

Supporting Information

Amine Functionalized Bifunctional Co^{III}-NHC Complexes: Highly Effective Phosphine-Free Catalysts for the α -Alkylation of Nitriles

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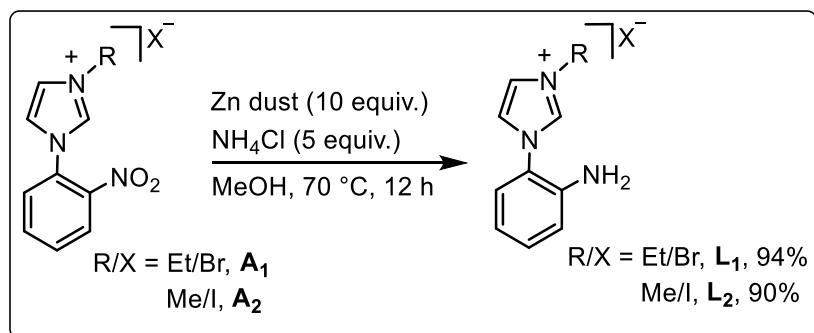
General experimental details

All experiments with metal complexes were performed using oven-dried glassware under an inert atmosphere using either standard Schlenk line or Glove box techniques. All solvents used for the synthesis were distilled, degassed by standard methods, and stored under inert atmosphere over 4 Å molecular sieves. All the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded using Bruker 400 and 500 MHz FT-NMR spectrometers, referenced internally to the residual solvent signals. ESI-MS spectra were measured using an Agilent 6545A Q-TOF Mass spectrometer. Chemicals e.g. cobalt precursor, $[\text{Co}(\text{Cp}^*)\text{Cl}_2]_2$ and ligands **L**₁₋₂ were synthesized by modified procedure and **L**₃₋₄ according to the literature procedures.^{1,2} All other chemicals were procured from commercial sources and used as received.

General procedure for the synthesis of ligand **L**₁₋₂

Compound **A**₁₋₂ were synthesized following the reported procedure.¹ Following that **A**₁/**A**₂ (1 equiv.), Zn dust (10 equiv.), and NH_4Cl (5 equiv.) were taken in an RB flask followed by the addition of methanol slowly. Then the reaction mixture was refluxed at 70 °C for 12 h. After the completion of reaction, the reaction mixture was filtered through a pad of celite using methanol. The obtained filtrate was then concentrated ~ 1 mL and diethyl ether was then added to induce precipitation which after isolation followed by drying in vacuo provided the desired ligands **L**₁₋₂ as a hygroscopic orange colour solids in 90-94% yield.

Synthesis and characterization of ligands **L**₁₋₂



Scheme S1: Synthesis of ligand **L**₁₋₂.

Ligand L₁: L₁ was synthesized according to the general procedure using 1.00 g of A₁, 2.20 g of Zn dust, and 0.89 g of NH₄Cl (yield: 0.84 g, 3.152 mmol, 94%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.49 (s, 1H), 8.02 (s, 1H), 7.86 (s, 1H), 7.28-7.22 (m, 2H), 6.91 (d, *J* = 11.7 Hz, 1H), 6.67 (t, *J* = 7.8 Hz, 1H), 5.56 (s, 2H), 4.25 (q, *J* = 8.4 Hz, 2H), 1.50 (t, *J* = 8.0 Hz, 3H) ppm. ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 143.8, 137.1, 131.1, 127.2, 123.8, 122.6, 119.8, 116.5, 116.0, 44.5, 14.7 ppm. MS (ESI, positive ions): *m/z* 188.1146 (calcd for [M-Br]⁺: *m/z* 188.1188)

Ligand L₂: L₂ was synthesized according to the general procedure using 0.20 g of A₂, 0.39 g of Zn dust, and 0.16 g of NH₄Cl (yield: 0.16 g, 0.543 mmol, 90%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.37 (s, 1H), 7.90 (s, 1H), 7.84 (s, 1H), 7.26 (t, *J* = 8.2 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.68 (t, *J* = 7.9 Hz, 1H), 5.51 (s, 2H), 3.90 (s, 3H) ppm. ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 143.8, 137.9, 131.2, 127.2, 124.0, 123.6, 119.6, 116.4, 116.0, 36.0 ppm. MS (ESI, positive ions): *m/z* 174.1028 (calcd for [M-I]⁺: *m/z* 174.1031)

NMR spectra of isolated ligands and complexes

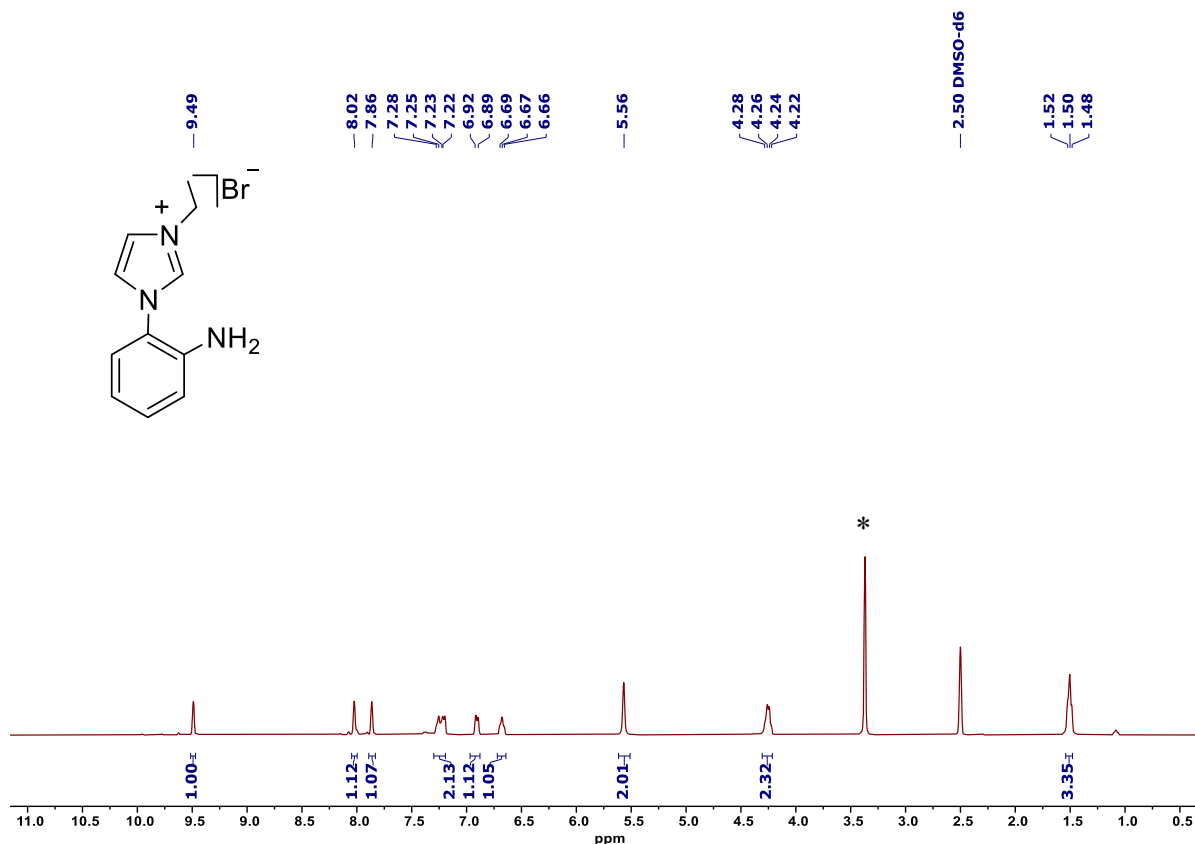


Figure S1. ¹H NMR spectrum of L₁ in DMSO-*d*₆. * indicates the solvent impurity of H₂O in DMSO-*d*₆.

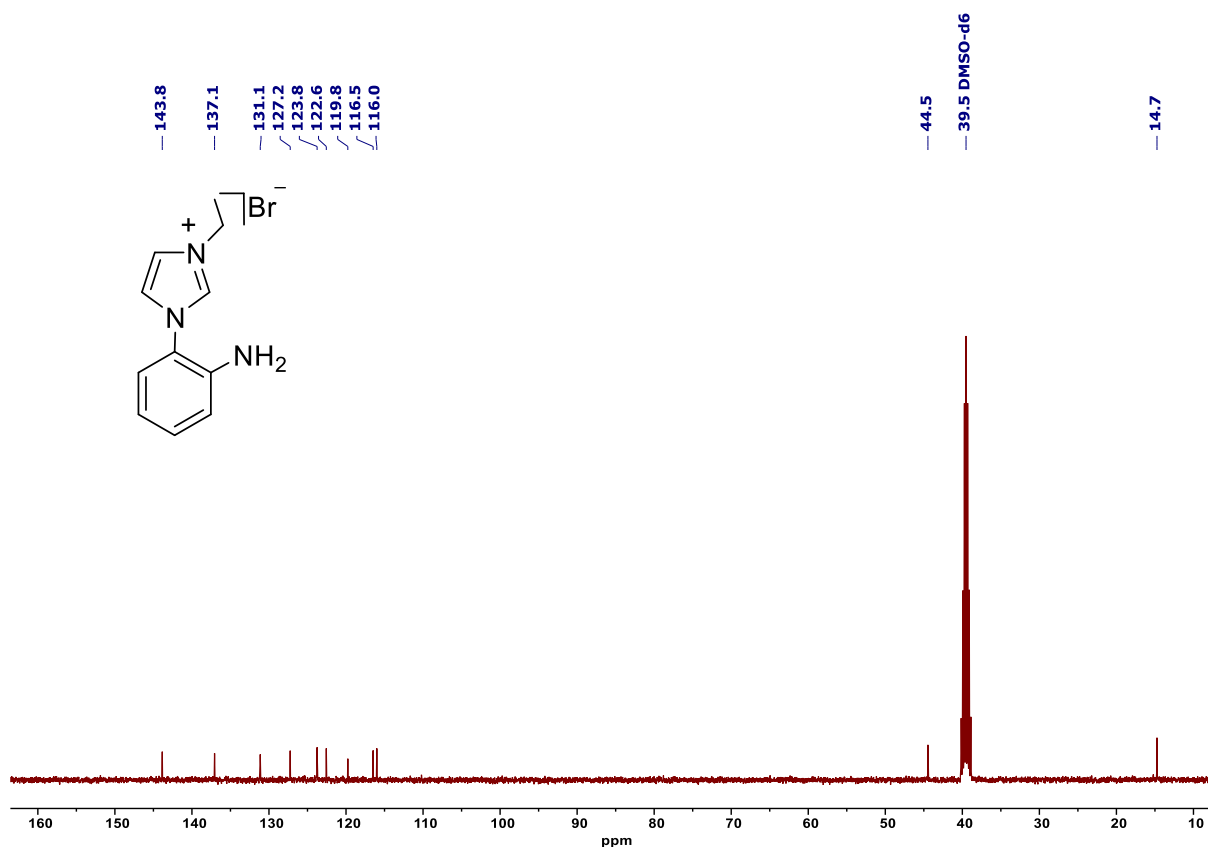


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of L1 in DMSO- d_6 .

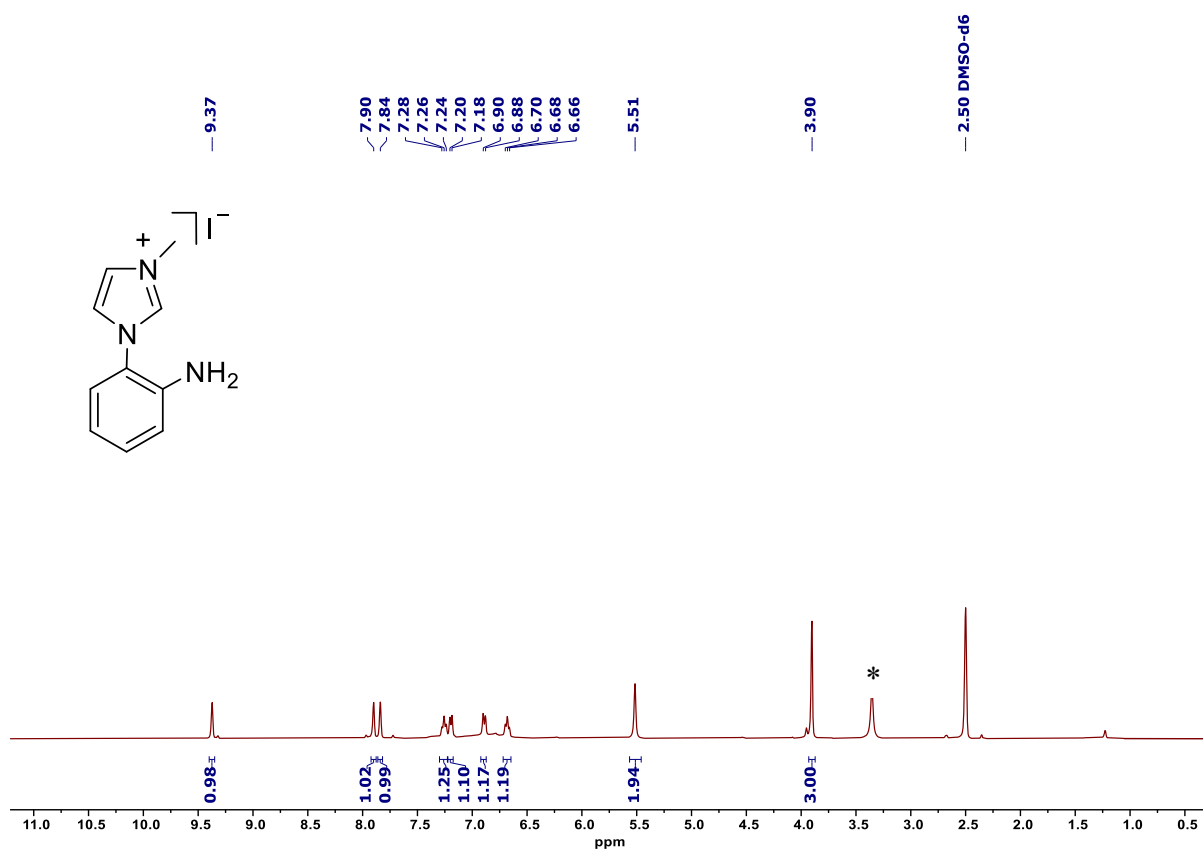


Figure S3. ^1H NMR spectrum of L2 in DMSO- d_6 . * indicates the solvent impurity of H $_2$ O in DMSO- d_6 .

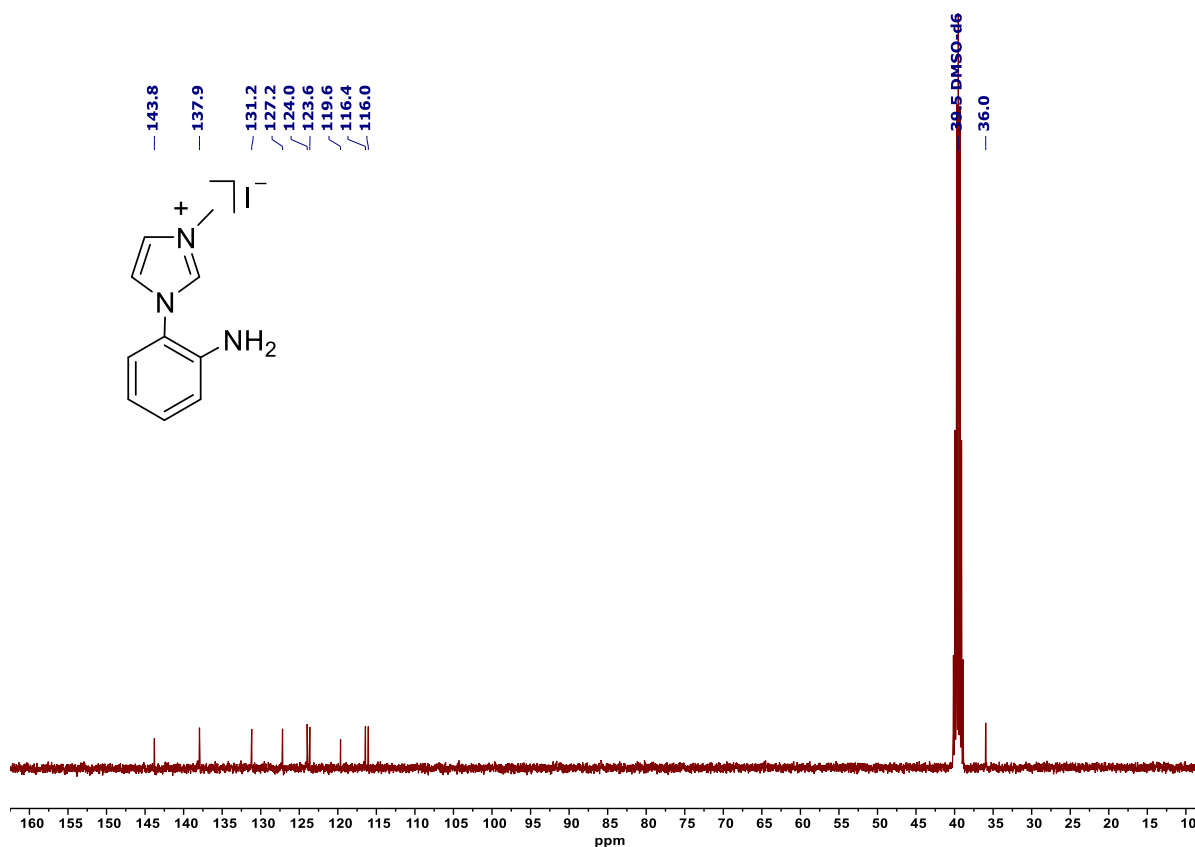
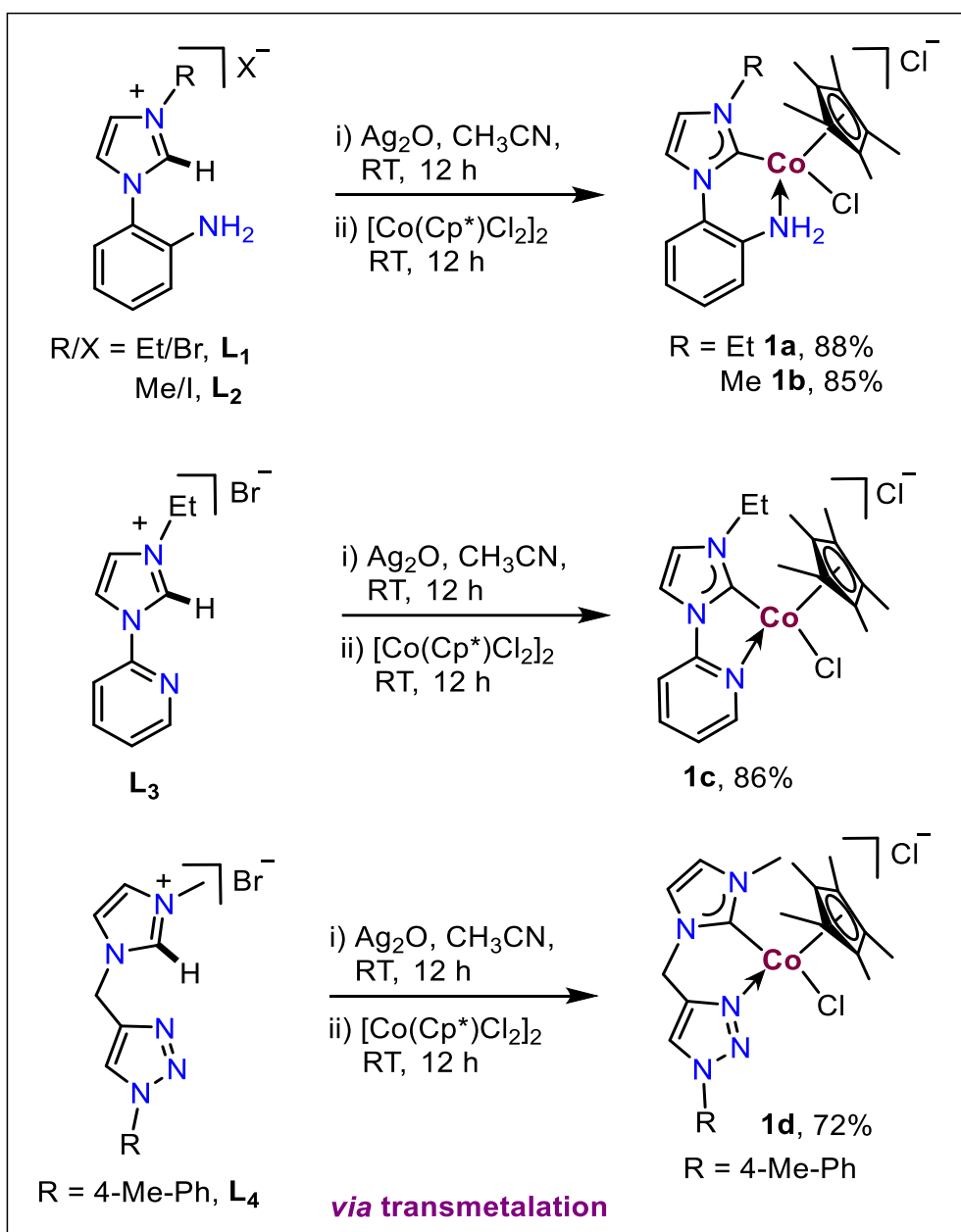


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **L2** in $\text{DMSO-}d_6$.

General procedure for the synthesis of complexes

The ligand **L1-4** (1 equiv.) and Ag_2O (0.6 equiv.) were taken in a Schenk tube under an inert condition, dry acetonitrile was then added to it and the reaction mixture was stirred under dark at room temperature. After 12 h of reaction, metal precursor $[\text{Co}(\text{Cp}^*)\text{Cl}_2]_2$ (0.5 equiv.) was added and again stirred for 12 h at RT. The crude reaction mixture was first filtered through a small pad of celite which was followed by purification *via* column chromatography using DCM/methanol as eluent. The obtained compound was then concentrated and diethyl ether was added to precipitate the compound, which was isolated as a reddish-pink solid in 70-80% yield.



Scheme S2. Synthesis of various Co^{III} -NHC complexes *via* transmetalation strategy.

Complex 1a: Complex **1a** was synthesized following the general procedure using **L1** (250 mg, 0.932 mmol) and isolated as an air-stable reddish-pink solid. Yield: 371 mg (0.820 mmol, 88%). ^1H NMR (500 MHz, CDCl_3) δ 8.30-8.27 (m, 1H), 8.27 (s, *br*, 1H), 8.00 (d, $J = 1.8$ Hz, 1H), 7.69 (d, $J = 1.9$ Hz, 1H), 7.59 (d, $J = 7.8$ Hz, 1H), 7.35 (t, $J = 7.1$ Hz, 1H), 7.28 (d, $J = 7.8$ Hz, 1H), 4.44-4.37 (m, 1H), 4.25-4.19 (m, 1H), 3.63 (*br*, 1H), 1.36 (t, $J = 7.2$ Hz, 3H), 1.14 (s, 15H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 174.5, 133.6, 133.2, 127.6, 127.4, 125.4, 124.7, 122.6, 121.2, 94.7, 46.5, 16.7, 9.3 ppm. MS (ESI, positive ions): m/z 416.1341 (calcd for $[\text{M-Cl}]^+$: m/z 416.1340).

Complex 1b: Complex **1b** was synthesized following the general procedure using **L2** (100 mg, 0.332 mmol) and isolated as an air-stable reddish-pink solid. Yield: 124 mg (0.282 mmol, 85%). ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 7.7$ Hz, 1H), 8.14 (s, *br*, 1H), 7.93 (s, 1H), 7.82 (s, 1H), 7.50 (d, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 6.1$ Hz, 2H), 4.12 (s, 3H), 3.23 (s, *br*, 1H), 1.16 (s, 15H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 134.1, 133.5, 128.8, 127.7, 127.1, 125.1, 121.7, 120.8, 94.7, 38.9, 9.3 ppm. MS (ESI, positive ions): m/z 402.1073 (calcd for $[\text{M}-\text{Cl}]^+$: m/z 402.1147).

Complex 1c: Complex **1c** was synthesized following the general procedure using **L3** (100 mg, 0.393 mmol) and isolated as a hygroscopic reddish-pink solid. Yield: 148 mg (0.338 mmol, 86%). ^1H NMR (500 MHz, CDCl_3) δ 9.44 (s, 1H), 9.02 (d, $J = 8.4$ Hz, 1H), 8.84 (d, $J = 5.8$ Hz, 1H), 8.17 (t, $J = 7.8$ Hz, 1H), 7.56 (s, 1H), 7.45 (t, $J = 7.26$ Hz, 1H), 4.63-4.50 (m, 2H), 1.59 (t, $J = 7.2$ Hz, 3H), 1.39 (s, 15H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 182.9, 153.9, 152.5, 142.9, 126.1, 123.5, 123.5, 115.2, 96.8, 46.6, 16.6, 10.1 ppm. MS (ESI, positive ions): m/z 402.1161 (calcd for $[\text{M}-\text{Cl}]^+$: m/z 402.1147).

Complex 1d: Complex **1d** was synthesized following the general procedure using **L4** (100 mg, 0.299 mmol) and isolated as an air-stable reddish-pink solid. Yield: 112 mg (0.215 mmol, 72%). ^1H NMR (500 MHz, CDCl_3) δ 9.24 (s, 1H), 7.84 (d, $J = 2.0$ Hz, 1H), 7.71 (d, $J = 8.5$ Hz, 2H), 7.31 (d, $J = 8.5$ Hz, 2H), 7.21 (d, $J = 1.8$ Hz, 1H), 6.54 (d, $J = 16.6$ Hz, 1H), 5.38 (d, $J = 16.6$ Hz, 1H), 4.06 (s, 3H), 2.41 (s, 3H), 1.39 (s, 15H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 169.3, 144.8, 140.6, 134.2, 130.6, 126.5, 125.7, 124.1, 120.9, 96.5, 44.7, 38.8, 21.3, 10.1 ppm. MS (ESI, positive ions): m/z 482.1706 (calcd for $[\text{M}-\text{Cl}]^+$: m/z 482.1522).

NMR spectra of the isolated complexes (1a-d)

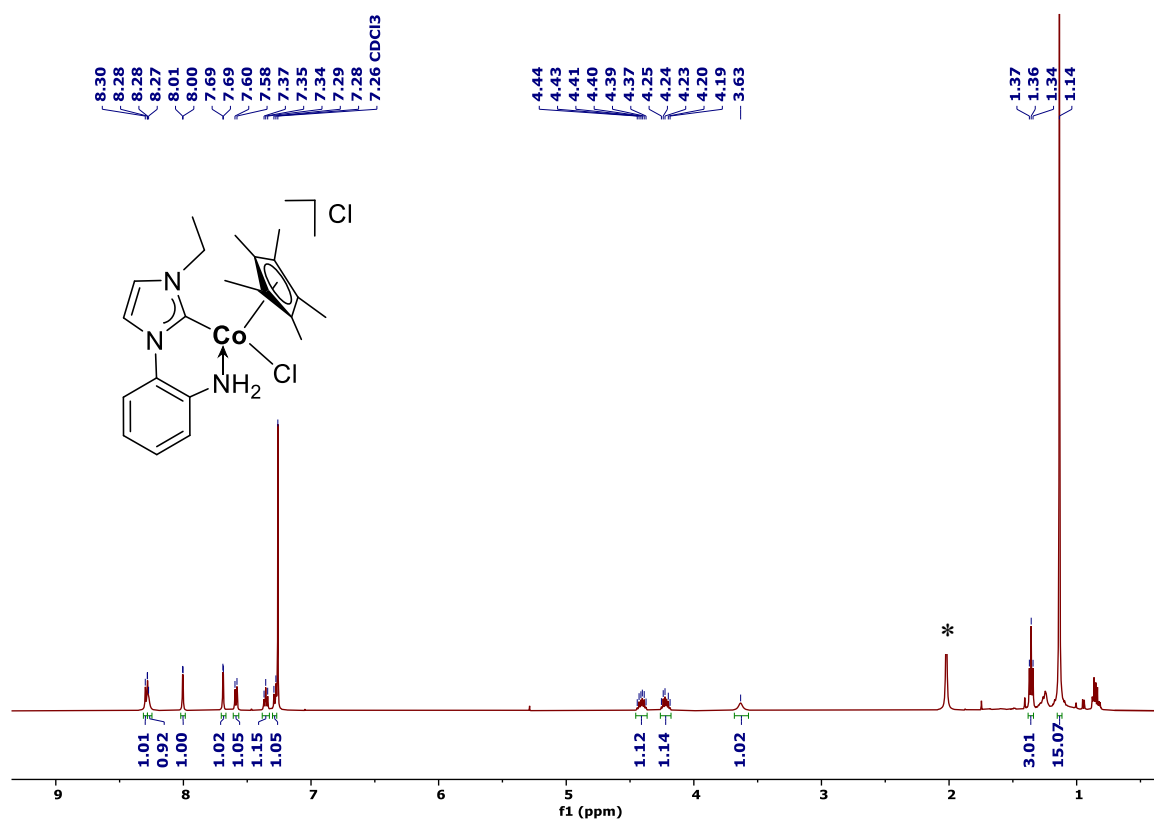


Figure S5. ¹H NMR spectrum of **1a** in CDCl₃. * indicates the solvent impurity of H₂O in CDCl₃.

