Supplementary Information

Deoxygenative Coupling of Alcohols with Aromatic Nitriles Enabled by Direct Visible Light Excitation

Yanjiao Xiong, Xuesong Wu*

Hubei Key Laboratory of Bioinorganic Chemistry & Materia Medica, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China.

*Corresponding authors

E-mail: xswu@hust.edu.cn

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1. General Information

Commercially Reagents: Commercially reagents were purchased from Energy Chemical, Bidepharm, Aladdin, TCI or Alfa Aesar and used without further purification. All experiments were performed in oven-dried glassware under an atmosphere of nitrogen. Diethyl ether was purchased from Sinopharm Chemical Reagent Co., Ltd. *N*,*N*-Dimethylacetamide was extra-dry solvent with molecular sieve (MS) purchased from Energy Chemical and stored within a N_2 filled glove box. All alcohols used in this research were purchased from Energy Chemical, Bidepharm, TCI, and Alfa Aesar, and used without further purification.

NMR Spectra: ^{1}H NMR spectra were recorded on a 400 or 600 MHz spectrometer (400 MHz: Bruker AV400; 600 MHz: Bruker Ascend^{TM} 600 MHz). Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent ($CDCl_3$: 7.26 ppm). $^{13}C\{^{1}H\}$ NMR spectra were recorded on the same spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm, t). Data are reported as follows: chemical shift δ/ppm, integration (^{1}H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants *J* in Hz, assignment. ^{19}F NMR spectra was recorded on the same spectrometer.

Gas Chromatograph (GC): All GC were recorded on Fuli GC9790II.

Infra-Red Spectrometer (IR): All IR were recorded on Bruker INVENIO-R.

High Resolution Mass Spectrometer (HRMS): All HRMS were recorded on high resolution Fourier transform mass spectrometer with BrukerDaltonics SolariX 7.0T from America. The detector is FT-MS, and the mass analyzer type is FT-ICR.

Melting Points: Melting points were determined on Hanon MP430 (Hanon Advanced Technology Group Co., Ltd) and were uncorrected.

UV/Vis Absorption Spectrometer: All UV/Vis absorption spectra were recorded on Shimadzu UV/Vis spectrophotometer UV-2600.

Fluorescence Spectrometer: All fluorescence spectra were recorded on Agilent CARY **ECLIPSE G9800AS24.**

Chromatography: Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silicagel 60 F254, 0.25 mm). Visualisation was by ultraviolet fluorescence (λ = 254 nm) and/or staining with I_2, phosphomolybdic acid or potassium permanganate ($KMnO_4$). Flash column chromatography was performed using 200-300 mesh silica gel.

Photoreactor: The photoreactors used in this research were purchased from Taobao (30 W blue LEDs).

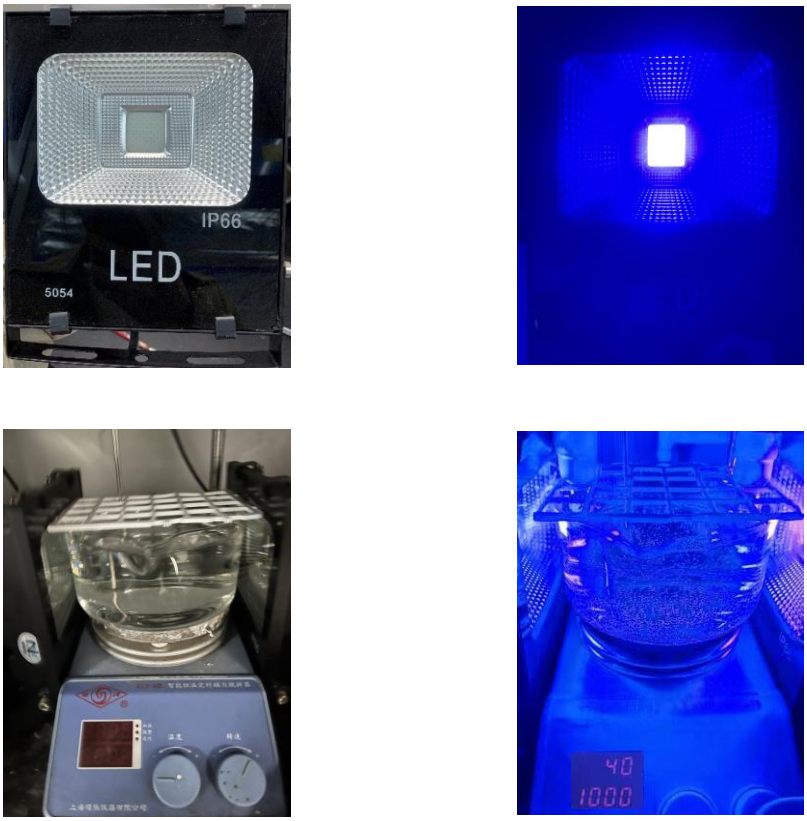


Figure S1. Photoreactor used in this research (30 W blue LEDs)

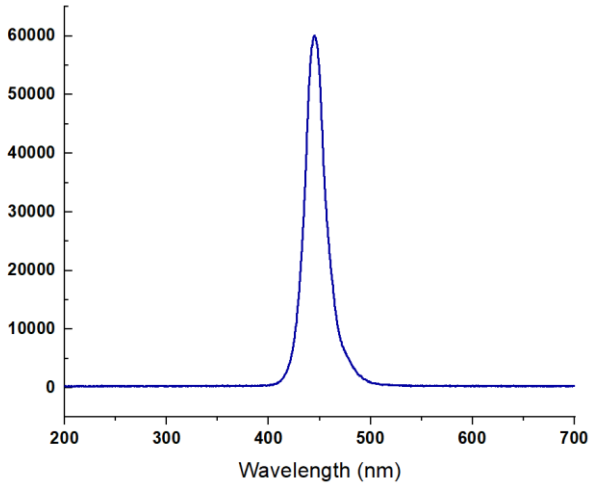
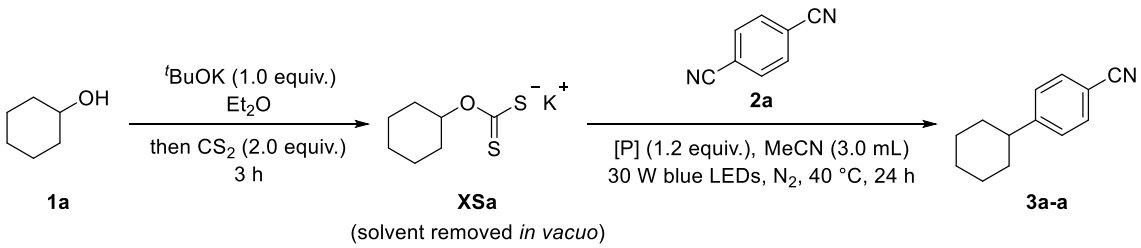


Figure S2. Emission spectra of the 30W blue LEDs, its emission wavelength range is from 401 nm to 510 nm, and its maximum emission wavelength is 445 nm. (The emission spectra was recorded on a Marine optical spectrometer USB2000+)

2. Detailed Optimization of Reaction Conditions

2.1 Optimization of Reaction Conditions

Table S1. Screening of PR_3[a]

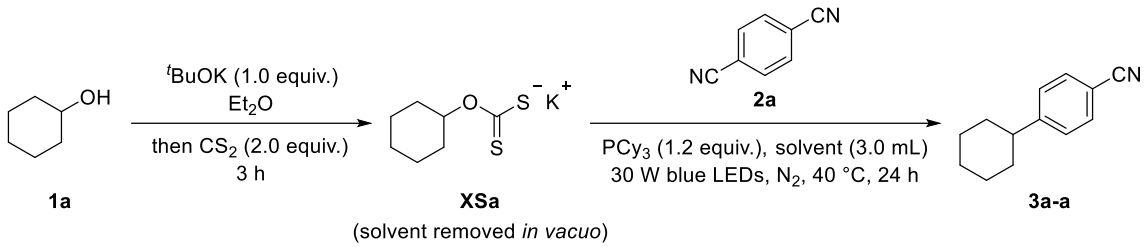


1a **XSa** (solvent removed *in vacuo*) **3a-a**

entry	[P]	yield (%)[b]
1	PPh_3	0
2	$P(PMP)_3$	5
3	PPh_2Me	0
4	$P(OEt)_3$	6
5	PCy_3	45
6	P^nBu_3	40
7	P^iPr_3	41

[a]Standard procedure: **1a** (0.30 mmol, 1.0 equiv.), ^{t}BuOK (0.30 mmol, 1.0 equiv.), Et_2O (3.0 mL), CS_2 (2.0 mmol, 2.0 equiv.), 3 h. After removing solvent *in vacuo*, then **2a** (0.30 mmol, 1.0 equiv.), [P] (0.36 mmol, 1.2 equiv.), MeCN (3.0 mL), 24 h blue LEDs irradiation. [b]Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

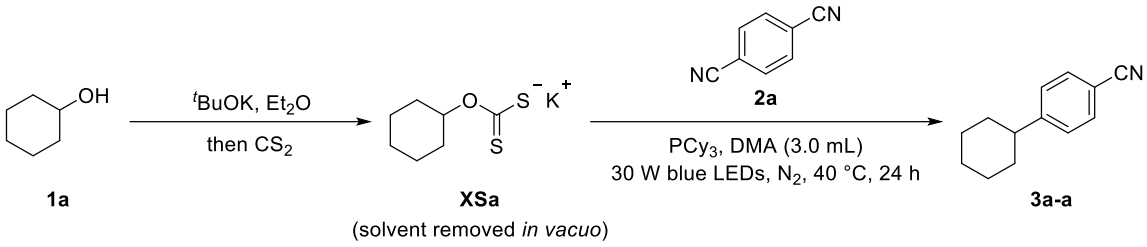
Table S2. Screening of Solvents[a]



entry	solvent	yield (%)[b]
1	MeCN	45
2	DCM	0
3	THF	26
4	$PhCF_3$	0
5	DMSO	37
6	DMF	49
7	DMA	52

[a]Standard procedure: **1a** (0.30 mmol, 1.0 equiv.), [t]BuOK (0.30 mmol, 1.0 equiv.), Et_2O (3.0 mL), CS_2 (2.0 mmol, 2.0 equiv.), 3 h. After removing solvent *in vacuo*, then **2a** (0.30 mmol, 1.0 equiv.), Pcy_3 (0.36 mmol, 1.2 equiv.), solvent (3.0 mL), 24 h blue LEDs irradiation. [b]Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

Table S3. Selection of Reagent Amount[a]

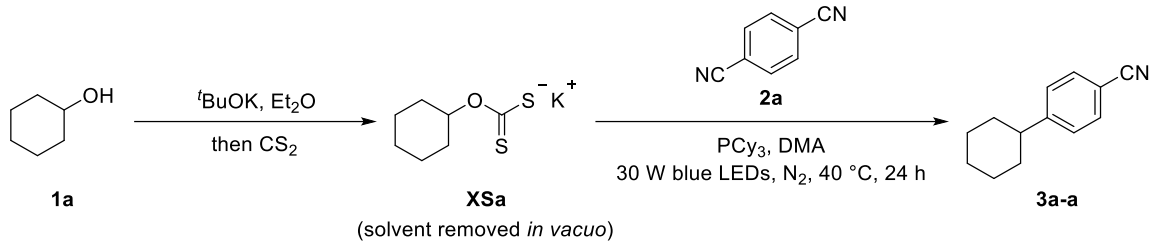


entry	**1a** (x mmol)	**2a** (y mmol)	yield (%)[b]
1	0.30	0.30	52
2	0.30	0.36	40
3	0.30	0.45	38
4	0.36	0.30	66
5	0.45	0.30	74
6	0.54	0.30	83
7	0.60	0.30	78

[a]Standard procedure: **1a** (x mmol), [t]BuOK (x mmol), Et_2O (3.0 mL), CS_2 (2x mmol), 3 h. After removing solvent *in vacuo*, then **2a** (y mmol), PCy_3 (1.2x mmol), DMA (3.0 mL), 24 h blue LEDs irradiation. [b]Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

2.2 Control Experiments

Table S4. Control Experiments[a]

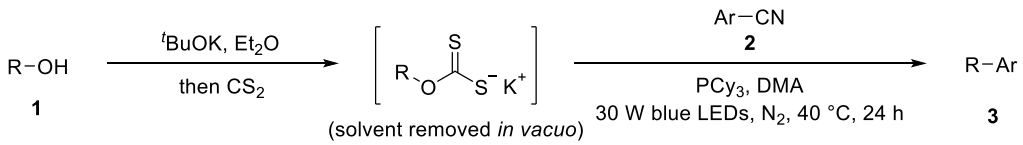


entry	^{t}BuOK	CS_2	PCy_3	light	yield (%)[b]
1	Yes	Yes	Yes	Yes	83
2	No	Yes	Yes	Yes	0
3	Yes	No	Yes	Yes	0
4	Yes	Yes	No	Yes	0
5	Yes	Yes	Yes	No	0
6	Yes	Yes	No	No	0

[a]Standard procedure: **1a** (0.54 mmol, 1.8 equiv.), ^{t}BuOK (0.54 mmol, 1.8 equiv.), Et_2O (3.0 mL), CS_2 (1.08 mmol, 3.6 equiv.), 3 h. After removing solvent *in vacuo*, then **2a** (0.30 mmol, 1.0 equiv.), PCy_3 (0.648 mmol, 2.16 equiv.), DMA (3.0 mL), 24 h blue LEDs irradiation. [b]Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

3. General Procedure and Characterization Data of Products

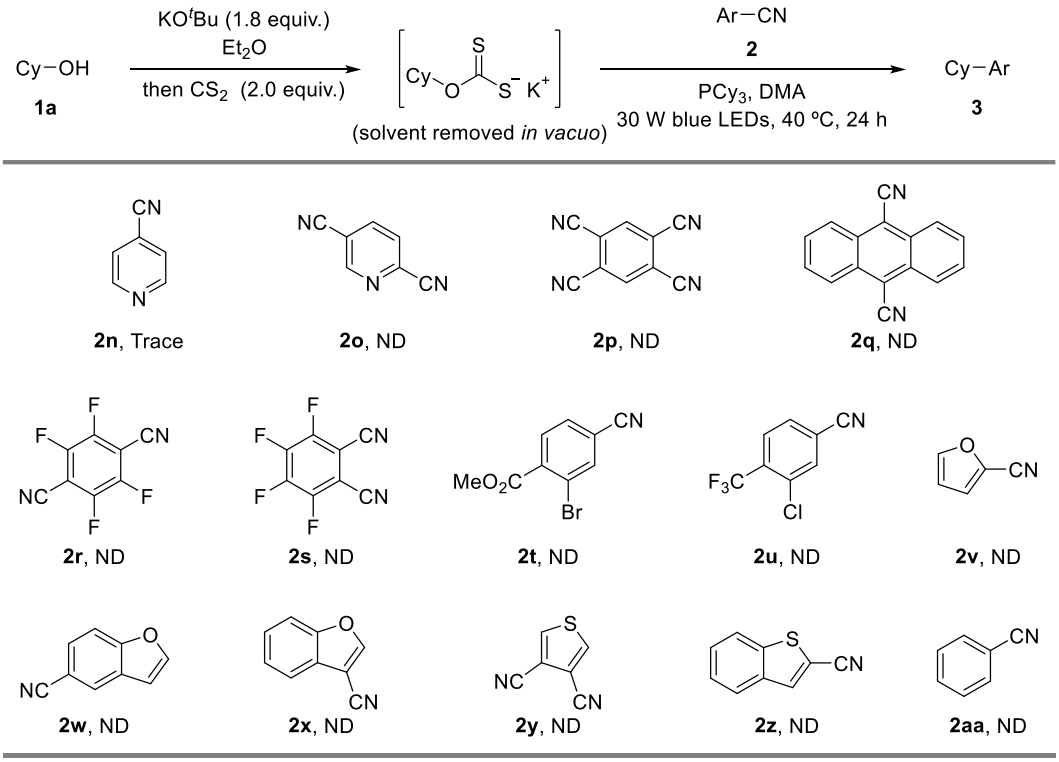
3.1 General Procedure for Deoxygenative Arylation of Alcohols



In a N_2-filled glovebox, an oven-dried 10 mL glass vial equipped with a magnetic stir bar was charged sequentially with alcohol **1** (0.54 mmol), ^{t}BuOK (60.6 mg, 0.54 mmol), and dry Et_2O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (82.2 mg, 65.0 µL, 1.08 mmol) via microsyringe and continued to be stirred for 3 hours at room temperature before removing the solvent *in vacuo*. The system was transferred into the glovebox, then aromatic nitrile **2** (0.30 mmol), PCy_3 (182 mg, 0.648 mmol), and DMA (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W

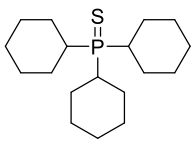
blue LEDs lamp (the distance was about 0.6 cm), maintained at 40 ℃ (in water bath), and stirred for 24 hours. Chemo- and stereoselectivity were determined from analysis of the reaction mixture by either ^{1}H NMR or LC-MS analysis. The mixture was diluted with saturated NaCl aqueous solution (30 mL) and extracted with ethyl acetate (10 mL x 5). The combined organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the product.

Table S8. Unsuccessful Aromatic Nitrile Substrates[a]



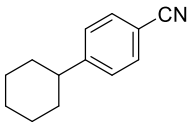
[a]Standard procedure: **1a** (0.54 mmol), ^{t}BuOK (0.54 mmol), Et_2O (3.0 mL), CS_2 (1.08 mmol), 3 h. After removing solvent in vacuo, then **2** (0.30 mmol), PCy_3 (0.648 mmol), DMA (3.0 mL), 24 h blue LEDs irradiation. ND: the desired product was not detected.

3.2 Characterization Data of Products



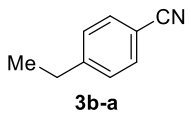
Tricyclohexylphosphine sulfide: The title compound was obtained from the reaction of alcohol **1a** and aromatic nitrile **2a**, and isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a white sollid (163 mg, 97% yield, Mp = 182 – 184 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.00 – 1.92

(m, 6H), 1.91 – 1.79 (m, 9H), 1.72 – 1.65 (m, 3H), 1.46 – 1.35 (m, 6H), 1.27 – 1.18 (m, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 37.1 (d, *J* = 44.6 Hz), 27.3 (d, *J* = 3.0 Hz), 27.1 (d, *J* = 12.2 Hz), 26.1 (d, *J* = 1.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.02. IR (ATR): *v* = 2921, 2849, 1441, 849, 747 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{18}H_{34}PS^+$: 313.2113, found 313.2117.



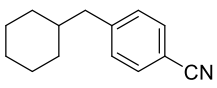
3a-a

4-Cyclohexylbenzonitrile (3a-a): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (45.1 mg, 81% yield). ^{1}H NMR (400 MHz, CDCl3) δ 7.61 – 7.49 (m, 2H), 7.34 – 7.26 (m, 2H), 2.63 – 2.46 (m, 1H), 1.91 – 1.75 (m, 5H), 1.48 – 1.28 (m, 5H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl3) δ 153.6, 132.3, 127.8, 119.3, 109.7, 44.9, 34.1, 26.7, 26.0. This compound is known.[1]



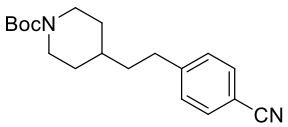
3b-a

4-Ethylbenzonitrile (3b-a): Synthesized according to the general procedure from alcohol **1b** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (23.0 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.33 – 7.26 (m, 2H), 2.76 – 2.63 (m, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.9, 132.3, 128.8, 119.3, 109.7, 29.2, 15.2. This compound is known.[2]



3c-a

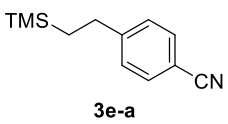
Methyl 2,5-diphenylpentanoate (3c-a): Synthesized according to the general procedure from alcohol **1c** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (40.2 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.26 – 7.18 (m, 2H), 2.53 (d, *J* = 7.2 Hz, 2H), 1.74 – 1.60 (m, 6H), 1.22 – 1.13 (m, 3H), 0.99 – 0.89 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.3, 132.0, 130.0, 119.4, 109.6, 44.3, 39.7, 33.1, 26.5, 26.3. This compound is known.[3]



3d-a

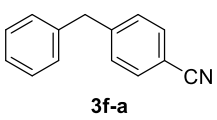
***tert*-Butyl 4-(4-cyanophenethyl)piperidine-1-carboxylate (3d-a)**: Synthesized according to the general procedure from alcohol **1d** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil (58.4

mg, 62% yield). ^{1}H NMR (400 MHz, CDCl3) δ 7.60 – 7.54 (m, 2H), 7.31 – 7.22 (m, 2H), 4.09 (s, 2H), 2.74 – 2.60 (m, 4H), 1.75 – 1.63 (m, 3H), 1.61 – 1.52 (m, 2H), 1.45 (s, 9H), 1.21 – 1.06 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.0, 148.3, 132.4, 129.2, 119.2, 109.8, 79.5, 44.2, 37.9, 35.7, 33.3, 32.1, 28.6. This compound is known.[4]



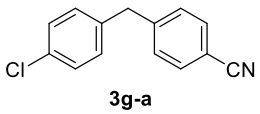
3e-a

4-(2-(Trimethylsilyl)ethyl)benzonitrile (3e-a): Synthesized according to the general procedure from alcohol **1e** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (45.8 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 2.70 – 2.63 (m, 2H), 0.88 – 0.82 (m, 2H), 0.02 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.1, 132.3, 128.7, 119.4, 109.4, 30.5, 18.4, -1.7. IR (ATR): *ν* = 2953, 2930, 2228, 1607, 1506, 1414, 1249, 1177, 864, 836 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{12}H_{18}NSi^+$: 204.1203, found 204.1200.



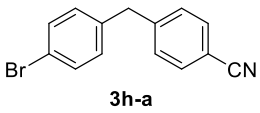
3f-a

4-Benzylbenzonitrile (3f-a): Synthesized according to the general procedure from alcohol **1f** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (42.9 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H), 7.37 – 7.24 (m, 5H), 7.20 – 7.15 (m, 2H), 4.05 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.8, 139.4, 132.4, 129.7, 129.1, 128.9, 126.8, 119.1, 110.2, 42.1. This compound is known.[5]



3g-a

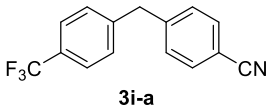
4-(4-Chlorobenzyl)benzonitrile (3g-a): Synthesized according to the general procedure from alcohol **1g** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a white solid (43.7 mg, 64% yield, Mp = 79 – 80 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 7.30 – 7.24 (m, 4H), 7.11 – 7.06 (m, 2H), 4.00 (s, 2H). ^{13}C{^{1}H} (101 MHz, $CDCl_3$) δ 146.2, 137.9, 132.7, 132.5, 130.4, 129.7, 129.0, 119.0, 110.4, 41.4. This compound is known.[5]



3h-a

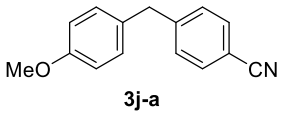
4-(4-Bromobenzyl)benzonitrile (3h-a): Synthesized according to the general procedure from alcohol **1h** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl

acetate (PE/EA = 100:1) as a white solid (49.5 mg, 61% yield, Mp = 123 – 124 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.98 (s, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 146.1, 138.4, 132.5, 132.0, 130.8, 129.7, 120.7, 119.0, 110.4, 41.4. This compound is known.[6]



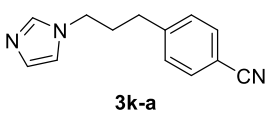
3i-a

4-(4-(Trifluoromethyl)benzyl)benzonitrile (3i-a): Synthesized according to the general procedure from alcohol **1i** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a light yellow oil. (44.7 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 4H), 7.24 – 7.17 (m, 4H), 4.02 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.6, 143.5, 132.6, 129.8, 129.4, 129.0 (q, *J* = 32.3 Hz), 125.9 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 272.7 Hz), 118.9, 110.7, 41.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.48. This compound is known.[5]



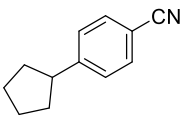
3j-a

4-(4-Methoxybenzyl)benzonitrile (3j-a): Synthesized according to the general procedure from alcohol **1j** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 50:1) as a white solid (45.5 mg, 68% yield, Mp = 149 – 151 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.95 (s, 2H), 3.77 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.4, 147.3, 132.3, 131.4, 130.0, 129.6, 119.1, 114.2, 109.9, 55.3, 41.1. This compound is known.[5]



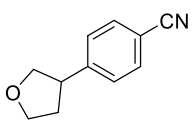
3k-a

4-(3-(1*H*-Imidazol-1-yl)propyl)benzonitrile (3k-a): Synthesized according to the general procedure from alcohol **1k** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil (31.3 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.29 – 7.26 (m, 2H), 6.26 (t, *J* = 2.0 Hz, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 2.65 (dd, *J* = 8.8, 6.8 Hz, 2H), 2.26 – 2.11 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.7, 139.6, 132.5, 129.4, 129.2, 119.1, 110.2, 105.6, 51.2, 32.9, 31.5. IR (ATR): ν = 2937, 2226, 1607, 1507, 1396, 1090, 1037, 844, 819, 750 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{13}H_{14}N_3S^+$: 212.1182, found:212.1176.



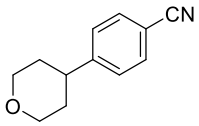
3l-a

4-Cyclopentylbenzonitrile (3l-a): Synthesized according to the general procedure from alcohol **1l** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (41.6 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 3.10 – 2.95 (m, 1H), 2.14 – 2.03 (m, 2H), 1.86 – 1.77 (m, 2H), 1.77 – 1.68 (m, 2H), 1.62 – 1.52 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.5, 132.2, 128.0, 119.4, 109.5, 46.2, 34.6, 25.7. This compound is known.[1]



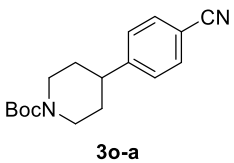
3m-a

4-(Tetrahydrofuran-3-yl)benzonitrile (3m-a): Synthesized according to the general procedure from alcohol **1m** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (38.0 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.15 – 4.04 (m, 2H), 3.96 – 3.88 (m, 1H), 3.75 (dd, *J* = 8.8, 6.6 Hz, 1H), 3.50 – 3.40 (m, 1H), 2.47 – 2.36 (m, 1H), 2.03 – 1.92 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.0, 132.6, 128.2, 119.0, 110.5, 74.4, 68.5, 45.2, 34.7. This compound is known.[1]



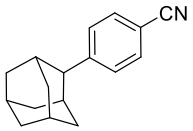
3n-a

4-(Tetrahydro-2*H*-pyran-4-yl)benzonitrile (3n-a): Synthesized according to the general procedure from alcohol **1n** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (40.4 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.13 – 4.05 (m, 2H), 3.60 – 3.48 (m, 2H), 2.88 – 2.77 (m, 1H), 1.87 – 1.71 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.3, 132.6, 127.7, 119.1, 110.4, 68.2, 41.9, 33.5. This compound is known.[7]



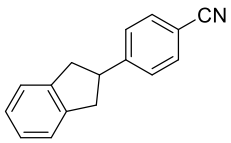
3o-a

***tert*-Butyl 4-(4-cyanophenyl)piperidine-1-carboxylate (3o-a):** Synthesized according to the general procedure from alcohol **1o** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a white solid (58.5 mg, 68% yield, Mp = 84 – 85 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.25 (s, 2H), 2.89 – 2.66 (m, 3H), 1.80 (d, *J* = 13.0 Hz, 2H), 1.65 – 1.54 (m, 2H), 1.47 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.9, 151.2, 132.5, 127.8, 119.0, 110.4, 79.8, 44.2, 43.0, 32.8, 28.6, 28.5. This compound is known.[1]



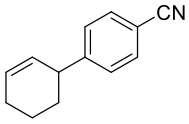
3p-a

4-(Adamantan-2-yl)benzonitrile (3p-a): Synthesized according to the general procedure from alcohol **1p** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a white solid (59.1 mg, 83% yield, Mp = 110 – 112 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 3.02 (s, 1H), 2.46 (s, 2H), 2.07 – 1.98 (m, 3H), 1.98 – 1.90 (m, 2H), 1.82 – 1.70 (m, 5H), 1.63 – 1.52 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.5, 132.1, 127.9, 119.4, 109.1, 47.3, 39.1, 37.7, 32.0, 31.1, 27.9, 27.7. This compound is known.[8]



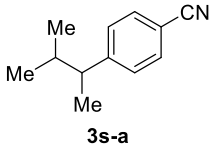
3q-a

4-(2,3-Dihydro-1*H*-inden-2-yl)benzonitrile (3q-a): Synthesized according to the general procedure from alcohol **1q** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a white solid (50.7 mg, 77% yield, Mp = 97 – 99 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.19 (m, 4H), 3.73 (q, *J* = 8.2 Hz, 1H), 3.40 (dd, *J* = 15.6, 8.0 Hz, 2H), 3.06 (dd, *J* = 15.6, 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.4, 142.3, 132.5, 128.0, 126.9, 124.5, 119.2, 110.2, 45.4, 40.8. This compound is known.[1]



3r-a

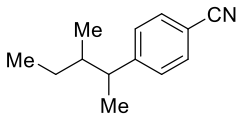
1',2',3',4'-Tetrahydro-[1,1'-biphenyl]-4-carbonitrile (3r-a): Synthesized according to the general procedure from alcohol **1r** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (44.5 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.99 – 5.92 (m, 1H), 5.68 – 5.61 (m, 1H), 3.49 – 3.42 (m, 1H), 2.14 – 2.06 (m, 2H), 2.06 – 1.99 (m, 1H), 1.97 – 1.87 (m, 1H), 1.67 – 1.60 (m, 1H), 1.55 – 1.47 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.4, 132.3, 129.8, 128.7, 128.6, 119.3, 110.0, 42.1, 32.4, 25.0, 21.0. This compound is known.[9]



3s-a

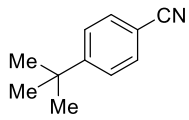
4-(3-Methylbutan-2-yl)benzonitrile (3s-a): Synthesized according to the general procedure from alcohol **1s** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (42.6 mg, 82% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 2.53 – 2.42 (m, 1H), 1.82 – 1.73 (m, 1H), 1.23 (d, *J* = 6.6 Hz,

3H), 0.94 (d, *J* = 7.2 Hz, 3H), 0.74 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 153.0, 132.1, 128.6, 119.4, 109.7, 47.3, 34.4, 21.2, 20.2, 18.6. This compound is known.[10]



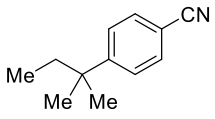
3t-a

4-(3-Methylpentan-2-yl)benzonitrile (3t-a): Synthesized according to the general procedure from alcohol **1t** and a colorless oil **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (46.6 mg, 83% yield, 1:1 *dr*). Data of one isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 1.8 Hz, 2H), 7.20 (d, *J* = 5.8 Hz, 2H), 2.59 – 2.54 (m, 1H), 1.51 – 1.40 (m, 2H), 1.15 (d, *J* = 7.0 Hz, 3H), 0.98 – 0.91 (m, 1H), 0.78 (t, *J* = 7.4 Hz, 3H), 0.66 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 152.7, 132.0, 128.5, 119.3, 109.6, 44.9, 40.6, 26.3, 17.3, 15.6, 11.3. Data of the other isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 1.8 Hz, 2H), 7.22 (d, *J* = 4.0 Hz, 2H), 2.65 – 2.59 (m, 1H), 1.57 – 1.47 (m, 2H), 1.19 (d, *J* = 7.0 Hz, 3H), 1.11 – 1.05 (m, 1H), 0.87 – 0.80 (m, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 153.2, 132.1, 128.7, 119.3, 109.7, 45.2, 40.9, 27.5, 18.7, 16.9, 11.6. IR (ATR): *ν* = 2965, 2931, 2877, 2228, 1607, 1504, 1459, 1379, 1067, 1016, 843 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{13}H_{18}N^+$: 188.1434, found:188.1431.



3u-a

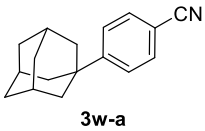
4-(*tert*-Butyl)benzonitrile (3u-a): Synthesized according to the general procedure from alcohol **1u** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (23.9 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 1.33 (s, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 156.8, 132.1, 126.3, 119.3, 109.4, 35.4, 31.1. This compound is known.[11]



3v-a

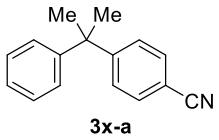
4-(*tert*-Pentyl)benzonitrile (3v-a): Synthesized according to the general procedure from alcohol **1v** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (24.5 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 1.66 (t, *J* = 7.6 Hz, 2H), 1.28 (s, 6H), 0.65 (t, *J* = 7.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 155.3, 132.0, 126.9, 119.3, 109.3, 38.7, 36.7, 28.2, 9.1. IR (ATR): *ν* = 2967, 2930, 2877, 2227, 1607, 1504, 1462, 1016, 839 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$

calcd. for $C_{12}H_{16}N^+$: 174.1277, found:174.1277.



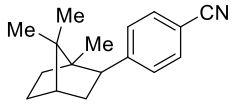
3w-a

4-(Adamantan-1-yl)benzonitrile (3w-a): Synthesized according to the general procedure from alcohol **1w** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a white solid (30.1 mg, 42% yield, Mp = 126 – 127 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 2.12 (s, 3H), 1.89 (d, *J* = 2.8 Hz, 6H), 1.83 – 1.73 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.8, 132.2, 126.0, 119.4, 109.4, 42.9, 37.0, 36.7, 28.8. This compound is known.[12]



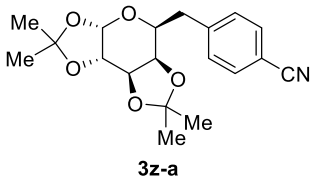
3x-a

4-(2-Phenylpropan-2-yl)benzonitrile (3x-a): Synthesized according to the general procedure from alcohol **1x** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (49.2 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.23 – 7.15 (m, 3H), 1.69 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.5, 149.2, 132.1, 128.5, 127.8, 126.8, 126.3, 119.2, 109.7, 43.6, 30.5. This compound is known.[13]



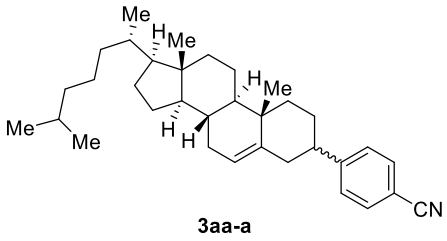
3y-a

4-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)benzonitrileMethyl (3y-a): Synthesized according to the general procedure from alcohol **1y** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a white solid (53.9 mg, 75% yield, 1.1:1 *dr*, Mp = 150 – 151 ℃). Data of one isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.14 – 3.06 (m, 1H), 2.23 – 2.14 (m, 1H), 1.70 – 1.58 (m, 3H), 1.53 – 1.46 (m, 1H), 1.21 – 1.13 (m, 2H), 1.03 (s, 3H), 0.94 (s, 3H), 0.72 (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.9, 131.6, 130.1, 119.4, 109.7, 50.7, 50.6, 50.3, 48.2, 45.4, 34.3, 28.5, 20.3, 18.7, 14.5. Data of the other isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 2.93 (t, *J* = 8.4 Hz, 1H), 2.33 – 2.24 (m, 1H), 1.92 – 1.81 (m, 3H), 1.81 – 1.78 (m, 1H), 1.35 – 1.31 (m, 2H), 0.84 (s, 3H), 0.75 (d, *J* = 1.6 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.5, 131.5, 130.1, 119.3, 109.3, 52.9, 50.5, 45.7, 40.7, 33.4, 28.4, 27.6, 21.3, 19.9, 14.8. IR (ATR): *ν* = 2952, 2879, 2222, 1601, 1500, 1456, 1388, 845, 831, 779 cm^{-1}. HRMS (ESI): m/z [M + H]$^+$ calcd. for $C_{17}H_{22}N^+$: 240.1747, found: 240.1744.



3z-a

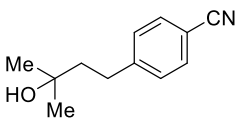
4-(((3a*S*,5*S*,5a*R*,8a*R*,8b*S*)-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl)benzonitrile (3z-a): Synthesized according to the general procedure from alcohol **1z** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as highly viscous and colorless oil (47.7 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.53 (d, *J* = 4.8 Hz, 1H), 4.59 (dd, *J* = 7.6, 2.4 Hz, 1H), 4.31 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.07 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.03 – 3.96 (m, 1H), 3.08 – 2.90 (m, 2H), 1.50 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H), 1.31 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.3, 132.3, 130.1, 119.2, 110.3, 109.5, 108.7, 96.8, 72.3, 71.0, 70.5, 68.0, 36.6, 26.2, 26.1, 25.0, 24.6. IR (ATR): *v* = 2986, 2932, 2227, 1608, 1455, 1382, 1256, 1212, 1070, 1001, 903, 862 cm^{-1}. HRMS (ESI): m/z [M +H]$^{+}$ calcd. for $C_{19}H_{24}NO_5^{+}$: 346.1649, found: 346.1655.



3aa-a

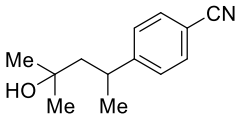
4-(10,13-Dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)benzonitrile (3aa-a): Synthesized according to the general procedure from alcohol **1aa** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a white solid (77.8 mg, 55% yield, 2.2:1 *dr*, Mp = 156 – 158 °C). Data of one isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.36 (d, *J* = 5.2 Hz, 1H), 2.62 – 2.52 (m, 1H), 2.42 – 2.35 (m, 1H), 2.06 – 1.96 (m, 4H), 1.66 – 1.45 (m, 12H), 1.13 – 1.00 (m, 14H), 0.87 (dd, *J* = 6.7, 2.1 Hz, 9H), 0.69 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.7, 142.1, 132.4, 127.8, 121.0, 119.3, 109.9, 56.9, 56.3, 50.6, 46.1, 42.5, 40.2, 39.9, 39.7, 39.7, 37.0, 36.3, 35.9, 32.1, 32.0, 29.8, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.1, 19.7, 18.9, 12.0. Data of the other isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 5.46 (d, *J* = 5.4 Hz, 1H), 3.13 (s, 1H), 2.86 – 2.77 (m, 1H), 2.45 – 2.42 (m, 1H), 2.20 – 2.08 (m, 4H), 1.89 – 1.78 (m, 6H), 1.78 – 1.70 (m, 6H), 1.23 (d, *J* = 13.0 Hz, 10H), 0.91 (dd, *J* = 10.1, 6.4 Hz, 12H), 0.68 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.6, 140.8, 131.8, 129.2, 122.4, 119.4, 109.2, 56.9, 56.3, 50.0, 46.1, 42.5, 40.2, 39.8, 39.7, 38.9, 37.4, 35.9, 35.3, 33.0, 31.9, 29.8, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 20.8, 19.8, 18.8, 12.0. IR (ATR): *v* =

2930, 2865, 2227, 1606. 1463, 1378, 1021, 834, 800 cm^{-1}. HRMS (APCI): m/z $[M - H]^-$ calcd.. for $C_{34}H_{48}N^-$: 470.3792, found: 470.3784.



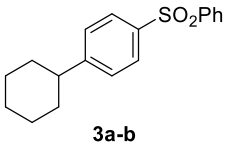
3ab-a

4-(3-Hydroxy-3-methylbutyl)benzonitrile (3ab-a): Synthesized according to the general procedure from alcohol **1ab** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil (40.3 mg, 71% yield, > 20:1 *rr*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 2.80 – 2.74 (m, 2H), 1.79 – 1.73 (m, 2H), 1.30 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.5, 132.4, 129.3, 119.2, 109.8, 70.8, 45.1, 31.1, 29.6. IR (ATR): *v* = 3433, 2969, 2228, 1607, 1505, 1453, 1377, 1214, 1149, 931, 850, 823 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{12}H_{16}NO^+$: 190.1226, found: 190.1227.



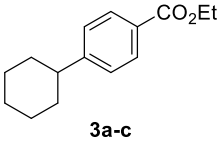
3ac-a

4-(4-Hydroxy-4-methylpentan-2-yl)benzonitrile (3ac-a): Synthesized according to the general procedure from alcohol **1ac** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil. (45.7 mg, 75% yield, > 20:1 *rr*). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.07 – 2.98 (m, 1H), 1.91 (dd, *J* = 14.4, 7.8 Hz, 1H), 1.76 (dd, *J* = 14.4, 4.8 Hz, 1H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.13 (s, 3H), 1.09 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 154.5, 132.4, 128.0, 119.1, 109.6, 71.2, 51.0, 36.6, 30.4, 29.8, 24.7. IR (ATR): *v* = 3485, 2967, 2929, 2228, 1607, 1504, 1457, 1145, 1019, 891, 838 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{13}H_{18}NO^+$: 204.1383, found: 204.1387.



3a-b

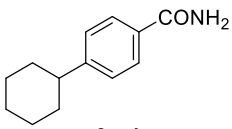
1-Cyclohexyl-4-(phenylsulfonyl)benzene (3a-b): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2b**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 20:1) as a white solid (64.8 mg, 72% yield, Mp = 97 – 98 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.88 – 7.81 (m, 2H), 7.58 – 7.45 (m, 3H), 7.35 – 7.29 (m, 2H), 2.60 – 2.47 (m, 1H), 1.89 – 1.72 (m, 5H), 1.41 – 1.22 (m, 5H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.1, 142.1, 138.9, 133.1, 129.3, 127.9, 127.9, 127.7, 44.7, 34.2, 26.7, 26.0. This compound is known.[14]



3a-c

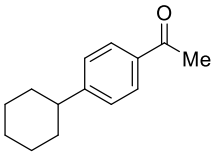
Ethyl 4-Cyclohexylbenzoate (3a-c): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2c**. The title compound was

isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 50:1) as a white solid (44.6 mg, 64% yield, Mp = 90 – 91 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.26 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.60 – 2.50 (m, 1H), 1.93 – 1.82 (m, 4H), 1.45 – 1.25 (m, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.9, 153.5, 129.8, 128.2, 127.0, 60.9, 44.8, 34.3, 26.9, 26.2, 14.5. This compound is known.[15]



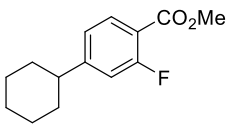
3a-d

4-Cyclohexylbenzamide (3a-d): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2d**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a white solid (32.4 mg, 53% yield, Mp = 201 – 203 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.21 – 5.53 (m, 2H), 2.61 – 2.50 (m, 1H), 1.92 – 1.81 (m, 4H), 1.76 (d, *J* = 13.4 Hz, 1H), 1.55 – 1.32 (m, 4H), 1.30 – 1.18 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.5, 152.7, 130.9, 127.6, 127.2, 44.7, 34.3, 26.9, 26.2. This compound is known.[16]



3a-e

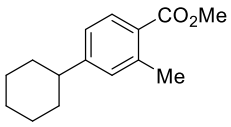
1-(4-Cyclohexylphenyl)ethan-1-one (3a-e): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2e**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a white solid (25.5 mg, 42% yield, Mp = 68 – 69 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 2.59 – 2.53(dd, *J* = 8.8, 2.8 Hz, 4H), 1.93 – 1.79 (m, 4H), 1.81 – 1.73 (m, 1H), 1.47 – 1.36 (m, 4H), 1.28 – 1.24 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.0, 153.8, 135.1, 128.6, 127.1, 44.8, 34.2, 26.8, 26.6, 26.1. This compound is known.[17]



3a-f

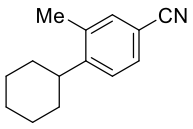
Methyl 4-cyclohexyl-2-fluorobenzoate (3a-f): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2f**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 50:1) as a white solid (36.9 mg, 52% yield, Mp = 77 – 79 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, *J* = 7.9 Hz, 1H), 7.08 – 6.91 (m, 2H), 3.91 (s, 3H), 2.59 – 2.46 (m, 1H), 1.91 – 1.81 (m, 4H), 1.78 – 1.73 (m, 1H), 1.44 – 1.34 (m, 4H), 1.29 – 1.24 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.2, 162.3 (d, *J* = 259.2 Hz), 156.2 (d, *J* = 8.2 Hz), 132.1, 122.7 (d, *J* = 3.2 Hz), 116.0 (d, *J* = 10.0 Hz), 115.2 (d, *J* = 22.3 Hz), 52.3, 44.5, 34.0, 26.7, 26.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ

-109.97 (dd, J = 16.0, 8.0 Hz). IR (ATR): ν = 2928, 2854, 1733, 1622, 1571, 1438, 1293, 1146, 1089, 948, 777 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{14}H_{18}FO_2^+$: 237.1285, found: 237.1282.

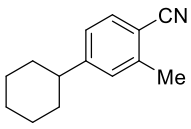


3a-g

Methyl 4-cyclohexyl-2-methylbenzoate (3a-g): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2g**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 50:1) as a colorless oil. (38.3 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 2.2 Hz, 1H), 7.10 – 7.04 (m, 2H), 3.87 (s, 3H), 2.58 (s, 3H), 2.53 – 2.45 (m, 1H), 1.89 – 1.82 (m, 4H), 1.79 – 1.73 (m, 1H), 1.46 – 1.35 (m, 4H), 1.28 – 1.24 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.2, 152.6, 140.5, 131.0, 130.5, 127.1, 124.3, 51.8, 44.7, 34.2, 26.9, 26.2, 22.1. IR (ATR): ν = 2927, 2853, 1723, 1609, 1449, 1269, 1086, 780 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd. for $C_{15}H_{21}O_2^+$: 233.1536, found: 233.1533.

