2.3 H$_{4p}$), 1.63 (d, *J* = 7.2 Hz, 2.3H$_{4p}$), 1.23 (t, *J* = 7.6 Hz, 0.69H$_{4q}$).

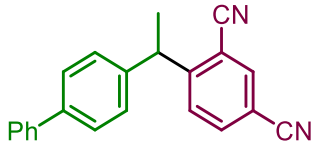
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 147.2, 142.8, 141.8, 136.6, 136.3, 132.4, 132.4, 129.7, 129.5, 129.0, 128.5, 128.4, 127.5, 119.2, 110.0, 109.9, 44.6, 41.7, 28.6, 21.6, 21.1, 15.7.

HRMS-ESI: *m/z* 244.1087 ([M+Na]$^+$, $C_{16}H_{15}NNa^+$ calcd. 244.1097).

The spectral data are consistent with those reported in the literature.[6, 7]

- Compounds **4s-*o*** and **4s-*m*** were prepared from 4-ethyl-1,1'-biphenyl **1a** (72.8 mg, 0.4 mmol) and benzene-1,2,4-tricarbonitrile **3b** (30.6 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1) to afford nitrile **4s-*o*** as a white solid (16 mg, yield: 26 %) and nitrile **4s-*m*** as a white solid (12 mg, yield: 19 %).

4-(1-([1,1'-biphenyl]-4-yl)ethyl)isophthalonitrile (4s-*o*):



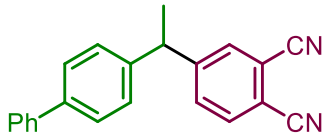
Rf: 0.14 (PE/Et_2O = 3/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.5 Hz, 1H), 7.80 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.60-7.54 (m, 4H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.46-7.41 (m, 2H), 7.38-7.29 (m, 3H), 4.72 (q, *J* = 7.2 Hz, 1H), 1.75 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (90 MHz, $CDCl_3$) δ 155.4, 141.3, 140.6, 140.4, 136.5, 136.2, 129.1, 129.0, 128.2, 127.7, 127.6, 127.2, 116.9, 116.2, 114.1, 111.7, 43.1, 21.2.

HRMS-ESI: *m/z* 331.1192 ([M+Na]$^+$, $C_{22}H_{16}N_2Na^+$ calcd. 331.1206).

4-(1-([1,1'-biphenyl]-4-yl)ethyl)phthalonitrile (4s-*m*):



Rf: 0.22 (PE/Et_2O = 3/1).

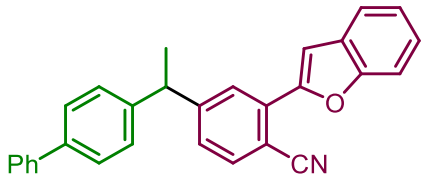
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.63-7.53 (m, 5H), 7.47-7.41 (m, 2H), 7.38-7.32 (m, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 1H), 1.71 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (90 MHz, $CDCl_3$) δ 153.1, 142.3, 140.6, 140.4, 133.8, 133.1, 133.0, 132.6, 129.0, 128.1, 127.9, 127.6, 127.2, 116.3, 115.6, 113.7, 44.5, 21.4.

HRMS-ESI: *m/z* 331.1194 ([M+Na]$^+$, $C_{22}H_{16}N_2Na^+$ calcd. 331.1206).

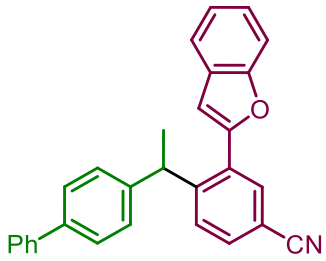
- Compounds **4t-*m*** and **4t-*o*** were prepared from 4-ethyl-1,1'-biphenyl **1a** (72.8 mg, 0.4 mmol) and 2-(benzofuran-2-yl)terephthalonitrile **3c** (48.8 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1, **Rf** = 0.67) to afford a 5:4 mixture of nitrile **4t-*o*** and nitrile **4t-*m*** as a colorless liquid (51 mg, yield: 64 %). **4t-*m*** and **4t-*o*** can be separated by preparative TLC (PE/DCM = 5/1).

4-(1-([1,1'-biphenyl]-4-yl)ethyl)-2-(benzofuran-2-yl)benzonitrile (4t-*m*):



Rf: 0.33 (PE/DCM = 5/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.8 Hz, 1H), 7.73-7.63 (m, 3H), 7.59-7.54 (m, 5H), 7.45-7.40 (m, 2H), 7.38-7.27 (m, 6H), 4.33 (q, *J* = 7.2 Hz, 1H), 1.77 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 152.3, 151.5, 143.7, 140.8, 139.8, 134.8, 133.3, 128.9, 128.1, 127.8, 127.6, 127.4, 127.2, 126.4, 125.8, 123.5, 122.1, 119.2, 111.4, 107.0, 106.1, 44.9, 21.6.
HRMS-ESI: *m/z* 422.1496 ([M+Na]$^+$, $C_{29}H_{21}NNaO^+$ calcd. 422.1515).

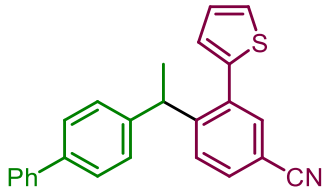
4-(1-([1,1'-biphenyl]-4-yl)ethyl)-3-(benzofuran-2-yl)benzonitrile (4t-*o*):



Rf: 0.28 (PE/DCM = 5/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.7 Hz, 1H), 7.66-7.60 (m, 2H), 7.58-7.54 (m, 3H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.48-7.40 (m, 3H), 7.39-7.28 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 0.9 Hz, 1H), 4.86 (q, *J* = 7.1 Hz, 1H), 1.71 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 153.3, 150.5, 143.7, 140.8, 139.6, 133.6, 132.4, 131.4, 129.7, 128.9, 128.7, 128.1, 127.4, 127.1, 125.2, 123.4, 121.5, 118.6, 111.5, 110.7, 106.9, 40.6, 22.0.
HRMS-ESI: *m/z* 422.1491 ([M+Na]$^+$, $C_{29}H_{21}NNaO^+$ calcd. 422.1515).

- Compounds **4u-*o*** and **4u-*m*** were prepared from 4-ethyl-1,1'-biphenyl **1a** (72.8 mg, 0.4 mmol) and 2-(thiophen-2-yl)terephthalonitrile **3d** (42 mg, 0.2 mmol), following general procedure **A** and purified by preparative TLC (PE/Et_2O = 3/1) to afford nitrile **4u-*o*** as a colorless liquid (11 mg, yield: 15 %) and nitrile **4u-*m*** as a colorless liquid (22 mg, yield: 30 %).

4-(1-([1,1'-biphenyl]-4-yl)ethyl)-3-(thiophen-2-yl)benzonitrile (4u-*o*):



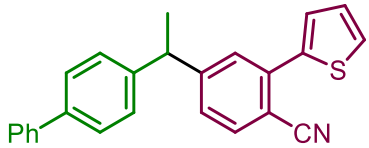
Rf: 0.62 (PE/Et_2O = 3/1).

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.68 (d, *J* = 1.8 Hz, 1H), 7.62-7.54 (m, 3H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.46-7.39 (m, 4H), 7.36-7.31 (m, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.10 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.98 (dd, *J* = 3.5, 1.1 Hz, 1H), 4.61 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (90 MHz, $CDCl_3$) δ 151.2, 144.0, 140.8, 139.8, 139.4, 135.4, 135.0, 131.9, 129.1, 128.9, 128.0, 127.9, 127.5, 127.4, 127.3, 127.1, 126.7, 118.7, 110.1, 40.4, 22.1.

HRMS-ESI: *m/z* 388.1112 ([M+Na]$^+$, $C_{25}H_{19}NNaS^+$ calcd. 388.1130).

4-(1-([1,1'-biphenyl]-4-yl)ethyl)-2-(thiophen-2-yl)benzonitrile (4u-*m*):



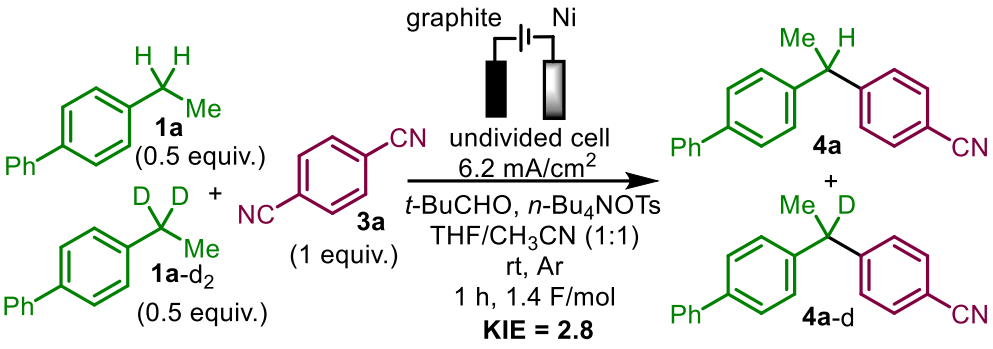
Rf: 0.55 (PE/Et_2O = 3/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.60-7.51 (m, 5H), 7.47-7.40 (m, 3H), 7.37-7.31 (m, 1H), 7.31-7.24 (m, 3H), 7.15 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 1H), 1.72 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (90 MHz, $CDCl_3$) δ 152.2, 143.6, 140.8, 139.8, 139.8, 137.9, 134.6, 129.2, 128.9, 128.3, 128.1, 127.8, 127.6, 127.4, 127.3, 127.2, 119.1, 108.0, 44.8, 21.6.

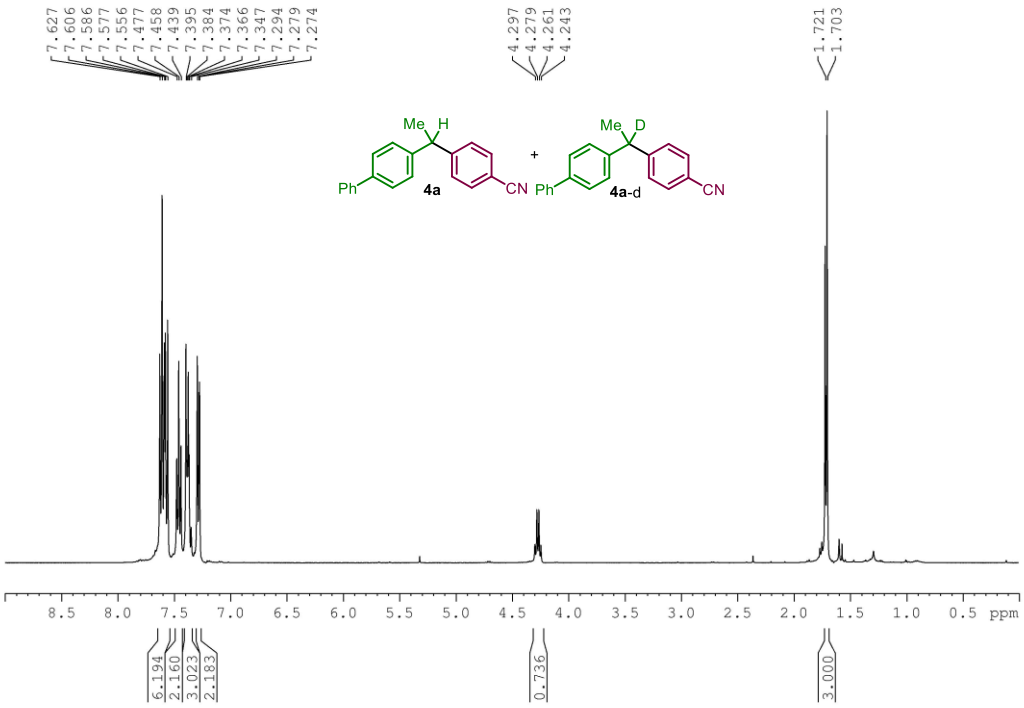
HRMS-ESI: *m/z* 388.1113 ([M+Na]$^+$, $C_{25}H_{19}NNaS^+$ calcd. 388.1130).

Competitive experiment between 1a and 1a-d_2

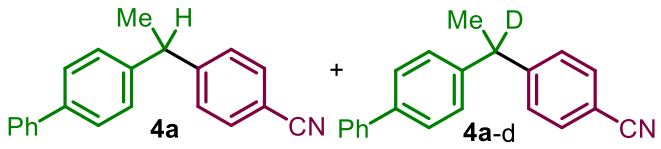


To the 5 mL vial with a stir bar were successively added benzylic substrate 4-ethyl-1,1'-biphenyl **1a** (18.2 mg, 0.1 mmol), **1a**-d_2 (18.4 mg, 0.1 mmol), 1,4-dicyanobenzene **3a** (25.6 mg, 0.2 mmol), *n*-Bu_4NOTs (0.2 mmol, 82.6 mg), pivaldehyde (0.2 mmol, 17.2 mg), 1.5 mL of CH_3CN and 1.5 mL of THF. The cell was then equipped with a graphite anode and a nickel-plated cathode, and then evacuated and backfilled with an argon balloon. This cycle was repeated three times. The reaction mixture was electrolyzed under a constant current of 7.5 mA (~ 6.25 mA/cm^2, 1.5 cm x 0.8 cm x 0.2 cm submerged) for 1 hours (1.4 F/mol) at room temperature. The reaction solution was concentrated under a vacuum and then purified by preparative TLC (PE/Et_2O = 3/1) to afford nitrile **4a** and **4a**-d as a white solid (13 mg, yield: 23%) in a ratio of 74:26.

^{1}H NMR (400 MHz, $CDCl_3$), **4a** and **4a**-d



4-(1-([1,1'-biphenyl]-4-yl)ethyl)benzonitrile (4a) and 4-(1-([1,1'-biphenyl]-4-yl)ethyl-1-d)benzonitrile (4a-d):



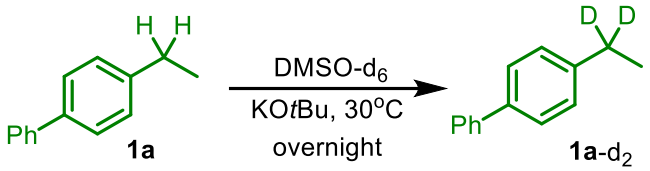
Rf: 0.62 (PE/Et_2O = 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.55 (m, 6H), 7.51-7.44 (m, 2H), 7.42-7.34 (m, 3H), 7.33-7.25 (m, 2H), 4.27 (q, *J* = 7.2 Hz, 0.74H), 1.72 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) 151.9, 143.8, 140.8, 139.7, 132.4, 128.9, 128.6, 128.1, 127.5, 127.4, 127.1, 119.1, 110.1, 44.7, 21.6$_{4a}$, 21.5$_{4a\text{-}d}$.

HRMS-ESI: **4a** *m/z* 306.1231 ([M+Na]$^+$, $C_{21}H_{17}NNa^+$ calcd. 306.1253). **4a**-d *m/z* 307.1280 ([M+Na]$^+$, $C_{21}H_{16}DNNa^+$ calcd. 307.1316).

Preparation of **1a**-d_2



To a 5mL flask charged with **1a** (1 mmol, 182 mg, 1.0 equiv.) and KO*t*Bu (1 mmol, 112 mg, 1.0 equiv.) was added DMSO-d_6 (1 mL) under argon atmosphere and the resulting reaction mixture was stirred at 30°C for overnight (oil bath). The reaction mixture was directly purified by flash column chromatography (PE) to give the **1a**-d_2 as a white solid (178 mg, 97% yield, 96% D-rate).

4-(ethyl-1,1-d_2)-1,1'-biphenyl (1a-d_2):

Rf: 0.61 (PE).

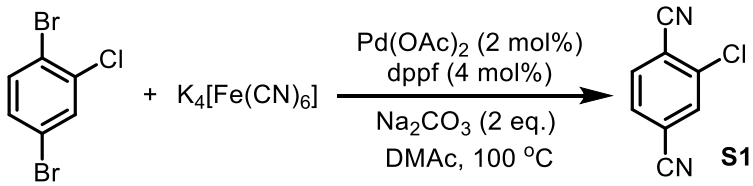
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.57 (m, 2H), 7.57- 7.50 (m, 2H), 7.48-7.40 (m, 2H), 7.38-7.32 (m, 1H), 7.32-7.27 (m, 2H), 2.75-2.64 (m, 0.09H, 96% D, benzylic C*H*), 1.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 141.3, 138.7, 128.8, 128.4, 127.2, 127.1, 127.1, 28.63-27.30 (m), 15.57.

The spectral data are consistent with those reported in the literature.[8]

Synthesis of substituted 1,4-dicyanoarenes 3b-d

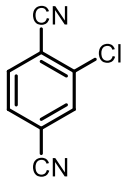
Compound **S1**



A dried Schlenk tube was charged with 1,4-dibromo-2-chlorobenzene (0.5 mmol, 135.2 mg), Na_2CO_3 (1.0 mmol, 106 mg 2.0 equiv.), $K_4[Fe(CN)_6]$ (0.25 mmol, 92.3 mg, 0.5 equiv.){$K_4[Fe(CN)_6]\cdot 3H_2O$ was grounded to a fine powder and dried in vacuum (ca. 2 mbar) at 80 °C overnight}, $Pd(OAc)_2$ (0.01 mmol, 2.24 mg, 2 mol%), and dppf (0.02

mmol, 11.1 mg, 4 mol%) in an argon atmosphere. Then 2.0 mL DMAc was added. The Schlenk tube was sealed and stirred at 130 °C overnight. After cooling to room temperature, the reaction mixture was filtered through celite and washed with 30 mL ethyl acetate. The solution was extracted with ethyl acetate (2 x 30 mL), the combined organic phases were washed with brine (2 x 30 mL), and then dried over Na_2SO_4. After evaporation of the solvents, the residue was subjected to purification by column chromatography (PE/EA = 5/1) to give the product **S1** (42 mg, 52%) as an off-white solid.[9]

2-chloroterephthalonitrile (S1):

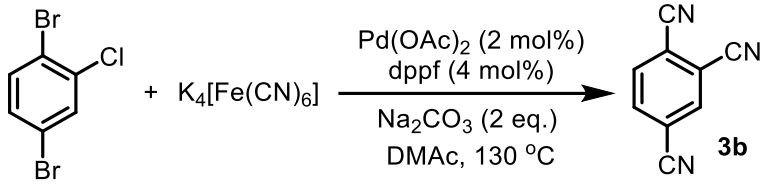


Rf: 0.53 (PE/EA = 5/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86-7.79 (m, 2H), 7.69 (dd, *J* = 8.0, 1.4 Hz, 1H).

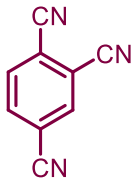
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 134.7, 133.3, 130.7, 117.9, 116.0, 114.5.

Compound **3b**



A dried Schlenk tube was charged with 1,4-dibromo-2-chlorobenzene (0.5 mmol, 135.2 mg), Na_2CO_3 (1.0 mmol, 106 mg 2.0 equiv.), $K_4[Fe(CN)_6]$ (0.25 mmol, 92.3 mg, 0.5 equiv.){$K_4[Fe(CN)_6]\cdot 3H_2O$ was grounded to a fine powder and dried in vacuum (ca. 2 mbar) at 80 °C overnight}, $Pd(OAc)_2$ (0.01 mmol, 2.24 mg, 2 mol%), and dppf (0.02 mmol, 11.1 mg, 4 mol%) in an argon atmosphere. Then 2.0 mL DMAc was added. The Schlenk tube was sealed and stirred at 130 °C overnight. After cooling to room temperature, the reaction mixture was filtered through celite and washed with 30 mL ethyl acetate. The solution was extracted with ethyl acetate (2 x 30 mL), the combined organic phase were washed with brine (2 x 30 mL), and then dried over Na_2SO_4. After evaporation of the solvents, the residue was subjected to purification by column chromatography (PE/EA = 5/1) to give the product **3b** (35 mg, 46%) as a yellow solid.[8]

benzene-1,2,4-tricarbonitrile (3b):

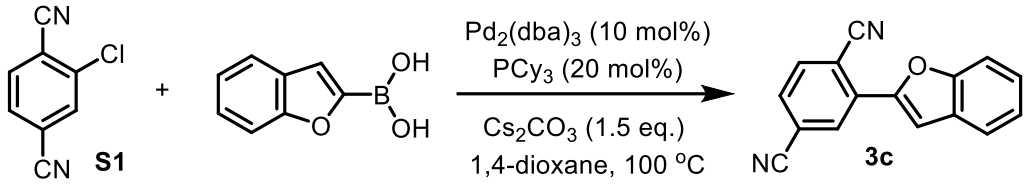


Rf: 0.22 (PE/EA = 5/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.4 Hz, 1H), 8.05 (dd, *J* = 8.1 Hz, 1.4, 1H), 7.99 (d, *J* = 8.1 Hz, 1H).

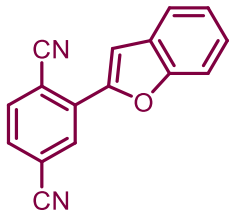
^{13}C NMR (90 MHz, $CDCl_3$) δ 136.6, 136.4, 134.5, 119.8, 117.8, 117.6, 115.3, 114.1, 113.6.
The spectral data are consistent with those reported in the literature.[10]

Compound **3c**



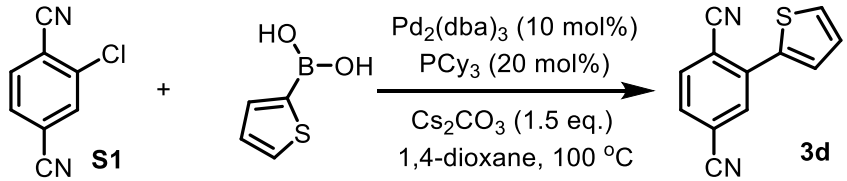
A dried Schlenk tube was charged with 2-chloroterephthalonitrile **S1** (0.2 mmol, 32.4 mg), Cs_2CO_3 (0.3 mmol, 97.7 mg, 1.5 equiv.), benzofuran-2-ylboronic acid (0.3 mmol, 48.6 mg, 1.5 equiv.), $Pd_2(dba)_3$ (0.02 mmol, 18.3 mg, 10 mol%), and PCy_3 (0.04 mmol, 11.2 mg, 20 mol%) in an argon atmosphere. Then 2.0 mL of 1,4-dioxane was added. The Schlenk tube is sealed and stirred at 100 °C overnight. After cooling to room temperature, the reaction mixture was filtered through celite and washed with 30 mL ethyl acetate. The solution was concentrated under vacuum to give the crude product. The residue was subjected to purification by column chromatography (PE/ Et_2O = 4/1) to give the product **3c** (38 mg, 78%) as a yellow solid.[11]

2-(benzofuran-2-yl)terephthalonitrile (3c):



Rf: 0.42 (PE/ Et_2O = 4/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.4 Hz, 1H), 7.87-7.80 (m, 2H), 7.70-7.62 (m, 2H), 7.59-7.53 (m, 1H), 7.45-7.38 (m, 1H), 7.34-7.27 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 148.9, 135.0, 134.0, 130.6, 130.4, 128.4, 126.9, 124.0, 122.5, 117.4, 117.2, 117.0, 111.6, 111.4, 108.8.
HRMS-ESI: *m/z* 267.0518 ($[M+Na]^+$, $C_{16}H_8N_2NaO^+$ calcd. 267.0529).

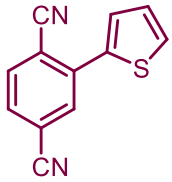
Compound **3d**



A dried Schlenk tube was charged with 2-chloroterephthalonitrile **8** (0.2 mmol, 32.4 mg), Cs_2CO_3 (0.3 mmol, 97.7 mg, 1.5 equiv.), thiophen-2-ylboronic acid (0.3 mmol, 37 mg, 1.5 equiv.), $Pd_2(dba)_3$ (0.02 mmol, 18.3 mg, 10 mol%), and PCy_3 (0.04 mmol, 11.2 mg, 20 mol%) in an argon atmosphere. Then 2.0 mL of 1,4-dioxane was added. The Schlenk tube was sealed and stirred at 100 °C overnight. After cooling to room

temperature, the reaction mixture was filtered through celite and washed with 30 mL ethyl acetate. The solution was concentrated under a vacuum to give the crude product. The residue was subjected to purification by column chromatography (PE/DCM/Et_2O = 6/1/1) to give the product **3d** (28 mg, 67%) as a yellow solid.[11]

2-(thiophen-2-yl)terephthalonitrile (3d):



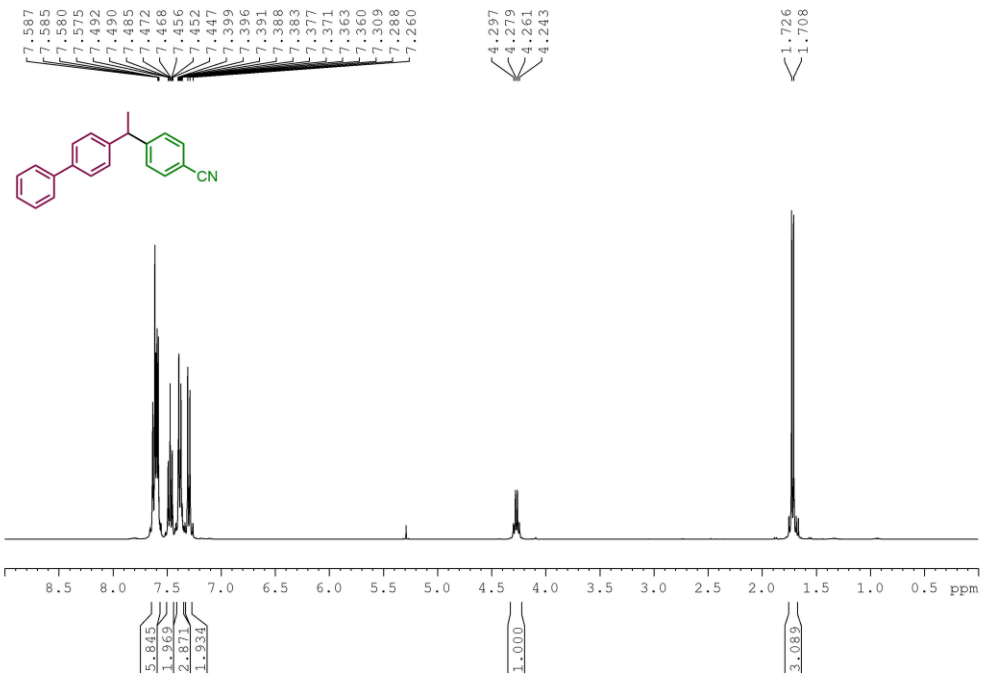
Rf: 0.45 (PE/DCM/Et_2O = 6/1/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (dd, *J* = 3.6 Hz, 1.0 Hz, 1H), 7.65 (dd, *J* = 8.0 Hz, 1.4 Hz, 1H), 7.54 (dd, *J* = 5.1 Hz, 1.0 Hz, 1H), 7.23-7.18 (m, 1H).

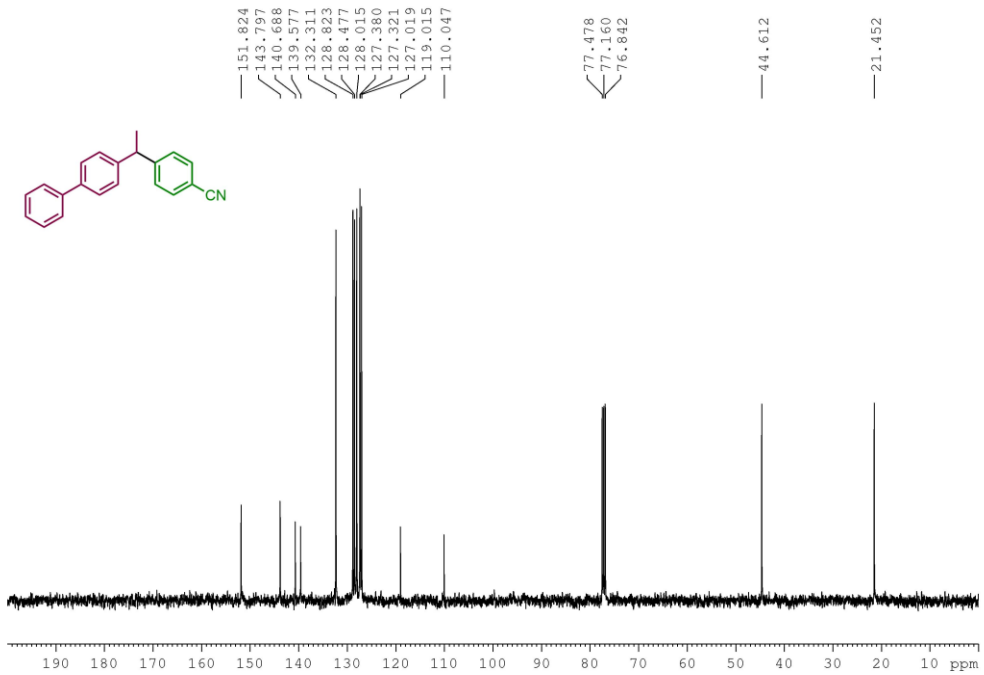
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.1, 135.1, 133.0, 130.3, 129.1, 129.0, 128.9, 117.4, 117.1, 117.0, 113.9.

E. NMR Spectra of products

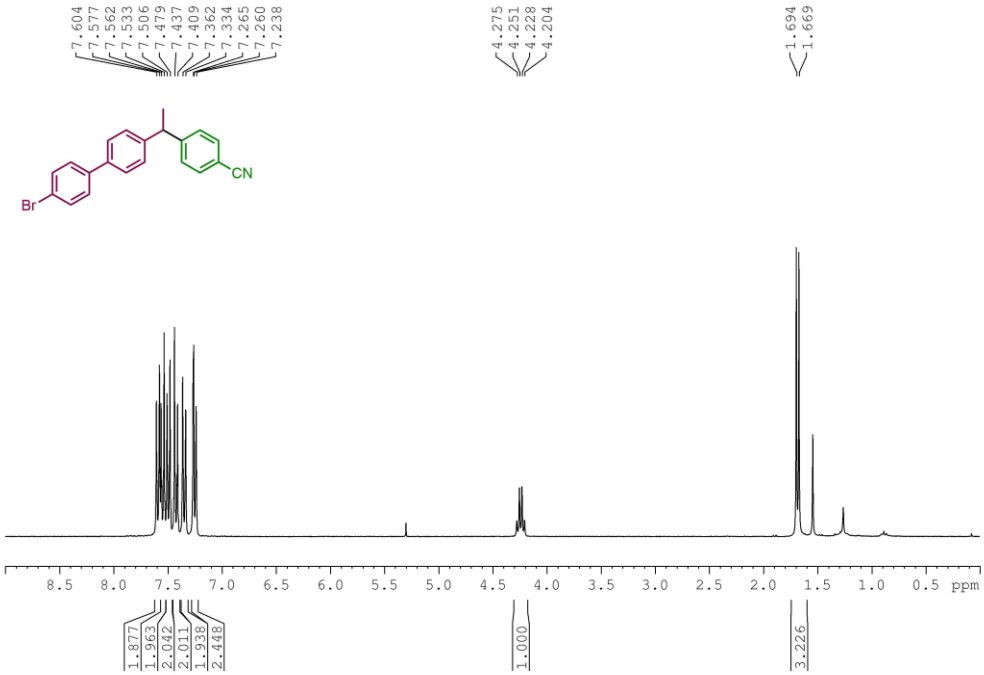
^{1}H NMR (400 MHz, $CDCl_3$), **4a**



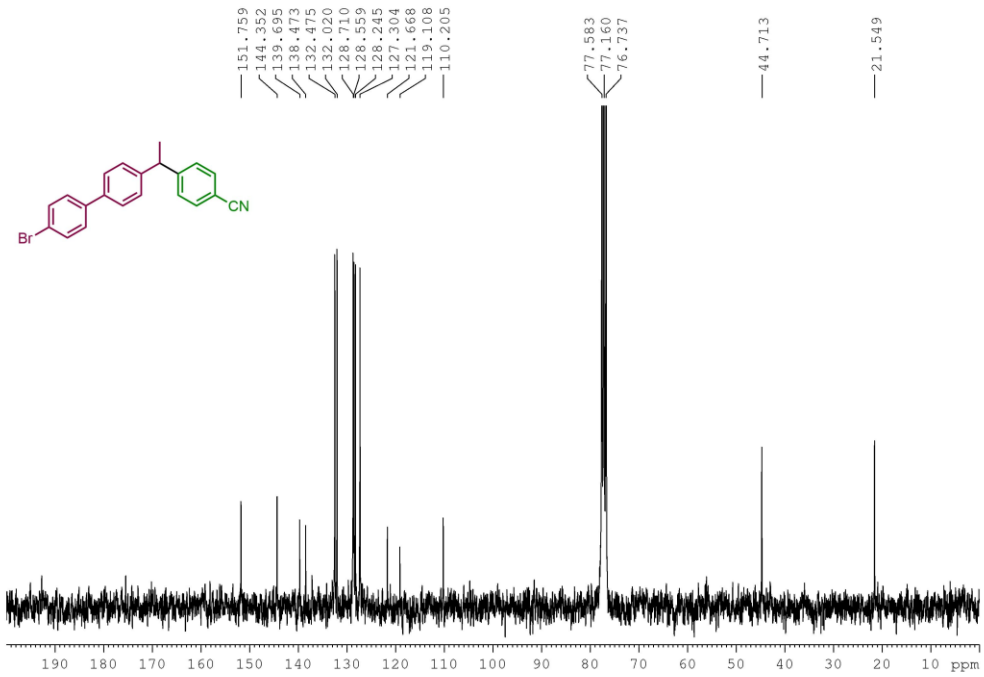
^{13}C NMR (100 MHz, $CDCl_3$), **4a**



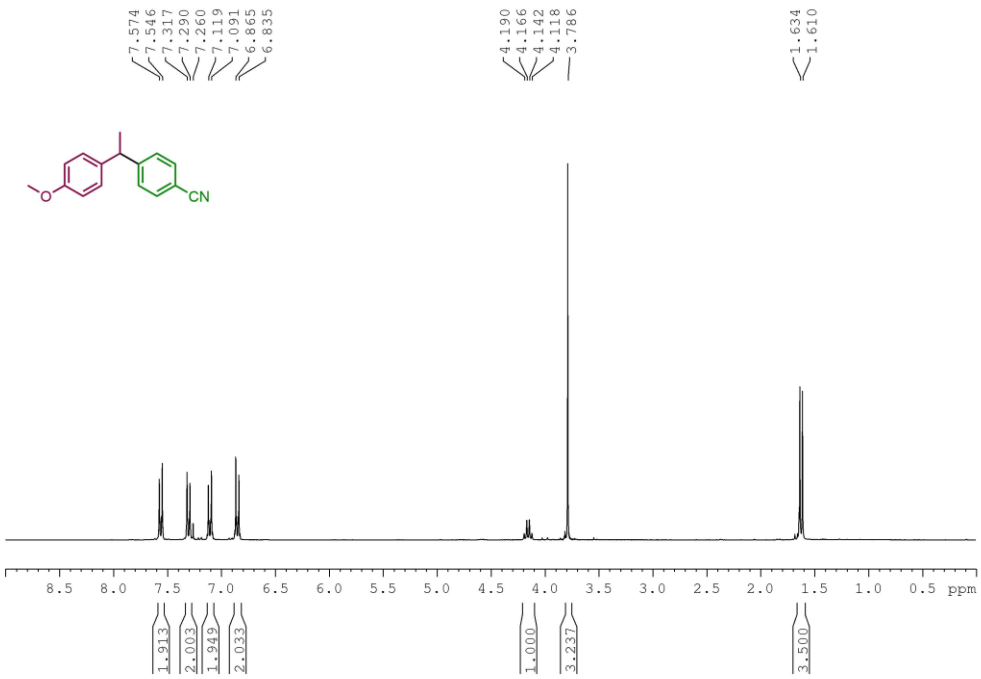
^{1}H NMR (300 MHz, $CDCl_3$), **4b**



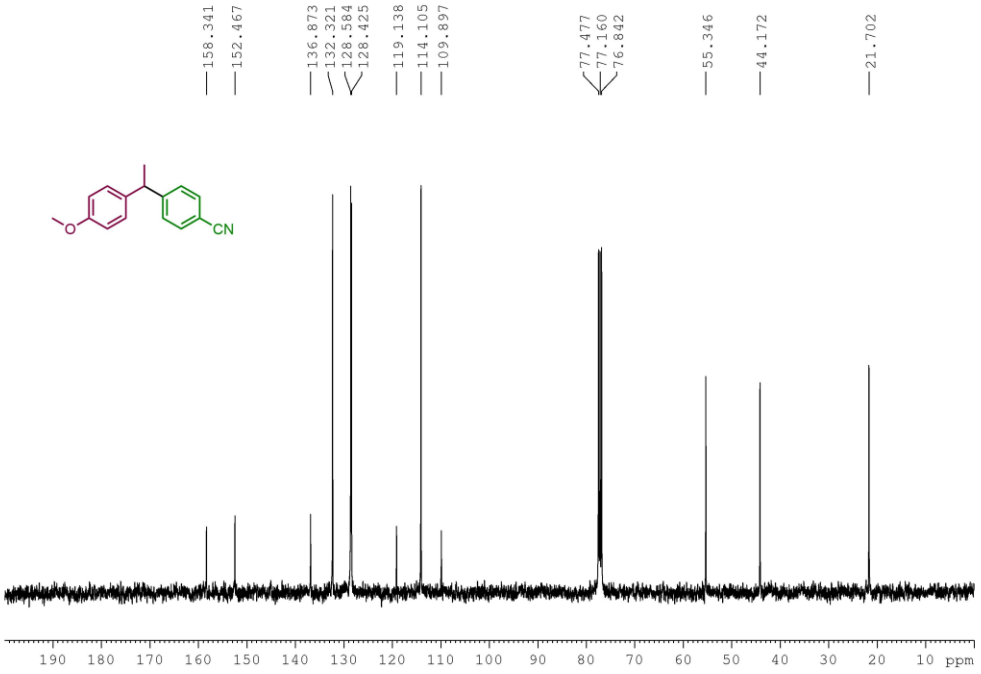
^{13}C NMR (75 MHz, $CDCl_3$), **4b**



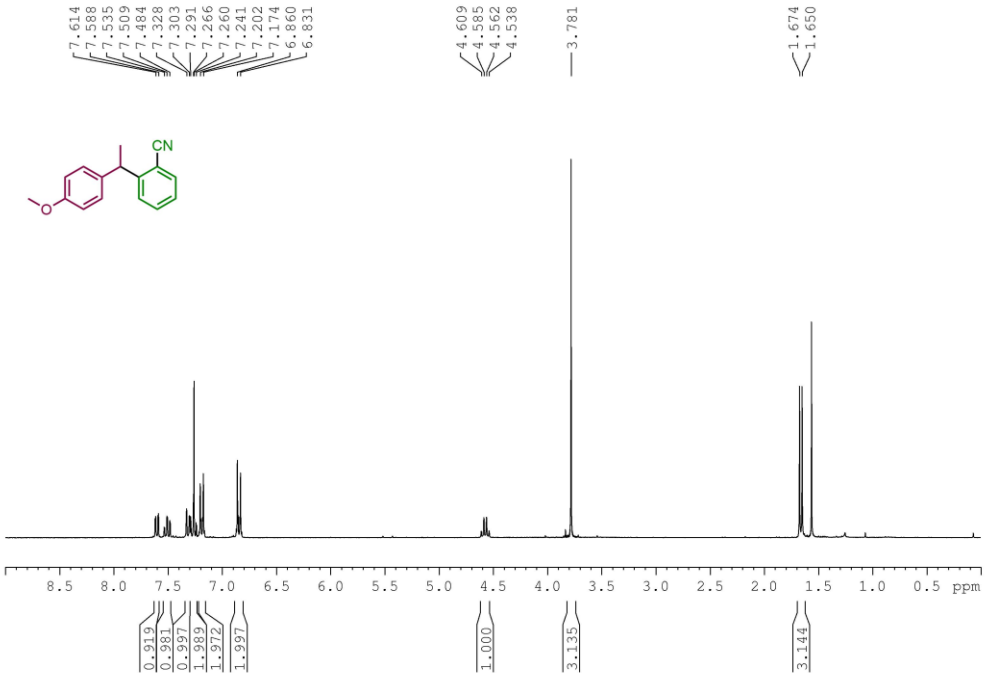
^{1}H NMR (300 MHz, $CDCl_3$), **4c-*p***