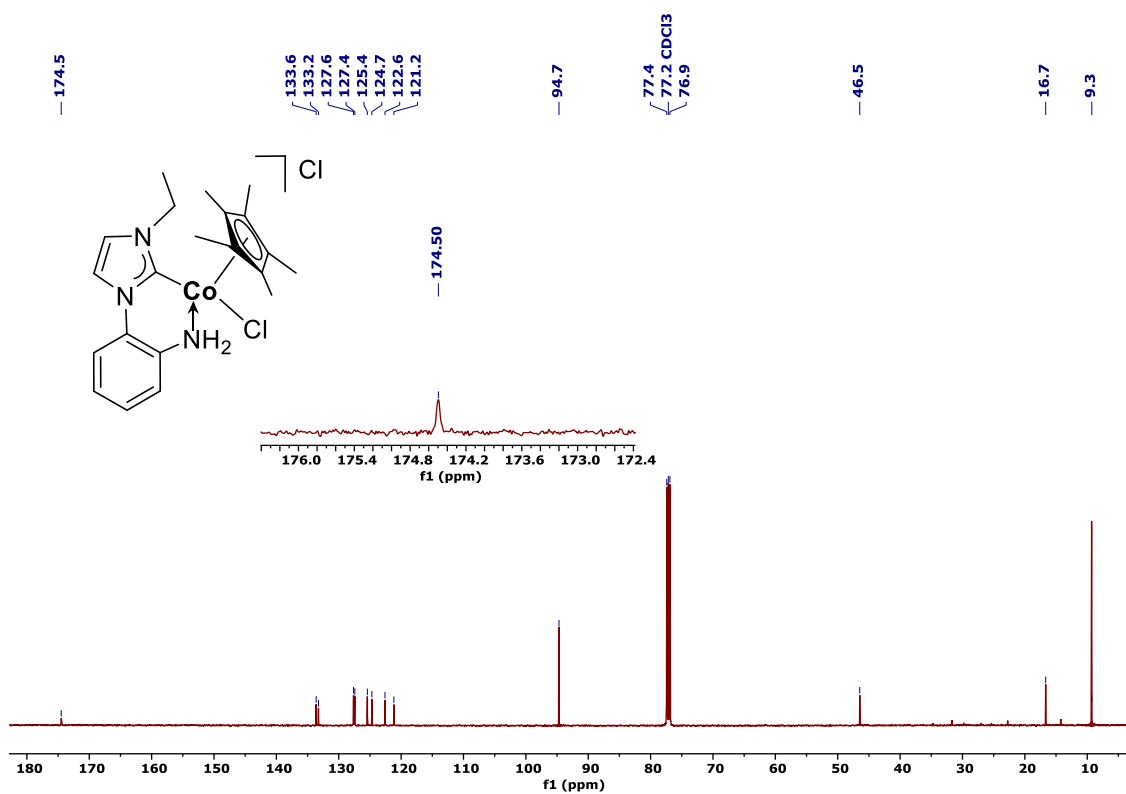


Figure S6. ¹³C{¹H} NMR spectrum of **1a** in CDCl₃.

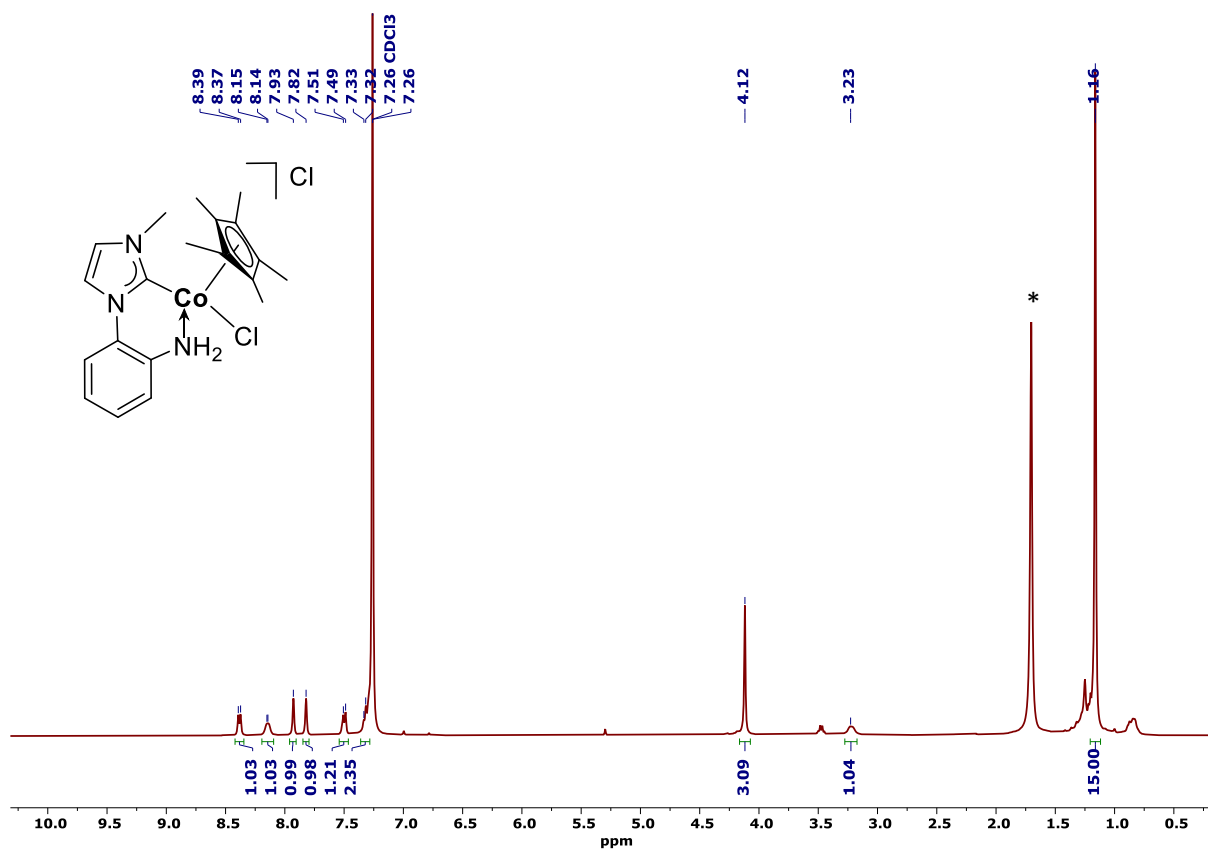


Figure S7. ^1H NMR spectrum of **1b** in CDCl_3 . * indicates the solvent impurity of H_2O in CDCl_3 .

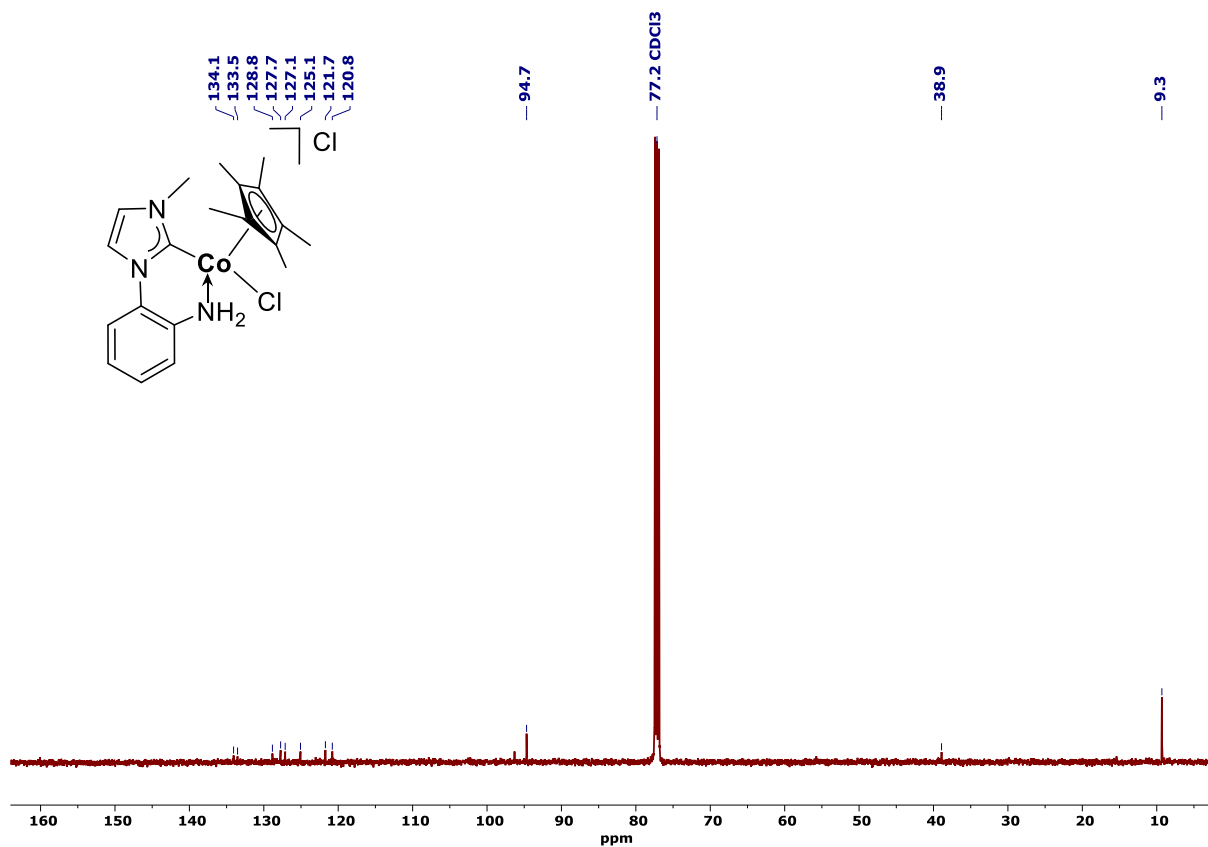


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1b** in CDCl_3 .

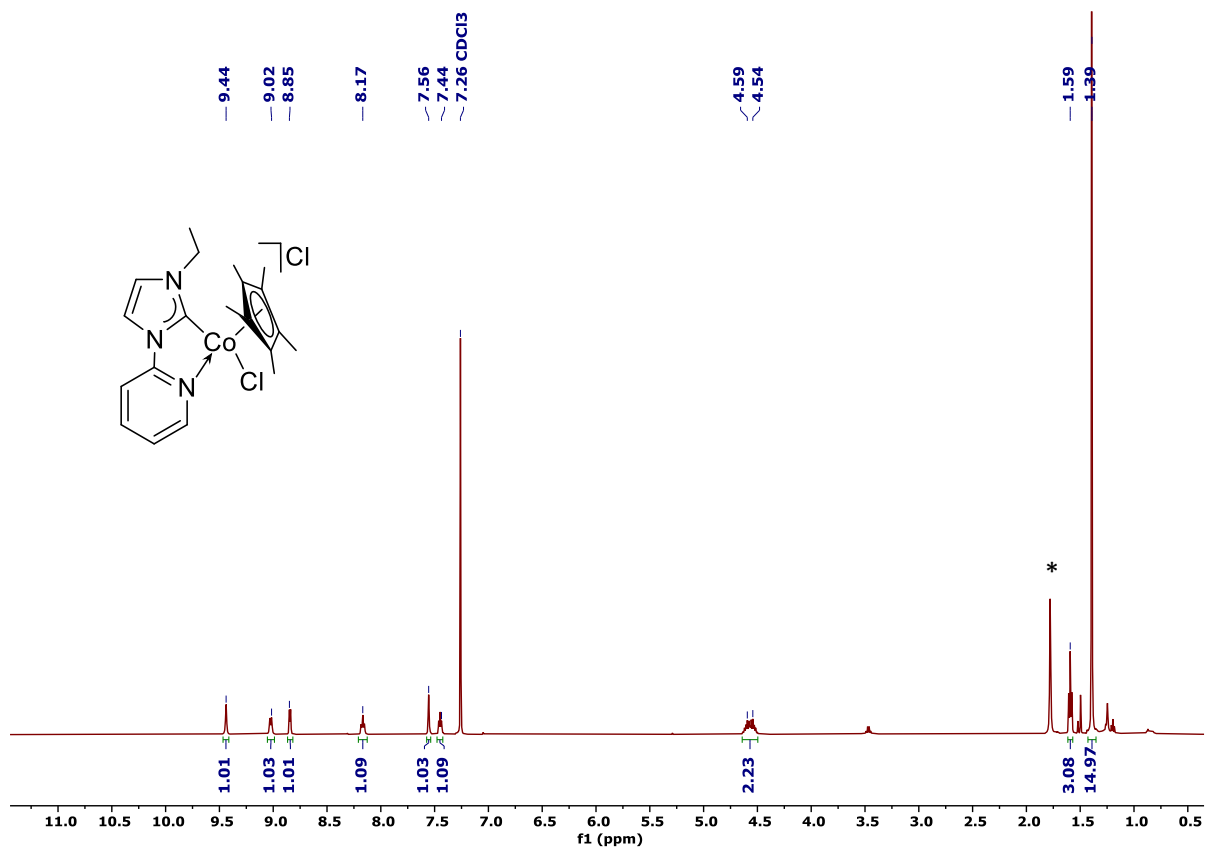


Figure S9. ^1H NMR spectrum of **1c** in CDCl_3 . * indicates the solvent impurity of H_2O in CDCl_3 .

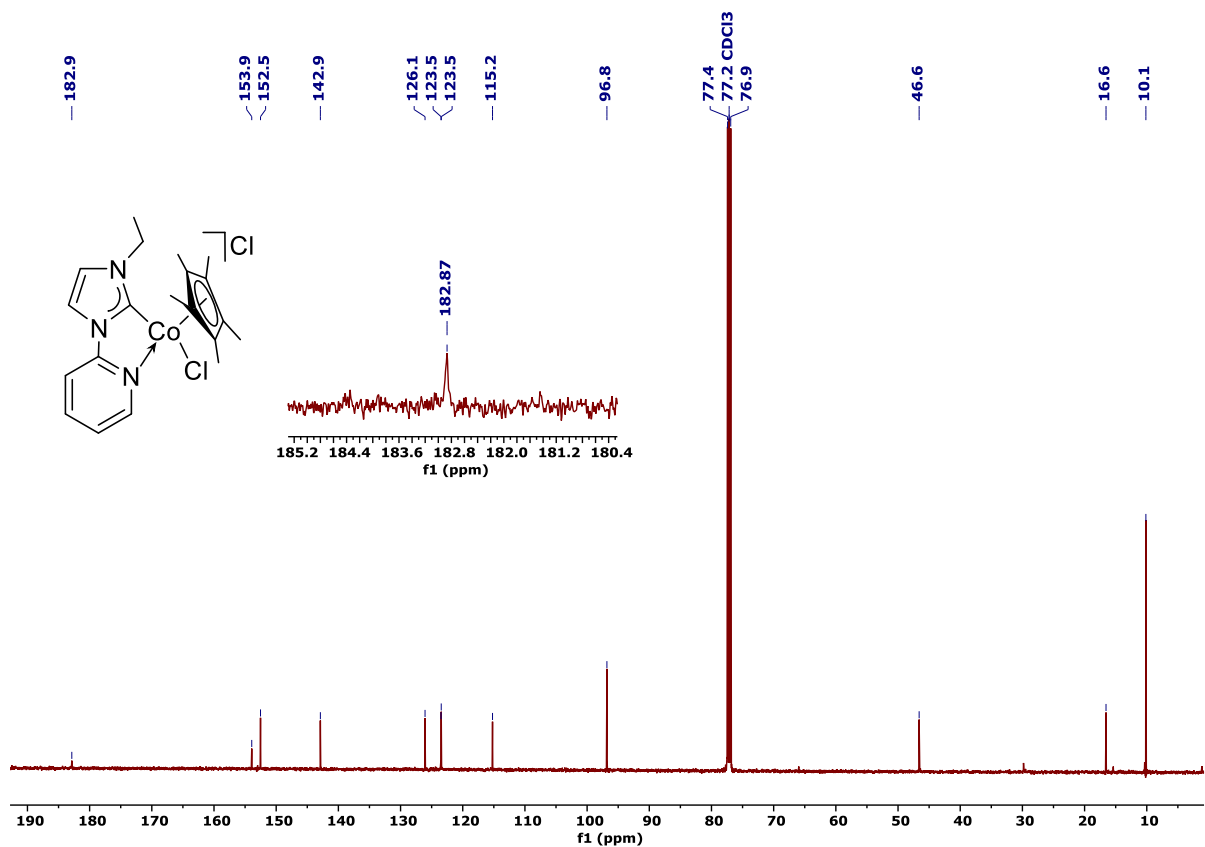


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1c** in CDCl_3 .

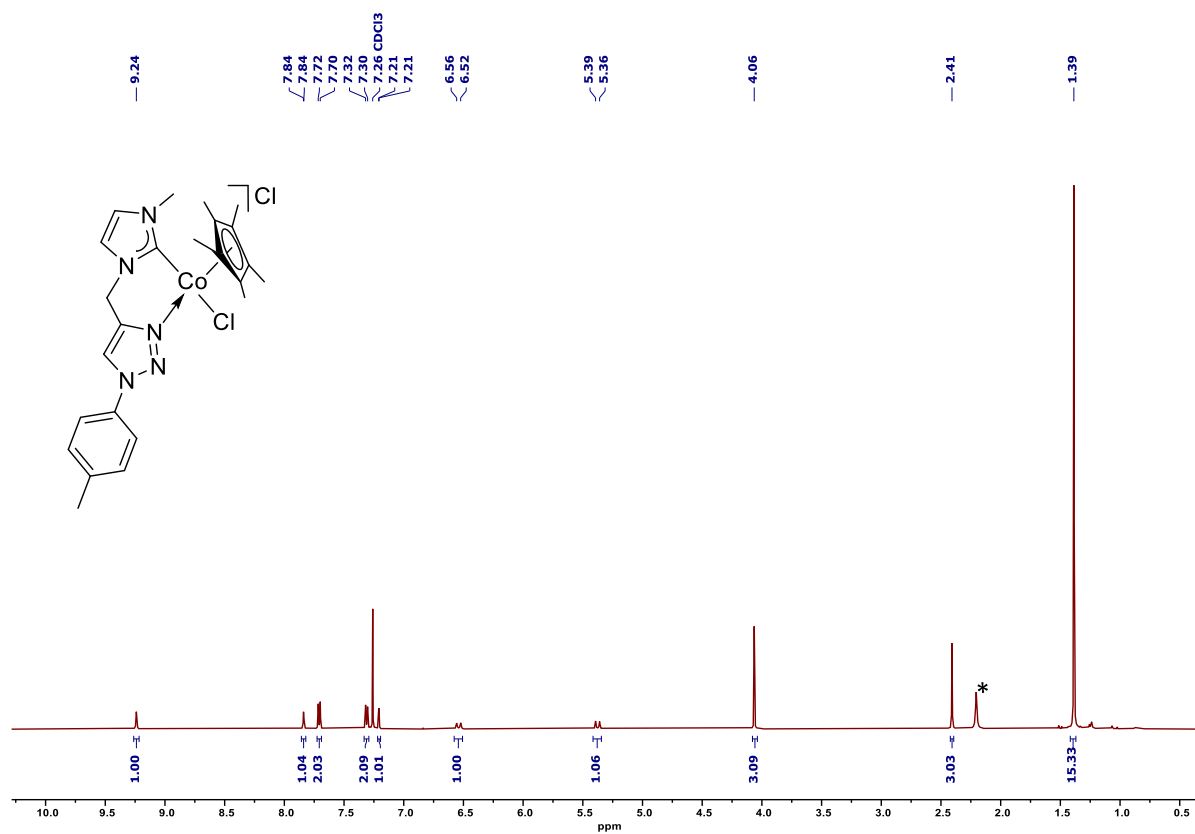


Figure S11. ^1H NMR spectrum of **1d** in CDCl_3 . * indicates the solvent impurity of H_2O in CDCl_3 .

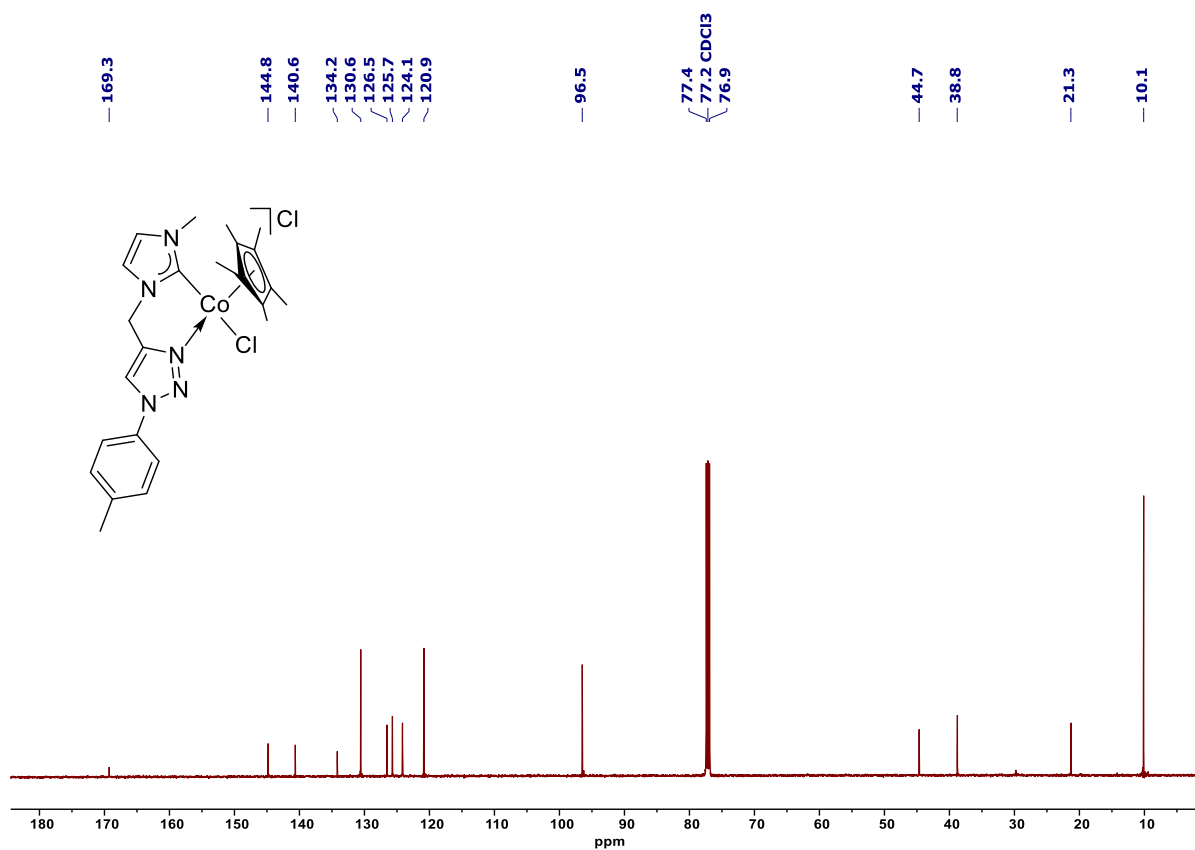


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1d** in CDCl_3 .

Detection of NH₂ proton position in ¹H NMR spectrum of 1a

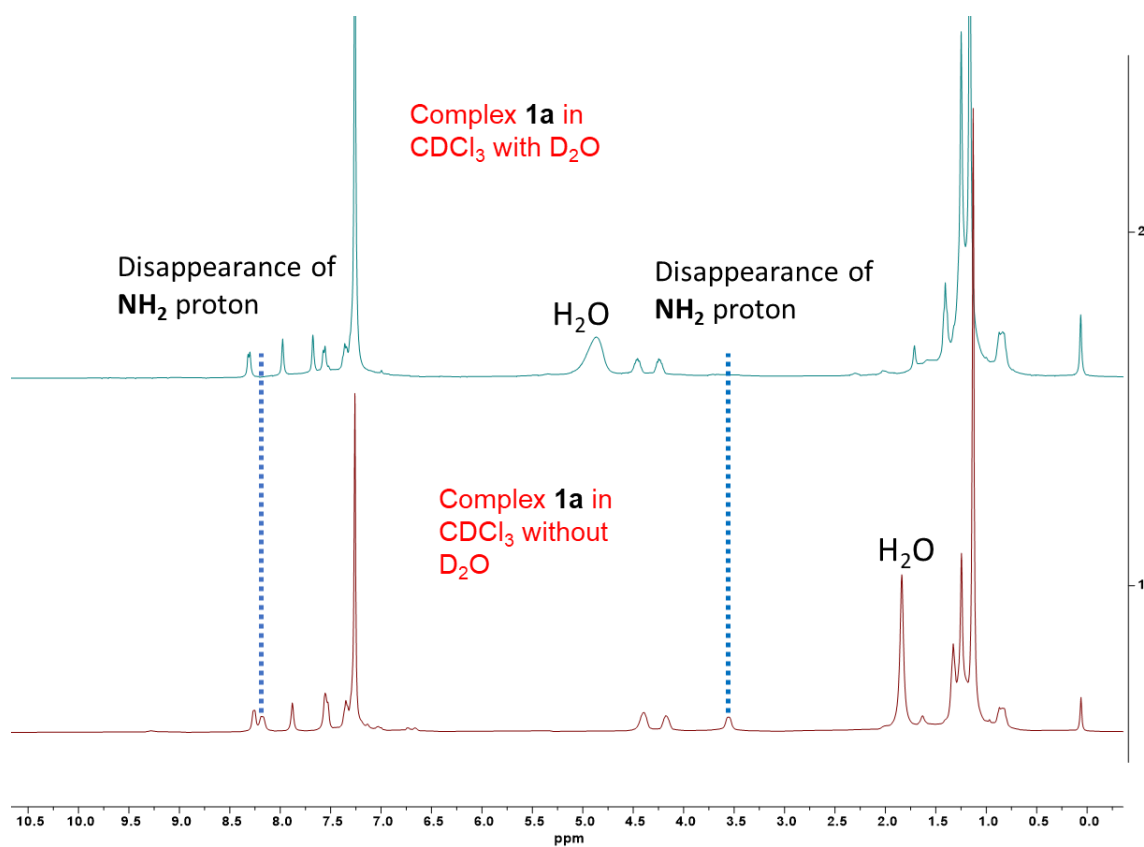


Figure S13. Comparison of ¹H NMR spectrum of 1a in CDCl₃ without D₂O and with D₂O.

ESI-MS (positive-ion) spectra of the synthesized complexes (1a-d)

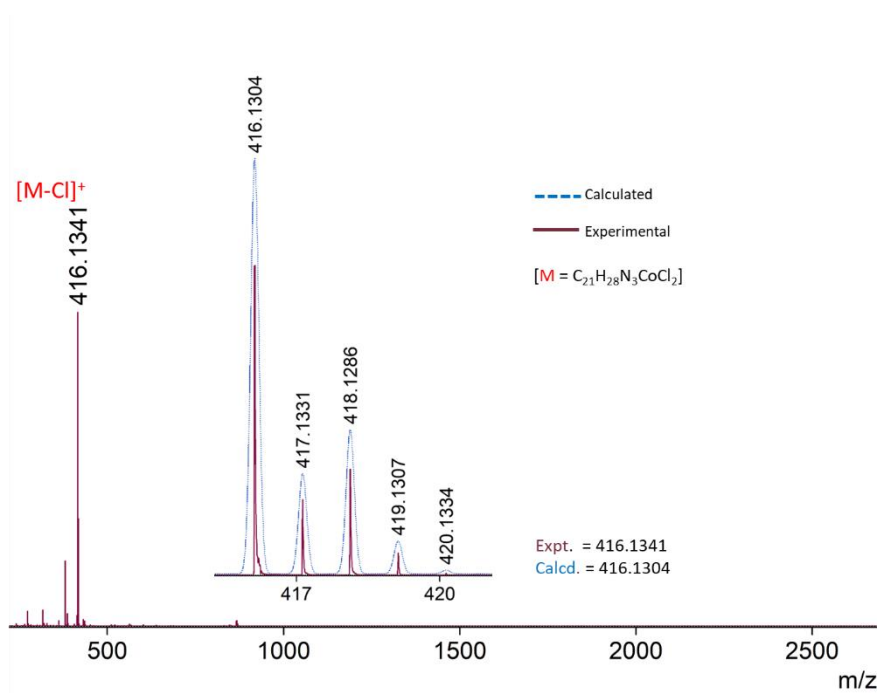


Figure S14. ESI-MS (positive ions) spectrum of the complex 1a.