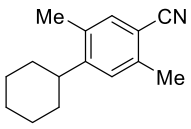


3a-h-1



3a-h-2

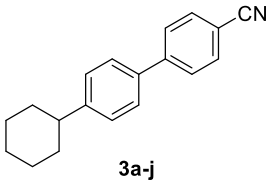
4-Cyclohexyl-3-methylbenzonitrile (3a-h-1)/4-Cyclohexyl-2-methylbenzonitrile (3a-h-2): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2h**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil. (49.6 mg, 83% yield, C_1:C_4 = 1:1). **3a-h-1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 1H), 7.41 (s, 1H), 7.29 (d, J = 8.0 Hz, 1H), 2.79 – 2.67 (m, 1H), 2.35 (s, 3H), 1.83 – 1.70 (m, 5H), 1.40 – 1.33 (m, 4H), 1.28 – 1.18 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.7, 136.6, 133.7, 130.1, 126.4, 119.5, 109.3, 40.5, 33.4, 26.8, 26.2, 19.3. IR (ATR): ν = 2928, 2853, 2226, 1607, 1498, 1449, 1268, 827 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{14}H_{18}N^+$: 200.1434, found: 200.1432. **3a-h-2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 1H), 7.14 (s, 1H), 7.10 (d, J = 8.0 Hz, 1H), 2.54 – 2.49 (m, 4H), 1.88 – 1.83 (m, 5H), 1.48 – 1.40 (m, 4H), 1.31 – 1.28 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.5, 142.0, 132.7, 129.0, 125.0, 118.7, 110.1, 44.9, 34.1, 27.0, 26.1, 20.7. This compound is known.[18]



3a-i

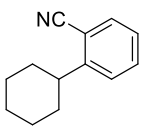
4-Cyclohexyl-2,5-dimethylbenzonitrile (3a-i): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2i**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 20:1) as a highly viscous and colorless oil (39.0 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.12 (s, 1H), 2.74 – 2.64 (m, 1H), 2.48 (s, 3H), 2.29 (s, 3H), 1.91 – 1.84 (m,

2H), 1.81 – 1.71 (m, 3H), 1.43 – 1.34 (m, 4H), 1.29 – 1.23 (m, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.4, 139.6, 133.9, 133.6, 127.5, 118.8, 109.6, 40.5, 33.4, 27.0, 26.3, 20.3, 18.8. This compound is known.[19]



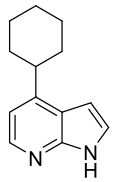
3a-j

4'-Cyclohexyl-[1,1'-biphenyl]-4-carbonitrile (3a-j): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2j**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 50:1) as a white solid (49.4 mg, 63% yield, Mp = 144 – 145 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.63 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* =8.0 Hz, 2H), 2.61 – 2.50 (m, 1H), 1.94 – 1.82 (m, 4H), 1.82 – 1.72 (m, 1H), 1.53 – 1.37 (m, 4H), 1.33 – 1.24 (m, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.0, 145.8, 136.8, 132.7, 127.8, 127.6, 127.3, 119.2, 110.7, 44.4, 34.5, 27.0, 26.2. IR (ATR): *v* = 2921, 2851, 2221, 1603, 1490, 1445, 1001, 814 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{19}H_{20}N^+$: 262.1590, found: 262.1587.



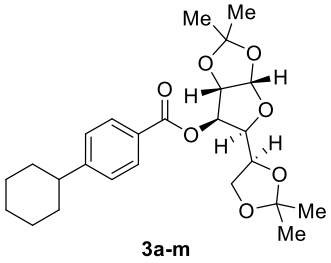
3a-k

2-Cyclohexylbenzonitrile (3a-k): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2k**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (24.1 mg, 43% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.23 (m, 1H), 3.05 – 2.90 (m, 1H), 1.93 – 1.85 (m, 4H), 1.82 – 1.76 (m, 1H), 1.54 – 1.40 (m, 4H), 1.31 – 1.24 (m, 1H). $^{13}C\ \{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 151.7, 133.1, 133.0, 126.7, 126.4, 118.4, 112.0, 42.9, 33.8, 26.7, 26.1. This compound is known.[20]



3a-l

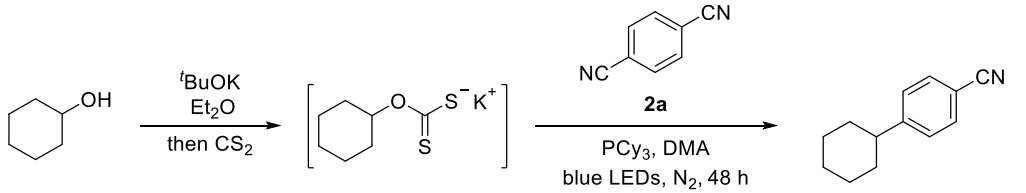
4-Cyclohexyl-1*H*-pyrrolo[2,3-*b*]pyridine (3a-l): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2l**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 2:1) as a white solid (24.7 mg, 41% yield, Mp = 158 – 162 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.24 (d, *J* = 4.8 Hz, 1H), 7.30 (d, *J* = 3.6 Hz, 1H), 6.94 (d, *J* = 4.8 Hz, 1H), 6.58 (d, *J* = 3.6 Hz, 1H), 3.02 – 2.91 (m, 1H), 2.05 – 1.96 (m, 3H), 1.95 – 1.87 (m, 2H), 1.84 – 1.78 (m, 1H), 1.61 – 1.45 (m, 4H). $^{13}C\ \{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 150.0, 148.6, 143.3, 124.0, 119.3, 113.0, 99.6, 42.0, 33.2, 27.0, 26.4. IR (ATR): *v* = 2922, 2848, 1587, 1500, 1445, 1342, 1328, 821, 796, 711 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{13}H_{17}N_2^+$: 201.1386, found: 201.1389



3a-m

5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-cyclohexylbenzoate (3a-m): Synthesized according to the general procedure from alcohol **1a** and aromatic nitrile **2m**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a white solid (80.1 mg, 53% yield, Mp = 142 – 144 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 5.6 Hz, 2H), 7.28 (d, *J* = 5.6 Hz, 2H), 5.93 (d, *J* = 2.4 Hz, 1H), 5.48 (d, *J* = 1.6 Hz, 1H), 4.60 (d, *J* = 2.4 Hz, 1H), 4.39 – 4.32 (m, 2H), 4.15 – 4.05 (m, 2H), 2.57 – 2.50 (m, 1H), 1.89 – 1.83 (m, 4H), 1.79 – 1.74 (m, 1H), 1.55 (s, 3H), 1.46 – 1.38 (m, 7H), 1.31 (s, 3H), 1.27 (s, 3H), 1.26 – 1.24 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 165.4, 154.3, 130.0, 127.21, 127.18, 112.5, 109.5, 105.3, 83.5, 80.1, 76.5, 72.7, 67.3, 44.9, 34.2, 27.0, 26.9, 26.8, 26.3, 26.1, 25.4. IR (ATR): *ν* = 2928, 2853, 1714, 1610, 1449, 1371, 1219, 1093, 1013, 847, 766 cm^{-1}. HRMS (ESI): m/z [M + Na]$^{+}$ calcd. for $C_{25}H_{34}NaO_7^{+}$: 469.2197, found: 469.2203.

4. Gram-Scale Reaction



1a **XSa** (solvent removed *in vacuo*) **3a-a**, 71% yield (1.3 g)

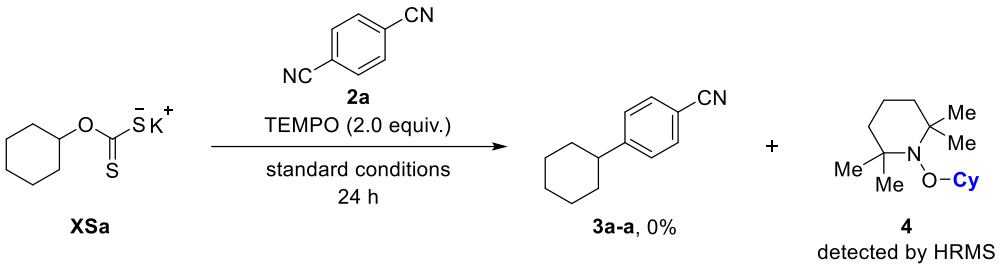
An oven-dried 150 mL eggplant flask equipped with a magnetic stir bar was charged sequentially with **1a** (1.84 g, 18.0 mmol), ^{t}BuOK (2.08 g, 18.0 mmol). The reaction vessel was evacuated and backfilled with nitrogen (three cycles) and anhydrous Et_2O (54 mL) was added under nitrogen atmosphere, a balloon was attached. Then the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (2.74 g, 2.18 mL, 36 mmol) via syringe and stirred for 3 hours before removing the solvent in vacuo. Then **2a** (1.31 g, 10 mmol), PCy_3 (6.18 g, 21.6 mmol), were added. The flask was sealed with a rubber plug, evacuated and backfilled with nitrogen (three cycles), and a nitrogen balloon was attached, followed by the addition of DMA (30 mL) via syringe. The reaction mixture was irradiated with a 30 W blue LEDs, and stirred for 48 hours. The mixture was diluted with saturated NaCl aqueous solution (300 mL) and extracted with

ethyl acetate (100 mL x 3). The combined organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the product **3a-a** (1.3 g, 71%).

5. Mechanism Studies

5.1 TEMPO Trapping Experiments

Table S8. TEMPO Trapping Experiments



XSa | **3a-a**, 0% | **4** detected by HRMS

In a nitrogen-filled glovebox, an oven-dried 10 mL vial equipped with a magnetic stir bar was charged sequentially with **XSa** (115.8 mg, 0.54 mmol), **2a** (38.4 mg, 0.30 mmol), PCy_3 (182 mg, 0.648 mmol), TEMPO (93.8 mg, 0.60 mmol), followed by addition of dry DMA (3.0 mL). The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W blue LEDs lamp (the distance was about 0.6 cm), maintained at 40 °C (in water bath), and stirred for 24 hours. The yield of **3a-a** was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. This result showed that the standard reaction was completely inhibited, and 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine **4** could be identified by HRMS (ESI, m/z), calcd. for $C_{15}H_{29}NO^+[M + H^+]$: 240.2322, found: 240.2323.

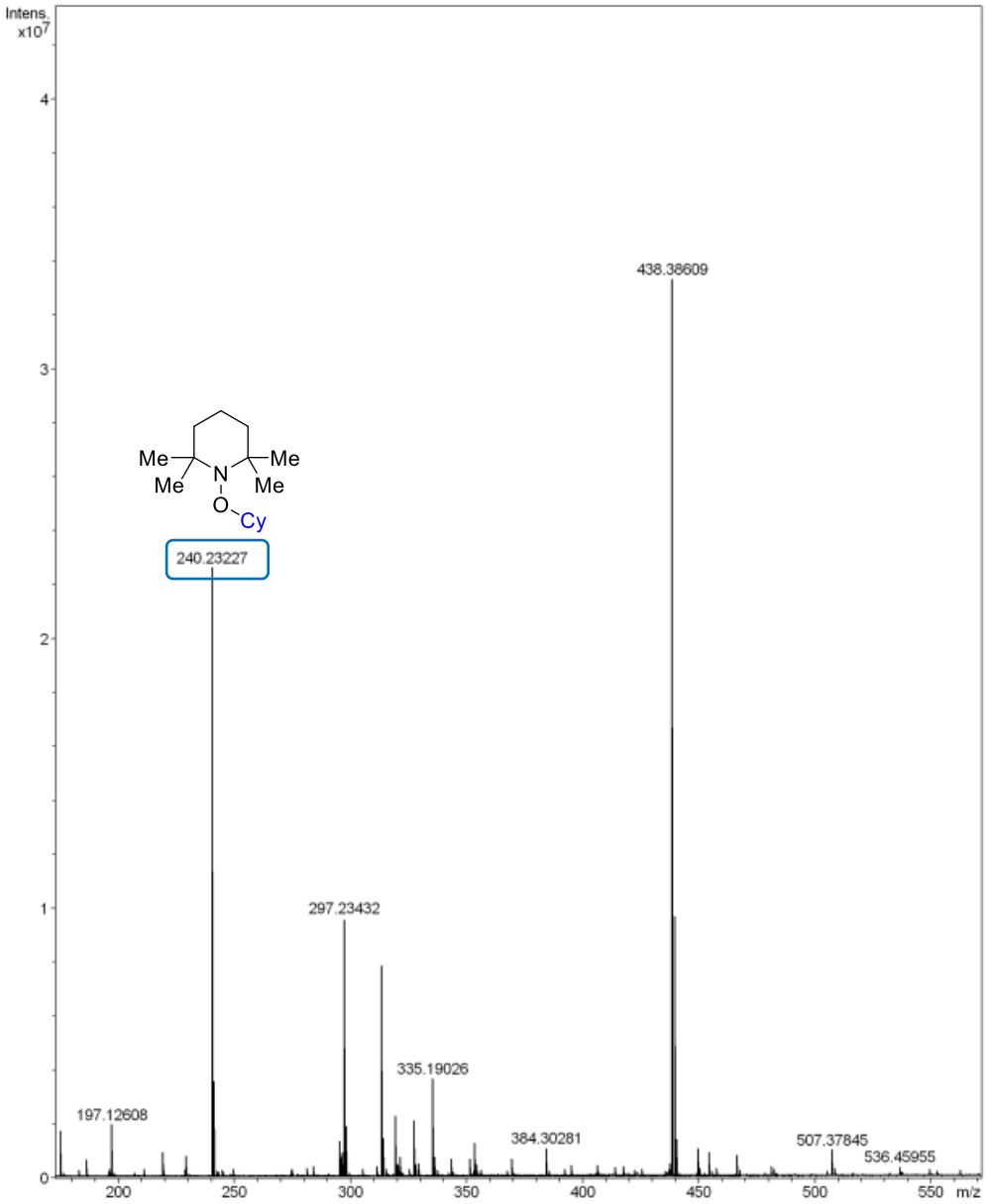
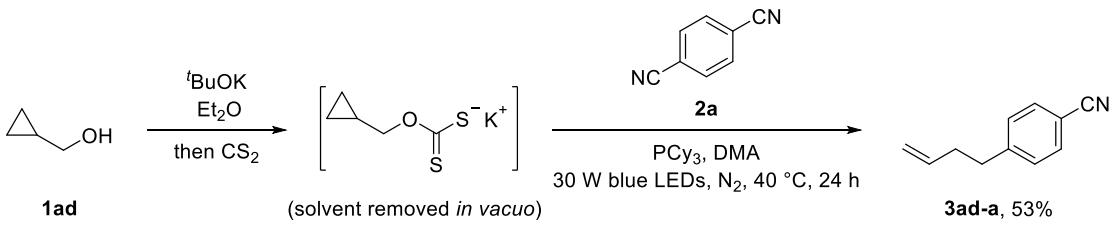


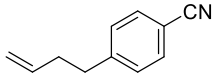
Figure S3. HRMS of 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine

5.2 Radical Clock Experiments



In a N_2-filled glovebox, an oven-dried 10 mL glass vial equipped with a magnetic stir bar was charged sequentially with alcohol **1ad** (38.9 mg, 0.54 mmol), ^{t}BuOK (60.6 mg, 0.54 mmol), and dry

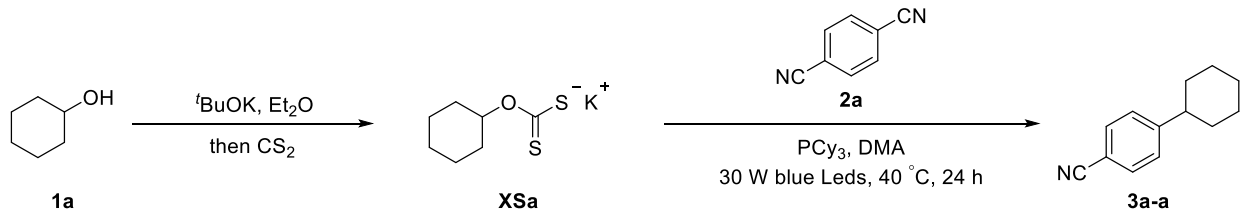
Et_2O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (82.2 mg, 65.0 μL, 1.08 mmol) via microsyringe and continued to be stirred for 3 hours at room temperature before removing the solvent *in vacuo*. The system was transferred into the glovebox, then aromatic nitrile **2a** (38.4 mg, 0.30 mmol), PCy_3 (182 mg, 0.648 mmol), and DMA (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W blue LEDs lamp (the distance was about 0.6 cm), maintained at 40 ℃ (in water bath), and stirred for 24 hours. The mixture was diluted with saturated NaCl aqueous solution (30 mL) and extracted with ethyl acetate (10 mL x 5). The combined organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford **3ad-a** (25.0 mg, 53% yield).



3ad-a

4-(But-3-en-1-yl)benzonitrile (3ad-a): Synthesized according to the general procedure from alcohol **1ad** and aromatic nitrile **2a**. The title compound was isolated by column chromatography eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a colorless oil (25.0 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.24 (d, *J* = 7.2 Hz, 2H), 5.87 – 5.73 (m, 1H), 5.07 – 4.96 (m, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.43 – 2.33 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.6, 137.1, 132.3, 129.4, 119.2, 115.9, 109.9, 35.5, 34.9. This compound is known.[3]

5.3 Light On-Off Experiments



1a **XSa** (solvent removed *in vacuo*) **3a-a**

In a N_2-filled glovebox, an oven-dried 10 mL glass vial equipped with a magnetic stir bar was charged sequentially with alcohol **1a** (54.1 mg, 0.54 mmol), ^{t}BuOK (60.6 mg, 0.54 mmol), and dry Et_2O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (82.2 mg, 65.0 μL, 1.08 mmol) via microsyringe and continued to be stirred for 3 hours at room temperature before removing the solvent *in vacuo*. The system was transferred into the glovebox, then aromatic

nitrile **2a** (38.4 mg, 0.30 mmol), PCy_3 (182 mg, 0.648 mmol), 1,2,4,5-tetramethylbenzene (8.1 mg, 0.06 mmol) and DMA (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W blue LEDs lamp (the distance was about 0.6 cm), maintained at 40 ℃ (in water bath), and stirred for 2 hours. The vial was wrapped in tin foil and a 30 μL sample of the reaction mixture was taken with a syringe and measured by GC. After being stirred for 2 hours at 40 ℃ (in water bath) in dark, a 30 μL sample of the reaction mixture was taken with a syringe and measured by GC. The reaction mixture was then irradiated with a 30 W blue LEDs lamp, and stirred for 2 hours at 40 ℃ (in water bath). Repeating this process three times.

The yield of **3a-a** was determined by GC using 1,2,4,5-tetramethylbenzene an internal standard.

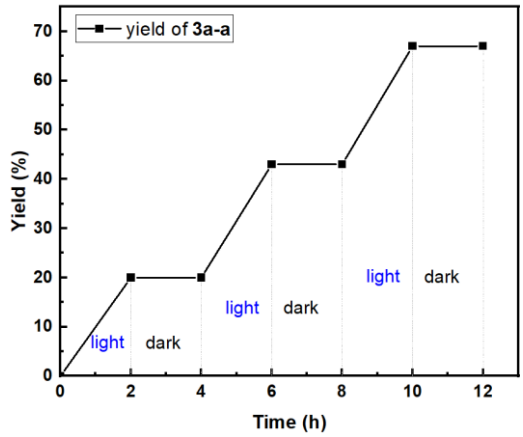


Figure S4. Light on-off experiments

5.4 Determination of Quantum Yields

Measurement of Photo Flux

The photon flux of blue LED was determined by standard ferrioxalate actinometry.

0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (328 mg, 0.750 mmol) in 5.0 mL of 0.20 M aqueous sulfuric acid.

0.15 M buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (54.1 mg, 0.300 mmol) and sodium acetate (1.23 g, 15.0 mmol) in 20 mL of 0.20 M aqueous sulfuric acid.

The actinometry measurements were done as follows:

To a 4 mL quartz cell was added 0.25 mL of the ferrioxalate solution. The vial was sealed and placed 2 cm away from a 10 W blue LEDs. After irradiation for 10 seconds, 0.75 mL of the aqueous

sulfuric acid and 1.0 mL of the buffered solution was added to the vial. The solution was then allowed to rest for 1 hour to allow the resultant ferrous ions to react completely with 1,10-phenanthroline. 50 µL of the resulting solution was taken as an aliquot and diluted with 3.0 mL of 0.20 M aqueous sulfuric acid. The absorbance of the resulting solution in a cuvette (l = 1.0 cm) at 510 nm was measured by UV/Vis spectrometer. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

The amount of ferrous ion formed was calculated as follows:

$$\text{mol } Fe^{2+} = \frac{v \times \Delta A}{l \times \varepsilon}$$

where V is the total volume (0.12 L) of the solution that was analyzed, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples, l is the path length (1.00 cm), and ε is the molar absorptivity at 510 nm (11,100 L/mol•cm).

The photon flux was calculated as follows:

$$\text{photo flux} = \frac{\text{mol } Fe^{2+}}{\Phi \times t \times f}$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 0.845, which was reported for a 0.15 M solution at λ = 457.9 nm) , t is the irradiation time, and f is the fraction of light absorbed at 450 nm (0.9931).

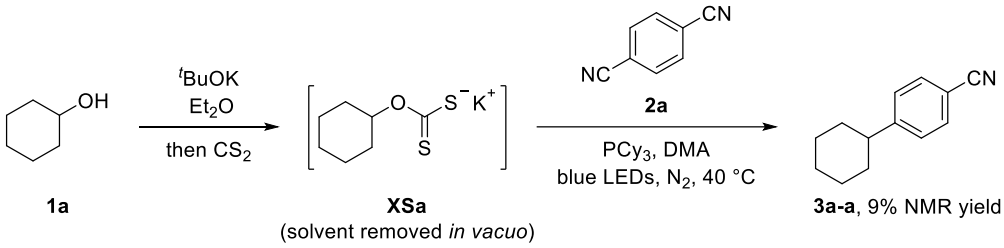
The fraction of light absorbed was determined by the following equation:

$$f = 1.0000 - 10^{-A}$$

where A is the measured absorbance (2.163) of the 0.15 M solution of potassium ferrioxalate at 450 nm.

The photo flux is 1.92×10^{-7} Einstein/s.

Determination of Quantum Yields



1a **XSa** (solvent removed *in vacuo*) **3a-a**, 9% NMR yield

In a N_2-filled glovebox, an oven-dried 10 mL glass vial equipped with a magnetic stir bar was charged sequentially with alcohol **1a** (54.1 mg, 0.54 mmol), ^{t}BuOK (60.6 mg, 0.54 mmol), and dry Et_2O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (82.2 mg, 65.0 µL, 1.08 mmol) via microsyringe and continued to be stirred for 3 hours at room temperature before removing the solvent *in vacuo*. The system was transferred into glovebox, then aromatic nitrile **2a** (38.4 mg, 0.30 mmol), PCy_3 (182 mg, 0.648 mmol) and DMA (3.0 mL) were added. The vial was sealed with a cap and transferred out of the glovebox. The reaction mixture was irradiated with a 10 W blue LEDs (λ = 456 nm, the distance was 2 cm) and stirred for 3600s. After irradiation, the moles of product **3a-a** formed for the model reaction were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard, and revealed 9% yield of **3a-a** (2.70×10^{-5} mol).

The quantum yield was determined as follows.

$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f}$$

where flux is the photon flux determined by ferrioxalate actinometry (1.92×10^{-7} Einstein/s), t is the time (3600 s), and f is the fraction of light absorbed by the irradiated reaction system at 450 nm, and the absorbance of the irradiated reaction system at 450 nm was 4.684. The fraction of light absorbed at 450 nm was calculated: $f = 1.0000 - 10^{-A} = 1.0000 - 10^{-4.684} = 0.99998$.

The quantum yield was calculated: **Φ = 0.039**

This result shows that the radical chain process is not main pathway.

5.5 Exclusion of EDA Complexes

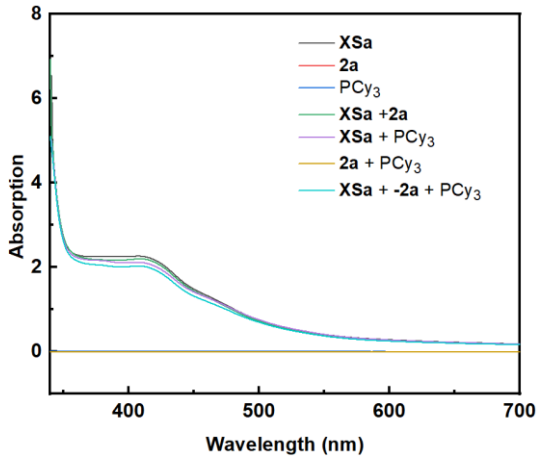


Figure S5. Exploration experiments of EDA complex between different reaction components

The UV/Vis absorption spectra of all solution was introduced to a 1 cm path length quartz cuvette and analyzed using a Shimadzu UV/Vis spectrophotometer UV-2600. **XSa**: 1.0 x 10^{-3} M in DMA. **2a**: 1.0 x 10^{-3} M in DMA. PCy_3: 1.0 x 10^{-3} M in DMA.

5.6 Luminescence Quenching Experiments of XSa

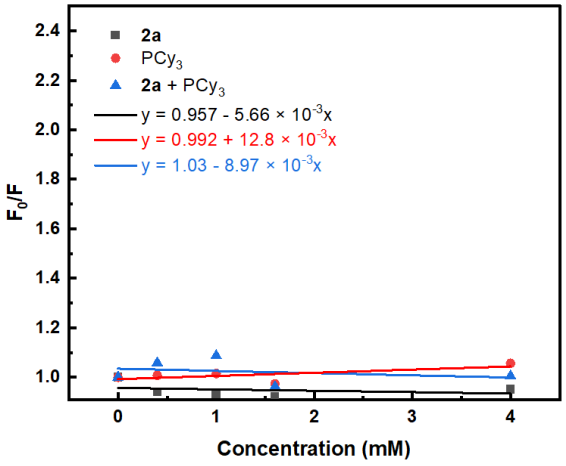


Figure S6. Fluorescence quenching of **XSa**

Fluorescence spectra was collected on Agilent CARY ECLIPSE G9800AS24 for all experiments. All solutions of **XSa** were excited at 390 nm and the emission intensity was collected at 484 nm. In a typical experiment, the emission spectrum of a 5×10^{-3} M solution of **XSa** in DMA collected. When substrate **2a** and PCy_3 were added, no changes in the fluorescence intensity of **XSa** were observed.

5.7 Visible Light Excitability of 1,4-Dicyanobenzene

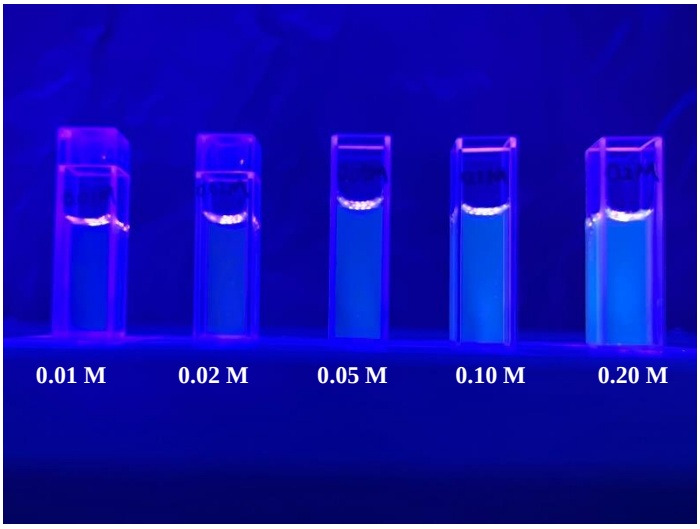


Figure S7. Irradiation of 1,4-dicyanobenzene

Different concentrations of 1,4-dicyanobenzene **2a** was subjected to the 30 W blue LED irradiation (solvent: DMA; concentrations: 0.01 M, 0.02 M, 0.05 M, 0.10 M, 0.20 M), the obvious fluorescence was observed. The experimental results indicate that the visible light excitability of 1,4-dicyanobenzene.

5.8 Luminescence Quenching Experiments of 1,4-Dicyanobenzene

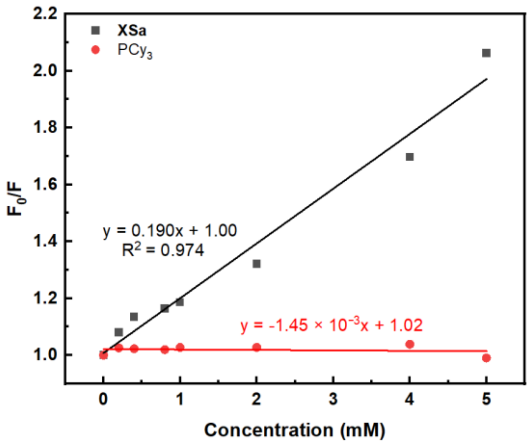
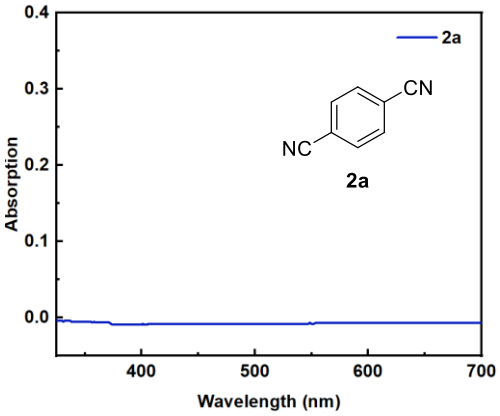


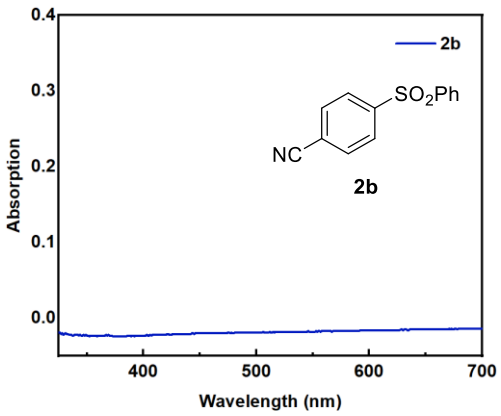
Figure S8. Fluorescence quenching of 1,4-dicyanobenzene

All solutions of 1,4-dicyanobenzene **2a** were excited at 390 nm and the emission intensity was collected at 419 nm. In a typical experiment, the emission spectrum of a 5×10^{-3} M solution of **2a** in DMA collected. The significant decrease of **2a** luminescence could be observed in the presence of **XSa**.

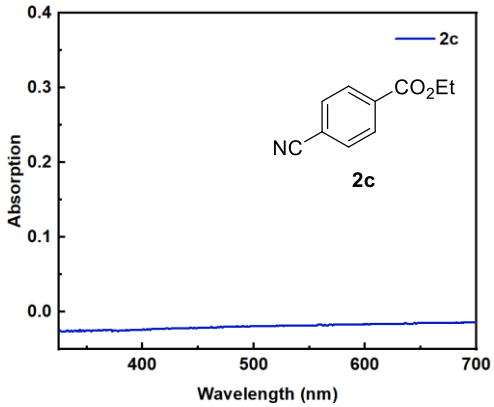
5.9 UV/Vis Absorption Spectra and Fluorescence Spectra of Aromatic Nitriles



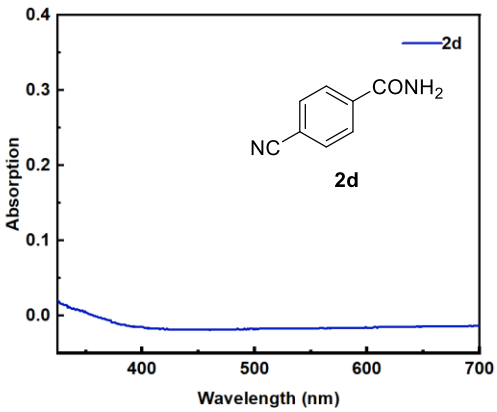
(A) UV/Vis absorption spectra of **2a**



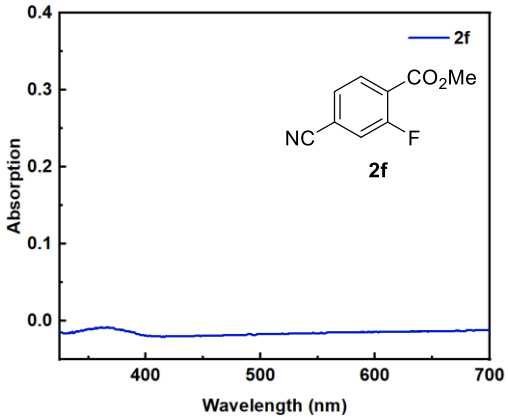
(B) UV/Vis absorption spectra of **2b**



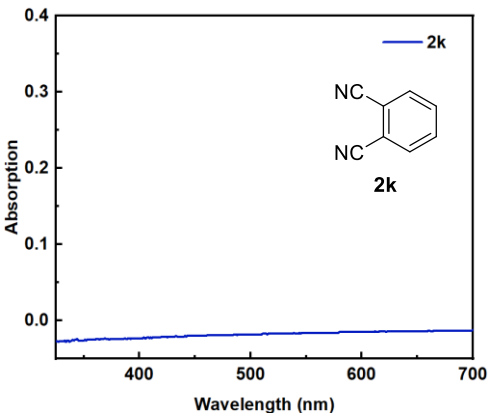
(C) UV/Vis absorption spectra of **2c**



(D) UV/Vis absorption spectra of **2d**



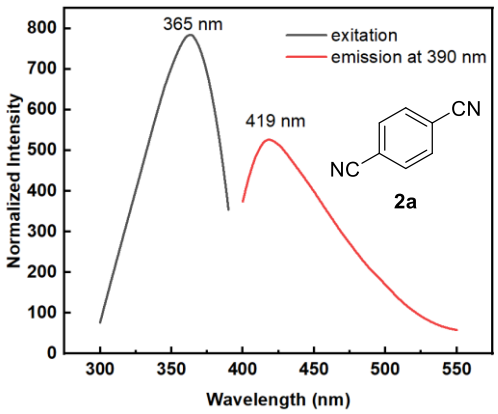
(E) UV/Vis absorption spectra of **2f**



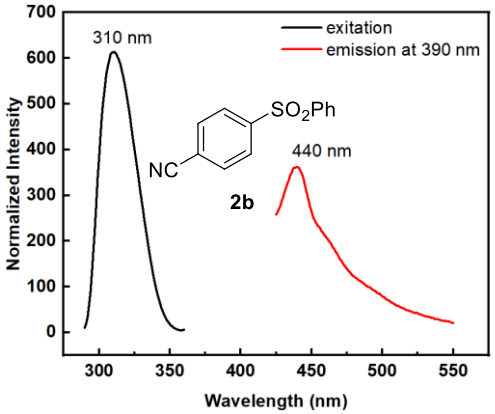
(F) UV/Vis absorption spectra **2k**

Figure S9. UV/Vis absorption spectra of **2a**, **2b**, **2c**, **2d**, **2f** and **2k**

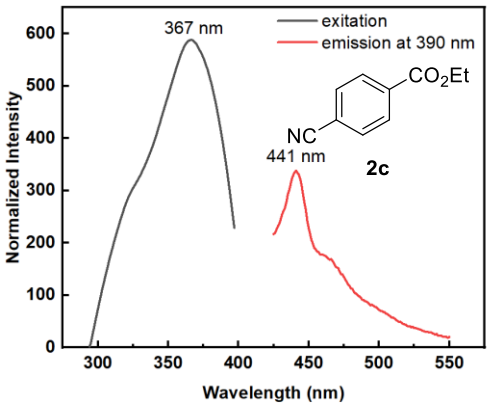
UV/Vis absorption spectra of **2a** (A), **2b** (B), **2c** (C), **2d** (D), **2f** (E) and **2k** (F) in DMA (1×10^{-3} M) were collected on Shimadzu UV/Vis spectrophotometer UV-2600 for all experiments. These aromatic nitriles mentioned above did not exhibit significant UV/Vis absorption.



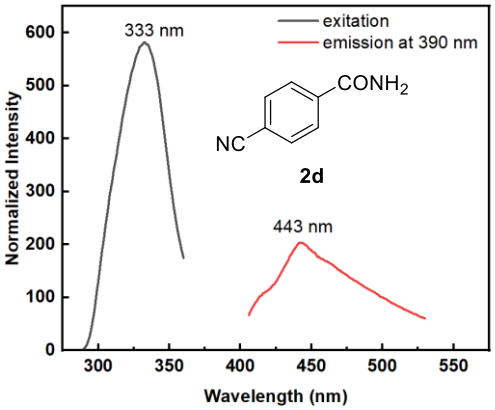
(A) Fluorescence spectra of **2a**



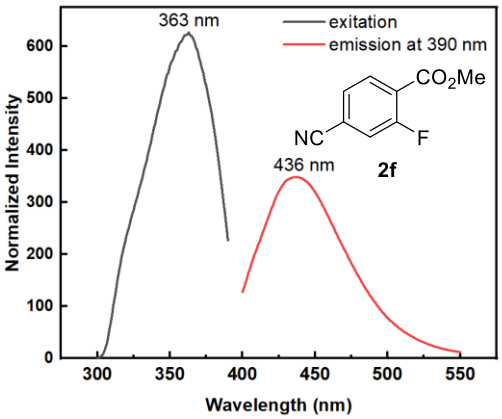
(B) Fluorescence spectra of **2b**



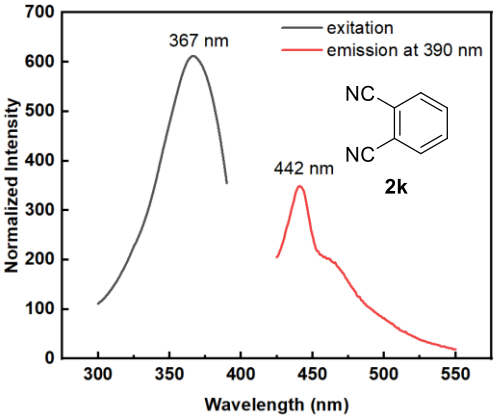
(C) Fluorescence spectra of **2c**



(D) Fluorescence spectra of **2d**



(E) Fluorescence spectra of **2f**



(F) Fluorescence spectra of **2k**

Figure S10. Fluorescence spectra of **2a**, **2b**, **2c**, **2d**, **2f** and **2k** in DMA

Fluorescence spectra of **2a** (A), **2b** (B), **2c** (C), **2d** (D), **2f** (E)and **2k** (F) in DMA (5×10^{-3} M) were collected on Agilent CARY ECLIPSE G9800AS24 for all experiments. Black line: exitation spectra, red line: emission spectra (excitation at 390 nm). The fluorescence spectrum of **2a** showed a exitation wavelength at 365 nm and emission wavelength at 419 nm. The fluorescence spectrum of

2b showed a exitation wavelength at 310 nm and emission wavelength at 440 nm. The fluorescence spectrum of **2c** showed a exitation wavelength at 367 nm and emission wavelength at 441 nm. The fluorescence spectrum of **2d** showed a exitation wavelength at 333 nm and emission wavelength at 443 nm. The fluorescence spectrum of **2f** showed a exitation wavelength at 363 nm and emission wavelength at 436 nm. The fluorescence spectrum of **2k** showed a exitation wavelength at 367 nm and emission wavelength at 442 nm.

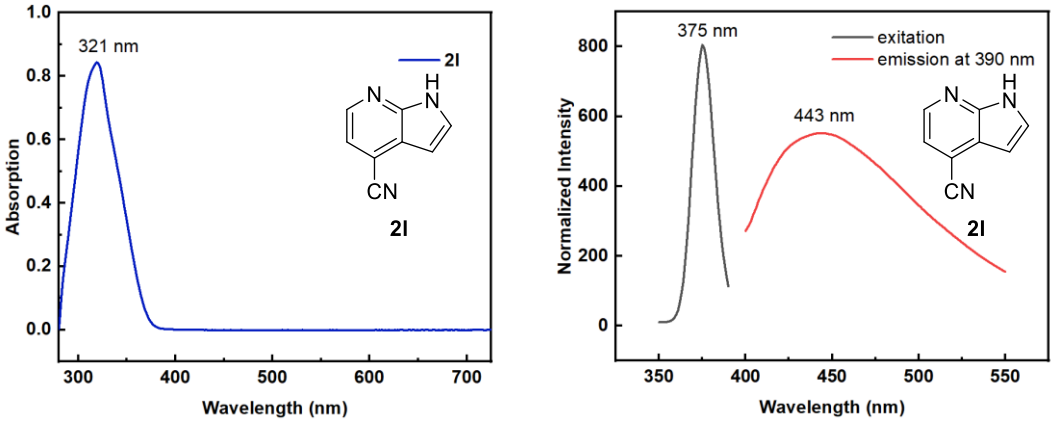


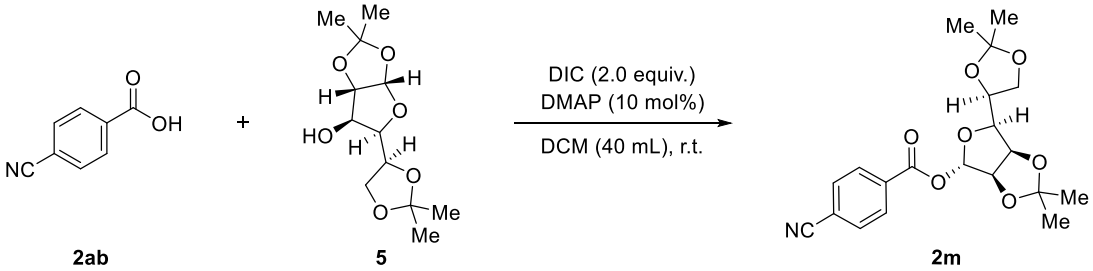
Figure S11. UV/Vis absorption and fluorescence spectra of **2l** in DMA

UV/Vis absorption spectra of **2l** (left) in DMA (1×10^{-4} M) was collected on Shimadzu UV/Vis spectrophotometer UV-2600 for all experiments. Fluorescence spectra of **2l** (right) in DMA (5×10^{-3} M) was collected on Agilent CARY ECLIPSE G9800AS24 for all experiments. Black line: exitation spectra, red line: emission spectra (excitation at 390 nm). The fluorescence spectrum of **2l** showed a exitation wavelength at 375 nm and emission wavelength at 443 nm.

6. Preparation and Characterization Data of Substrates

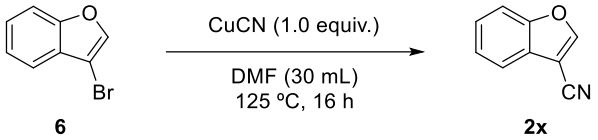
6.1 Preparation of Aromatic Nitriles

Preparation of 2m:



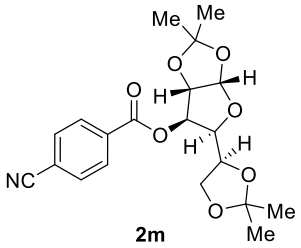
A 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with **2ab** (589 mg, 4.0 mmol), DIC (505 mg, 4.0 mmol), DMAP (24.4 mg, 0.20 mmol), **5** (521 mg, 2.0 mmol) and DCM (40 mL). The mixture was kept stirring for 16 hours at room temperature. The mixture was diluted with DCM (30 mL) and wash with 0.10 M HCl aqueous, 5% $NaHCO_3$ aqueous, NaCl sat. aqueous. The organics were combined, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash silica chromatography gave desired compound **2m** (623 mg, 80% yield).

Preparation of 2x:



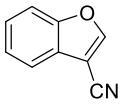
A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with **6** (589 mg, 5.0 mmol). Then, DMF (30 mL) was added to this flask to form a clear solution. Afterwards, CuCN (448 mg, 5 mmol) was added to the solution. The mixture was kept stirring for 16 hours (oil bath) at 125 °C. Then, the mixture was concentrated under reduced pressure, and 20 mL aqueous ammonia and 20 mL EtOAc were added after cooling the flask to room temperature. The organics were combined, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash silica chromatography gave desired compound **2x** (365 mg, 51%).

6.2 Characterization Data of Aromatic Nitriles



2m

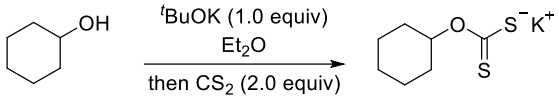
(3a*S*,5*S*,6*R*,6a*S*)-5-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-cyanobenzoate (2m): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a white solid (623 mg, 80% yield, Mp = 88 – 90 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 5.93 (d, *J* = 3.6 Hz, 1H), 5.49 (d, *J* = 2.4 Hz, 1H), 4.61 (d, *J* = 3.6 Hz, 1H), 4.33 – 4.26 (m, 2H), 4.10 (dd, *J* = 9.0, 4.8 Hz, 1H), 4.05 (dd, *J* = 8.8, 4.0 Hz, 1H), 1.53 (s, 3H), 1.38 (s, 3H), 1.30 (s, 3H), 1.23 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.7, 133.4, 132.5, 130.3, 117.9, 117.0, 112.6, 109.7, 105.2, 83.4, 80.0, 77.5, 72.6, 67.5, 27.0, 26.8, 26.3, 25.3. IR (ATR): *ν* = 2987, 2890, 1728, 1374, 1265, 1072, 1017, 841, 766 cm^{-1}. HRMS (ESI): m/z [M + Na]$^{+}$ calcd.. for $C_{20}H_{23}NNaO_7^{+}$: 412.1367, found 412.1368.