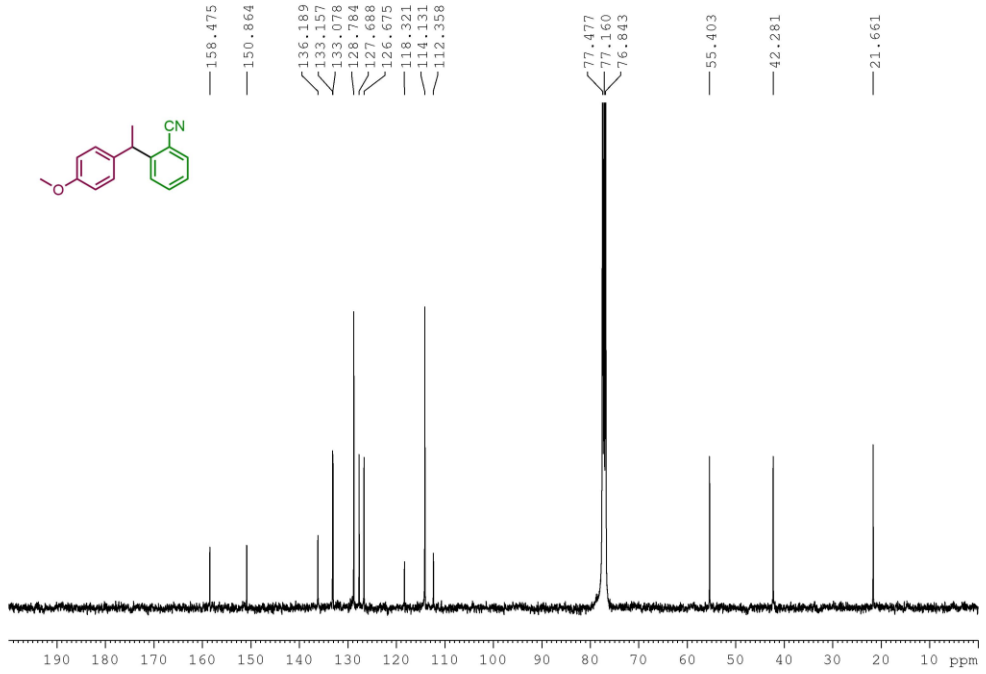
^{13}C NMR (100 MHz, $CDCl_3$), **4c-*p***



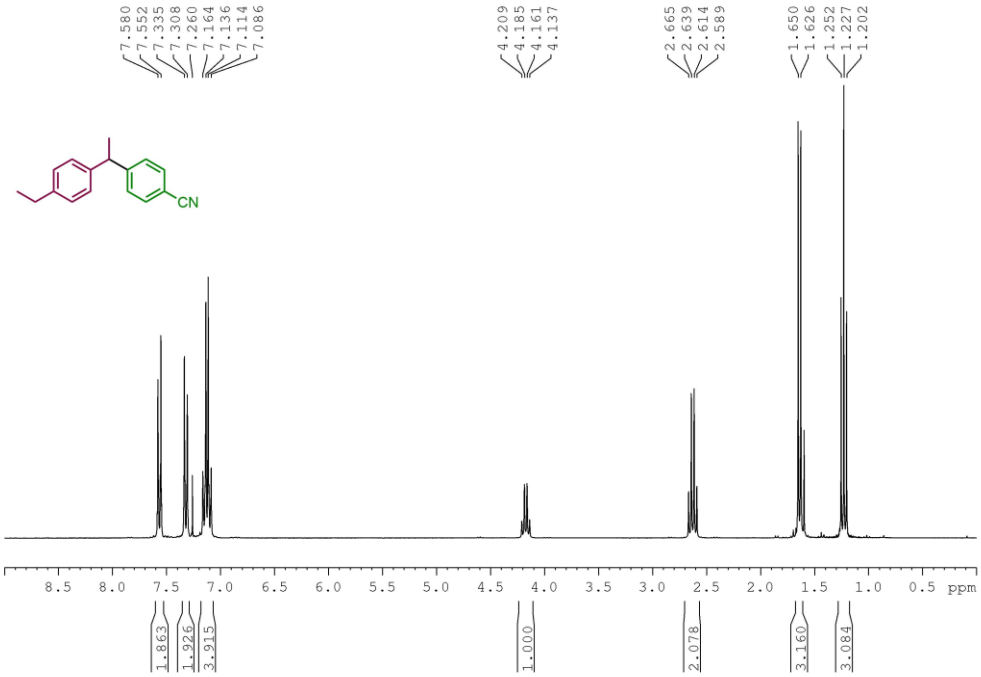
^{1}H NMR (300 MHz, $CDCl_3$), **4c-*o***



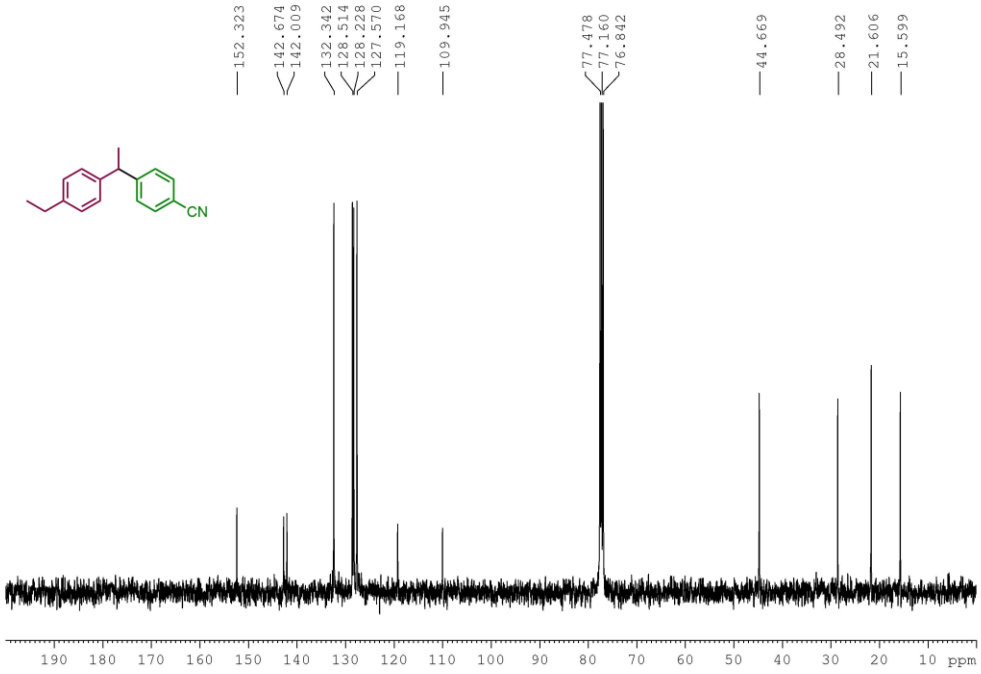
^{13}C NMR (100 MHz, $CDCl_3$), **4c-*o***



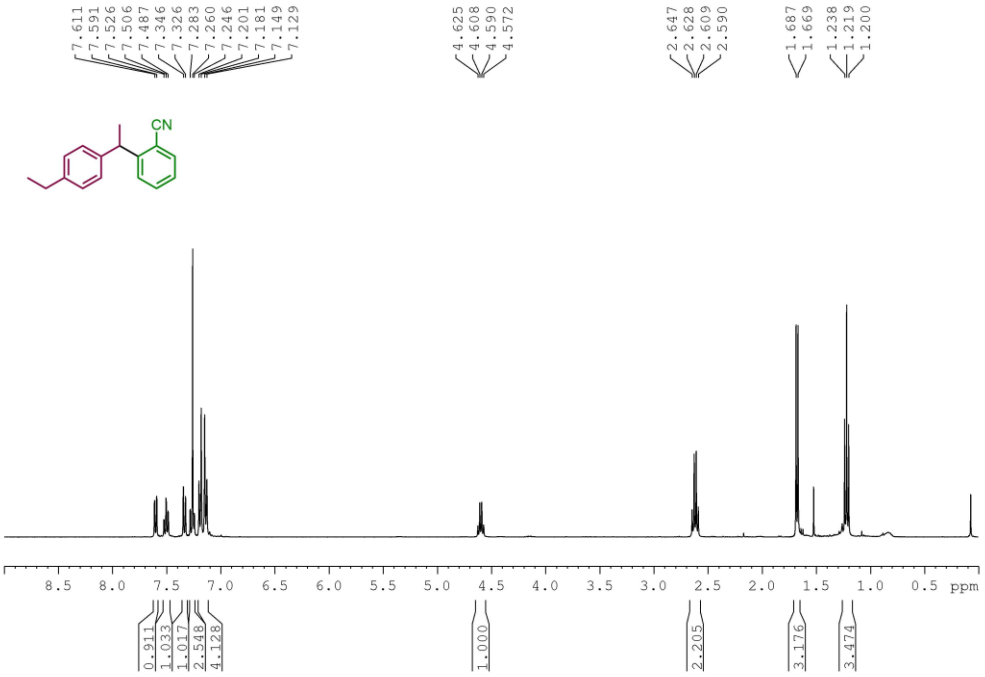
^{1}H NMR (300 MHz, $CDCl_3$), **4d-*p***



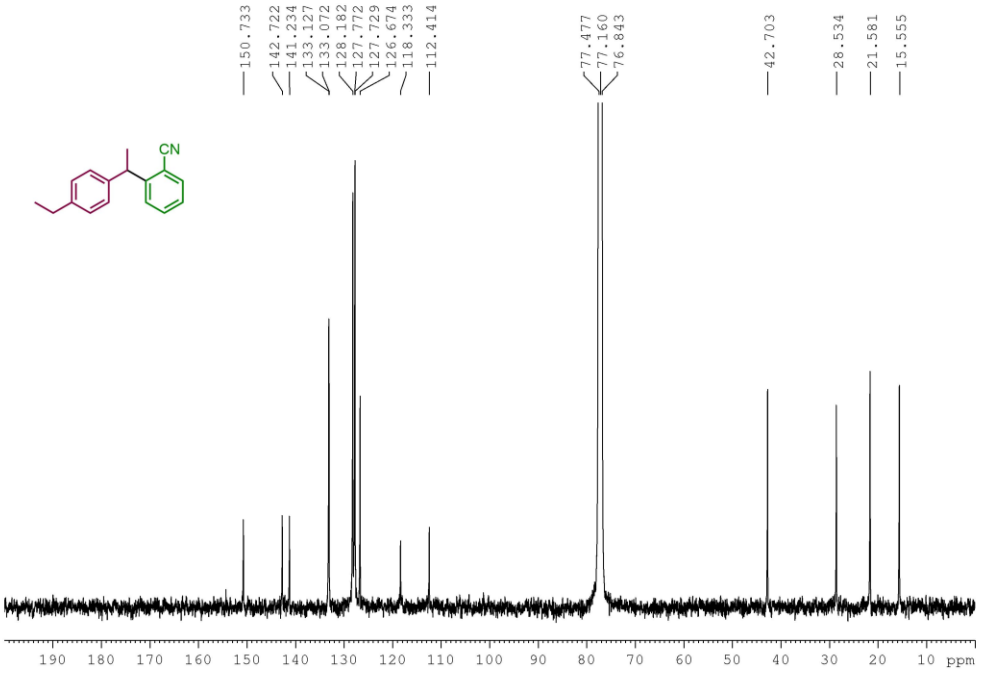
^{13}C NMR (100 MHz, $CDCl_3$), **4d-*p***



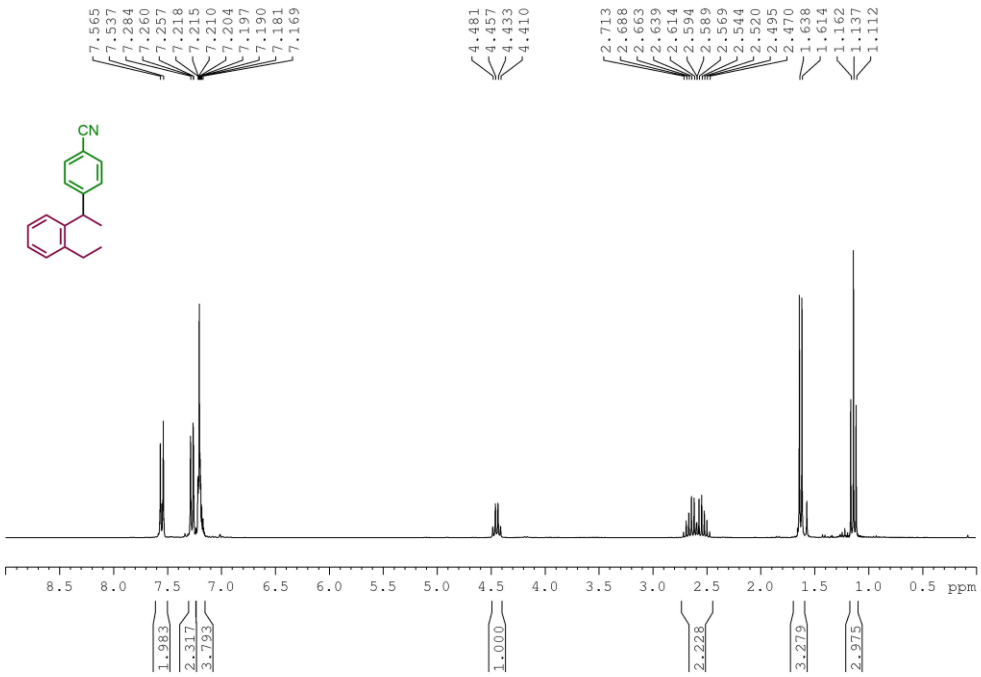
^{1}H NMR (400 MHz, $CDCl_3$), **4d-*o***



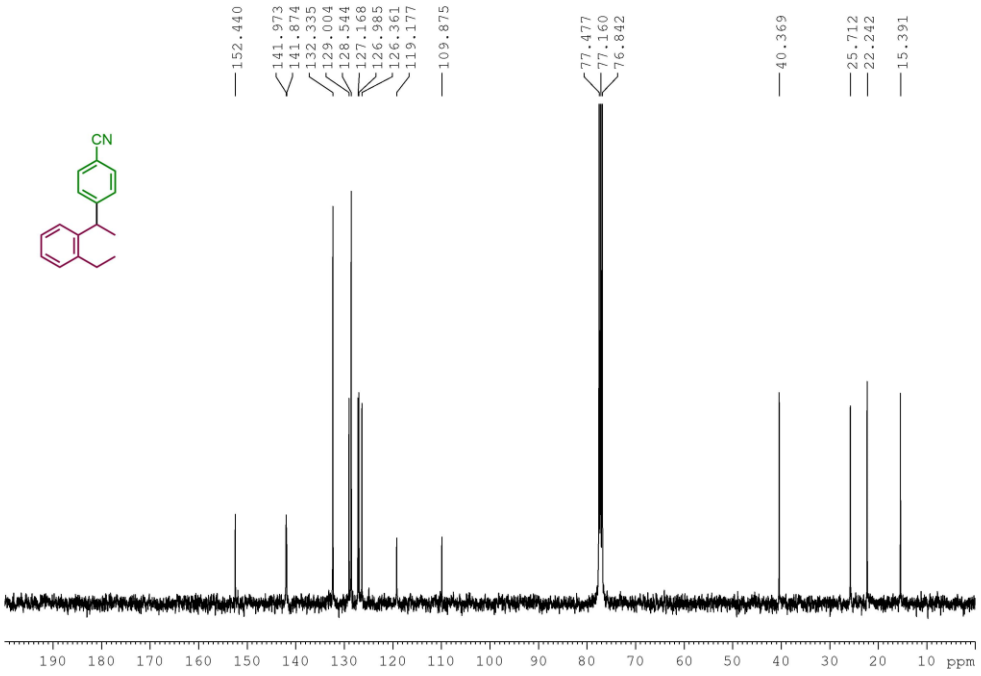
^{13}C NMR (100 MHz, $CDCl_3$), **4d-*o***



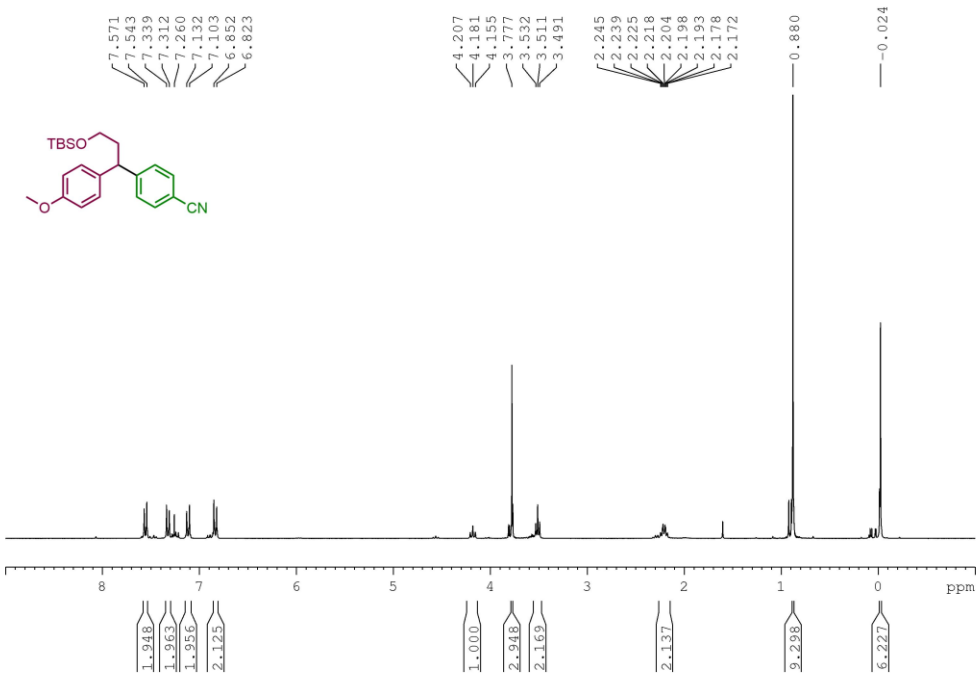
^{1}H NMR (300 MHz, $CDCl_3$), **4e**



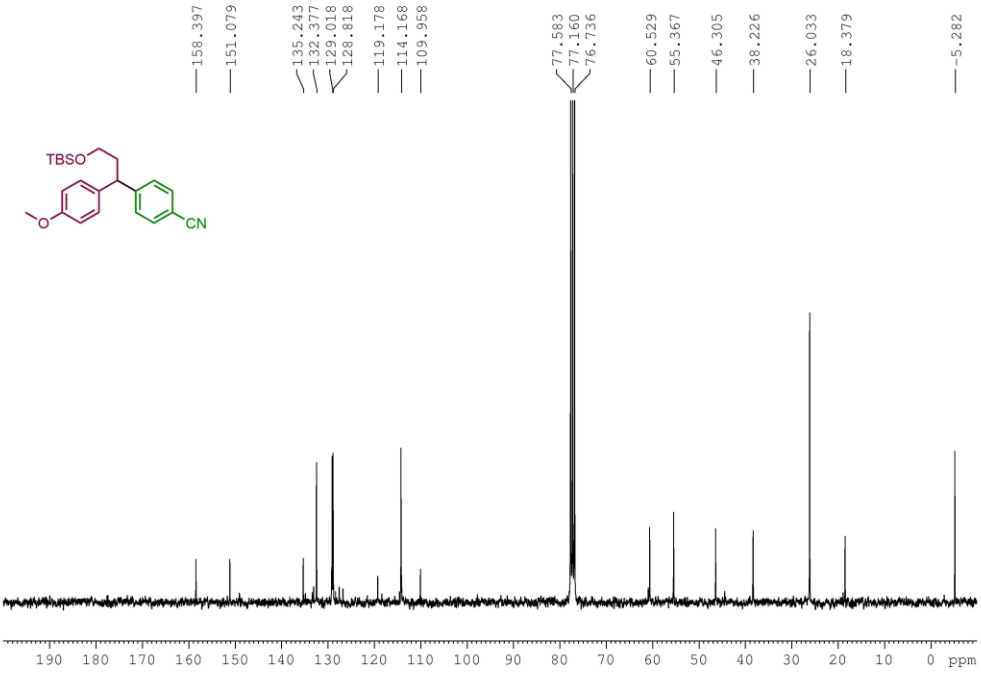
^{13}C NMR (100 MHz, $CDCl_3$), **4e**



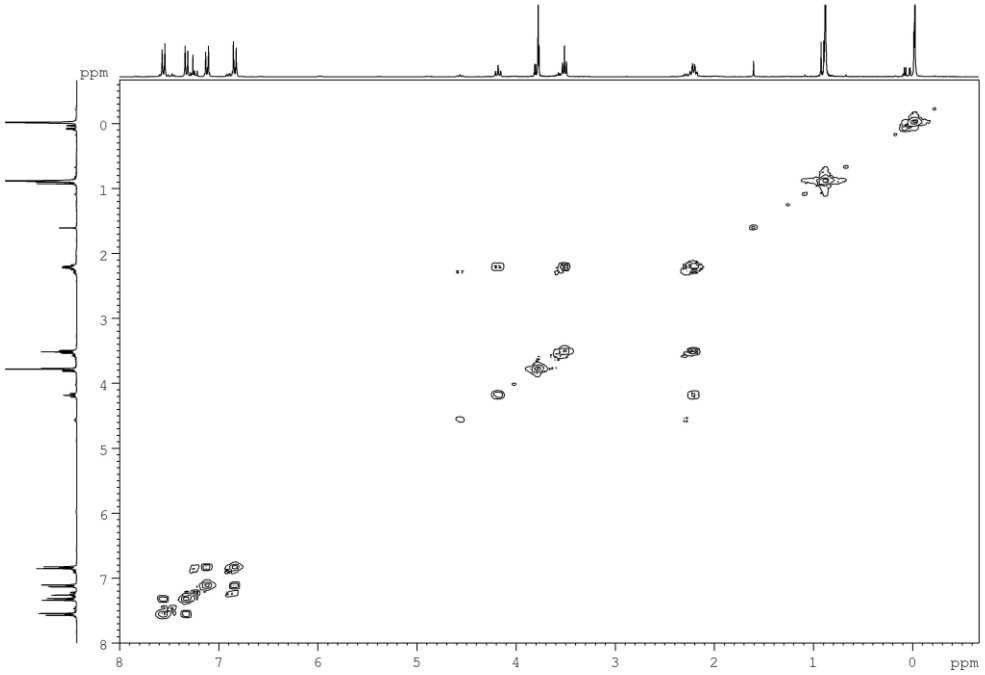
^{1}H NMR (300 MHz, $CDCl_3$), **4f**



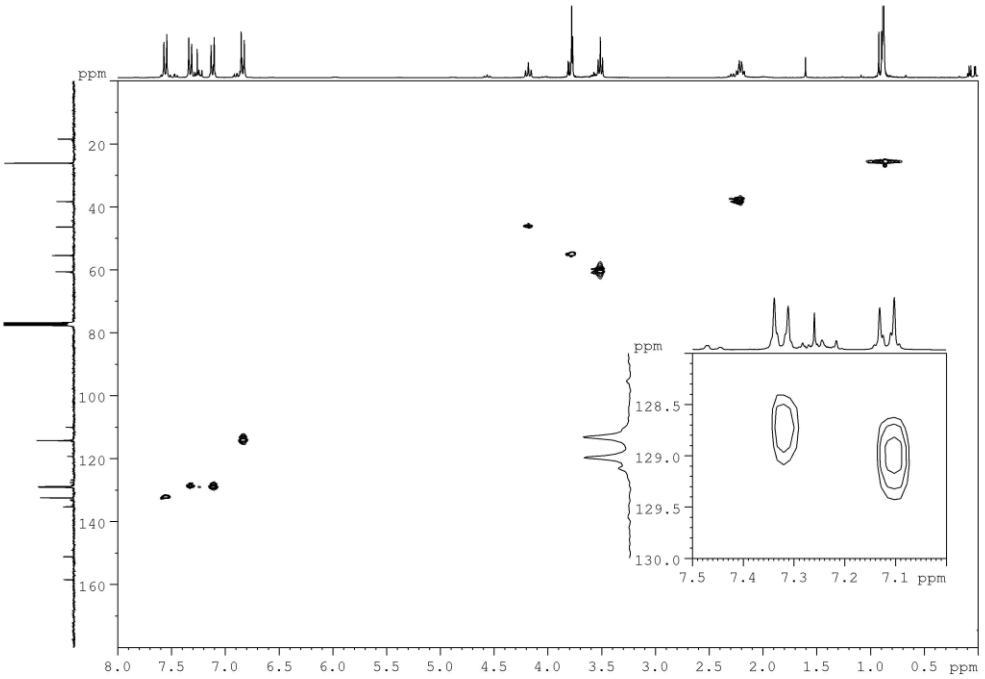
^{13}C NMR (75 MHz, $CDCl_3$), **4f**



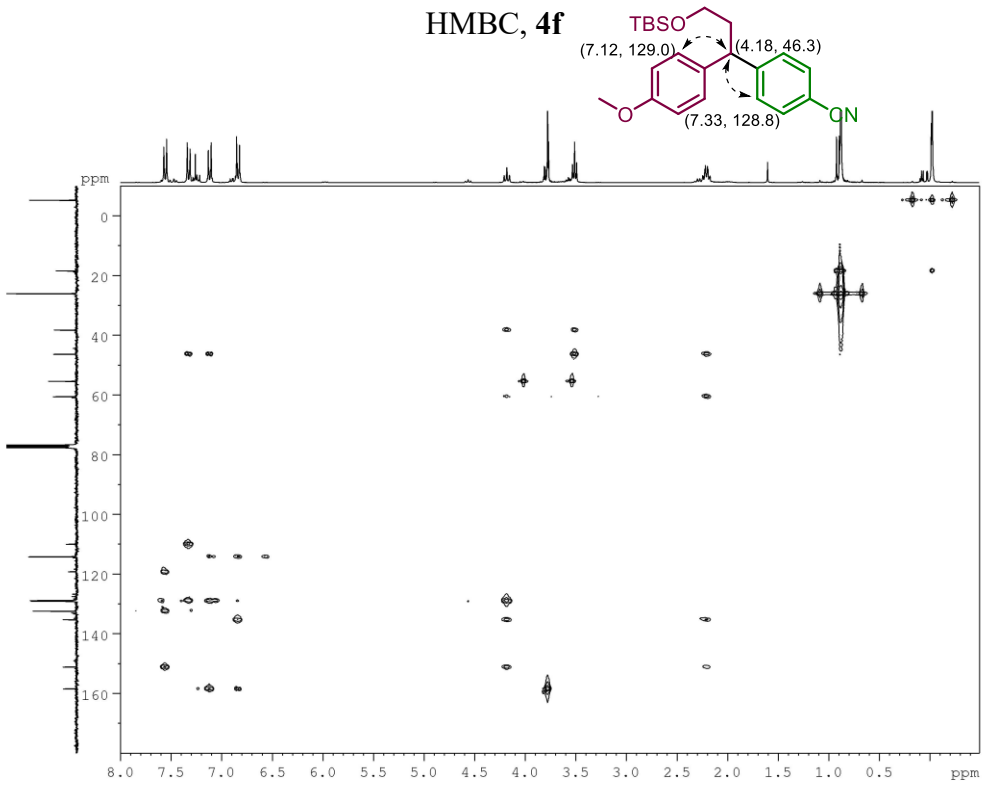
COSY, **4f**



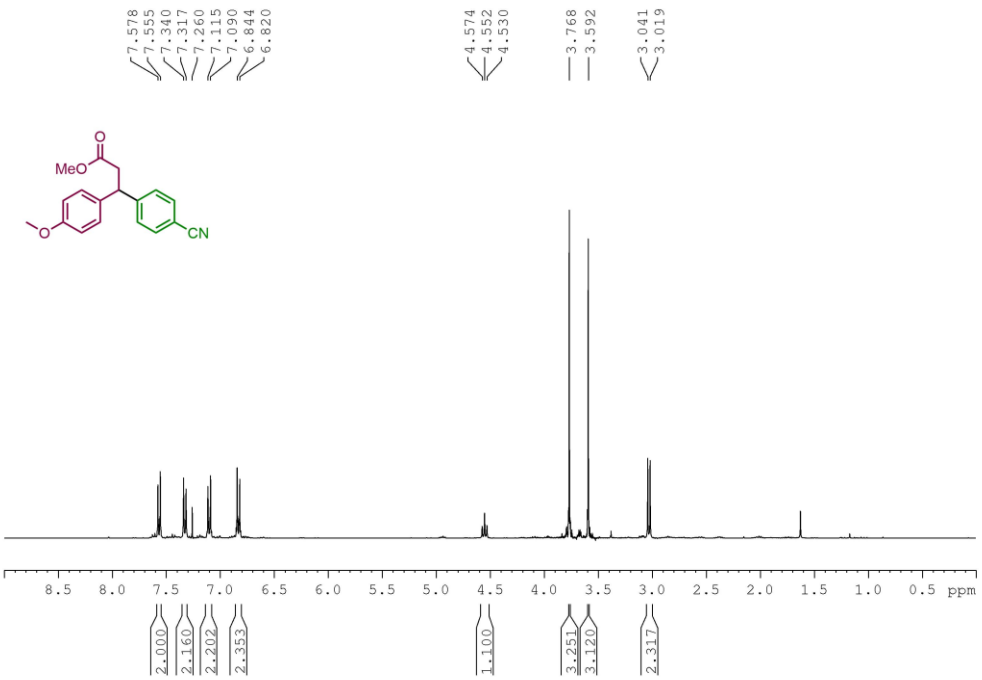
HSQC, **4f**



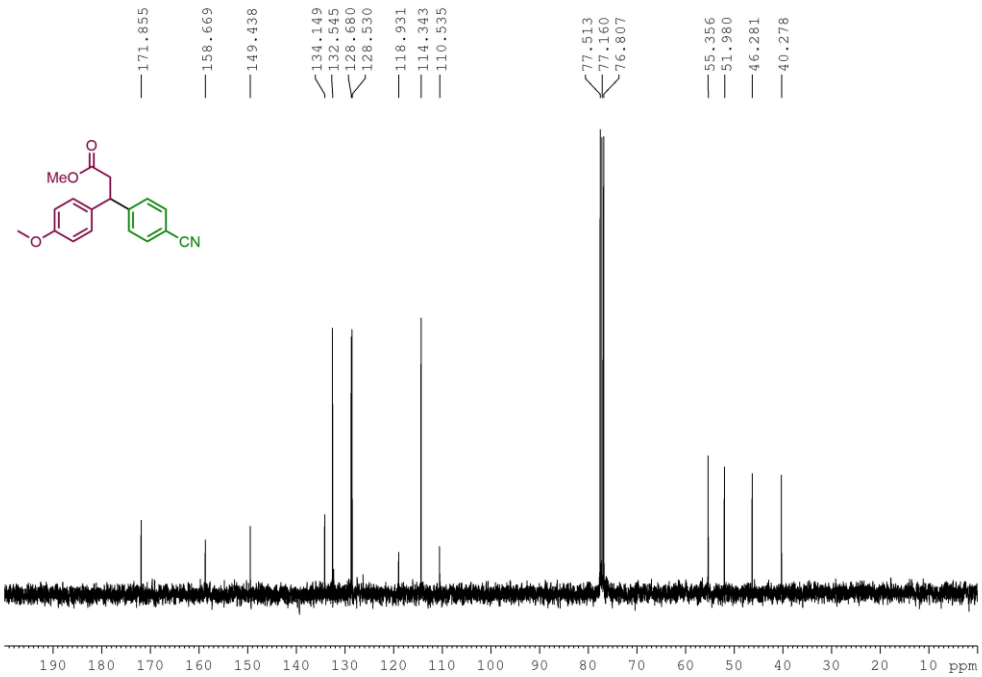
HMBC, **4f**


TBSO
(7.12, 129.0)
(4.18, 46.3)
O
(7.33, 128.8)
CN
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