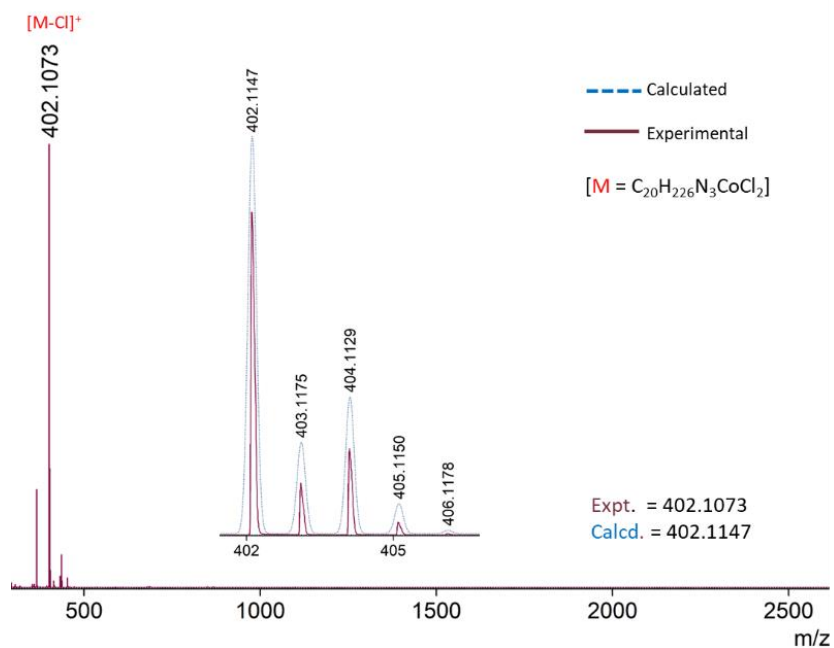


Figure S15. ESI-MS (positive ions) spectrum of the complex **1b**.

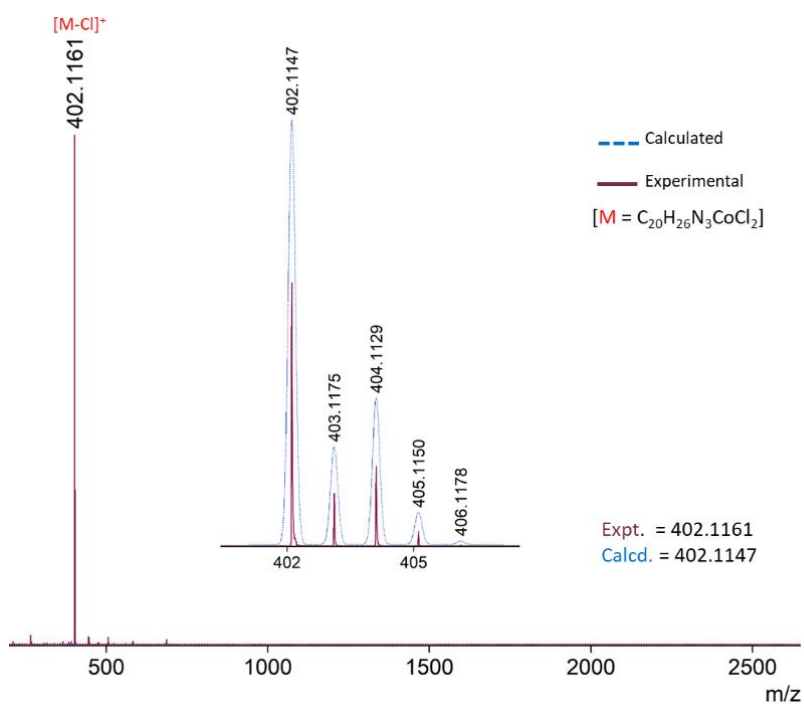


Figure S16. ESI-MS (positive ions) spectrum of the complex **1c**.

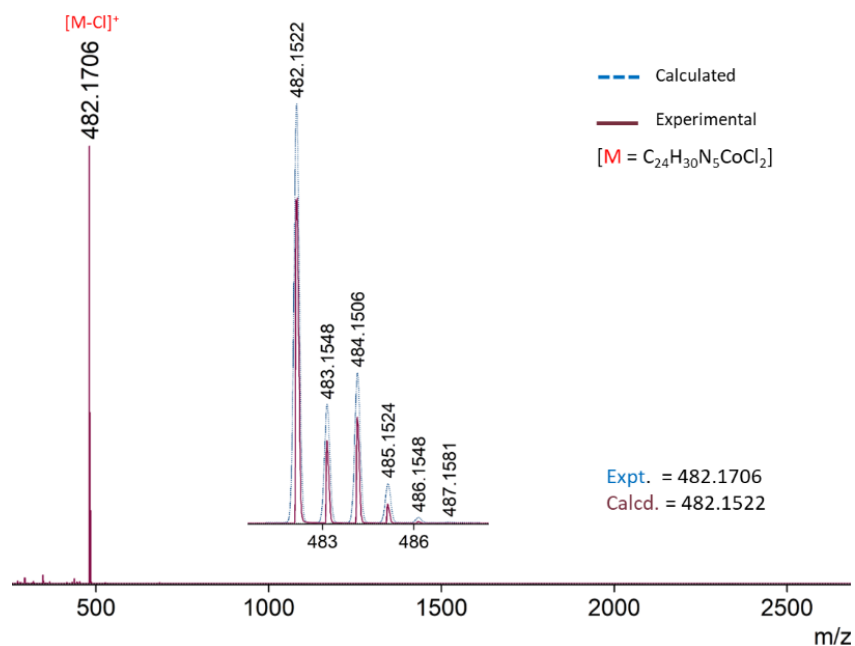
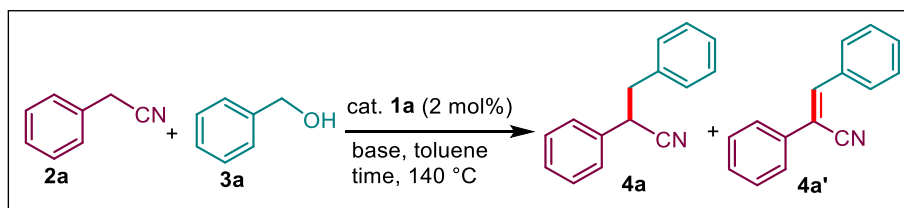


Figure S17. ESI-MS (positive ions) spectrum of the complex **1d**.

Optimization studies:

Screening of base^a



Entry	Cat.	Base	Conv. (%)	Ratio (4a/4a')
1	1a	LiO ^t Bu	26	27/73
2	1a	NaO ^t Bu	56	82/18
3	1a	KO ^t Bu	100	100/0
4	1a	CsOH	95	100/0
5	1a	Cs ₂ CO ₃	82	76/24

^aReaction conditions: **2a** (0.25 mmol), **3a** (0.5 mmol), base (20 mol%), **1a** (2 mol%) in toluene at 140 °C for 12 h. Conversion of **2a** was determined by GC-MS using mesitylene as an internal standard.

Screening of alcohol equivalence^a

Entry	Alcohol equivalence	Conv. (%)	Ratio (4a/4a')
1	1	68	98/2
2	1.5	96	89/11
3	2	100	100/0

^aReaction conditions: **2a** (0.25 mmol), **3a** (x equiv.), KO^tBu (20 mol%), **1a** (2 mol%) in toluene at 140 °C for 6 h. Conversion of **2a** was determined by GC-MS using mesitylene as an internal standard.

Screening of base equivalence^a

Entry	Base loading (x equiv.)	Conv. (%)	Ratio (4a/4a')
1	0.15	93	100/0
2	0.2	100	100/0
3	0.3	100	100/0

^aReaction conditions: **2a** (0.25 mmol), **3a** (0.5 mmol), KO^tBu (x equiv.), **1a** (2 mol%) in toluene at 140 °C for 6 h. Conversion of **2a** was determined by GC-MS using mesitylene as an internal standard.

General procedure for the α -alkylation of nitriles using isolated catalyst

An oven-dried pressure tube was charged with catalyst **1a** (0.01 mmol, 2 mol %), KO^tBu (0.1 mmol, 20 mol%), nitrile (0.5 mmol), and alcohol (1 mmol) in toluene (1 mL). Then the reaction mixture was kept in a preheated oil bath at 140 °C. After completion of the reaction, the pressure tube was cooled to room temperature. The pure products were isolated using column chromatography with ethyl acetate and hexane as eluents.

General procedure for α -alkylation of nitriles using *in situ* generated catalyst

To a pressure tube, [Co(Cp*)Cl₂]₂ (0.002 mmol, 1 mol %), ligand (0.004 mmol, 2 mol%), KO^tBu (0.04 mmol, 20 mol%), were stirred in toluene (1 mL) at 80 °C for 1 h. Then, nitrile (0.2 mmol) and alcohol (0.4 mmol) were added and the reaction mixture was kept in a preheated oil bath at 140 °C for 6 h. After that, the pressure tube was cooled to room temperature. The progress of the reaction was monitored using GC-MS analysis.

Procedure for the calculation of TON for α -alkylation of nitriles

First the catalyst stock solution was prepared by dissolving the catalyst **1a** in dichloromethane solution. An oven dried pressure tube was charged with catalyst **1a** (0.01 mol%) and all the volatiles were dried in high vacuum. After that, KO^tBu (22 mg, 0.2 mmol), nitrile **2a** (117 mg, 1.0 mmol), and benzyl alcohol (216 mg, 2 mmol) were added under inert condition. Then the

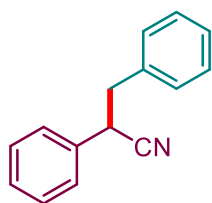
reaction mixture was heated for 12 h at 140 °C and after completion of the reaction, small portion of aliquot was taken for GC-MS analysis. The data based on GC-MS analysis shows 64% conversion of nitrile with 55% selectivity towards product **4a** which gives TON of 5500 and TOF 458 h⁻¹.

General synthetic method for the α -alkylation of nitriles in large scale

An oven-dried pressure tube (25 mL) was charged with catalyst **1a** (0.1 mmol, 2 mol%), KO^tBu (1 mmol, 20 mol%), nitrile (5 mmol), and alcohol (10 mmol), followed by the addition of toluene (6 mL). Then, the tube was kept in an oil bath at 140 °C and heated for 6 h. After completion of the reaction, the desired product **4a** (81% yield) and **6a** (77% yield) were isolated by column chromatography with ethyl acetate and hexane as eluents.

Characterization data of isolated compounds:

2,3-diphenylpropanenitrile (Compound-4a):³ Following the general procedure, the titled

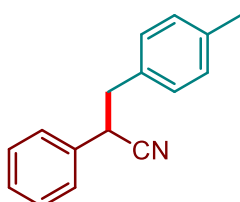


compound was isolated as colourless liquid (92 mg, 0.44 mmol, 89% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane).

¹H NMR (400 MHz, CDCl₃) δ 7.29-7.16 (m, 8H), 7.05 (d, J = 7.7 Hz, 2H), 3.91 (t, J = 7.4 Hz, 1H), 3.13-3.02 (m, 2H) ppm. ¹³C{¹H} NMR (101 MHz,

CDCl₃) δ 136.4, 135.3, 129.3, 129.1, 128.7, 128.3, 127.6, 127.5, 120.5, 42.3, 39.9 ppm.

2-phenyl-3-(*p*-tolyl)propanenitrile (Compound-4b):³ Following the general procedure, the

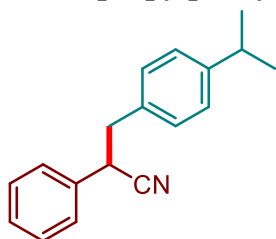


titled compound was isolated as colourless liquid (93 mg, 0.42 mmol, 84% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane).

¹H NMR (400 MHz, CDCl₃) δ 7.29-7.23 (m, 3H), 7.19-7.15 (m, 2H), 7.02 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 8.1 Hz, 2H), 3.88 (t, J = 7.5

Hz, 1H), 3.09-2.98 (m, 2H), 2.24 (s, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 137.1, 135.4, 133.3, 129.4, 129.2, 129.1, 128.2, 127.6, 120.6, 41.9, 40.0, 21.2 ppm.

3-(4-isopropylphenyl)-2-phenylpropanenitrile (Compound-4c):⁴ Following the general

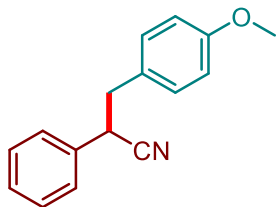


procedure, the titled compound was isolated as white solid (100 mg, 0.40 mmol, 80% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane).

¹H NMR (400 MHz, CDCl₃) δ 7.40-7.33 (m, 3H), 7.32-7.27 (m, 2H), 7.19-7.16 (m, 2H), 7.11-7.08 (m, 2H), 3.98 (dd, J = 8.7, 6.2 Hz, 1H), 3.19-3.08 (m, 2H), 2.93-2.86 (m, 1H), 1.25

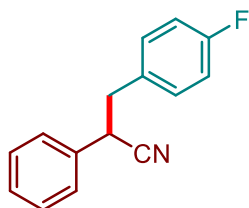
(d, $J = 7.0$ Hz, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.2, 135.6, 133.8, 129.2, 129.1, 128.3, 127.6, 126.8, 120.6, 42.0, 40.1, 33.9, 24.1 ppm.

3-(4-methoxyphenyl)-2-phenylpropanenitrile (Compound-4d):³ Following the general



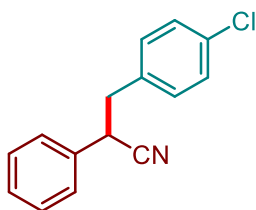
procedure, the titled compound was isolated as colourless liquid (89 mg, 0.37 mmol, 75% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.23 (m, 3H), 7.18-7.15 (m, 2H), 6.96 (d, $J = 8.8$ Hz, 2H), 6.74 (d, $J = 8.8$ Hz, 2H), 3.89-3.86 (m, 1H), 3.70 (s, 3H), 3.08-2.97 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 159.0, 135.4, 130.4, 129.1, 128.4, 128.3, 127.6, 120.6, 114.1, 55.3, 41.5, 40.2 ppm.

3-(4-fluorophenyl)-2-phenylpropanenitrile (Compound-4e):³ Following the general



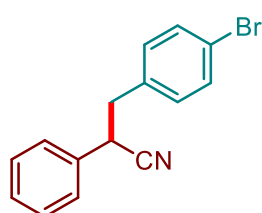
procedure, the titled compound was isolated as white solid (99 mg, 0.44 mmol, 88% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.29-7.24 (m, 3H), 7.17-7.14 (m, 2H), 7.00-6.97 (m, 2H), 6.91-6.86 (m, 2H), 3.89 (dd, $J = 8.1, 6.4$ Hz, 1H), 3.09-3.01 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 163.3, 161.3, 135.0, 132.0, 132.0, 131.0, 130.9, 129.2, 128.4, 127.6, 120.3, 115.7, 115.5, 41.4, 39.9 ppm.

3-(4-chlorophenyl)-2-phenylpropanenitrile (Compound-4f):³ Following the general



procedure, the titled compound was isolated as white solid (99 mg, 0.41 mmol, 82% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.34 (m, 3H), 7.26-7.22 (m, 4H), 7.03 (d, $J = 8.4$ Hz, 2H), 3.98 (t, $J = 7.2$ Hz, 1H), 3.18-3.08 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 134.9, 134.7, 133.5, 130.7, 129.2, 128.9, 128.5, 127.6, 120.2, 41.5, 39.7 ppm.

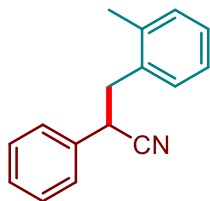
3-(4-bromophenyl)-2-phenylpropanenitrile (Compound-4g):³ Following the general



procedure, the titled compound was isolated as white solid (112 mg, 0.39 mmol, 78% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.9$ Hz, 2H), 7.36-7.34 (m, 3H), 7.25-7.22 (m, 2H), 6.98 (d, $J = 7.8$ Hz, 2H), 3.98 (t, $J = 7.1$ Hz, 1H), 3.17-3.07 (t, $J = 6.1$ Hz, 2H)

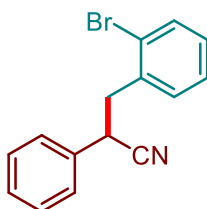
ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 135.2, 134.8, 131.8, 131.1, 129.2, 128.5, 127.6, 121.6, 120.2, 41.6, 39.6 ppm.

2-phenyl-3-(*o*-tolyl)propanenitrile (Compound-4h):⁴ Following the general procedure, the



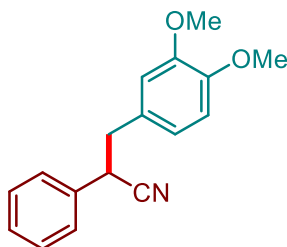
titled compound was isolated as colourless liquid (76 mg, 0.36 mmol, 72% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.34 (m, 3H), 7.30-7.27 (m, 2H), 7.19-7.14 (m, 4H), 3.97 (dd, $J = 8.7, 6.5$ Hz, 1H), 3.27-3.11 (m, 2H), 2.24 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.4, 135.6, 134.8, 130.7, 130.2, 129.2, 128.4, 127.7, 127.5, 126.4, 120.6, 39.6, 38.9, 19.4 ppm.

3-(2-bromophenyl)-2-phenylpropanenitrile (Compound-4i):⁵ Following the general



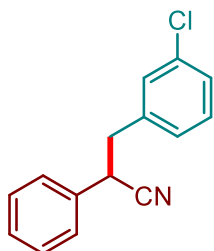
procedure, the titled compound was isolated as white solid (107 mg, 0.37 mmol, 75% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.7$ Hz, 1H), 7.39-7.35 (m, 6H), 7.19-7.15 (m, 2H), 4.21 (t, $J = 7.4$ Hz, 1H), 3.33-3.19 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 136.4, 136.0, 135.4, 133.2, 132.1, 129.5, 129.3, 128.5, 128.0, 127.4, 124.6, 120.2, 43.0, 37.9 ppm.

3-(3,4-dimethoxyphenyl)-2-phenylpropanenitrile (Compound-4j):⁶ Following the general



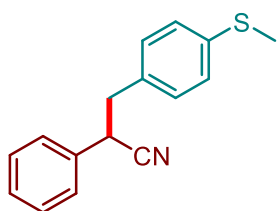
procedure, the titled compound was isolated as white solid (96 mg, 0.36 mmol, 72% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.37-7.30 (m, 3H), 7.25-7.23 (m, 2H), 6.78 (d, $J = 8.1$ Hz, 1H), 6.69 (dd, $J = 8.2, 2.1$ Hz, 1H), 6.52 (d, $J = 2.1$ Hz, 1H), 3.98 (m, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.16-3.06 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.9, 148.5, 135.3, 129.1, 128.8, 128.3, 127.7, 121.6, 120.6, 112.6, 111.3, 56.0, 55.9, 41.9, 40.0 ppm.

3-(3-chlorophenyl)-2-phenylpropanenitrile (Compound-4k):⁷ Following the general



procedure, the titled compound was isolated as white solid (104 mg, 0.43 mmol, 86% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.34 (m, 3H), 7.28-7.26 (m, 2H), 7.25-7.23 (m, 2H), 7.11 (t, $J = 2.0$ Hz, 1H), 7.04-7.02 (m, 1H), 4.02-3.98 (m, 1H), 3.20-3.08 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 138.3, 134.9, 134.5, 130.0, 129.5, 129.3, 128.6, 127.8, 127.6, 120.1, 41.9, 39.6 ppm.

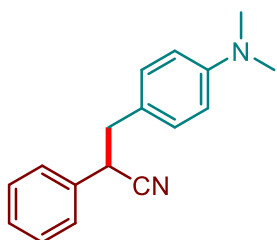
3-(4-(methylthio)phenyl)-2-phenylpropanenitrile (Compound-4l): Following the general



procedure, the titled compound was isolated as colourless liquid (99 mg, 0.39 mmol, 78% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.34 (m, 3H), 7.27 (s, 2H), 7.19 (d, $J = 8.3$ Hz, 2H), 7.06 (d, $J = 8.3$ Hz, 2H), 3.99 (t, $J = 7.3$ Hz, 1H), 3.19-3.08 (m, 2H), 2.48 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 137.7, 135.2, 133.1, 129.8, 129.2, 128.4, 127.6, 126.8, 120.4, 41.8, 39.9, 15.9 ppm.

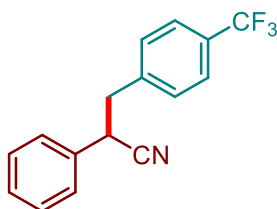
3-(4-(dimethylamino)phenyl)-2-phenylpropanenitrile (Compound-4m):⁵ Following the



general procedure, the titled compound was isolated as yellow solid (88 mg, 0.35 mmol, 70% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.37-7.31 (m, 3H), 7.28 (d, $J = 1.8$ Hz, 2H), 7.01 (d, $J = 8.9$ Hz, 2H), 6.66 (d, $J = 8.7$ Hz, 2H), 3.93 (dd, $J = 8.4, 6.4$ Hz, 1H), 3.13-3.03 (m, 2H),

2.93 (s, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 150.0, 135.8, 130.0, 129.1, 128.2, 127.7, 124.2, 120.9, 112.8, 41.6, 40.7, 40.5 ppm.

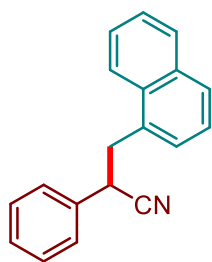
2-phenyl-3-(4-(trifluoromethyl)phenyl)propanenitrile (Compound-4n):⁵ Following the



general procedure, the titled compound was isolated as orange colour solid (103 mg, 0.37 mmol, 75% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.1$ Hz, 2H), 7.40-7.33 (m, 3H), 7.25-7.23 (m, 4H), 4.04 (t, $J = 7.2$ Hz, 1H), 3.28-3.18 (m, 2H) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 134.7, 129.8, 129.3, 128.6, 127.6, 125.7, 125.7, 120.0, 41.9, 39.5 ppm.

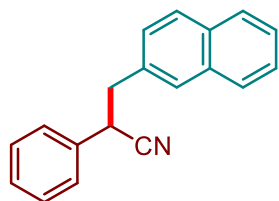
3-(naphthalen-1-yl)-2-phenylpropanenitrile (Compound-4o):³ Following the general



procedure, the titled compound was isolated as colourless liquid (111 mg, 0.43 mmol, 86% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.94 (dd, $J = 15.0, 8.1$ Hz, 2H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.60-7.52 (m, 2H), 7.43-7.32 (m, 7H), 4.19 (t, $J = 7.7$ Hz, 1H), 3.70-3.59 (m, 2H) ppm.

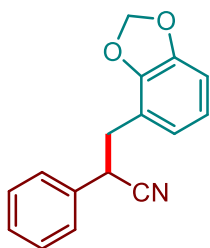
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 135.7, 134.1, 132.3, 131.4, 129.4, 129.2, 128.4, 128.4, 128.2, 127.5, 126.7, 125.9, 125.6, 122.7, 39.7, 38.9 ppm.

3-(naphthalen-2-yl)-2-phenylpropanenitrile (Compound-4p):⁴ Following the general



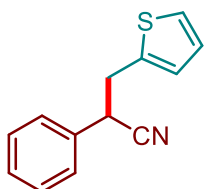
procedure, the titled compound was isolated as white solid (105 mg, 0.41 mmol, 82% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.67 (m, 3H), 7.51 (s, 1H), 7.38-7.37 (m, 2H), 7.24 (m, s, 3H), 7.20-7.13 (m, 3H), 4.00 (t, *J* = 7.1 Hz, 1H), 3.29-3.17 (m, 2H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 135.3, 133.8, 133.5, 132.7, 129.2, 128.4, 128.3, 128.2, 127.8, 127.8, 127.6, 127.2, 126.3, 126.1, 120.5, 42.4, 39.8 ppm.

3-(benzo[d][1,3]dioxol-4-yl)-2-phenylpropanenitrile (Compound-4q):⁴ Following the



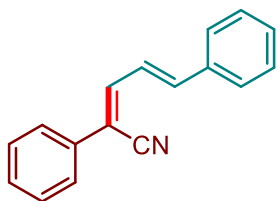
general procedure, the titled compound was isolated as colourless liquid (99 mg, 0.39 mmol, 79% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.33 (m, 3H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.62-6.58 (m, 2H), 5.95 (s, 2H), 3.95 (t, *J* = 7.2 Hz, 1H), 3.10-3.06 (m, 2H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 147.9, 147.0, 135.2, 130.0, 129.1, 128.3, 127.6, 122.6, 120.5, 109.6, 108.5, 101.2, 42.1, 40.1 ppm.

2-phenyl-3-(thiophen-2-yl)propanenitrile (Compound-4r):³ Following the general procedure, the titled compound was isolated as colourless liquid (79 mg, 0.37 mmol, 74%



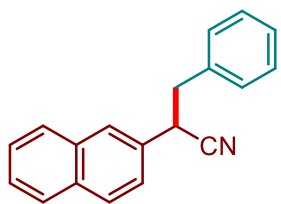
yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.28 (m, 5H), 7.18 (d, *J* = 5.3 Hz, 1H), 6.95-6.92 (m, 1H), 6.86 (d, *J* = 3.8 Hz, 1H), 4.05 (t, *J* = 7.1 Hz, 1H), 3.48-3.33 (m, 2H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 138.0, 134.9, 129.2, 128.5, 127.6, 127.2, 127.1, 125.0, 120.2, 40.2, 36.3 ppm.

2,5-diphenylpenta-2,4-dienitrile (Compound-4s):³ Following the general procedure, the titled compound was isolated as white solid (83 mg, 0.36 mmol, 72%



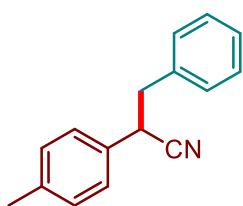
yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.65-7.63 (m, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.43-7.35 (m, 8H), 7.06-7.01 (m, 1H) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 141.7, 141.4, 136.0, 133.5, 129.7, 129.3, 129.2, 129.1, 127.7, 125.8, 125.4, 117.1, 113.4 ppm.

3-phenyl-2-(p-tolyl)propanenitrile (Compound-4t):⁴ Following the general procedure, the titled compound was isolated as colourless liquid (104 mg, 0.40 mmol, 81% yield) using silica



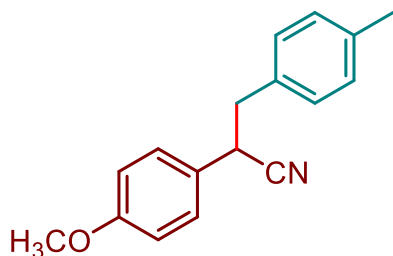
gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.87-7.80 (m, 3H), 7.75 (s, 1H), 7.53-7.51 (m, 2H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.32-7.28 (m, 3H), 7.17 (d, *J* = 7.5 Hz, 2H), 4.18 (t, *J* = 7.1 Hz, 1H), 3.32-3.21 (m, 2H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 136.4, 133.3, 133.0, 132.6, 129.4, 129.1, 128.8, 128.0, 127.9, 127.6, 126.8, 126.8, 126.7, 125.1, 120.5, 42.2, 40.1 ppm.

2-(naphthalen-2-yl)-3-phenylpropanenitrile (Compound-4u):⁹ Following the general



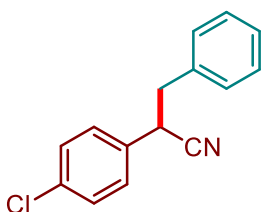
procedure, the titled compound was isolated as colourless liquid (81 mg, 0.36 mmol, 73% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.27 (m, 3H), 7.19-7.15 (m, 6H), 3.97 (dd, *J* = 8.5, 6.4 Hz, 1H), 3.21-3.10 (m, 2H), 2.36 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 138.1, 136.6, 132.4, 129.8, 129.3, 128.7, 127.4, 120.6, 42.3, 39.5, 21.2 ppm.