2x

Benzofuran-3-carbonitrile (2x): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 20:1) as a light yellow solid (623 mg, 80% yield, Mp = 94 – 95 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.78 – 7.72 (m, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.38 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.6, 152.1, 126.8, 124.9, 120.4, 112.4, 95.1. This compound is known.[21]

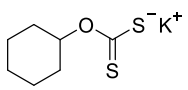
6.3 Preparation of Xanthate Salt



1a **XSa**

In a N_2-filled glovebox, an oven-dried 100 mL round-bottom flask equipped with a magnetic stir bar was charged sequentially with alcohol **1a** (501 mg 5.0 mmol), ^{t}BuOK (561 mg, 5.0 mmol), and dry Et_2O (50 mL). The flask was sealed with a septum cap and transferred out of the glovebox, and a balloon was attached. The reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (0.76 g, 0.60 mL, 10.0 mmol) via syringe and continued to be stirred for 3 hours at room temperature. The precipitate formed was collected by filtration, washed with Et_2O (3 × 30 mL), and dried *in vacuo* to afford **XSa** (997 mg, 93% yield).

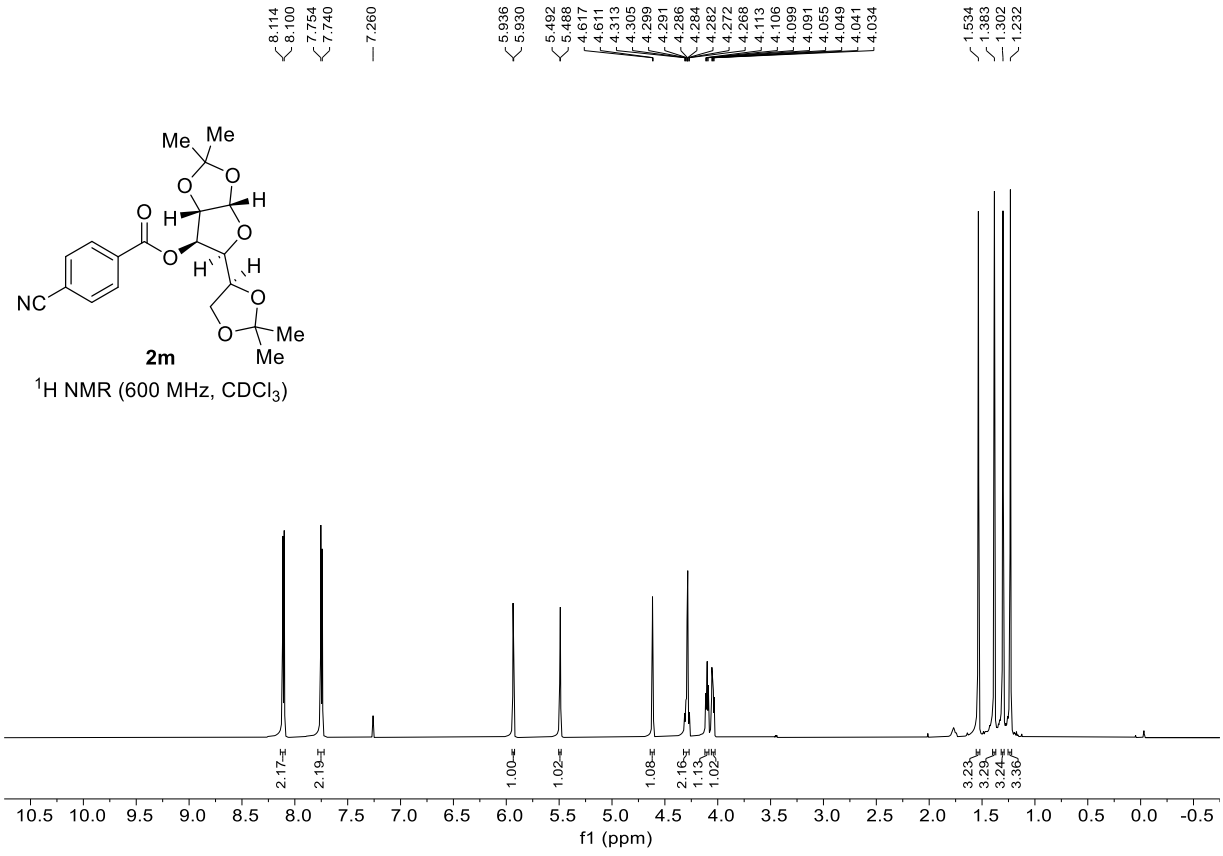
6.4 Characterization Data of Xanthate Salt



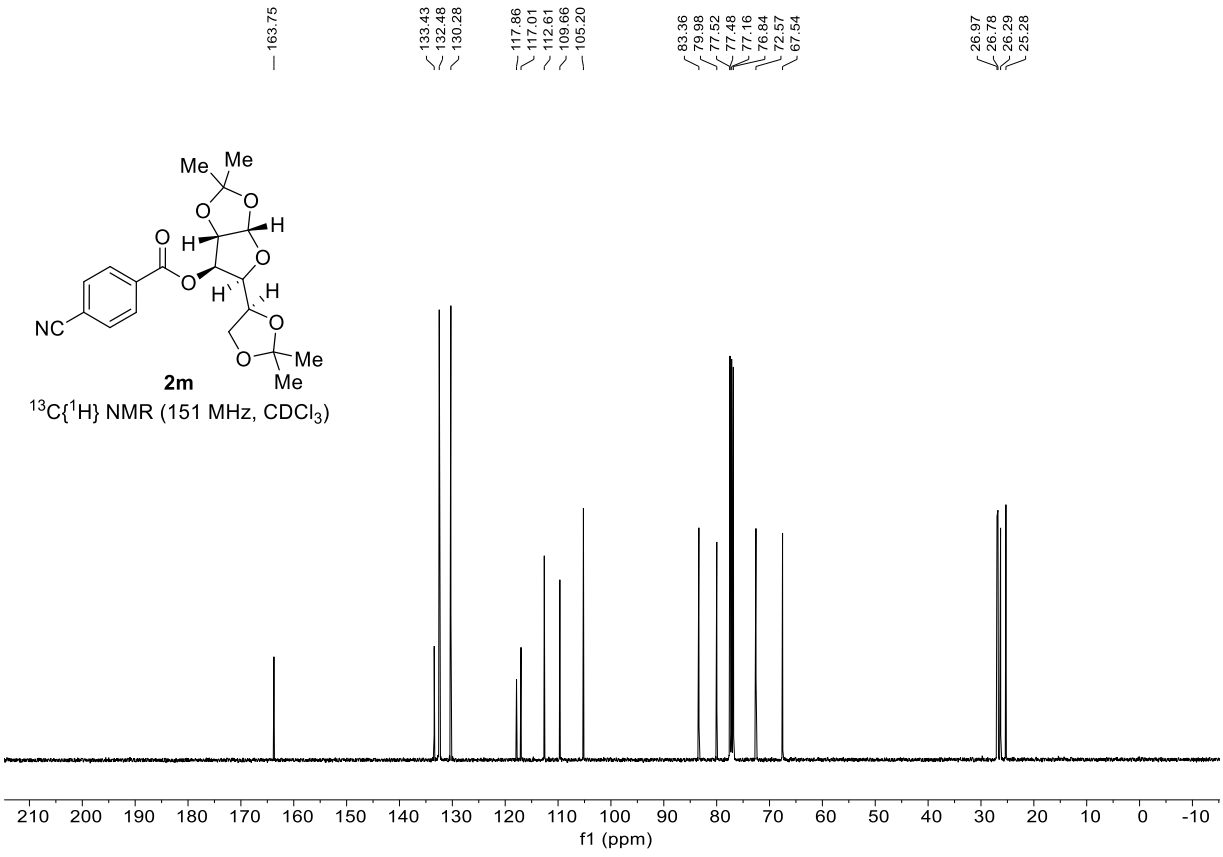
XSa

Potassium *O*-cyclohexyl carbonodithioate (XSa): The title compound was isolated by filtration as a pale-yellow solid (997 mg, 93% yield). ^{1}H NMR (400 MHz, d_6-DMSO) δ 5.27 – 5.12 (m, 1H), 1.94 – 1.77 (m, 2H), 1.74 – 1.59 (m, 2H), 1.56 – 1.40 (m, 1H), 1.37 – 1.11 (m, 5H). ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO) δ 229.8, 78.0, 32.0, 25.7, 24.4. This compound is known.[22]

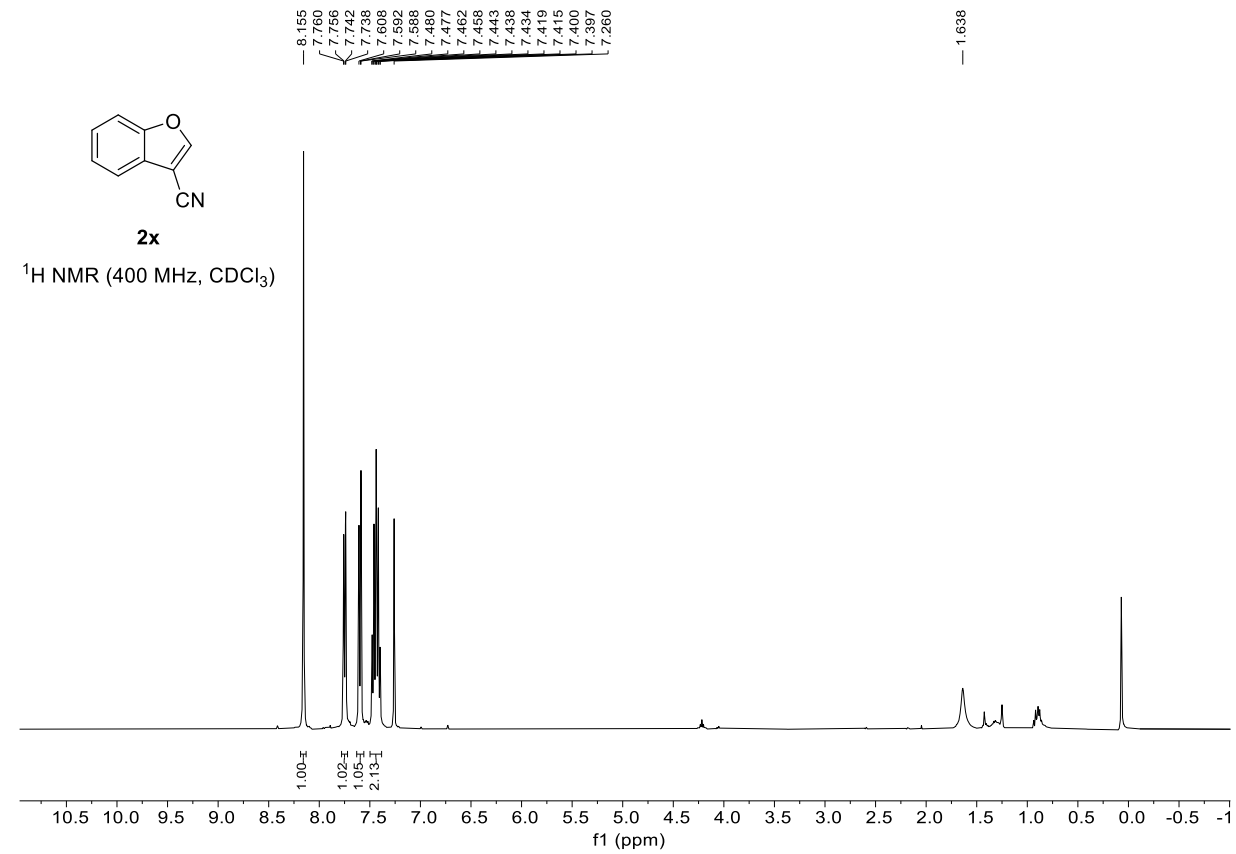
7. NMR Spectra



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

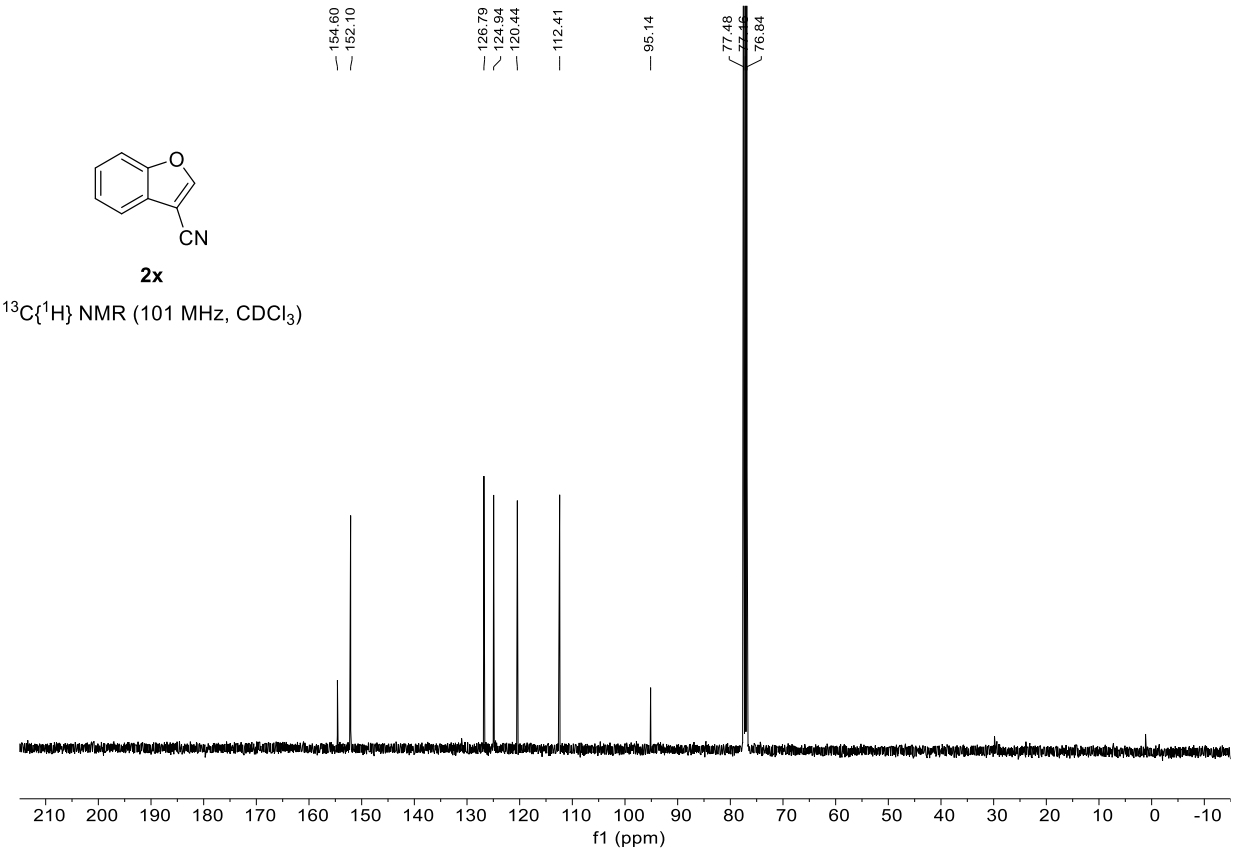


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



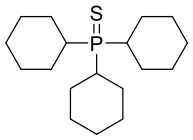
2x

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

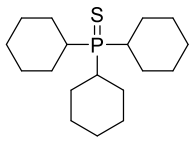


2x

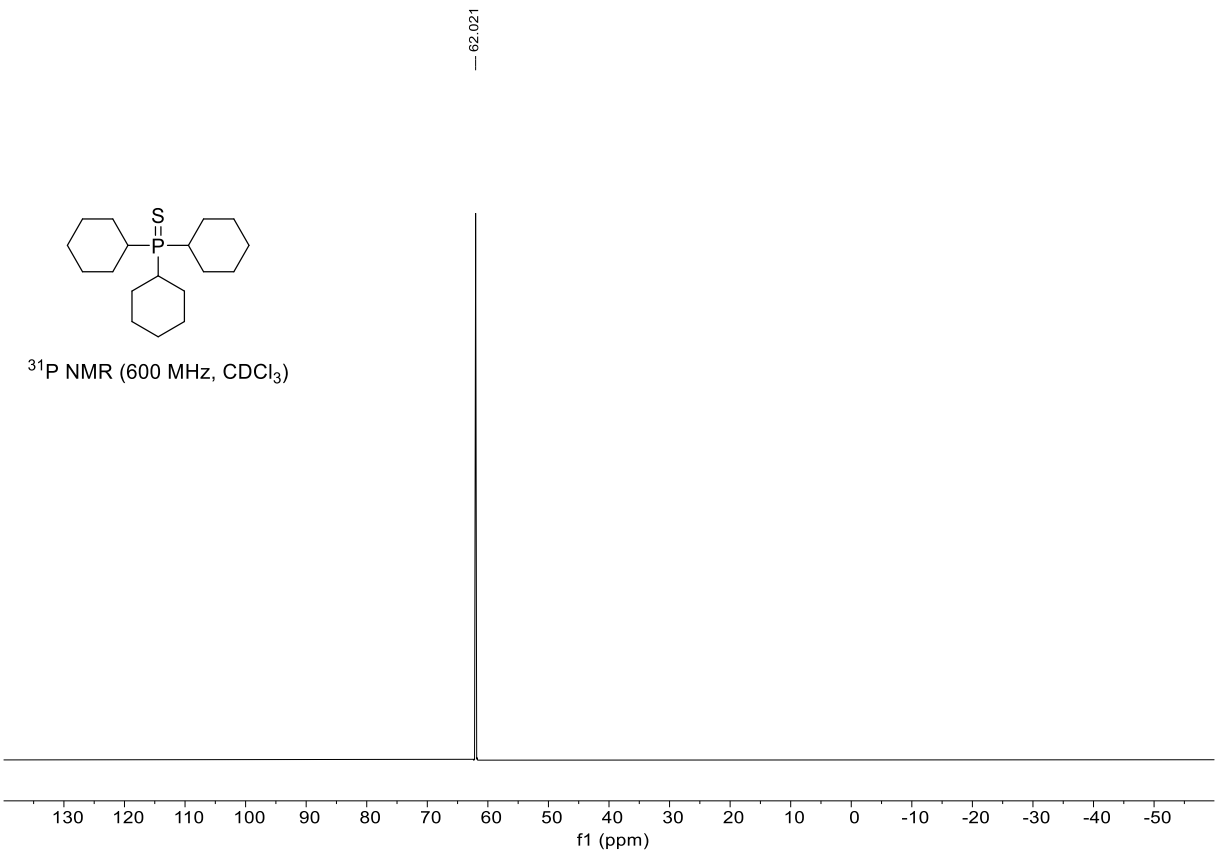
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



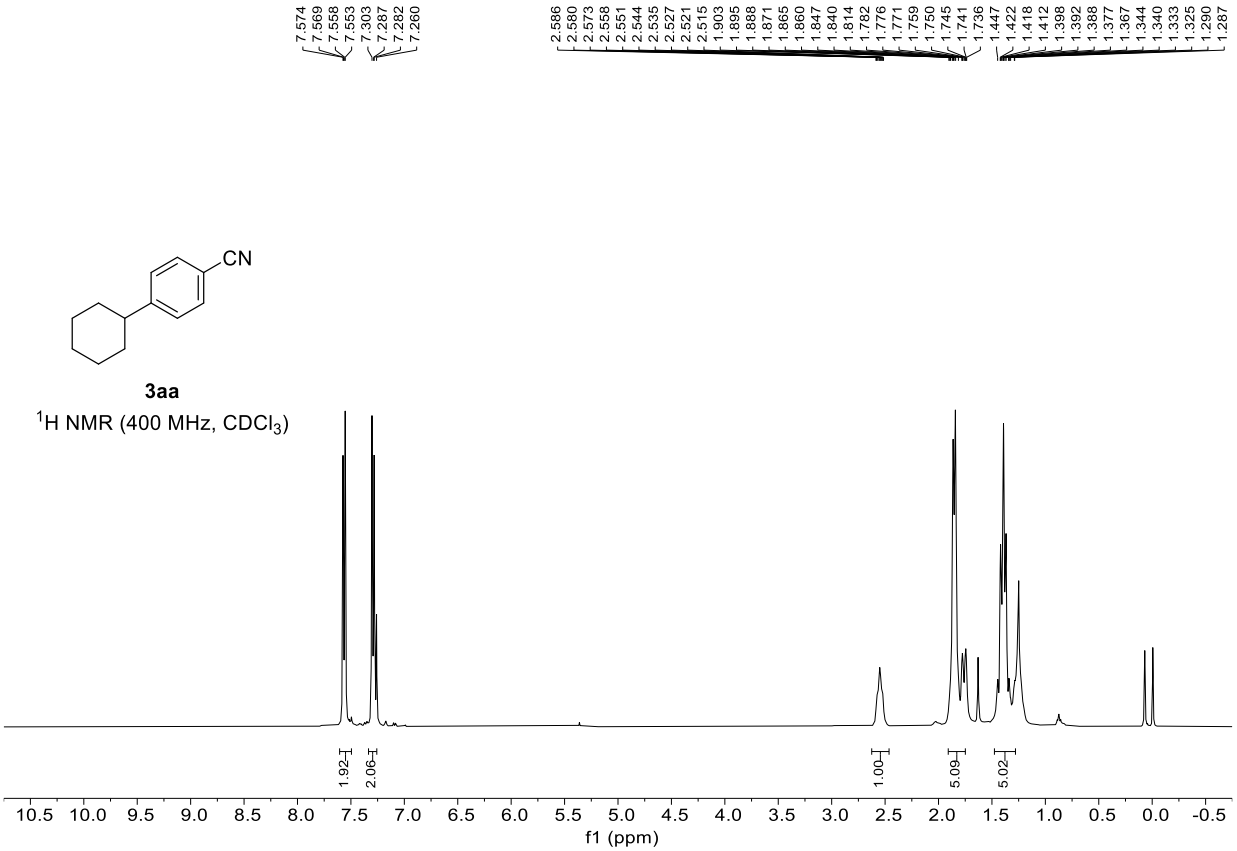
^{1}H NMR (600 MHz, $CDCl_3$)

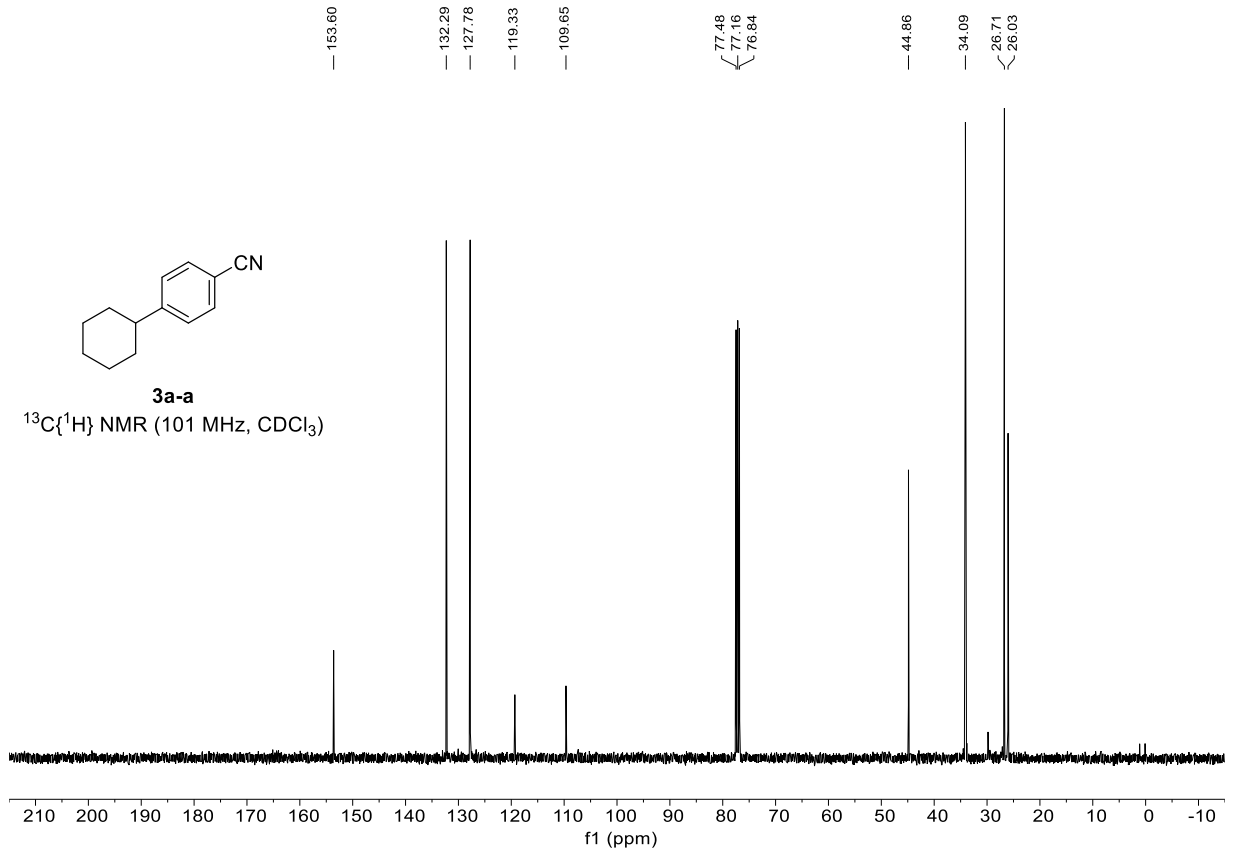


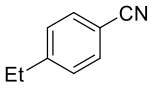
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



^{31}P NMR (600 MHz, $CDCl_3$)

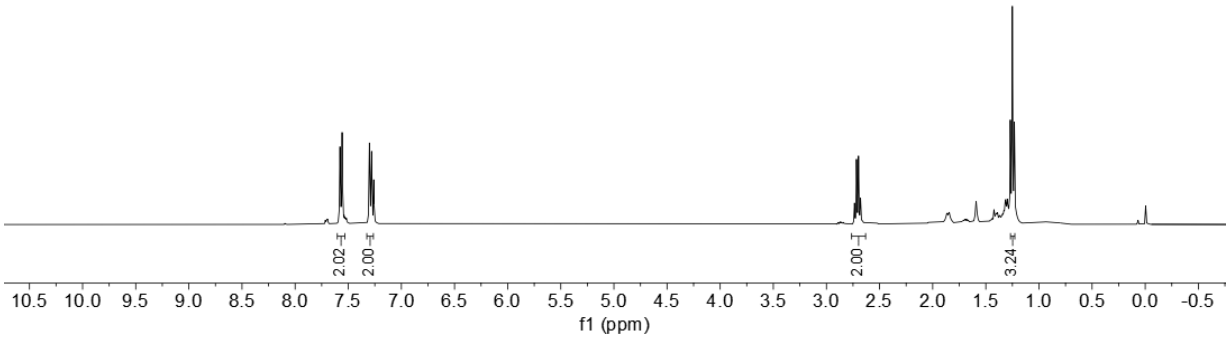

7.574
7.569
7.558
7.553
7.303
7.287
7.282
7.260
2.586
2.580
2.573
2.558
2.551
2.544
2.535
2.527
2.521
2.515
1.903
1.895
1.888
1.871
1.865
1.860
1.847
1.840
1.814
1.782
1.776
1.771
1.759
1.750
1.745
1.741
1.736
1.447
1.422
1.418
1.412
1.398
1.392
1.388
1.377
1.367
1.344
1.340
1.333
1.325
1.290
1.287
CN
3aa
1H NMR (400 MHz, CDCl3)
1.92
2.06
1.00
5.09
5.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

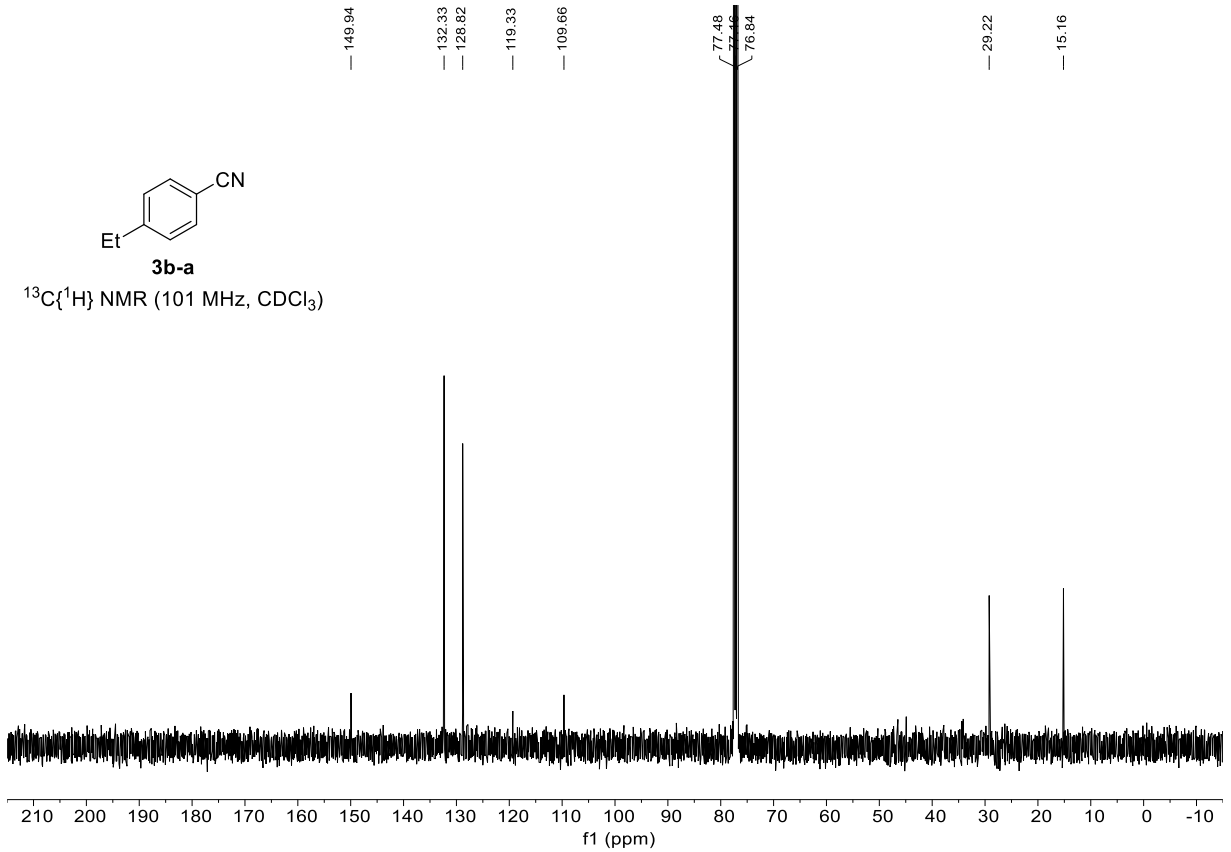

153.60
132.29
127.78
119.33
109.65
77.48
77.16
76.84
44.86
34.09
26.71
26.03
CN
3a-a
13C{1H} NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3b-a

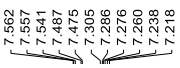
^{1}H NMR (400 MHz, $CDCl_3$)

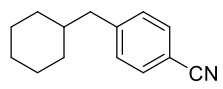




3b-a

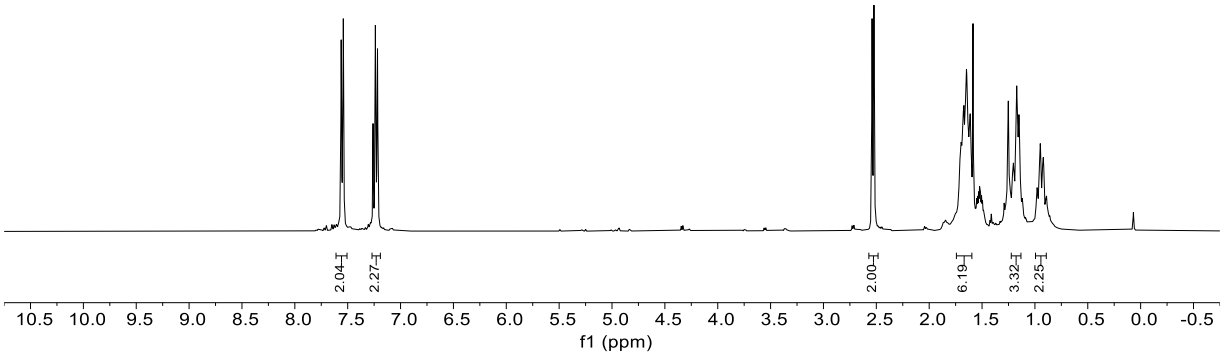
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

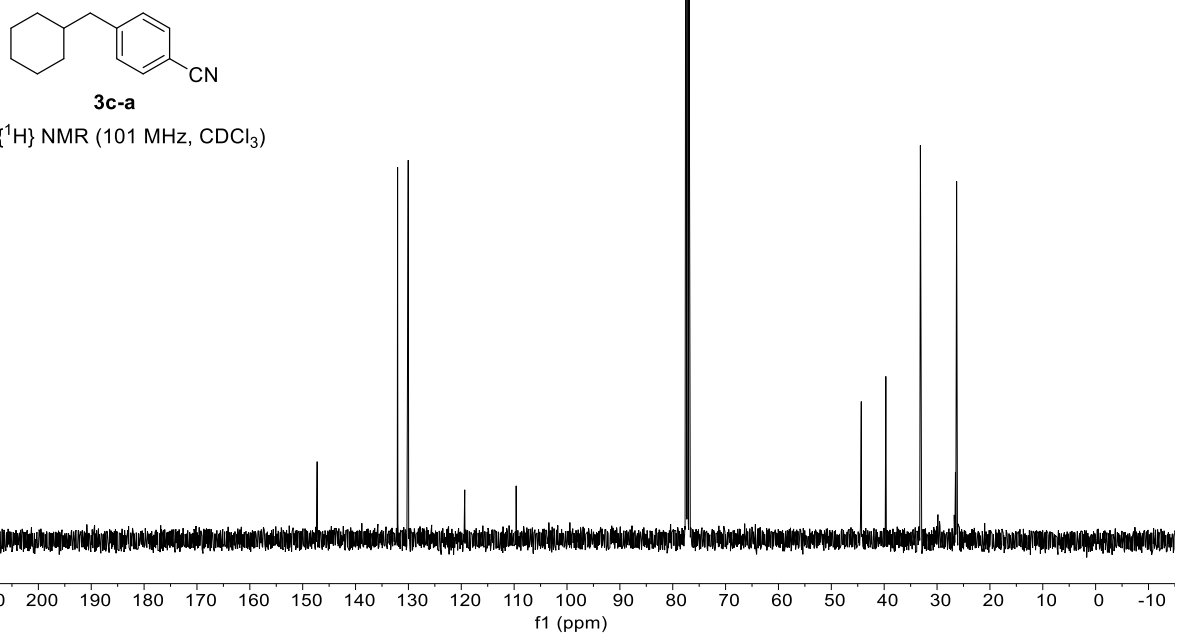




3c-a

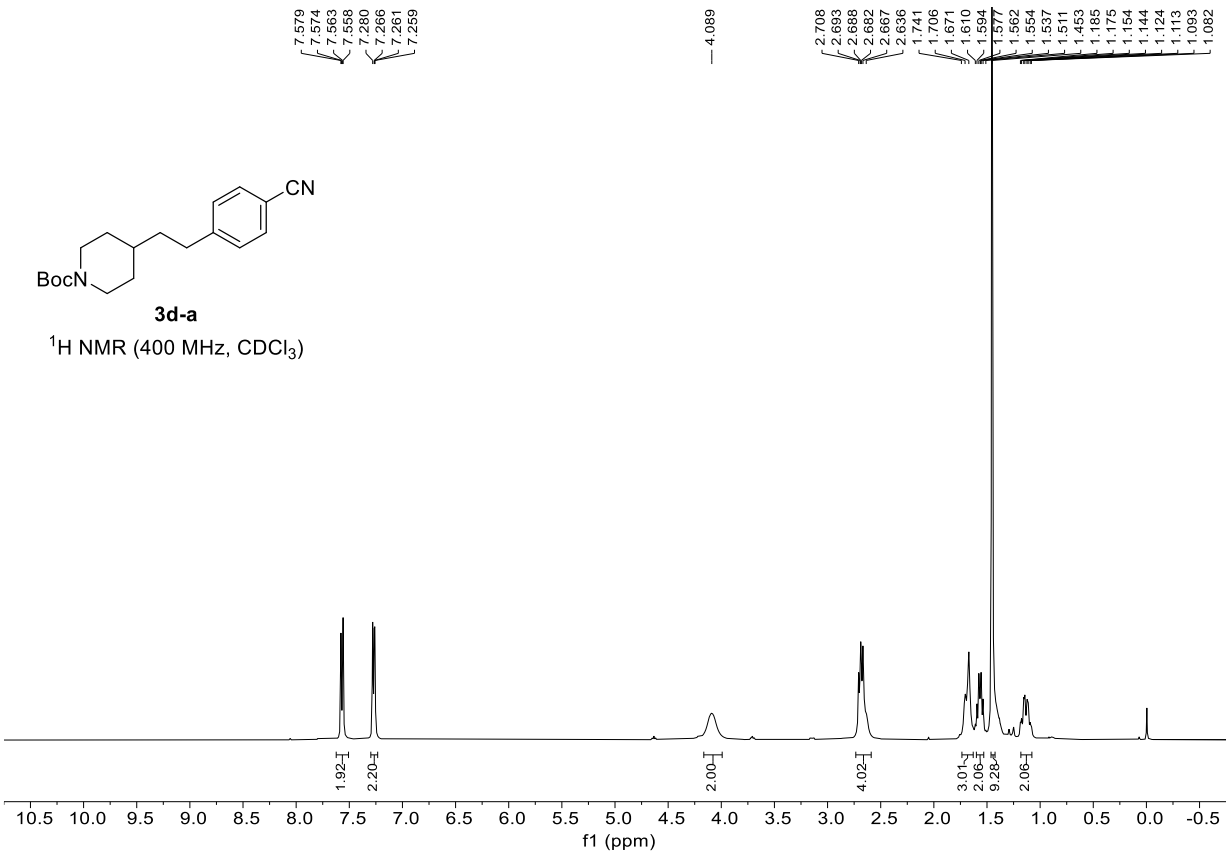
^{1}H NMR (400 MHz, $CDCl_3$)





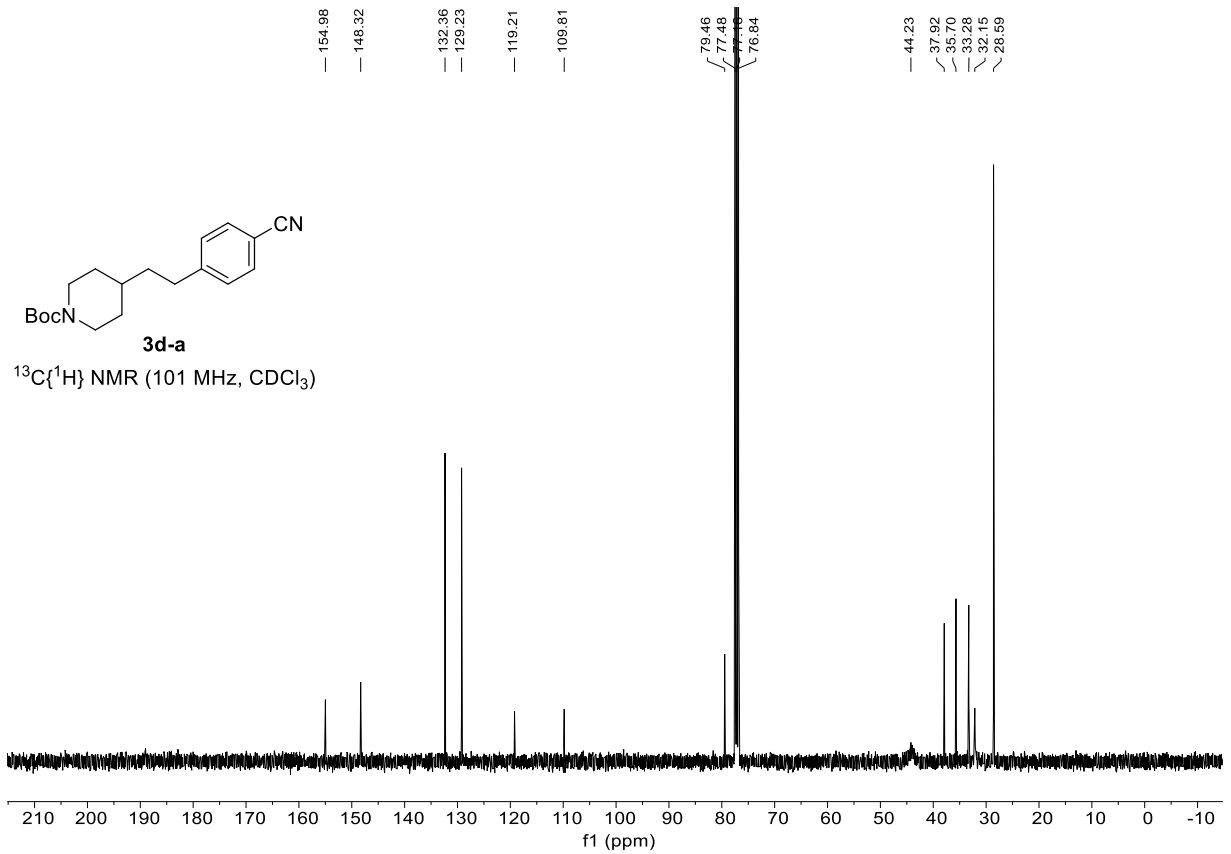
3c-a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