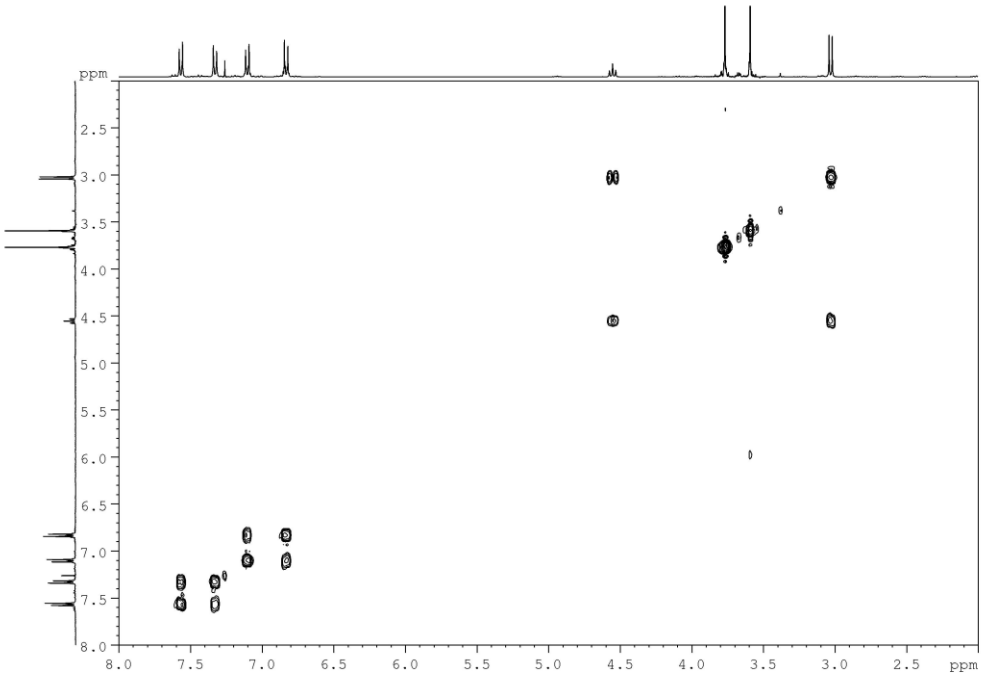
^{1}H NMR (360 MHz, $CDCl_3$), **4g**



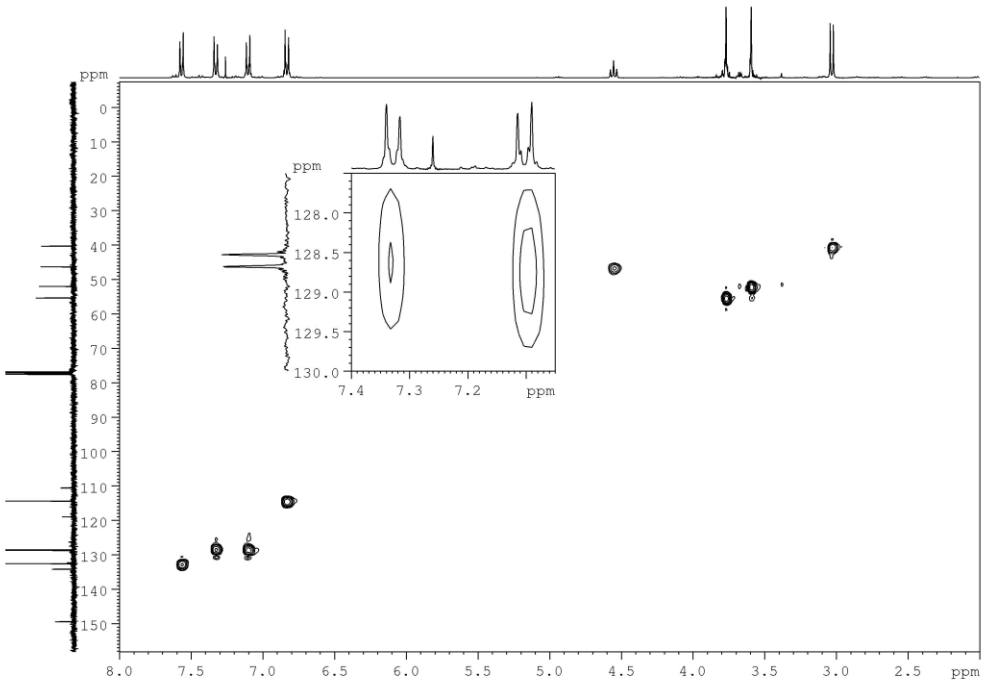
^{13}C NMR (90 MHz, $CDCl_3$), **4g**



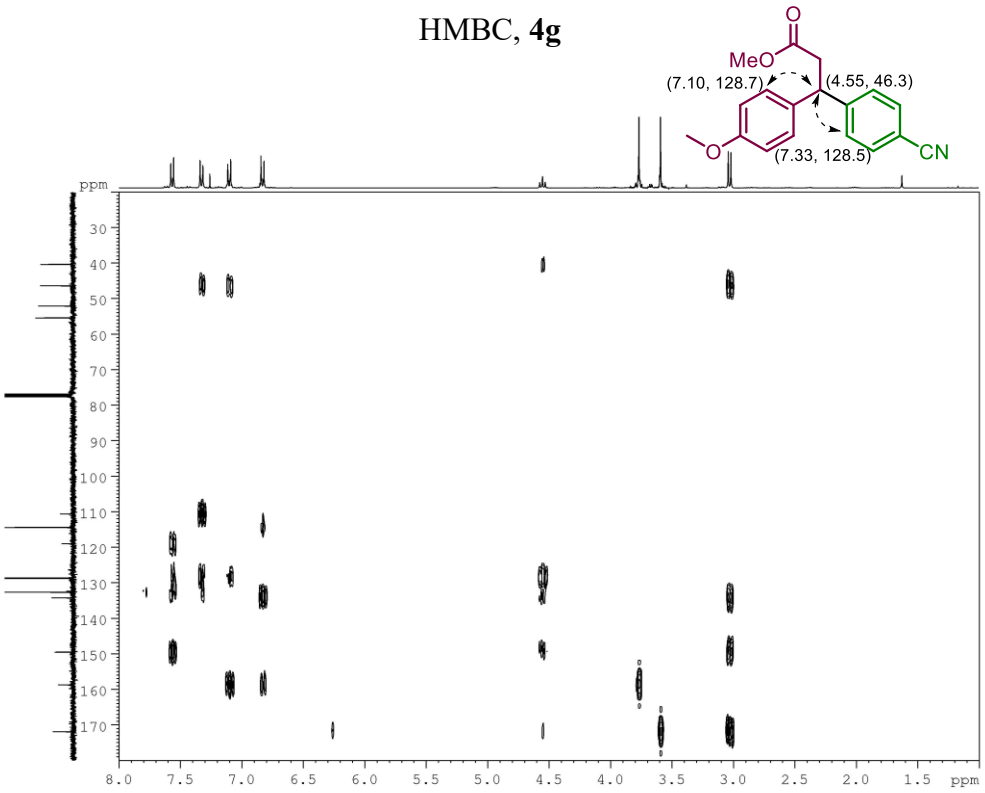
COSY, **4g**



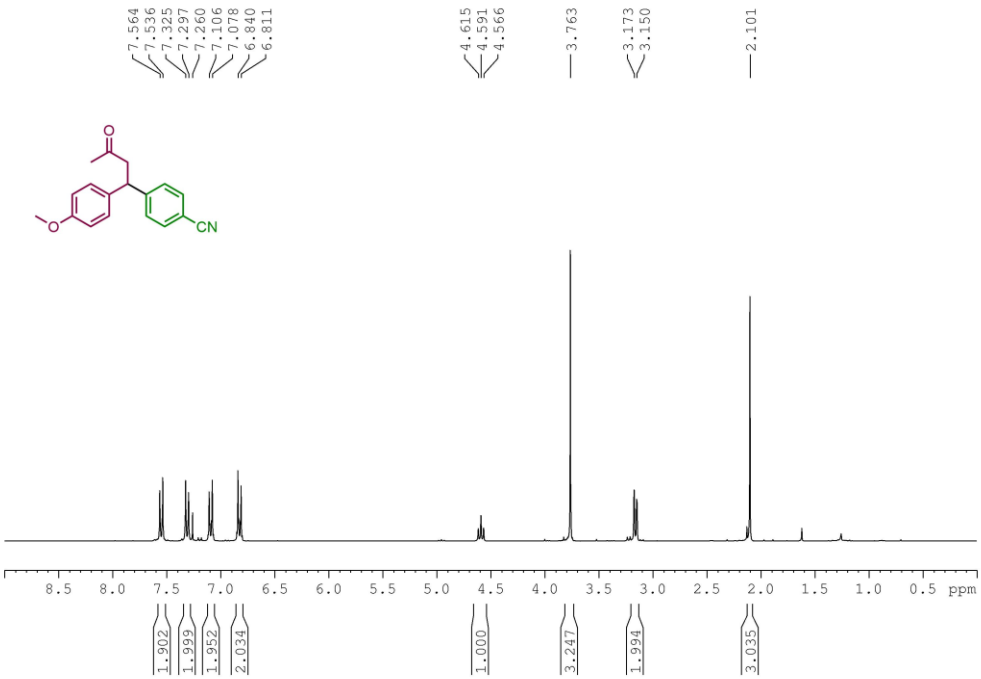
HSQC, **4g**



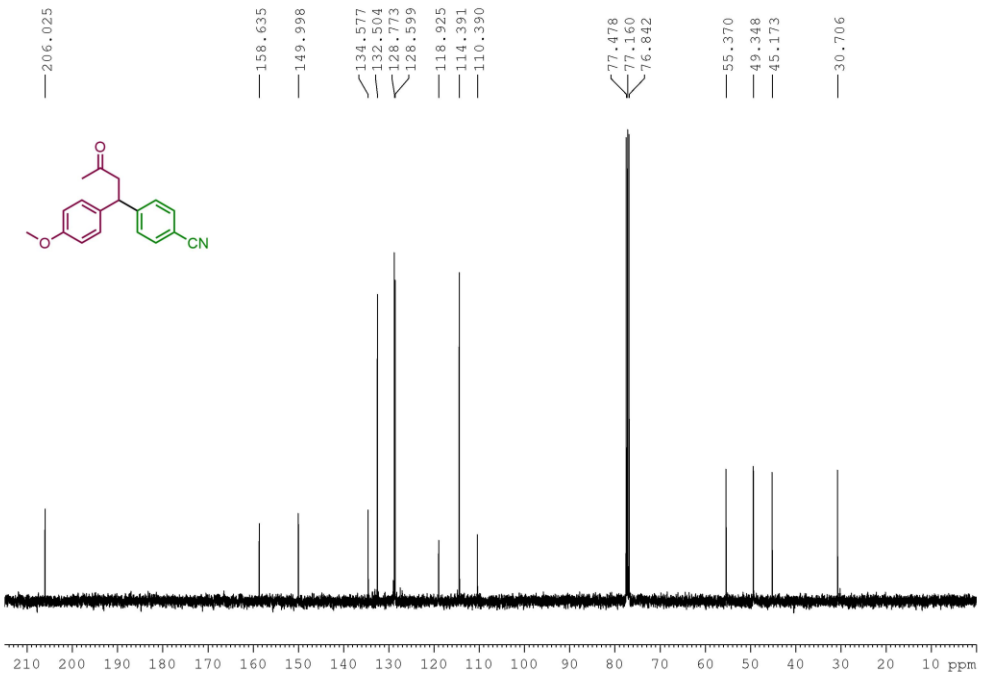
HMBC, **4g**


O
MeO
(7.10, 128.7)
(4.55, 46.3)
O
(7.33, 128.5)
CN
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

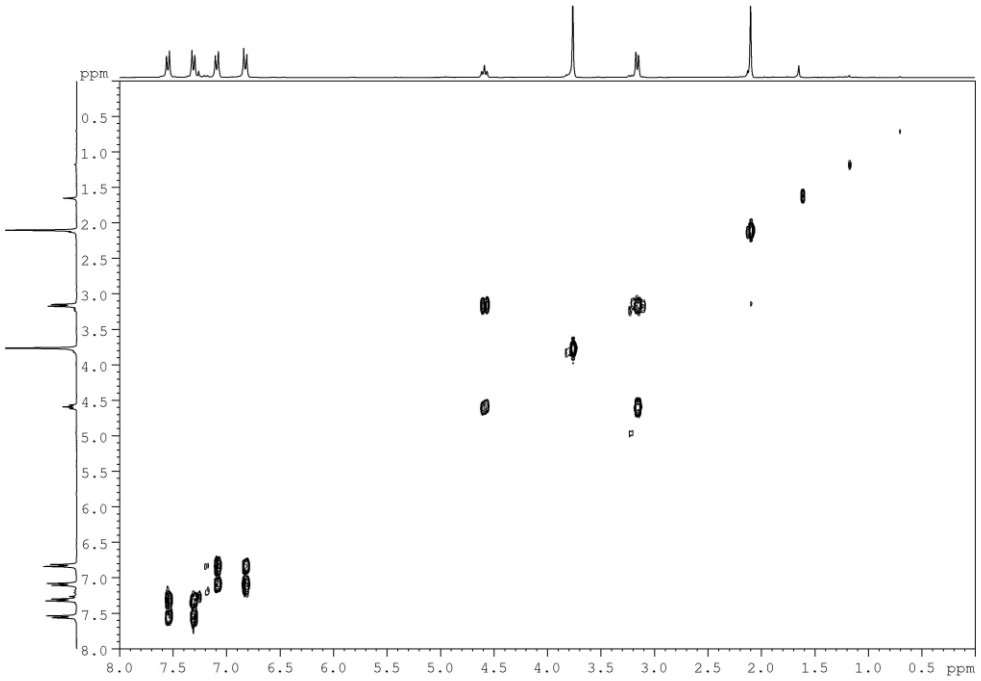
^{1}H NMR (300 MHz, $CDCl_3$), **4h**



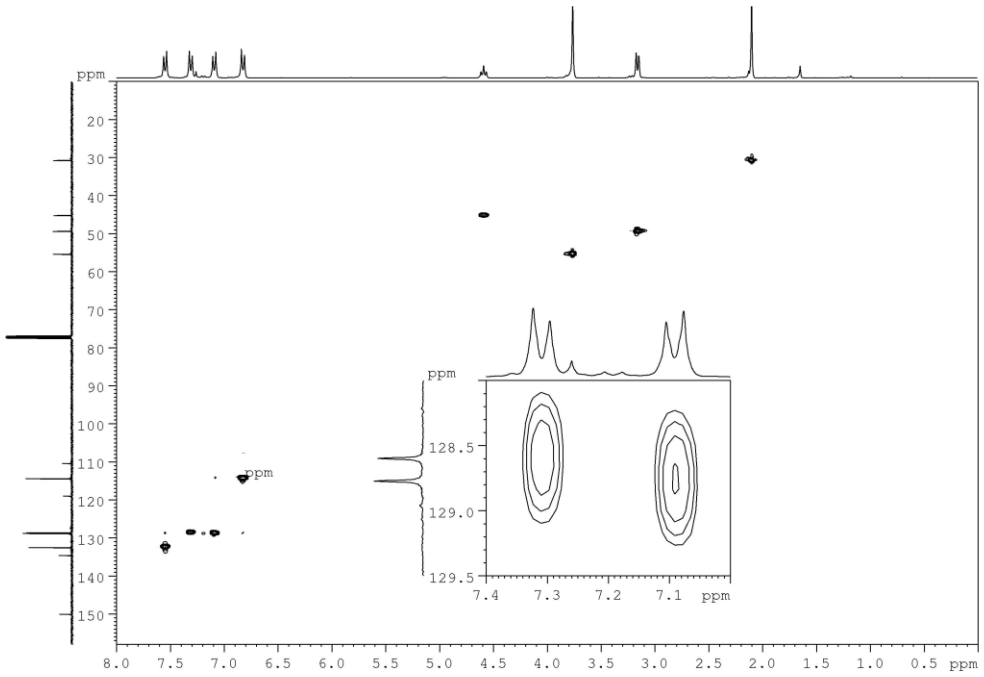
^{13}C NMR (100 MHz, $CDCl_3$), **4h**



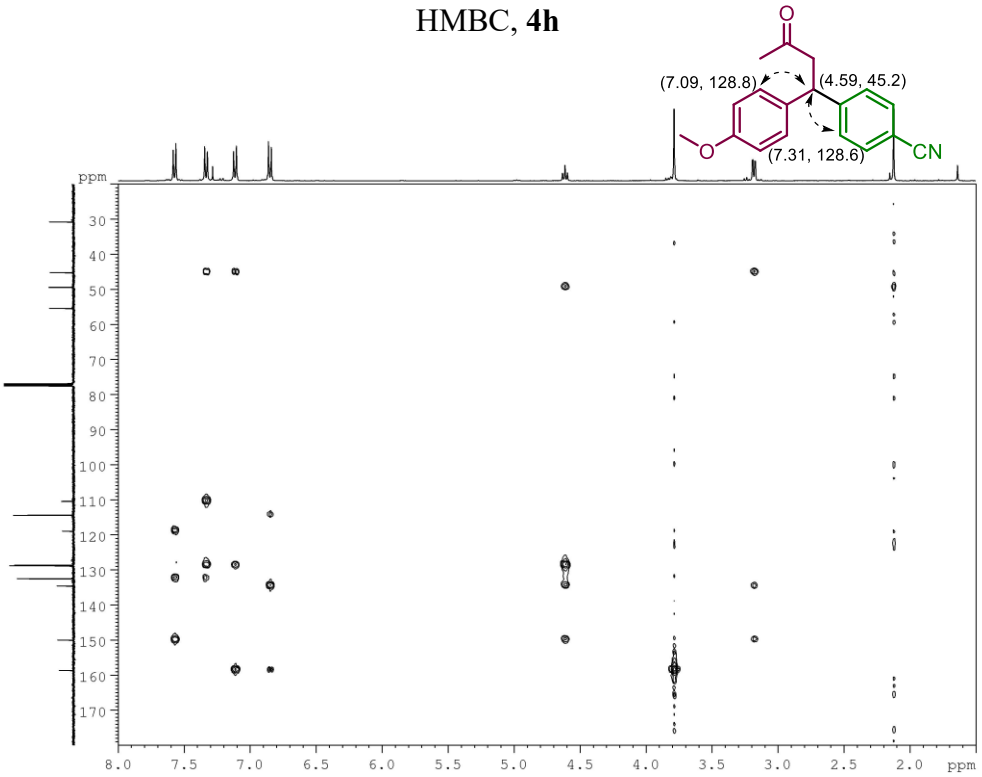
COSY, **4h**



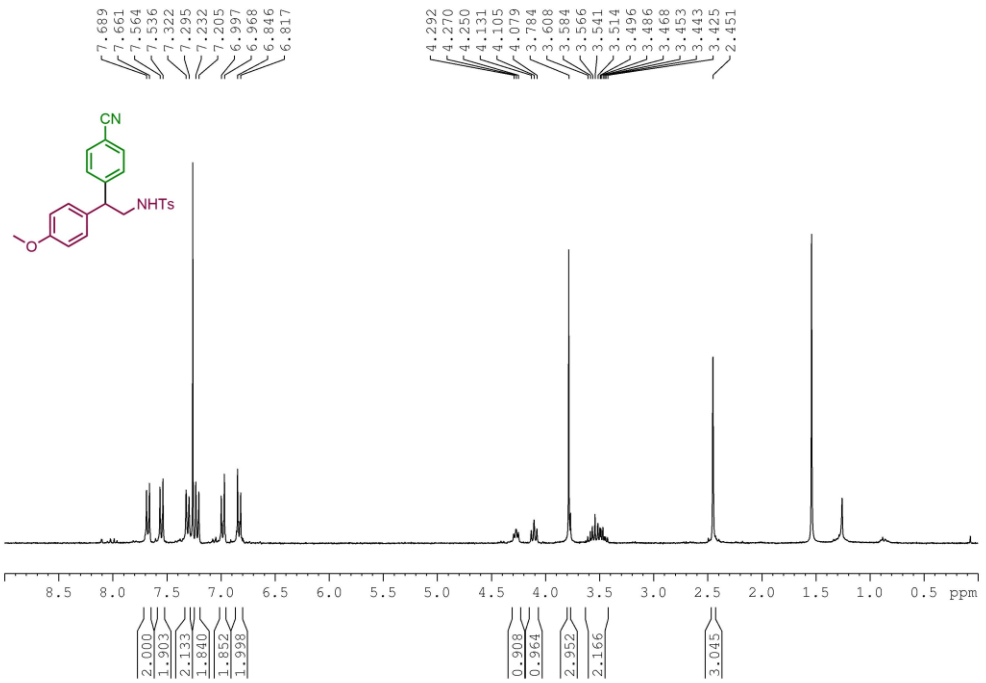
HSQC, **4h**



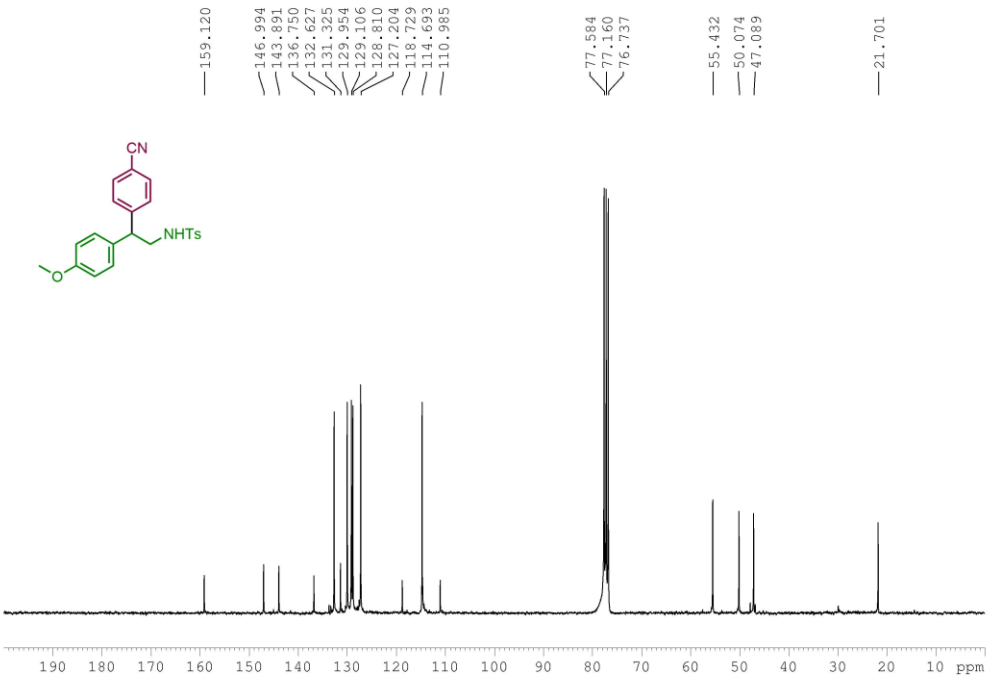
HMBC, **4h**


O
(7.09, 128.8)
(4.59, 45.2)
O
(7.31, 128.6)
CN
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

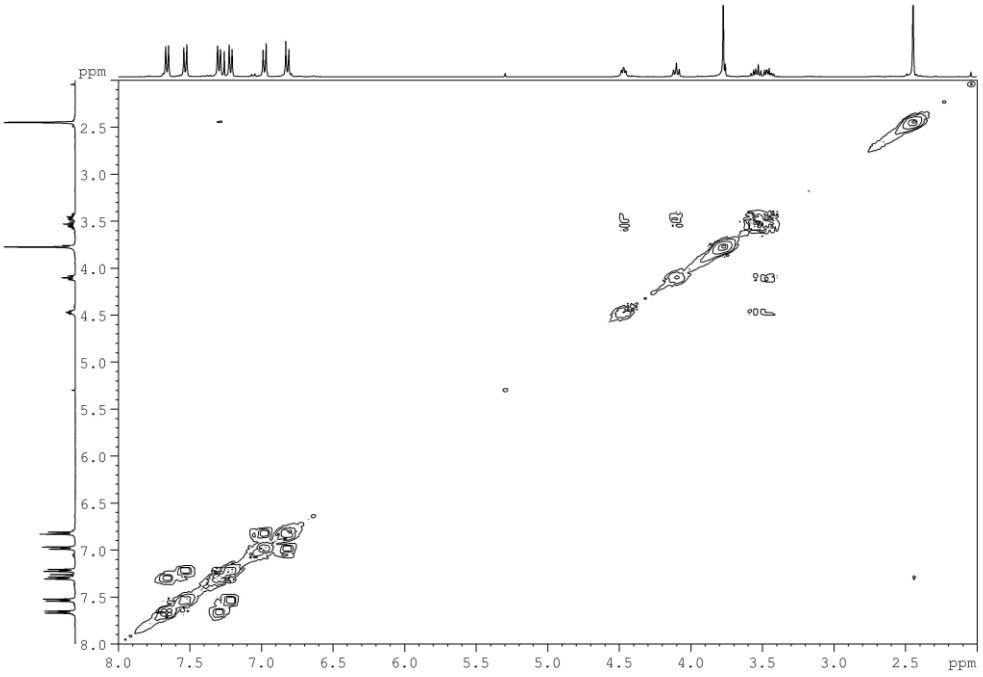
^{1}H NMR (300 MHz, $CDCl_3$), **4i**



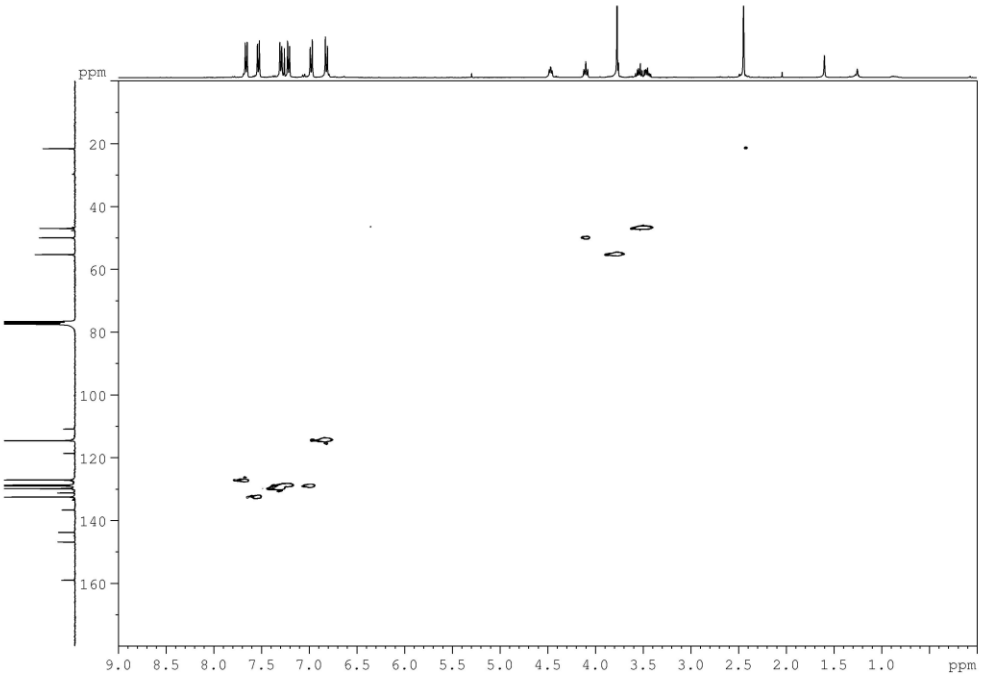
^{13}C NMR (75 MHz, $CDCl_3$), **4i**



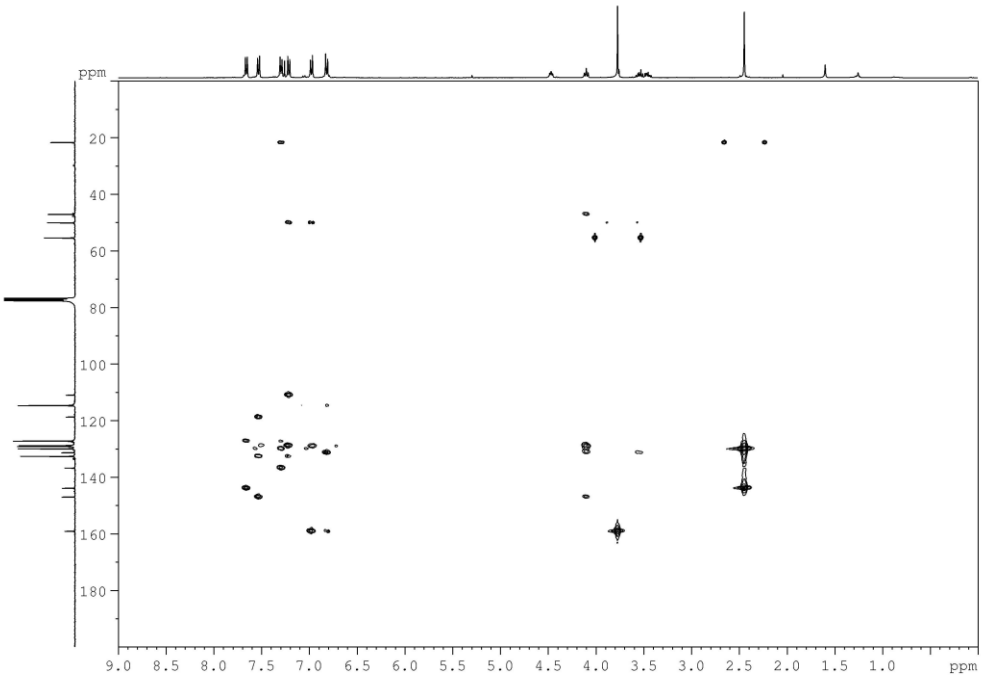
COSY, **4i**



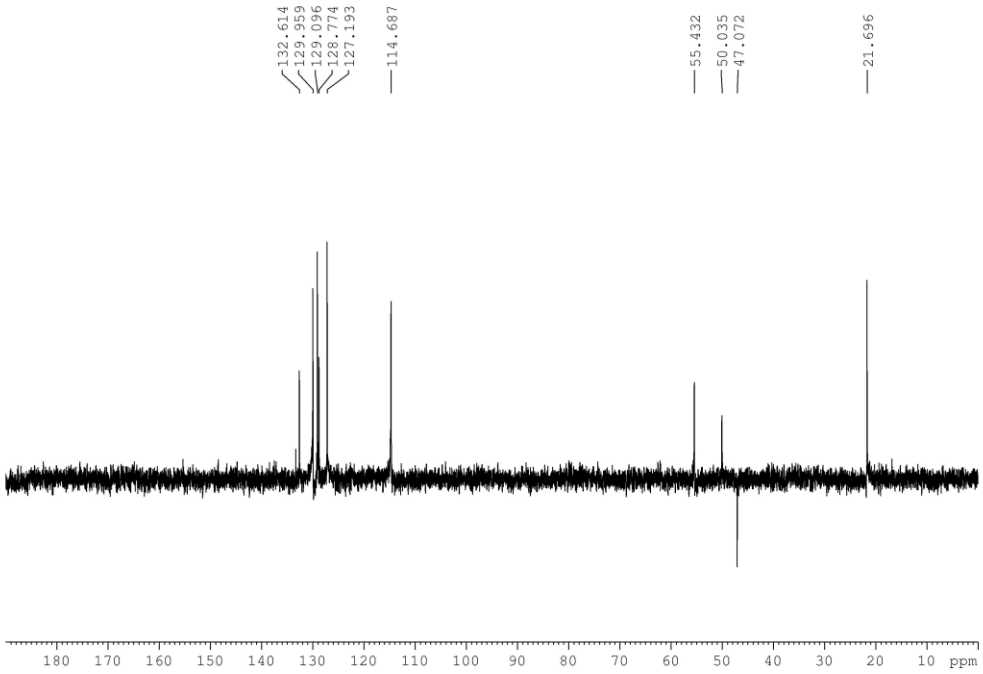
HSQC, **4i**



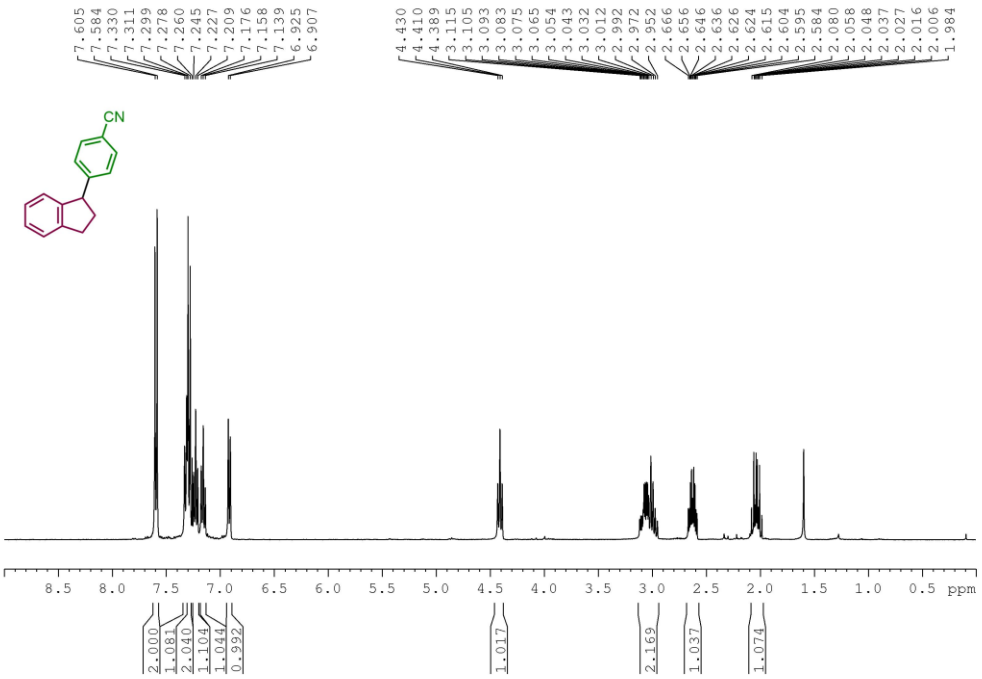
HMBC, **4i**



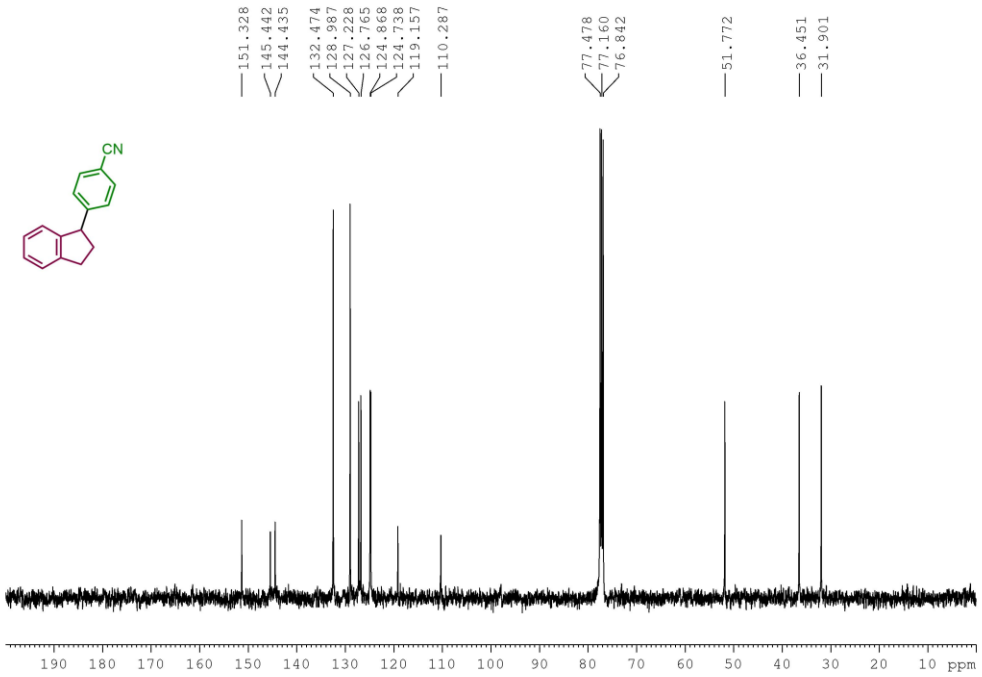
Dept 135, **4i**



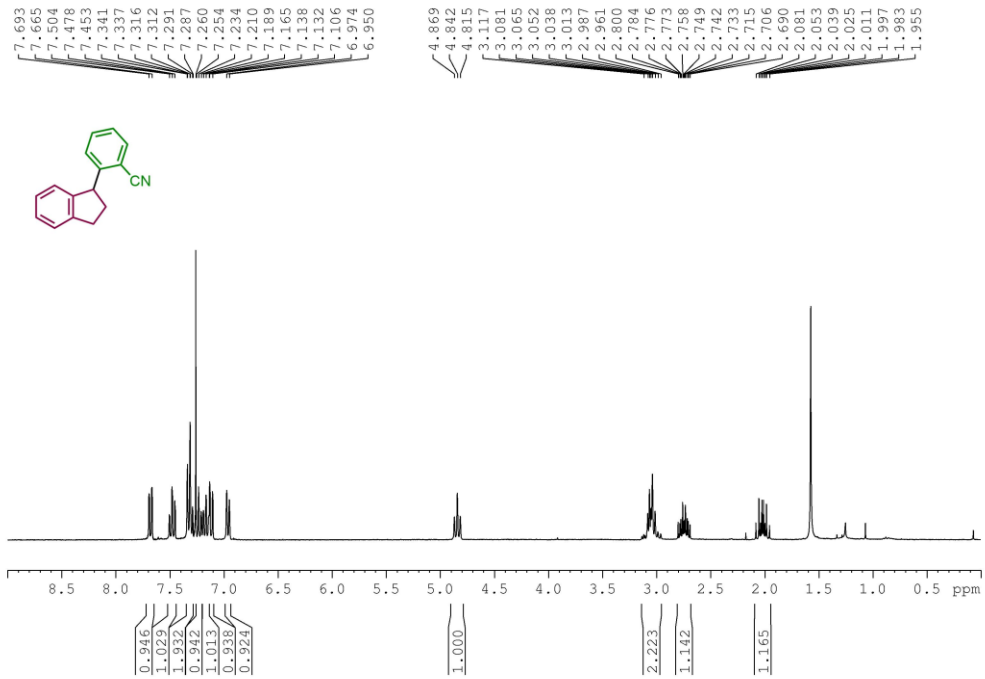
^{1}H NMR (400 MHz, $CDCl_3$), **4j-*p***