2-(4-methoxyphenyl)-3-(p-tolyl)propanenitrile (Compound-4v):⁴ Following the general



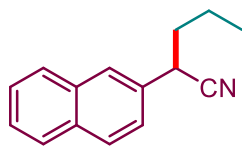
procedure, the titled compound was isolated as colourless liquid (98 mg, 0.38 mmol, 78% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.18 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 3.93 (dd, *J* = 8.3, 6.5 Hz, 1H), 3.81 (s, 3H), 3.16-3.05 (m, 2H), 2.33 (s, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 159.5, 137.0, 133.5, 129.4, 129.2, 128.7, 127.8, 120.8, 55.4, 42.0, 39.2, 21.2 ppm.

2-(4-chlorophenyl)-3-phenylpropanenitrile (Compound-4w):⁴ Following the general



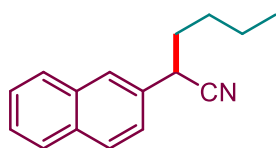
procedure, the titled compound was isolated as white solid (96 mg, 0.4 mmol, 80% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.26-7.19 (m, 5H), 7.09 (d, *J* = 10.9 Hz, 2H), 7.03 (d, *J* = 7.5 Hz, 2H), 3.91 (t, *J* = 7.3 Hz, 1H), 3.14-3.00 (m, 2H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 135.9, 134.4, 133.7, 129.4, 129.3, 129.0, 128.9, 127.7, 120.1, 42.1, 39.3 ppm.

2-(naphthalen-2-yl)pentanenitrile (Compound-6a):¹⁰ Following the general procedure, the



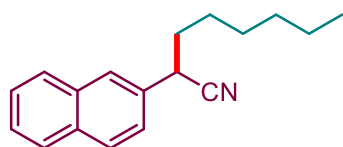
titled compound was isolated as pale yellow liquid (86 mg, 0.41 mmol, 82% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.87-7.82 (m, 4H), 7.54-7.49 (m, 2H), 7.41 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.96 (dd, *J* = 8.5, 6.3 Hz, 1H), 2.05-1.90 (m, 2H), 1.57-1.49 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 133.5, 133.0, 129.2, 128.0, 127.9, 126.8, 126.6, 126.4, 125.0, 121.0, 37.9, 37.5, 20.4, 13.5 ppm.

2-(naphthalen-2-yl)hexanenitrile (Compound-6b): Following the general procedure, the



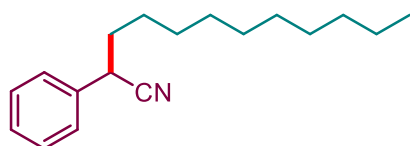
titled compound was isolated as pale yellow liquid (89 mg, 0.40 mmol, 80% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.88-7.82 (m, 4H), 7.55-7.50 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 3.95 (t, *J* = 8.7 Hz, 1H), 2.03-1.92 (m, 2H), 1.53-1.48 (m, 2H), 1.45-1.37 (m, 2H), 0.91 (t, *J* = 6.4 Hz, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 133.4, 133.4, 132.9, 129.1, 128.0, 127.8, 126.8, 126.6, 126.4, 124.9, 121.1, 37.7, 35.6, 29.2, 22.2, 13.9 ppm.

2-(naphthalen-2-yl)octanenitrile (Compound-6c):¹¹ Following the general procedure, the titled compound was isolated as pale yellow liquid (111 mg, 0.44 mmol, 88% yield) using silica



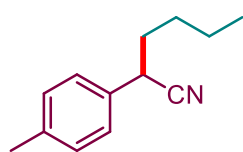
gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.88-7.82 (m, 4H), 7.52-7.51 (m, 2H), 7.41 (d, *J* = 8.3 Hz, 1H), 3.95 (t, *J* = 7.0 Hz, 1H), 2.02-1.94 (m, 2H), 1.54-1.49 (m, 2H), 1.35-1.29 (m, 6H), 0.88 (s, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 133.4, 133.4, 132.9, 129.1, 128.0, 127.8, 126.8, 126.5, 126.4, 124.9, 121.1, 37.7, 35.9, 31.6, 28.8, 27.1, 22.6, 14.1 ppm.

2-phenyldodecanenitrile (Compound-6d): Following the general procedure, the titled



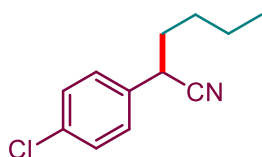
compound was isolated as pale-yellow liquid (100 mg, 0.39 mmol, 78% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.36 (m, 2H), 7.34-7.30 (m, 3H), 3.78-3.75 (m, 1H), 1.96-1.82 (m, 2H), 1.53-1.40 (m, 2H), 1.26 (br, 14H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 136.2, 129.2, 128.1, 127.3, 121.1, 37.7, 37.5, 36.0, 32.0, 29.6, 29.6, 29.4, 29.1, 27.2, 22.8, 14.2 ppm.

2-(p-tolyl)hexanenitrile (Compound-6e): Following the general procedure, the titled



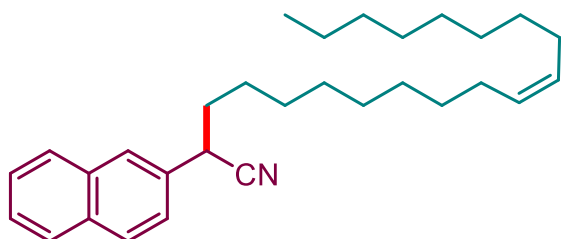
compound was isolated as pale colourless liquid (66 mg, 0.35 mmol, 71% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.20 (q, $J = 8.2$ Hz, 4H), 3.75-3.72 (m, 1H), 2.35 (s, 3H), 1.95-1.81 (m, 2H), 1.52-1.33 (m, 4H), 0.91 (t, $J = 7.2$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 137.9, 133.2, 129.8, 127.2, 121.2, 37.1, 35.7, 29.2, 22.2, 21.1, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{17}\text{NNa}$ 210.1259; Found 210.1248.

2-(4-chlorophenyl)hexanenitrile (Compound-6f): Following the general procedure, the



titled compound was isolated as pale colourless liquid (79 mg, 0.38 mmol, 76% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.34 (m, $J = 8.5$ Hz, 2H), 7.27 (s, *br*, 1H), 7.25 (s, *br*, 1H), 3.76-3.73 (m, 1H), 1.95-1.80 (m, 2H), 1.50-1.32 (m, 4H), 0.91 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 134.7, 134.2, 129.4, 128.7, 120.6, 37.0, 35.6, 29.2, 22.2, 13.9 ppm.

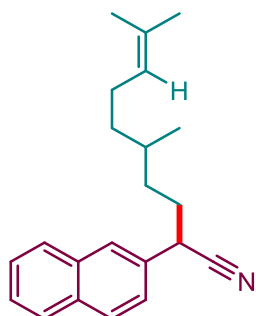
2-(naphthalen-2-yl)icos-11-enenitrile (Compound-6g): Following the general procedure,



the titled compound was isolated as pale colourless liquid (117 mg, 0.42 mmol, 85% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.87-7.81 (m, 4H), 7.54-7.49 (m, 2H), 7.41 (dd, $J = 8.4, 2.3$ Hz, 1H), 5.39-5.32 (m, 2H), 3.94 (dd, $J = 8.6, 6.2$ Hz, 1H), 2.03-1.94 (m, 6H), 1.55-1.49 (m, 2H), 1.37-1.28 (m, 22H), 0.91-0.88 (m, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 133.5, 133.5, 132.9, 130.1, 129.9, 129.1, 128.0, 127.8, 126.8, 126.6, 126.4, 124.9, 121.0, 37.7, 35.9, 29.9, 29.8, 29.8, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.3, 29.1, 27.4, 27.3, 27.2, 22.8, 14.2 ppm. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{43}\text{N}$ 418.3474; Found 418.3454.

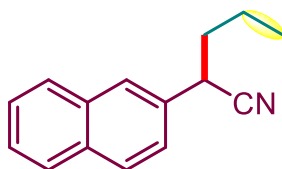
5,9-dimethyl-2-(naphthalen-2-yl)dec-8-enenitrile-2-(naphthalen-2-yl)octanenitrile

(Compound-6h): Following the general procedure, the titled compound was isolated as pale



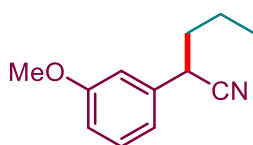
yellow liquid (127 mg, 0.41 mmol, 83% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.89-7.82 (m, 4H), 7.55-7.49 (m, 2H), 7.41 (d, $J = 8.7$ Hz, 1H), 5.07 (t, $J = 8.0$ Hz, 1H), 3.94-3.89 (m, 1H), 2.02-1.90 (m, 4H), 1.68 (s, 3H), 1.58 (s, 3H), 1.48 (s, 2H), 1.34-1.26 (m, 2H), 1.17-1.12 (m, 1H), 0.89 (d, $J = 6.8$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 133.4, 132.9, 131.5, 129.1, 128.0, 127.8, 126.8, 126.6, 126.4, 126.4, 124.9, 124.6, 121.1, 121.1, 37.9, 36.9, 36.7, 34.3, 33.6, 33.5, 32.1, 25.8, 25.5, 25.5, 19.5, 19.4, 17.8 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{27}\text{NNa}$ 328.2041; Found 328.2025.

2-(naphthalen-2-yl)pentanenitrile (Compound-6i):¹⁰ Following the general procedure, the



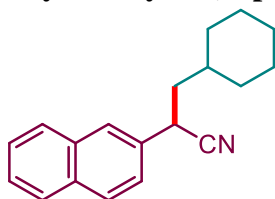
titled compound was isolated as pale yellow liquid (65 mg, 0.31 mmol, 62% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.82 (m, 4H), 7.53-7.49 (m, 2H), 7.40 (dd, $J = 8.6, 2.0$ Hz, 1H), 3.96 (dd, $J = 8.5, 6.3$ Hz, 1H), 2.06-1.90 (m, 2H), 1.61-1.58 (m, 1H), 1.53-1.49 (m, 1H), 0.98 (t, $J = 7.4$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 133.4, 132.9, 129.2, 128.0, 127.9, 126.8, 126.6, 126.4, 125.0, 121.1, 37.9, 37.5, 20.5, 13.6 ppm.

2-(3-methoxyphenyl)pentanenitrile (Compound-6j): Following the general procedure, the



titled compound was isolated as pale yellow liquid (71 mg, 0.37 mmol, 75% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.28 (m, 1H), 6.92-6.84 (m, 3H), 3.82 (s, 3H), 3.73 (dd, $J = 8.5, 6.3$ Hz, 1H), 1.97-1.81 (m, 2H), 1.52-1.34 (m, 4H), 0.91 (t, $J = 7.27$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 160.2, 137.7, 130.2, 121.0, 119.7, 113.4, 113.2, 55.5, 37.5, 35.7, 29.3, 22.2, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{NH}_4]^+$ Calcd for $\text{C}_{13}\text{H}_{17}\text{NONH}_4$ 221.1654; Found 221.1653.

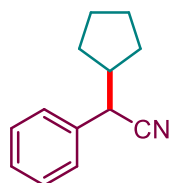
3-cyclohexyl-2-(naphthalen-2-yl)propanenitrile (Compound-6k): Following the general



procedure, the titled compound was isolated as colourless liquid (92 mg, 0.35 mmol, 70% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.87-7.81 (m, 4H), 7.54-7.49 (m, 2H), 7.42-7.39 (m, 1H), 7.26 (s, 1H), 4.02

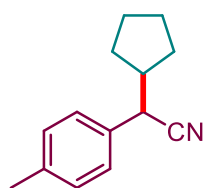
(dd, $J = 9.8, 6.2$ Hz, 1H), 1.98-1.94 (m, 1H), 1.88-1.86 (m, 1H), 1.80-1.67 (m, 5H), 1.59-1.58 (m, 1H), 1.31-1.28 (m, 1H), 1.23-1.14 (m, 2H), 1.04-0.96 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 134.0, 133.6, 133.0, 129.2, 128.0, 127.9, 126.8, 126.6, 126.3, 125.0, 121.2, 43.7, 35.5, 35.2, 33.5, 32.6, 26.5, 26.1, 26.0 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{21}\text{NNa}$ 286.1572; Found 286.1558.

2-cyclopentyl-2-phenylacetonitrile (Compound-6l):¹² Following the general procedure, the



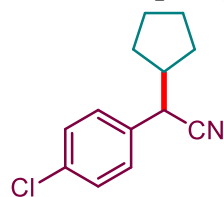
titled compound was isolated as colourless liquid (74 mg, 0.4 mmol, 80% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.31 (m, 5H), 3.71 (d, $J = 7.7$ Hz, 1H), 2.31 (q, $J = 6.8$ Hz, 1H), 1.88-1.83 (m, 1H), 1.73-1.69 (m, 3H), 1.58-1.44 (m, 2H), 1.39-1.34 (m, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ δ 136.0, 129.0, 128.0, 127.7, 120.7, 45.4, 42.6, 31.1, 30.4, 25.0, 24.9 ppm.

2-cyclopentyl-2-(p-tolyl)acetonitrile (Compound-6m):¹² Following the general procedure,



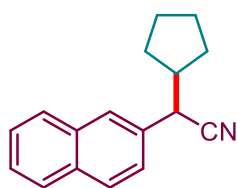
the titled compound was isolated as colourless liquid (46 mg, 0.38 mmol, 76% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.21-7.16 (m, 4H), 3.67 (d, $J = 7.7$ Hz, 1H), 2.35 (s, 3H), 2.31-2.27 (m, 1H), 1.88-1.82 (m, 1H), 1.74-1.69 (m, 3H), 1.59-1.49 (m, 3H), 1.37-1.30 (m, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 137.8, 133.0, 129.6, 127.6, 120.8, 45.3, 42.2, 31.0, 30.3, 25.0, 24.9, 21.1 ppm.

2-(4-chlorophenyl)-2-cyclopentylacetonitrile (Compound-6n):¹² Following the general



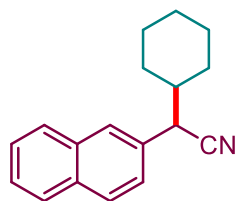
procedure, the titled compound was isolated as white solid (87 mg, 0.39 mmol, 79% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.33 (m, 2H), 7.27-7.26 (m, 1H), 7.25-7.24 (m, 1H), 3.69 (d, $J = 7.8$ Hz, 1H), 2.31-2.23 (m, 1H), 1.87-1.81 (m, 1H), 1.72-1.67 (m, 3H), 1.61-1.54 (m, 2H), 1.51-1.44 (m, 1H), 1.37-1.28 (m, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 134.5, 134.1, 129.3, 129.1, 120.2, 45.3, 42.1, 31.1, 30.3, 25.0, 24.9 ppm.

2-cyclopentyl-2-(naphthalen-2-yl)acetonitrile (Compound-6o): Following the general



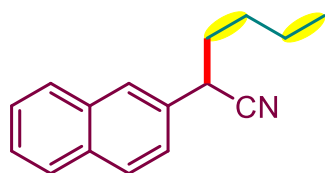
procedure, the titled compound was isolated as white solid (92 mg, 0.39 mmol, 78% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.80 (m, 3H), 7.80 (s, 1H), 7.53-7.50 (m, 2H), 7.42 (d, $J = 8.4$ Hz, 1H), 3.89 (d, $J = 7.7$ Hz, 1H), 2.47-2.38 (m, 1H), 1.90-1.84 (m, 1H), 1.75-1.68 (m, 3H), 1.62-1.53 (m, 3H), 1.43-1.38 (m, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 133.4, 133.3, 132.9, 129.0, 128.0, 127.8, 126.7, 126.5, 125.3, 120.7, 45.3, 42.7, 31.1, 30.4, 25.1, 25.0 ppm.

2-cyclohexyl-2-(naphthalen-2-yl)acetonitrile (Compound-6p):¹² Following the general



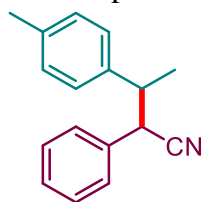
procedure, the titled compound was isolated as colourless liquid (92 mg, 0.37 mmol, 74% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.86-7.83 (m, 3H), 7.78 (s, 1H), 7.54-7.48 (m, 2H), 7.38-7.36 (m, 1H), 3.80 (d, $J = 6.6$ Hz, 1H), 1.88-1.84 (m, 1H), 1.76-1.67 (m, 3H), 1.60-1.58 (m, 2H), 1.23-1.19 (m, 5H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 133.4, 133.0, 132.2, 128.9, 128.0, 127.9, 127.3, 126.8, 126.6, 125.6, 120.2, 44.7, 42.9, 31.5, 29.8, 26.1, 26.0, 26.0 ppm.

2-(naphthalen-2-yl)hexanenitrile (Compound-6q): Following the general procedure, the



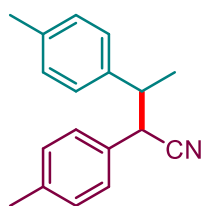
titled compound was isolated as pale yellow liquid (71 mg, 0.32 mmol, 65% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.82 (m, 4H), 7.54-7.49 (m, 2H), 7.41 (dd, $J = 8.6, 2.0$ Hz, 1H), 3.94 (m, 1H), 2.03-1.96 (m, 2H), 1.53-1.48 (m, 1H), 1.42-1.35 (m, 1H), 0.92 (t, $J = 7.2$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 133.5, 133.4, 132.9, 132.9, 129.1, 128.0, 127.8, 126.8, 126.6, 126.4, 124.9, 121.1, 37.7, 35.6, 29.3, 22.2, 13.9 ppm.

2-phenyl-3-(p-tolyl)butanenitrile (Compound-6r): Following the general procedure, the titled compound was isolated as colourless liquid (83 mg, 0.35 mmol, 71% yield) using silica

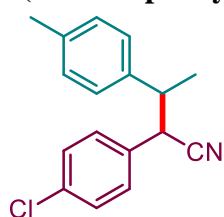


gel column chromatography (2-5% ethyl acetate in hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.31-7.30 (m, 3H), 7.13-7.08 (m, 2H), 7.10-7.08 (m, 2H), 7.01-6.99 (m, 2H), 3.92 (d, $J = 7.2$ Hz, 1H), 3.23-3.16 (m, 1H), 2.32 (s, 3H), 1.35 (d, $J = 7.0$ Hz, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 138.2, 137.2, 134.5, 129.3, 128.8, 128.4, 128.2, 127.8, 120.2, 45.8, 44.7, 21.2, 19.1 ppm. HRMS (ESI) m/z : $[\text{M}+\text{NH}_4]^+$ Calcd for $\text{C}_{17}\text{H}_{17}\text{NNH}_4$ 253.1705; Found 253.1701.

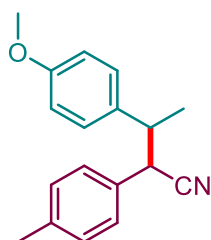
2,3-di-p-tolylbutanenitrile (Compound-6s): Following the general procedure, the titled compound was isolated as white solid (82 mg, 0.33 mmol, 66% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.12-7.09 (m, 4H), 7.02-7.00 (m, 4H), 3.87 (d, *J* = 7.3 Hz, 1H), 3.22-3.15 (m, 1H), 2.34-2.33 (m, 6H), 1.32 (d, *J* = 7.1 Hz, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 138.3, 138.0, 137.1, 131.4, 129.4, 129.2, 128.2, 127.7, 120.4, 45.4, 44.6, 21.2, 19.0 ppm. HRMS (ESI) *m/z*: [M+NH₄]⁺ Calcd for C₁₈H₁₉NNH₄ 267.1861; Found 267.1861.



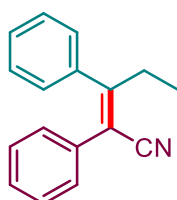
2-(4-chlorophenyl)-3-(p-tolyl)butanenitrile (Compound-6t): Following the general procedure, the titled compound was isolated as white solid (92 mg, 0.34 mmol, yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.27 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.03-6.95 (m, 4H), 3.93 (d, *J* = 4.2 Hz, 1H), 3.20-3.16 (m, 1H), 2.32 (s, 3H), 1.37 (d, *J* = 7.0 Hz, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 137.5, 137.4, 134.2, 132.9, 129.7, 129.3, 129.0, 127.8, 119.7, 45.1, 44.5, 21.2, 18.9 ppm.



3-(4-methoxyphenyl)-2-(p-tolyl)butanenitrile (Compound-6u): Following the general procedure, the titled compound was isolated as colourless liquid (85 mg, 0.32 mmol, 68 % yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (500 MHz, CDCl₃) δ 7.23-7.28 (m, 3H), 7.19-7.18 (m, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.92 (d, *J* = 6.4 Hz, 1H), 3.78 (s, 3H), 3.19-3.14 (m, 1H), 1.44 (d, *J* = 7.0 Hz, 3H) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 158.9, 134.9, 134.0, 128.8, 128.6, 128.1, 128.1, 119.9, 114.1, 55.4, 46.3, 44.4, 17.5 ppm. HRMS (ESI) *m/z*: [M+NH₄]⁺ Calcd for C₁₇H₁₇NONH₄ 269.1654; Found 269.1650.



2,3-diphenylpent-2-enenitrile (Compound-6v):^{13a} Following the general procedure, the titled compound was isolated as yellow liquid (72 mg, 0.31 mmol, 64% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.26-7.23 (m, 4H), 7.17-7.04 (m, 6H), 3.01-2.94 (m, 2H), 1.09 (t, *J* = 7.6 Hz, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 161.5, 137.9, 133.9, 129.6, 128.6, 128.4, 128.1, 119.0, 111.4, 32.5, 12.8 ppm. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd C₁₇H₁₅NNa 256.1102; Found 256.1116.



^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the isolated compounds from catalytic reactions

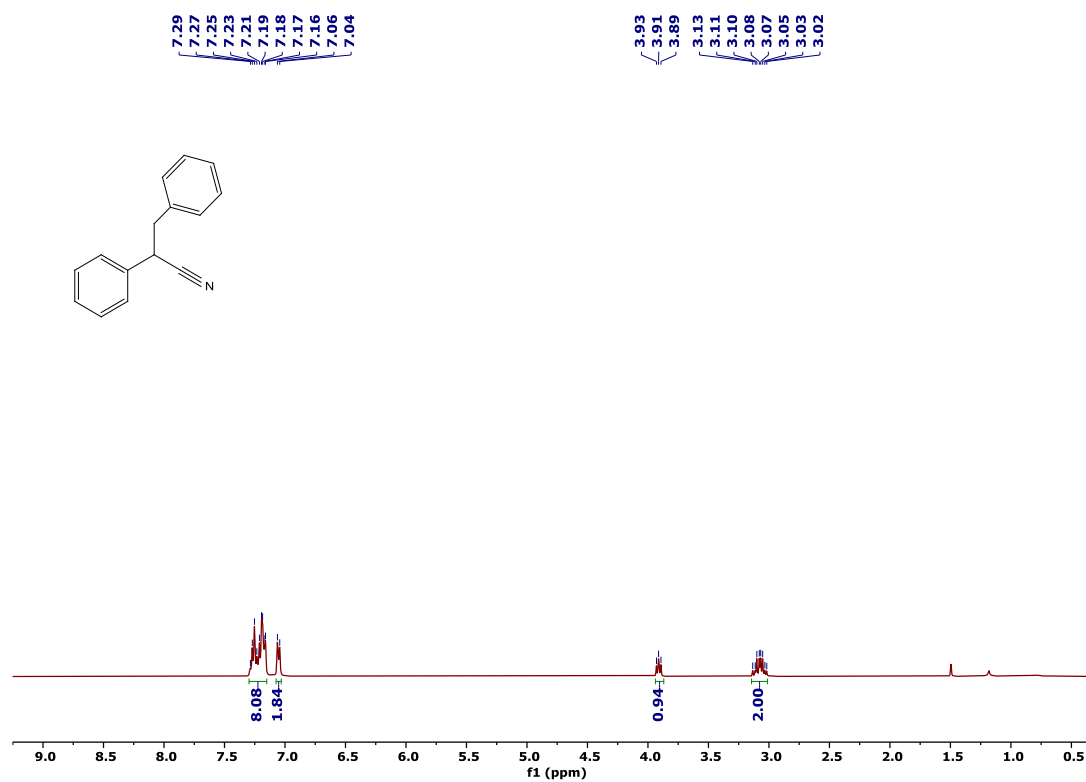


Figure S18. ^1H NMR spectrum of **4a** in CDCl_3 .

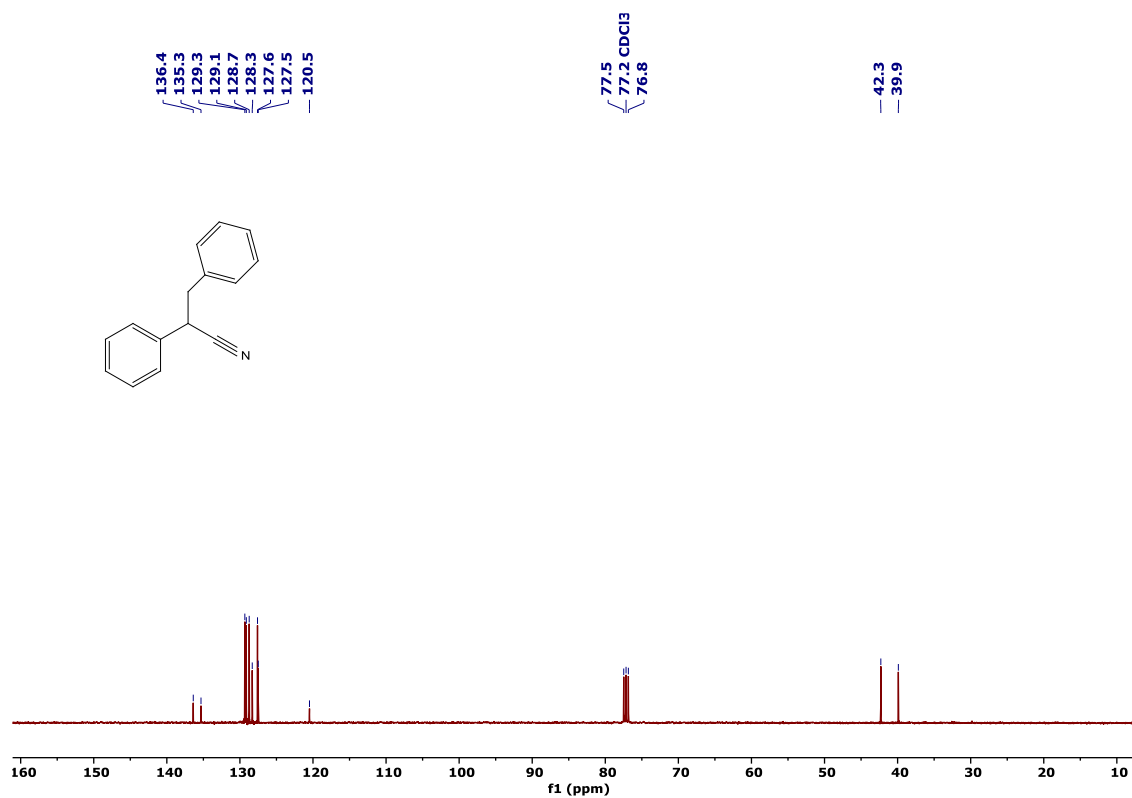


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4a** in CDCl_3 .