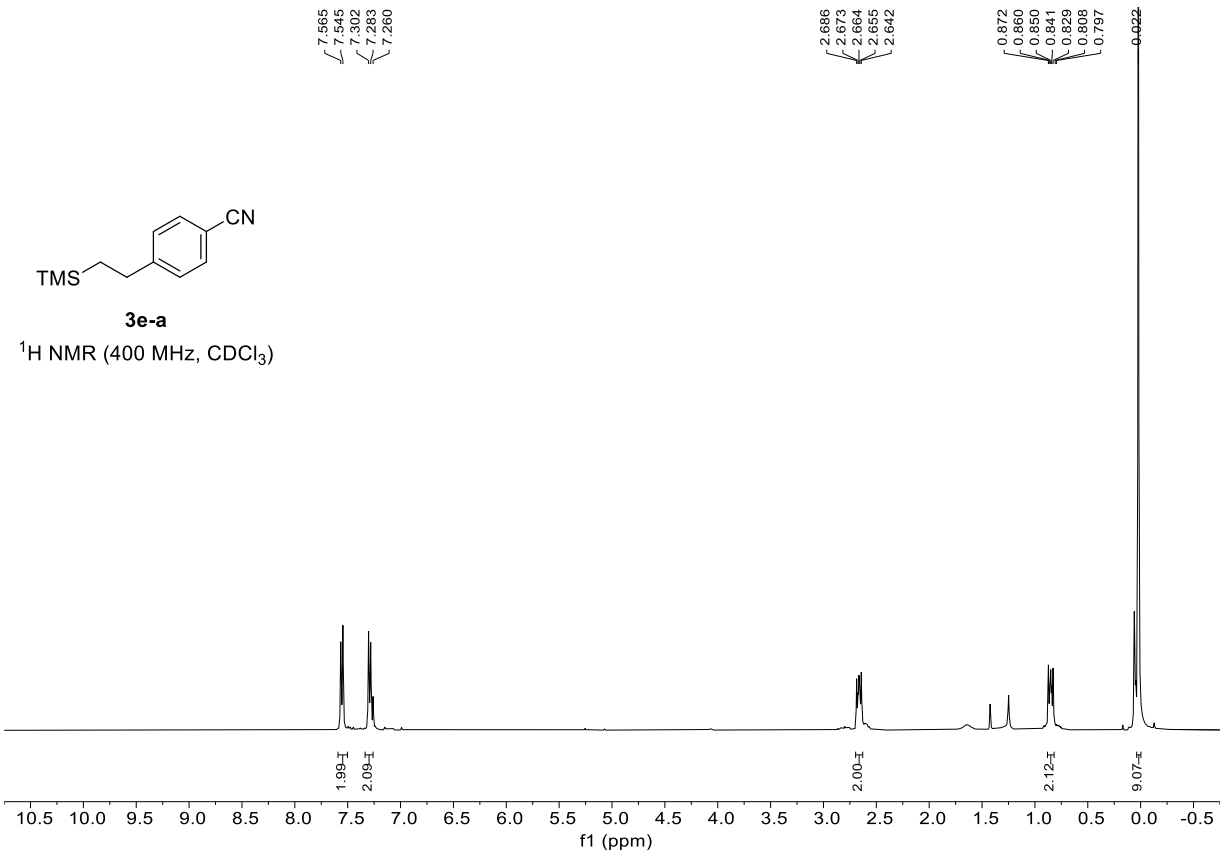
3d-a

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



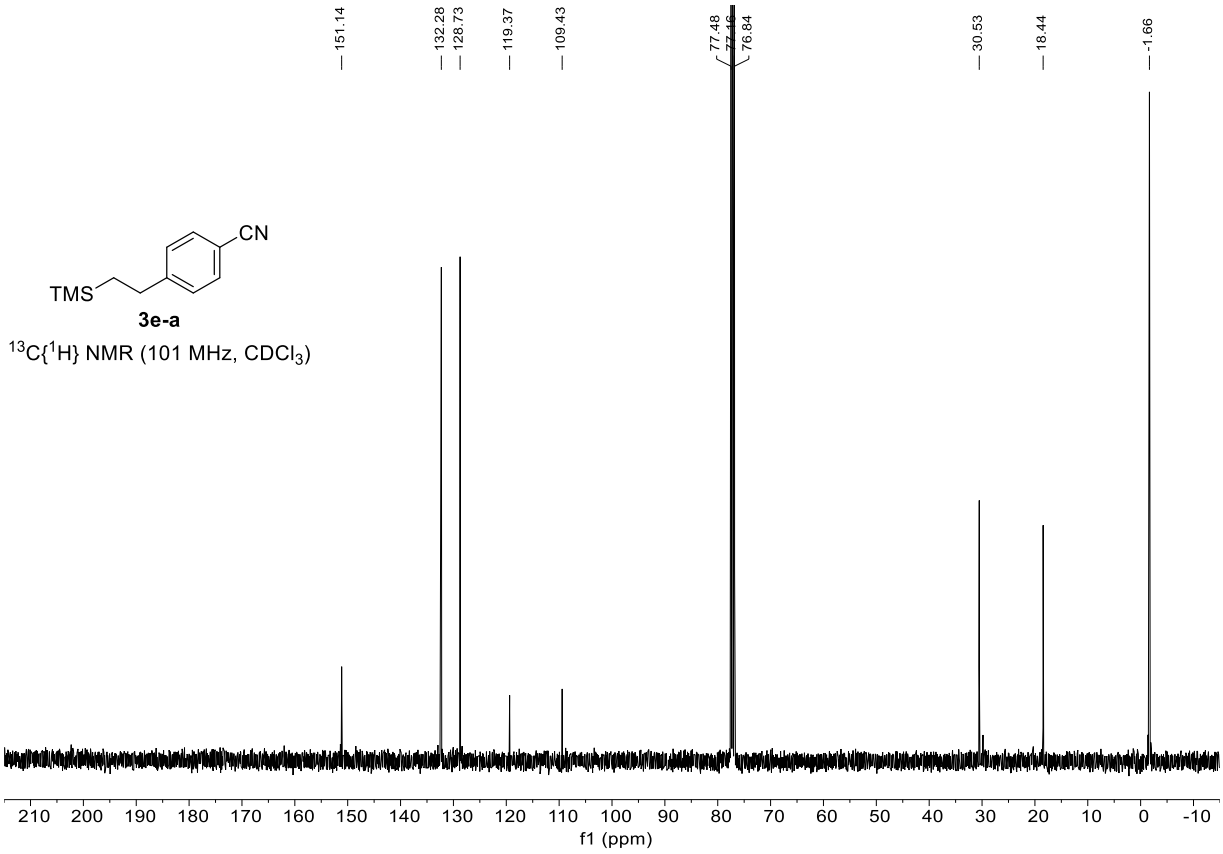
3d-a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



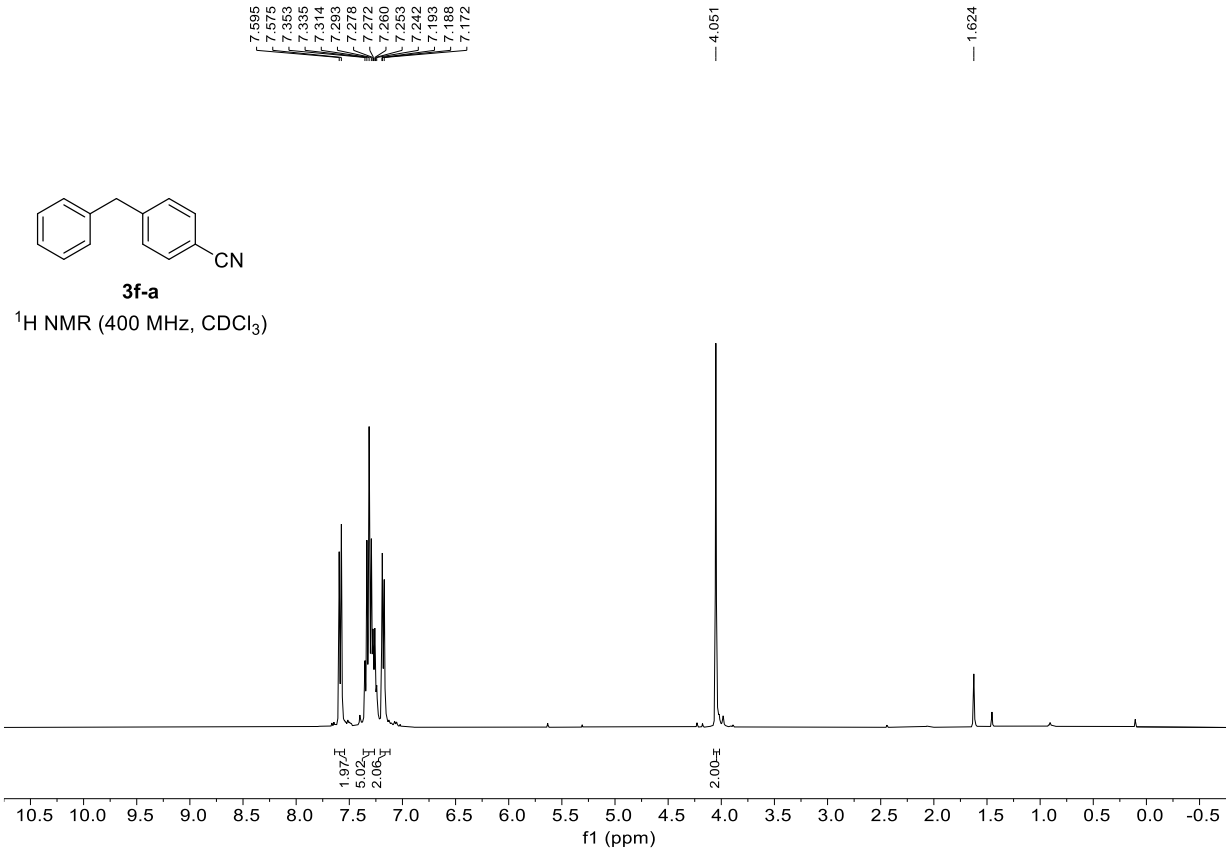
3e-a

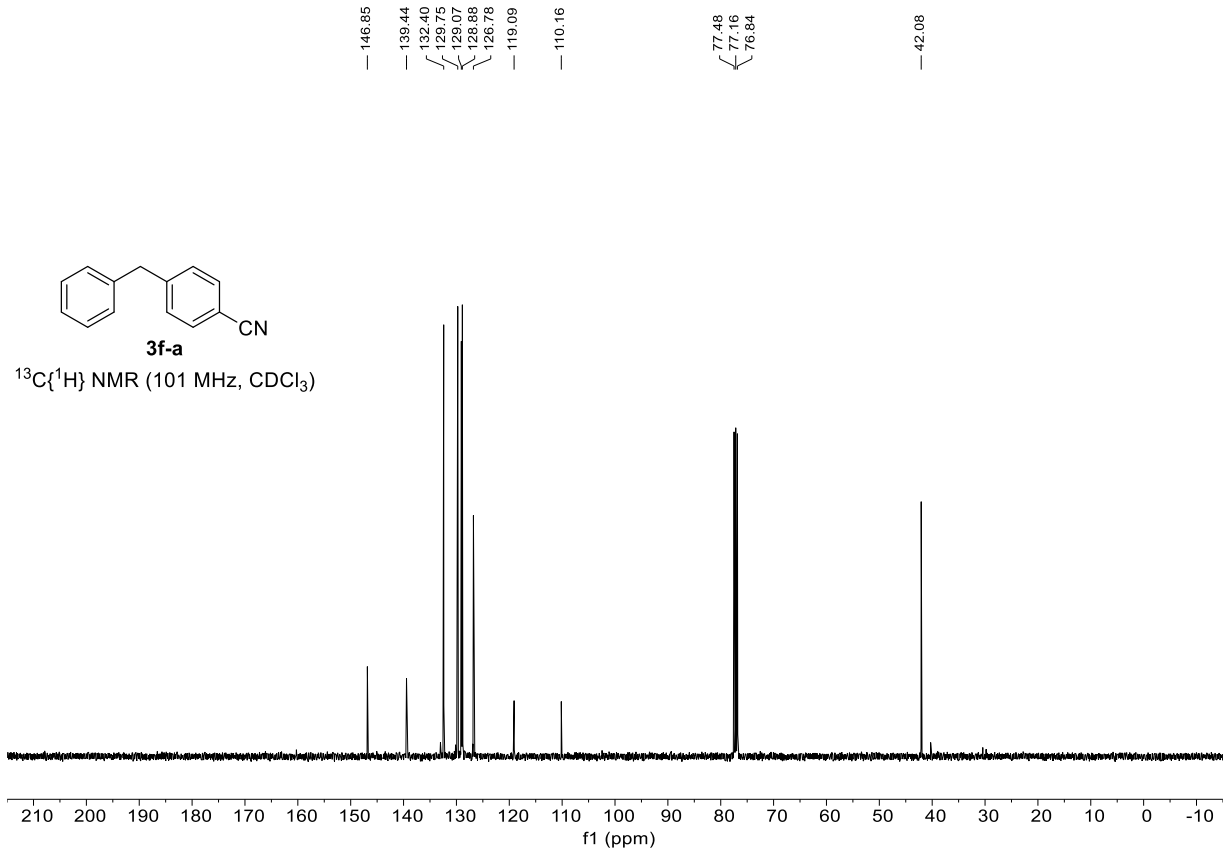
^{1}H NMR (400 MHz, $CDCl_3$)

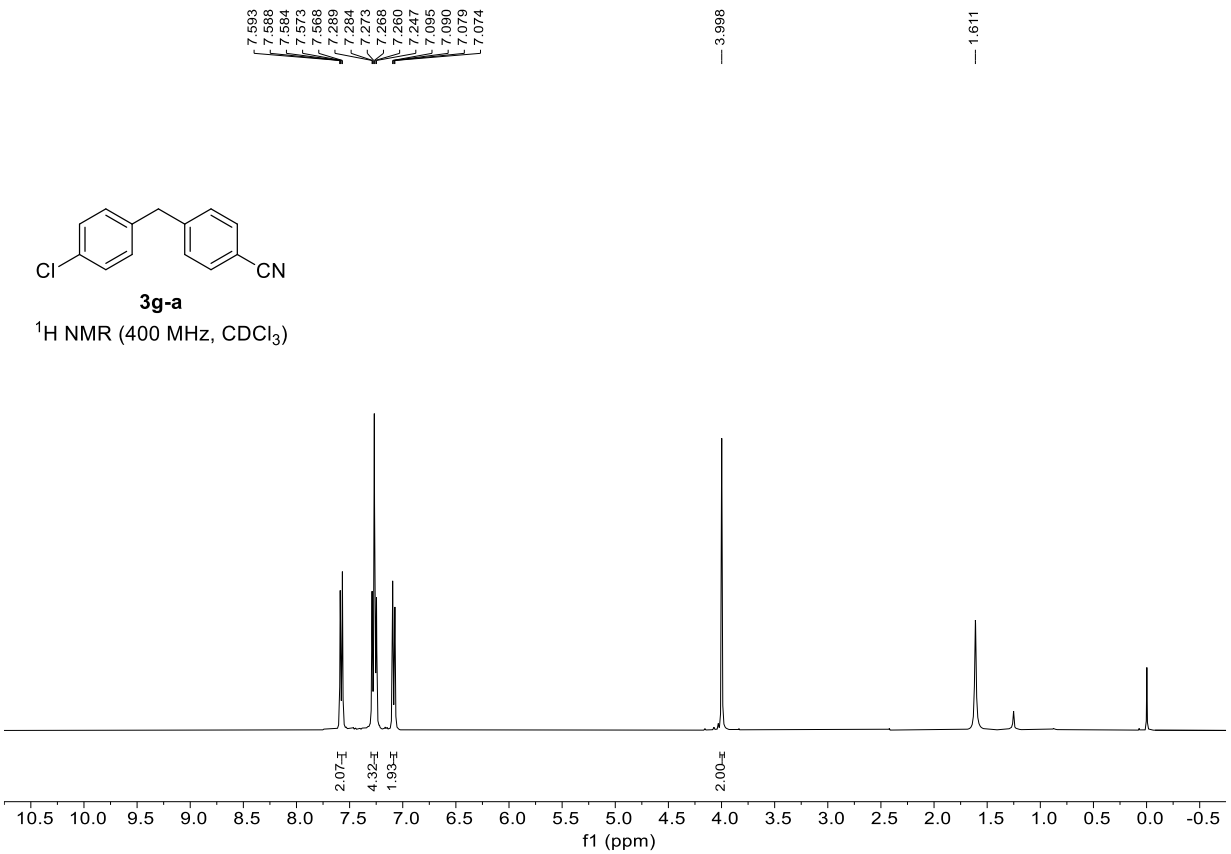


3e-a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

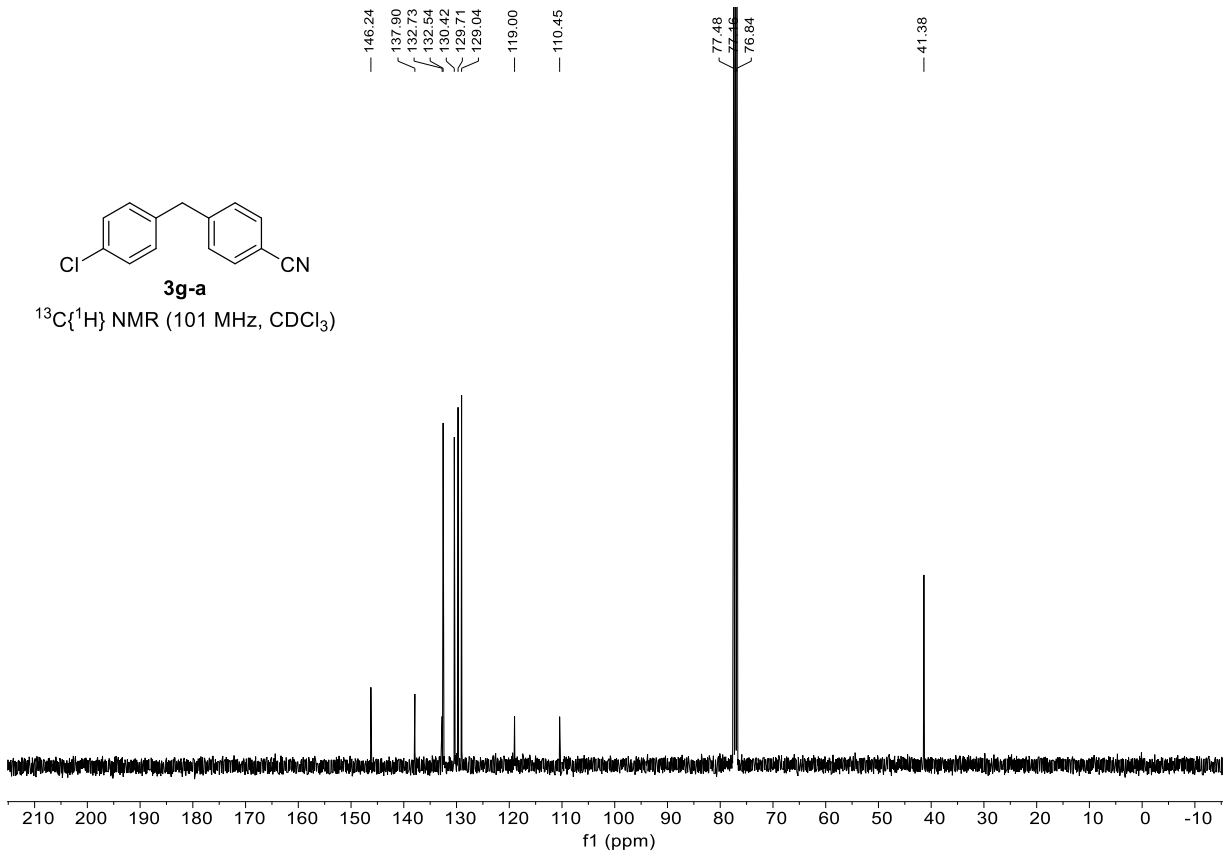

7.595
7.575
7.353
7.335
7.314
7.293
7.278
7.272
7.260
7.253
7.242
7.193
7.188
7.172
4.051
1.624
CN
3f-a
1H NMR (400 MHz, CDCl3)
1.97
5.02
2.06
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


146.85
139.44
132.40
129.75
129.07
128.88
126.78
119.09
110.16
77.48
77.16
76.84
42.08
CN
3f-a
13C{1H} NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



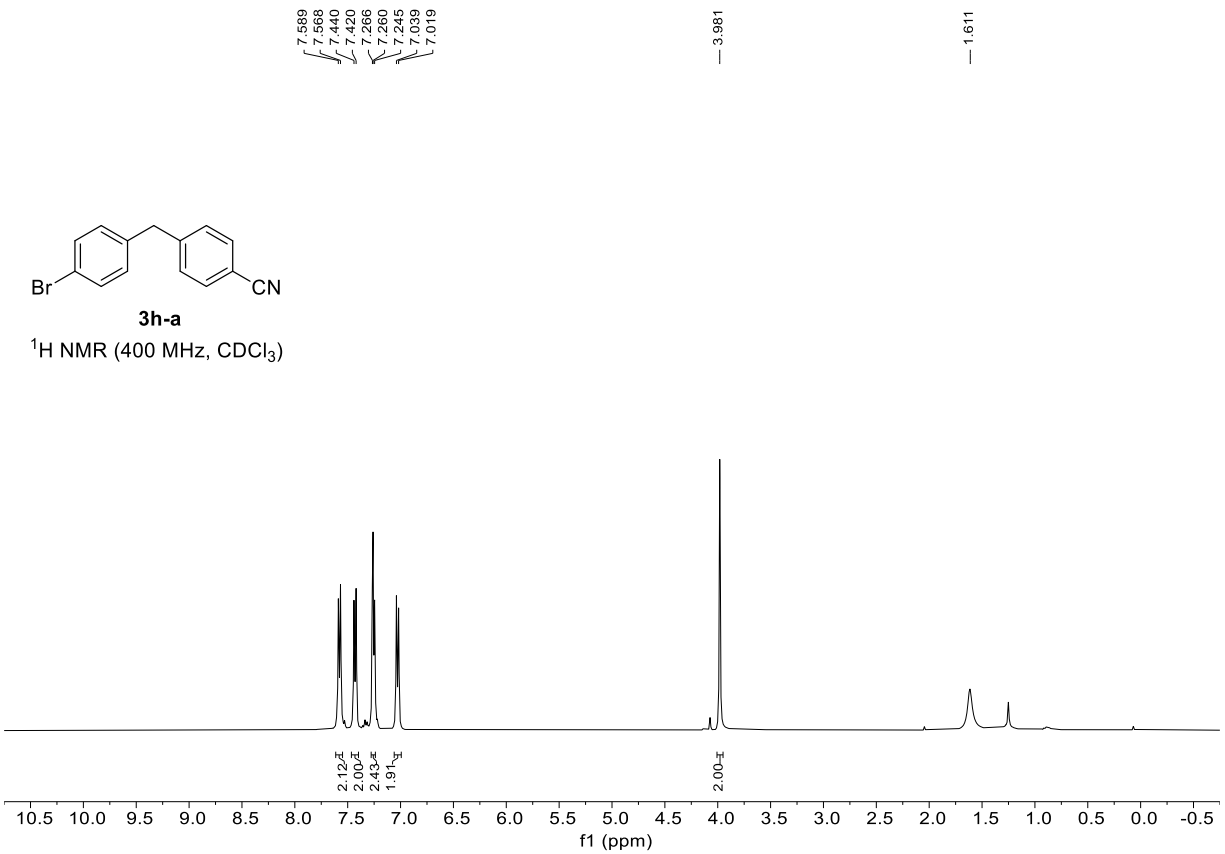
3g-a

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



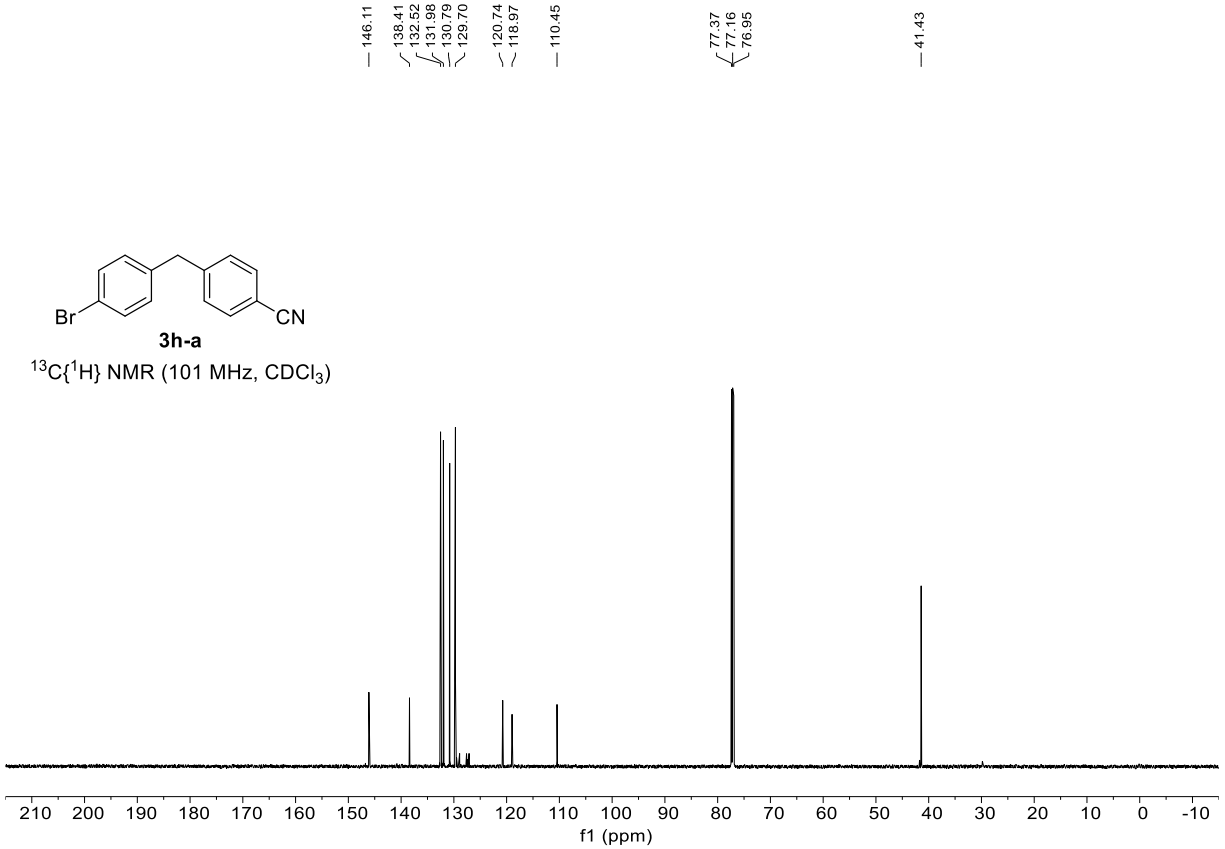
3g-a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



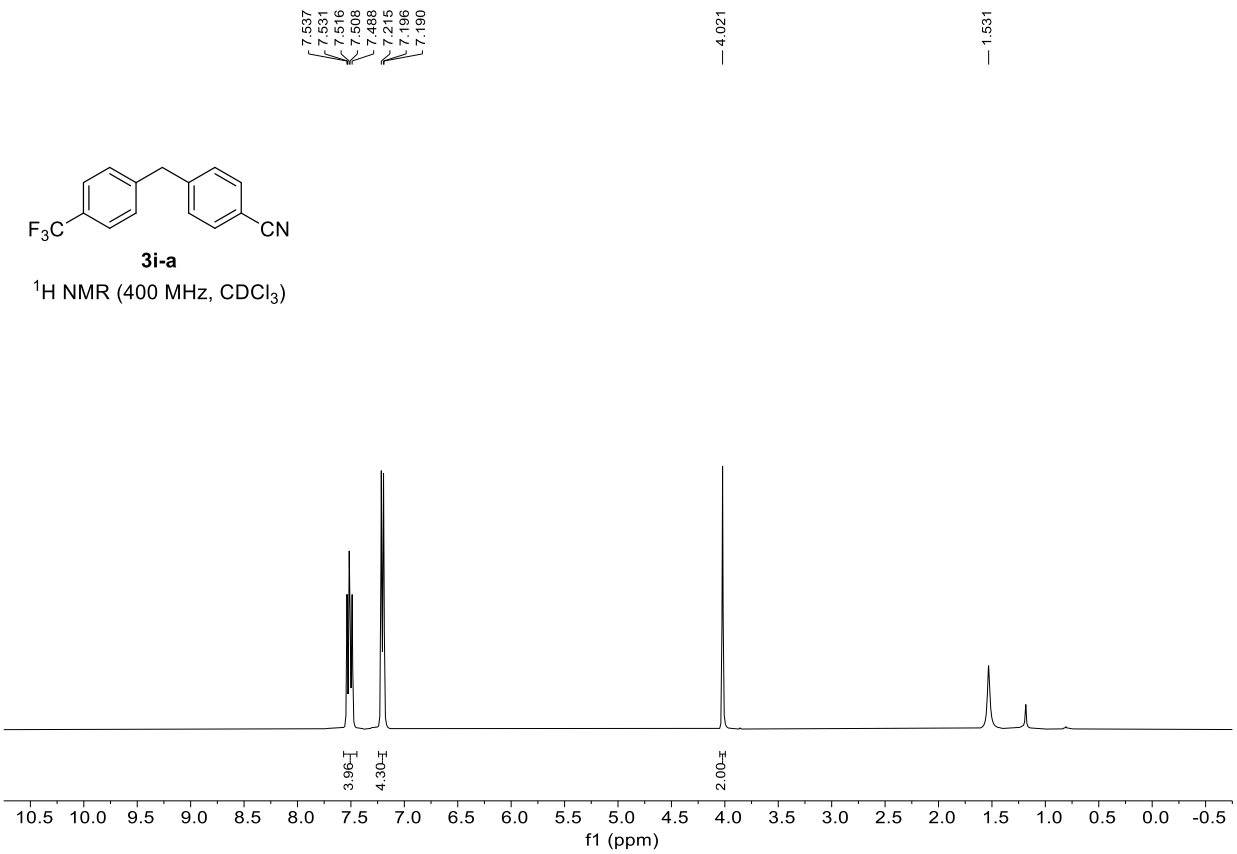
3h-a

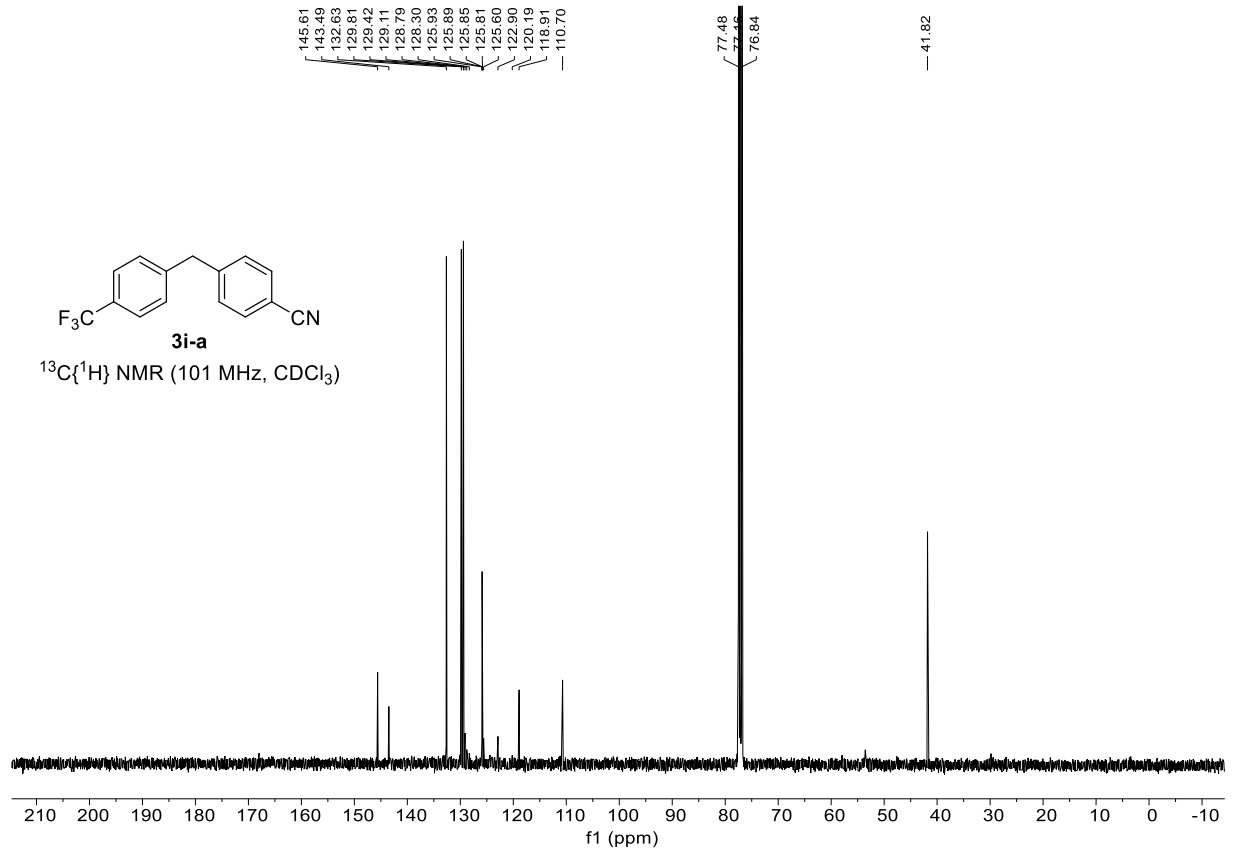
^{1}H NMR (400 MHz, $CDCl_3$)

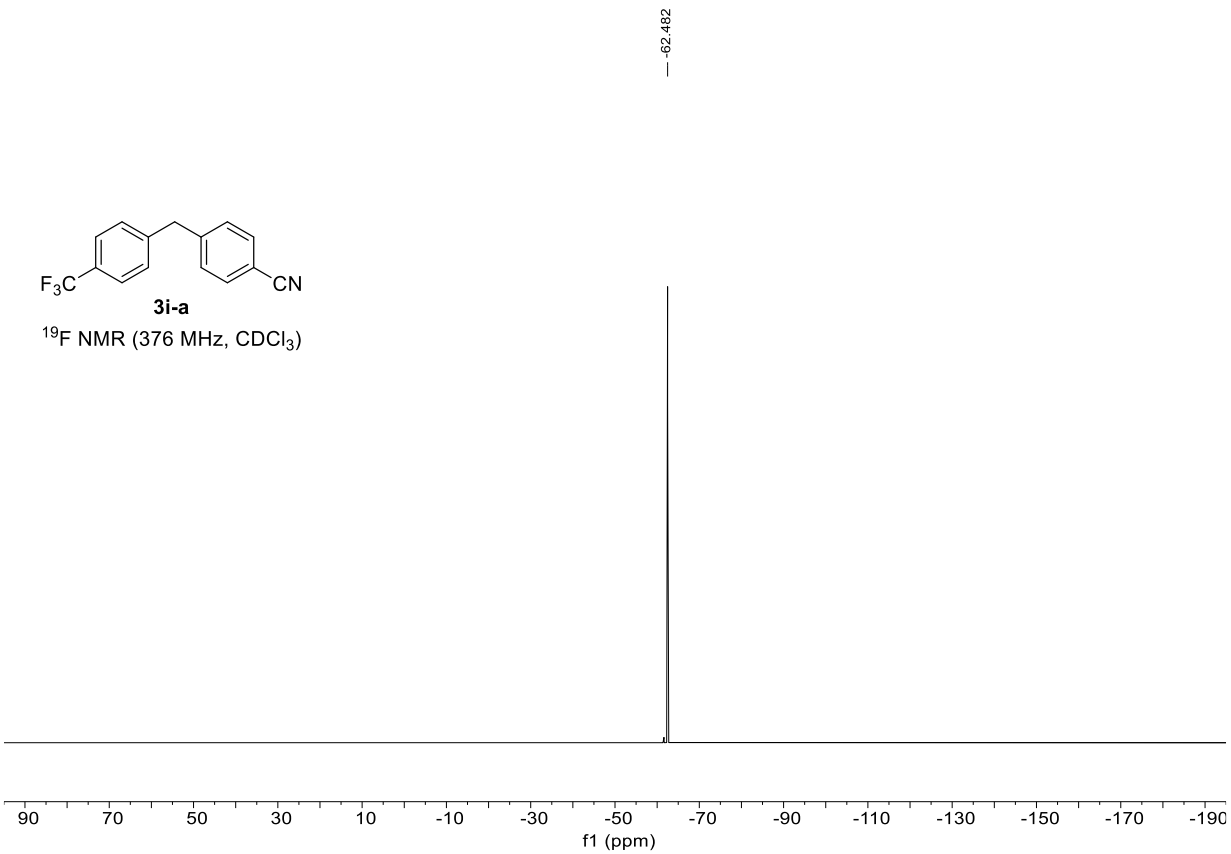


3h-a

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

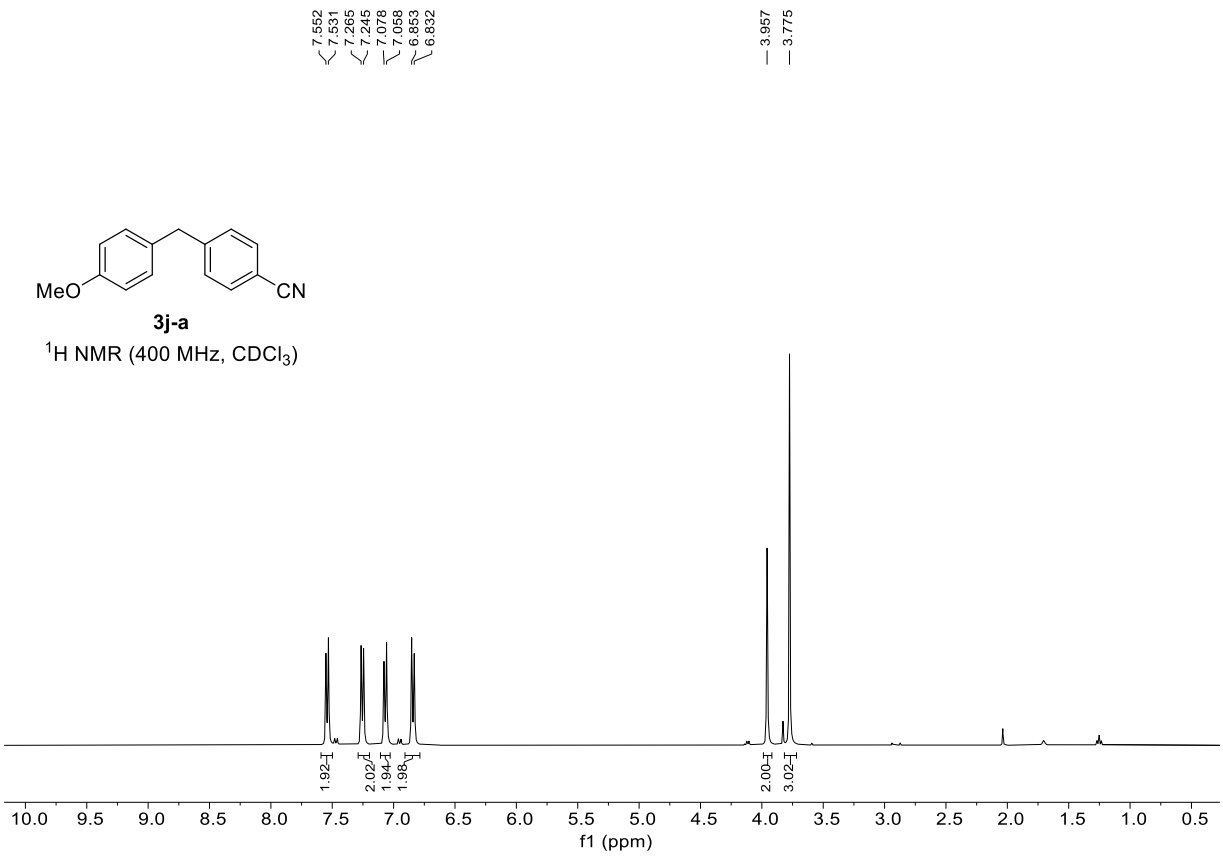

7.537
7.531
7.516
7.508
7.488
7.215
7.196
7.190
4.021
1.531
F3C
CN
3i-a
1H NMR (400 MHz, CDCl3)
3.96
4.30
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


145.61
143.49
132.63
129.81
129.42
129.11
128.79
128.30
125.93
125.89
125.85
125.81
125.60
122.90
120.19
118.91
110.70
77.48
77.16
76.84
41.82
F3C
CN
3i-a
13C{1H} NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



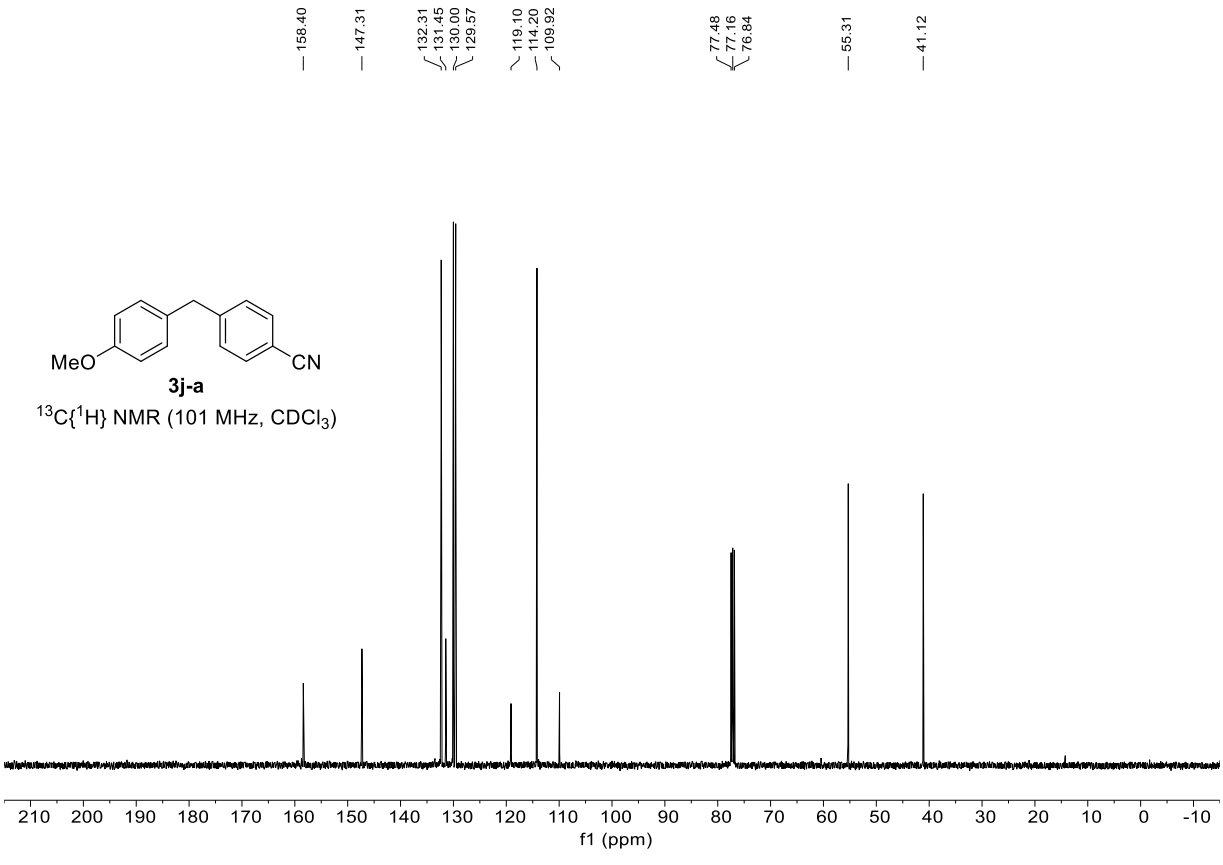
3i-a

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



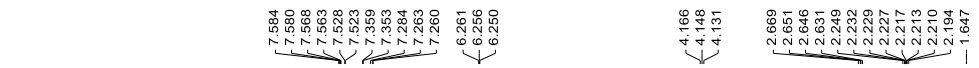
3j-a

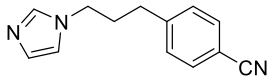
^{1}H NMR (400 MHz, $CDCl_3$)



3j-a

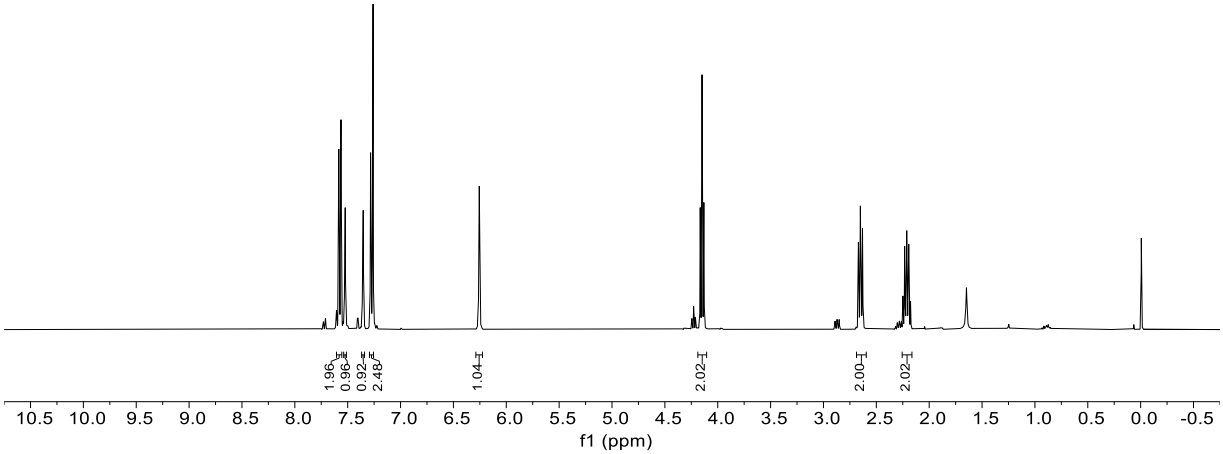
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

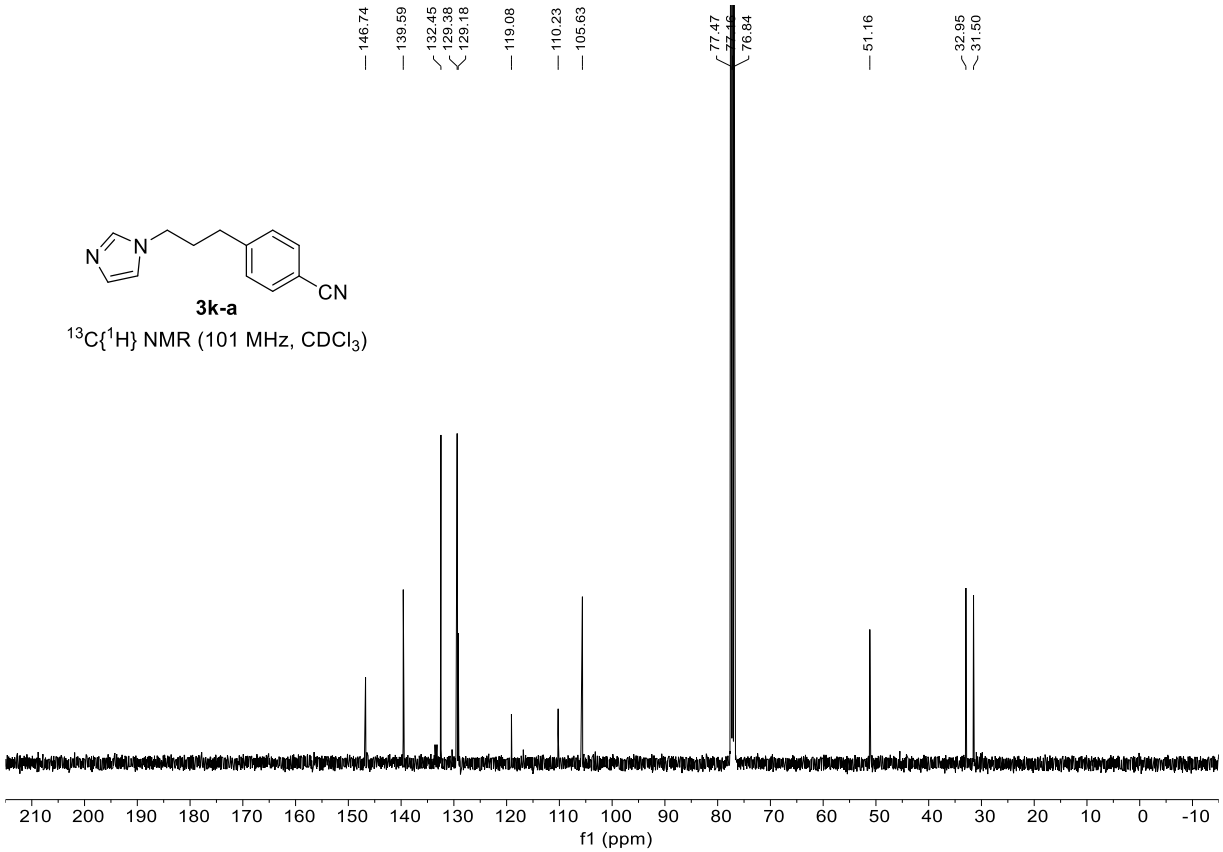




3k-a

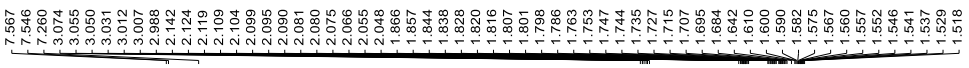
^{1}H NMR (400 MHz, $CDCl_3$)