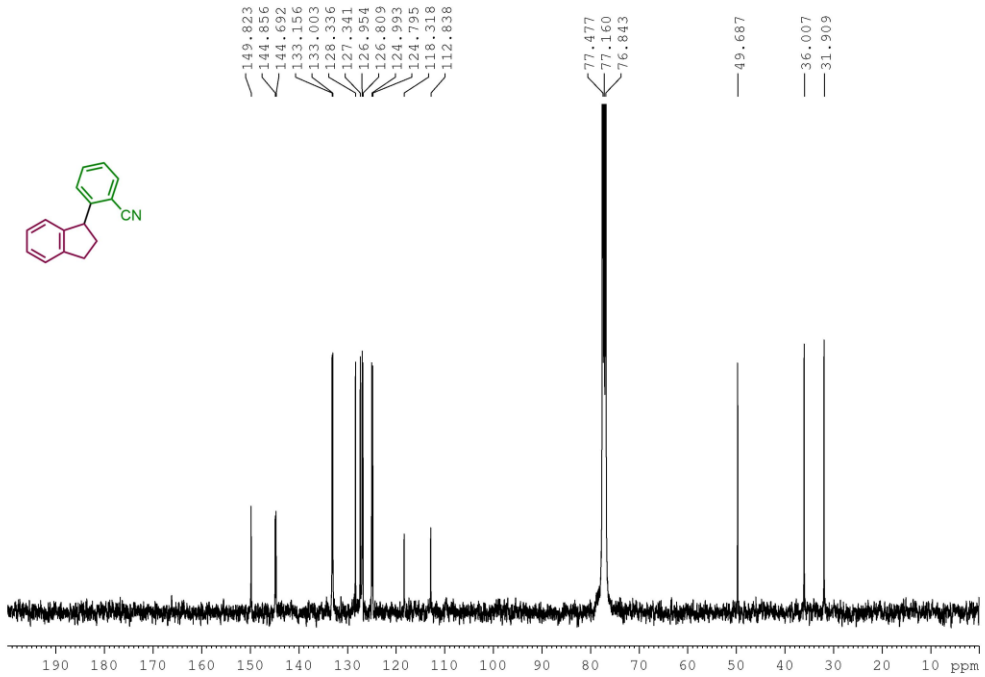
^{13}C NMR (100 MHz, $CDCl_3$), **4j-*p***



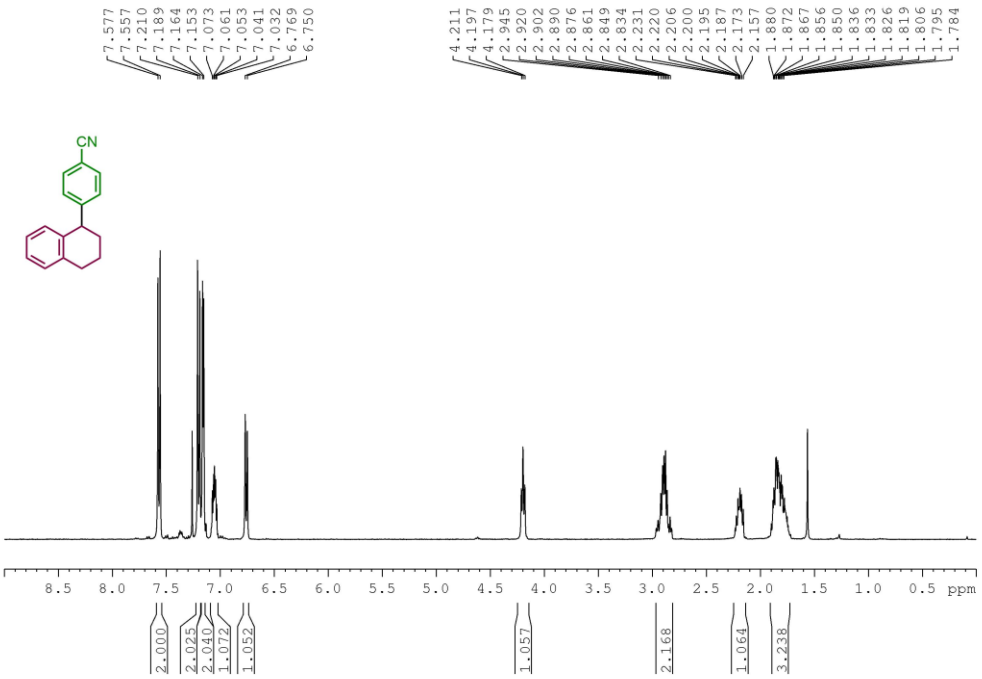
^{1}H NMR (300 MHz, $CDCl_3$), **4j-*o***



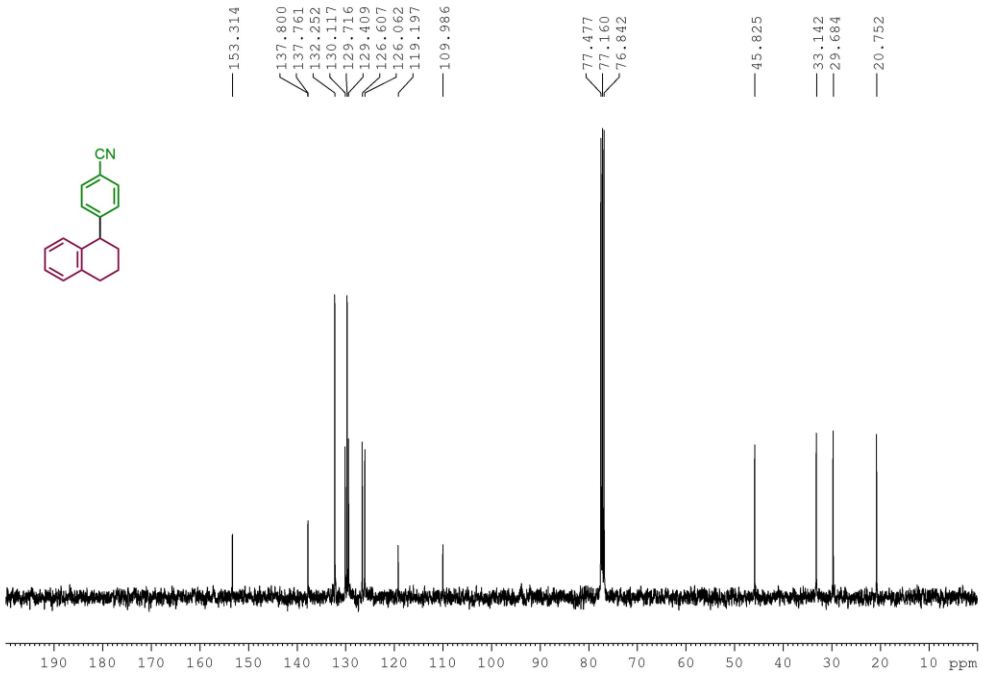
^{13}C NMR (100 MHz, $CDCl_3$), **4j-*o***



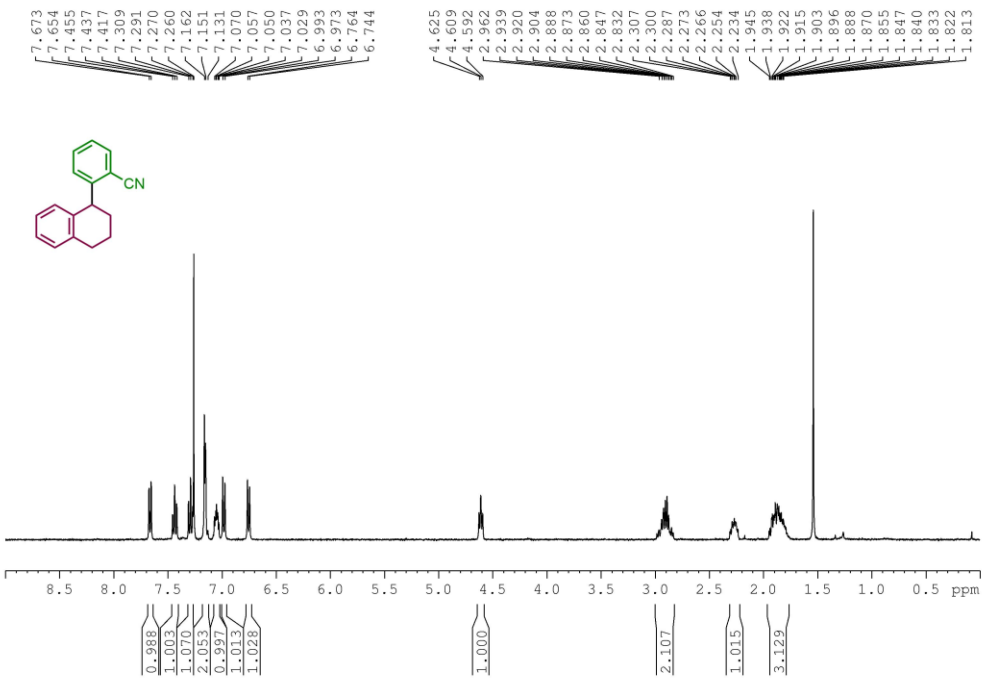
^{1}H NMR (400 MHz, $CDCl_3$), **4k-*p***



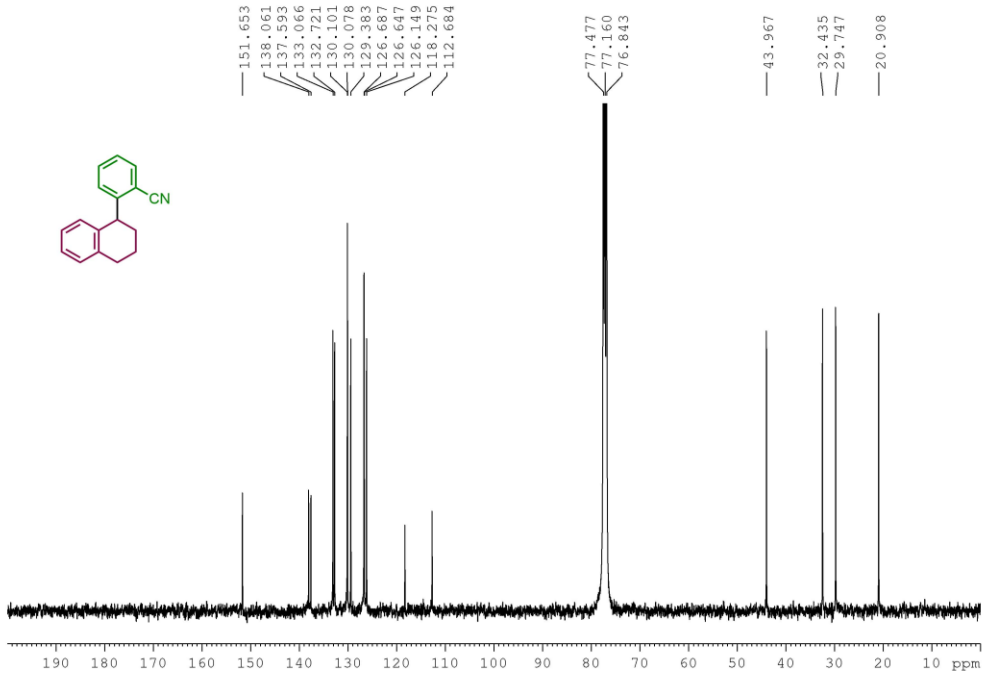
^{13}C NMR (100 MHz, $CDCl_3$), **4k-*p***



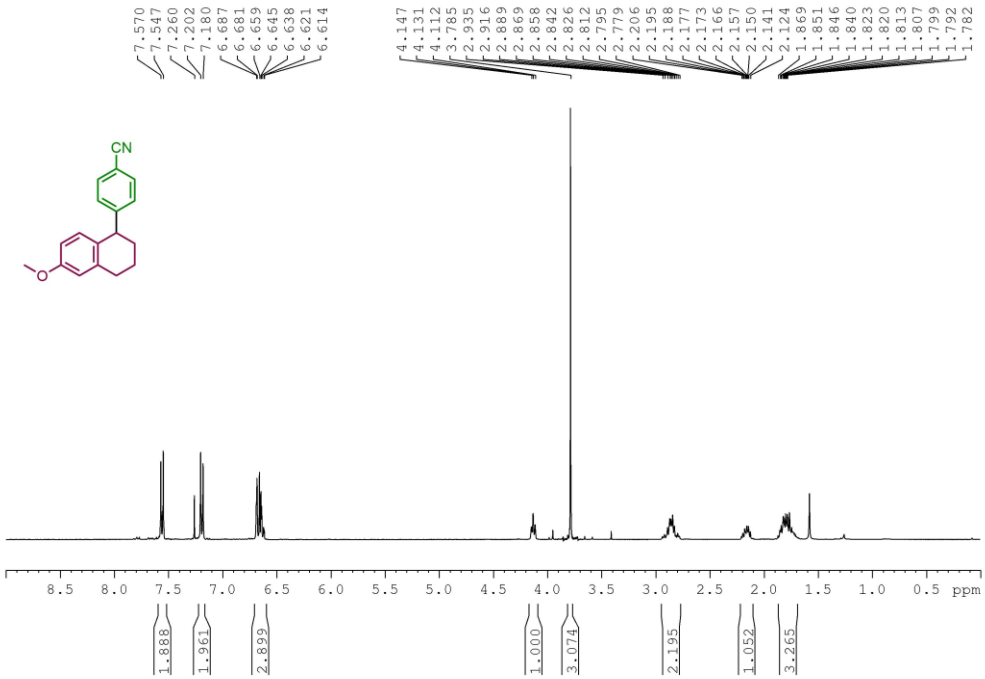
^{1}H NMR (400 MHz, $CDCl_3$), **4k-*o***



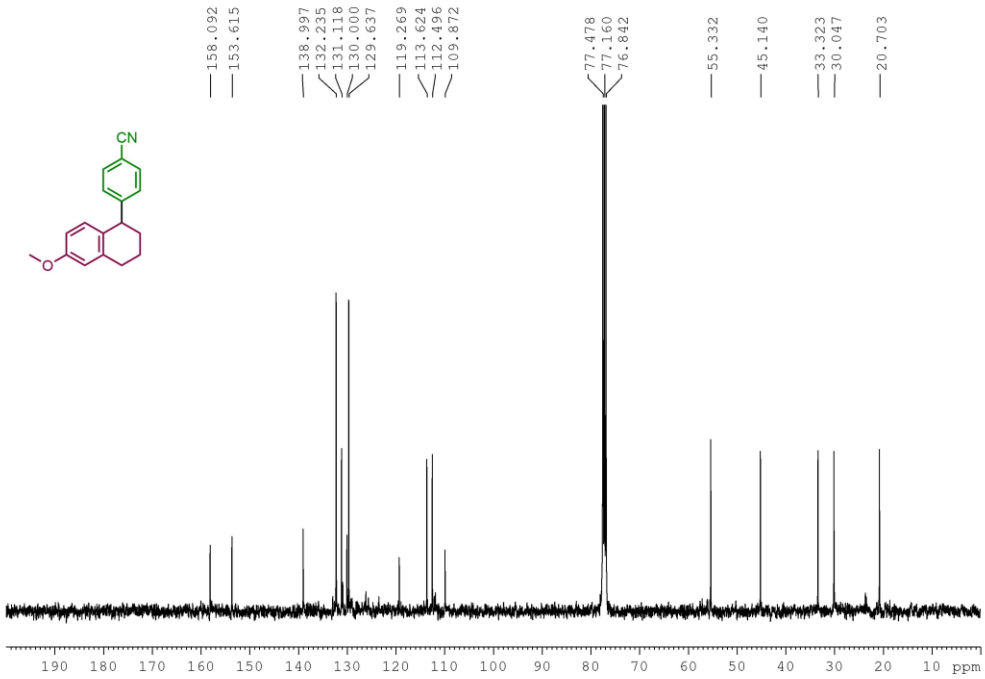
^{13}C NMR (100 MHz, $CDCl_3$), **4k-*o***



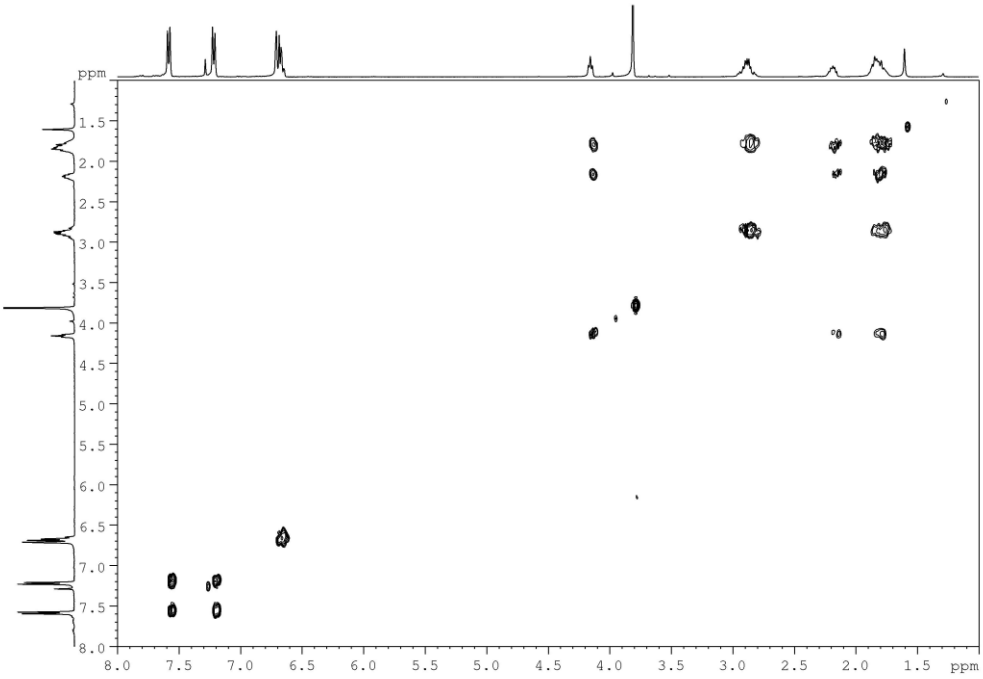
^{1}H NMR (360 MHz, $CDCl_3$), **4l**



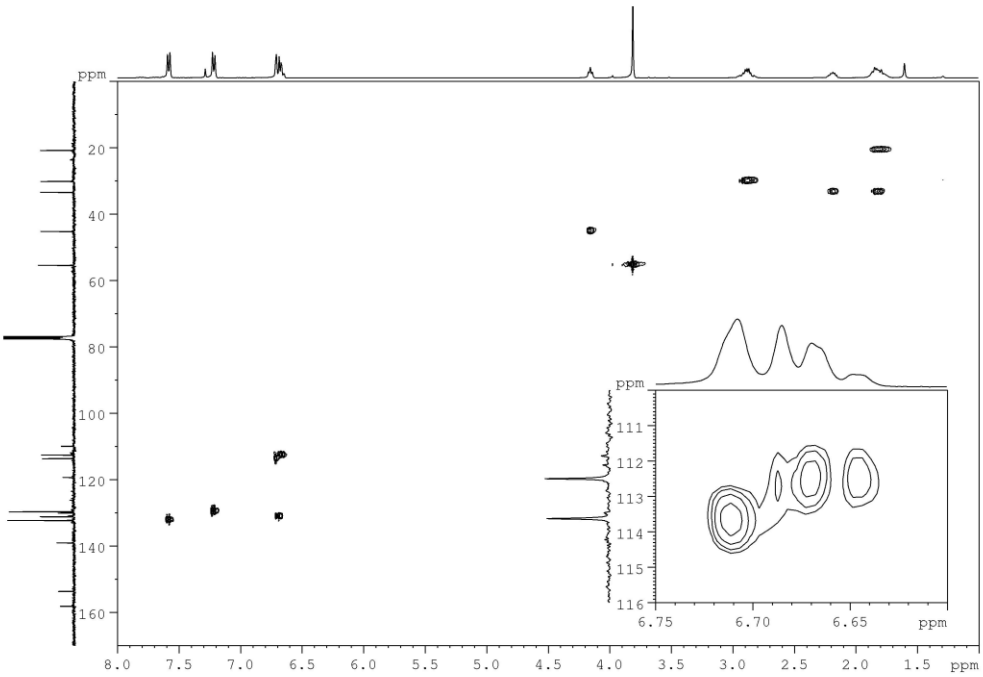
^{13}C NMR (100 MHz, $CDCl_3$), **4l**



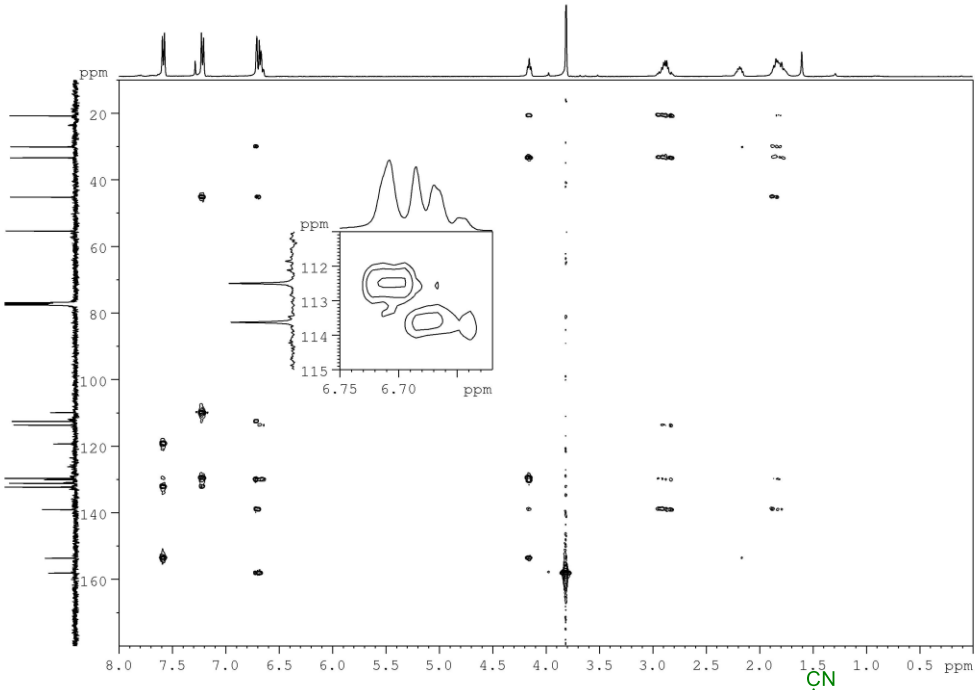
COSY, **4l**



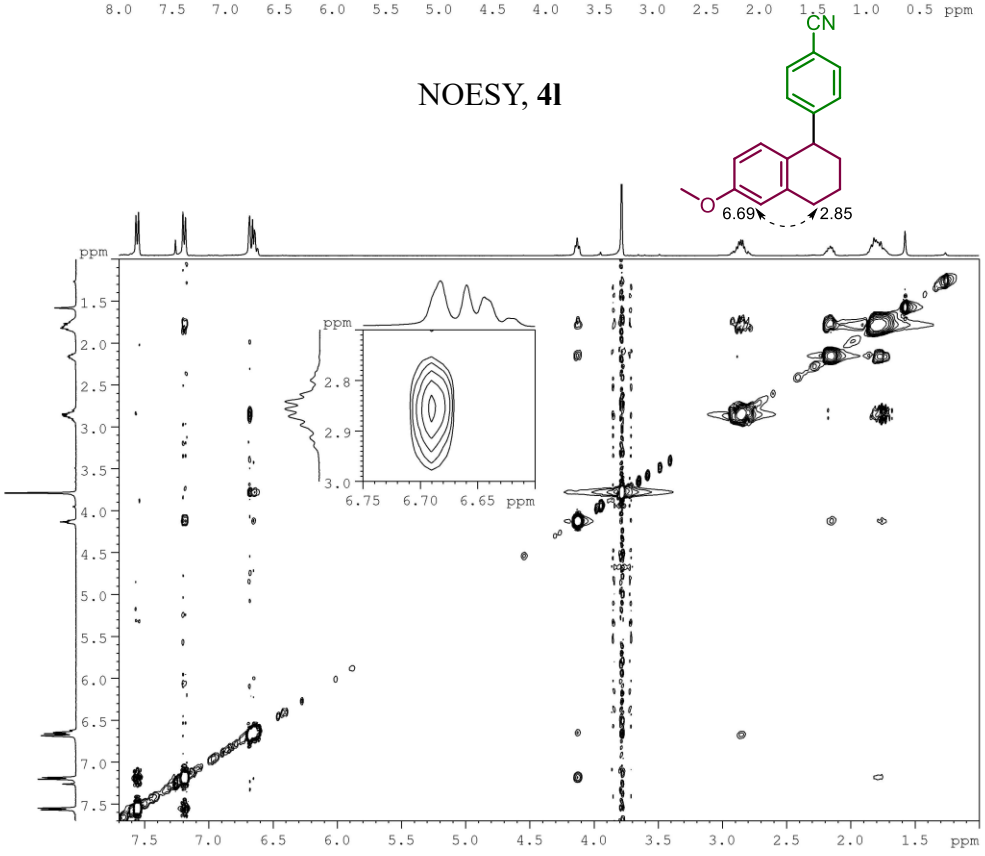
HSQC, **4l**



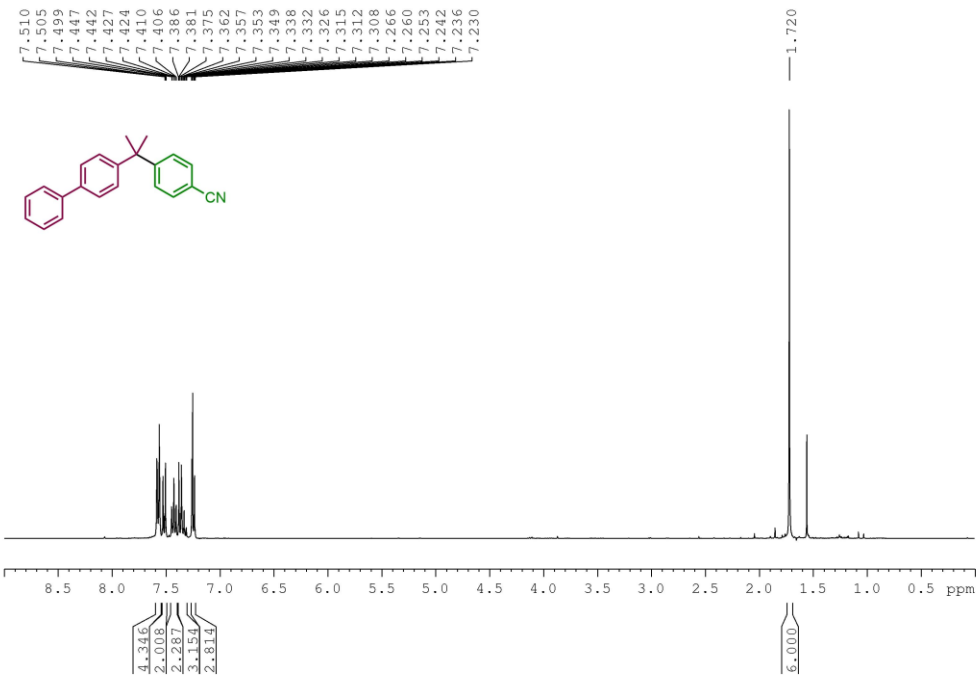
HMBC, **4l**



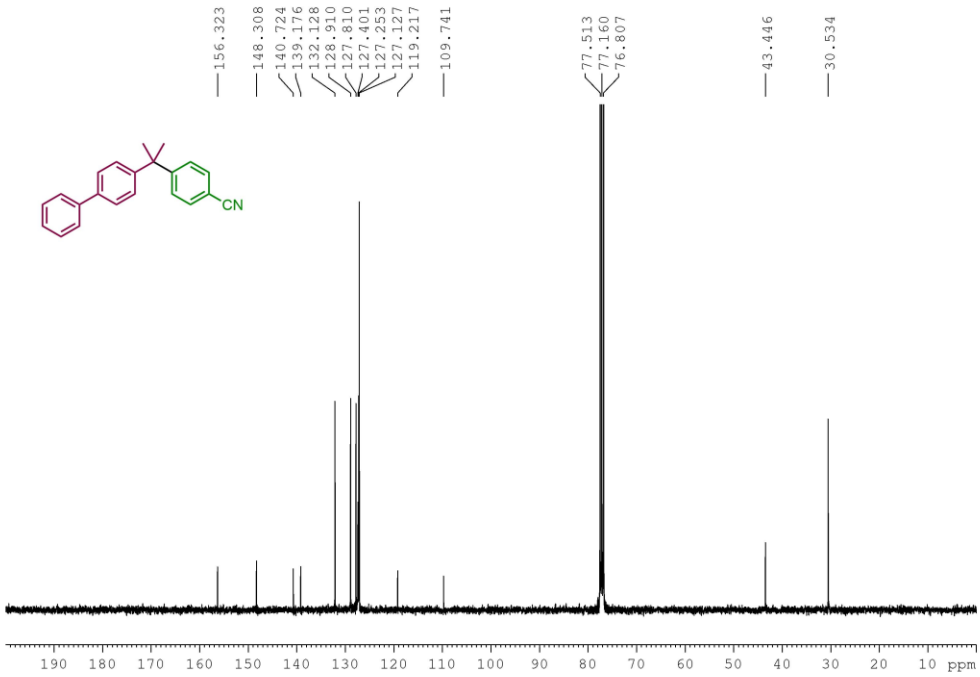
NOESY, **4l**



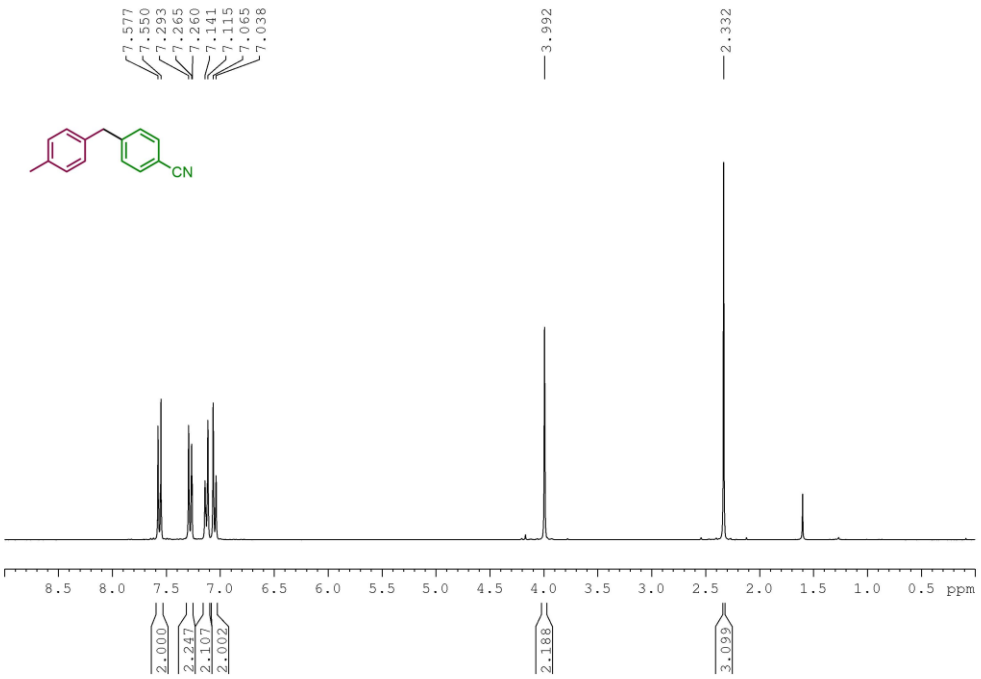
^{1}H NMR (360 MHz, $CDCl_3$), **4m**



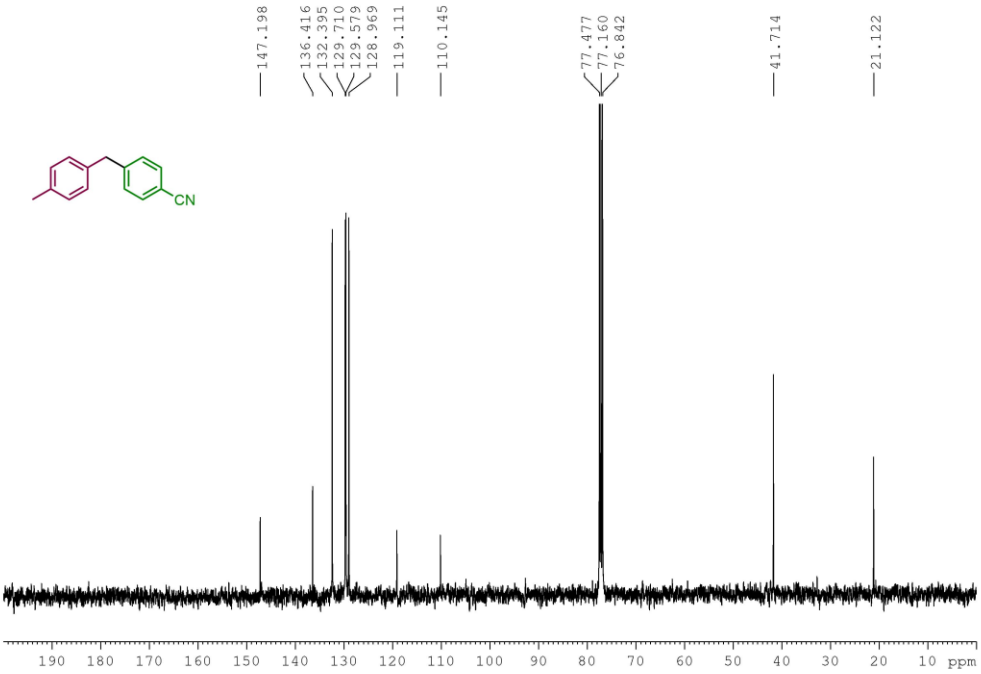
^{13}C NMR (90 MHz, $CDCl_3$), **4m**



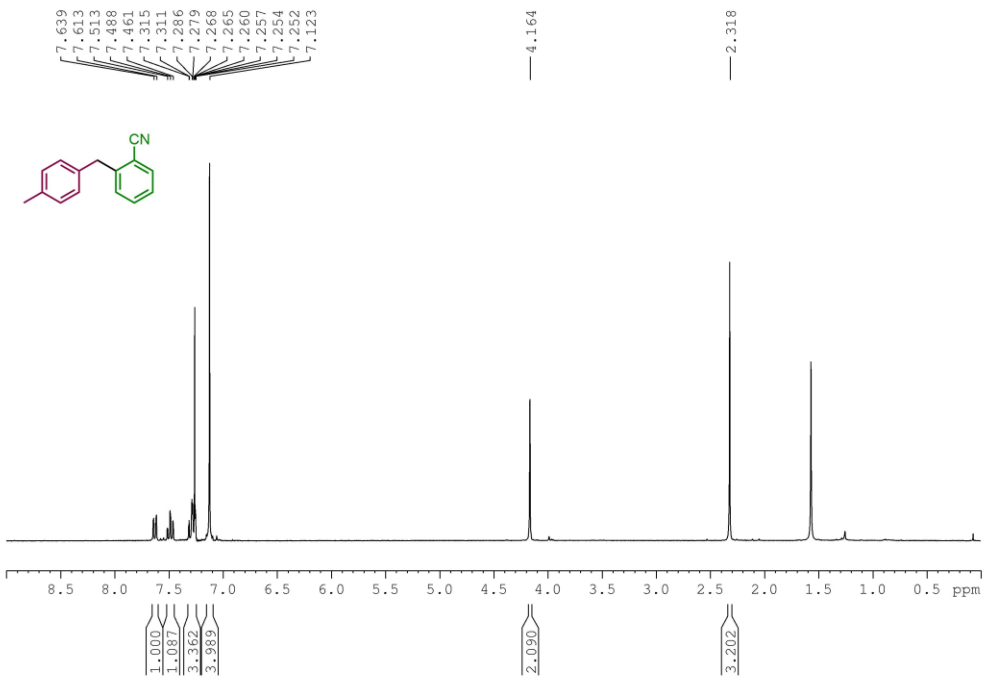
^{1}H NMR (300 MHz, $CDCl_3$), **4n-*p***