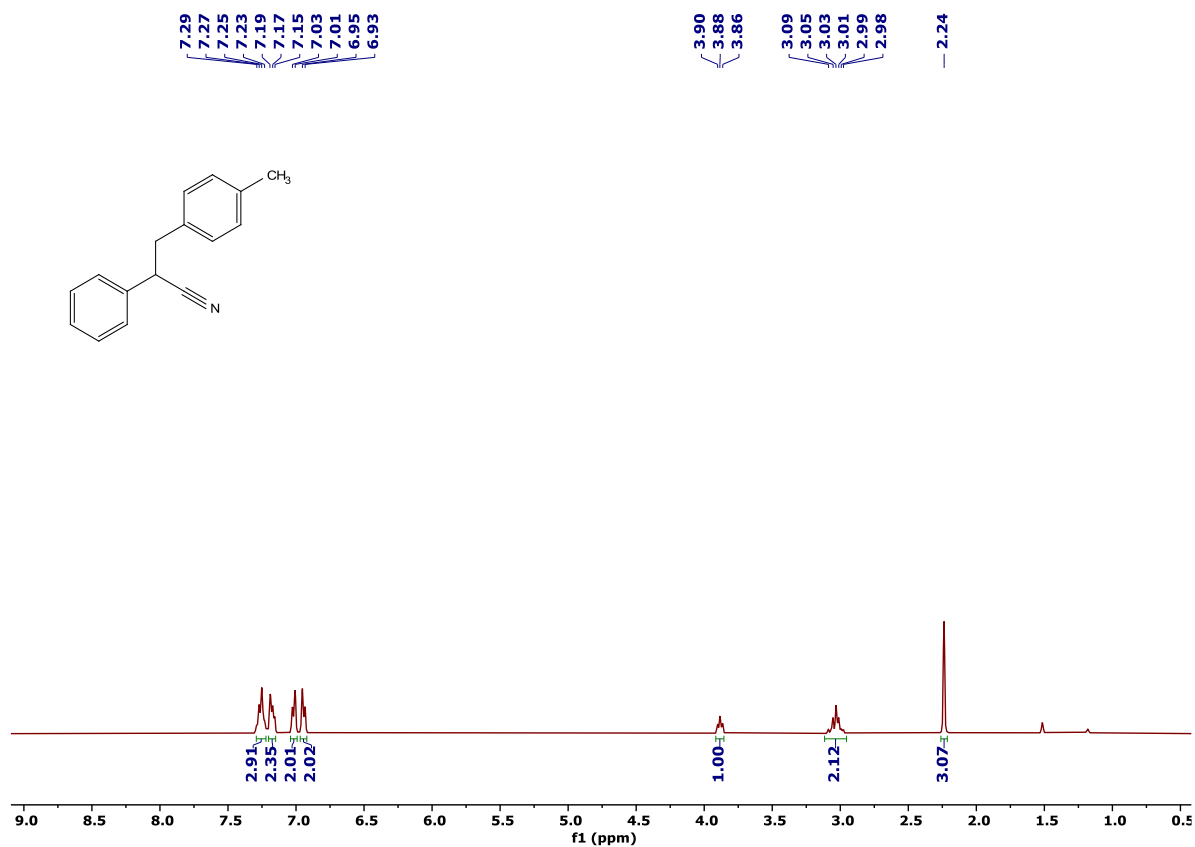


Figure S20. $^1\text{H NMR}$ spectrum of **4b** in CDCl_3 .

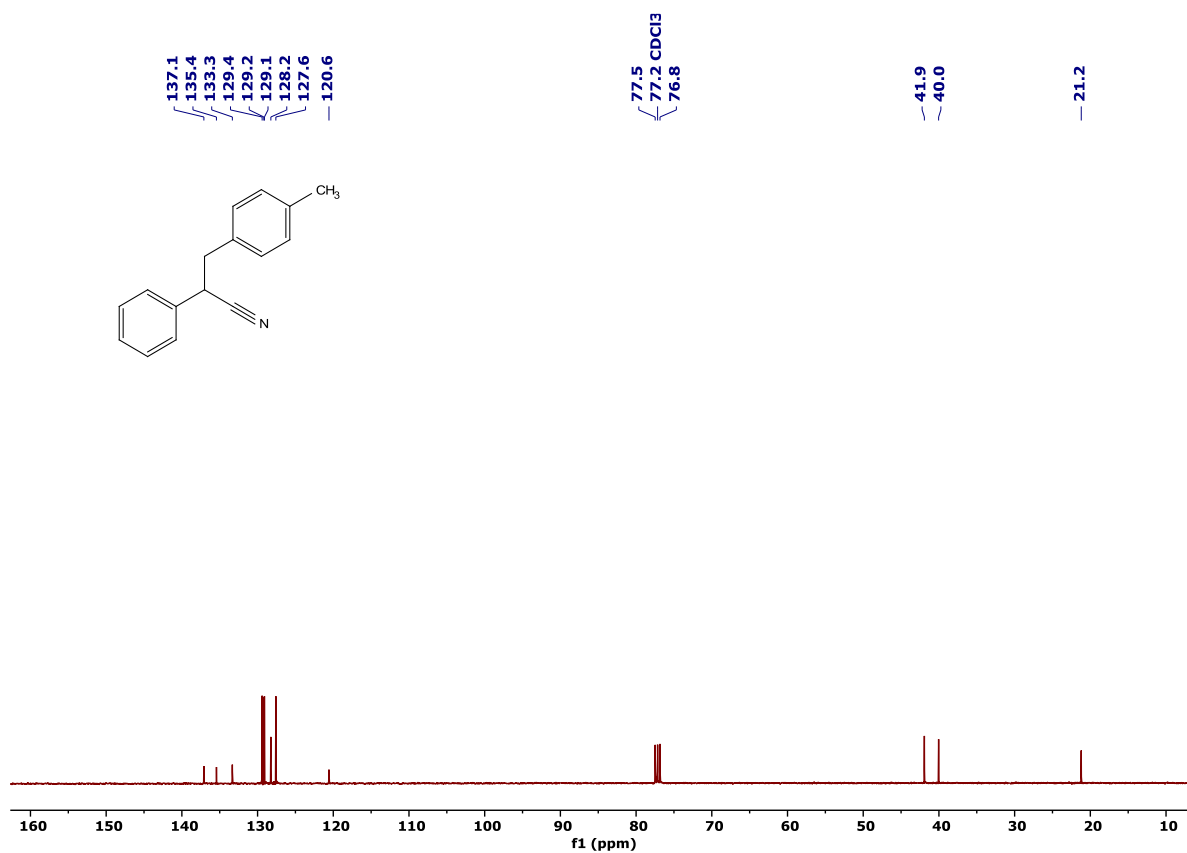


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4b** in CDCl_3 .

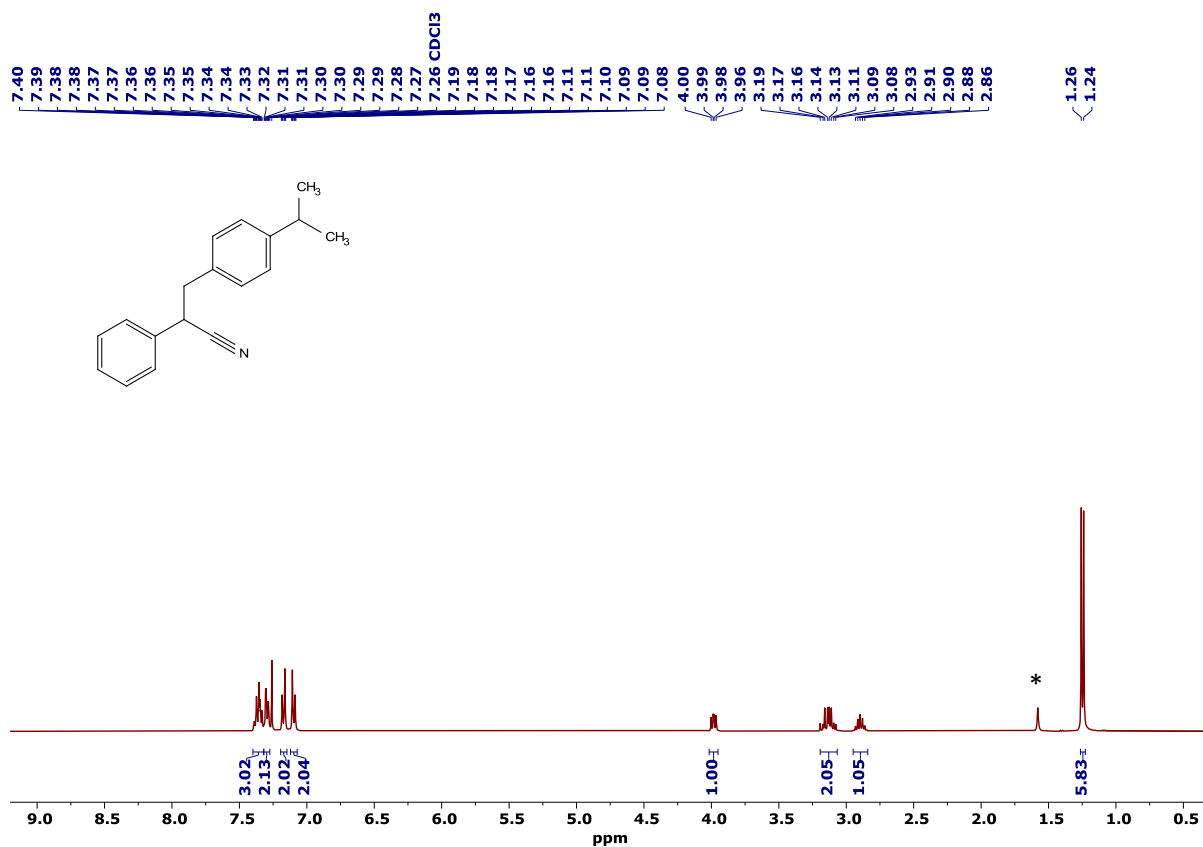


Figure S22. ¹H NMR spectrum of **4c** in CDCl₃. * indicates the solvent impurity of H₂O.

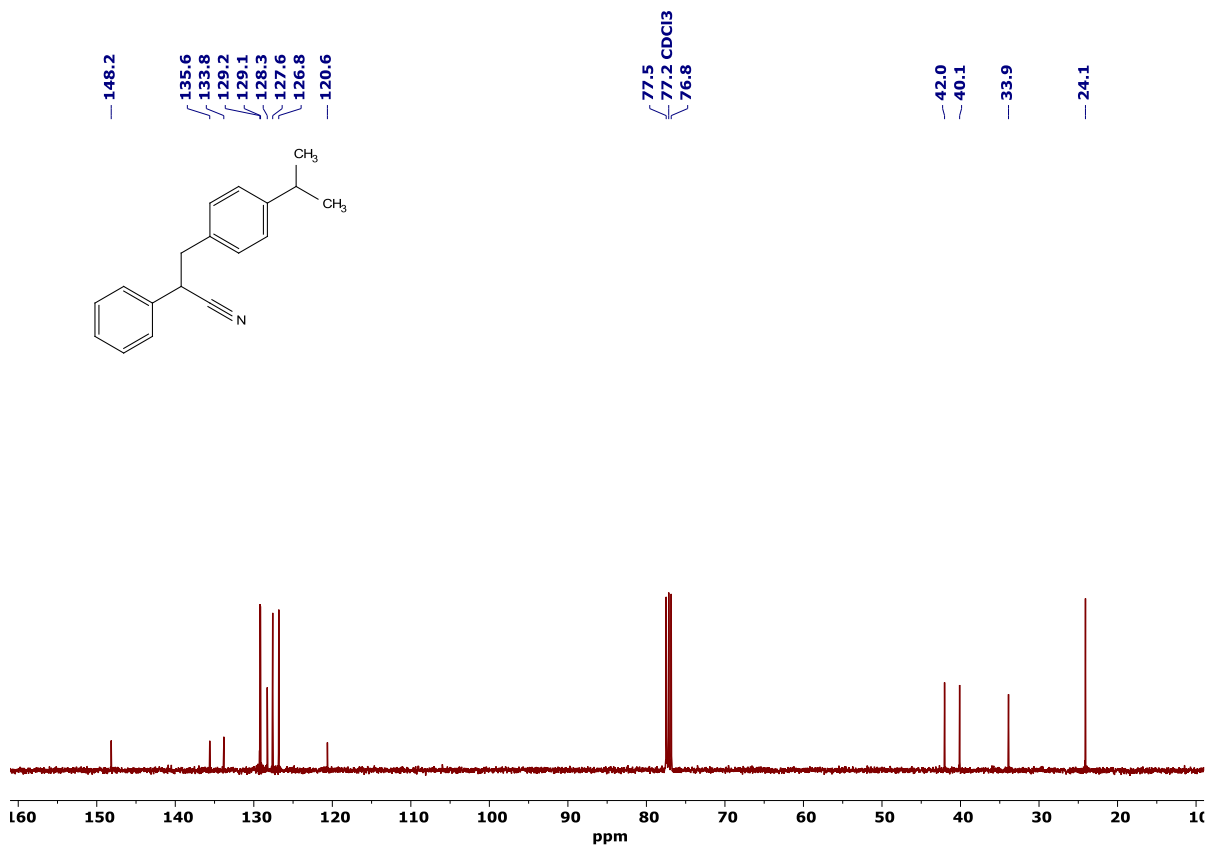


Figure S23. ¹³C{¹H} NMR spectrum of **4c** in CDCl₃.

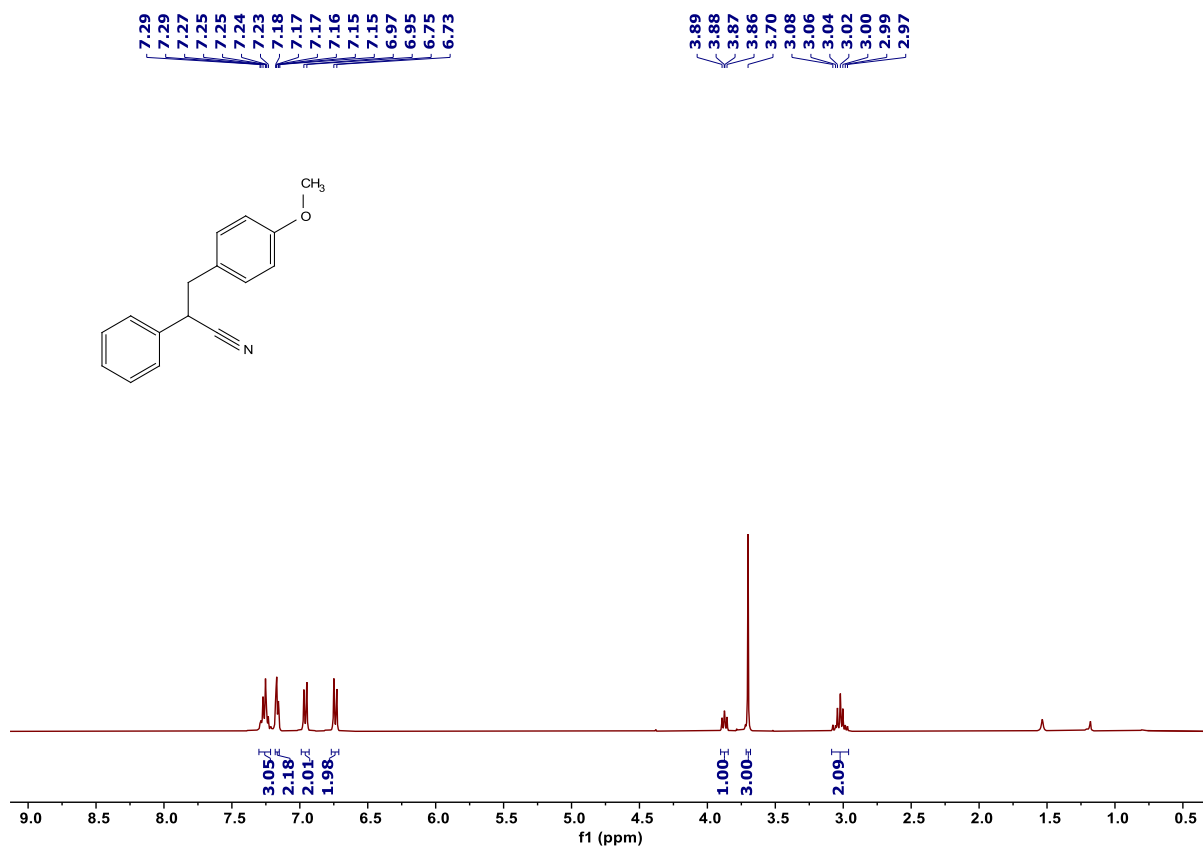


Figure S24. ^1H NMR spectrum of **4d** in CDCl_3 .

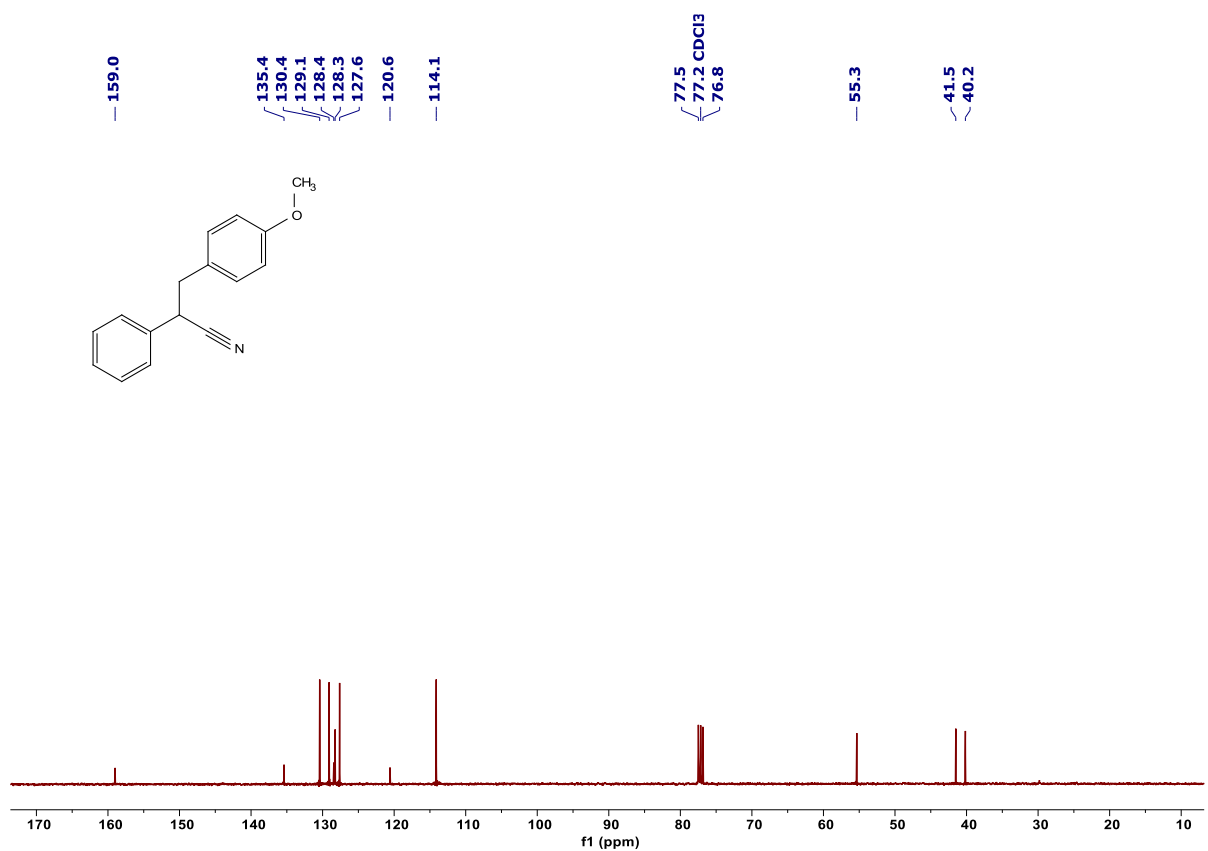


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4d** in CDCl_3 .

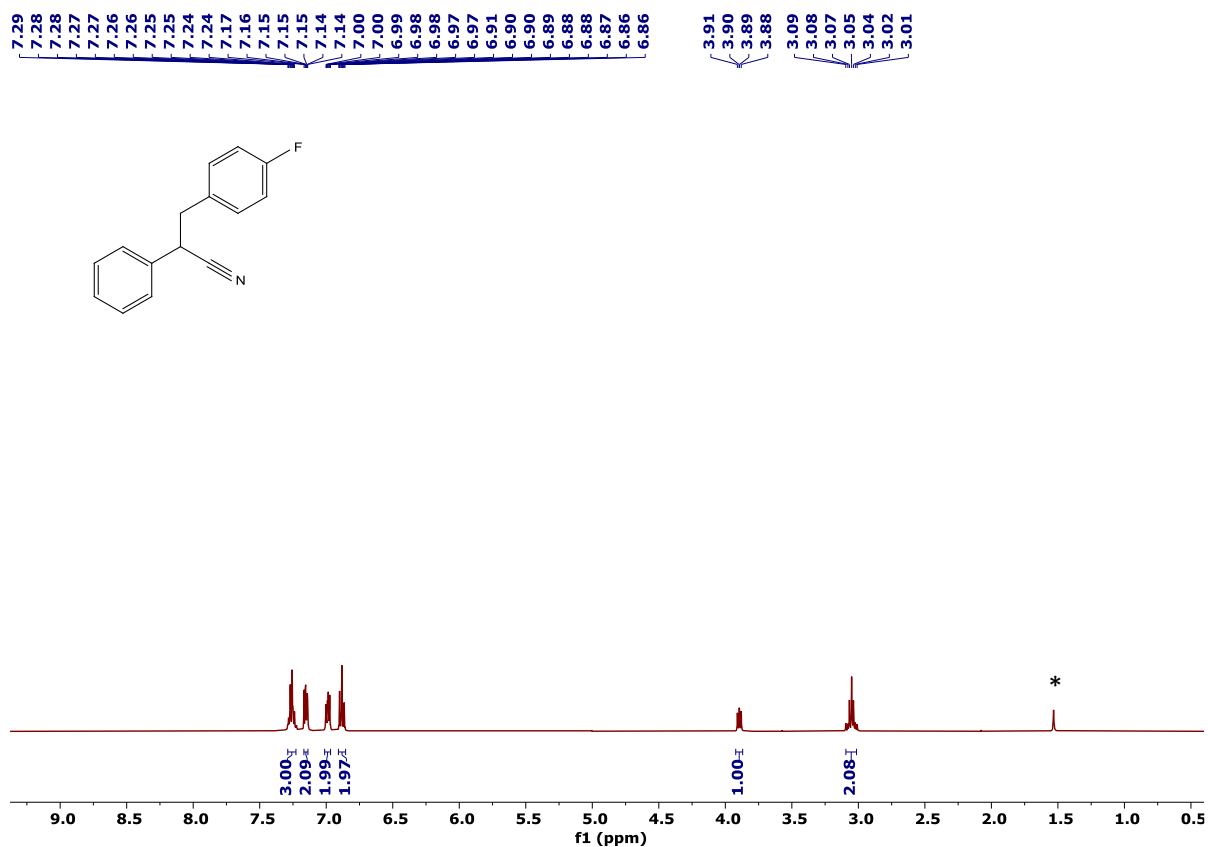


Figure S26. ¹H NMR spectrum of 4e in CDCl₃. * indicates the solvent impurity of H₂O.

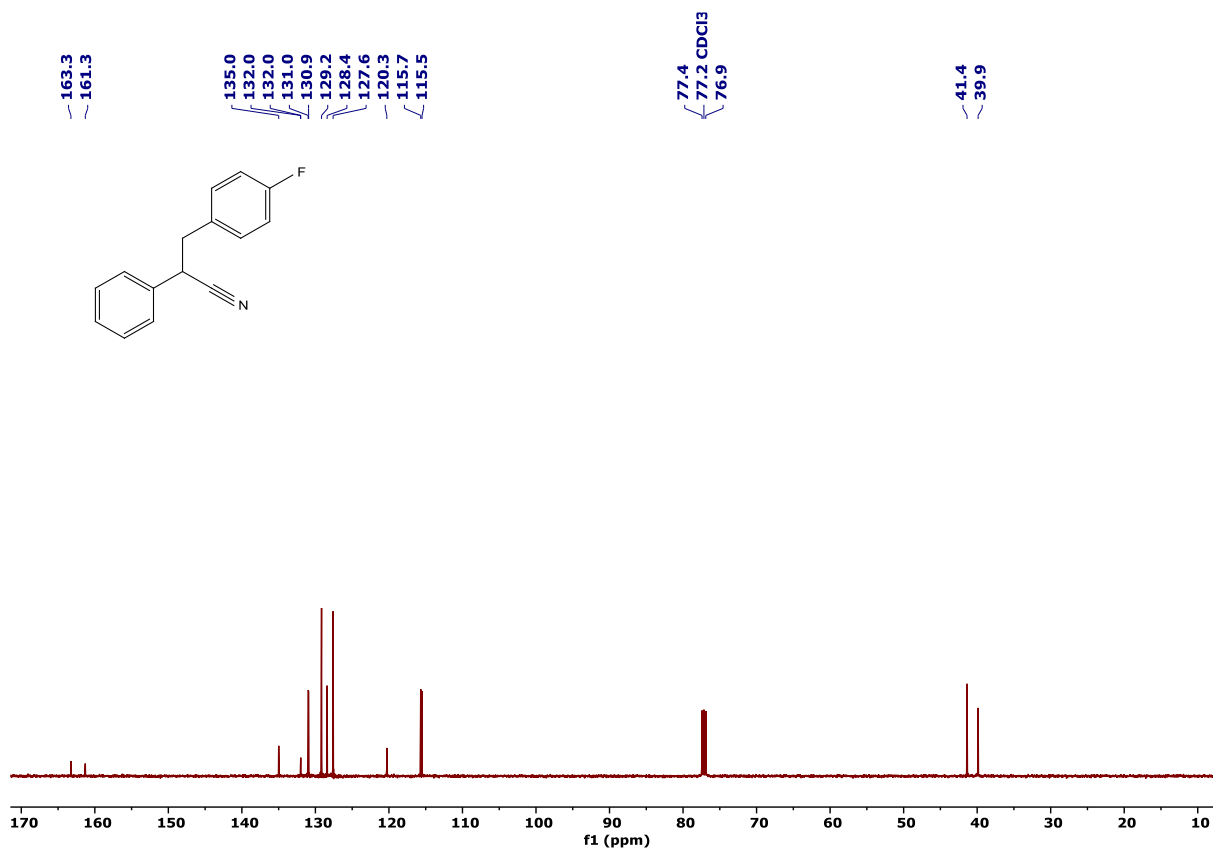


Figure S27. ¹³C{¹H} NMR spectrum of 4e in CDCl₃.

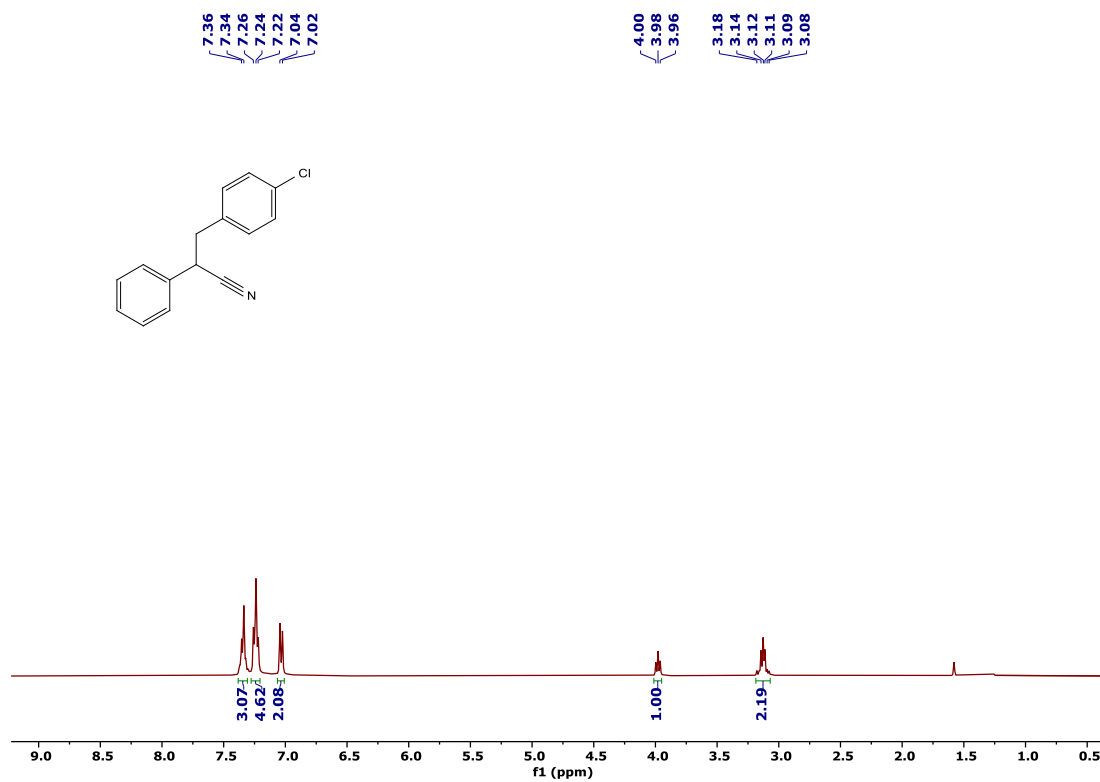


Figure S28. ^1H NMR spectrum of **4f** in CDCl_3 .