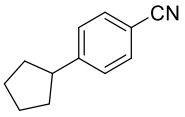




3k-a

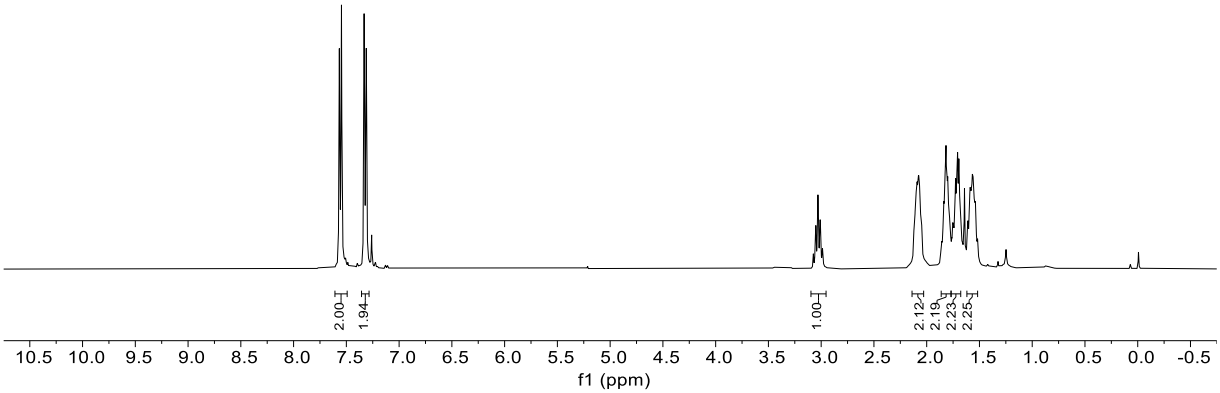
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

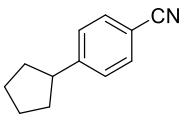




3l-a

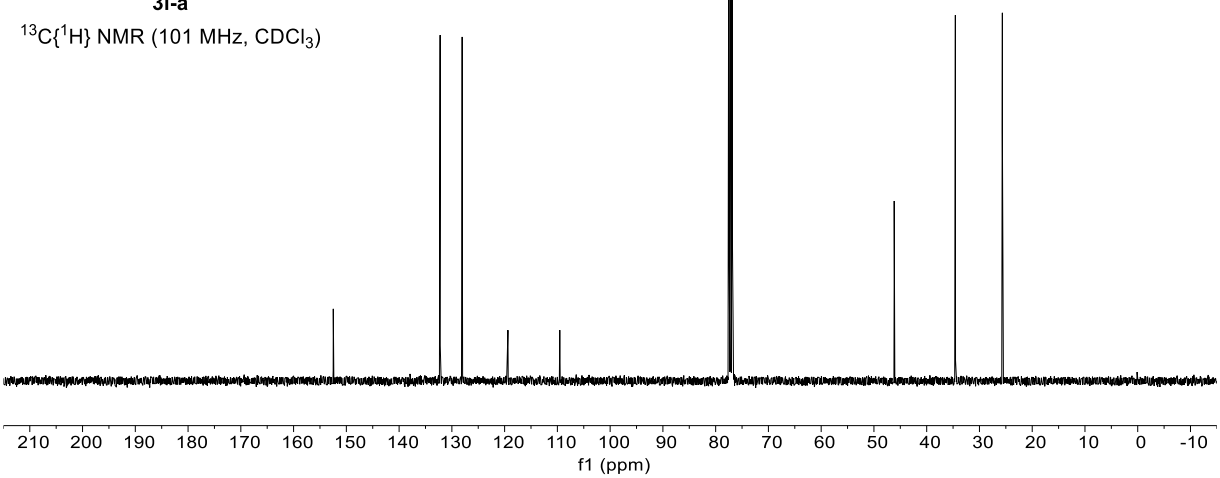
^{1}H NMR (400 MHz, $CDCl_3$)

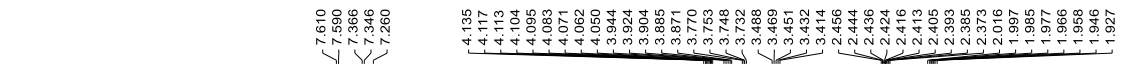


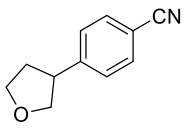


3l-a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

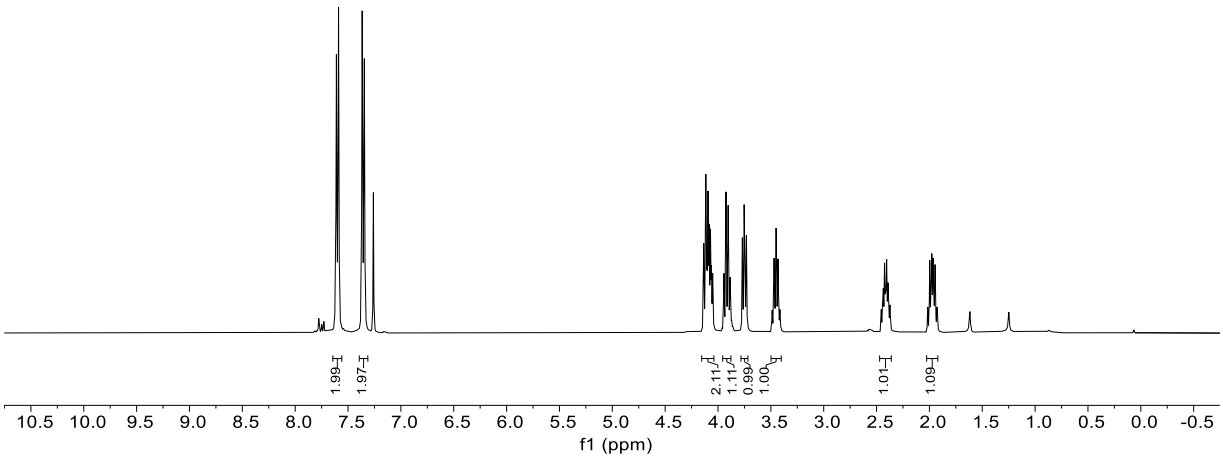


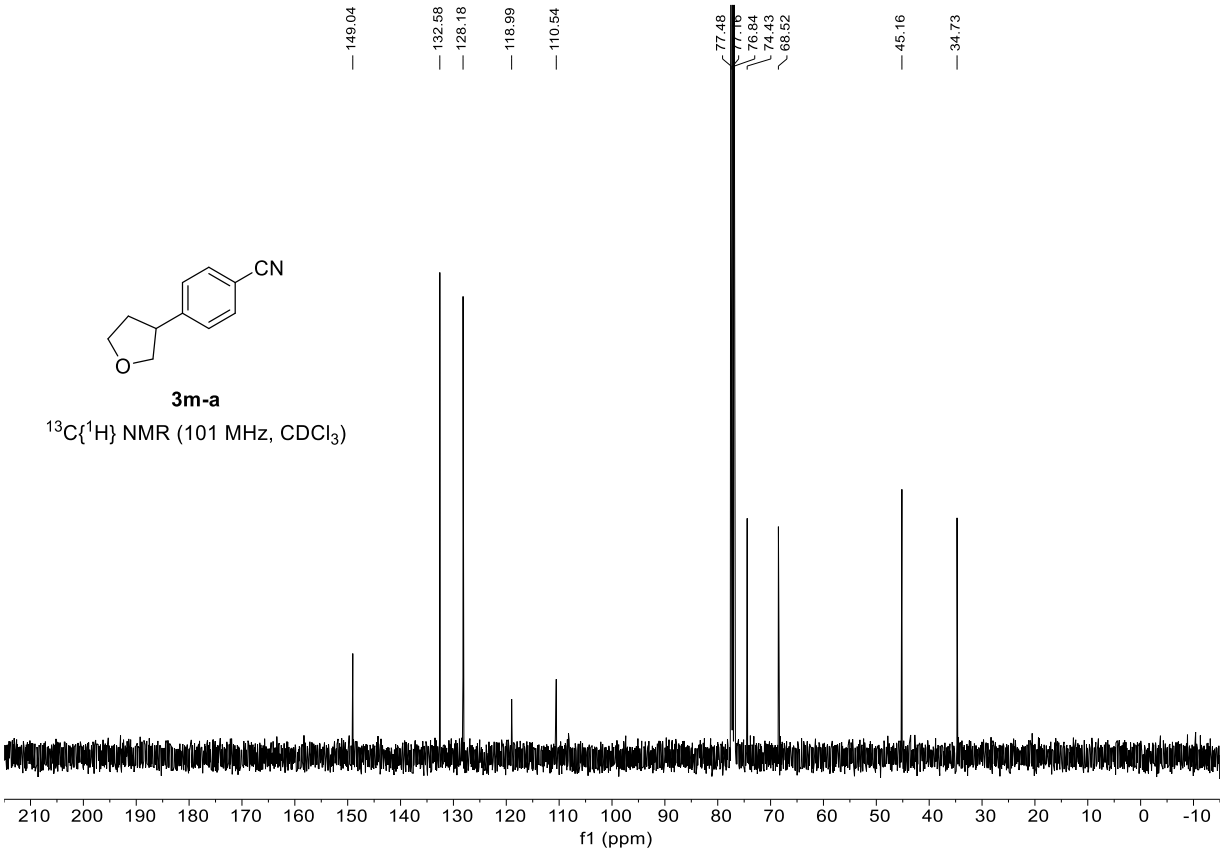




3m-a

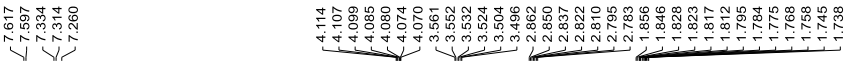
^{1}H NMR (400 MHz, $CDCl_3$)

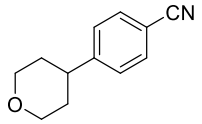




3m-a

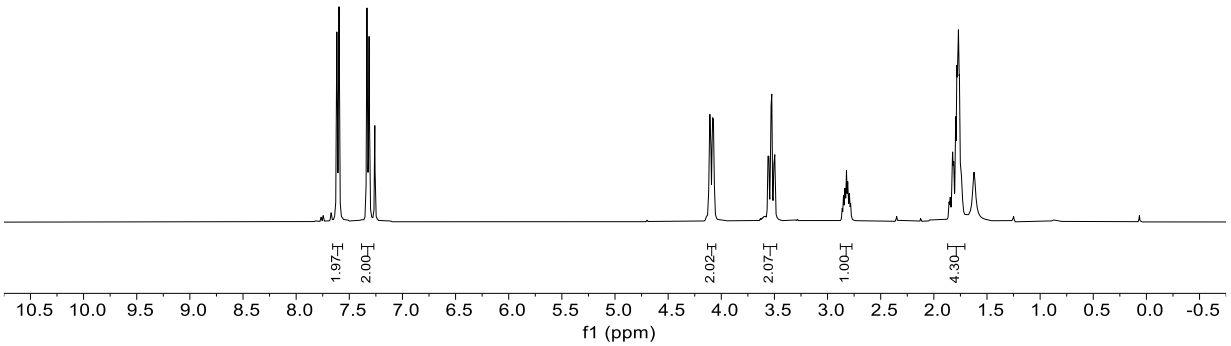
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

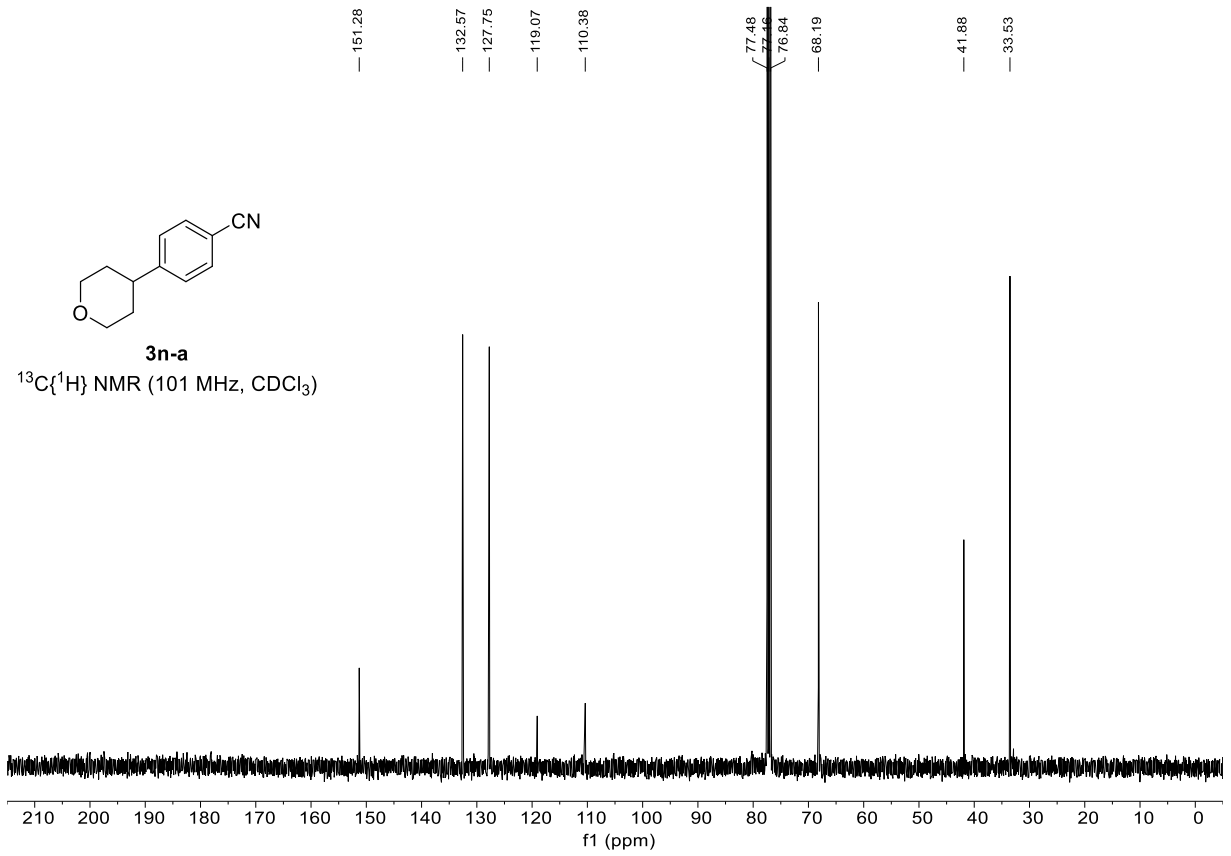




3n-a

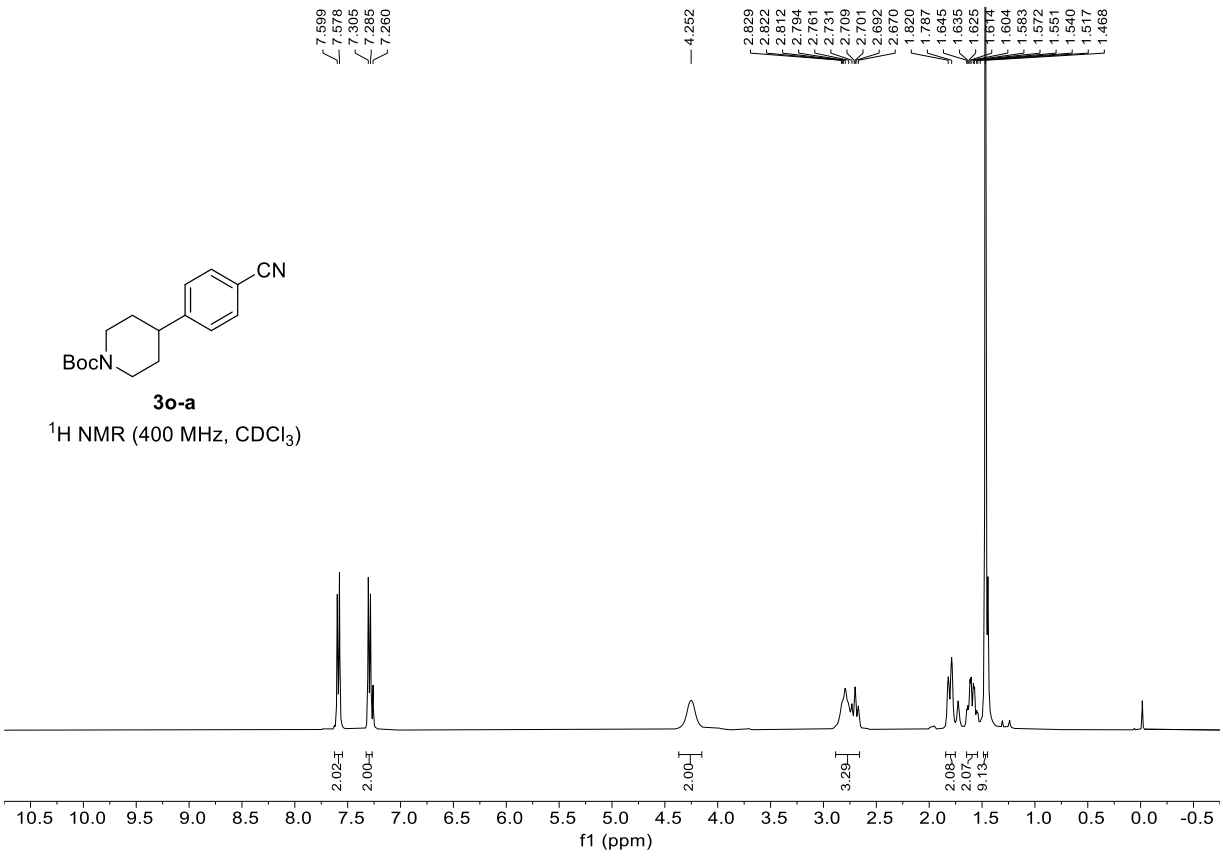
^{1}H NMR (400 MHz, $CDCl_3$)





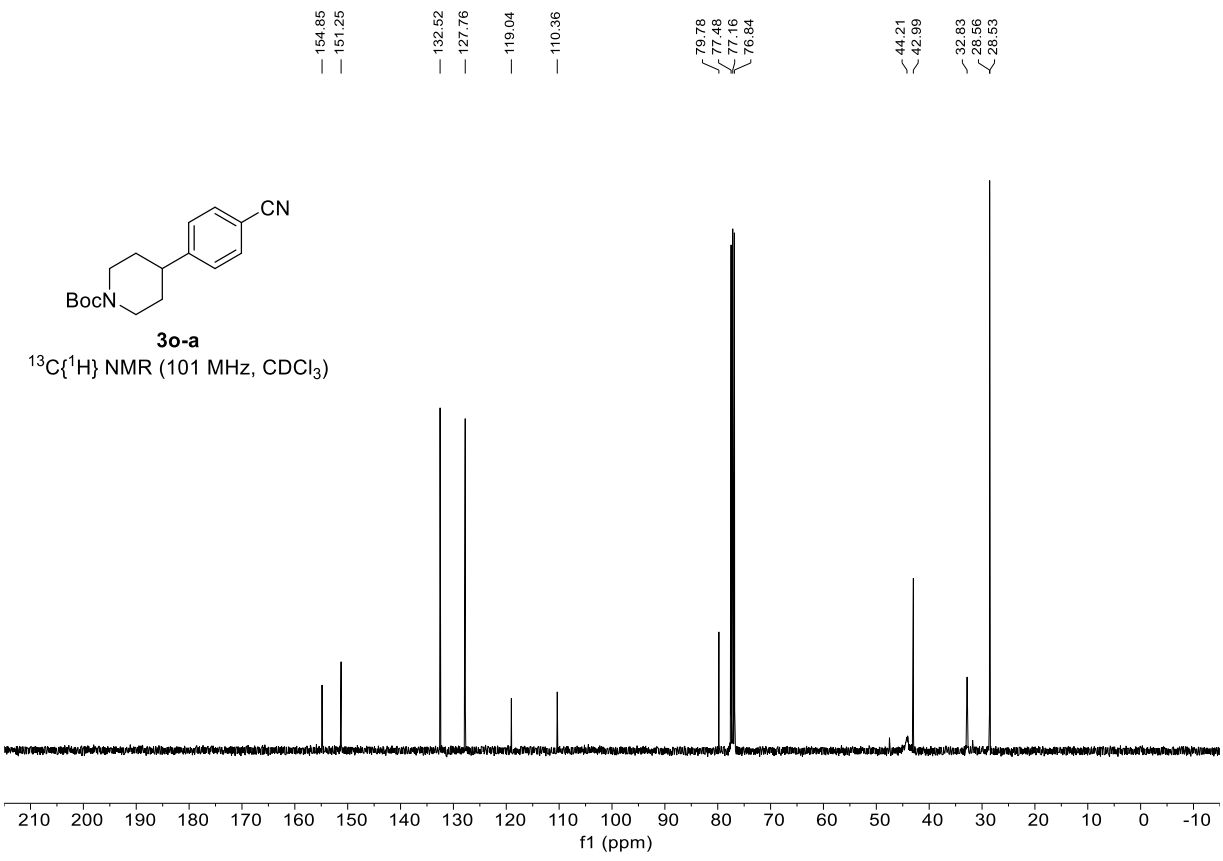
3n-a

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



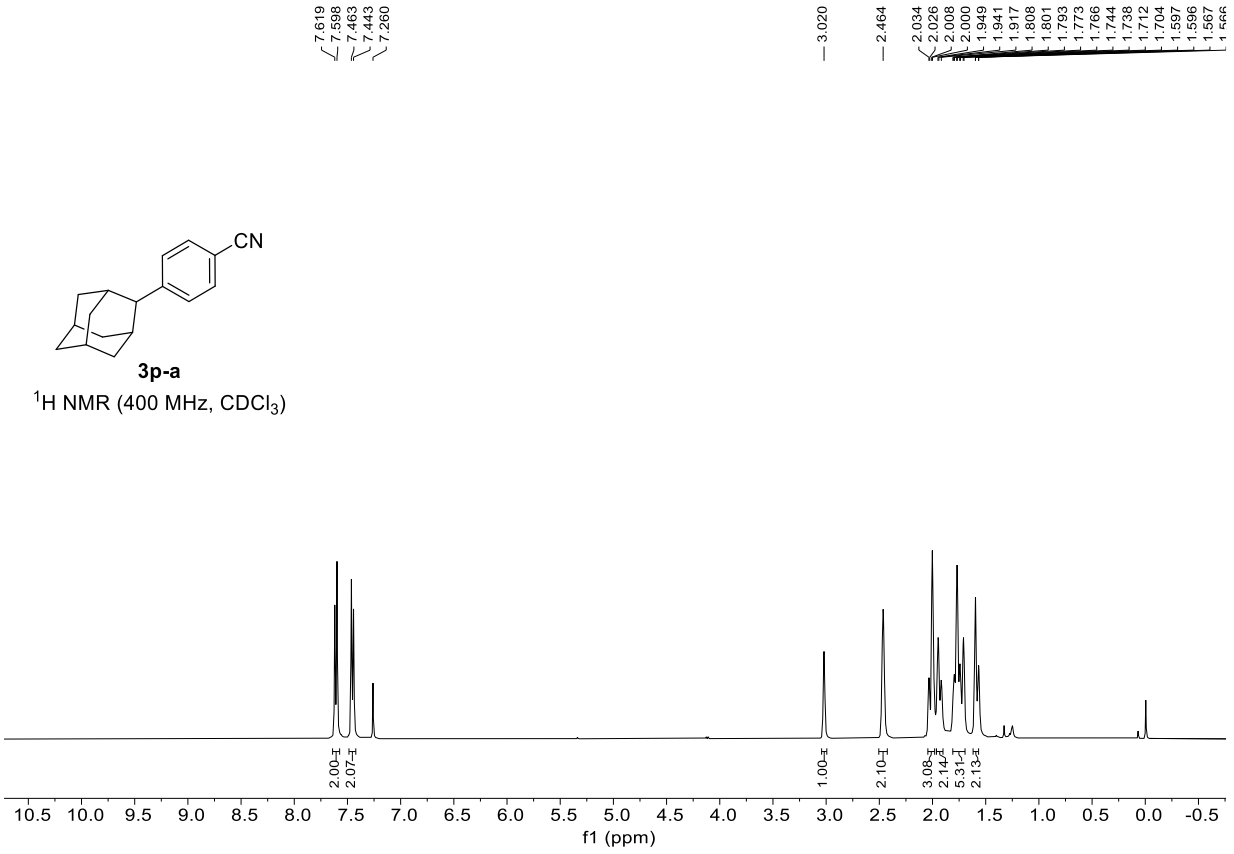
3o-a

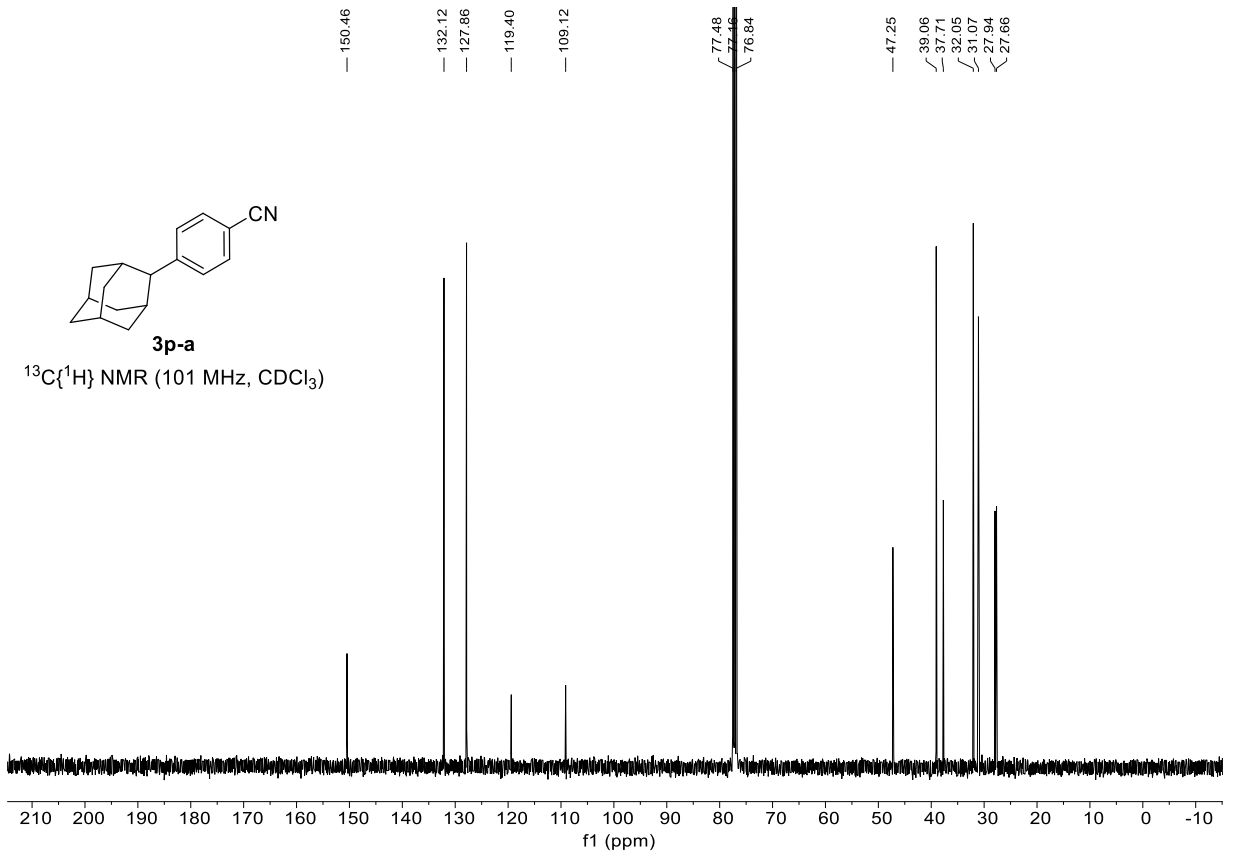
^{1}H NMR (400 MHz, $CDCl_3$)

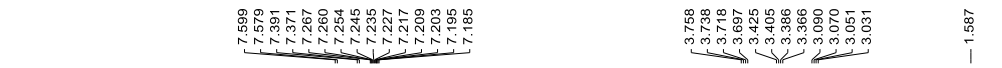


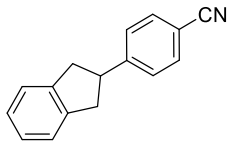
3o-a

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)


7.619
7.598
7.463
7.443
7.260
3.020
2.464
2.034
2.026
2.008
2.000
1.949
1.941
1.917
1.808
1.801
1.793
1.773
1.766
1.744
1.738
1.712
1.704
1.597
1.596
1.567
CN
3p-a
1H NMR (400 MHz, CDCl3)
2.00
2.07
1.00
2.10
3.08
2.14
5.31
2.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

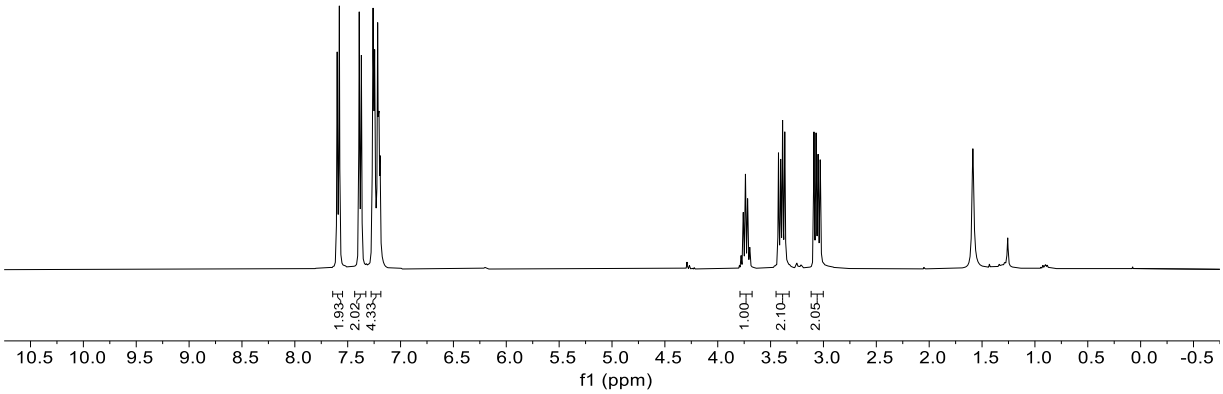

150.46
132.12
127.86
119.40
109.12
77.48
77.16
76.84
47.25
39.06
37.71
32.05
31.07
27.94
27.66
CN
3p-a
13C{1H} NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

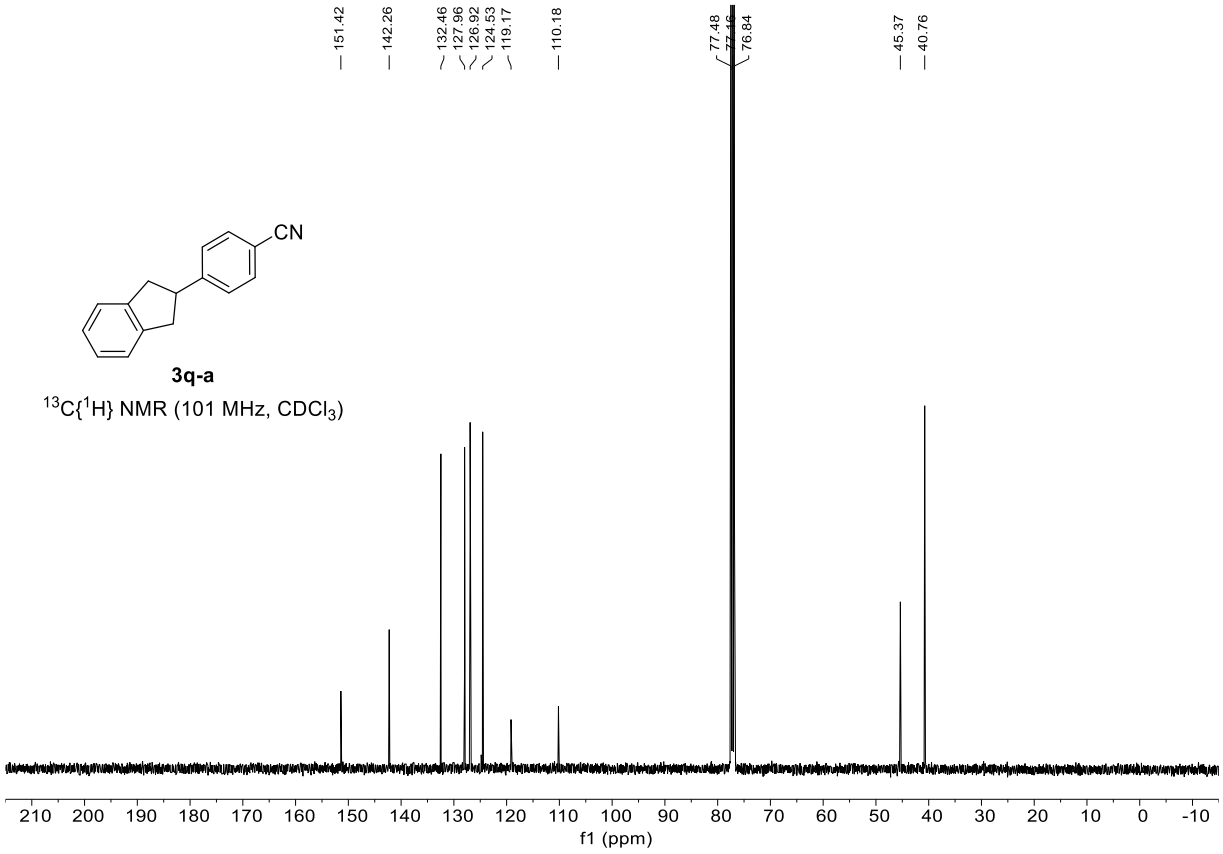




3q-a

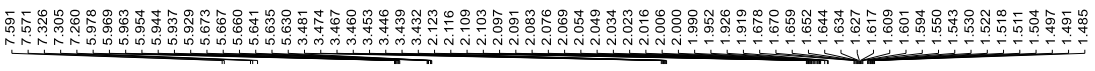
^{1}H NMR (400 MHz, $CDCl_3$)

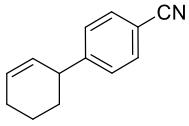




3q-a

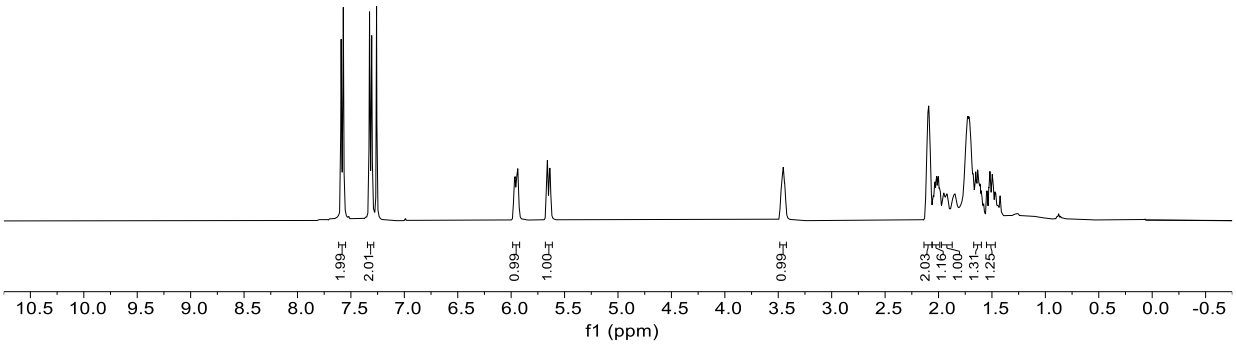
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

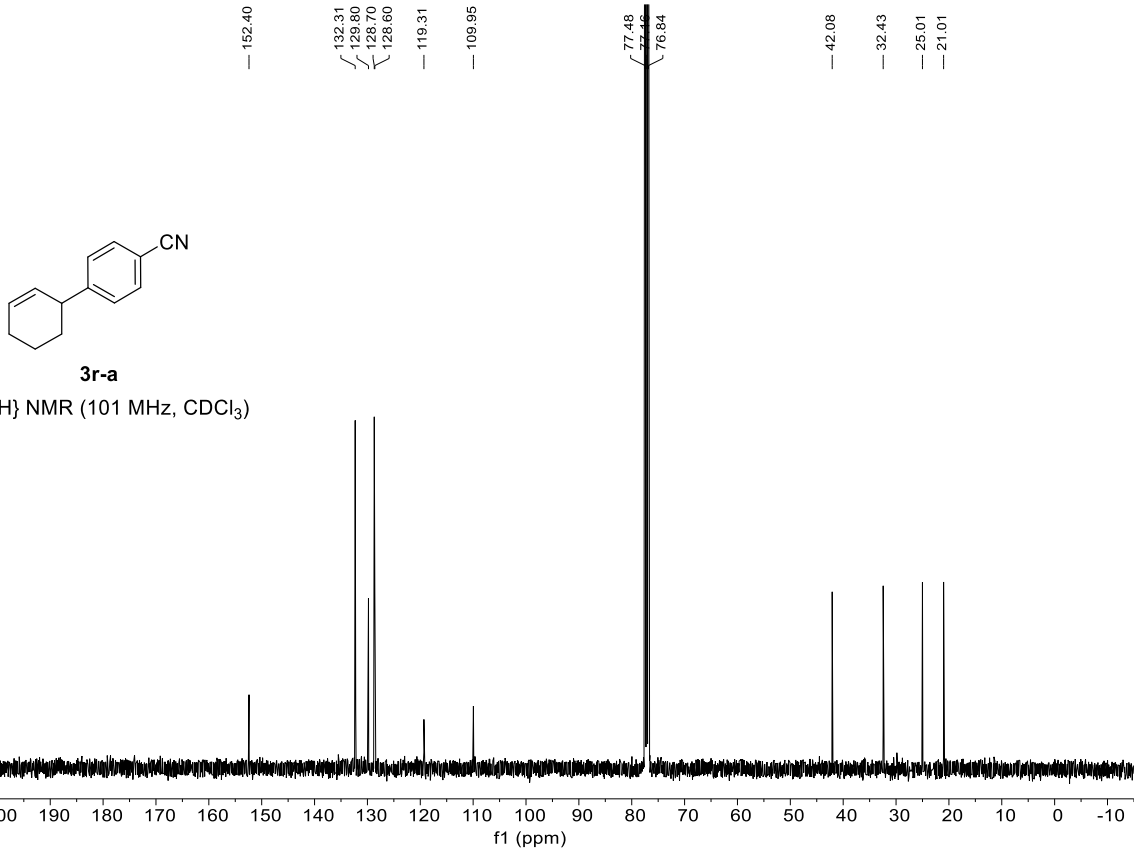




3r-a

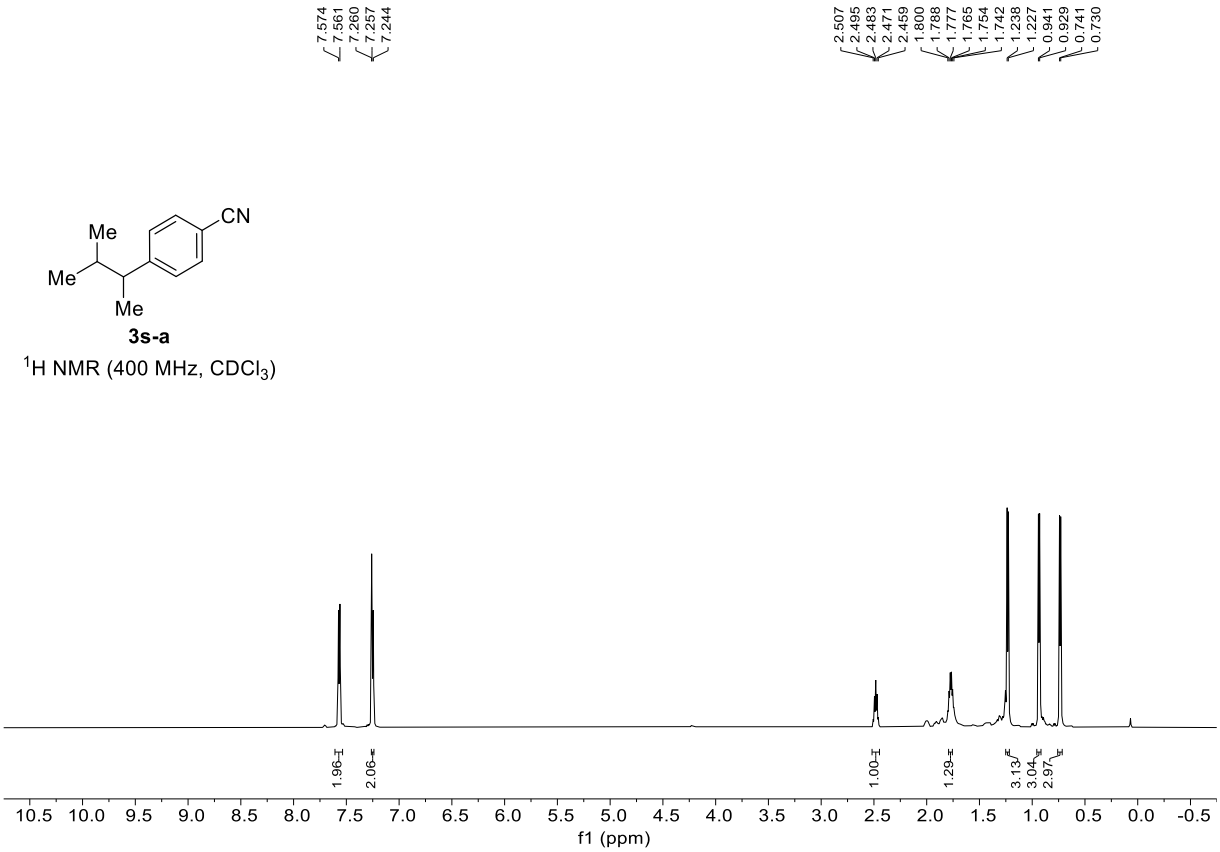
^{1}H NMR (400 MHz, $CDCl_3$)