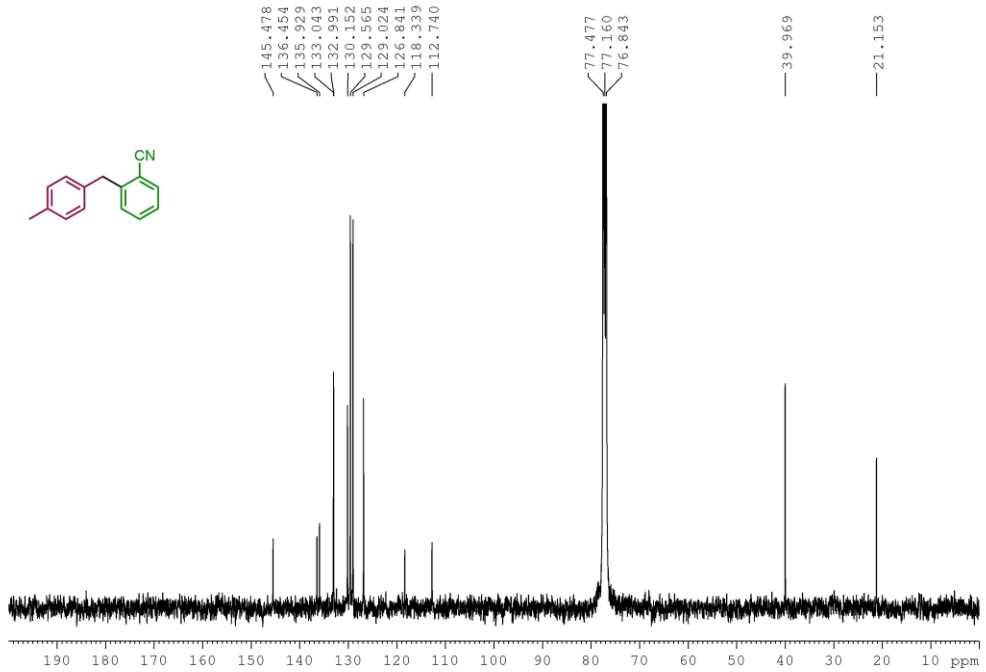
^{13}C NMR (100 MHz, $CDCl_3$), **4n-*p***



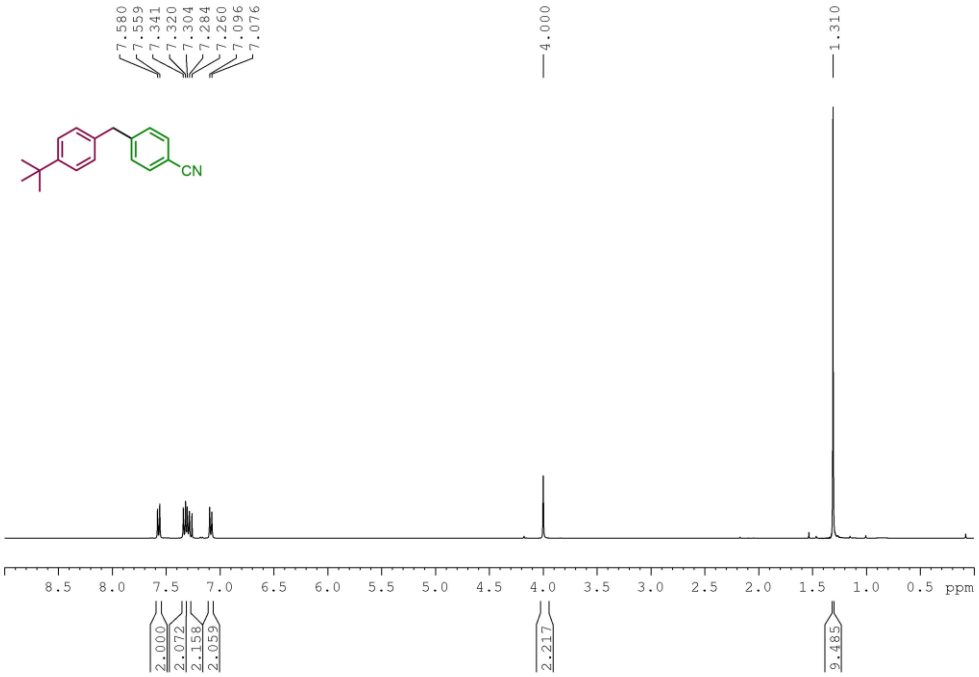
^{1}H NMR (300 MHz, $CDCl_3$), **4n-*o***



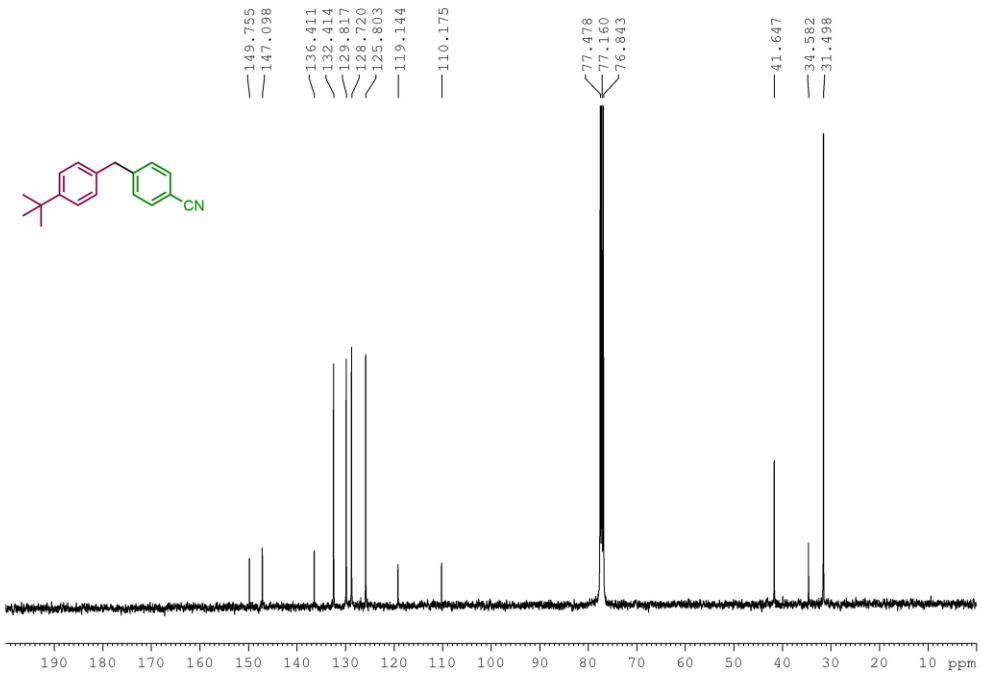
^{13}C NMR (100 MHz, $CDCl_3$), **4n-*o***



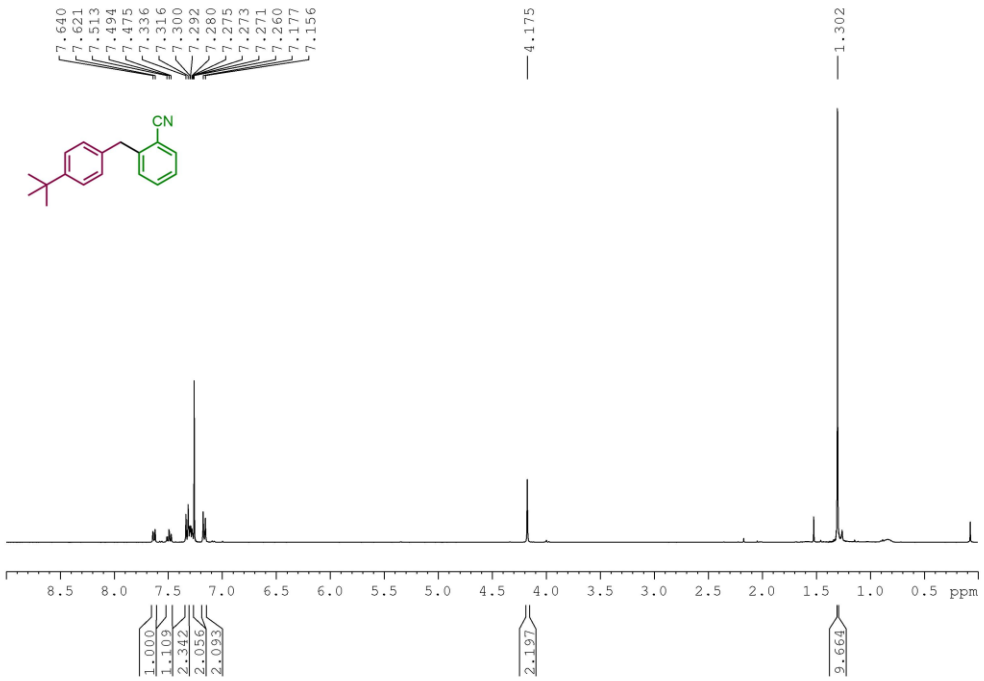
^{1}H NMR (400 MHz, $CDCl_3$), **4o-*p***



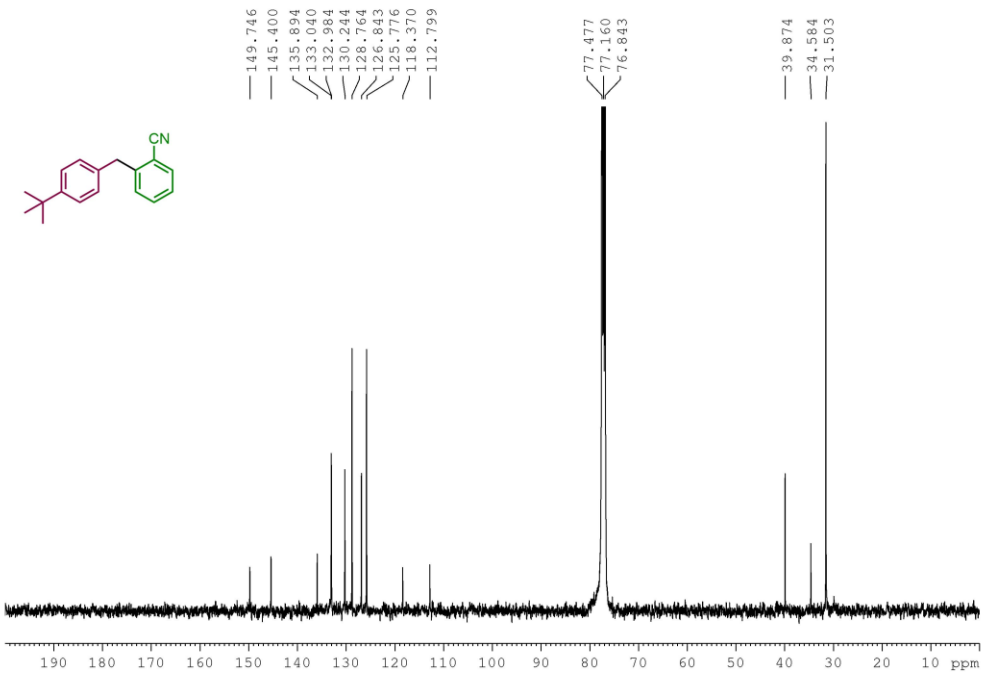
^{13}C NMR (100 MHz, $CDCl_3$), **4o-*p***



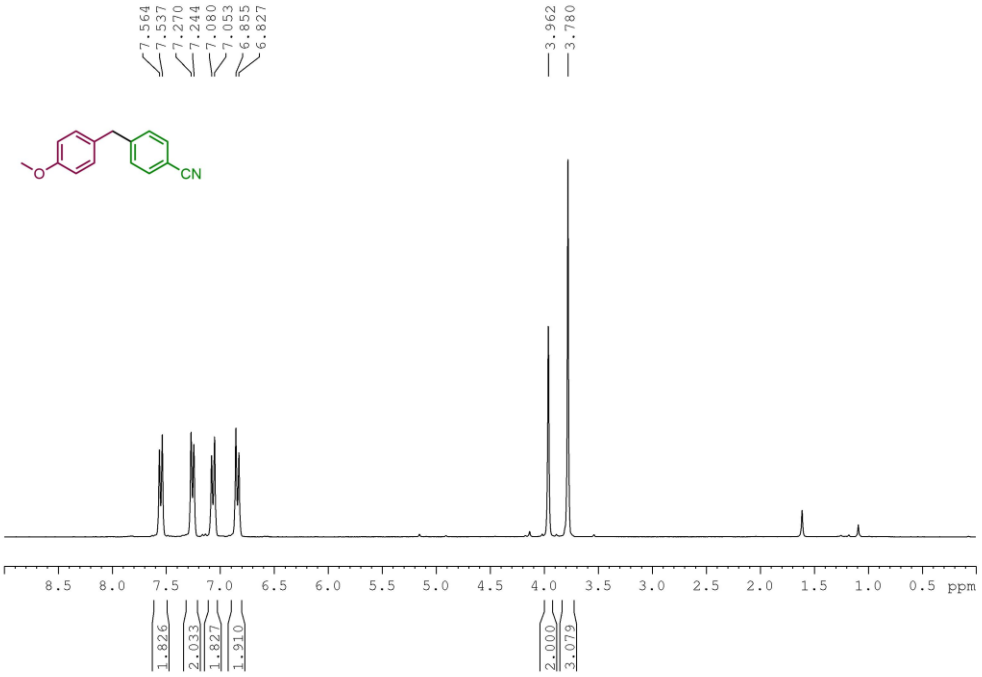
^{1}H NMR (400 MHz, $CDCl_3$), **4o-*o***



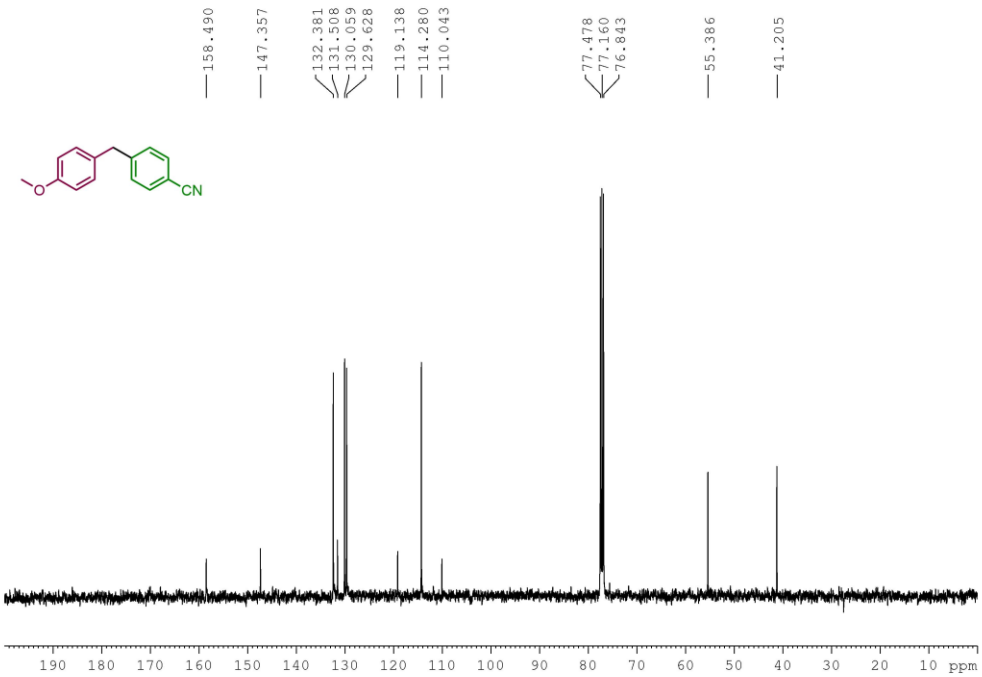
^{13}C NMR (100 MHz, $CDCl_3$), **4o-*o***



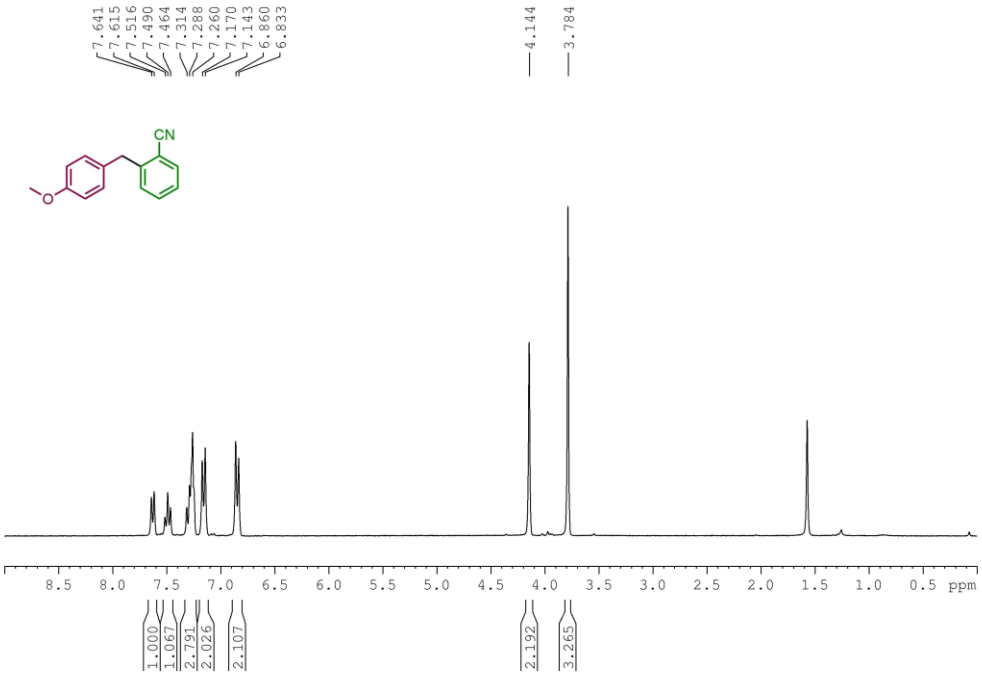
^{1}H NMR (300 MHz, $CDCl_3$), **4p-*p***



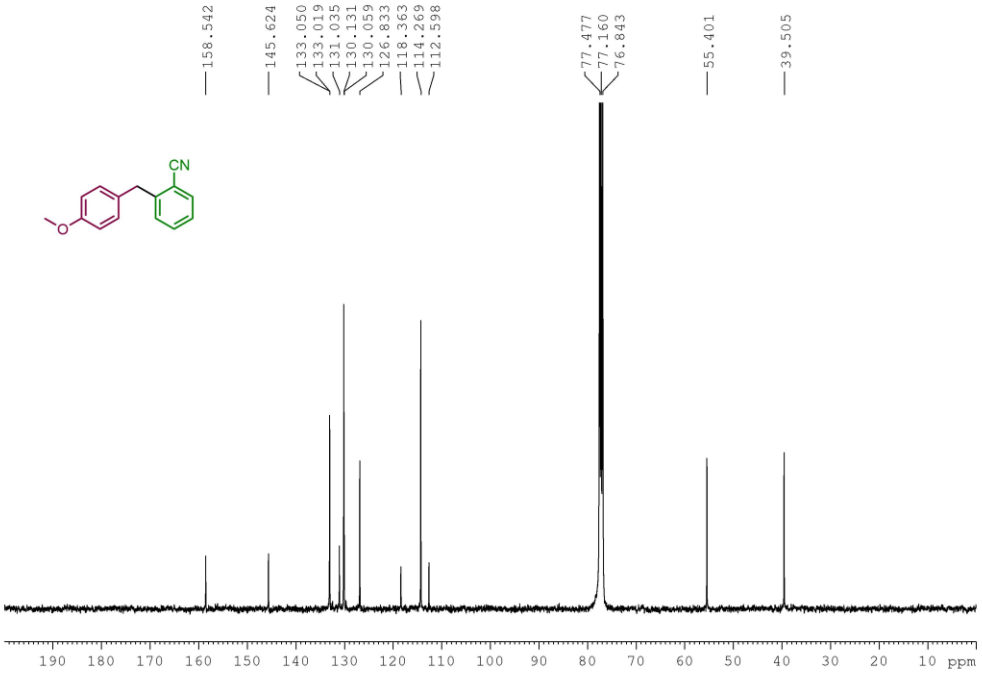
^{13}C NMR (100 MHz, $CDCl_3$), **4p-*p***



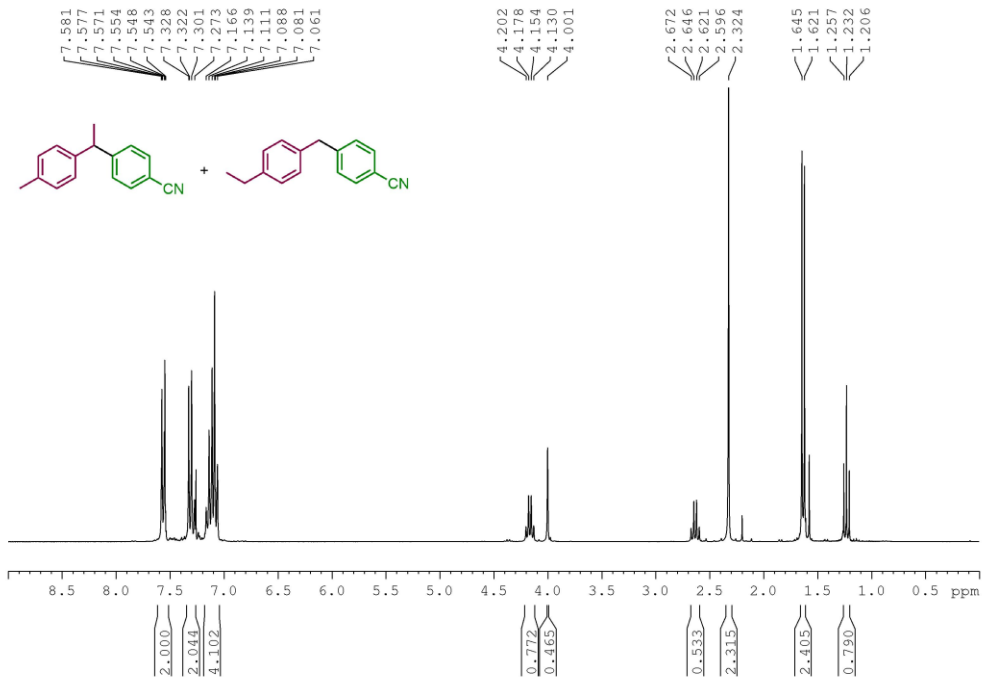
^{1}H NMR (300 MHz, $CDCl_3$), **4p-*o***



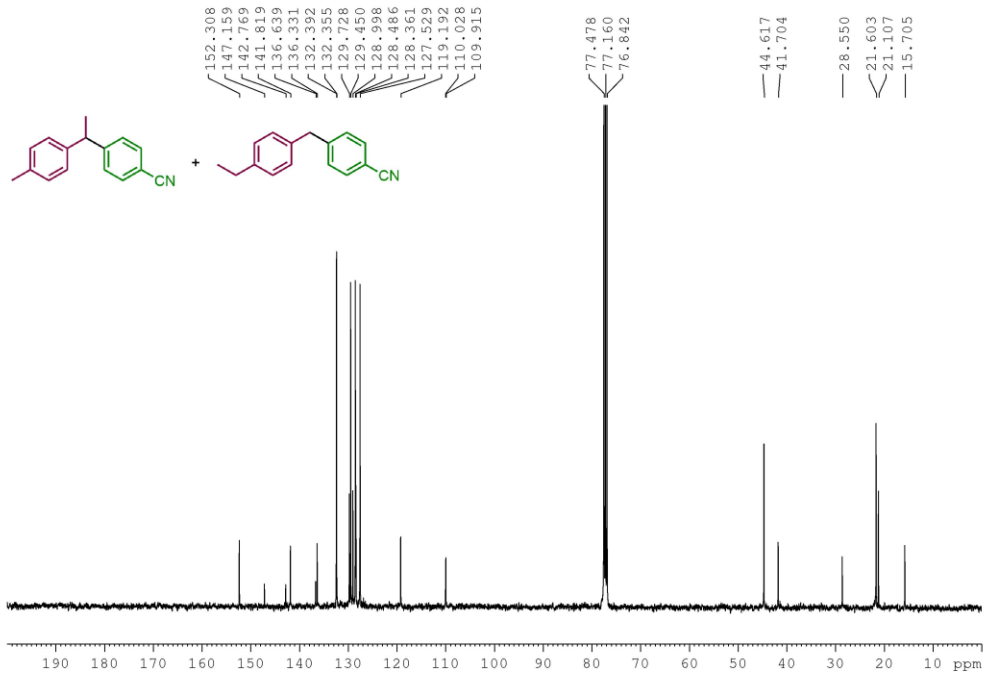
^{13}C NMR (100 MHz, $CDCl_3$), **4p-*o***



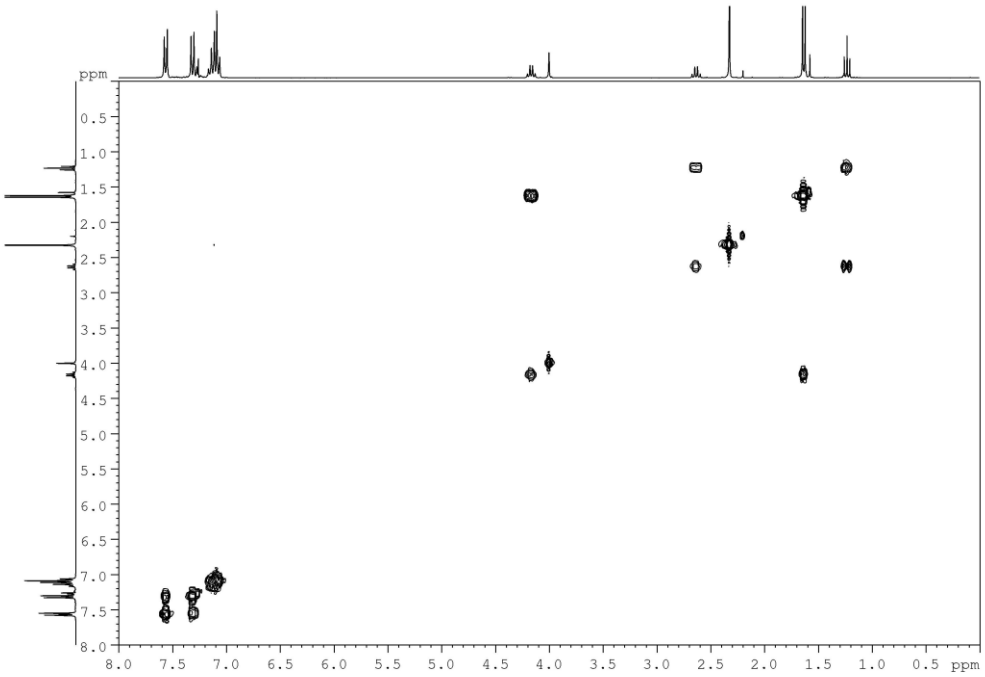
^{1}H NMR (300 MHz, $CDCl_3$), **4q/4r**



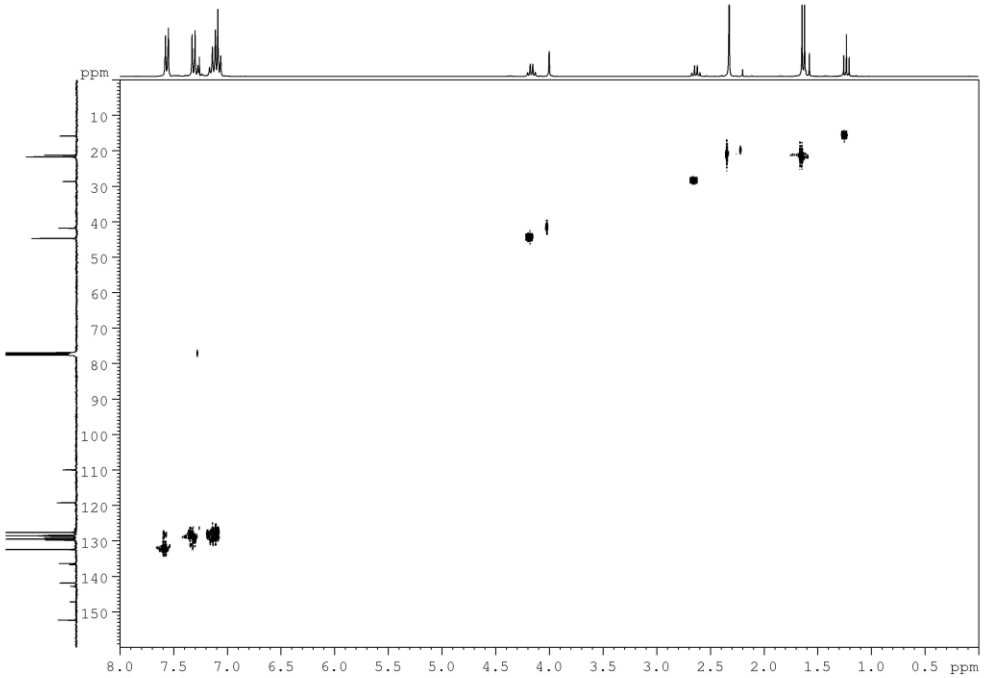
^{13}C NMR (100 MHz, $CDCl_3$), **4q/4r**



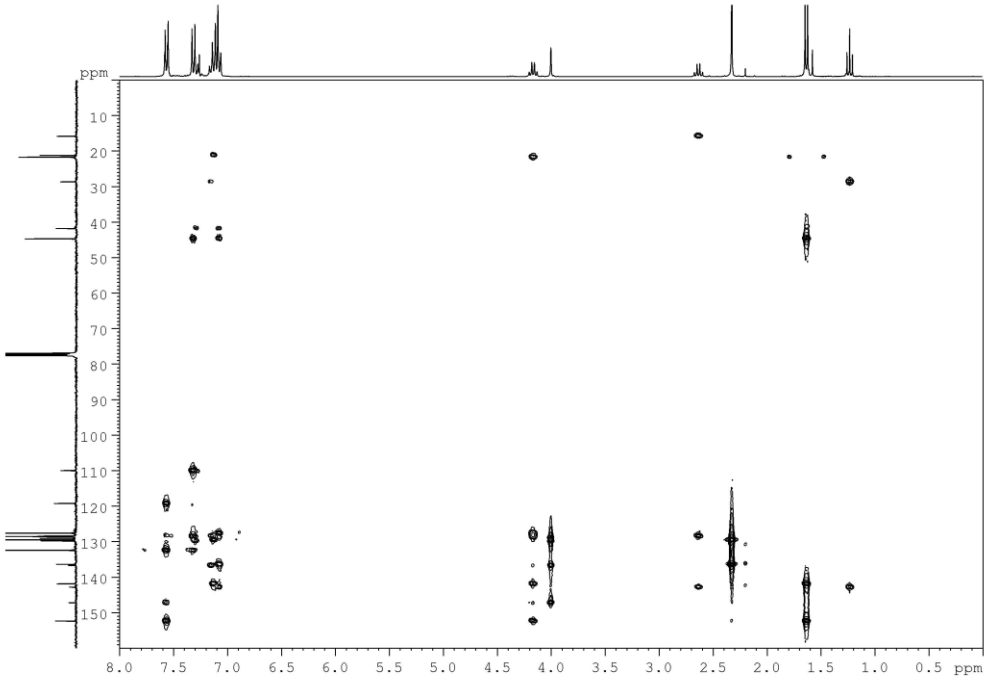
COSY, **4q/4r**



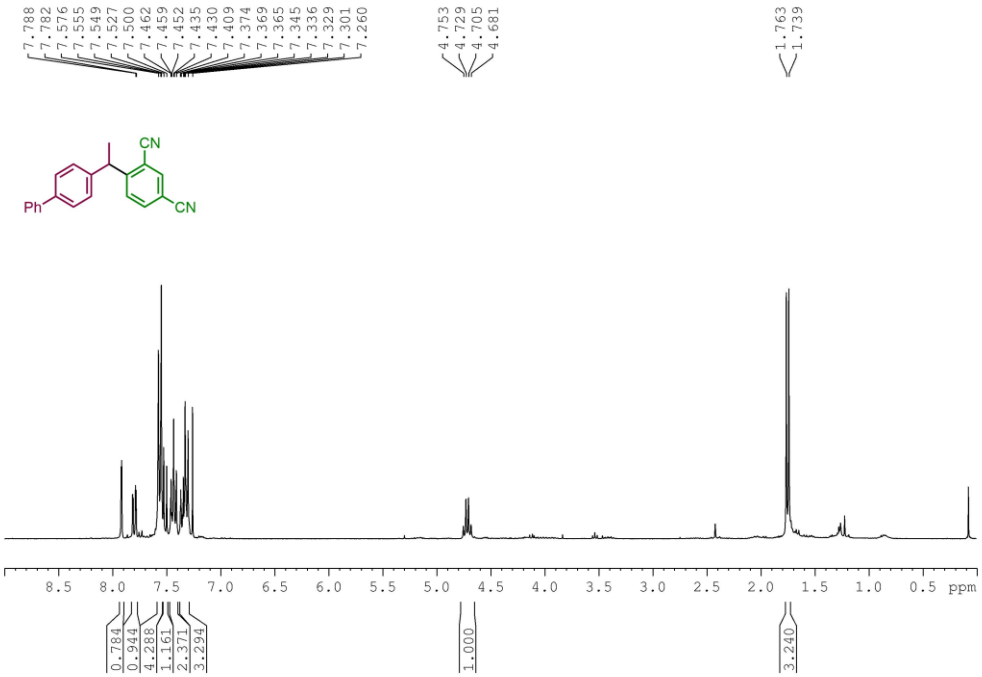
HSQC, **4q/4r**



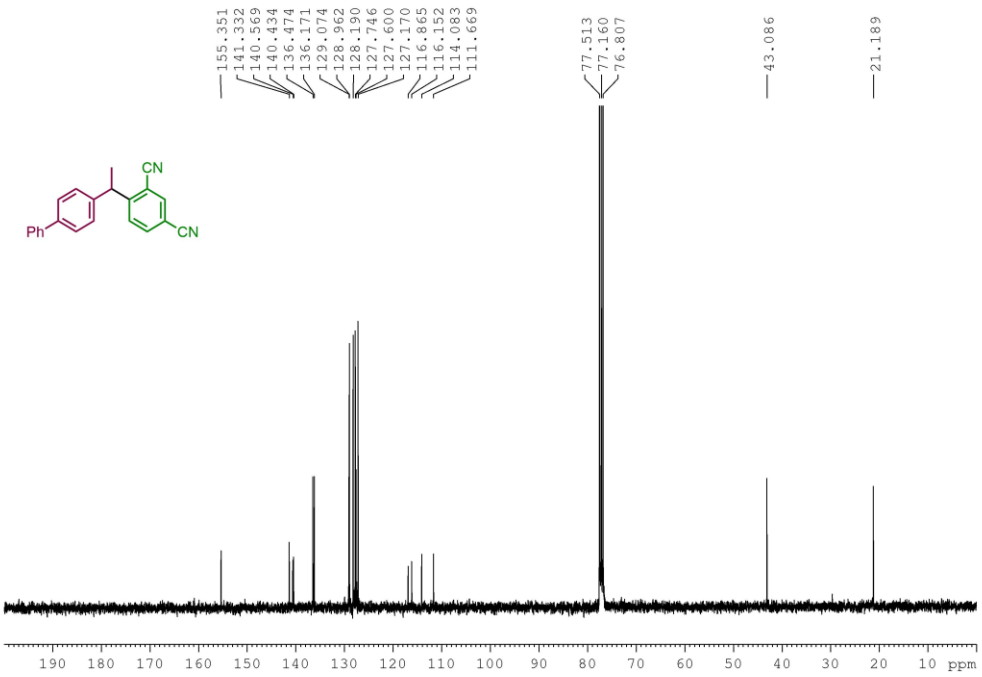
HMBC, **4q/4r**


ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

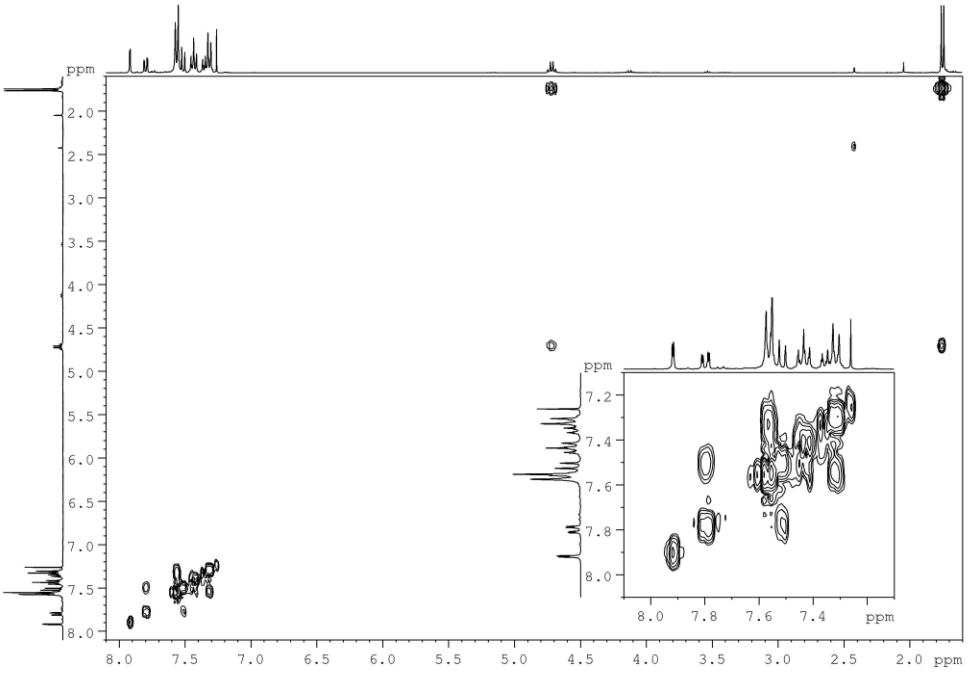
^{1}H NMR (300 MHz, $CDCl_3$), **4s-*o***