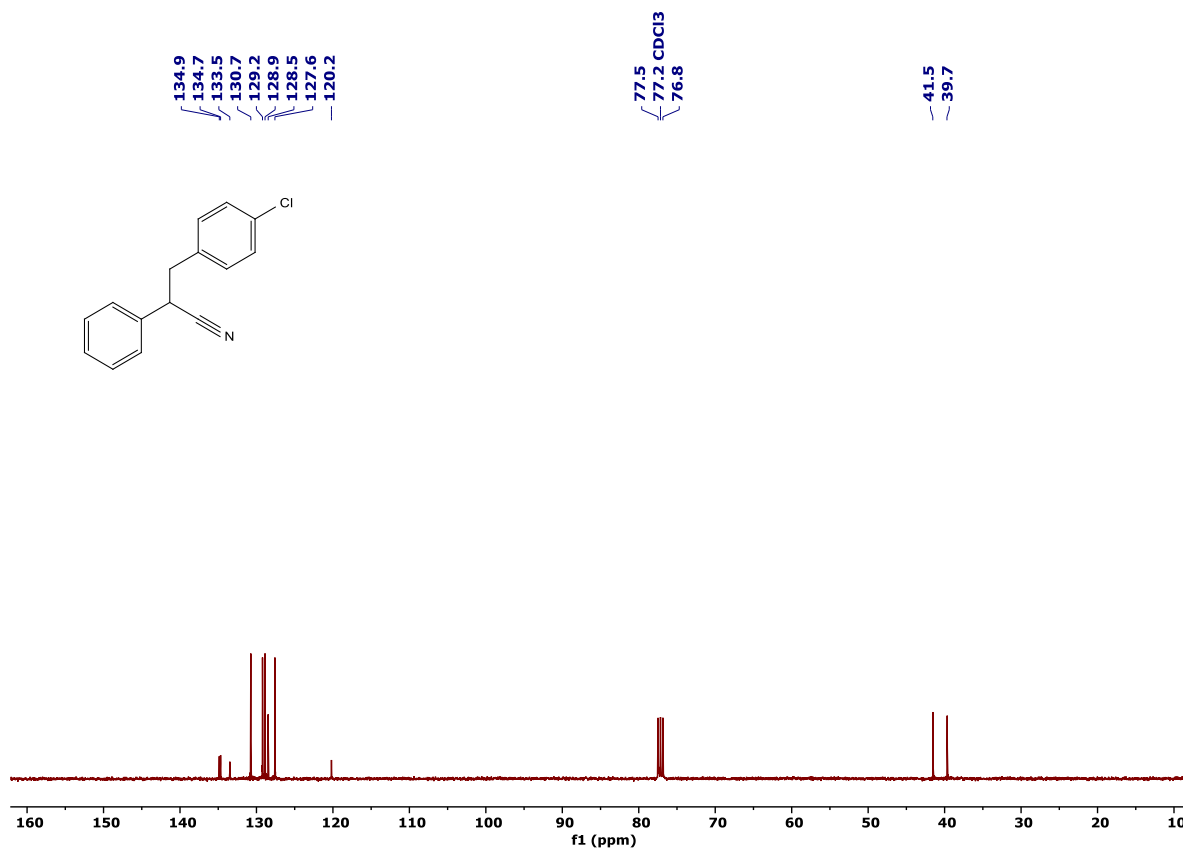


Figure S29. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4f** in CDCl_3 .

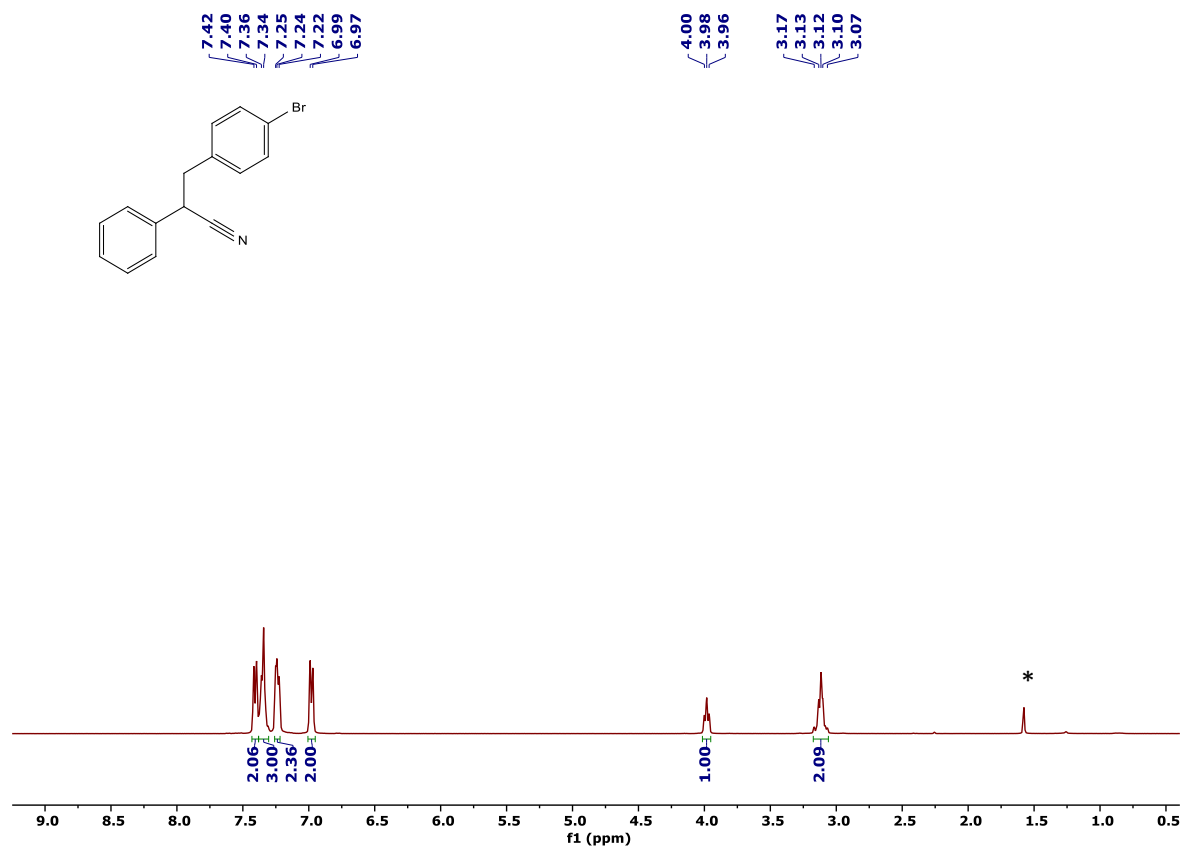


Figure S30. ¹H NMR spectrum of **4g** in CDCl₃. * indicates the solvent impurity of H₂O.

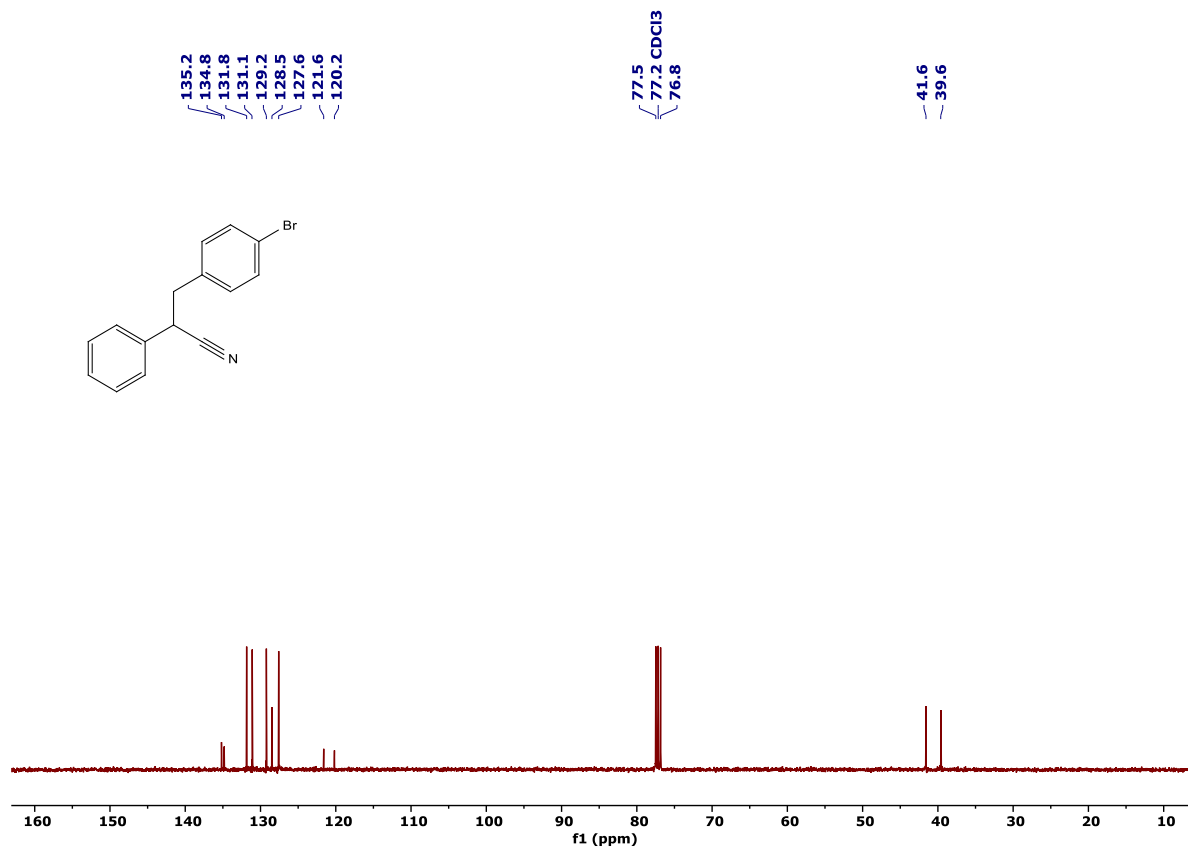


Figure S31. ¹³C{¹H} NMR spectrum of **4g** in CDCl₃.

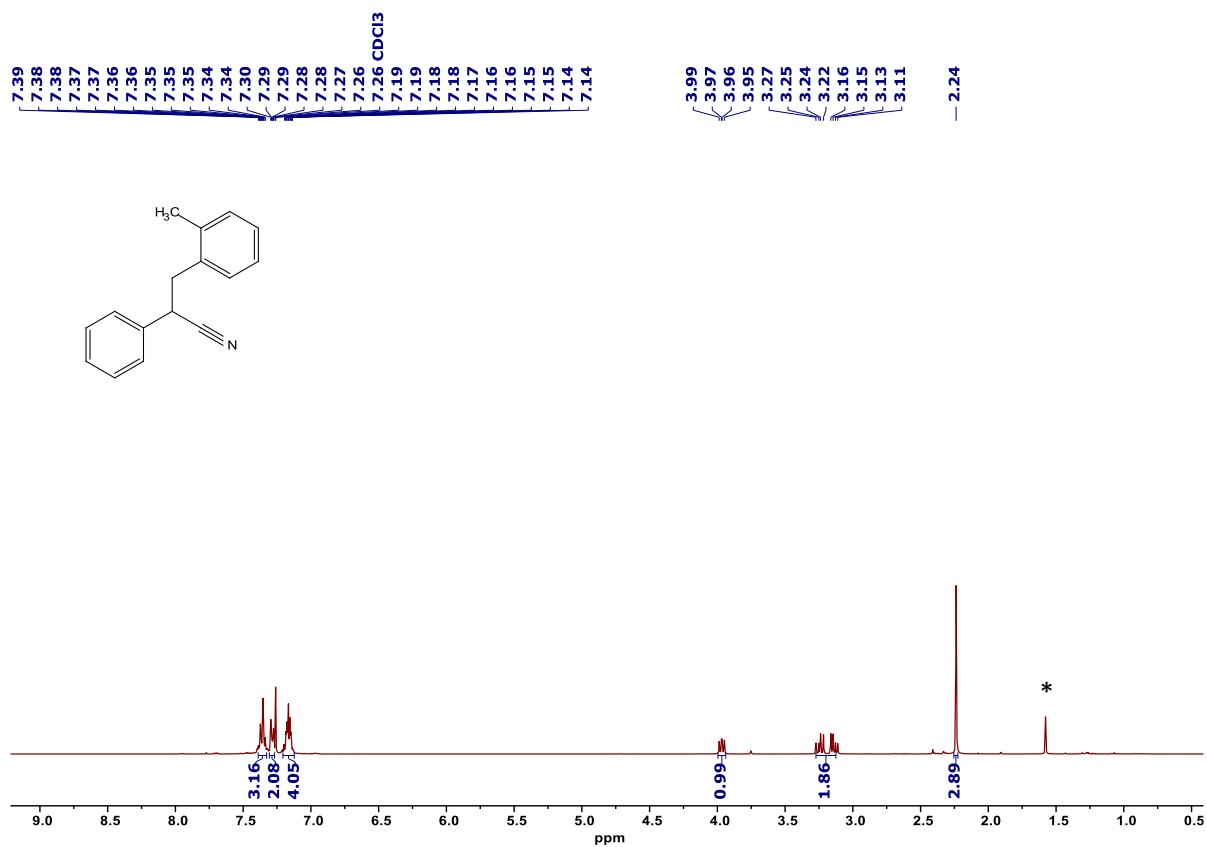


Figure S32. $^1\text{H NMR}$ spectrum of **4h** in CDCl_3 . * indicates the solvent impurity of H_2O .

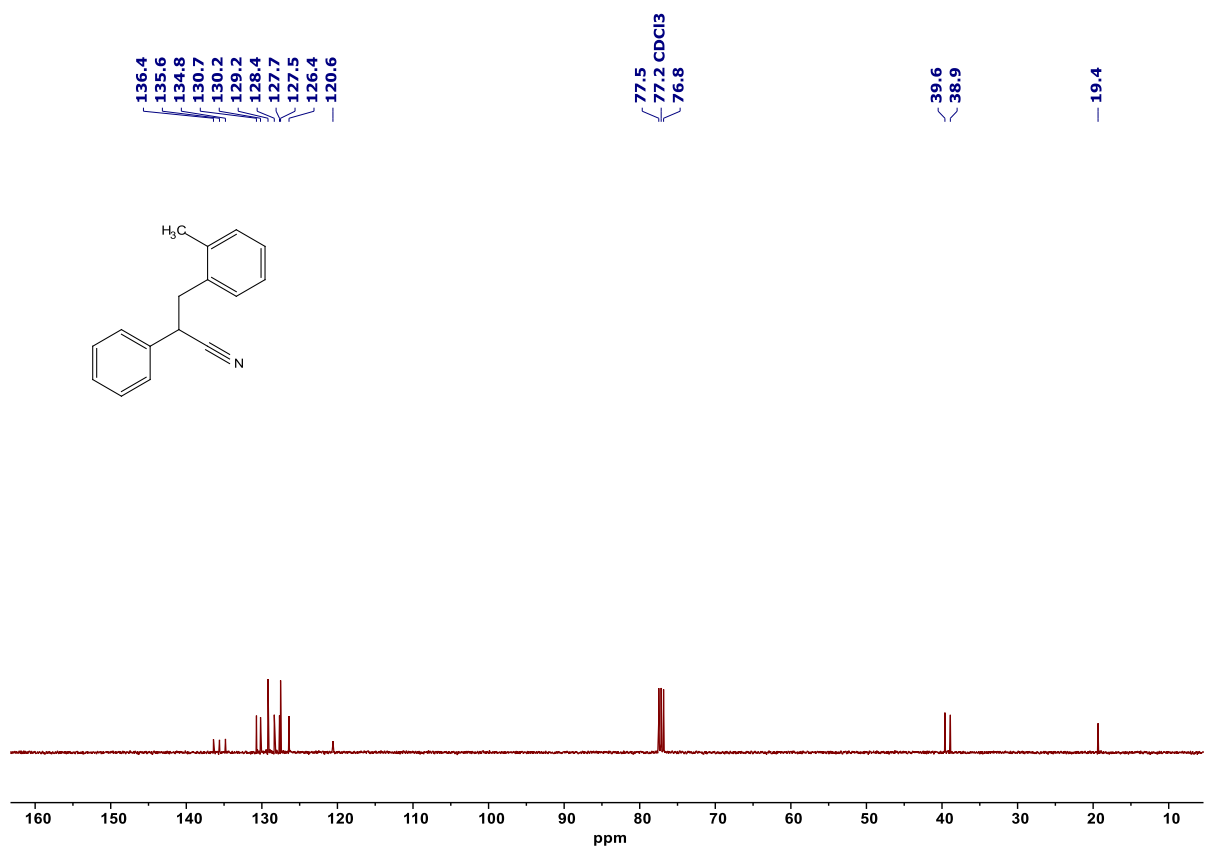


Figure S33. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4h** in CDCl_3 .

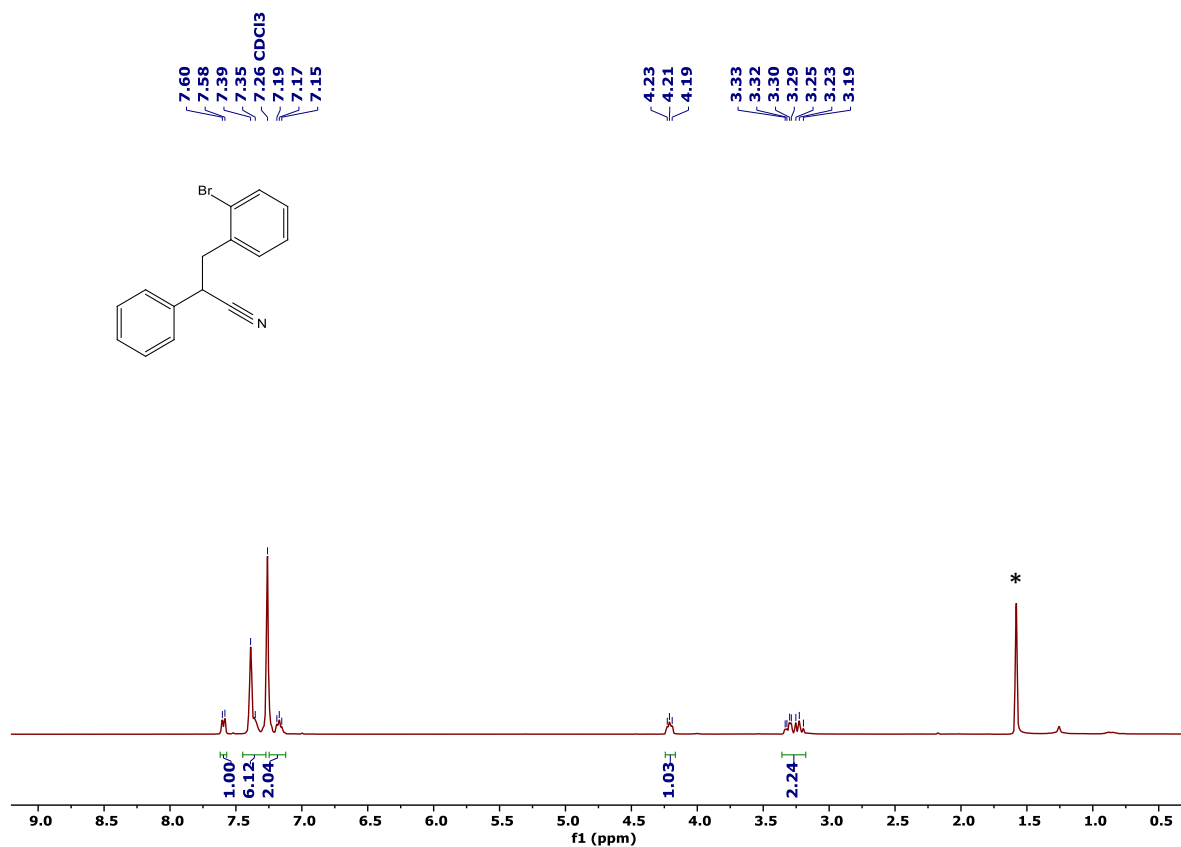


Figure S34. ¹H NMR spectrum of **4i** in CDCl₃. * indicates the solvent impurity of H₂O.

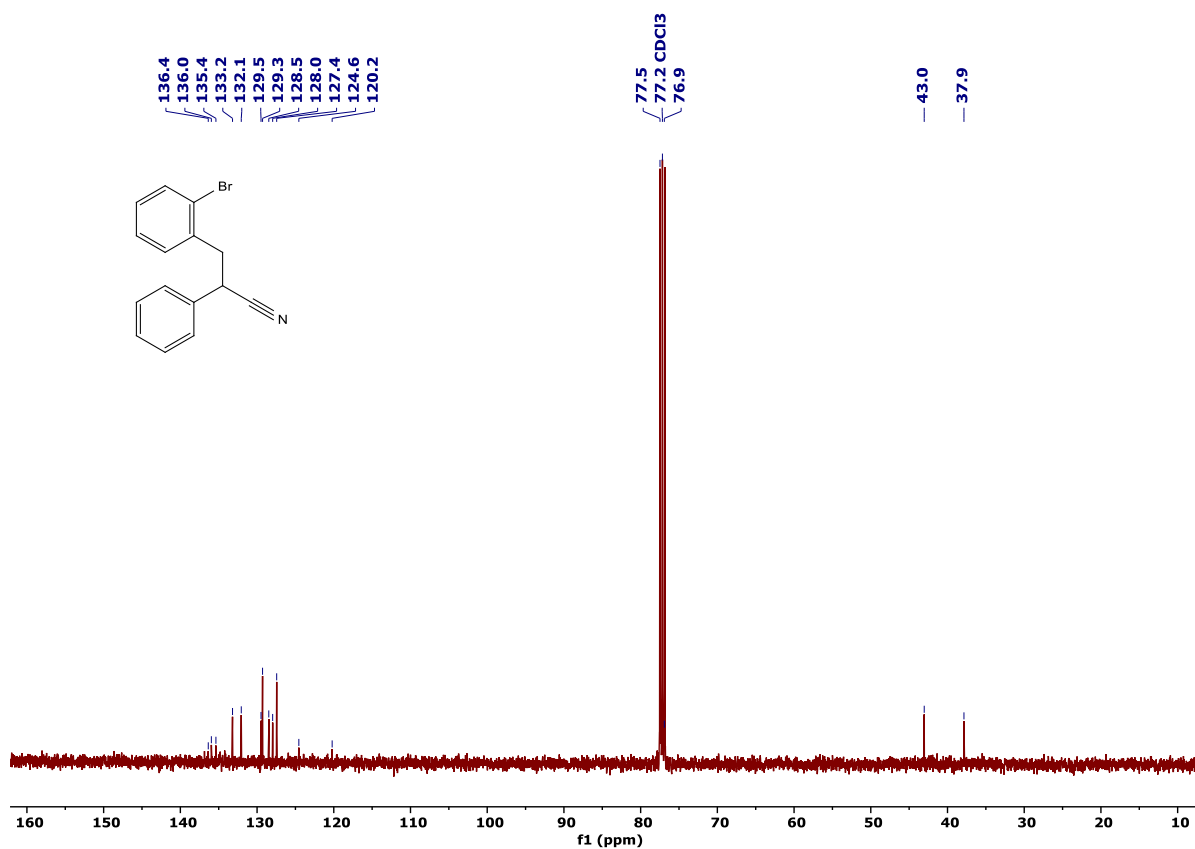


Figure S35. ¹³C{¹H} NMR spectrum of **4i** in CDCl₃.

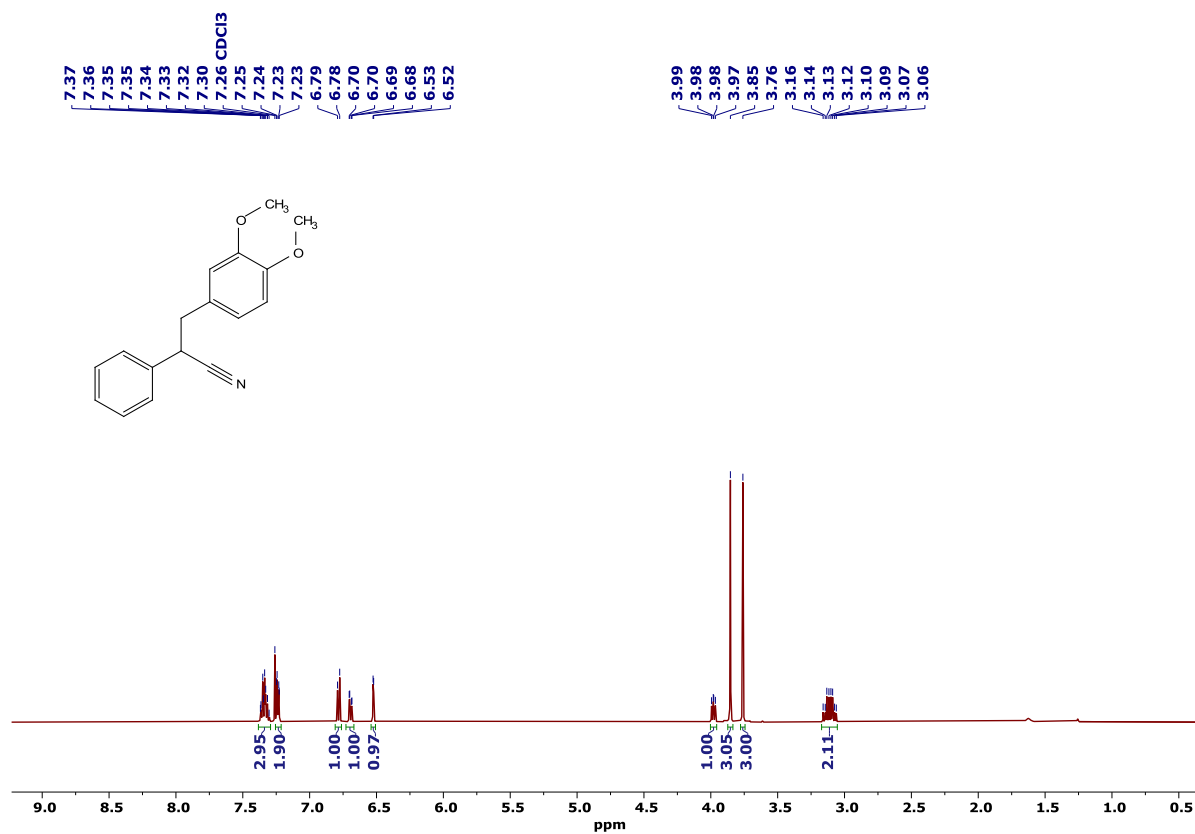


Figure S36. ¹H NMR spectrum of **4j** in CDCl₃.

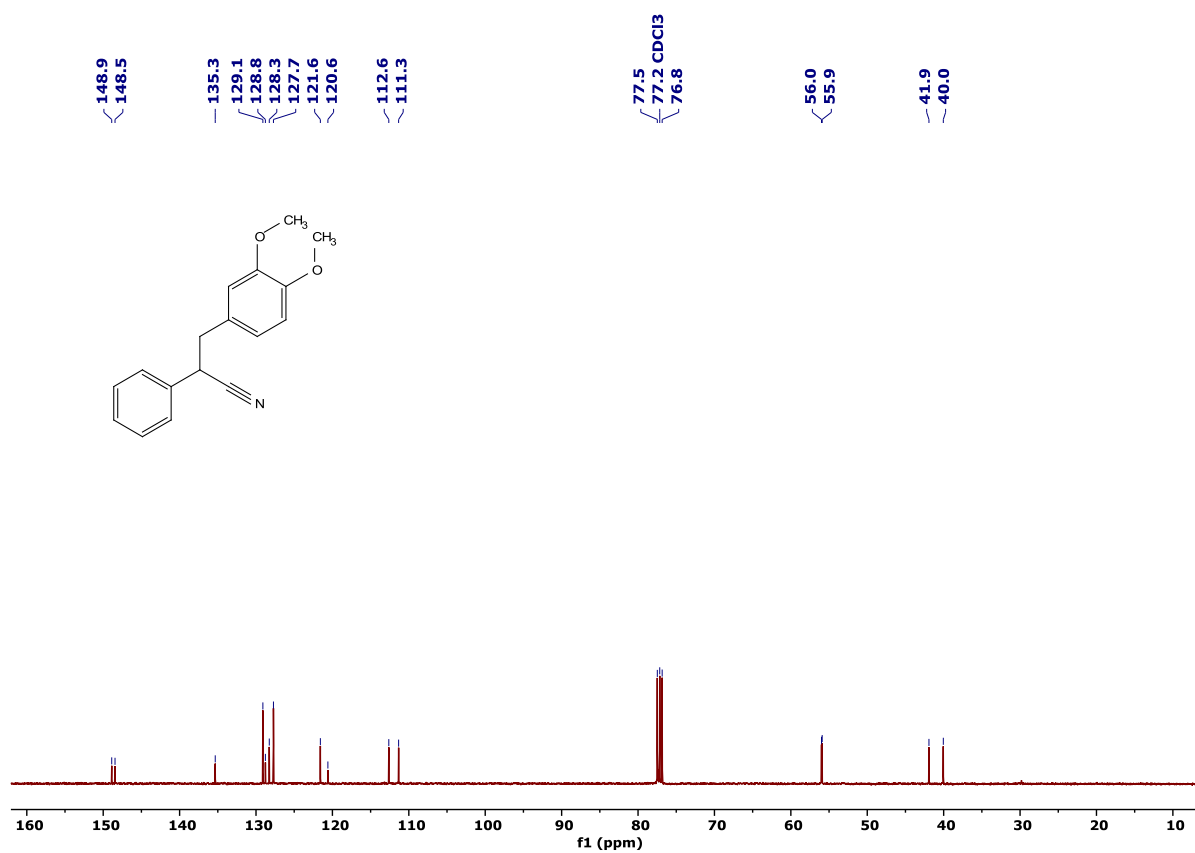


Figure S37. ¹³C {¹H} NMR spectrum of **4j** in CDCl₃.