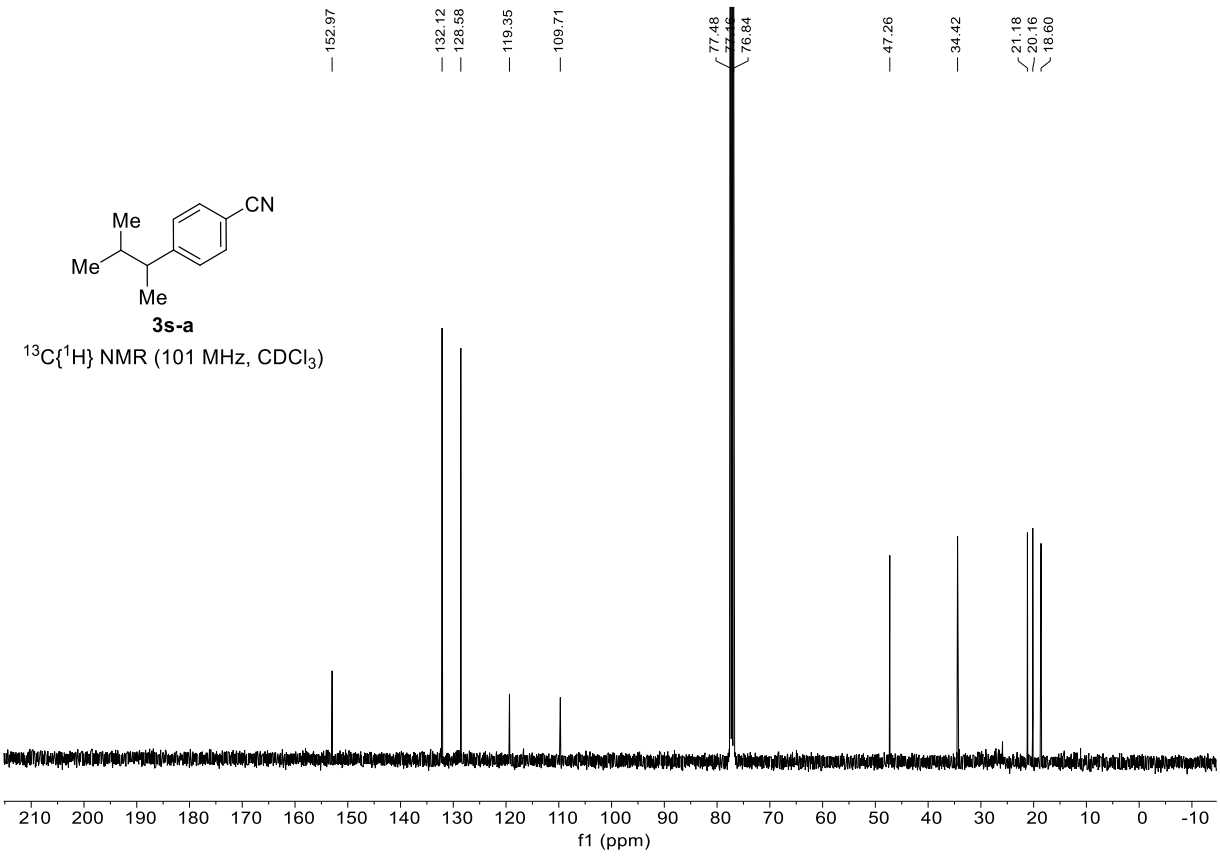
3r-a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



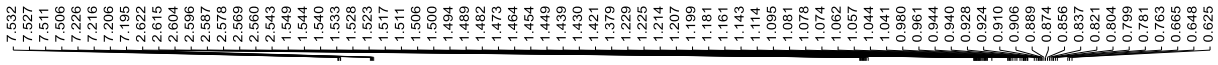
3s-a

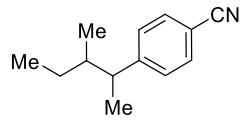
^{1}H NMR (400 MHz, $CDCl_3$)



3s-a

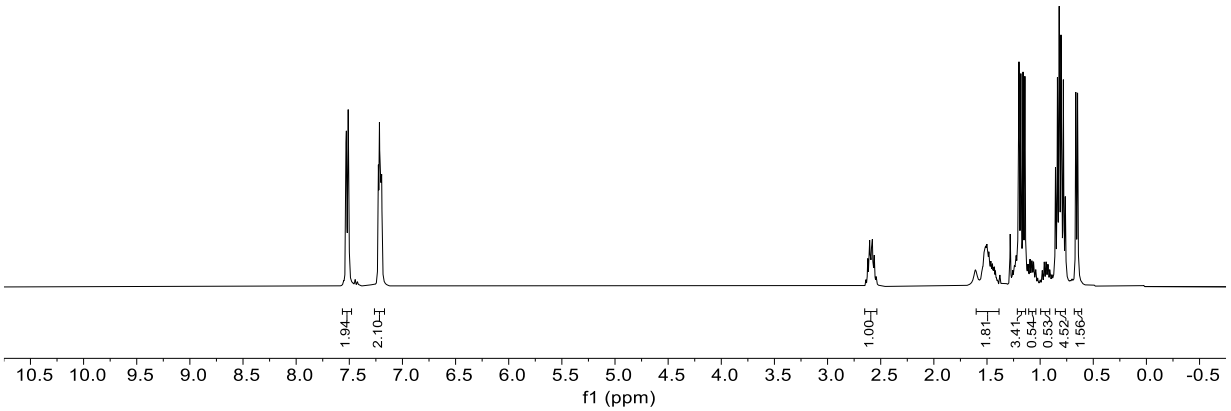
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

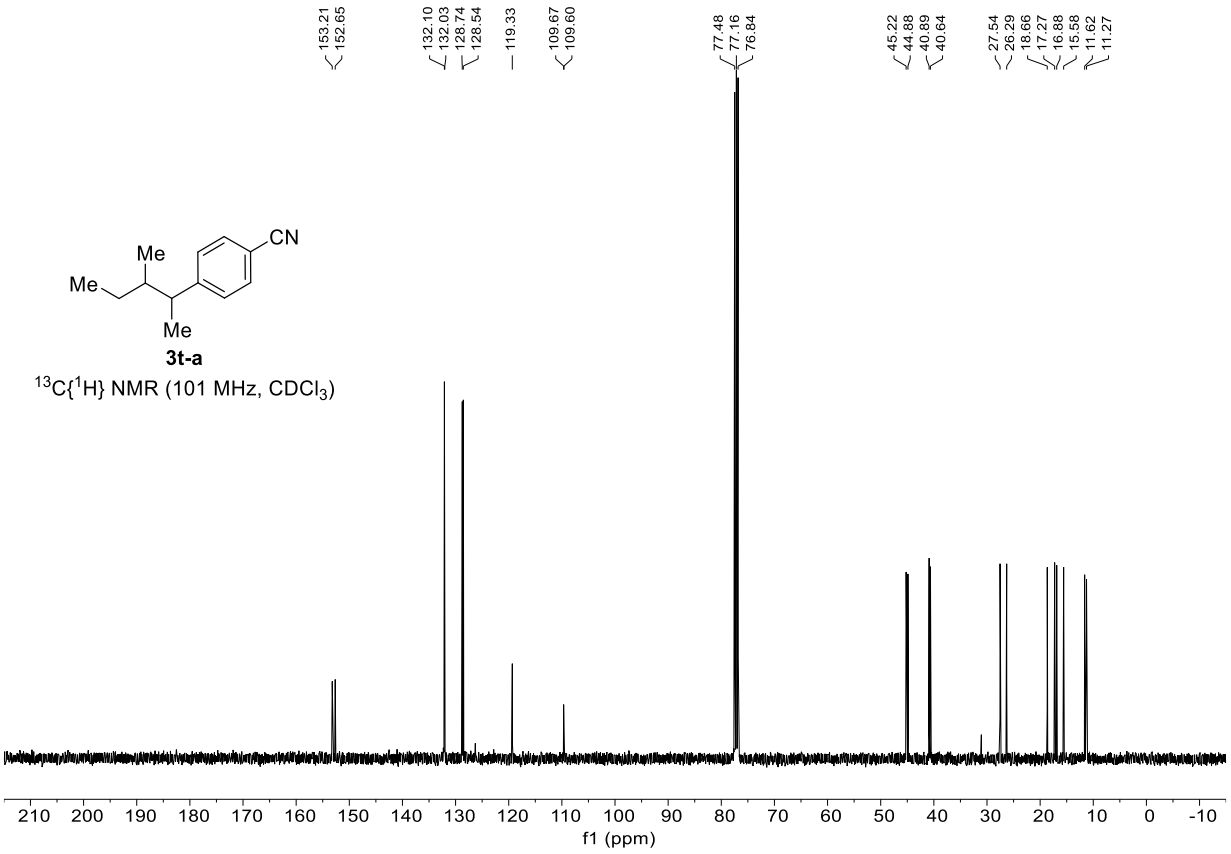




3t-a

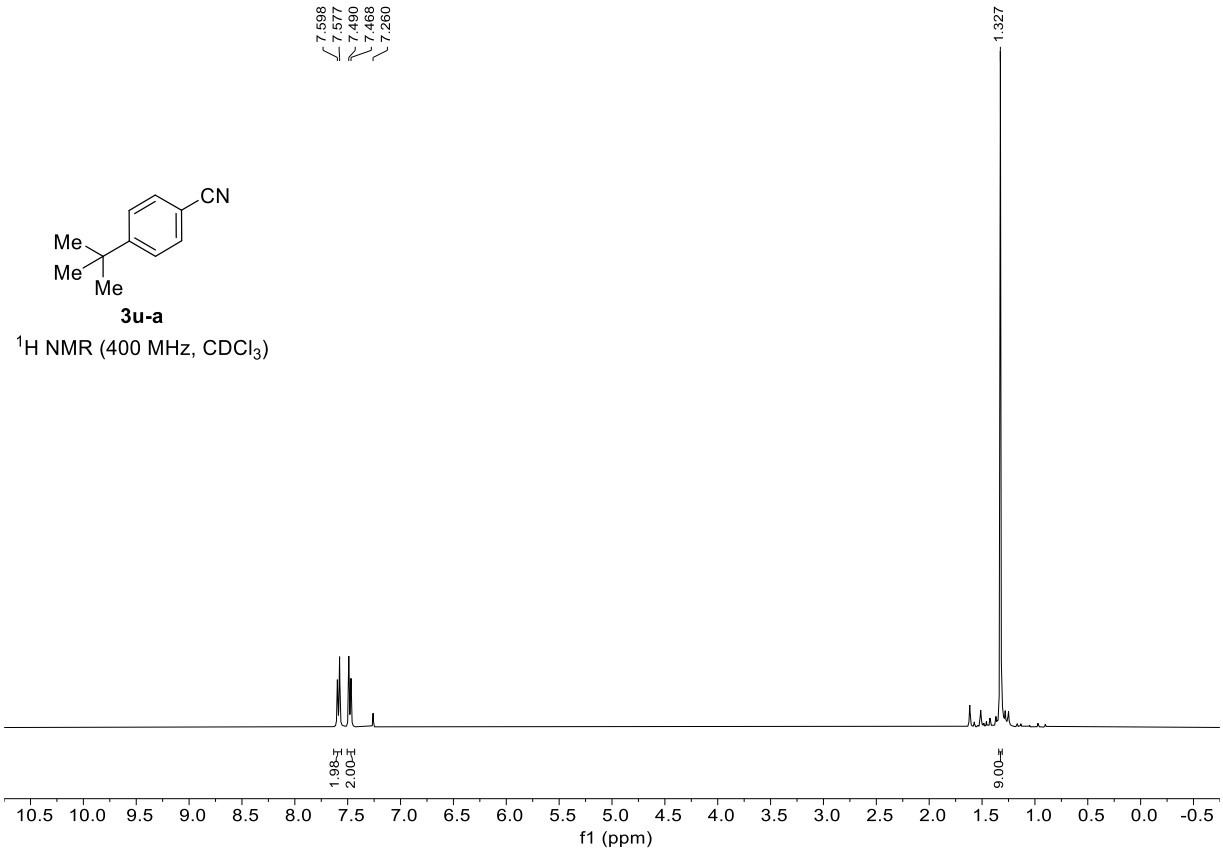
^{1}H NMR (400 MHz, $CDCl_3$)





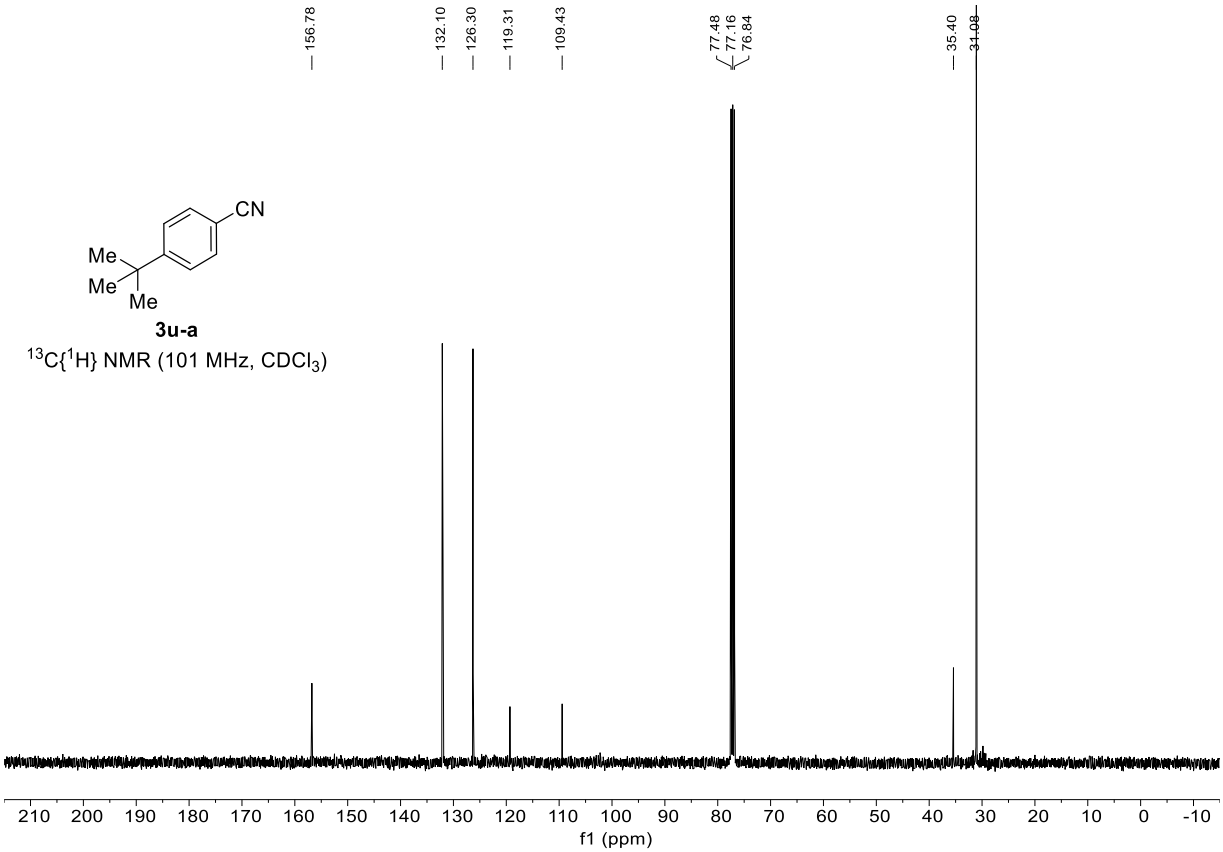
3t-a

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



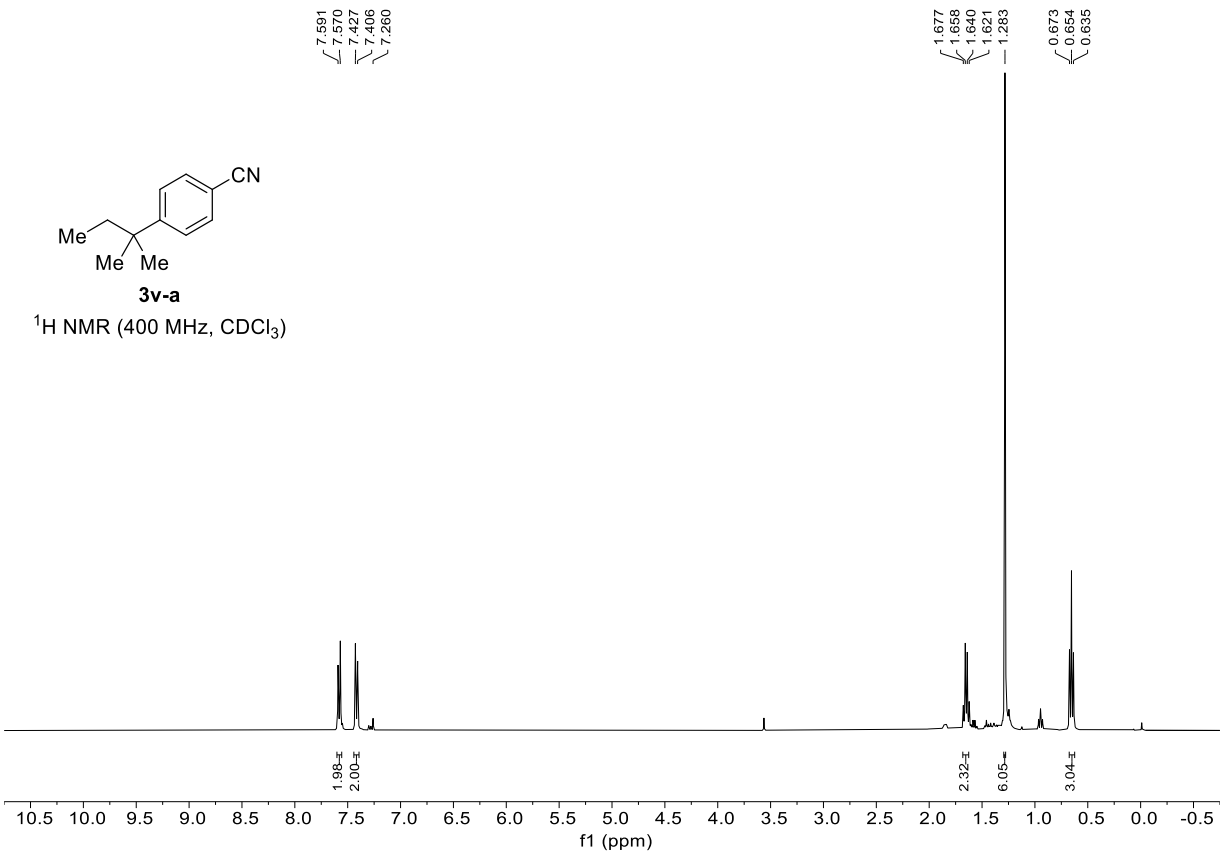
3u-a

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



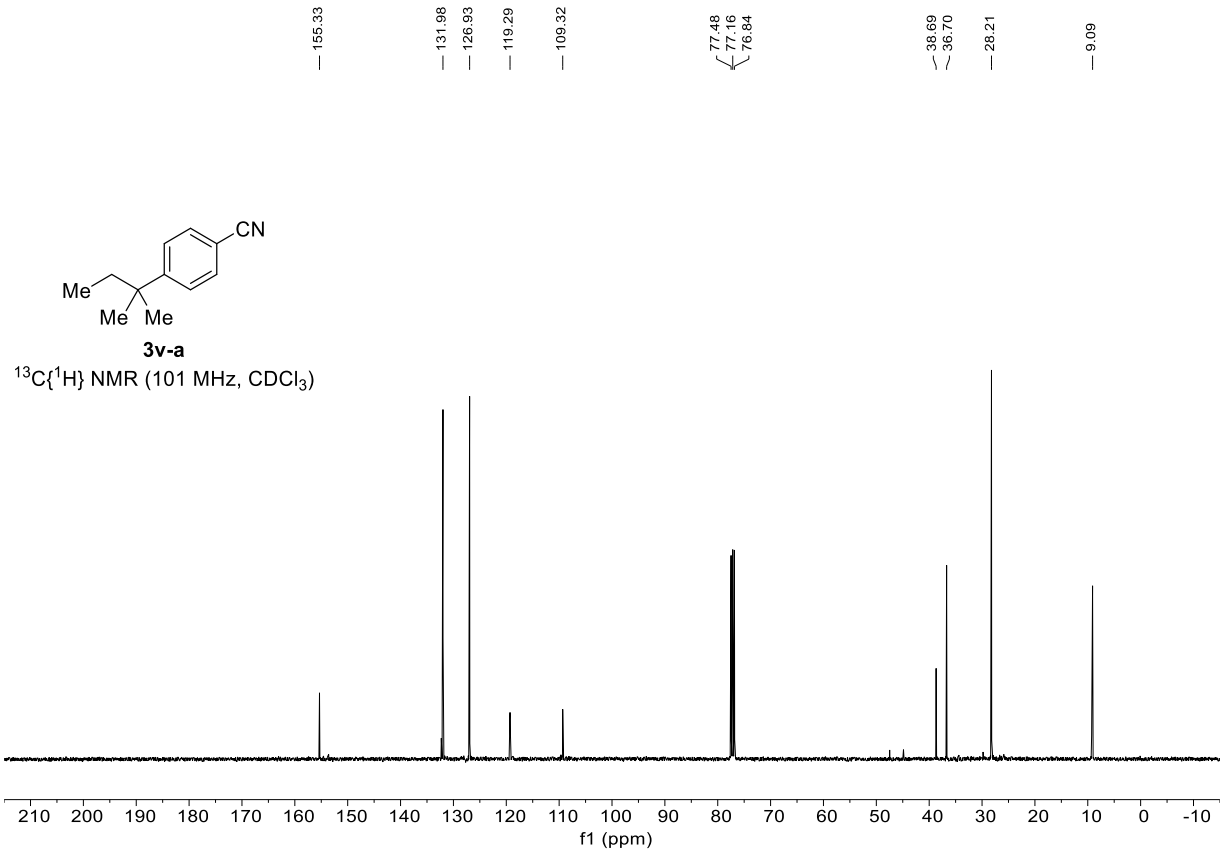
3u-a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



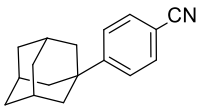
3v-a

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



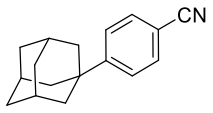
3v-a

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



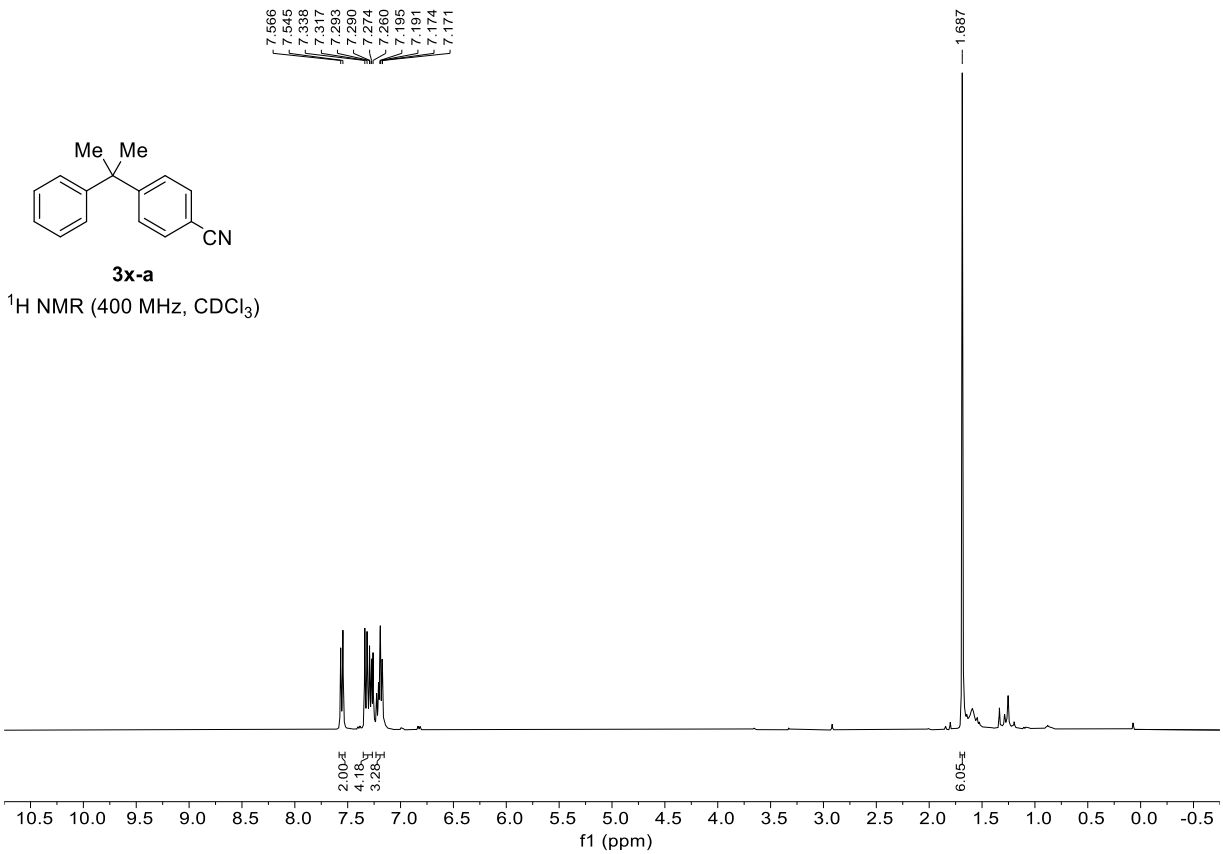
3w-a

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



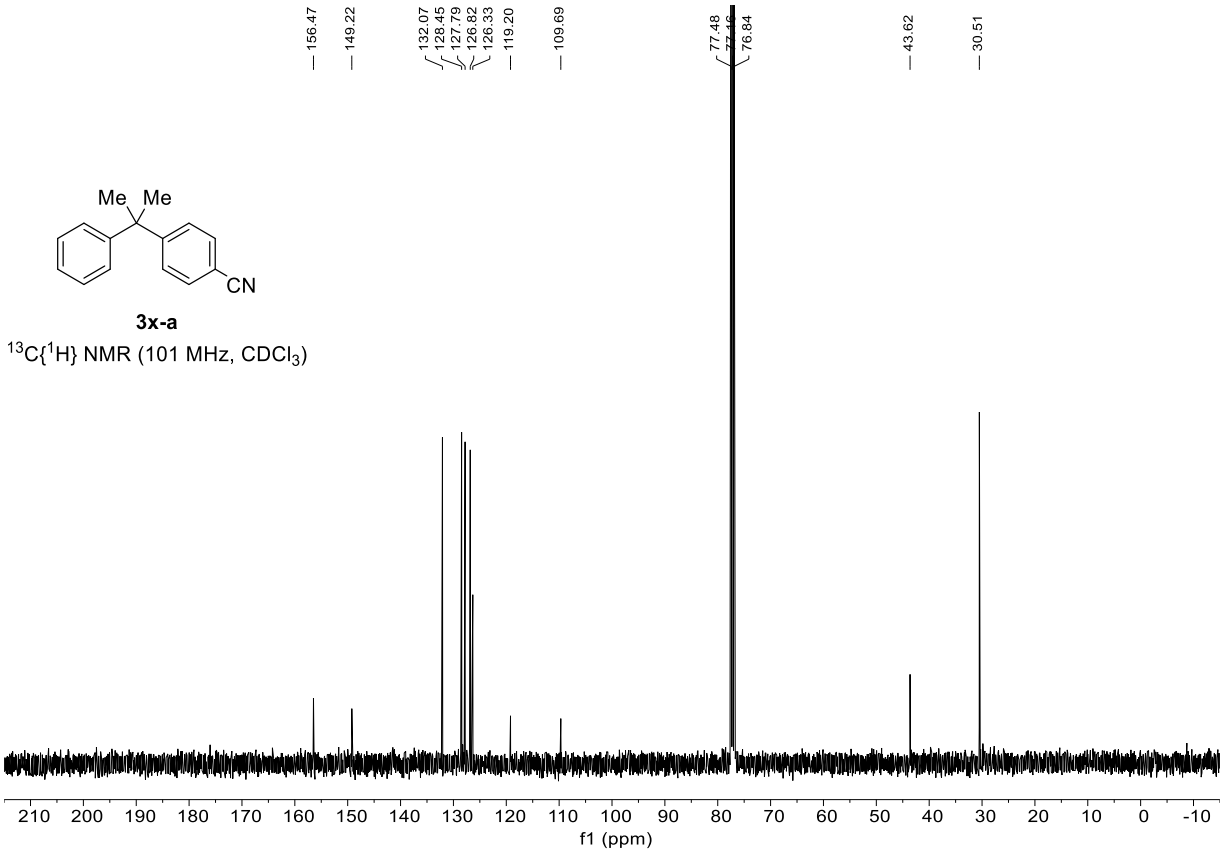
3w-a

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



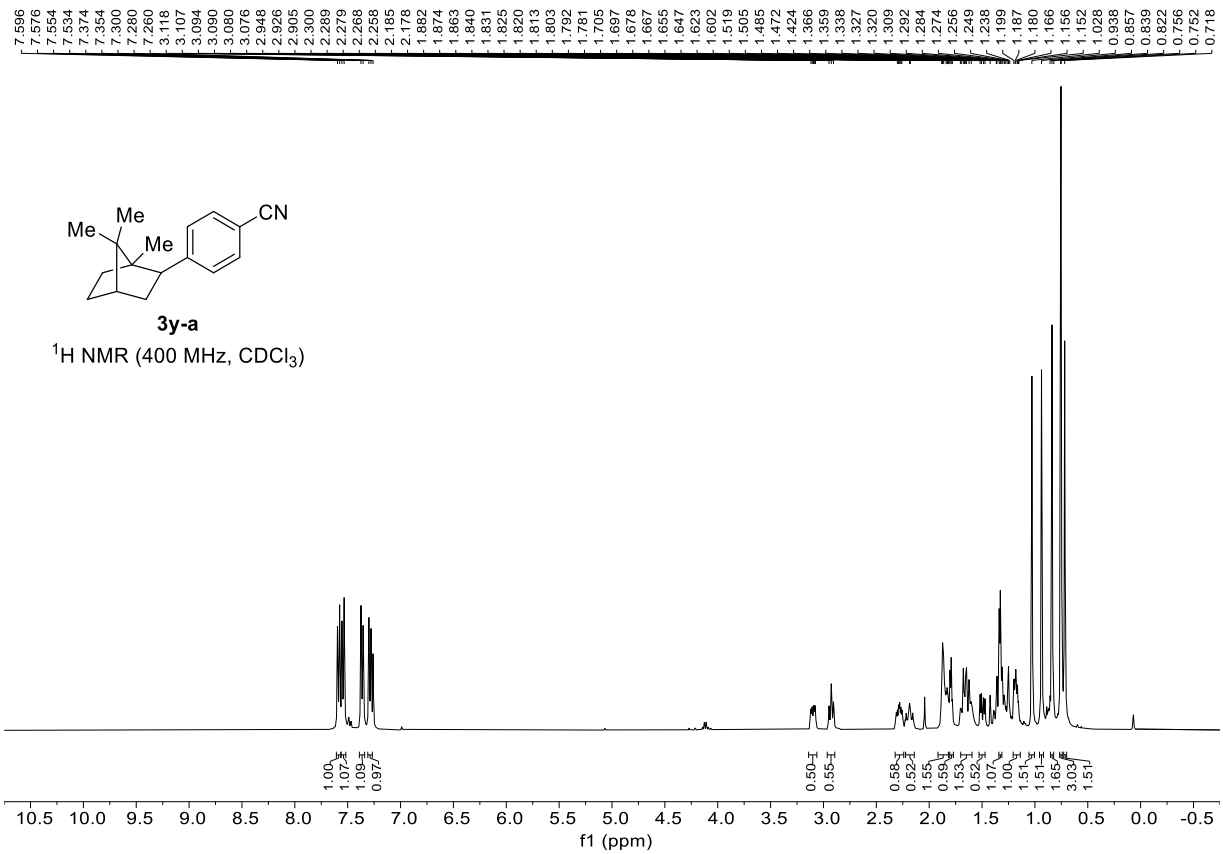
3x-a

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



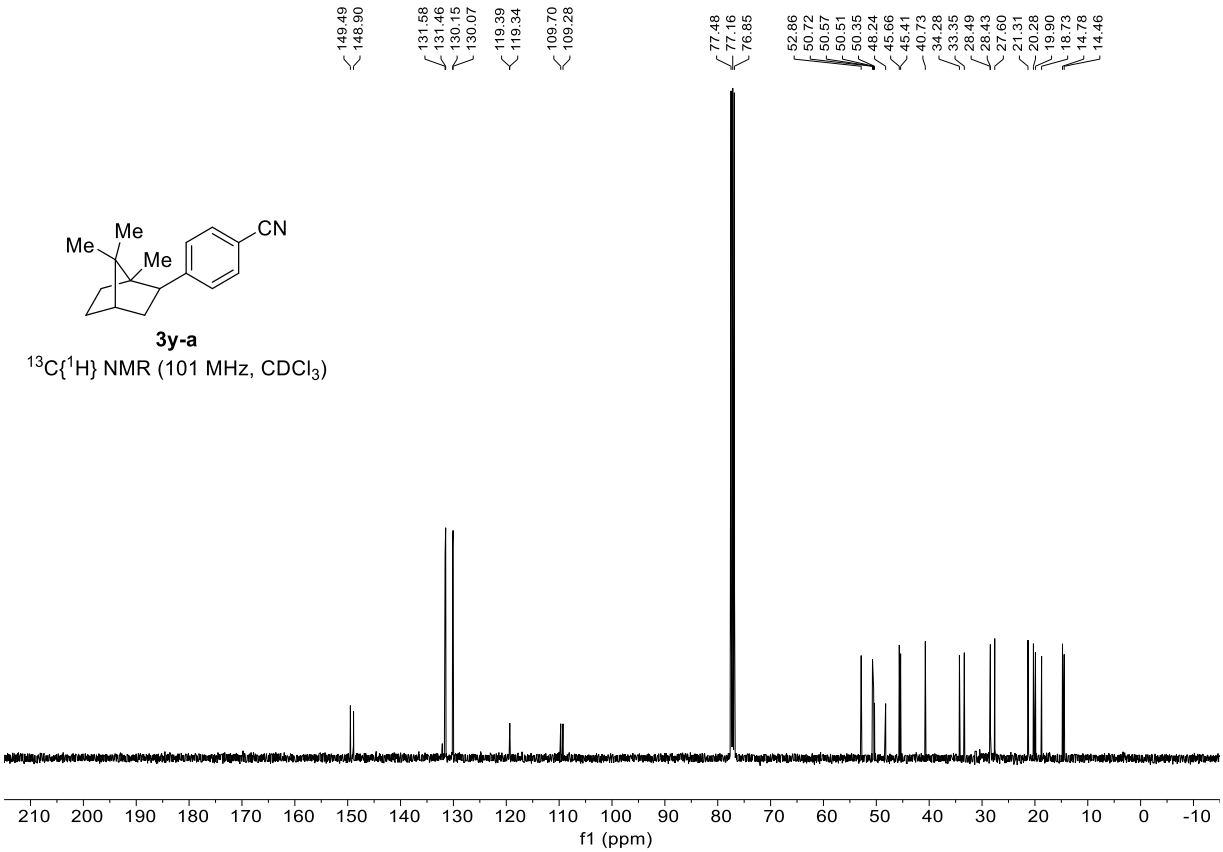
3x-a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



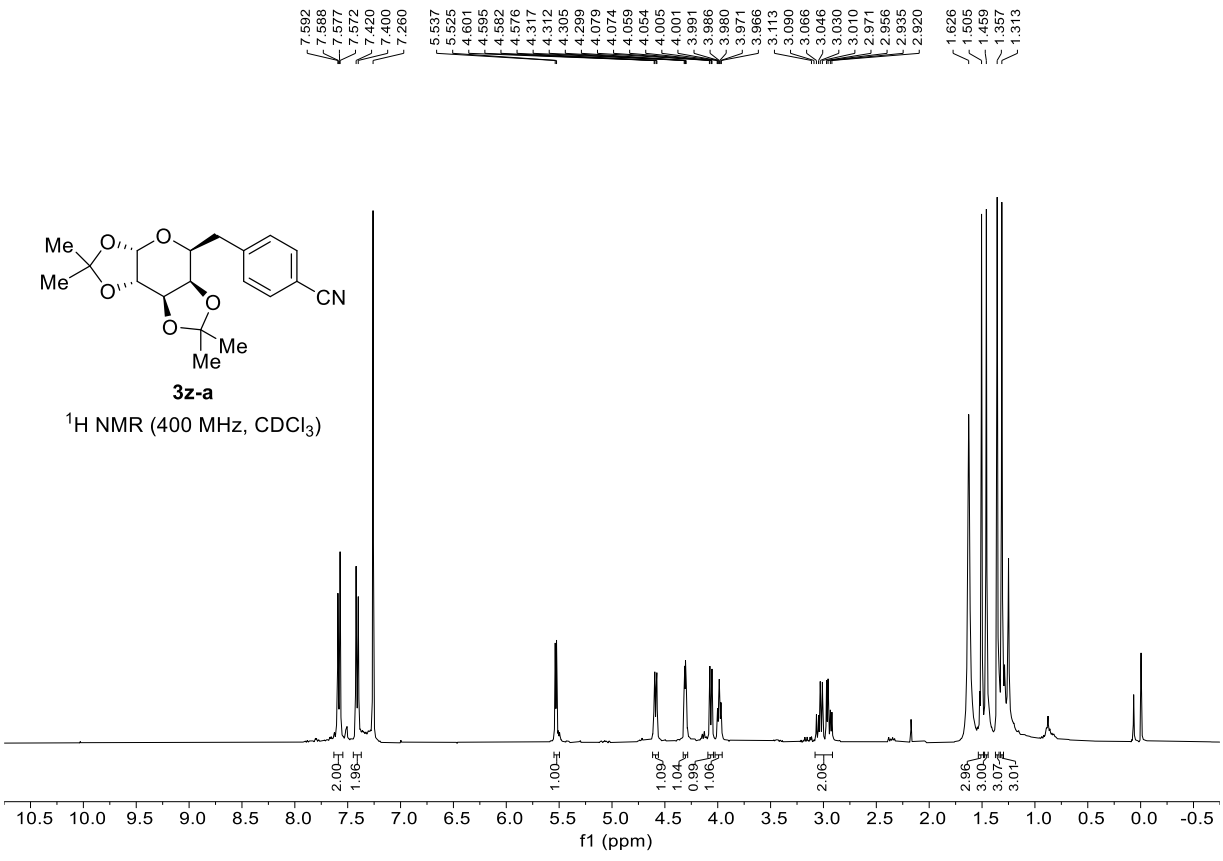
3y-a

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



3y-a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)


7.592
7.588
7.577
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7.420
7.400
7.260
5.537
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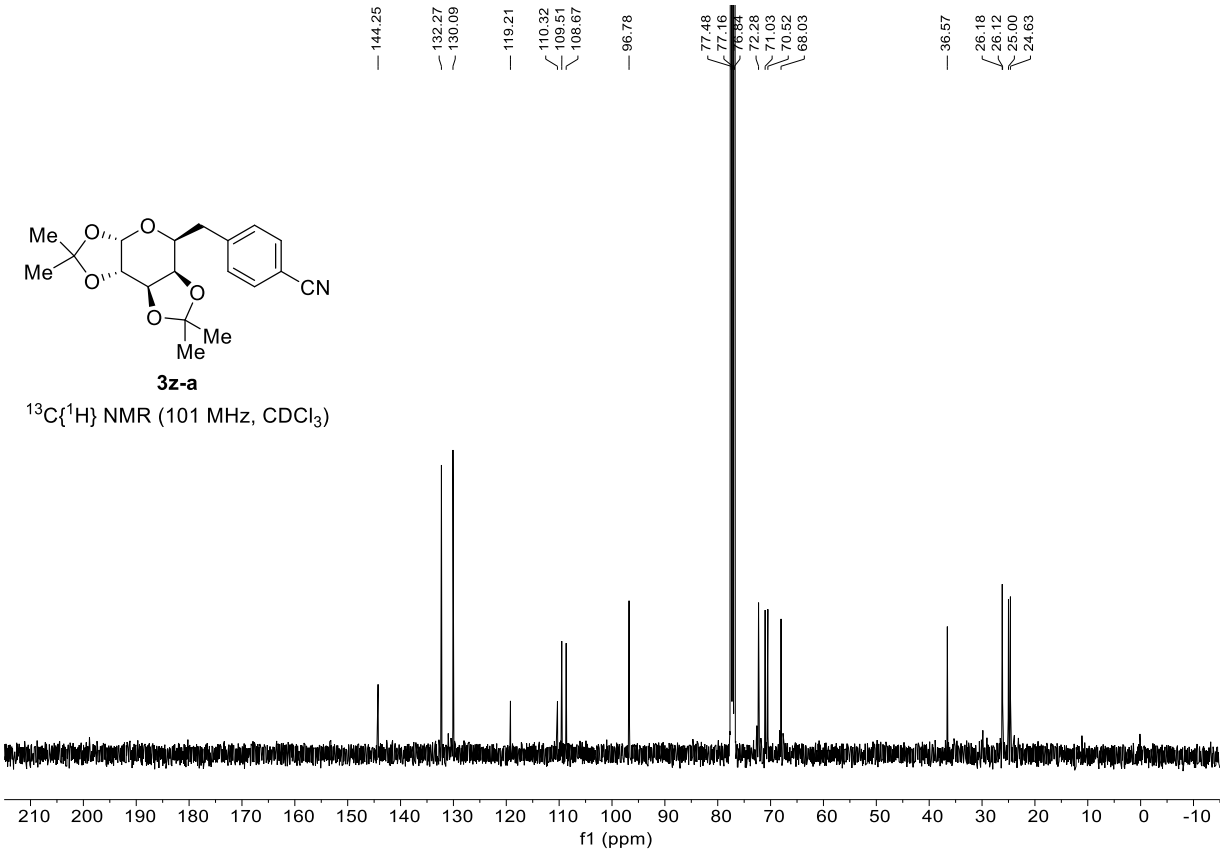
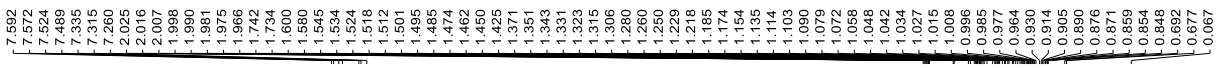
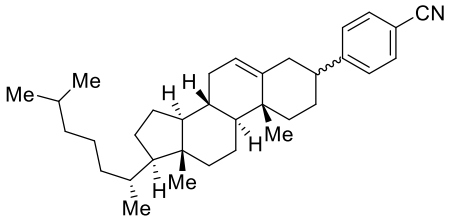
4.601
4.595
4.582
4.576
4.317
4.312
4.305
4.299
4.079
4.074
4.059
4.054
4.005
4.001
3.991
3.986
3.980
3.971
3.966
3.113
3.090
3.066
3.046
3.030
3.010
2.971
2.956
2.935
2.920
1.626
1.505
1.459
1.357
1.313
Me
Me
O
O
O
O
O
Me
Me
CN
3z-a
1H NMR (400 MHz, CDCl3)
2.00
1.96
1.00
1.09
1.04
0.99
1.06
2.06
2.96
3.00
3.07
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

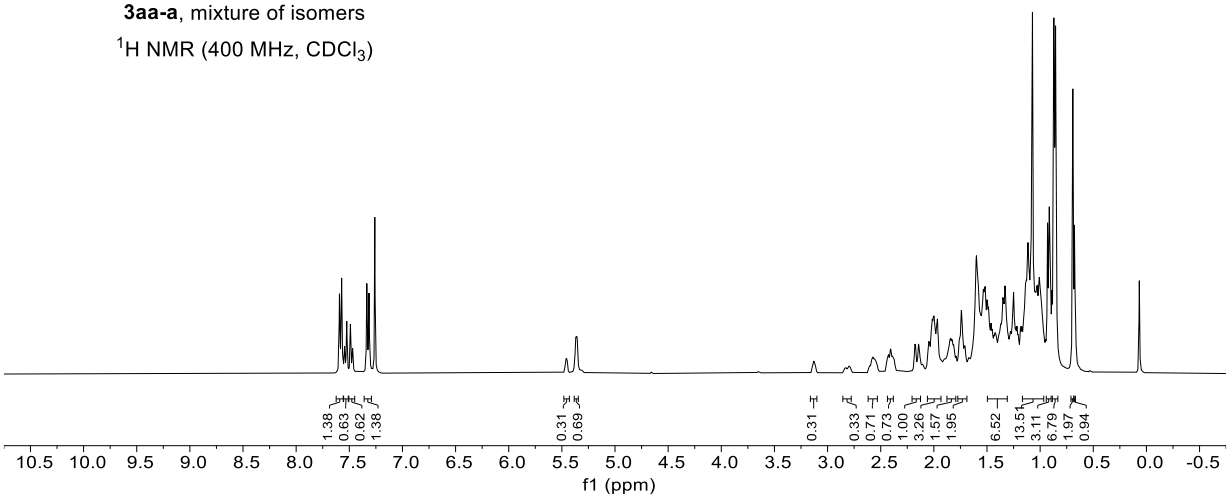

144.25
132.27
130.09
119.21
110.32
109.51
108.67
96.78
77.48
77.16
76.84
72.28
71.03
70.52
68.03
36.57
26.18
26.12
25.00
24.63
Me
Me
O
O
O
O
O
Me
Me
CN
3z-a
13C{1H} NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