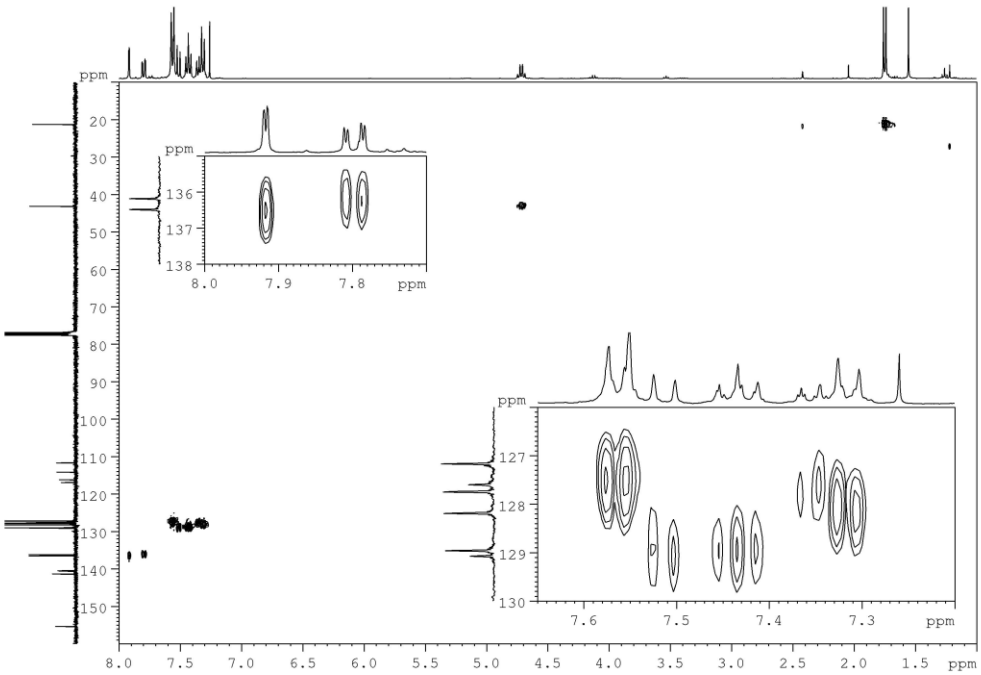
^{13}C NMR (90 MHz, $CDCl_3$), **4s-*o***



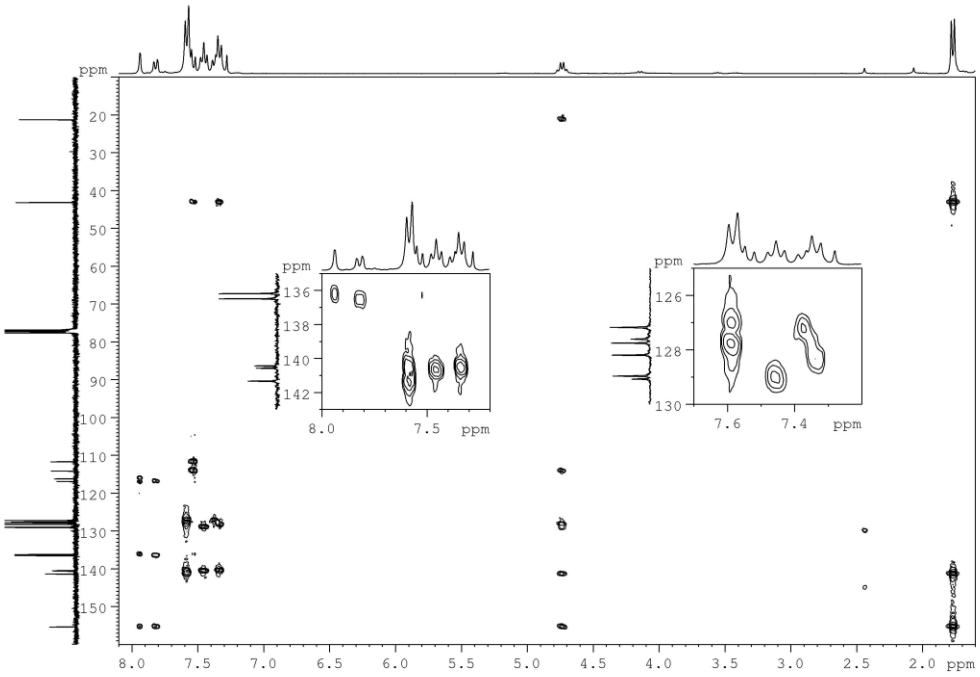
COSY, **4s-*o***



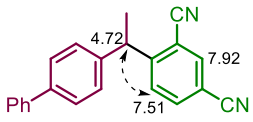
HSQC, **4s-*o***

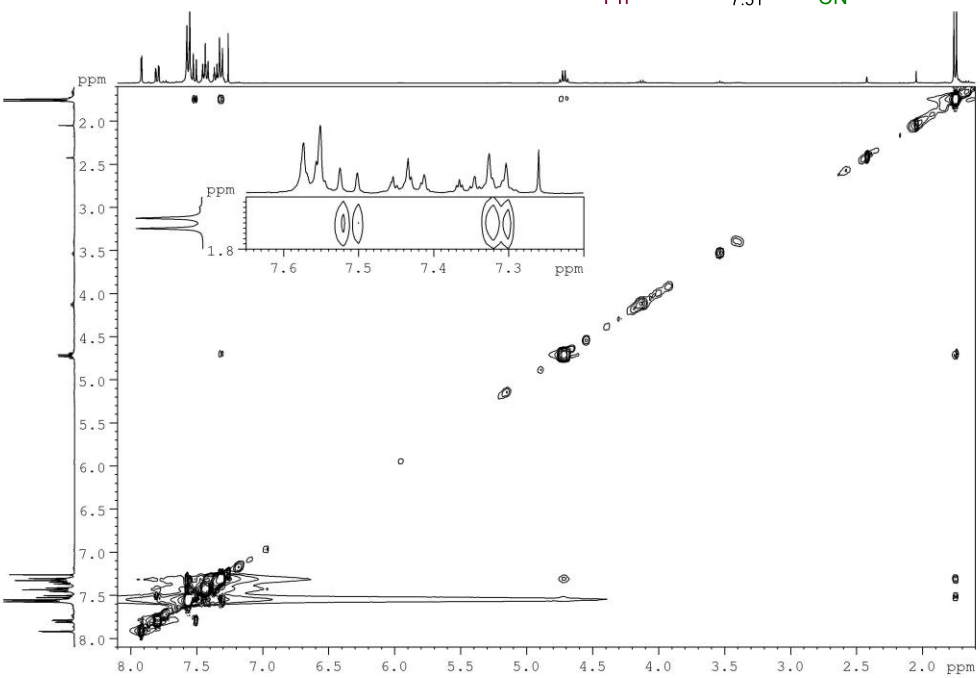


HMBC, **4s-*o***

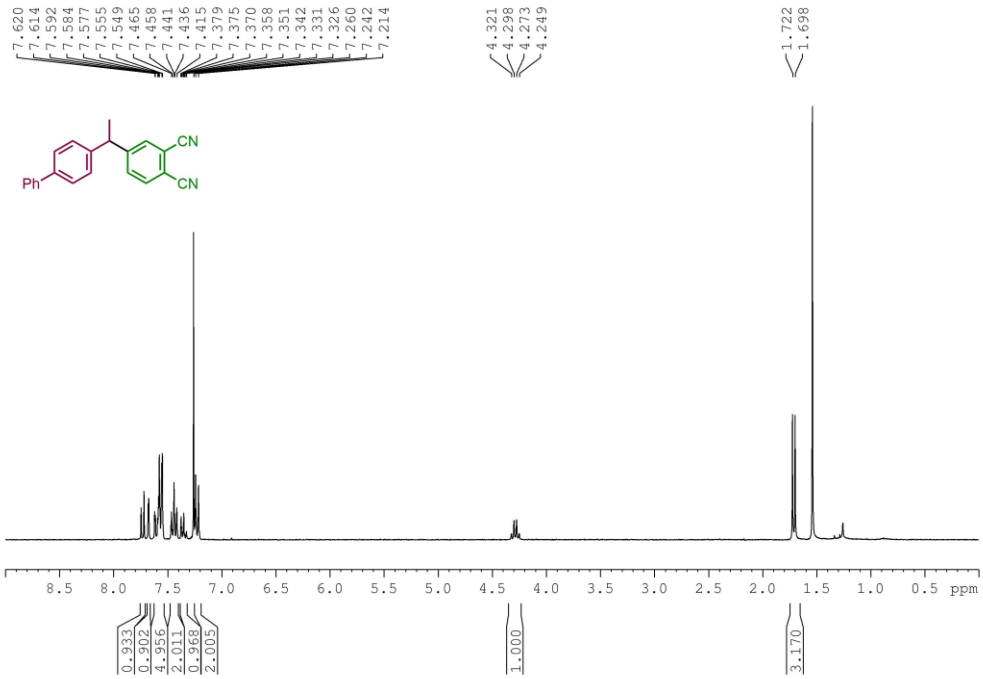


NOESY, **4s-*o***

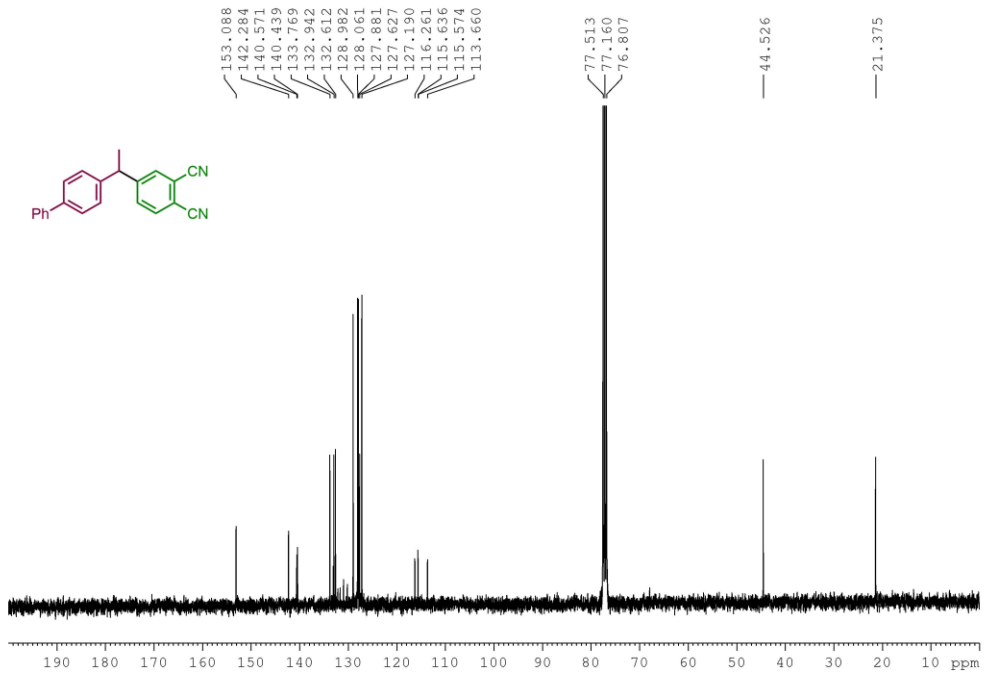




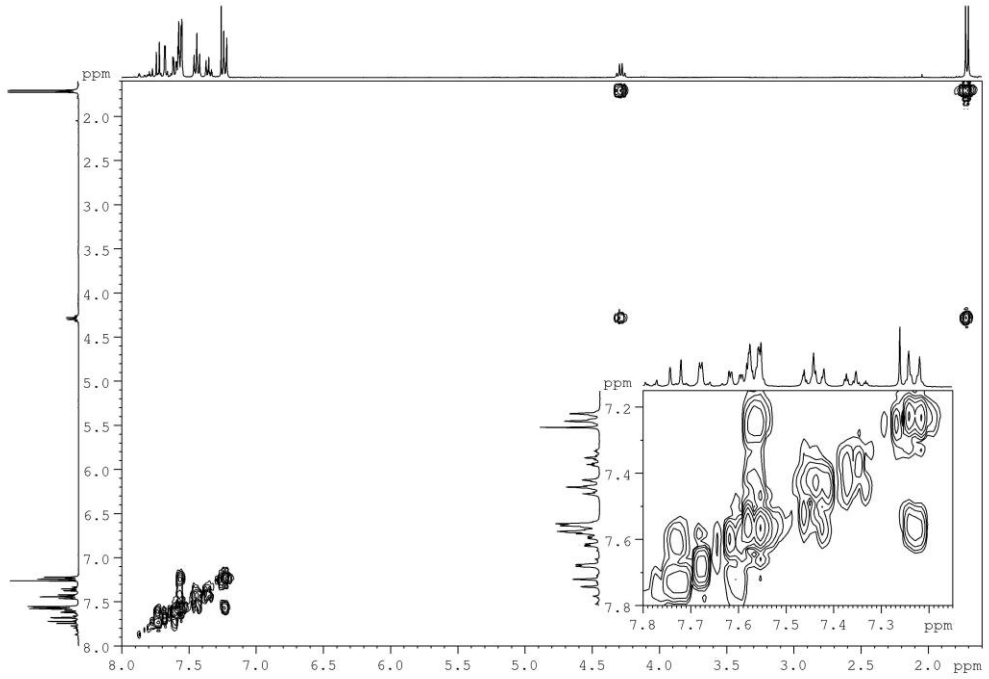
^{1}H NMR (300 MHz, $CDCl_3$), **4s-*m***



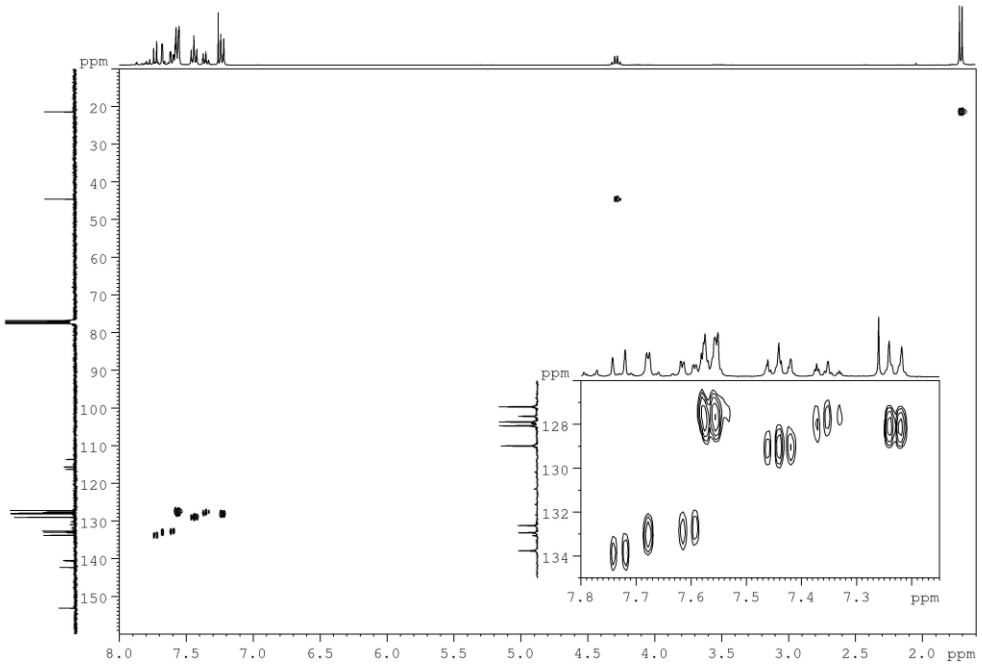
^{13}C NMR (90 MHz, $CDCl_3$), **4s-*m***



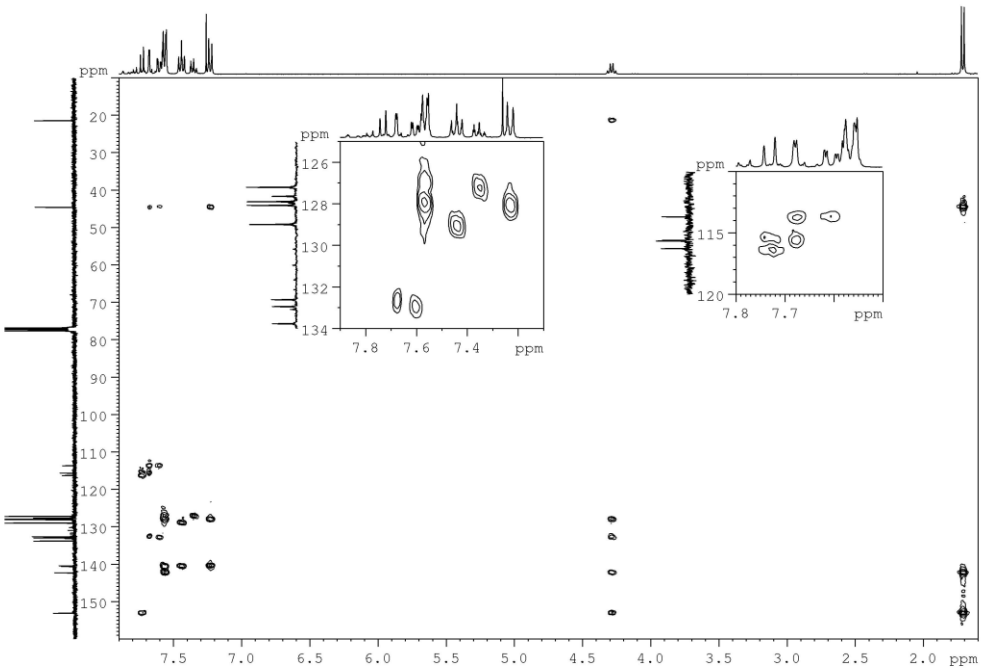
COSY, **4s-*m***



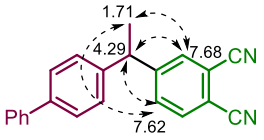
HSQC, **4s-*m***

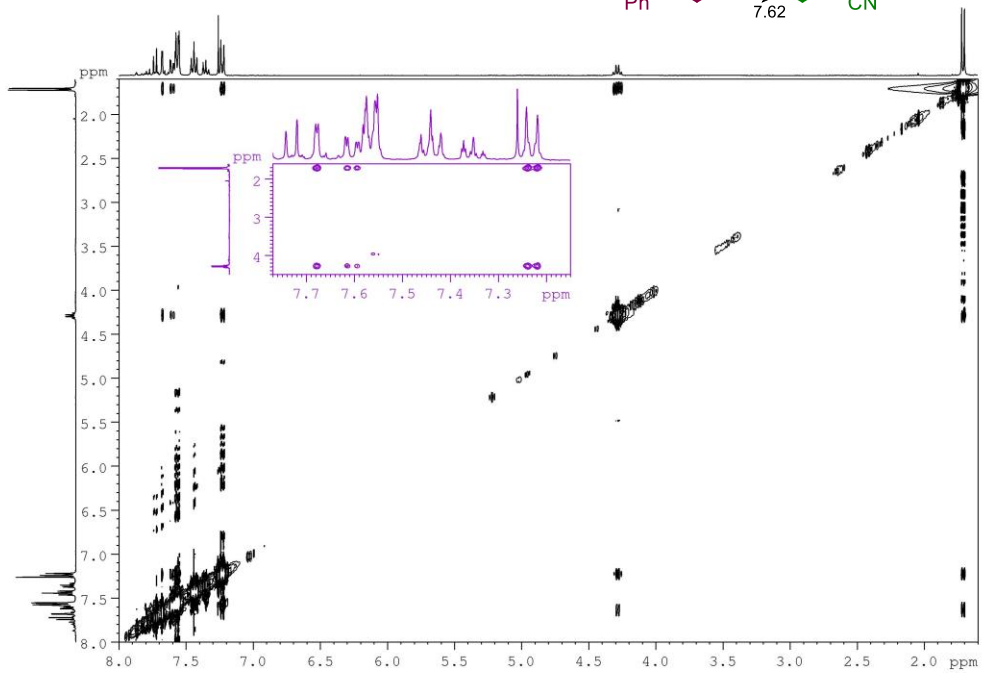


HMBC, **4s-*m***

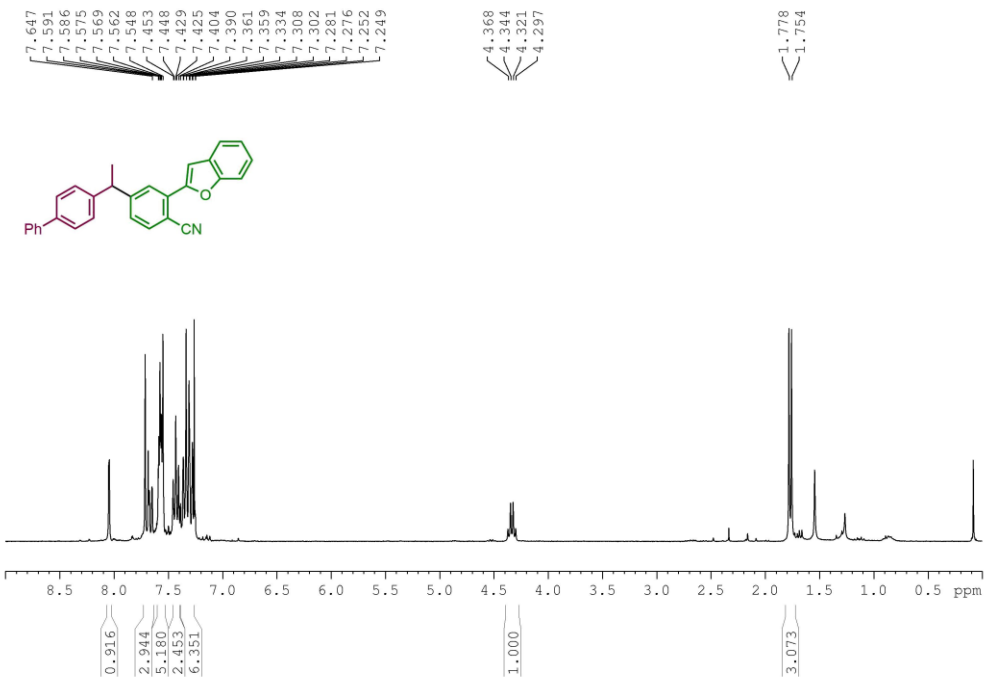


NOESY, **4s-*m***

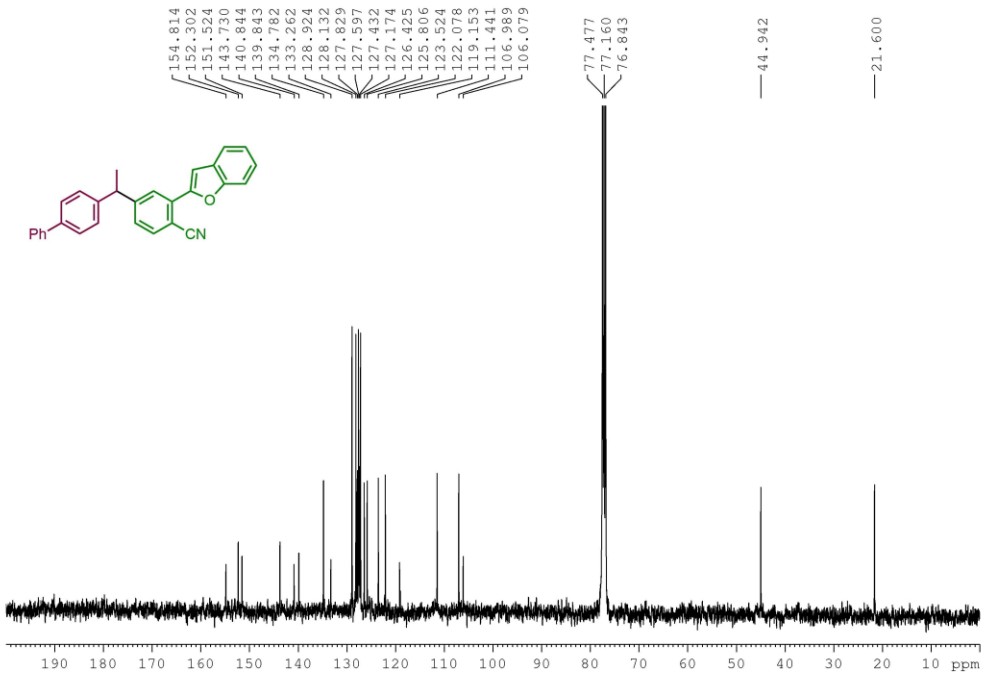




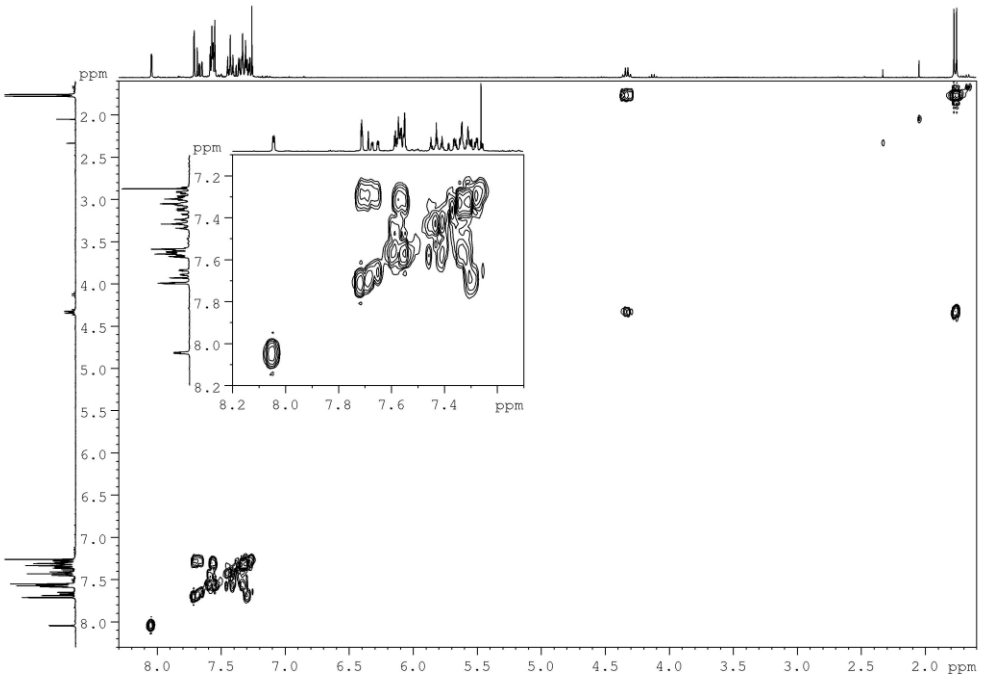
^{1}H NMR (300 MHz, $CDCl_3$), **4t-*m***



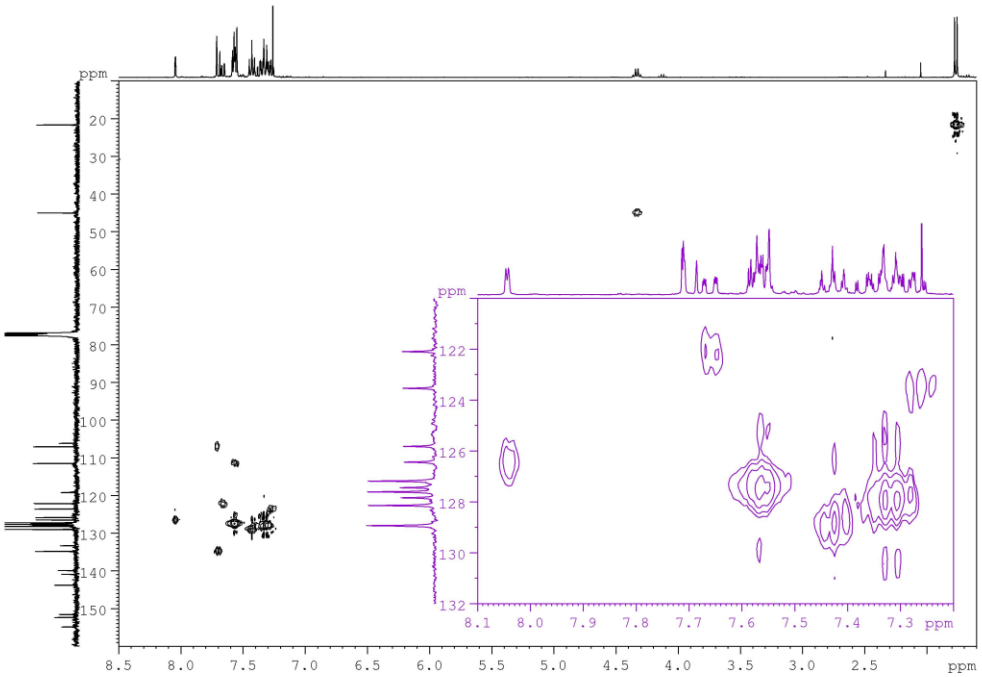
^{13}C NMR (100 MHz, $CDCl_3$), **4t-*m***