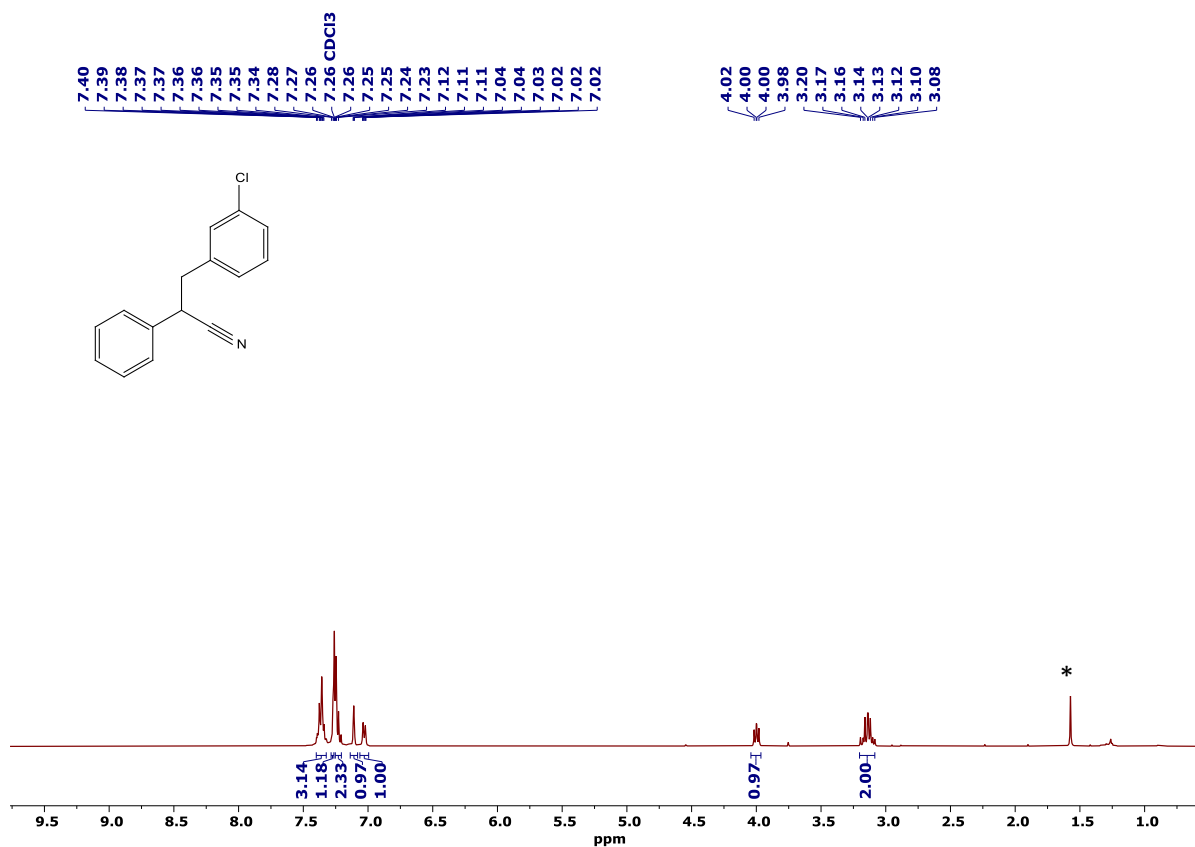


Figure S38. ¹H NMR spectrum of **4k** in CDCl₃. * indicates the solvent impurity of H₂O.

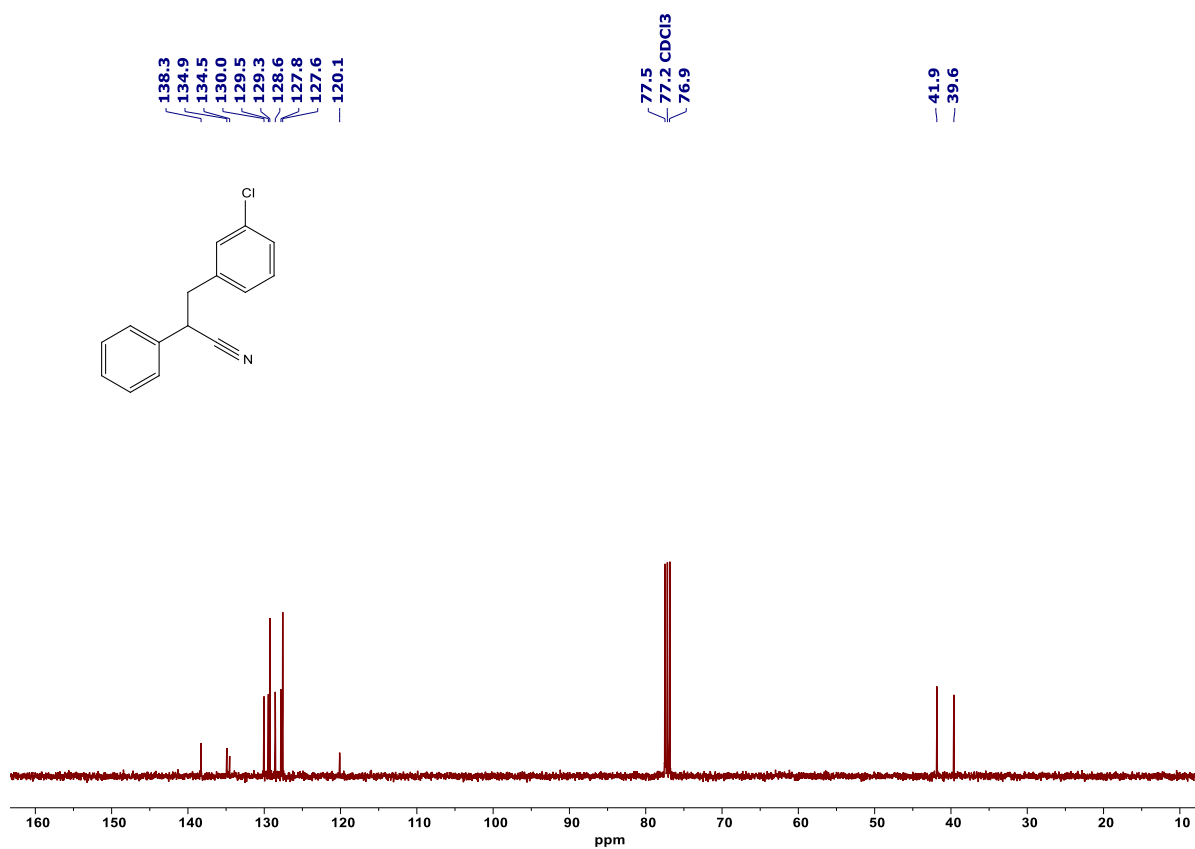


Figure S39. ¹³C{¹H} NMR spectrum of **4k** in CDCl₃.

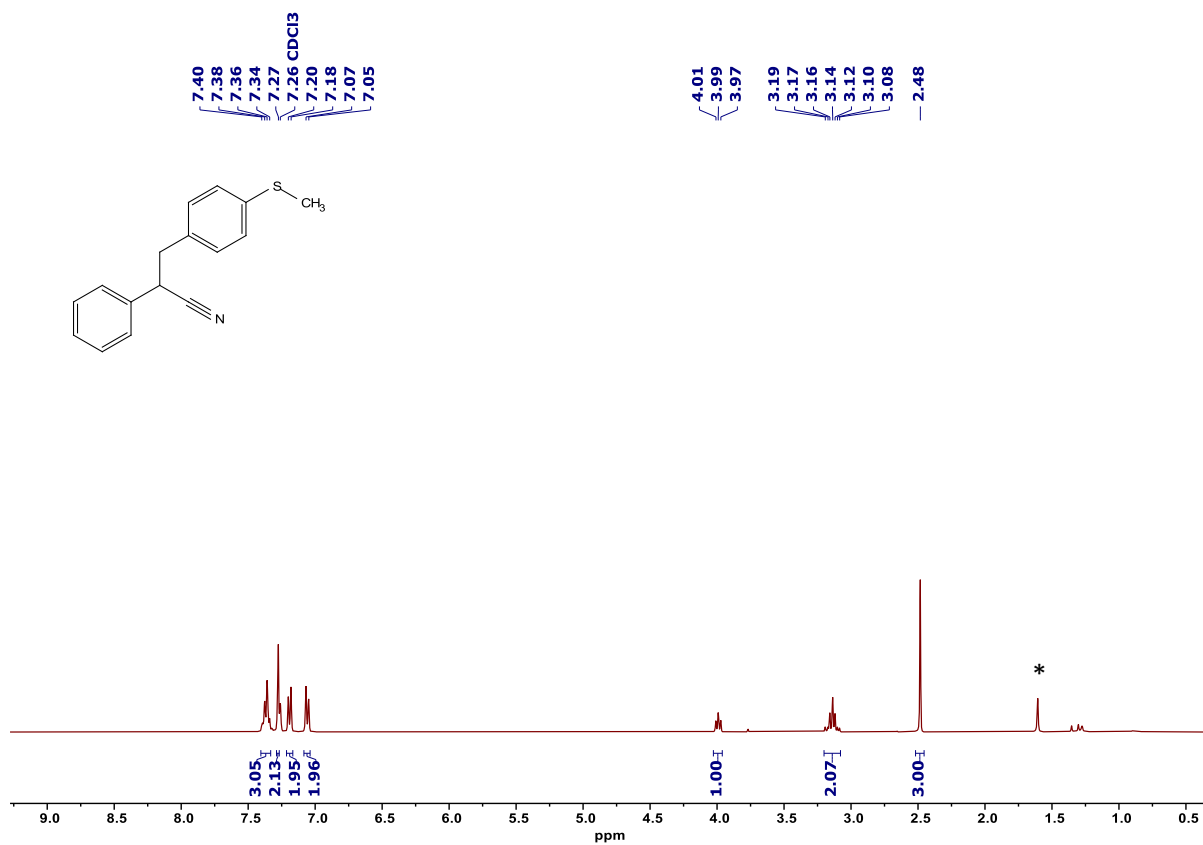


Figure S40. ¹H NMR spectrum of **4I** in CDCl₃. * indicates the solvent impurity of H₂O.

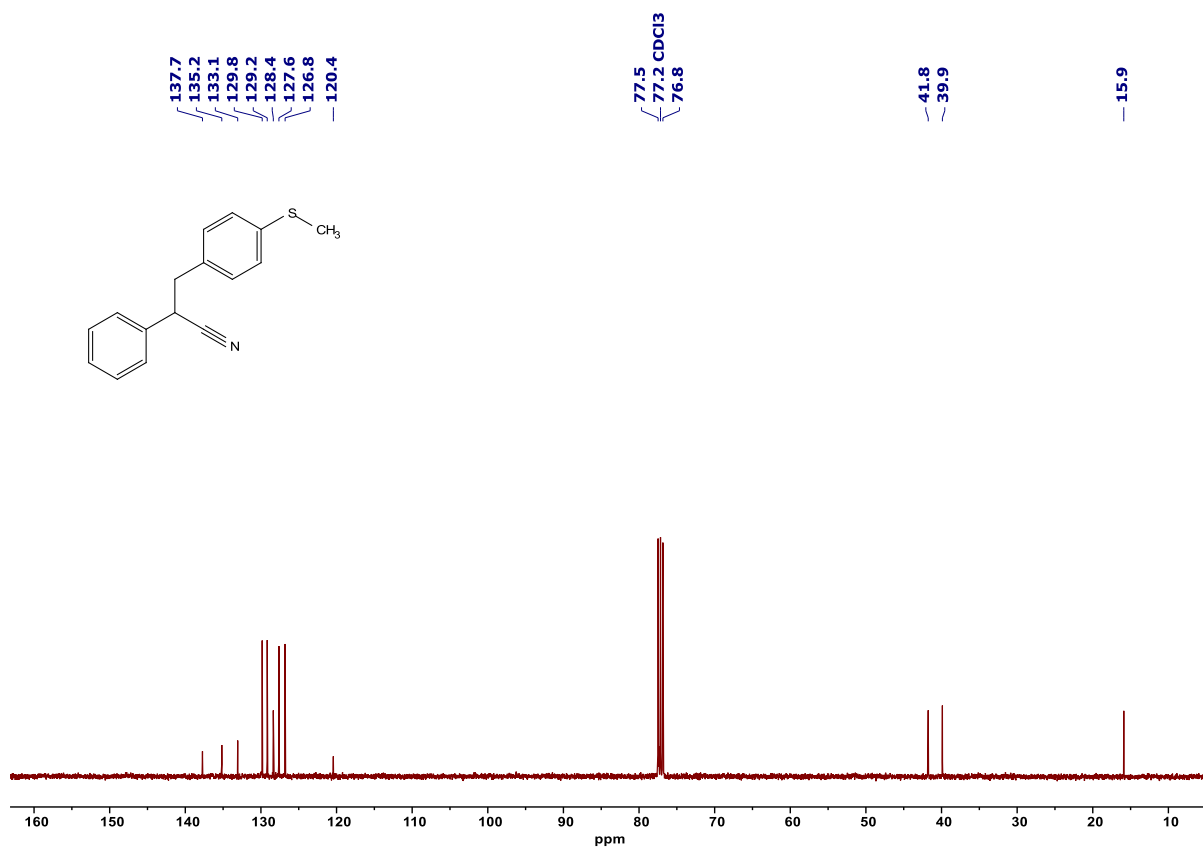


Figure S41. ¹³C{¹H} NMR spectrum of **4I** in CDCl₃.

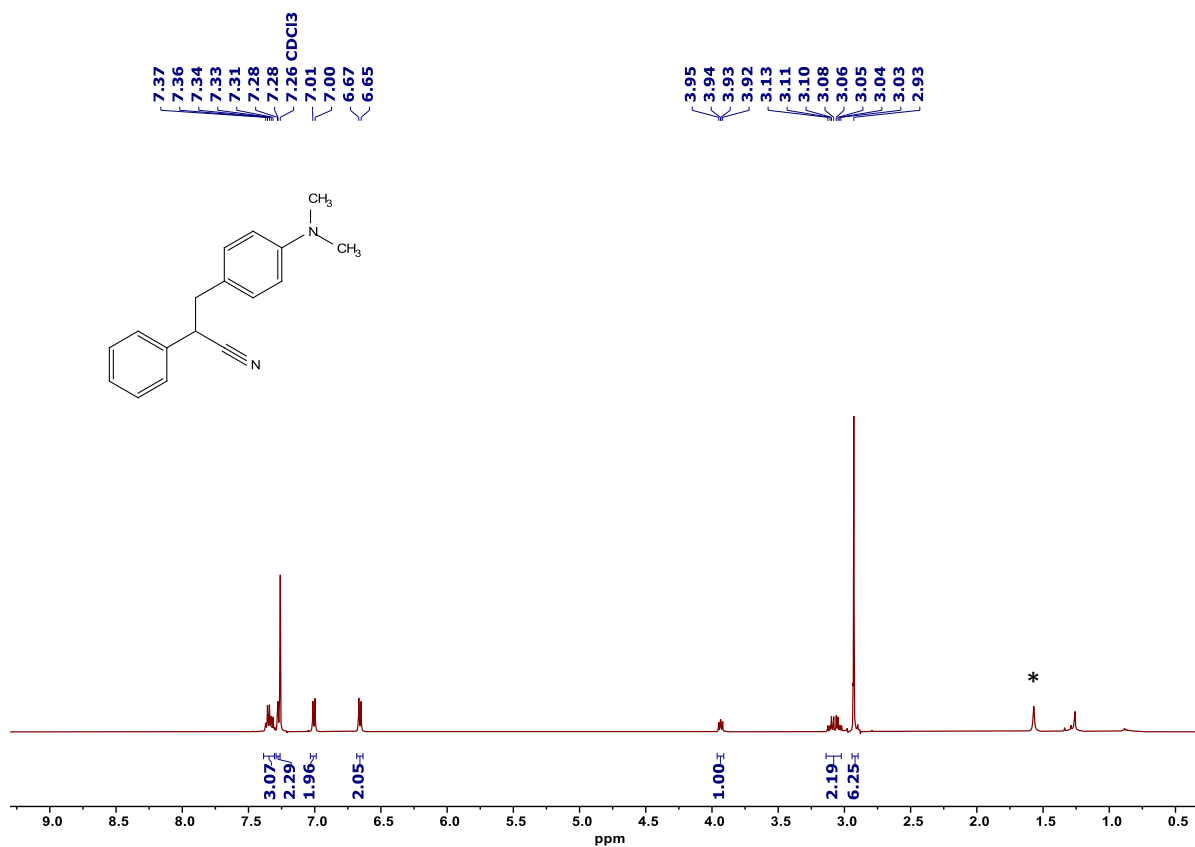


Figure S42. ¹H NMR spectrum of **4m** in CDCl₃. * indicates the solvent impurity of H₂O.

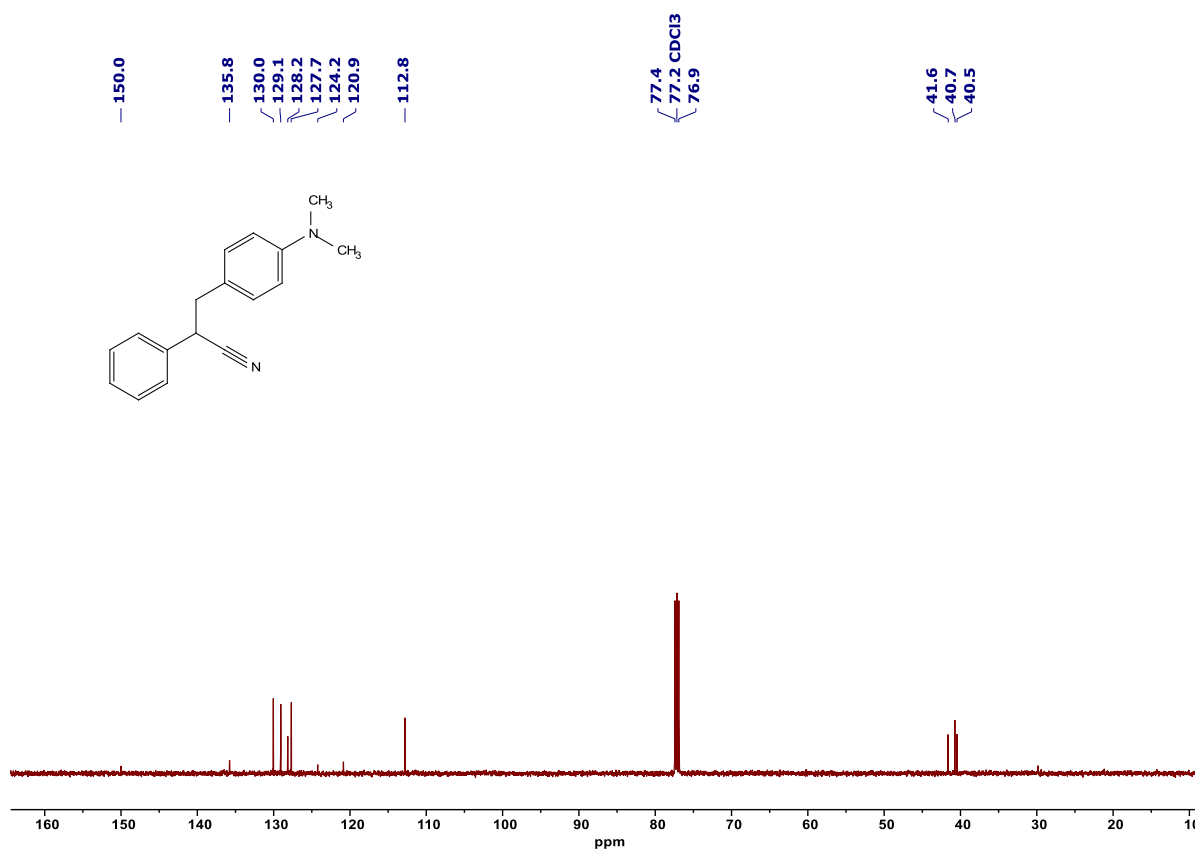


Figure S43. ¹³C{¹H} NMR spectrum of **4m** in CDCl₃.

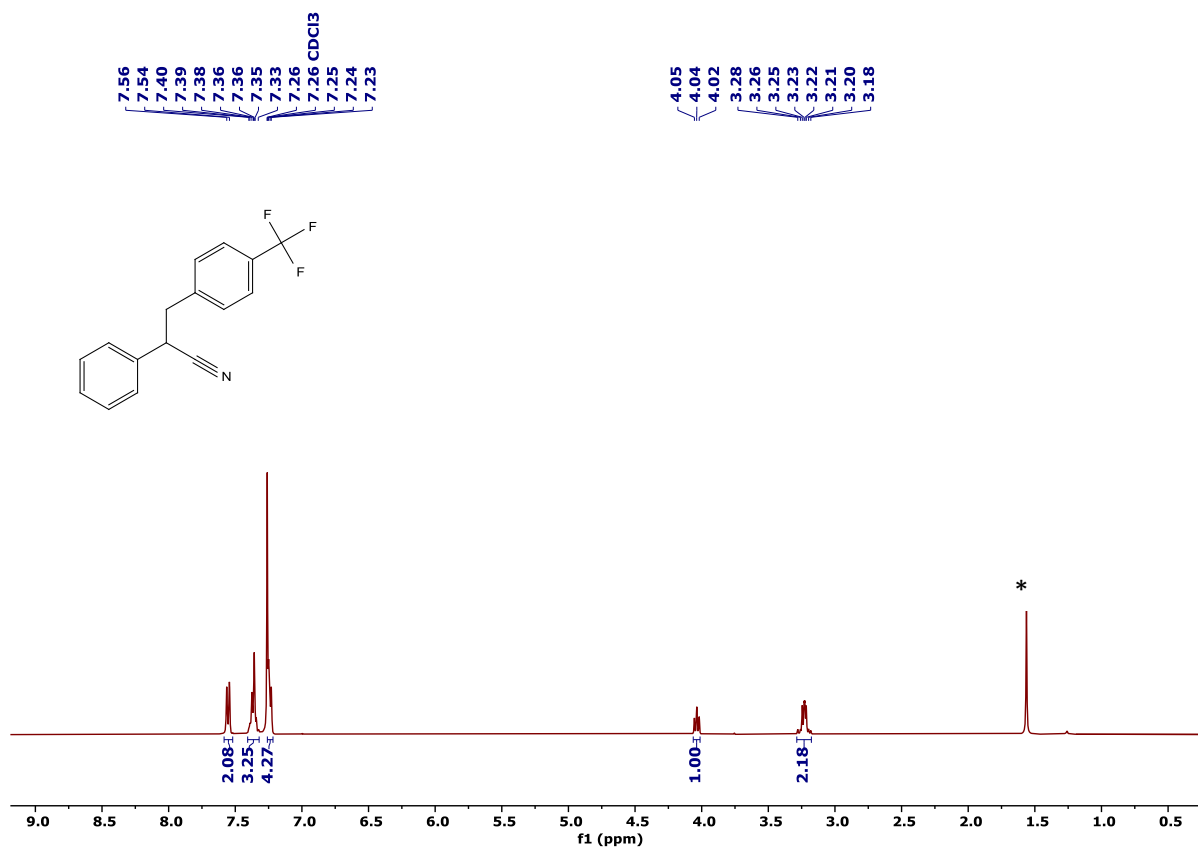


Figure S44. ¹H NMR spectrum of **4n** in CDCl₃. * indicates the solvent impurity of H₂O.

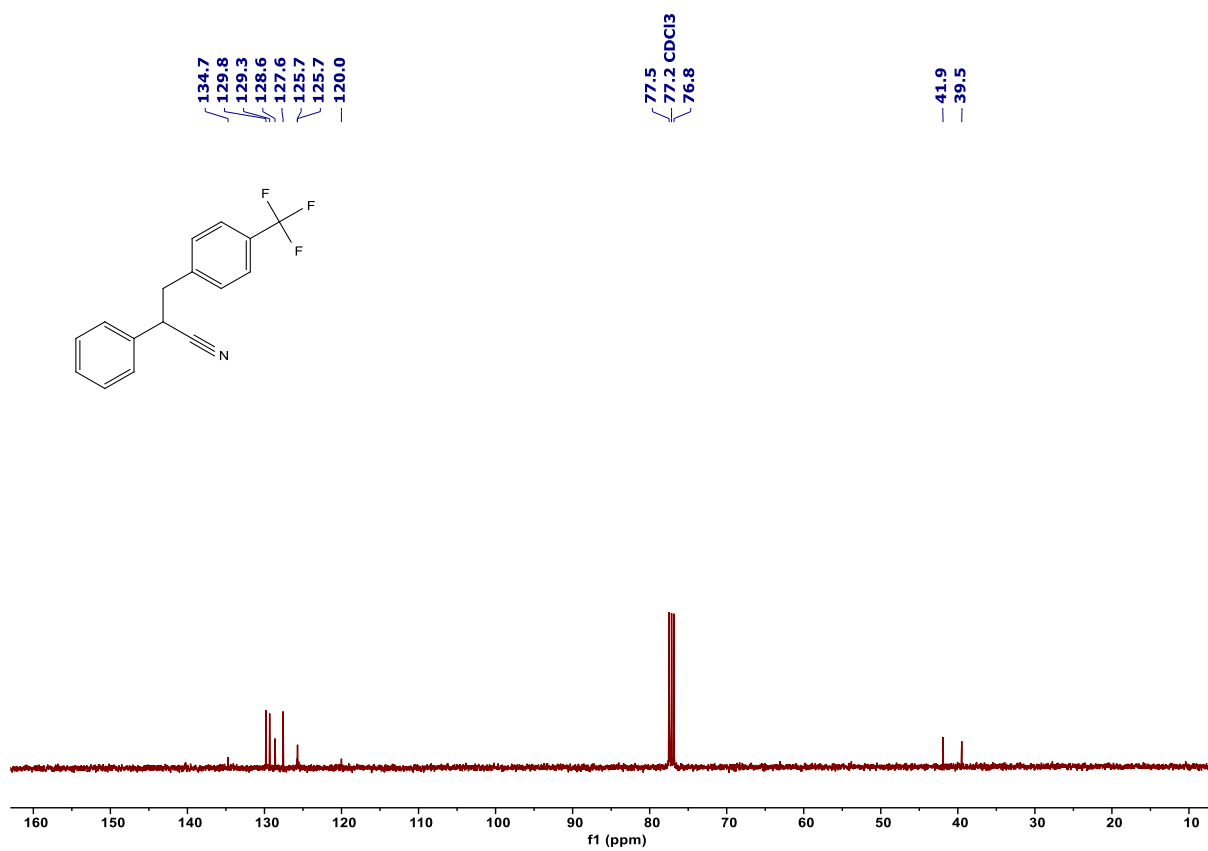


Figure S45. ¹³C{¹H} NMR spectrum of **4n** in CDCl₃.