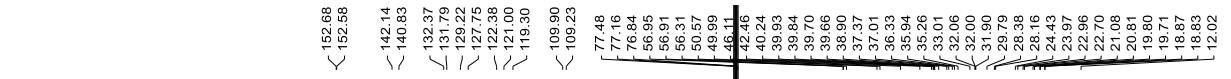


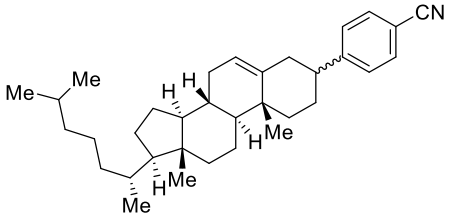


3aa-a, mixture of isomers

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

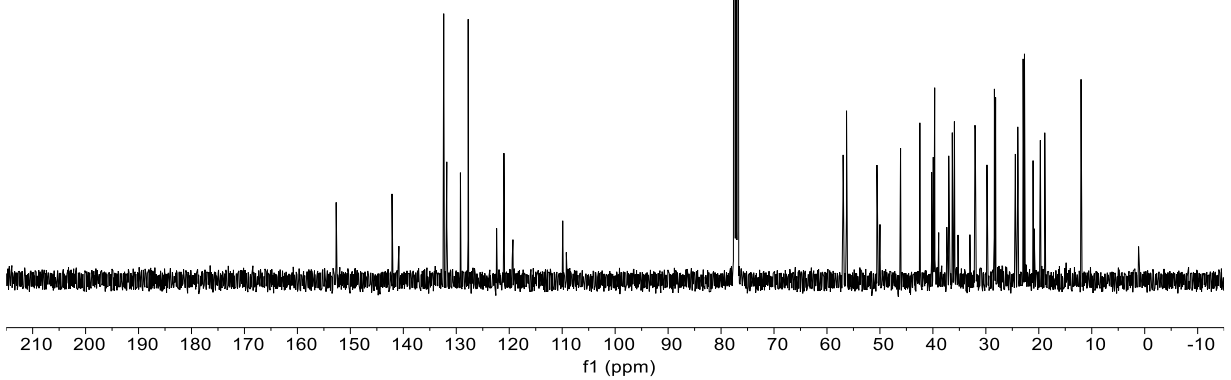


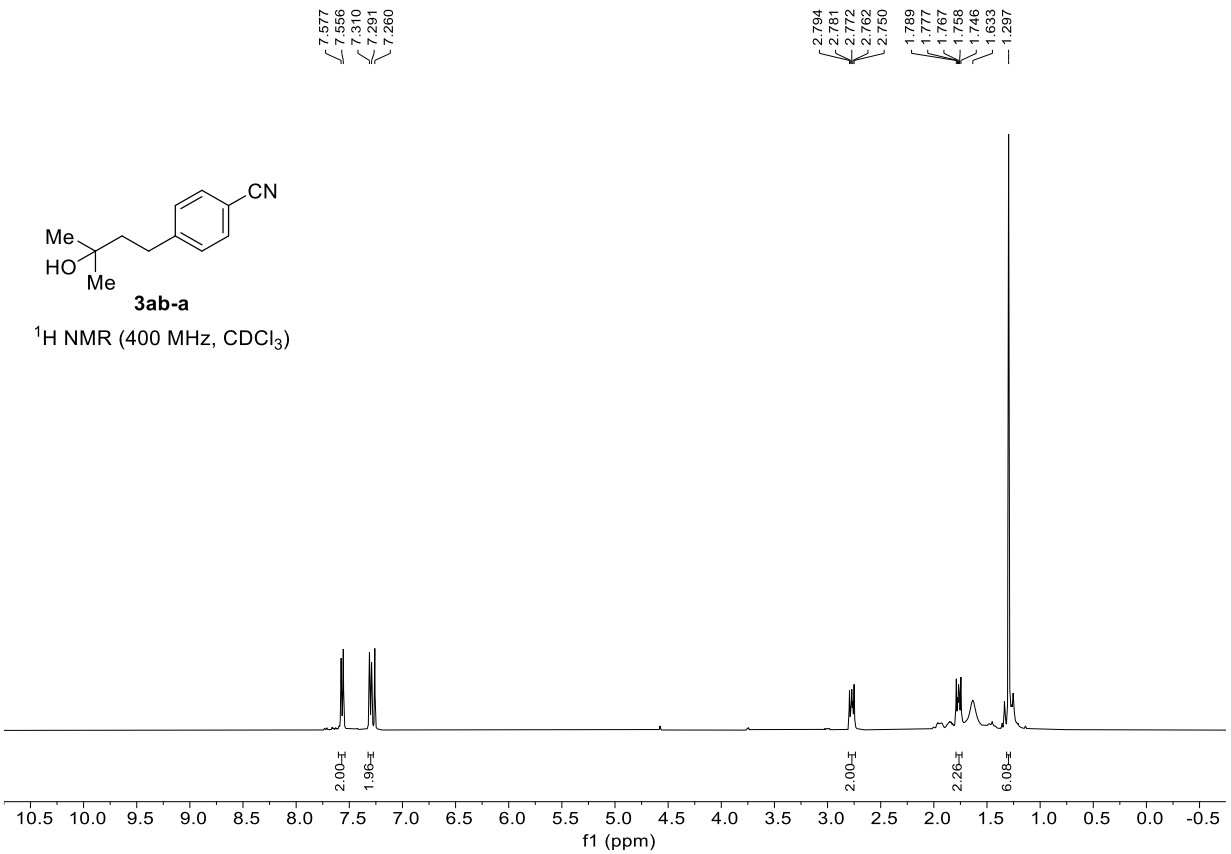




3aa-a, miture of isomers

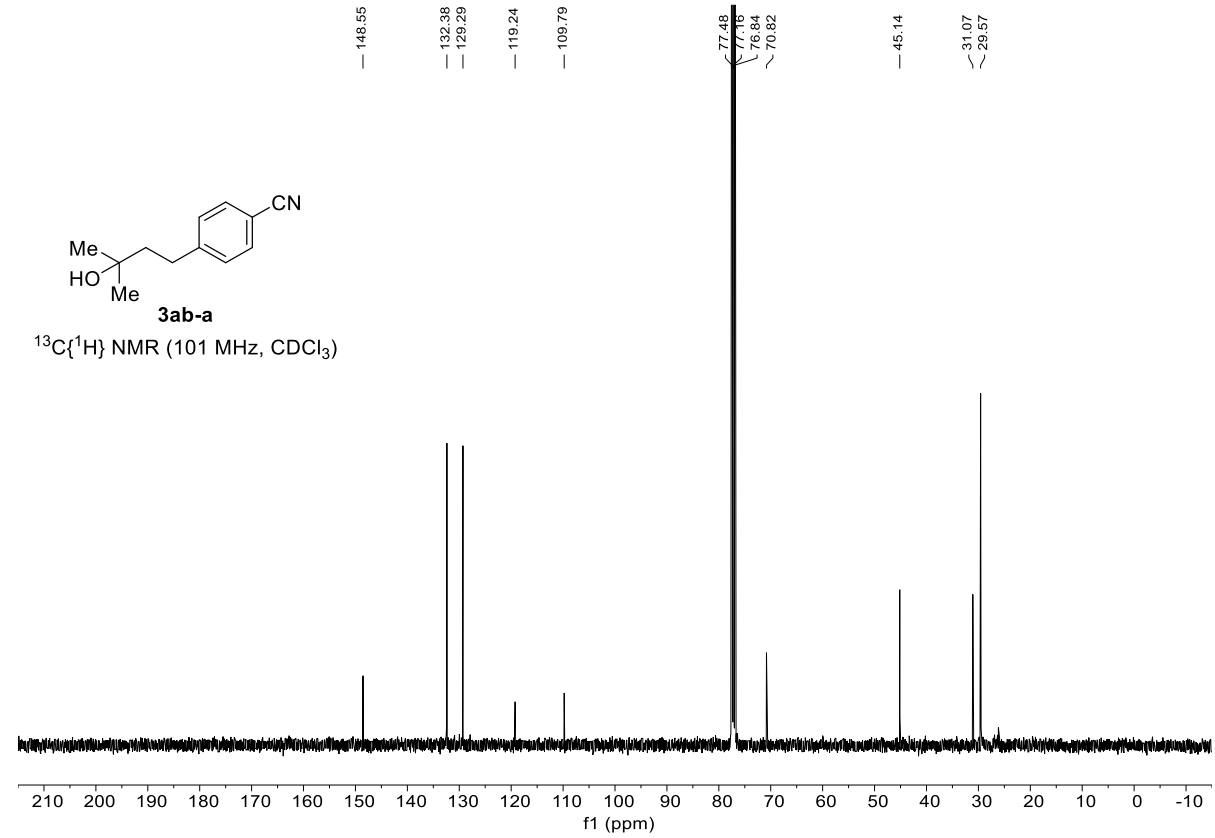
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)





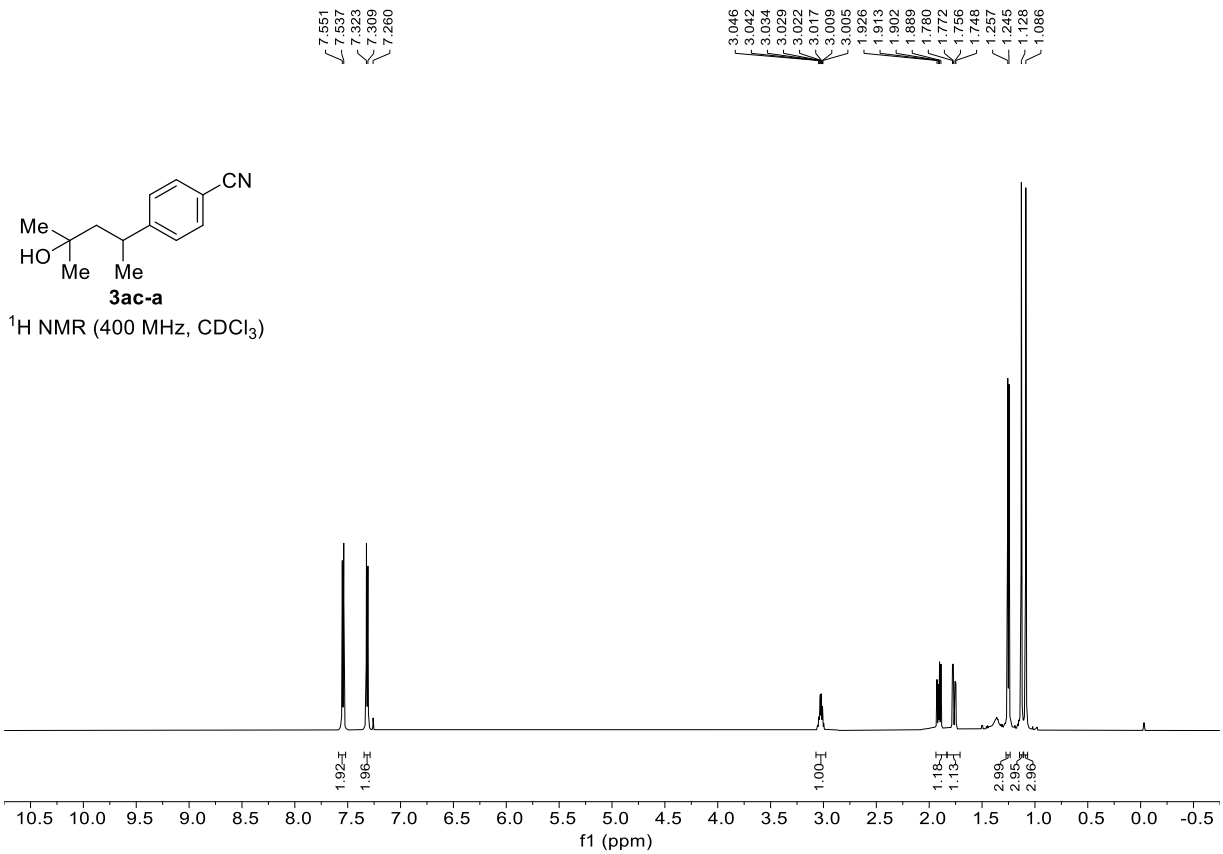
3ab-a

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



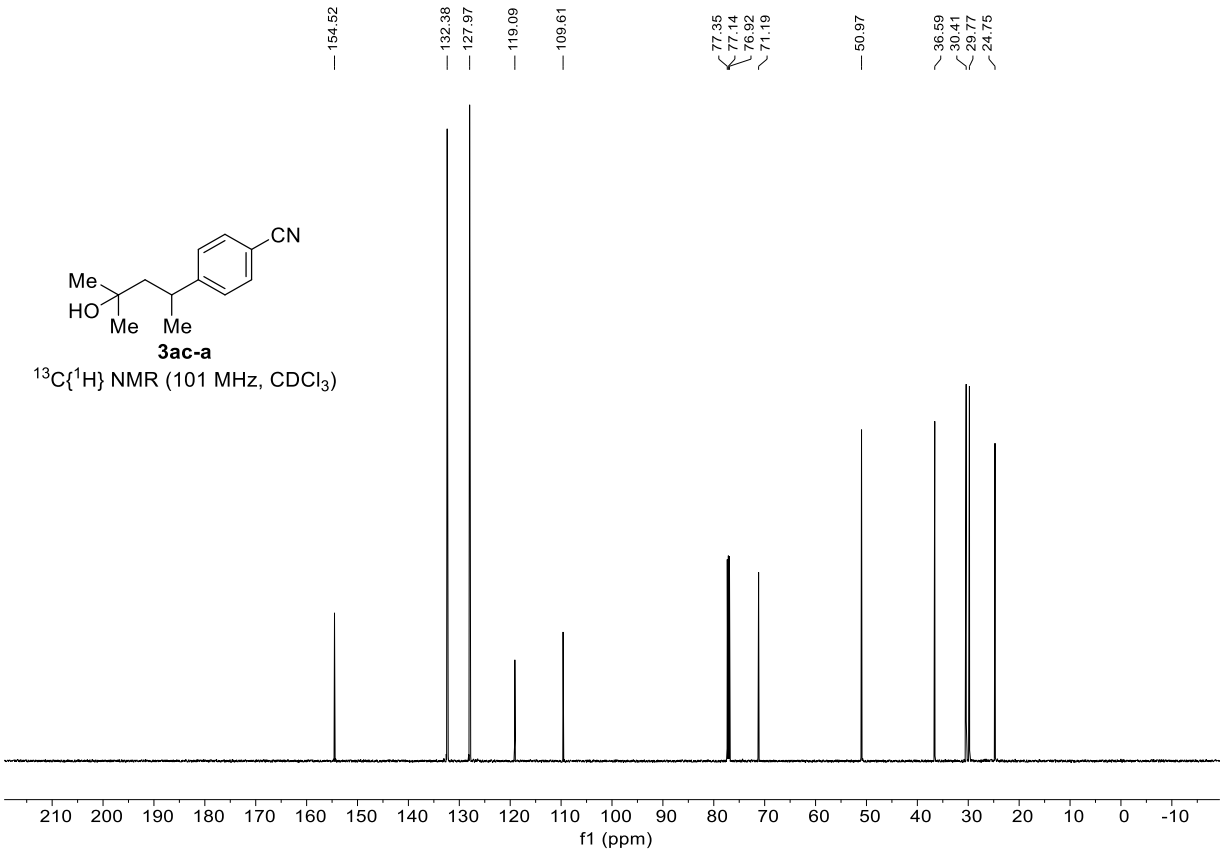
3ab-a

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



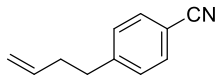
3ac-a

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



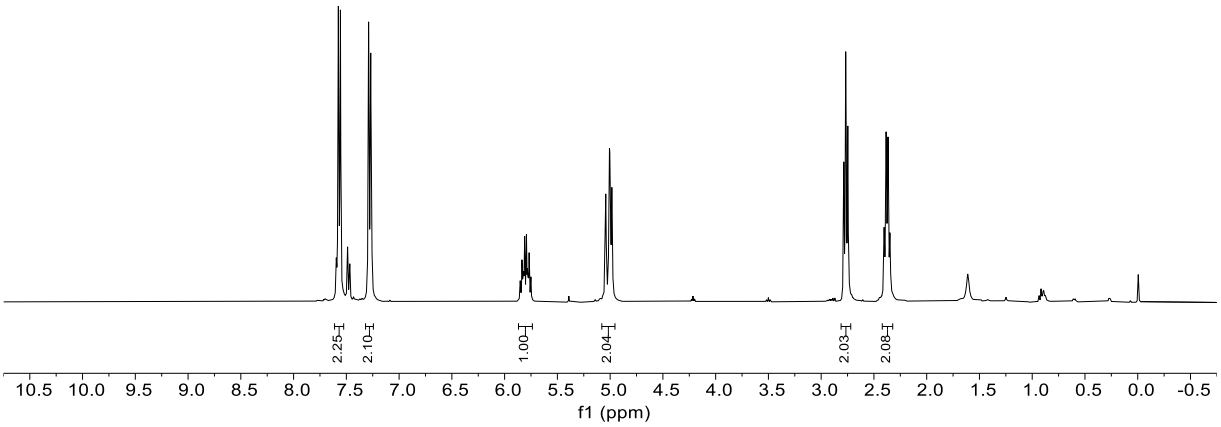
3ac-a

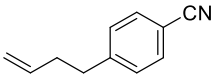
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



3ad-a

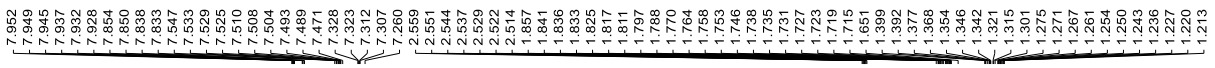
^{1}H NMR (400 MHz, $CDCl_3$)

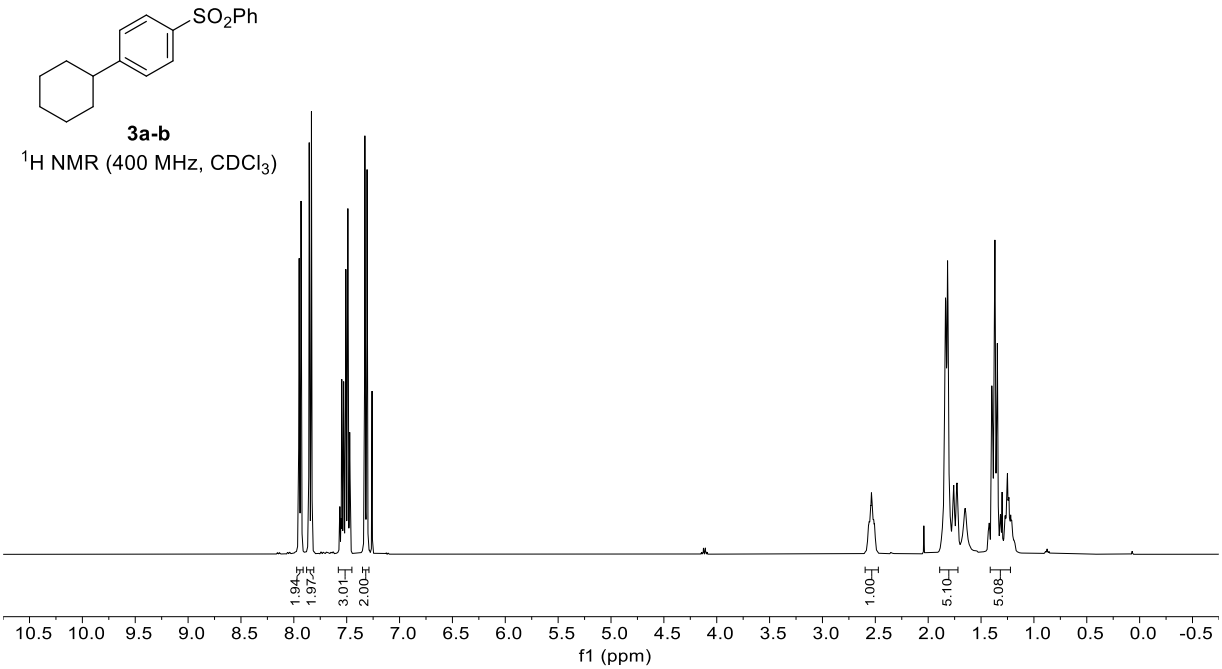




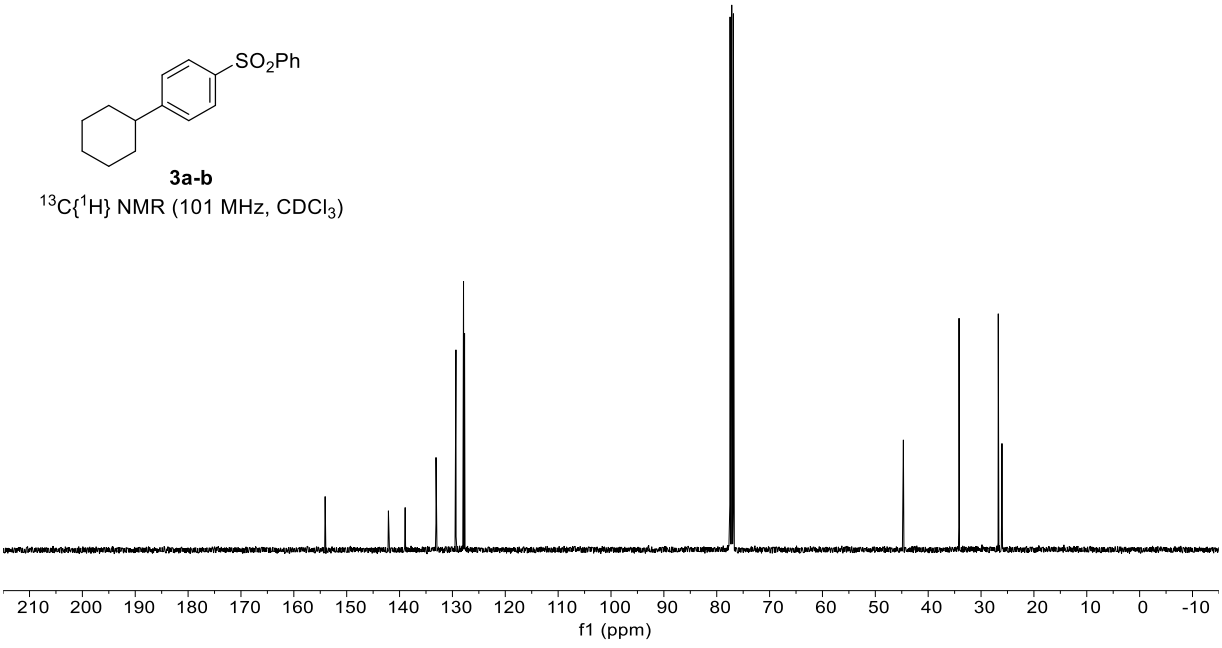
3ad-a

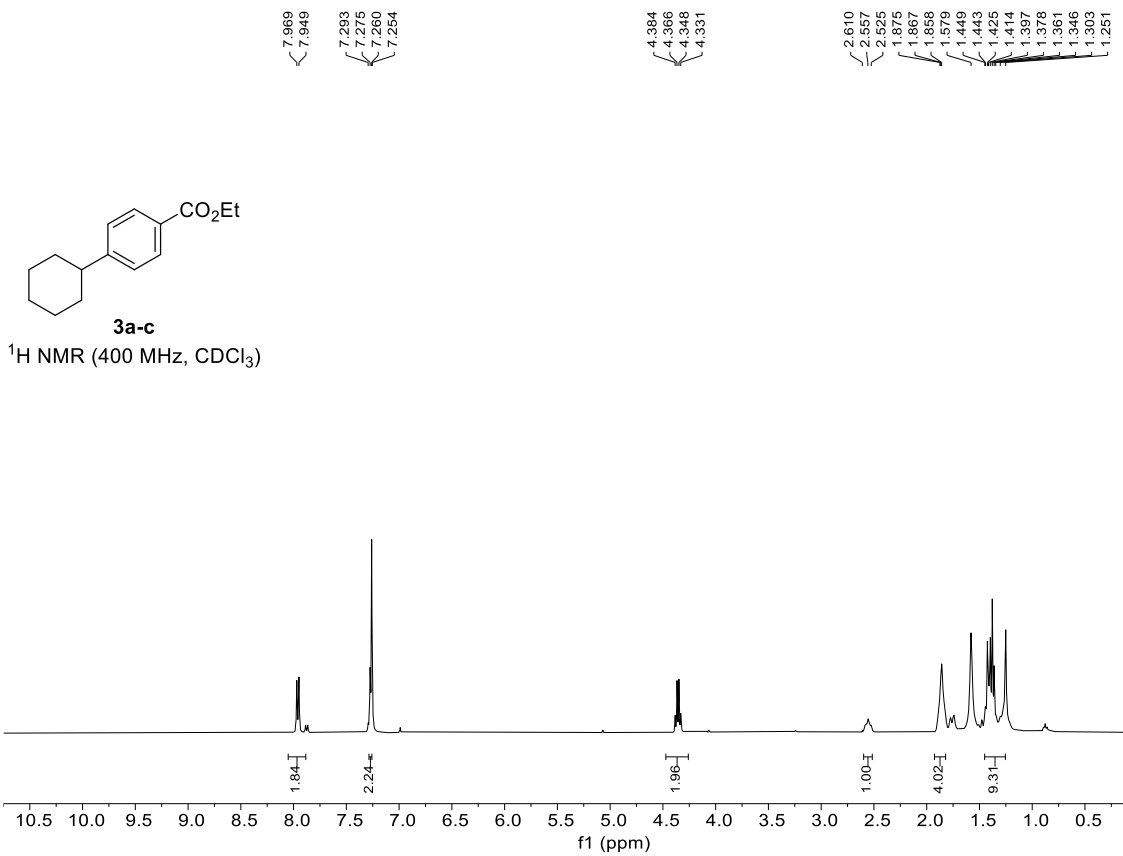
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)


7.952
7.949
7.945
7.937
7.932
7.928
7.854
7.850
7.838
7.833
7.547
7.533
7.529
7.525
7.510
7.508
7.504
7.493
7.489
7.471
7.328
7.323
7.312
7.307
7.260
2.559
2.551
2.544
2.537
2.529
2.522
2.514
1.857
1.841
1.836
1.833
1.825
1.817
1.811
1.797
1.788
1.770
1.764
1.758
1.753
1.746
1.738
1.735
1.731
1.727
1.723
1.719
1.715
1.651
1.399
1.392
1.377
1.368
1.354
1.346
1.342
1.321
1.315
1.301
1.275
1.271
1.267
1.261
1.254
1.250
1.243
1.236
1.227
1.220
1.213


SO2Ph
3a-b
1H NMR (400 MHz, CDCl3)
1.94
1.97
3.01
2.00
1.00
5.10
5.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

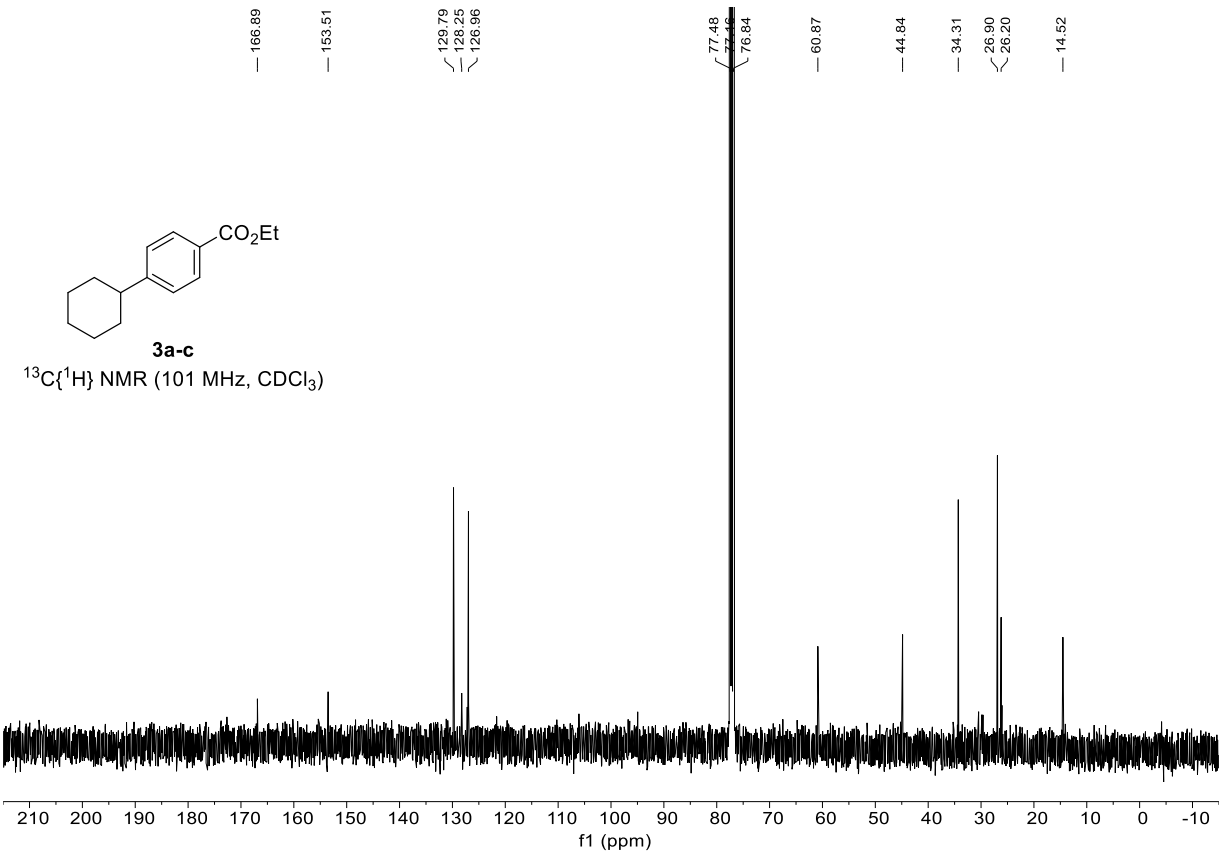

154.08
142.11
138.94
133.10
129.33
127.91
127.90
127.70
77.48
77.16
76.84
44.69
34.16
26.74
26.04


SO2Ph
3a-b
13C{1H} NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



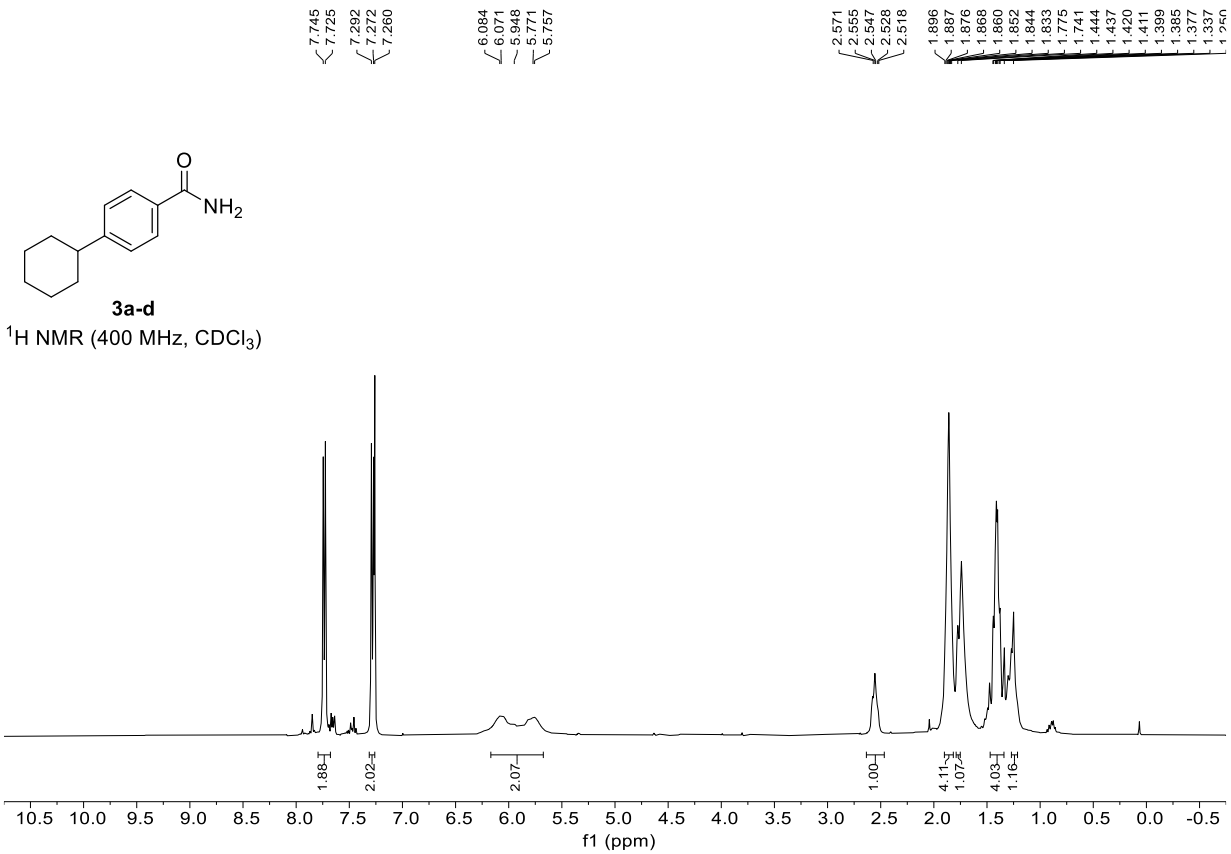
3a-c

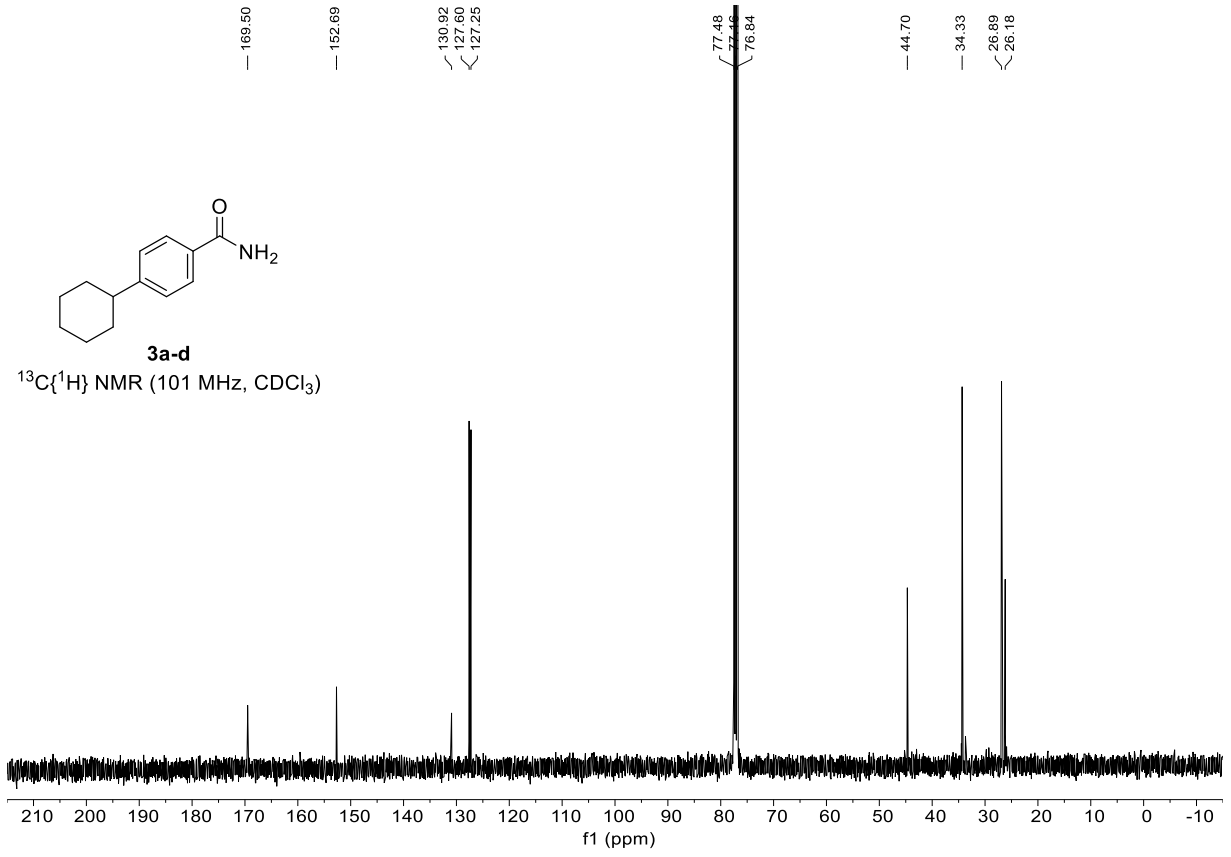
^{1}H NMR (400 MHz, $CDCl_3$)

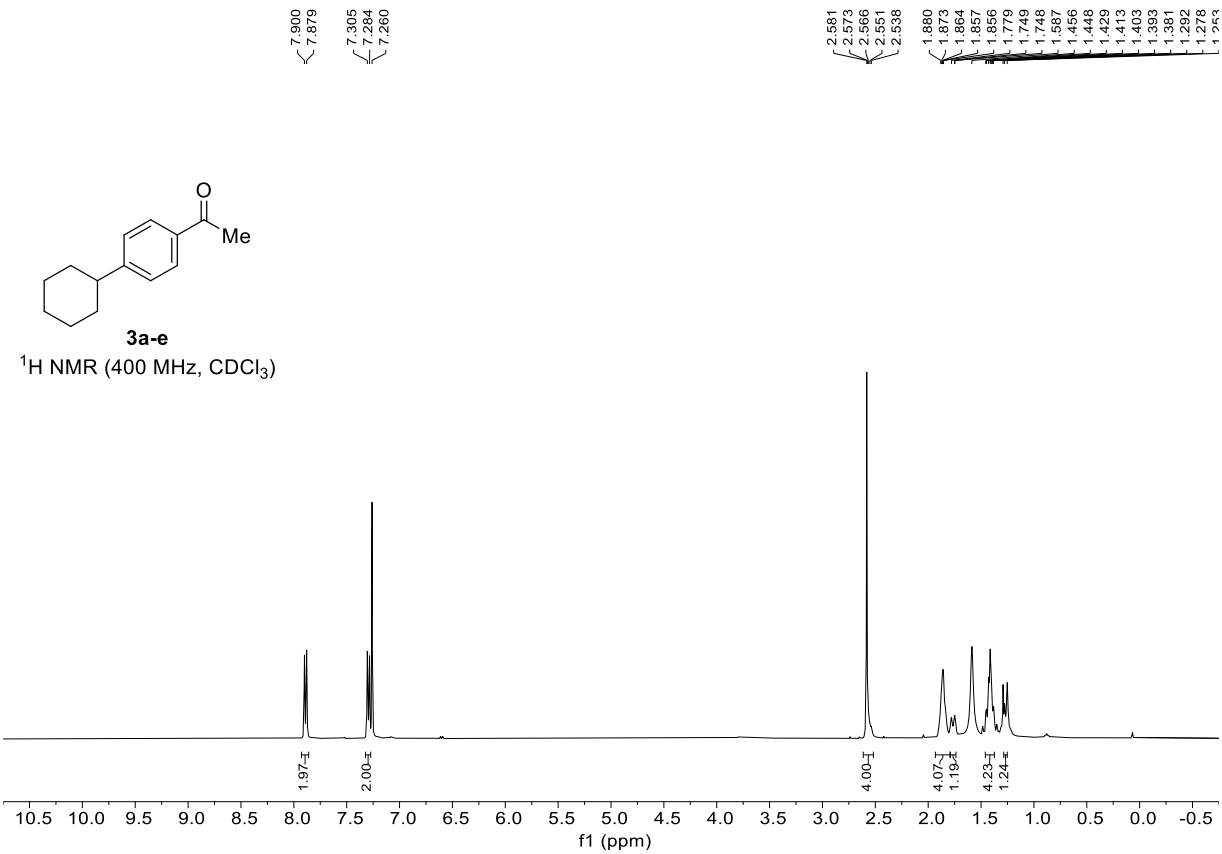


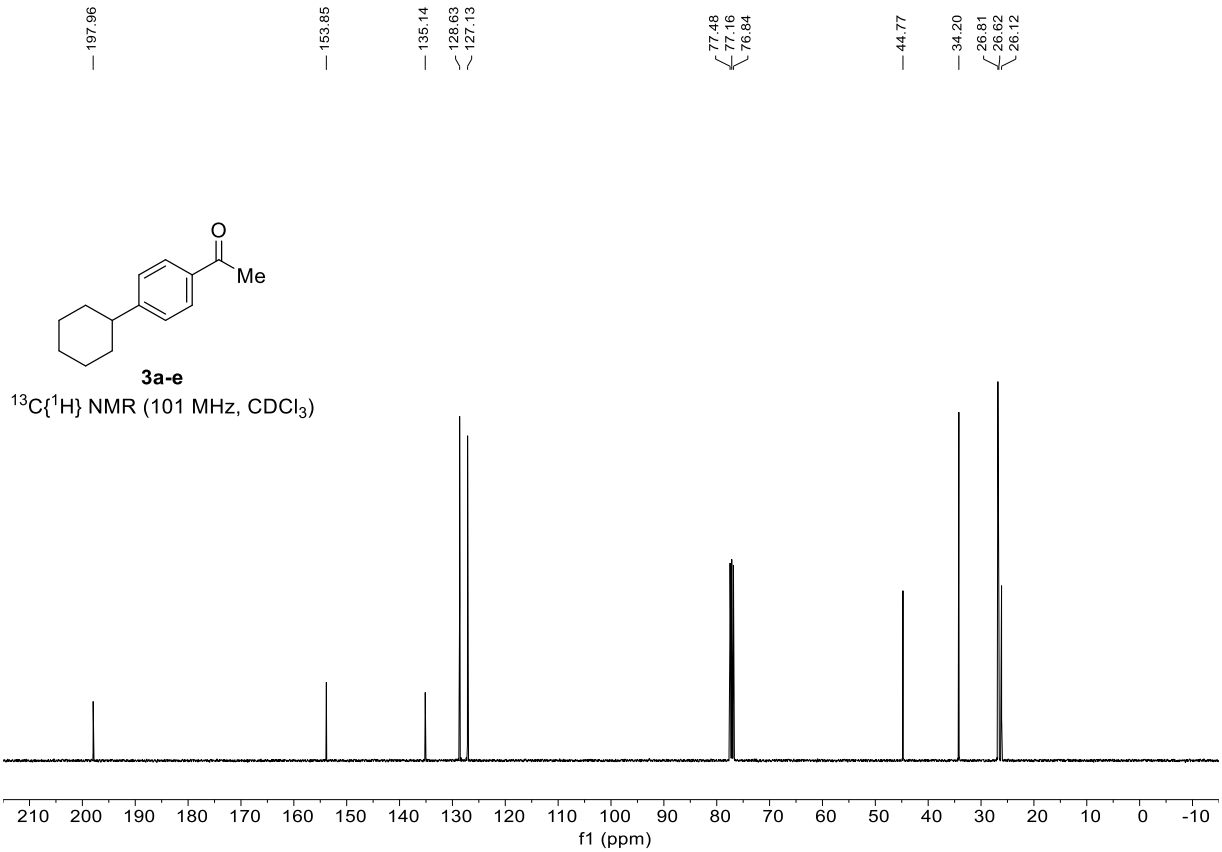
3a-c

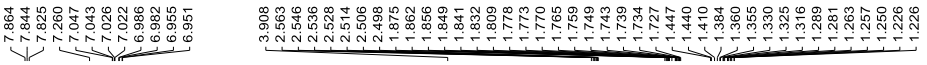
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

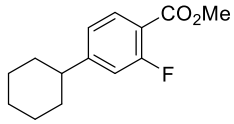

7.745
7.725
7.292
7.272
7.260
6.084
6.071
5.948
5.771
5.757
2.571
2.555
2.547
2.528
2.518
1.896
1.887
1.876
1.868
1.860
1.852
1.844
1.833
1.775
1.741
1.444
1.437
1.420
1.411
1.399
1.385
1.377
1.337
O
NH2
3a-d
1H NMR (400 MHz, CDCl3)
1.88
2.02
2.07
1.00
4.11
1.07
4.03
1.16
f1 (ppm)


169.50
152.69
130.92
127.60
127.25
77.48
77.16
76.84
44.70
34.33
26.89
26.18
O
NH2
3a-d
13C{1H} NMR (101 MHz, CDCl3)
f1 (ppm)


7.900
7.879
7.305
7.284
7.260
2.581
2.573
2.566
2.551
2.538
1.880
1.873
1.864
1.857
1.856
1.779
1.749
1.748
1.587
1.456
1.448
1.429
1.413
1.403
1.393
1.381
1.292
1.278
O
Me
3a-e
1H NMR (400 MHz, CDCl3)
1.97
2.00
4.00
4.07
1.19
4.23
1.24
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