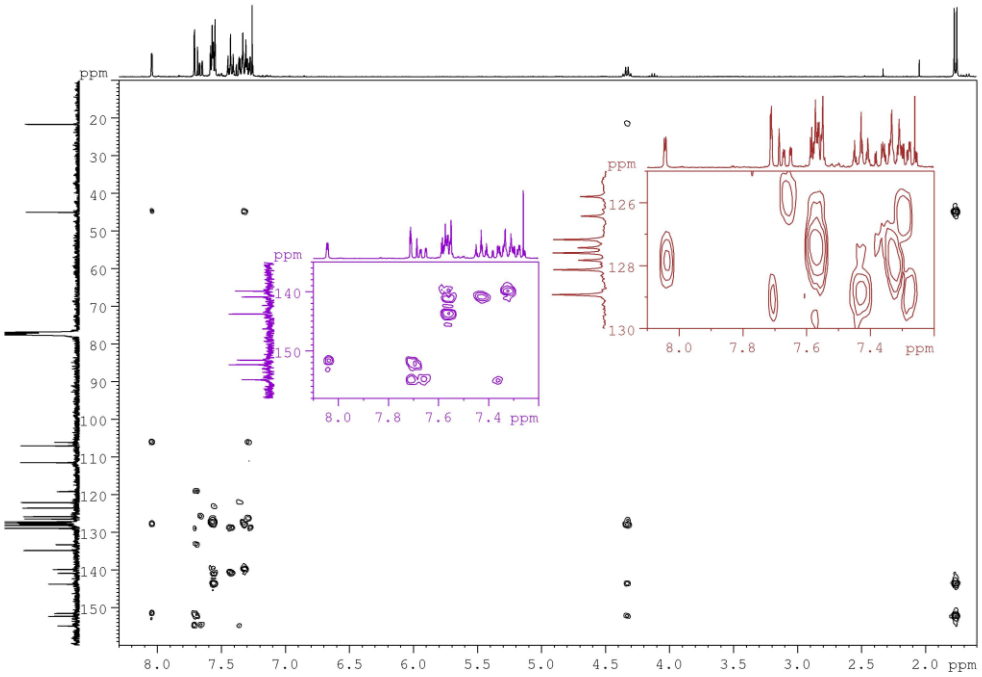
COSY, **4t-*m***



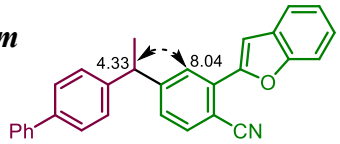
HSQC, **4t-*m***

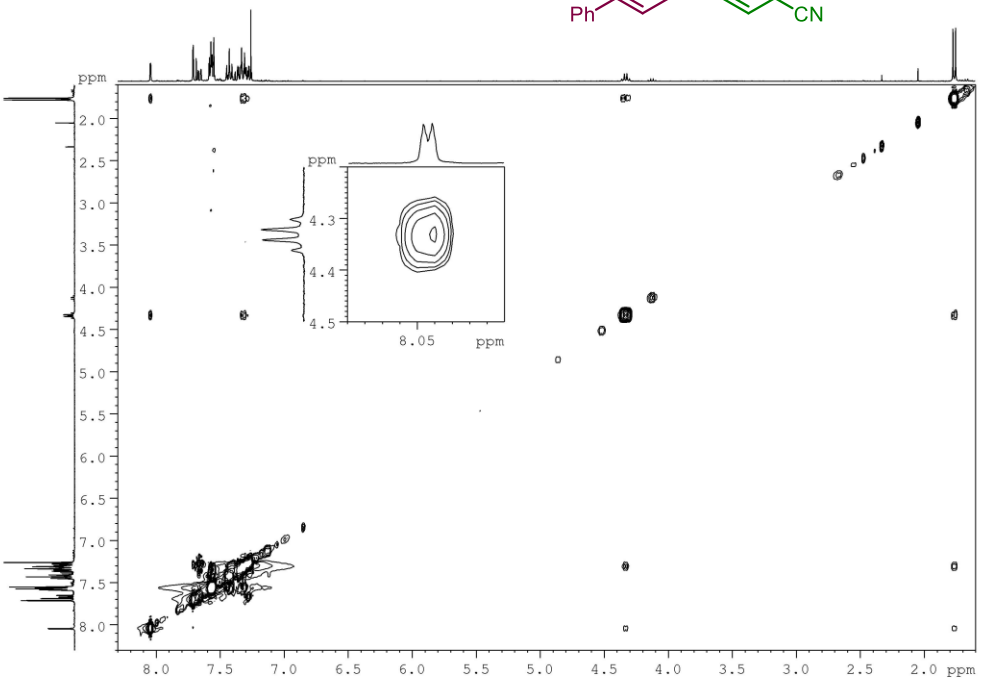


HMBC, **4t-*m***

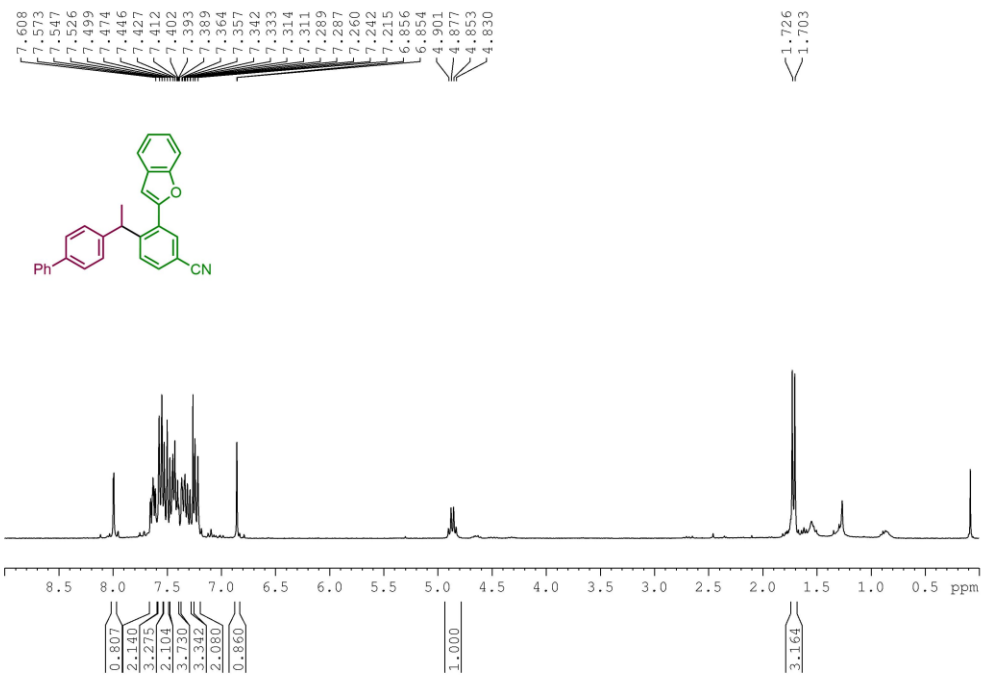


NOESY, **4t-*m***

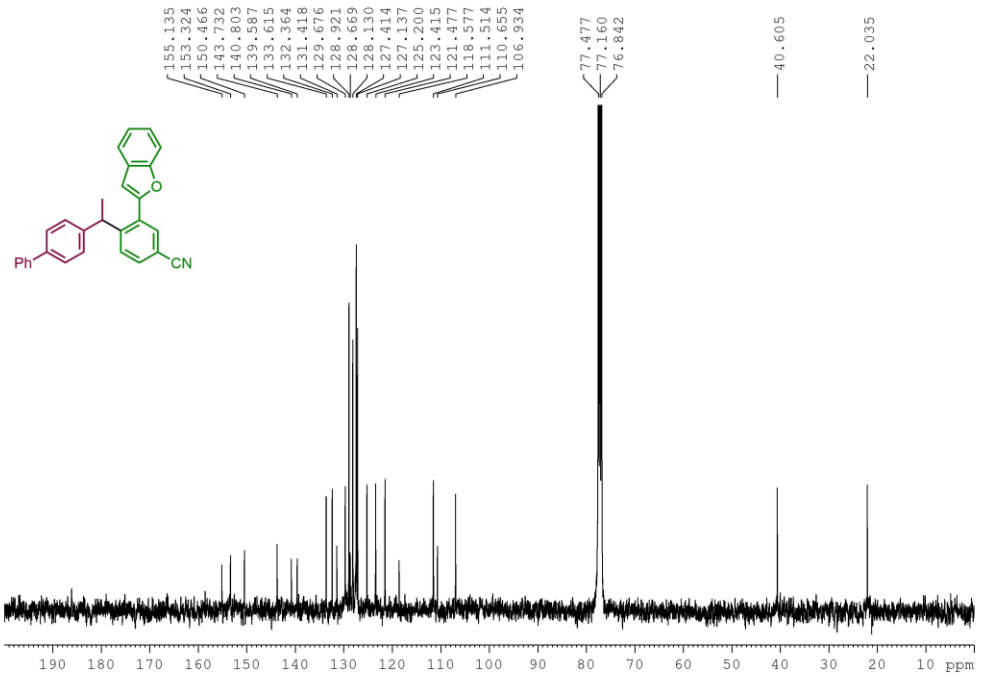




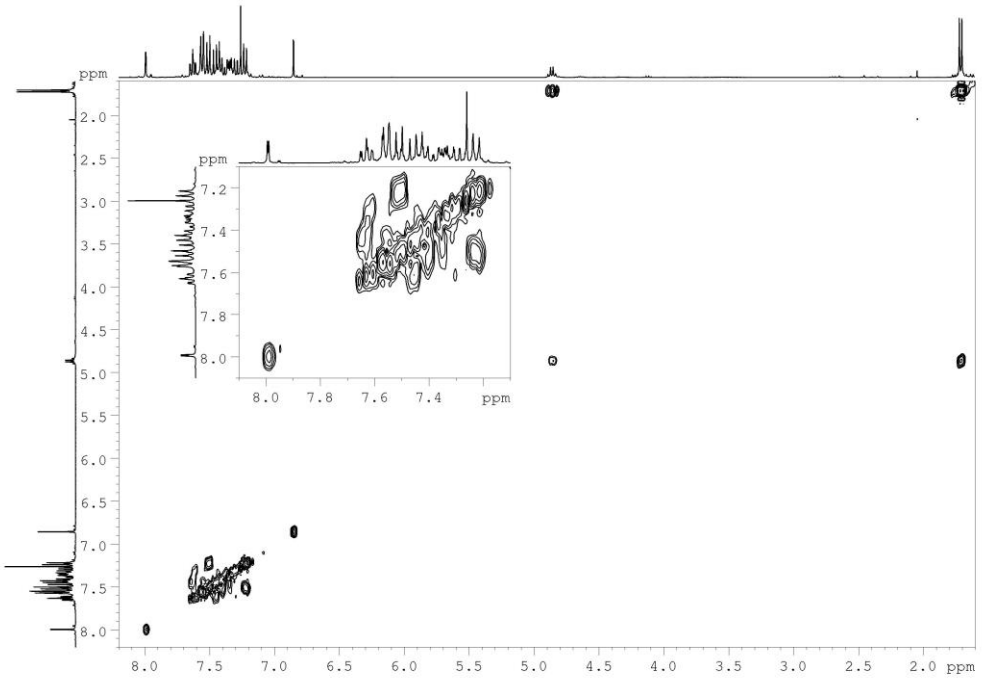
^{1}H NMR (300 MHz, $CDCl_3$), **4t-*o***



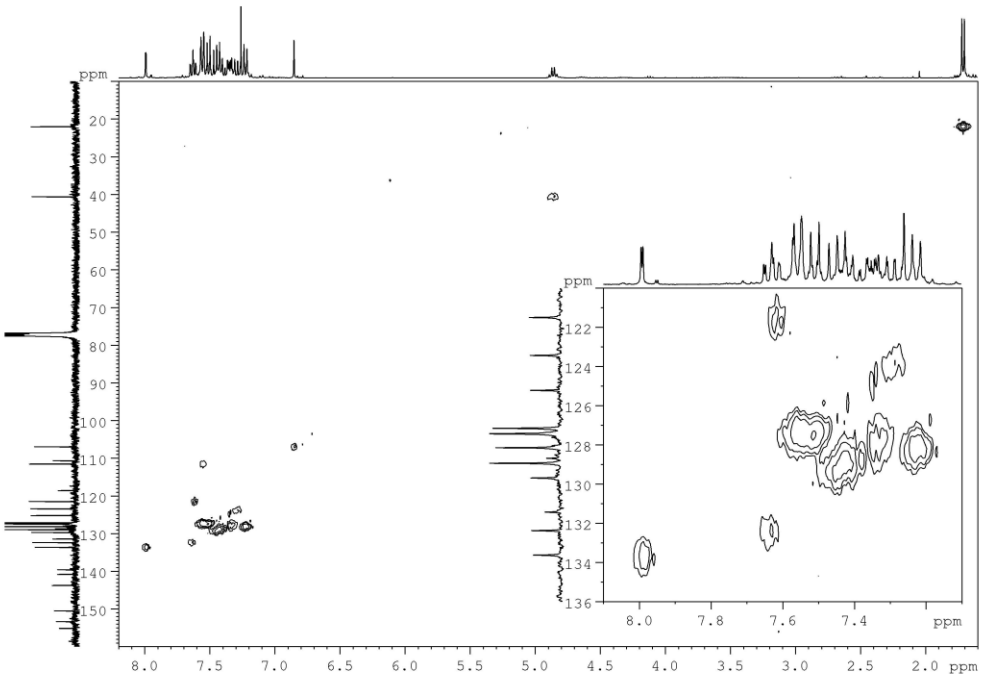
^{13}C NMR (100 MHz, $CDCl_3$), **4t-*o***



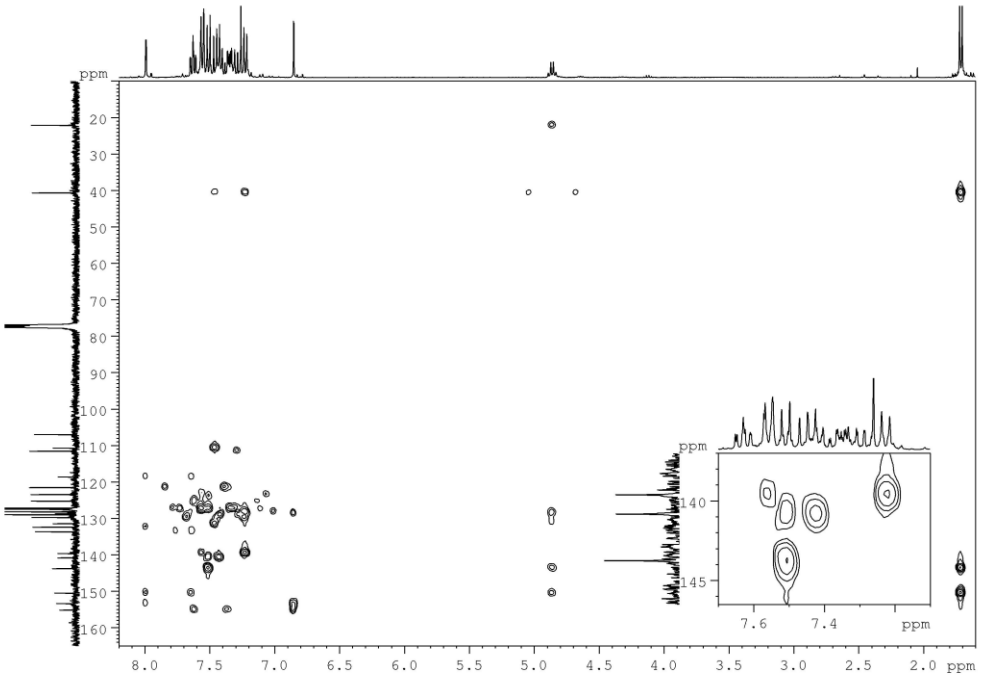
COSY, **4t-*o***



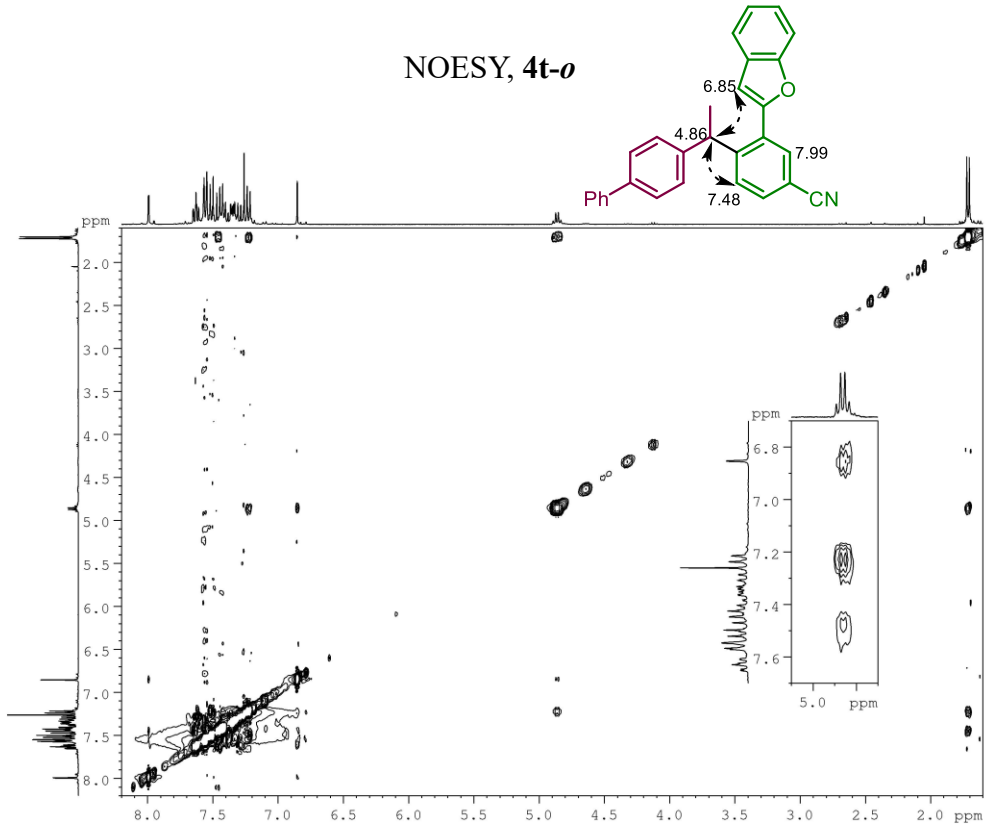
HSQC, **4t-*o***



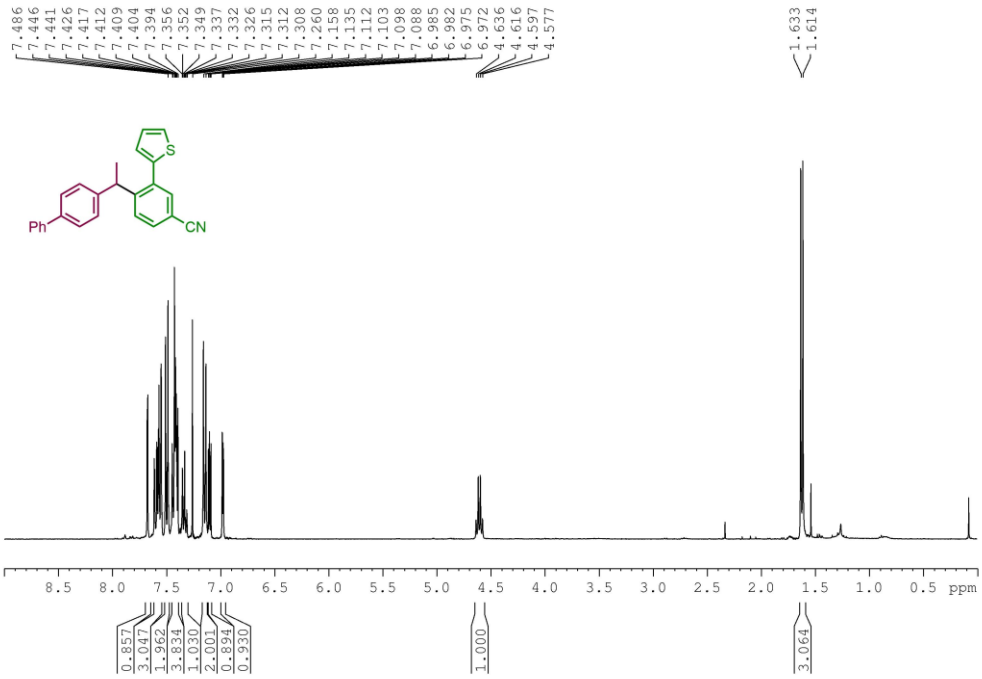
HMBC, **4t-*o***



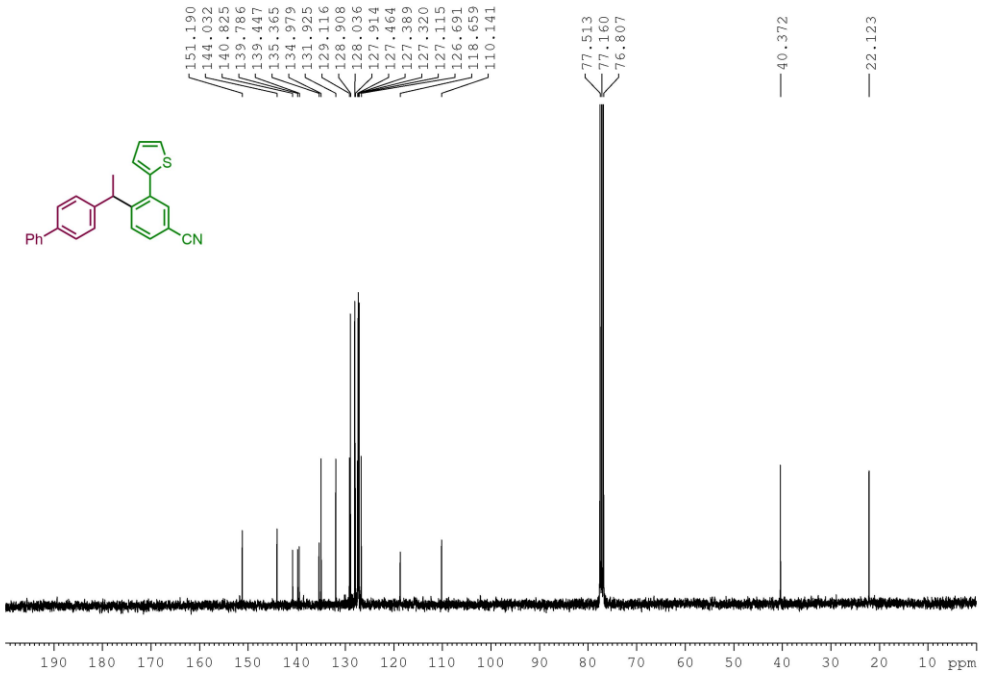
NOESY, **4t-*o***



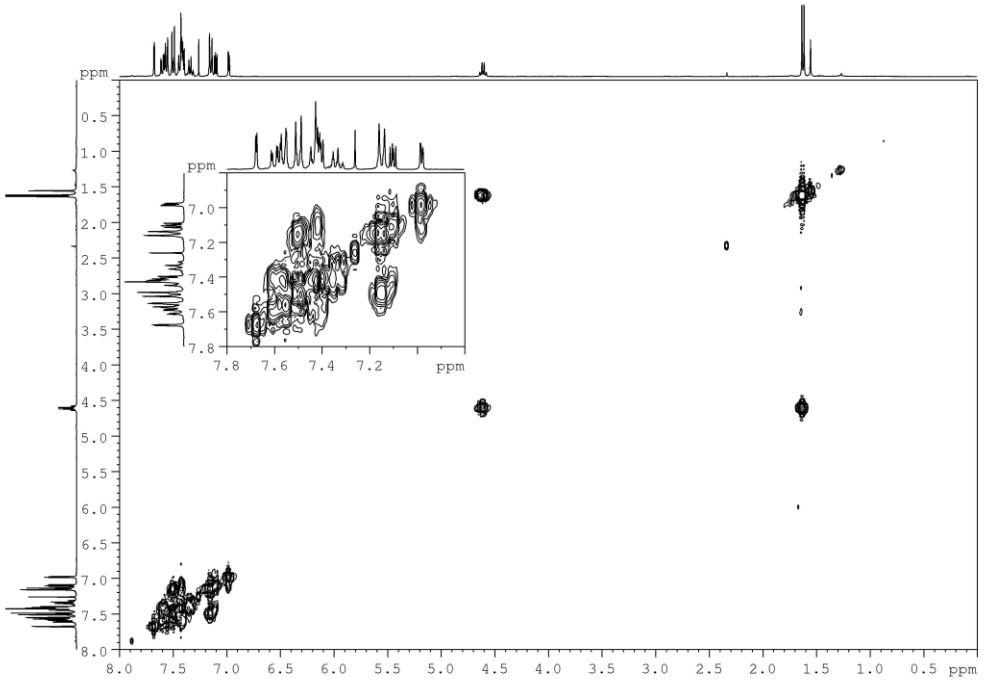
^{1}H NMR (360 MHz, $CDCl_3$), **4u-*o***



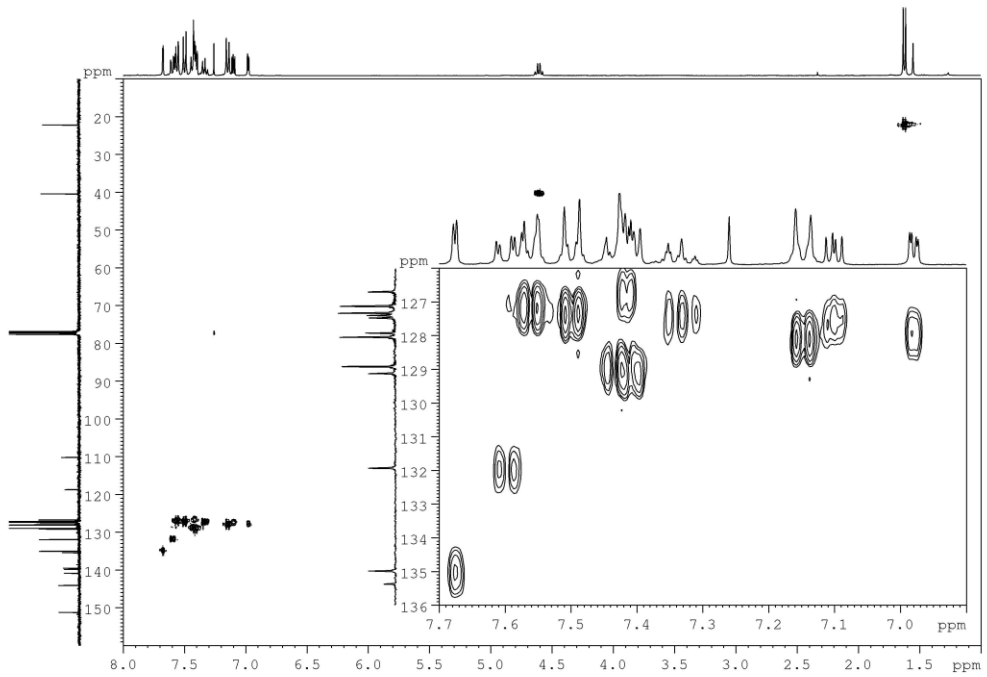
^{13}C NMR (90 MHz, $CDCl_3$), **4u-*o***



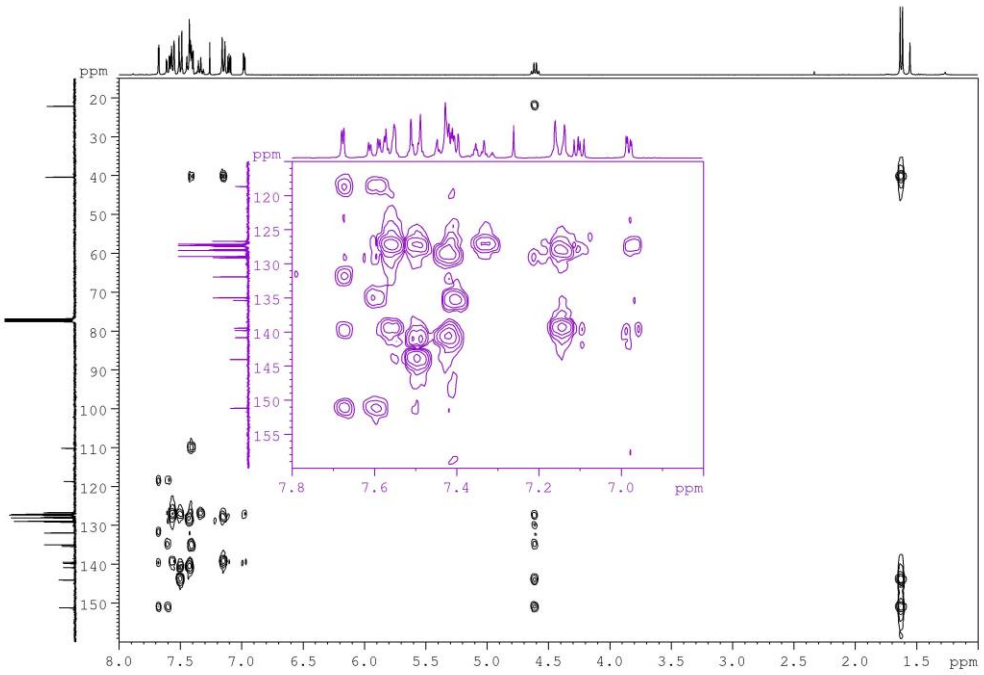
COSY, **4u-*o***



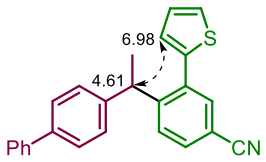
HSQC, **4u-*o***

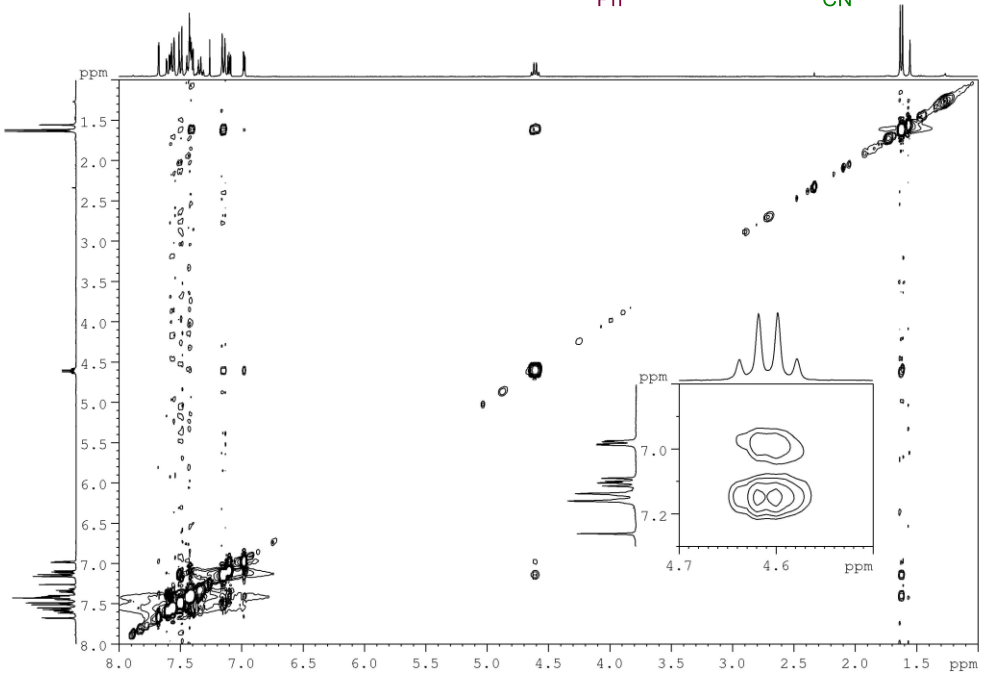


HMBC, **4u-*o***

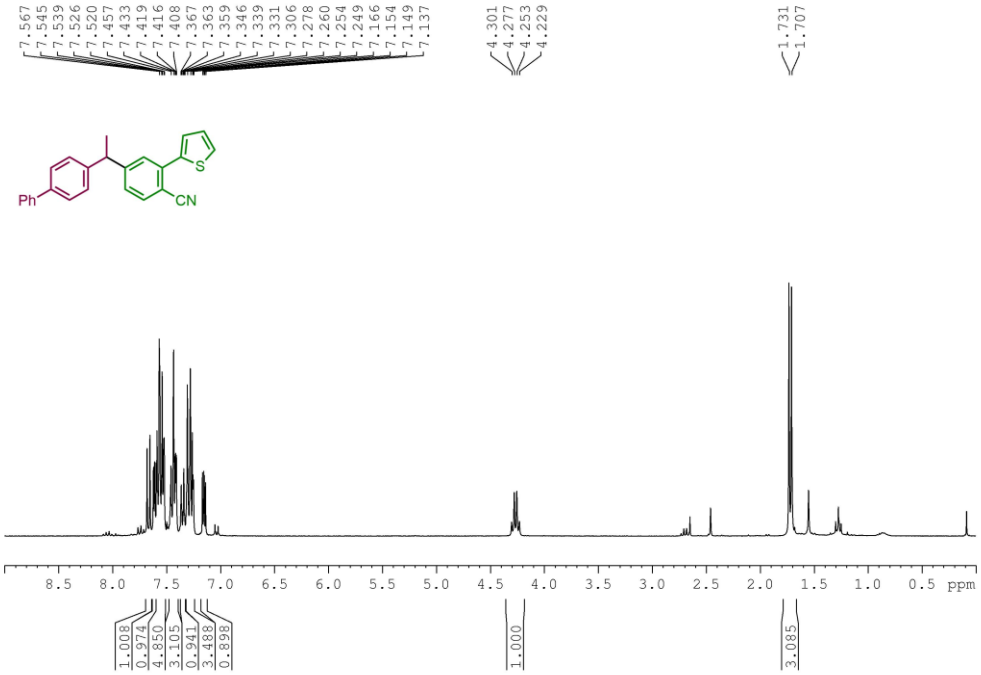


NOESY, **4u-*o***

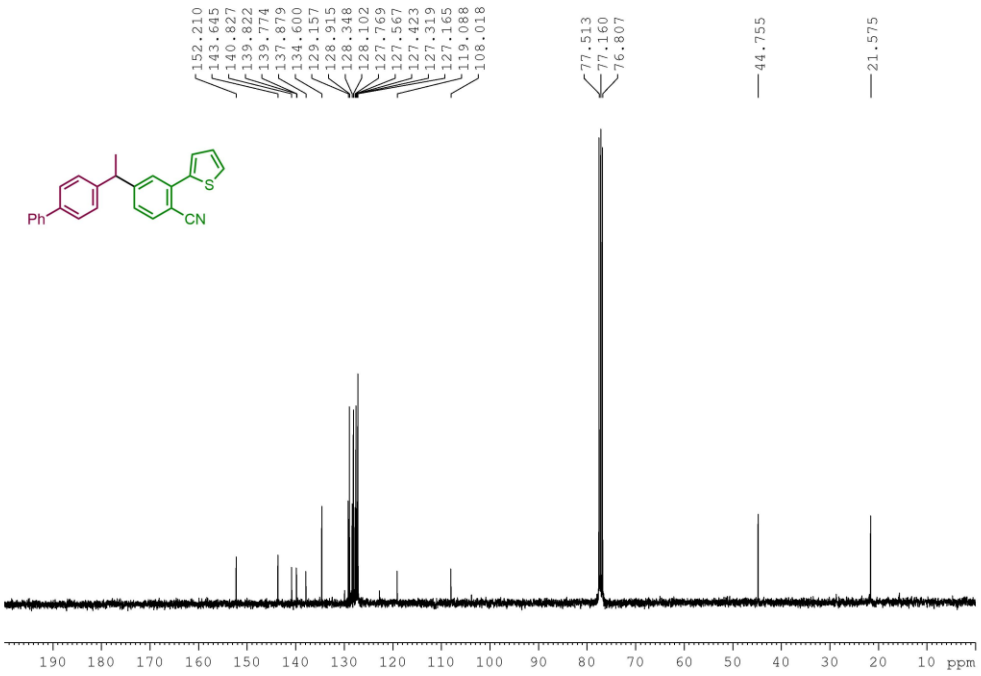




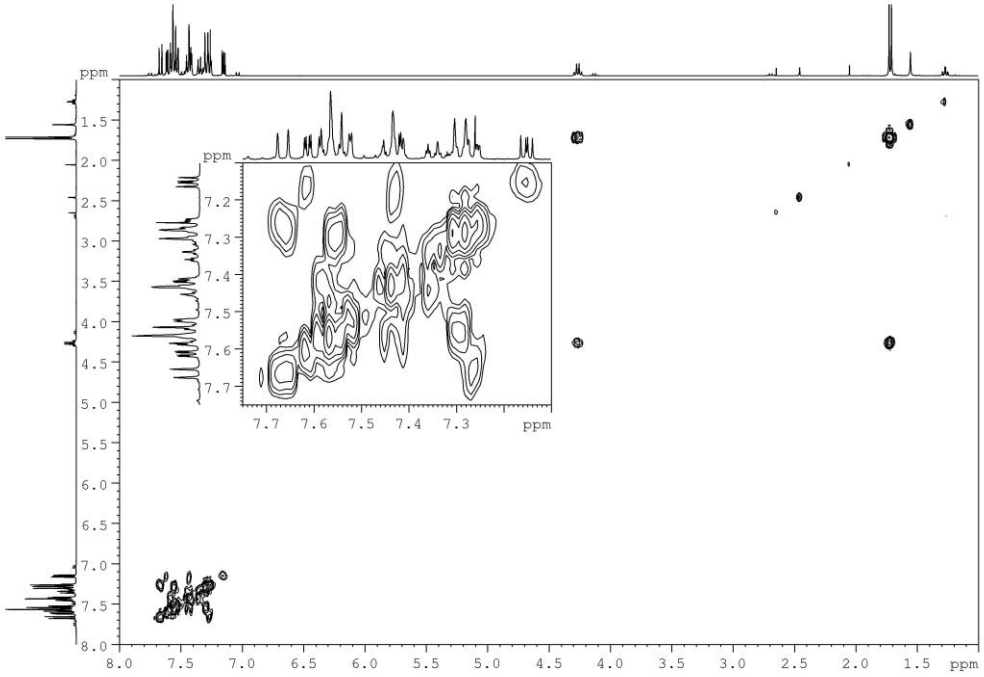
^{1}H NMR (300 MHz, $CDCl_3$), **4u-*m***



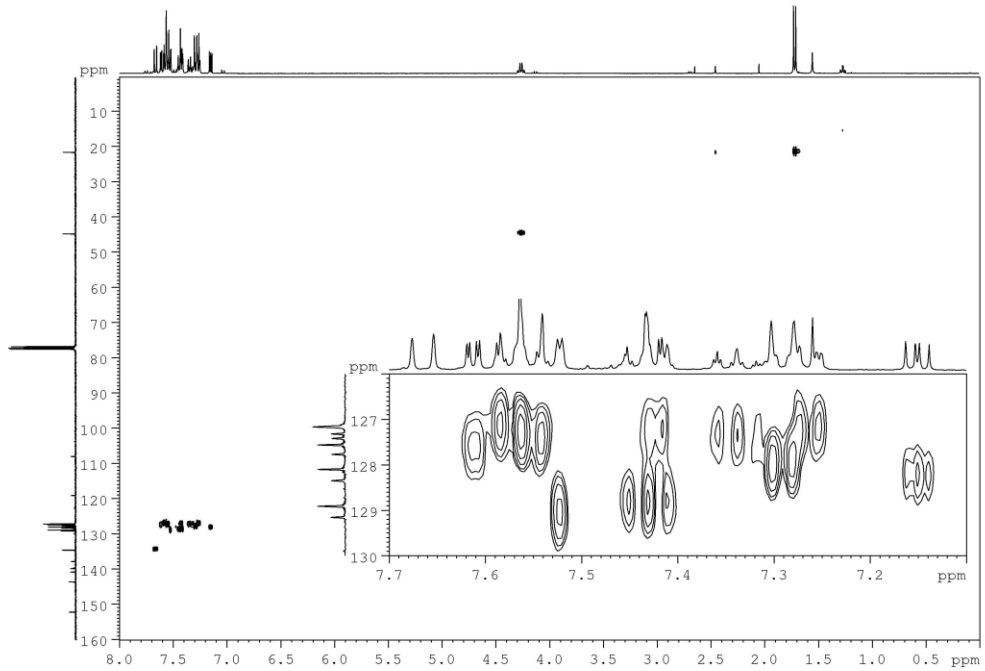
^{13}C NMR (90 MHz, $CDCl_3$), **4u-*m***