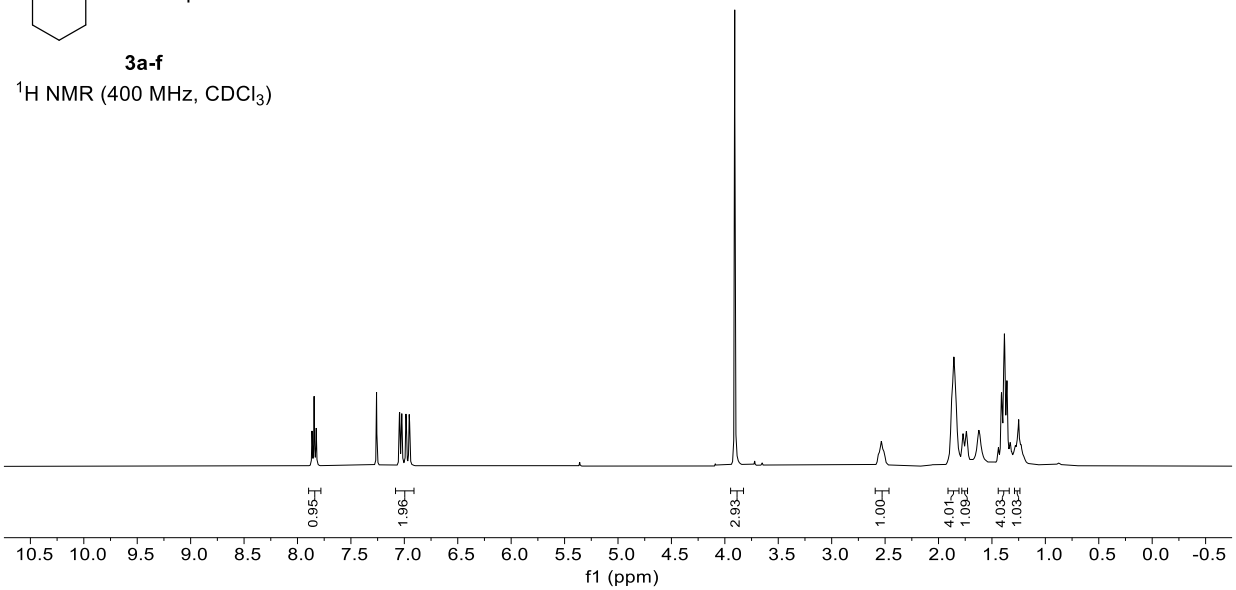

197.96
153.85
135.14
128.63
127.13
77.48
77.16
76.84
44.77
34.20
26.81
26.62
26.12
O
Me
3a-e
13C{1H} NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

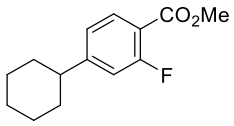




3a-f

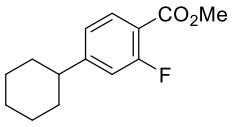
^{1}H NMR (400 MHz, $CDCl_3$)





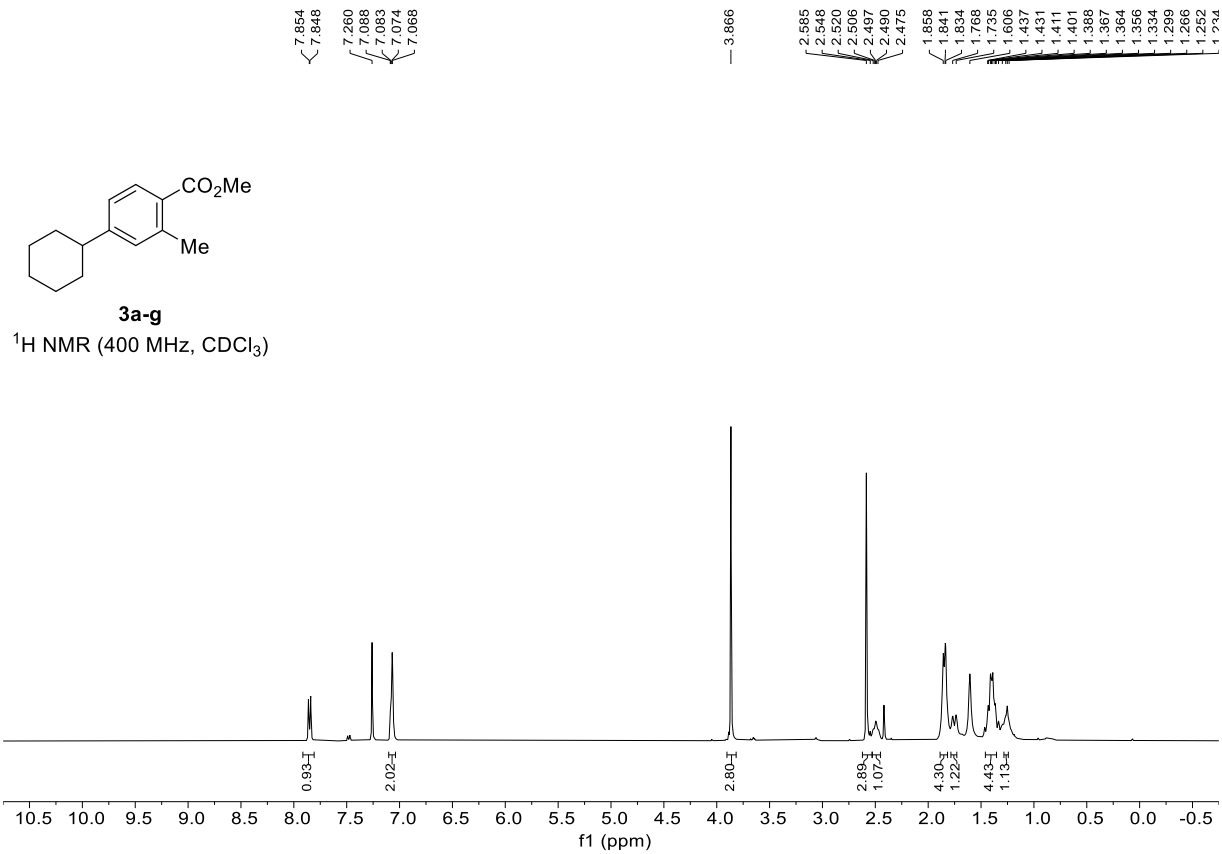
3af

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



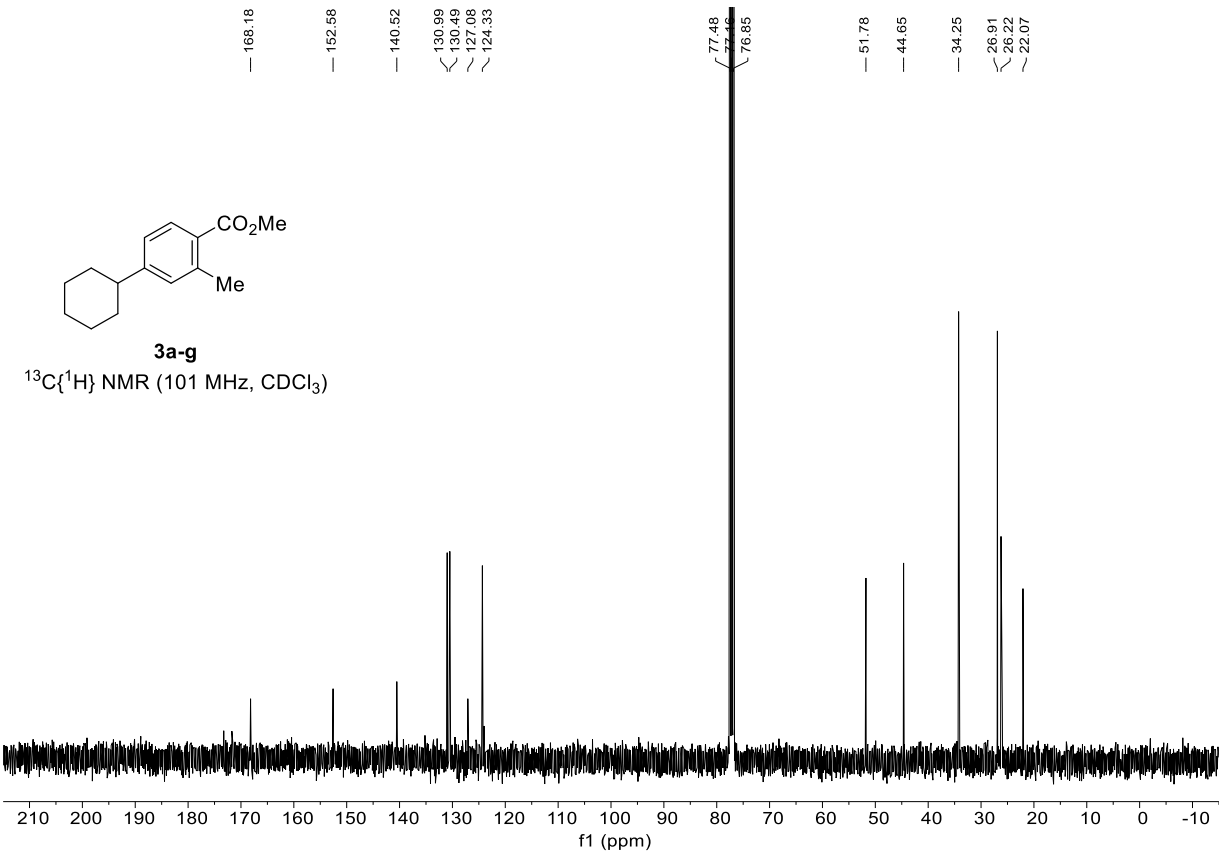
3a-f

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



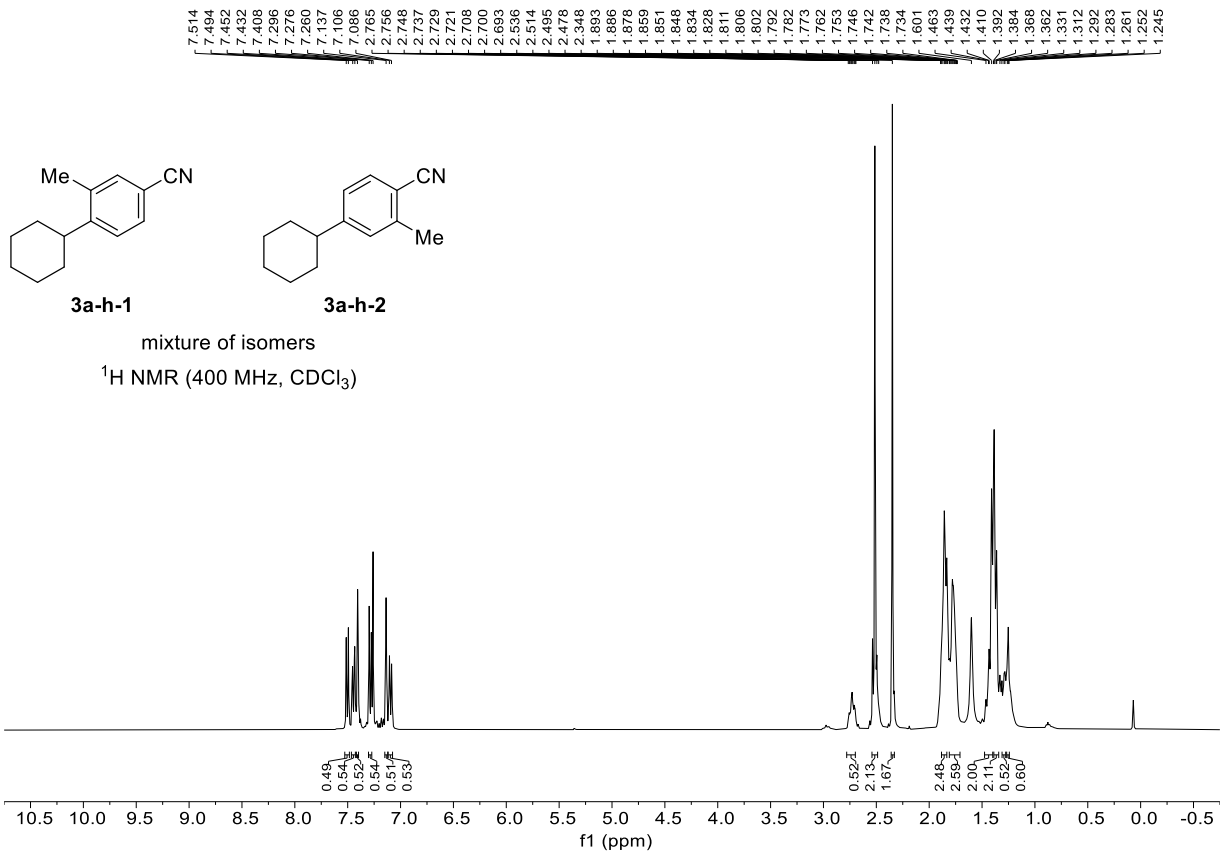
3a-g

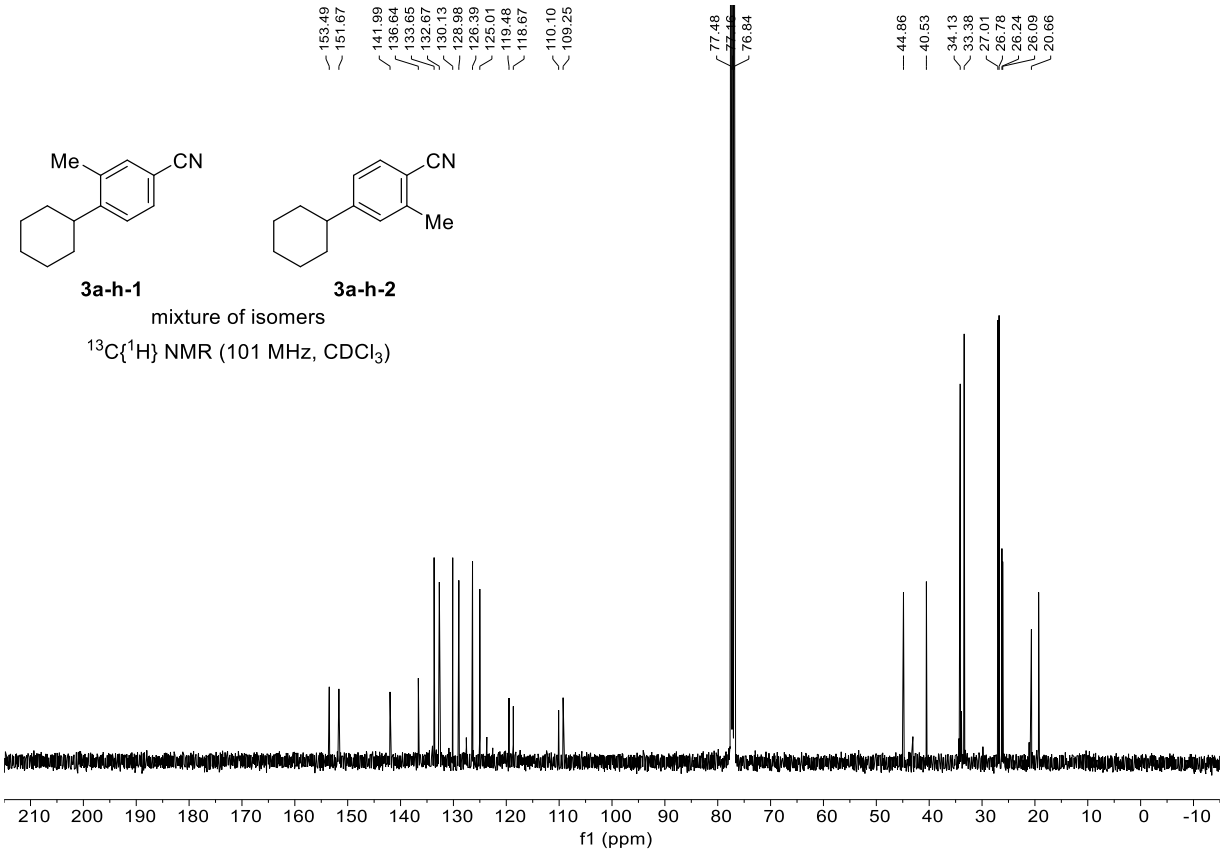
^{1}H NMR (400 MHz, $CDCl_3$)

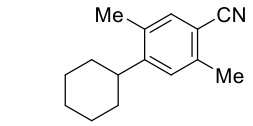


3a-g

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)


7.514 7.494 7.452 7.432 7.408 7.296 7.276 7.260 7.137 7.106 7.086 2.765 2.756 2.748 2.737 2.729 2.721 2.708 2.700 2.693 2.536 2.514 2.495 2.478 2.348 1.893 1.886 1.878 1.859 1.851 1.848 1.834 1.828 1.811 1.806 1.802 1.792 1.782 1.773 1.762 1.753 1.746 1.742 1.738 1.734 1.601 1.463 1.439 1.432 1.410 1.392 1.384 1.368 1.362 1.331 1.312 1.292 1.283 1.261 1.252 1.245
Me
CN
CN
Me
3a-h-1
3a-h-2
mixture of isomers
1H NMR (400 MHz, CDCl3)
0.49 0.54 0.52 0.54 0.51 0.53
0.52 2.13 1.67
2.46 2.59 2.00 2.11 0.52 0.60
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


153.49 151.67 141.99 136.64 133.65 132.67 130.13 128.98 126.39 125.01 119.48 118.67 110.10 109.25
77.48 77.16 76.84
44.86 40.53 34.13 33.38 27.01 26.78 26.24 26.09 20.66
Me
CN
CN
Me
3a-h-1
3a-h-2
mixture of isomers
13C{1H} NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

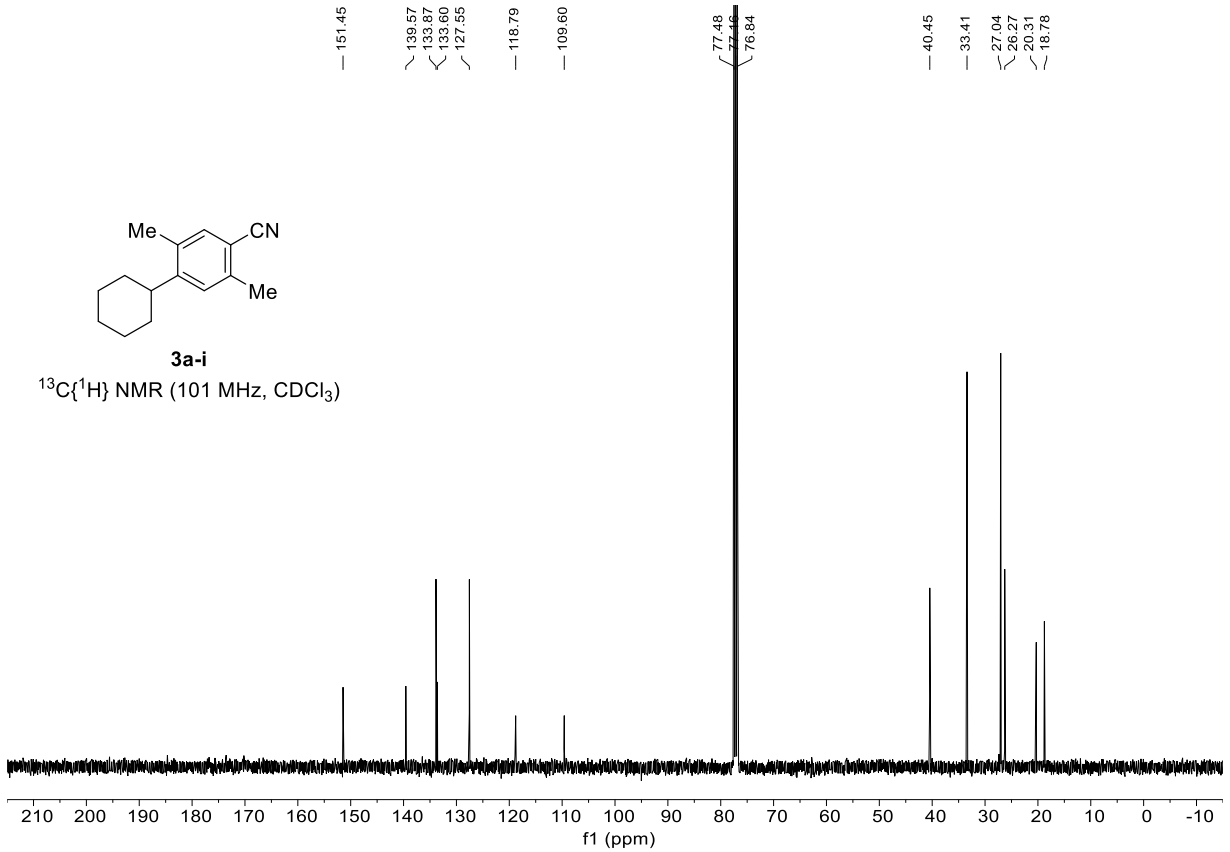


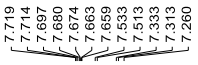
3a-i

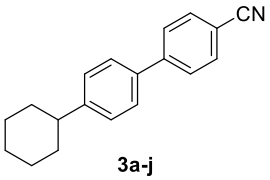
^{1}H NMR (400 MHz, $CDCl_3$)

3a-i

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

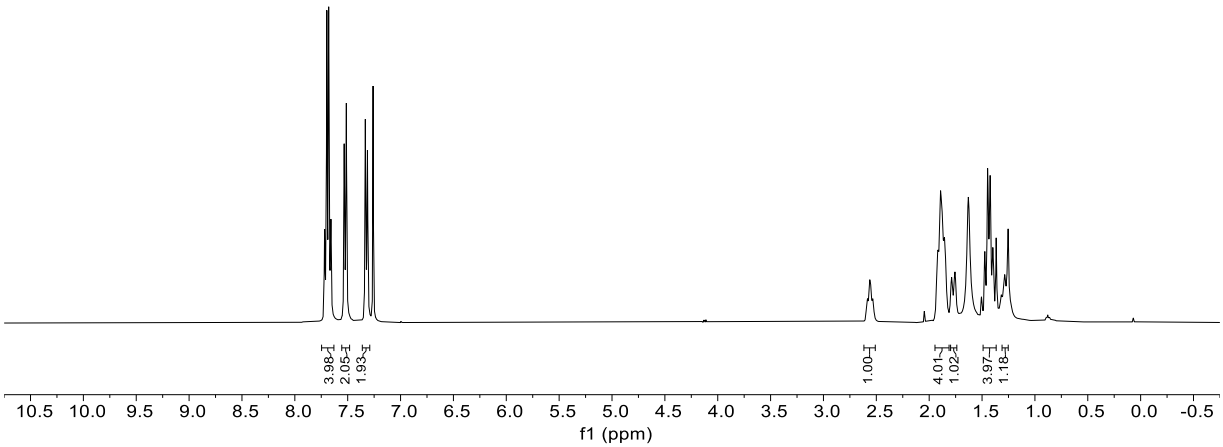


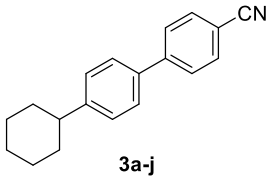




3a-j

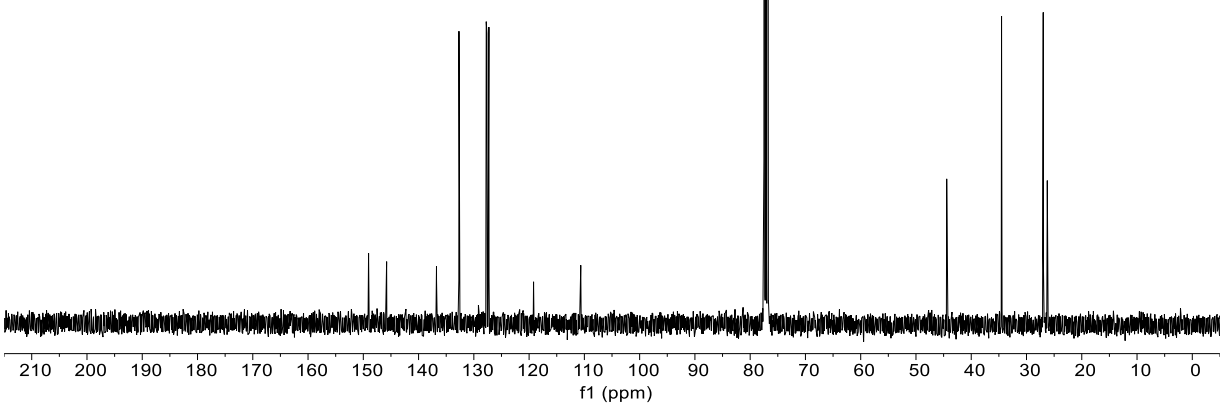
^{1}H NMR (400 MHz, $CDCl_3$)

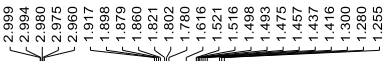


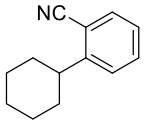


3a-j

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

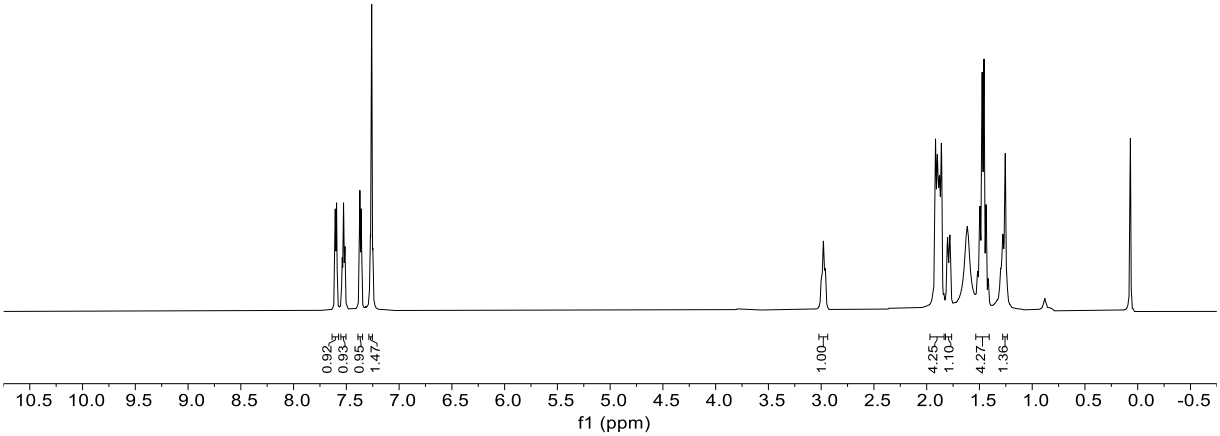


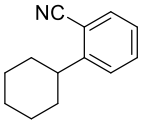




3a-k

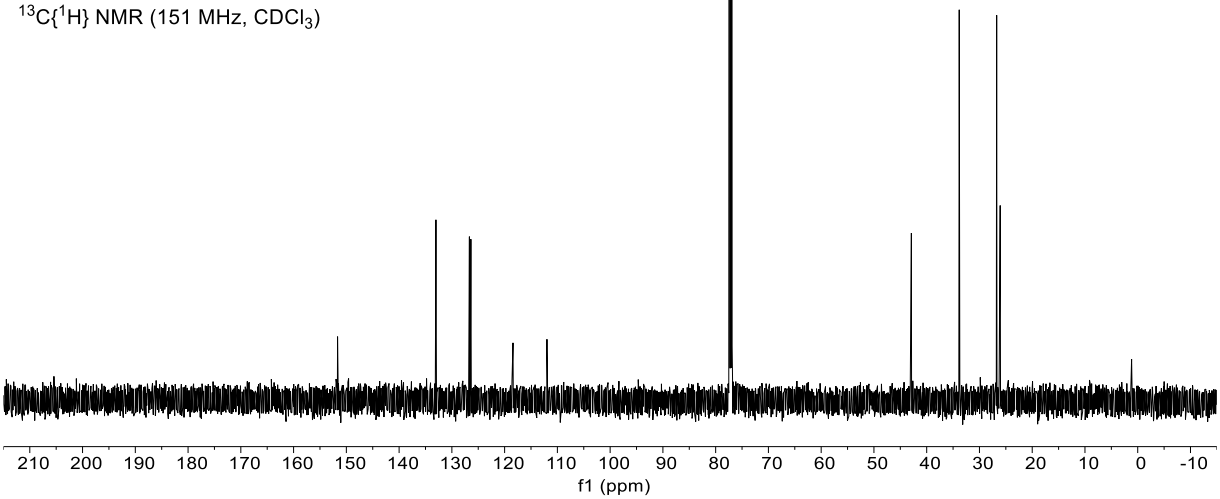
^{1}H NMR (600 MHz, $CDCl_3$)

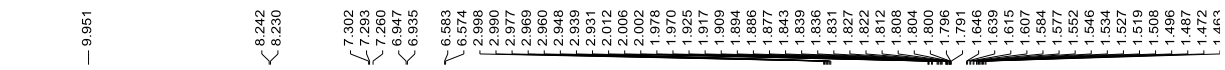


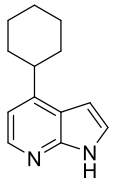


3a-k

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

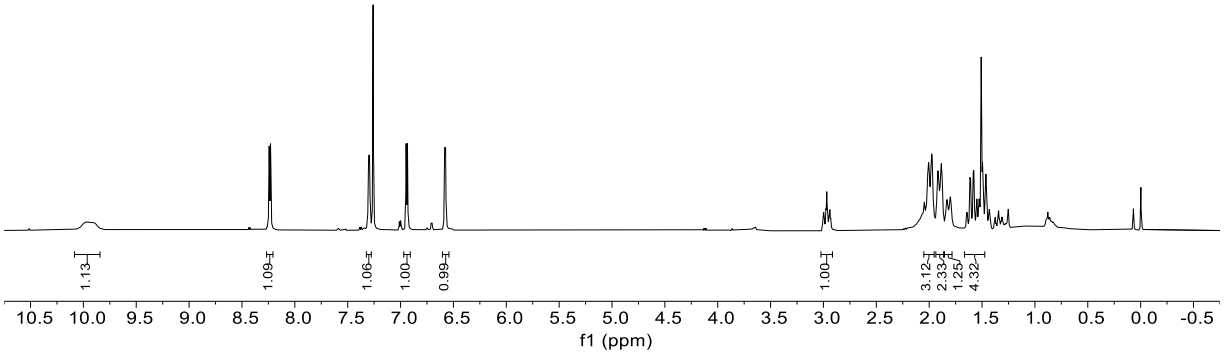


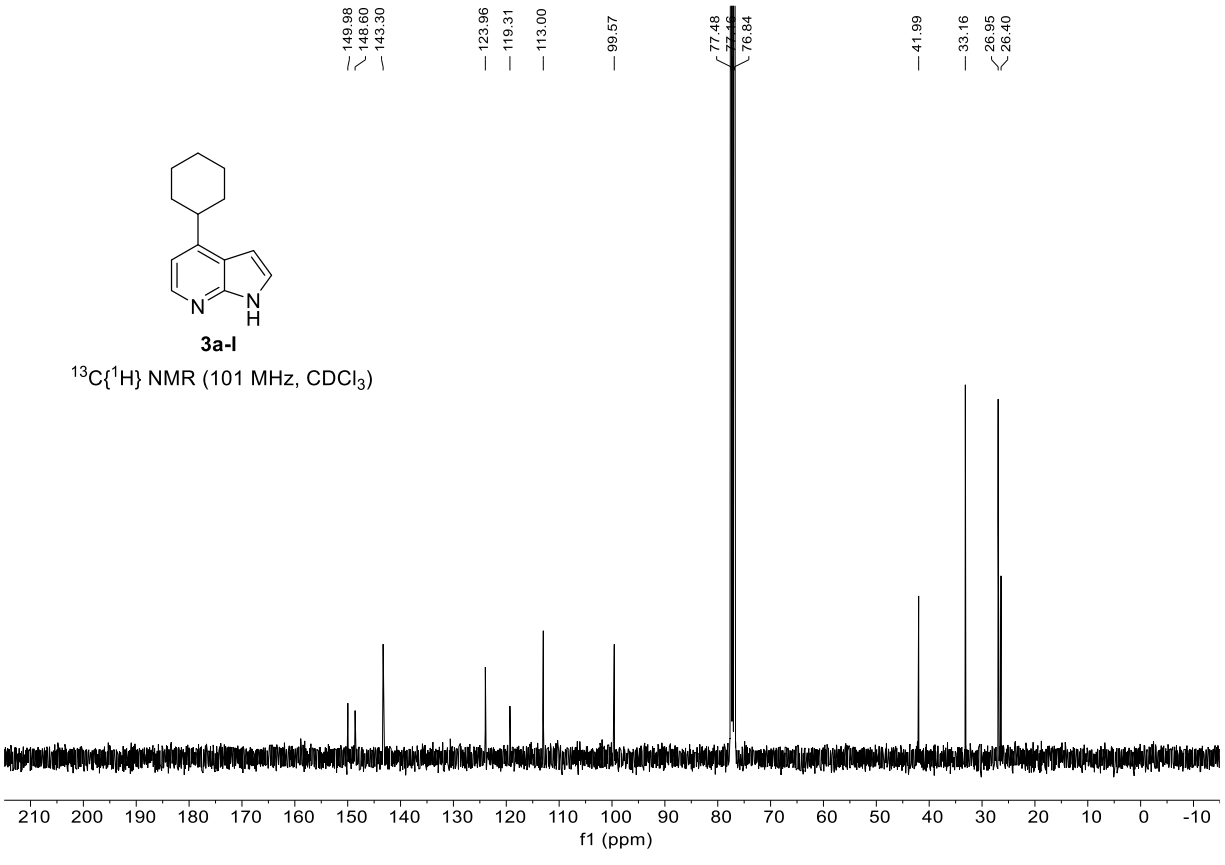




3a-l

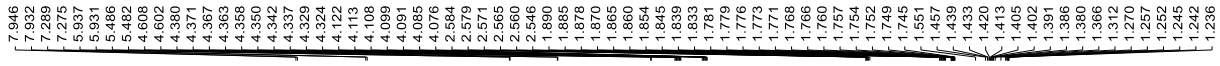
^{1}H NMR (400 MHz, $CDCl_3$)

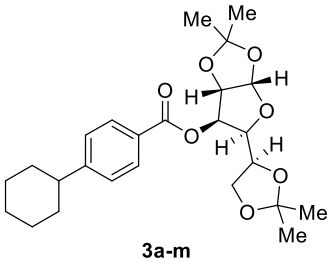




3a-l

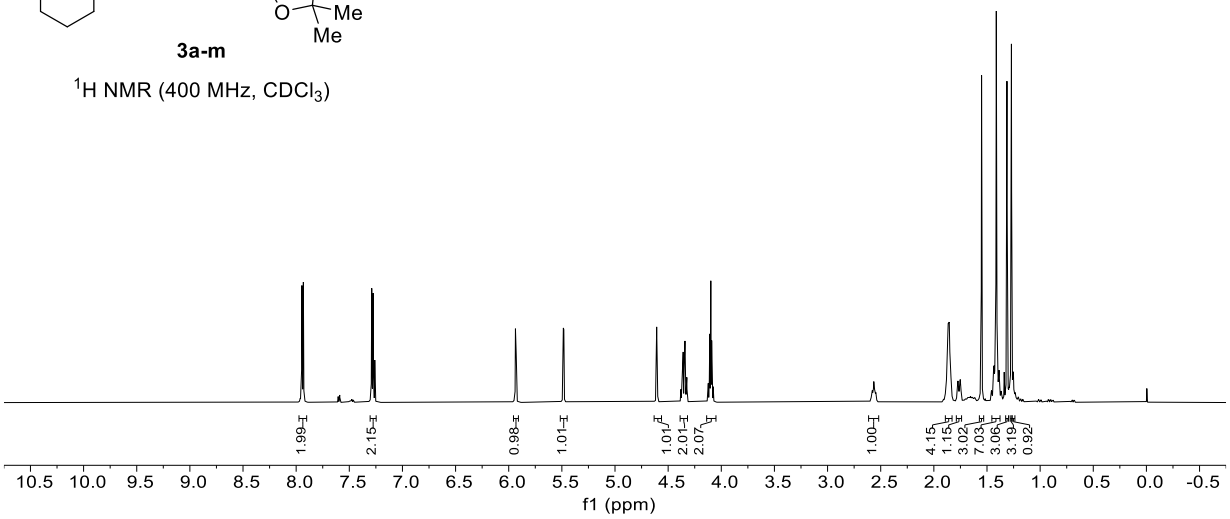
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

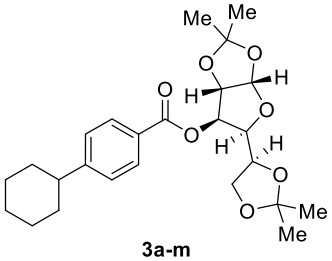




3a-m

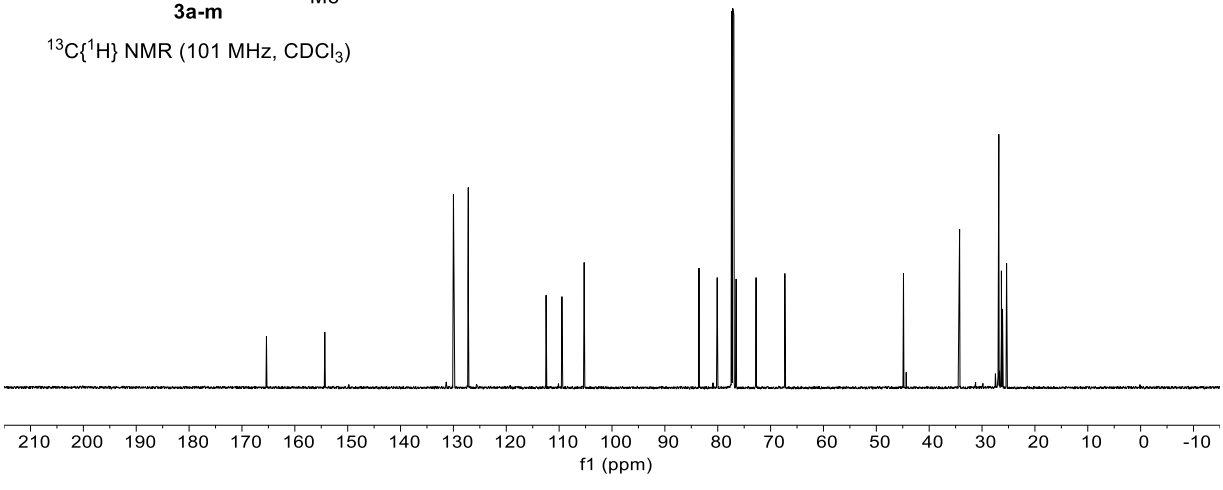
^{1}H NMR (400 MHz, $CDCl_3$)

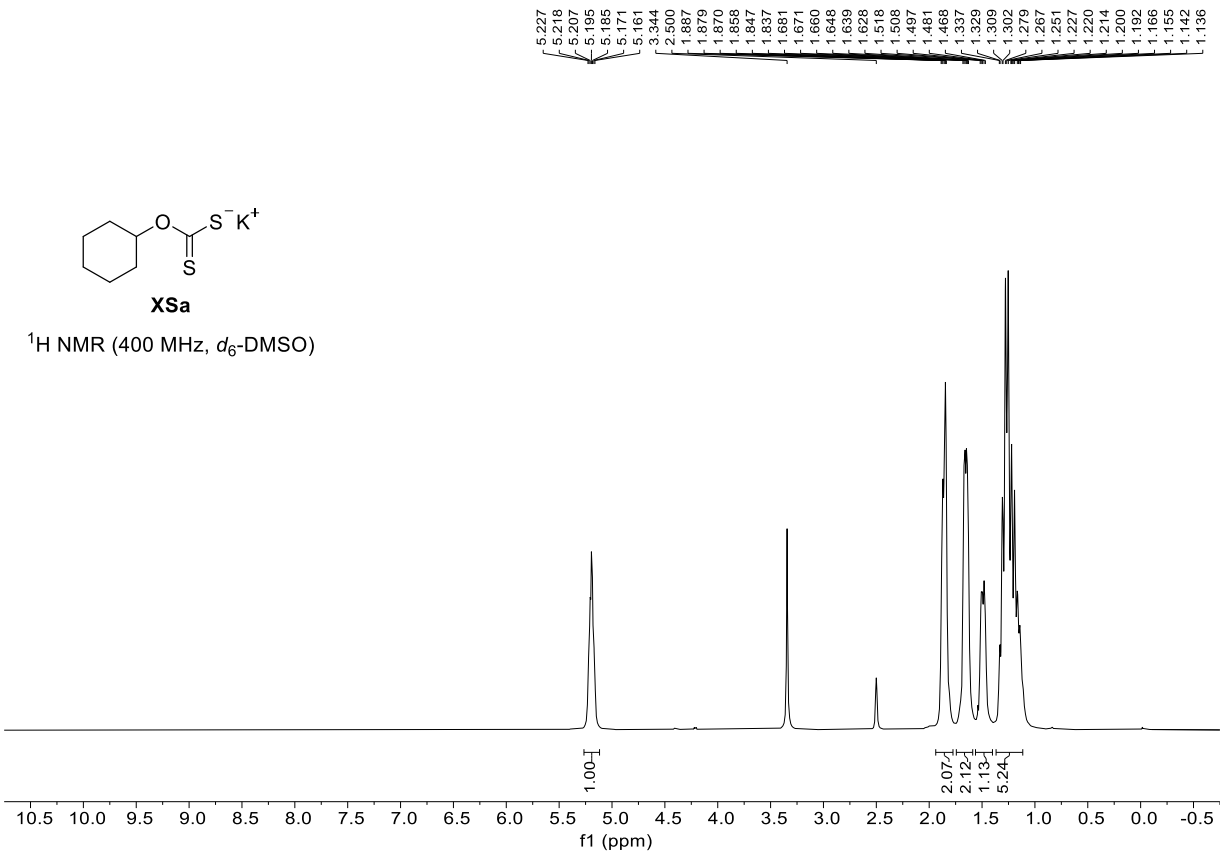


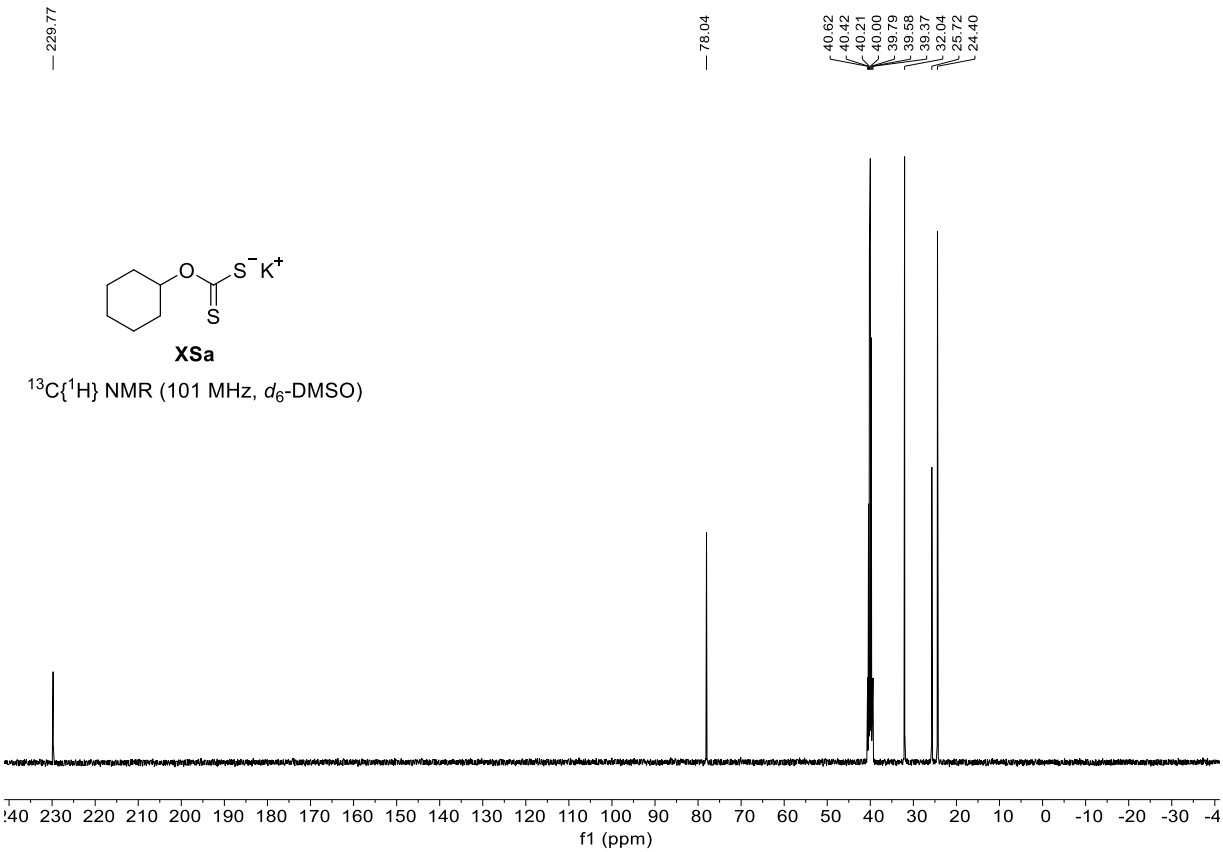


3a-m

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)




5.227
5.218
5.207
5.195
5.185
5.171
5.161
3.344
2.500
1.887
1.879
1.870
1.858
1.847
1.837
1.681
1.671
1.660
1.648
1.639
1.628
1.518
1.508
1.497
1.481
1.468
1.337
1.329
1.309
1.302
1.279
1.267
1.251
1.227
1.220
1.214
1.200
1.192
1.166
1.155
1.142
1.136
O
S
K
S
XSa
1H NMR (400 MHz, d6-DMSO)
1.00
2.07
2.12
1.13
5.24
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


229.77
78.04
40.62
40.42
40.21
40.00
39.79
39.58
39.37
32.04
25.72
24.40
O
S
K
S
XSa
13C{1H} NMR (101 MHz, d6-DMSO)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -4
f1 (ppm)

8. References

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