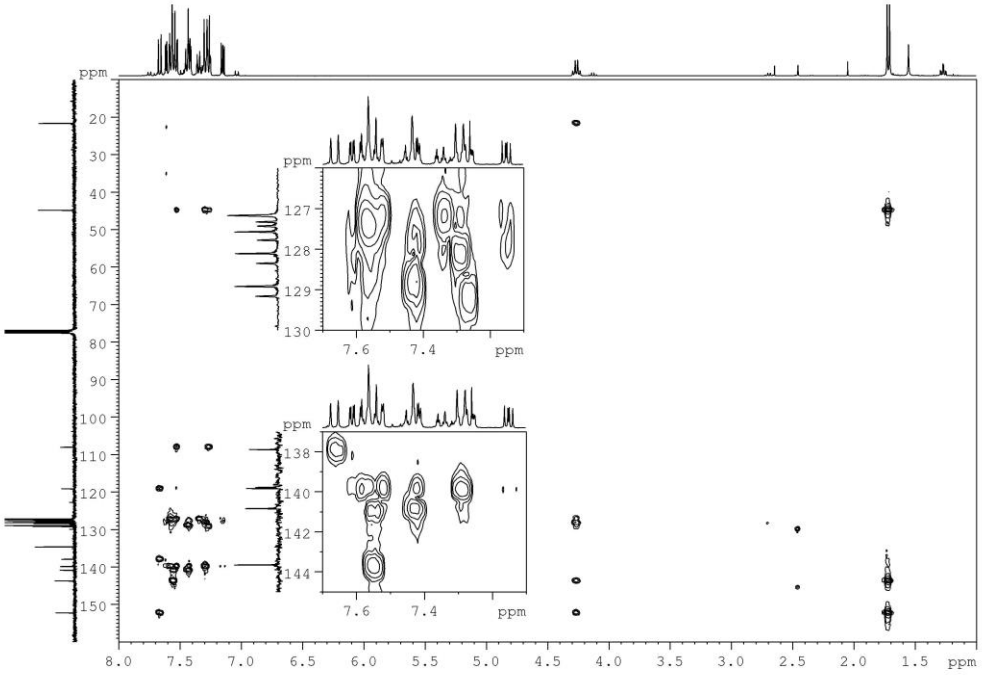
COSY, **4u-*m***



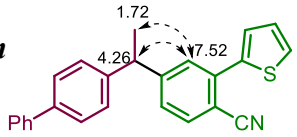
HSQC, **4u-*m***

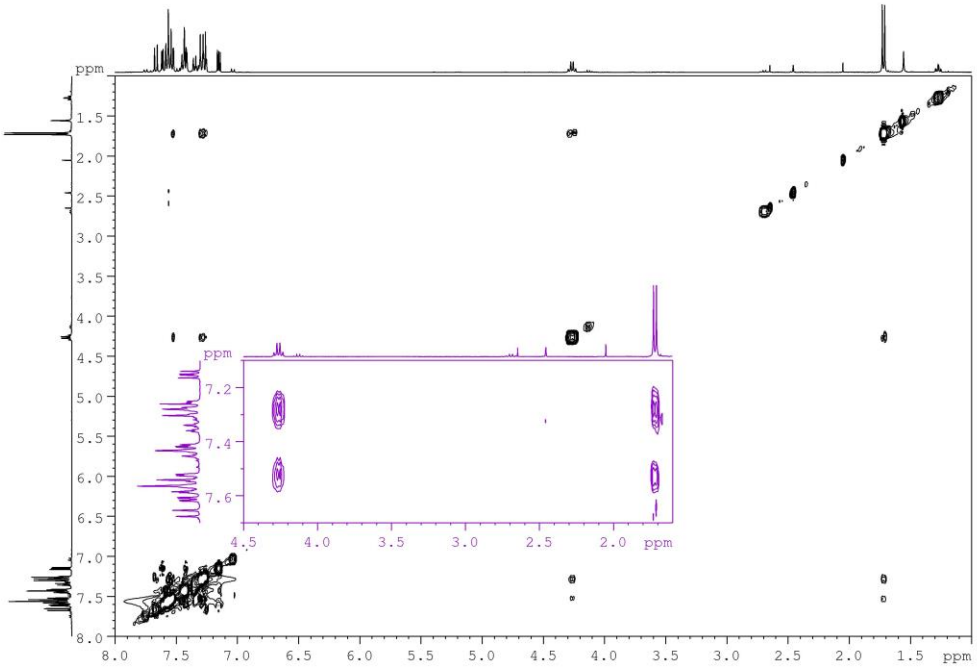


HMBC, **4u-*m***

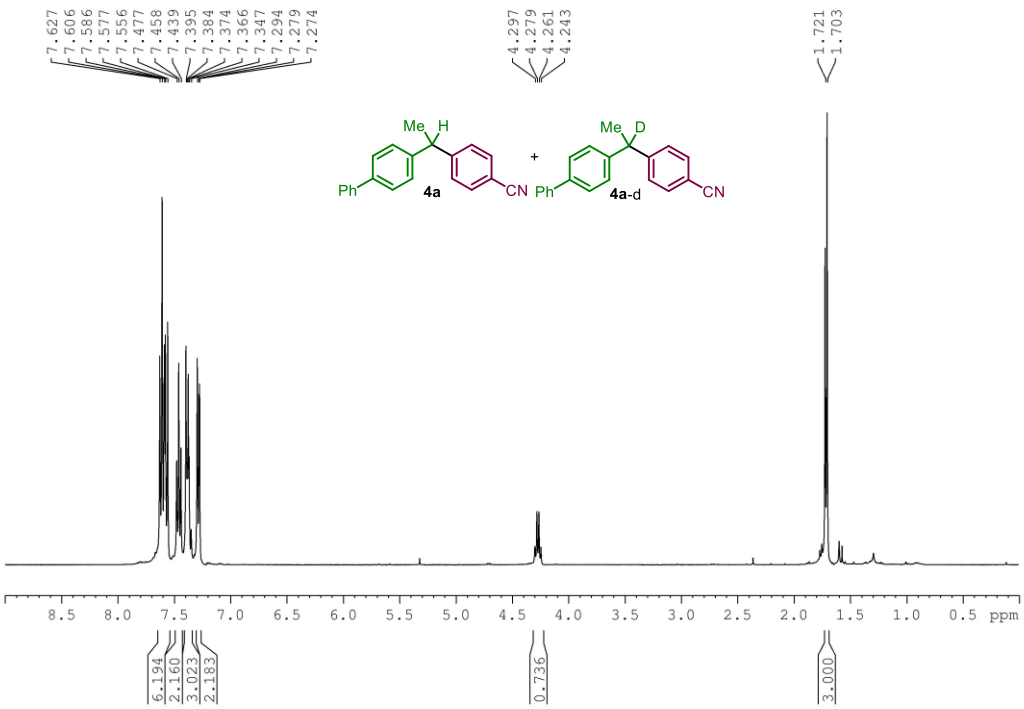


NOESY, **4u-*m***

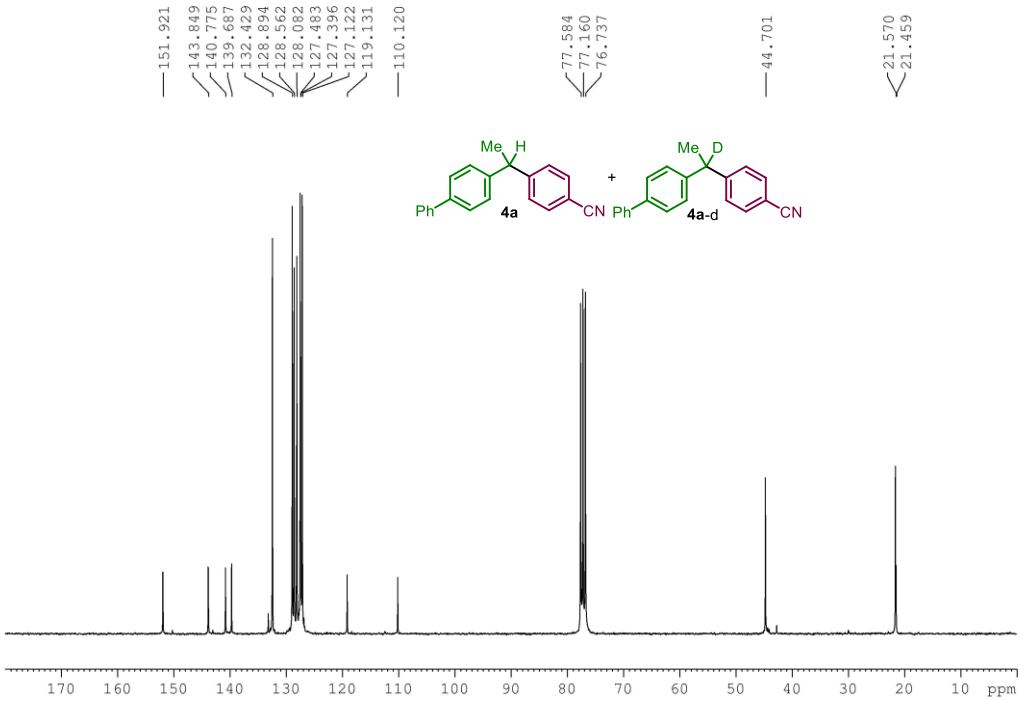




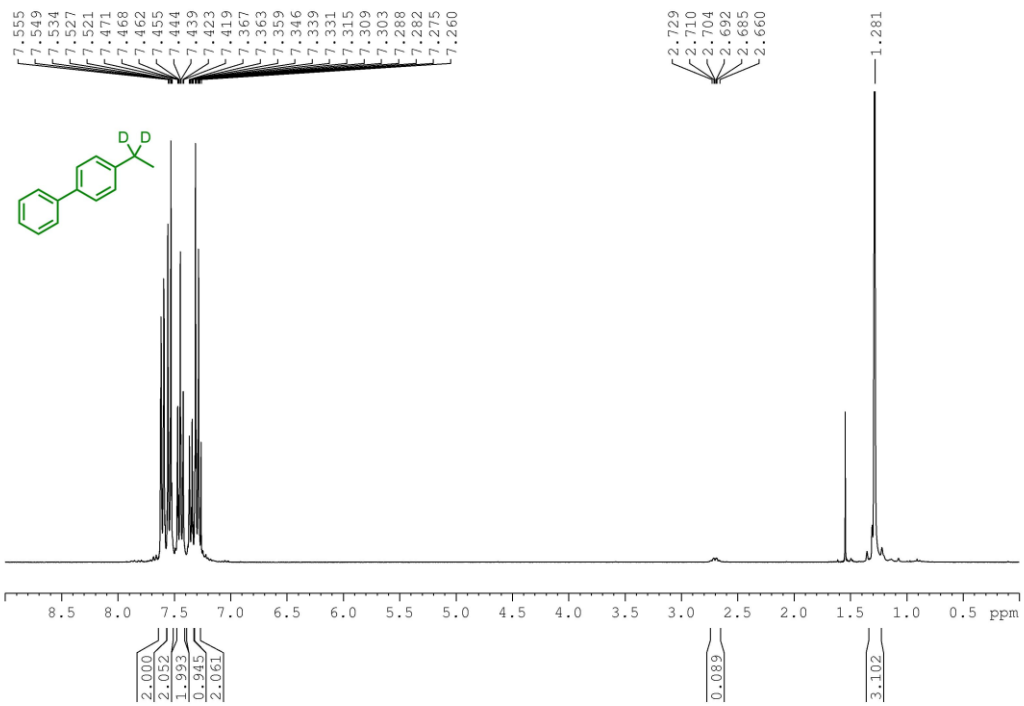
^{1}H NMR (400 MHz, $CDCl_3$), **4a** and **4a**-d



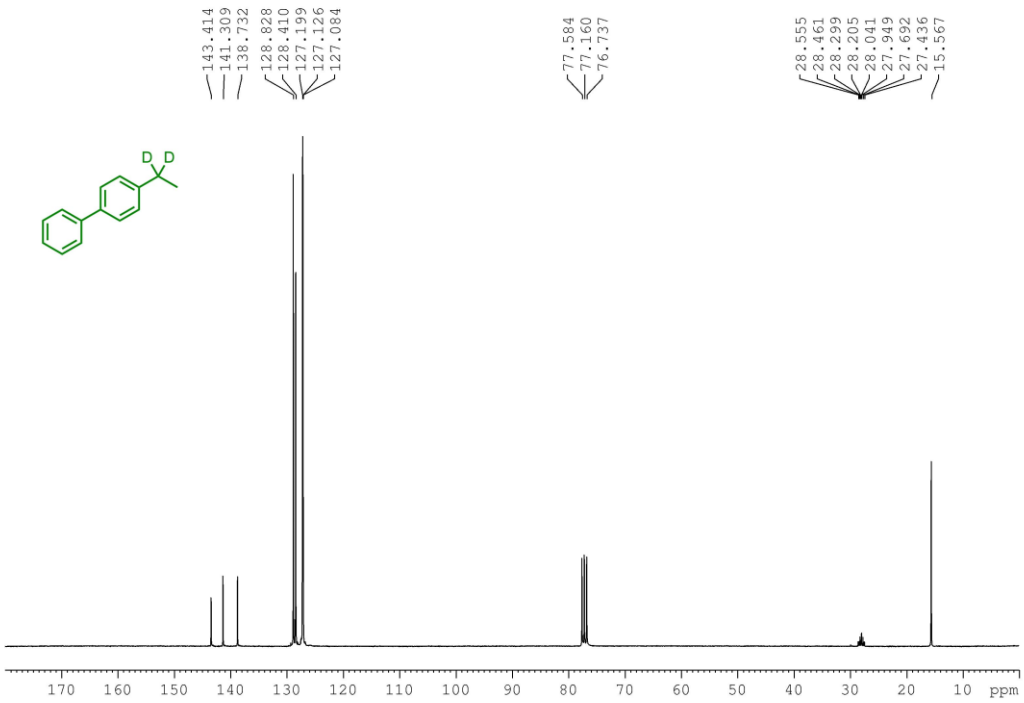
^{13}C NMR (75 MHz, $CDCl_3$), **4a** and **4a**-d



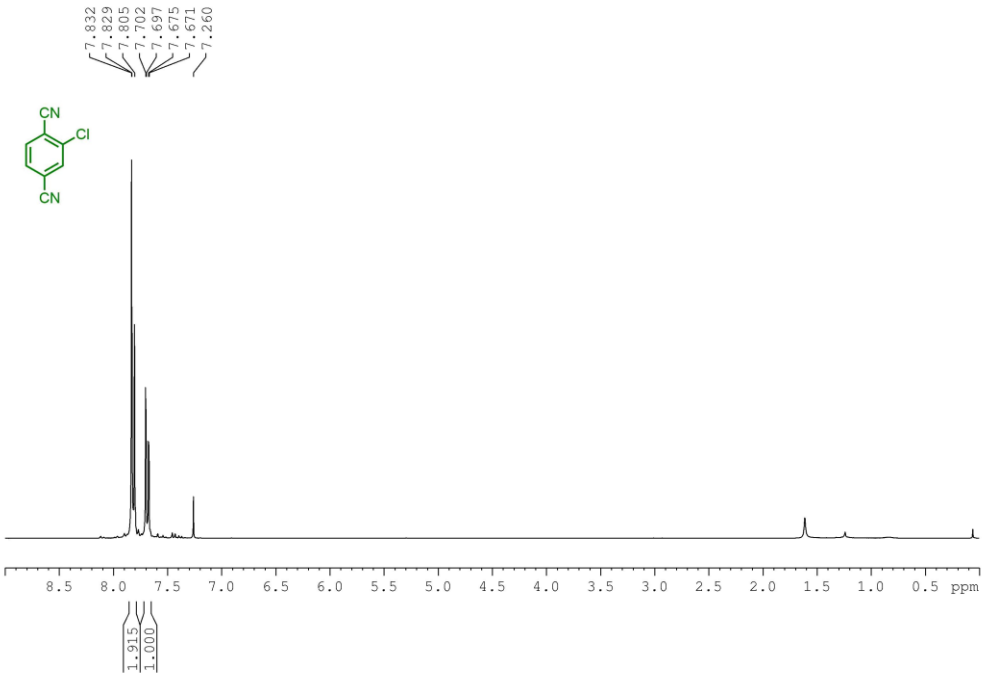
^{1}H NMR (300 MHz, $CDCl_3$), **1a**-d_2



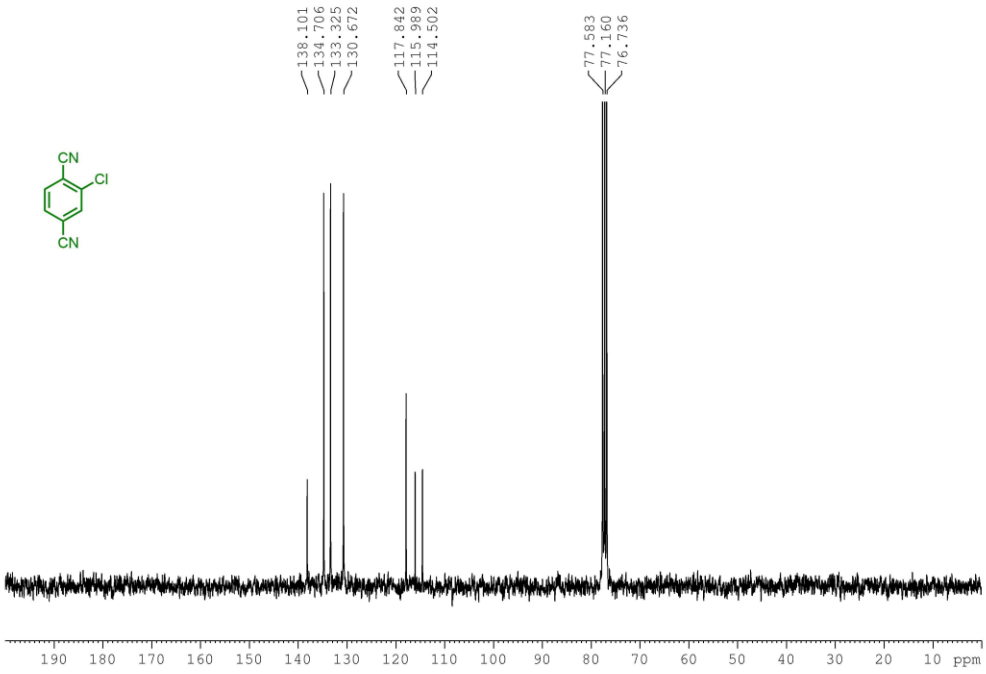
^{13}C NMR (75 MHz, $CDCl_3$), **1a**-d_2



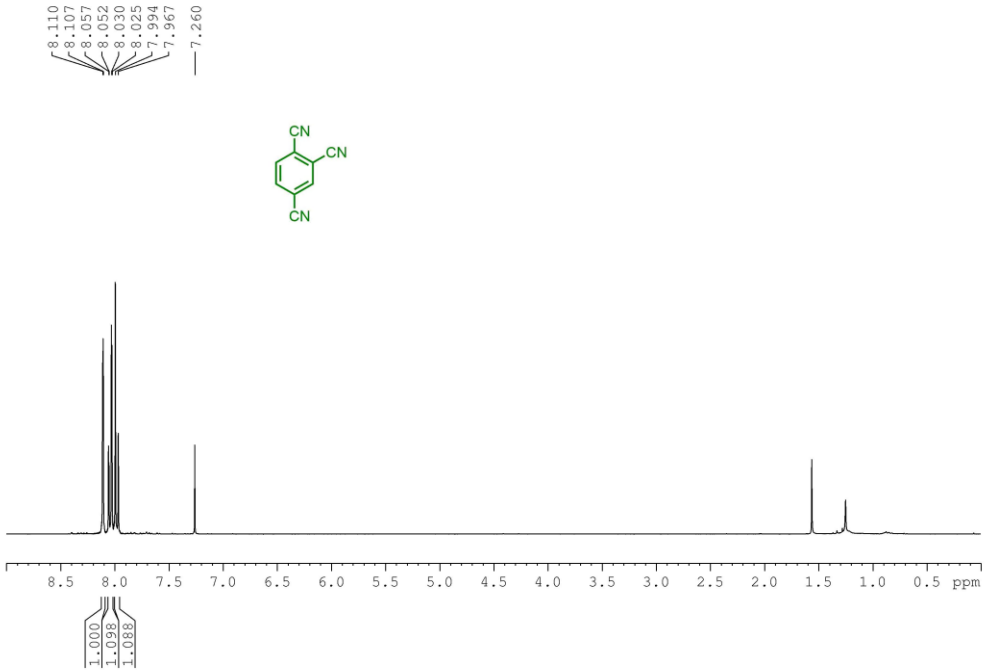
^{1}H NMR (300 MHz, $CDCl_3$), **S1**



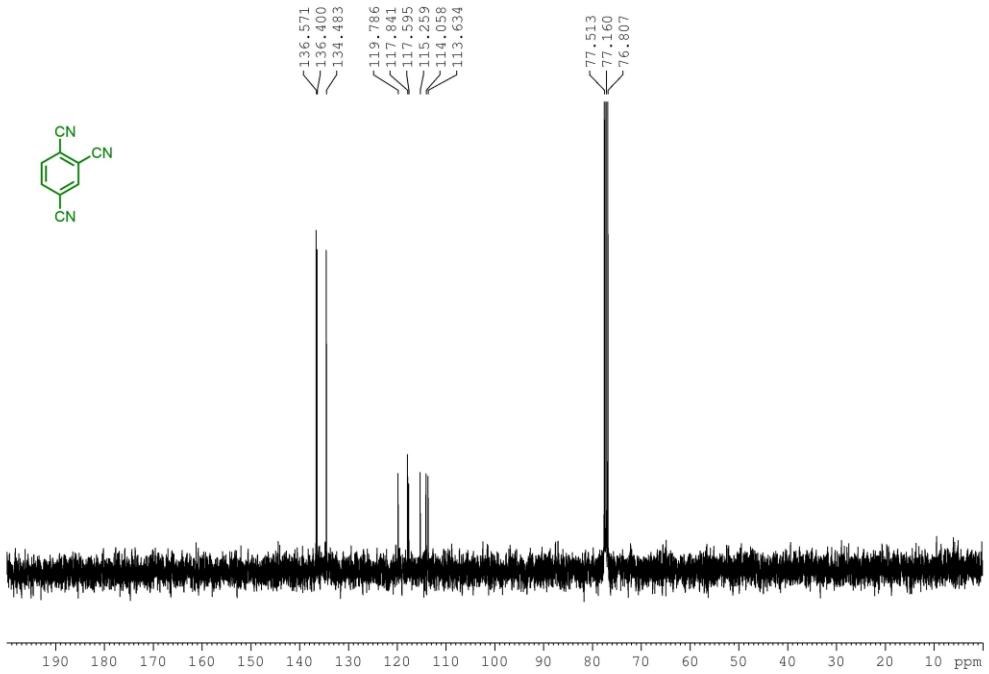
^{13}C NMR (75 MHz, $CDCl_3$), **S1**



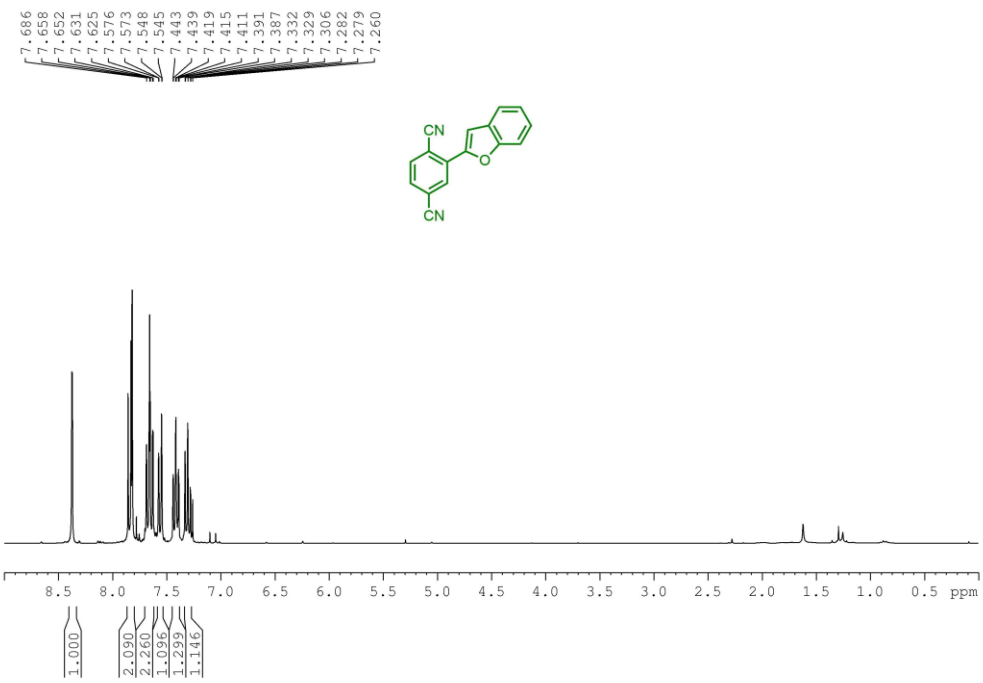
^{1}H NMR (300 MHz, $CDCl_3$), **3b**



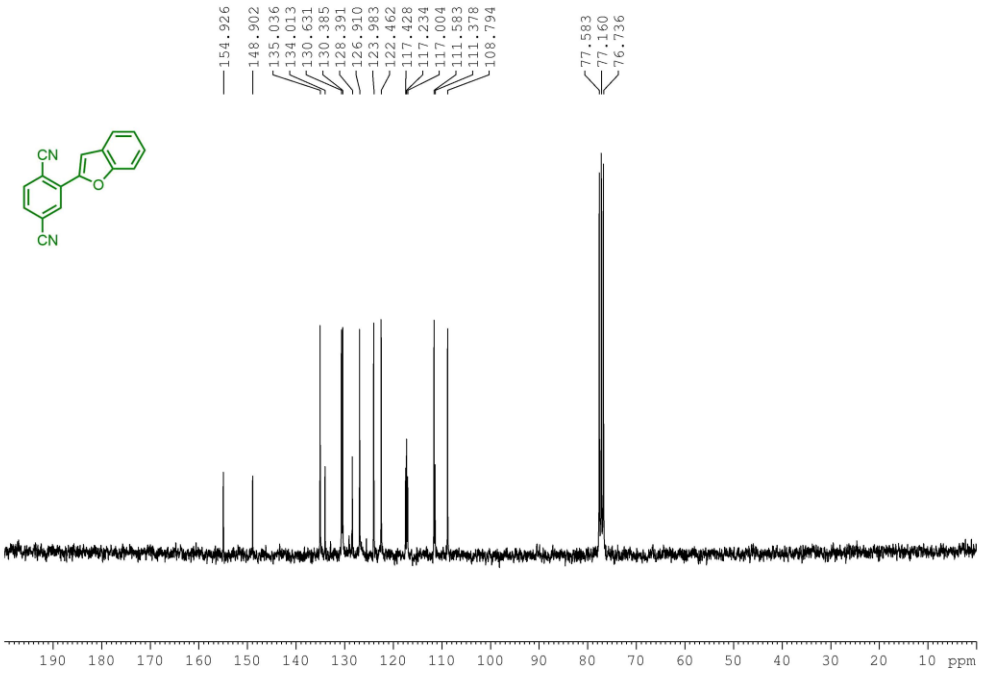
^{13}C NMR (90 MHz, $CDCl_3$), **3b**



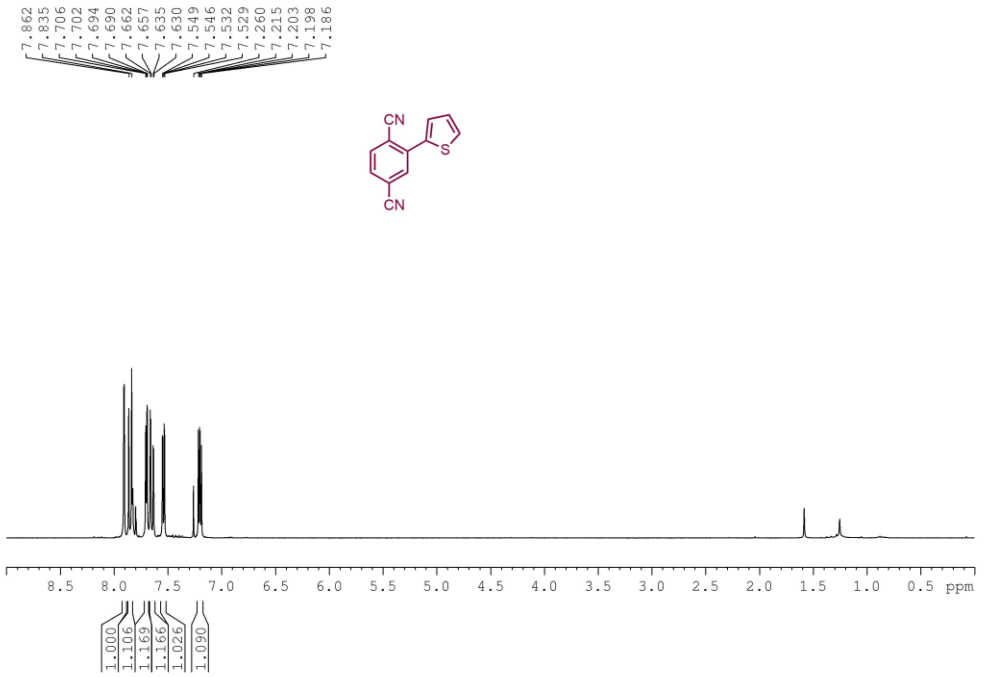
^{1}H NMR (300 MHz, $CDCl_3$), **3c**



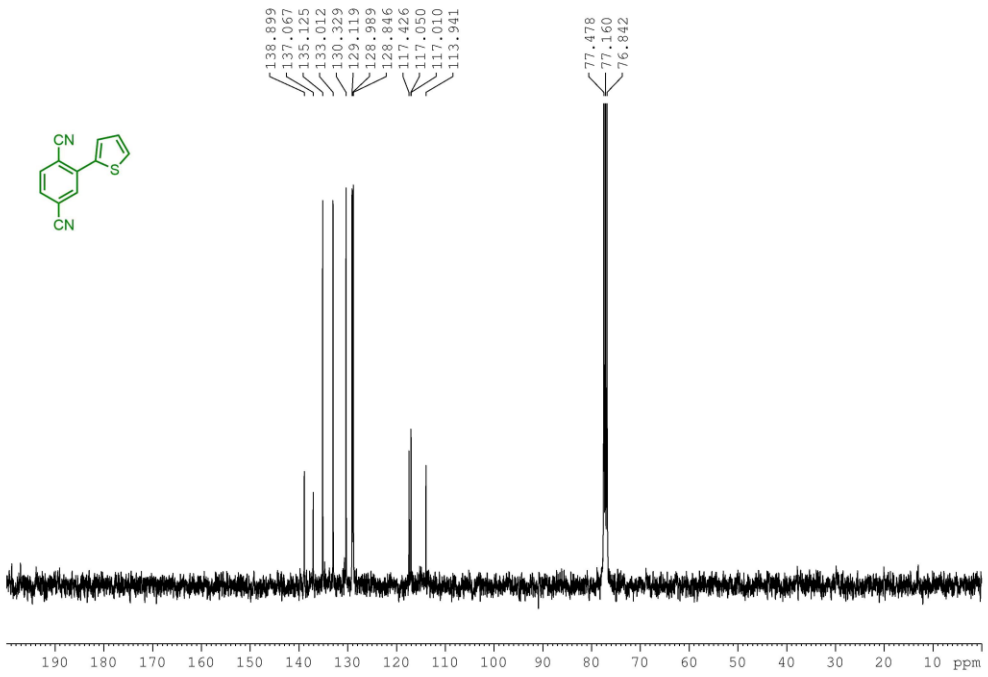
^{13}C NMR (75 MHz, $CDCl_3$), **3c**



^{1}H NMR (300 MHz, $CDCl_3$), **3d**



^{13}C NMR (100 MHz, $CDCl_3$), **3d**



F. References

(1) Miao, M.; Liao, L.-L.; Cao, G.-M.; Zhou, W.-J.; Yu, D.-G. Visible-Light-Mediated External-Reductant-Free Reductive Cross Coupling of Benzylammonium Salts with (Hetero)Aryl Nitriles. *Sci. China Chem.* **2019**, *62* (11), 1519-1524.

(2) Tanaka, H.; Sakai, K.; Kawamura, A.; Oisaki, K.; Kanai, M. Sulfonamides as New Hydrogen Atom Transfer (HAT) Catalysts for Photoredox Allylic and Benzylic C–H Arylations. *Chem. Commun.* **2018**, *54* (26), 3215-3218.

(3) Zhang, S.; Gao, W.; Shi, J.; Li, J.; Li, F.; Liang, Y.; Zhan, X.; Li, M.-B. Regioselective umpolung addition of dicyanobenzene to α,β-unsaturated alkenes enabled by electrochemical reduction. *Org. Chem. Front.* **2022**, *9*, 1261-1266.

(4) Wang, Q.-L.; Sun, Z.; Huang, H.; Mao, G.; Deng, G.-J. Stoichiometric Couplings of Methylarenes through Visible-Light-Induced Bromo Radical Formation from Aryl Halides. *Green Chem.* **2022**, *24* (8), 3293-3299.

(5) Elliott, Q.; dos Passos Gomes, G.; Evoniuk, C. J.; Alabugin, I. V. Testing the Limits of Radical-Anionic CH-Amination: A 10-Million-Fold Decrease in Basicity Opens a New Path to Hydroxyisoindolines via a Mixed C–N/C–O-Forming Cascade. *Chem. Sci.* **2020**, *11* (25), 6539-6555.

(6) Miyai, T.; Onishi, Y.; Baba, A. Novel Reductive Friedel-Crafts Alkylation of Aromatics Catalyzed by Indium Compounds: Chemoselective Utilization of Carbonyl Moieties as Alkylating Reagents. *Tetrahedron* **1999**, *55* (4), 1017-1026.

(7) Zhang, D.; Xu, Z.; Tang, T.; Le, L.; Wang, C.; Kambe, N.; Qiu, R. Pd-Catalyzed Cross-Coupling of *Sb* -Aryl Stibines with Halogenomethyl Arenes to Give Unsymmetirc Diarylmethanes. *Org. Lett.* **2022**, *24* (17), 3155-3160.

(8) Tie, L.; Shan, X.-H.; Qu, J.-P.; Kang, Y.-B. α-Trideuteration of Methylarenes. *Org. Chem. Front.* **2021**, *8* (12), 2981–2984.

(9) Schareina, T.; Zapf, A.; Beller, M. Potassium Hexacyanoferrate(II)-a New Cyanating Agent for the Palladium-Catalyzed Cyanation of Aryl Halides. *Chem. Commun.* **2004**, 1388-1389.

(10) Platonova, Y. B.; Volov, A. N.; Tomilova, L. G. Palladium(II) Phthalocyanines Efficiently Promote Phosphine-Free Sonogashira Cross-Coupling Reaction at Room Temperature. *Journal of Catalysis* **2020**, *391*, 224-228.

(11) Cho, S.-D.; Kim, H.-K.; Yim, H.; Kim, M.-R.; Lee, J.-K.; Kim, J.-J.; Yoon, Y.-J. Suzuki–Miyaura Coupling Reaction of Aryl Chlorides Using Di(2,6-Dimethylmorpholino)Phenylphosphine as Ligand. *Tetrahedron* **2007**, *63* (6), 1345-1352.