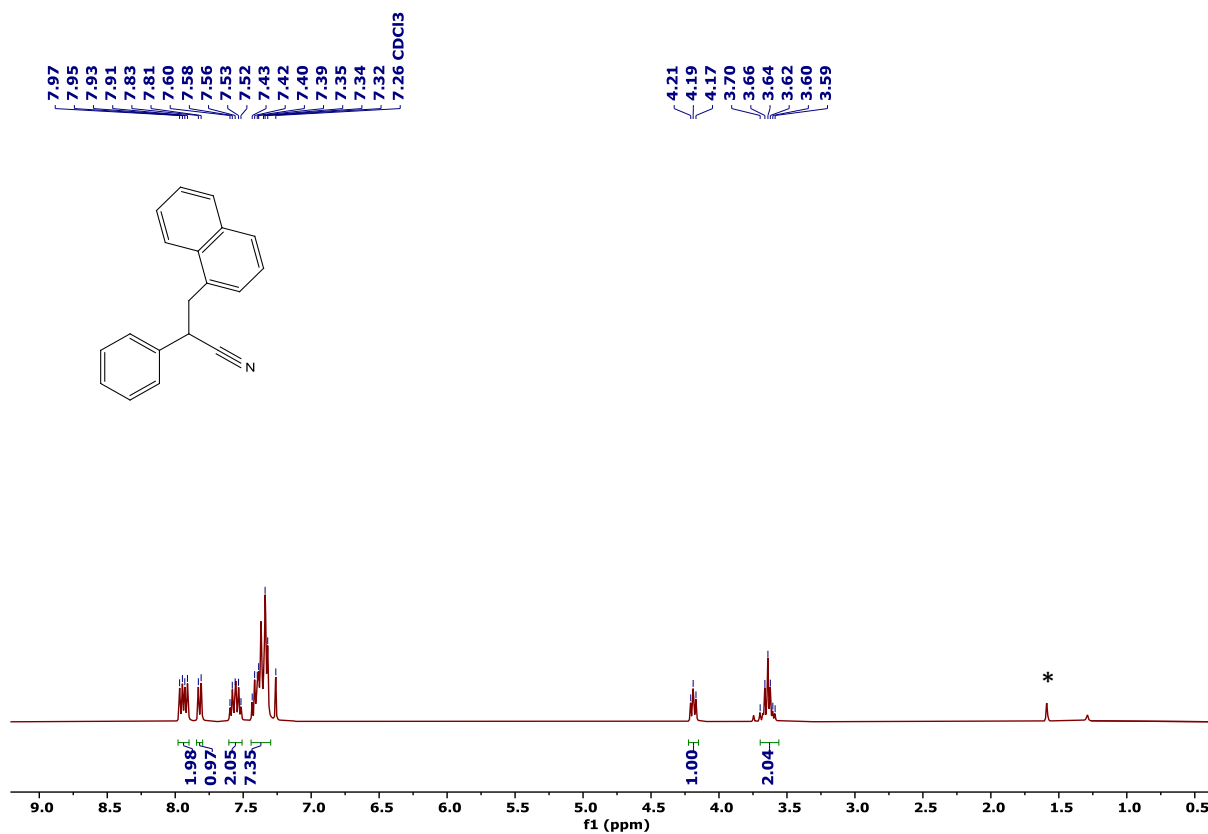


Figure S46. ¹H NMR spectrum of **4O** in CDCl₃. * indicates the solvent impurity of H₂O.

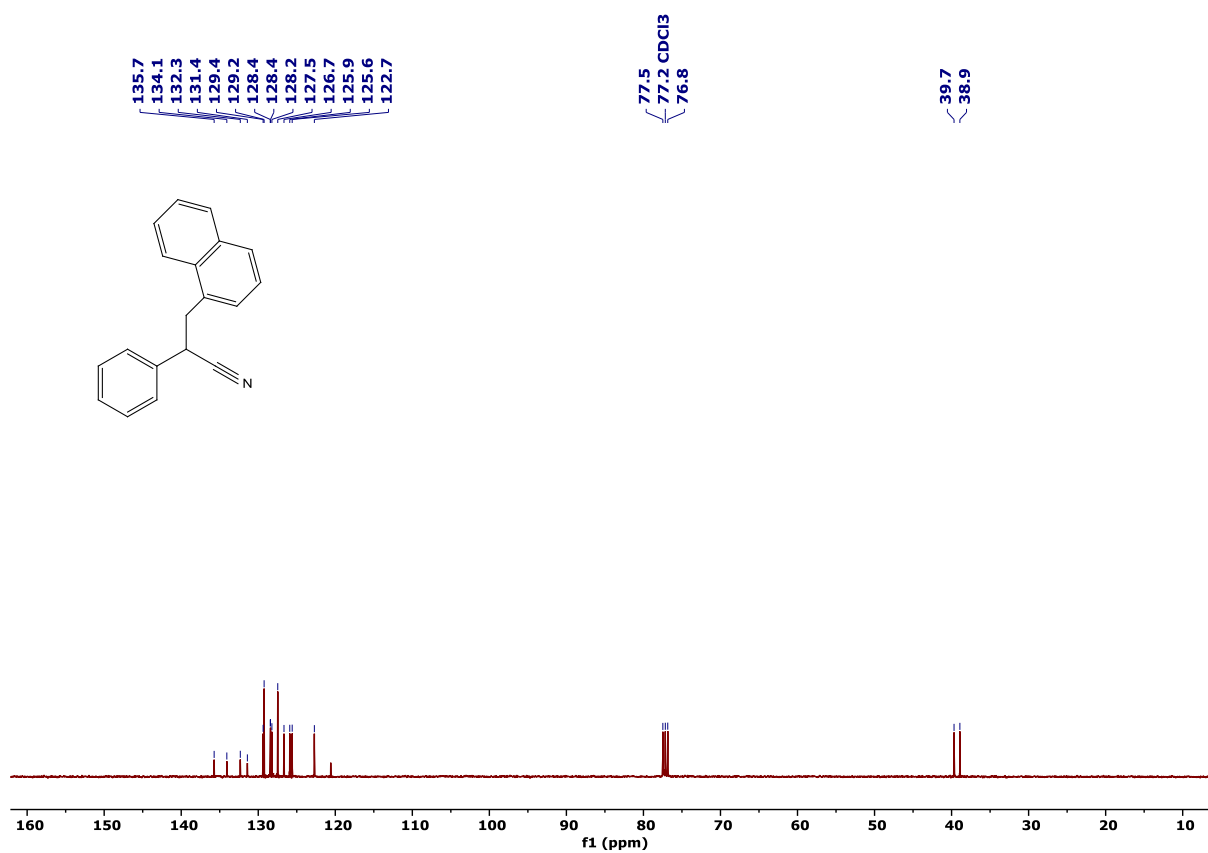


Figure S47. ¹³C {¹H} NMR spectrum of **4O** in CDCl₃.

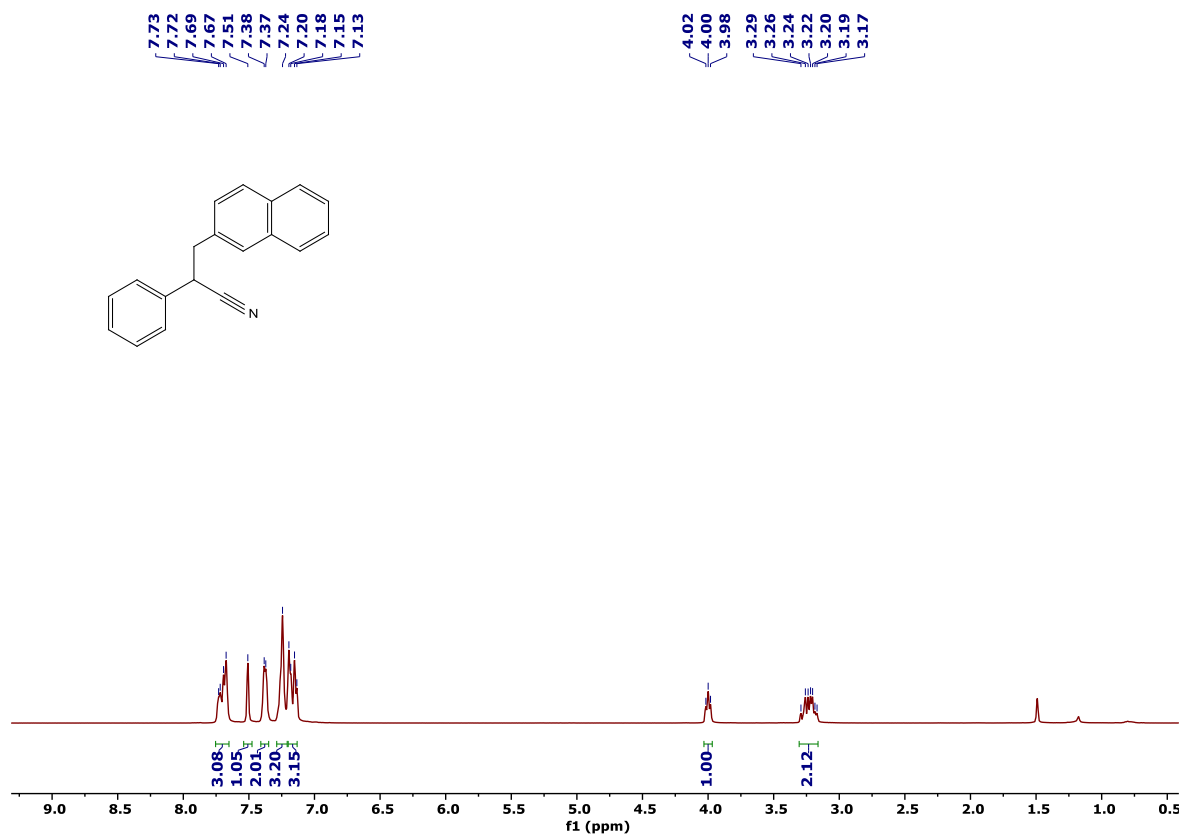


Figure S48. ¹H NMR spectrum of **4p** in CDCl₃.

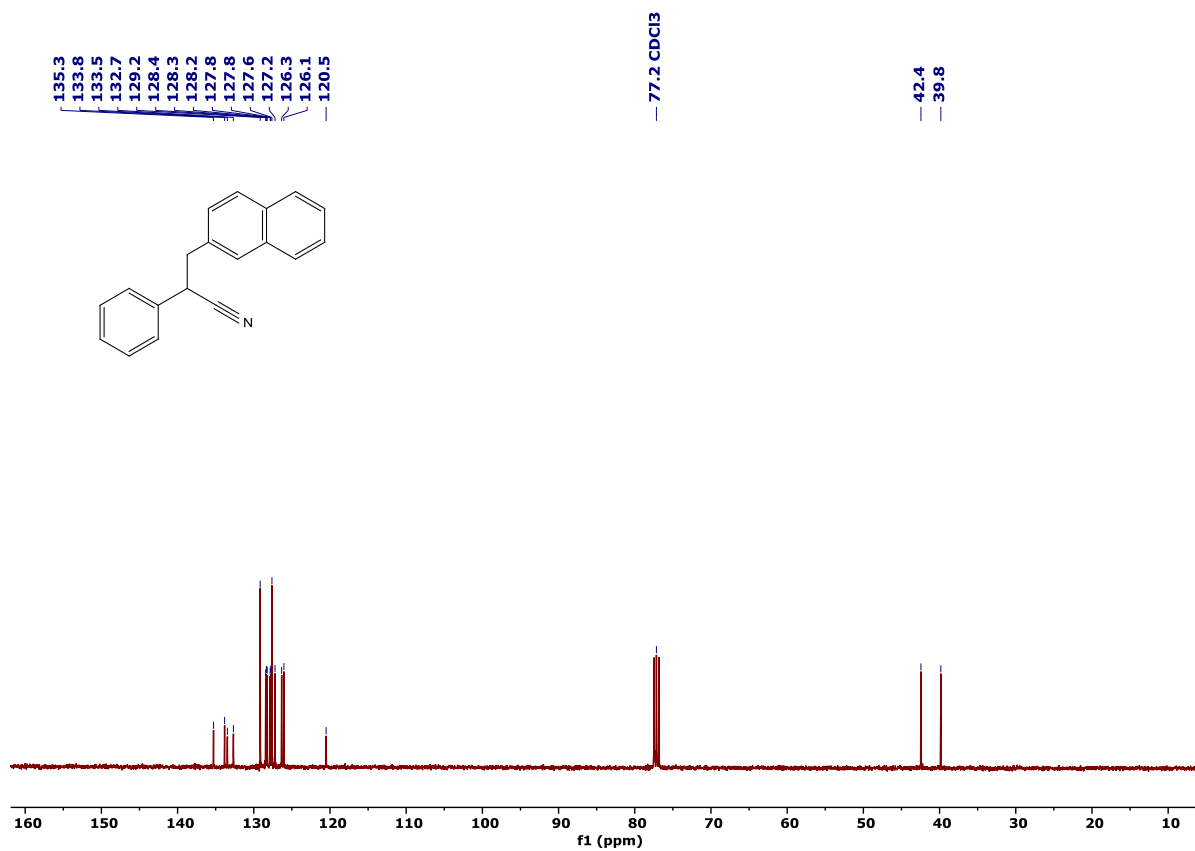


Figure S49. ¹³C {¹H} NMR spectrum of **4q** in CDCl₃.

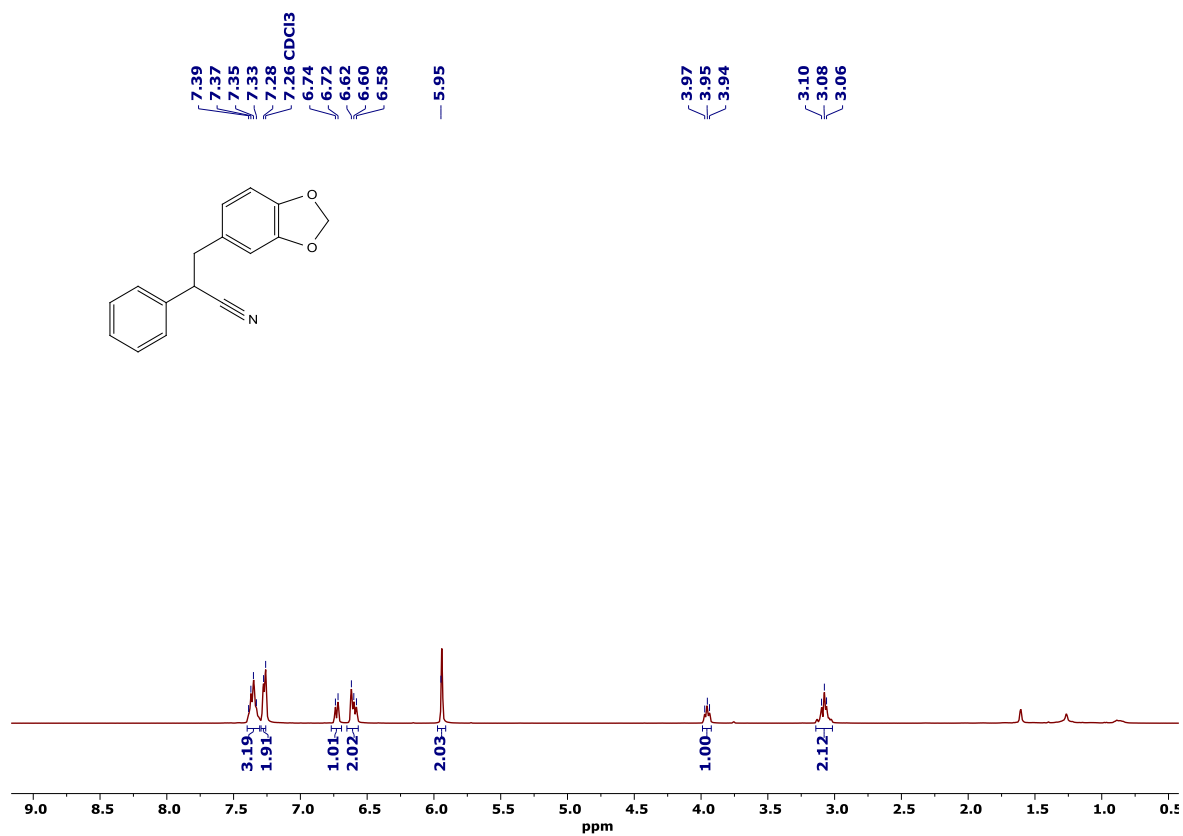


Figure S50. ^1H NMR spectrum of **4q** in CDCl_3 .

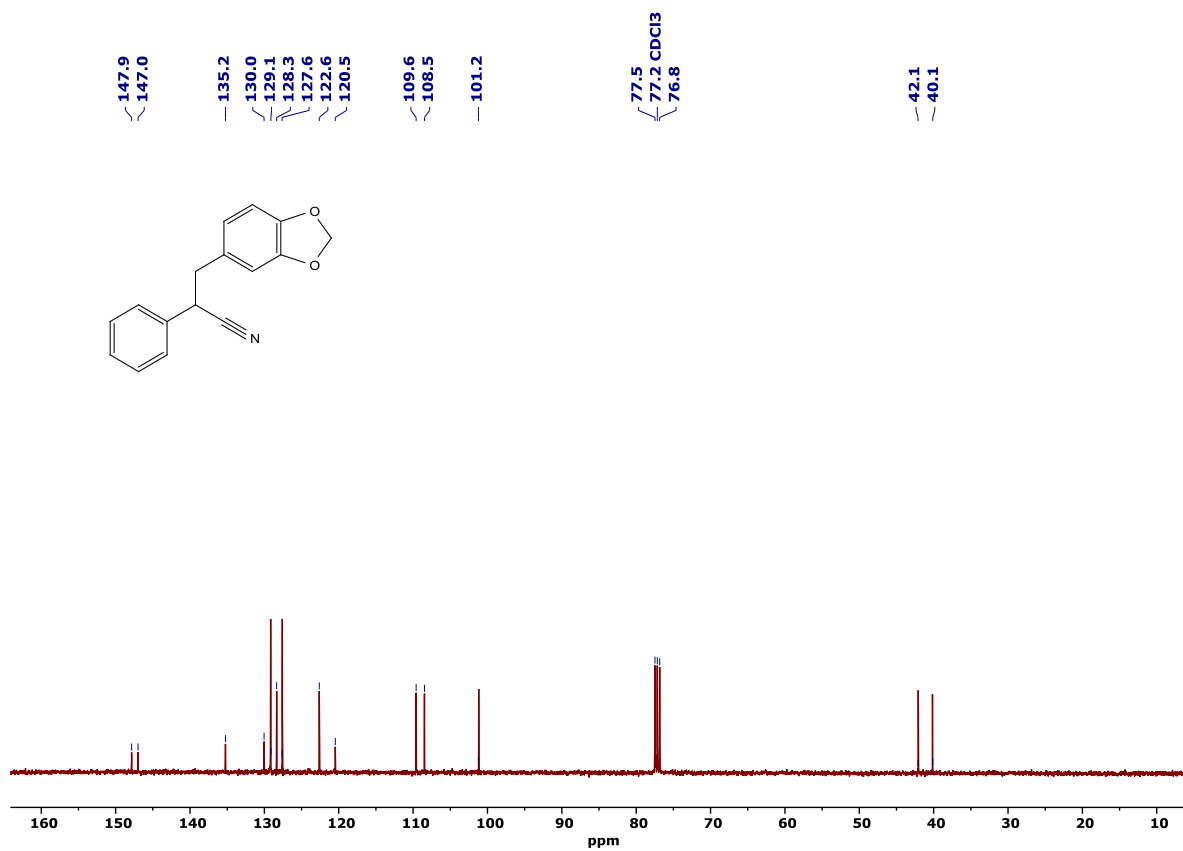


Figure S51. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4q** in CDCl_3 .

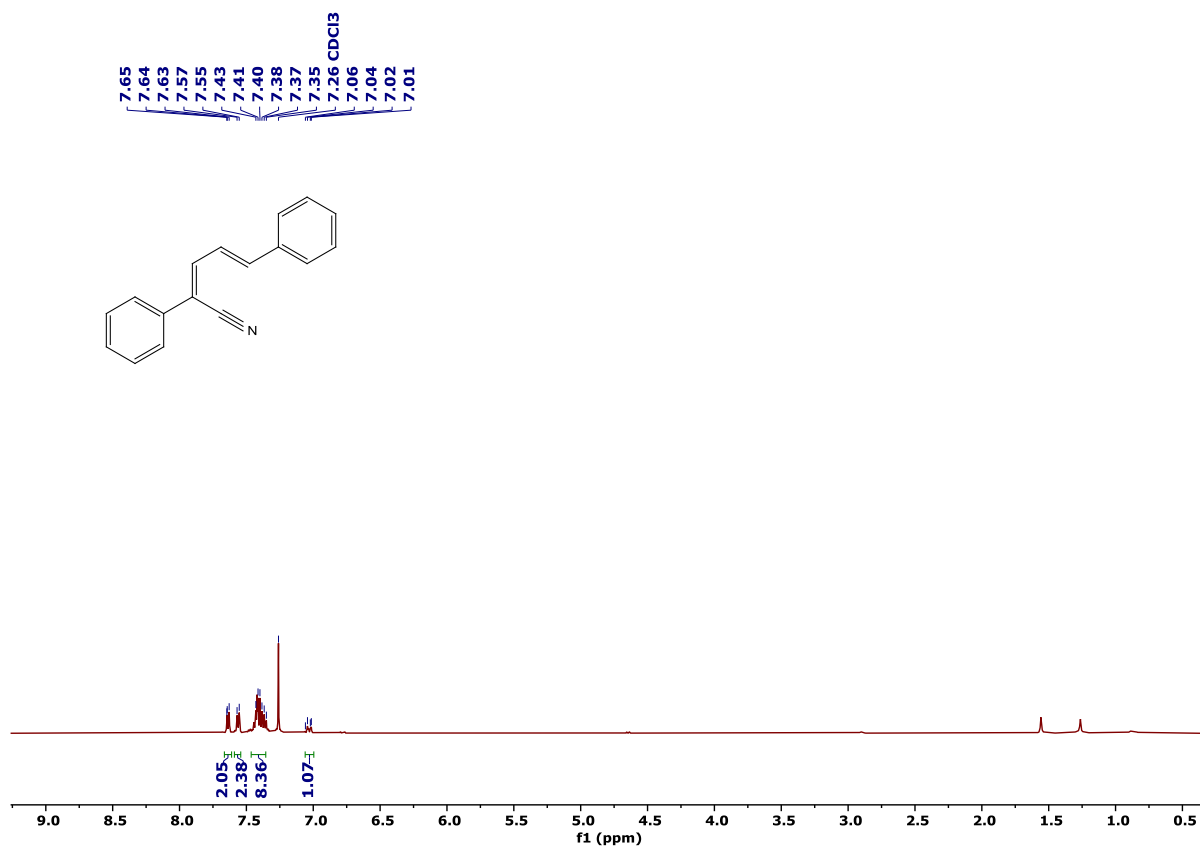


Figure S54. ¹H NMR spectrum of 4s in CDCl₃.

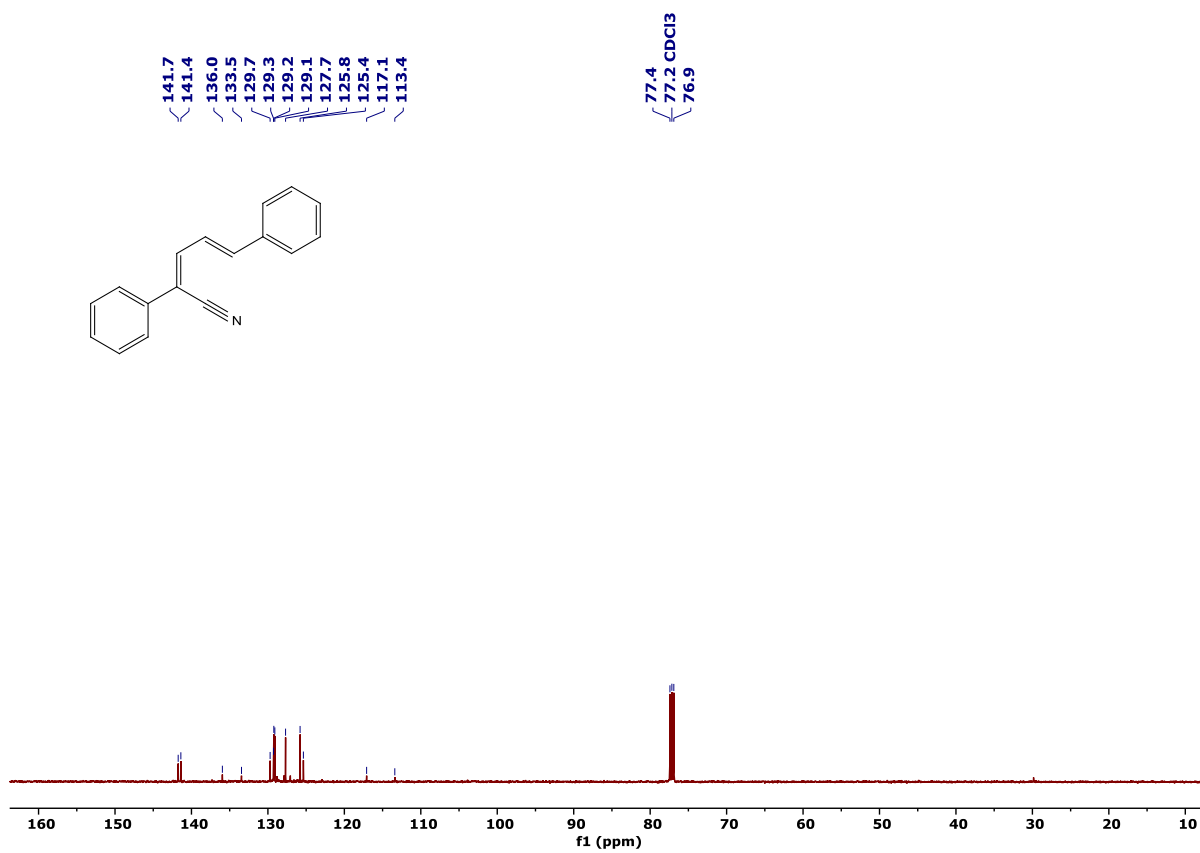


Figure S55. ¹³C{¹H} NMR spectrum of 4s in CDCl₃.

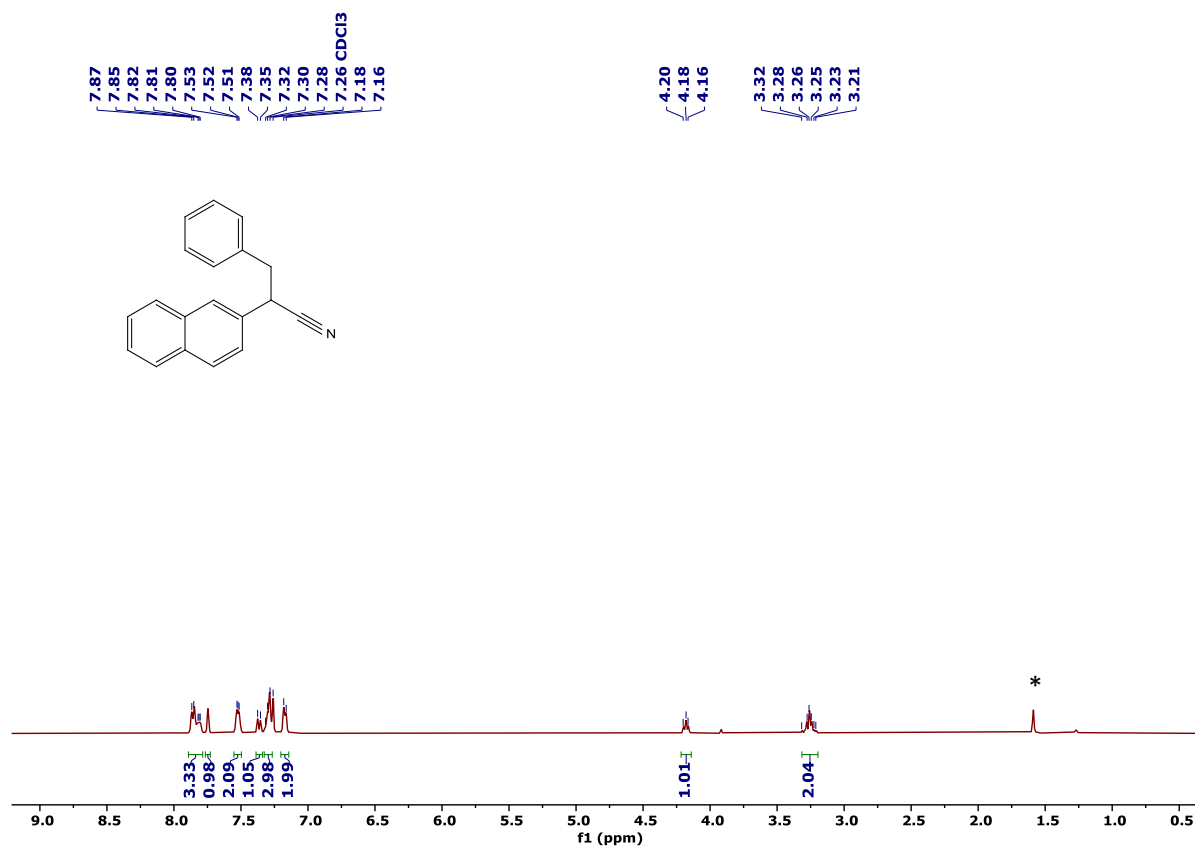


Figure S56. ¹H NMR spectrum of 4t in CDCl₃. * indicates the solvent impurity of H₂O.

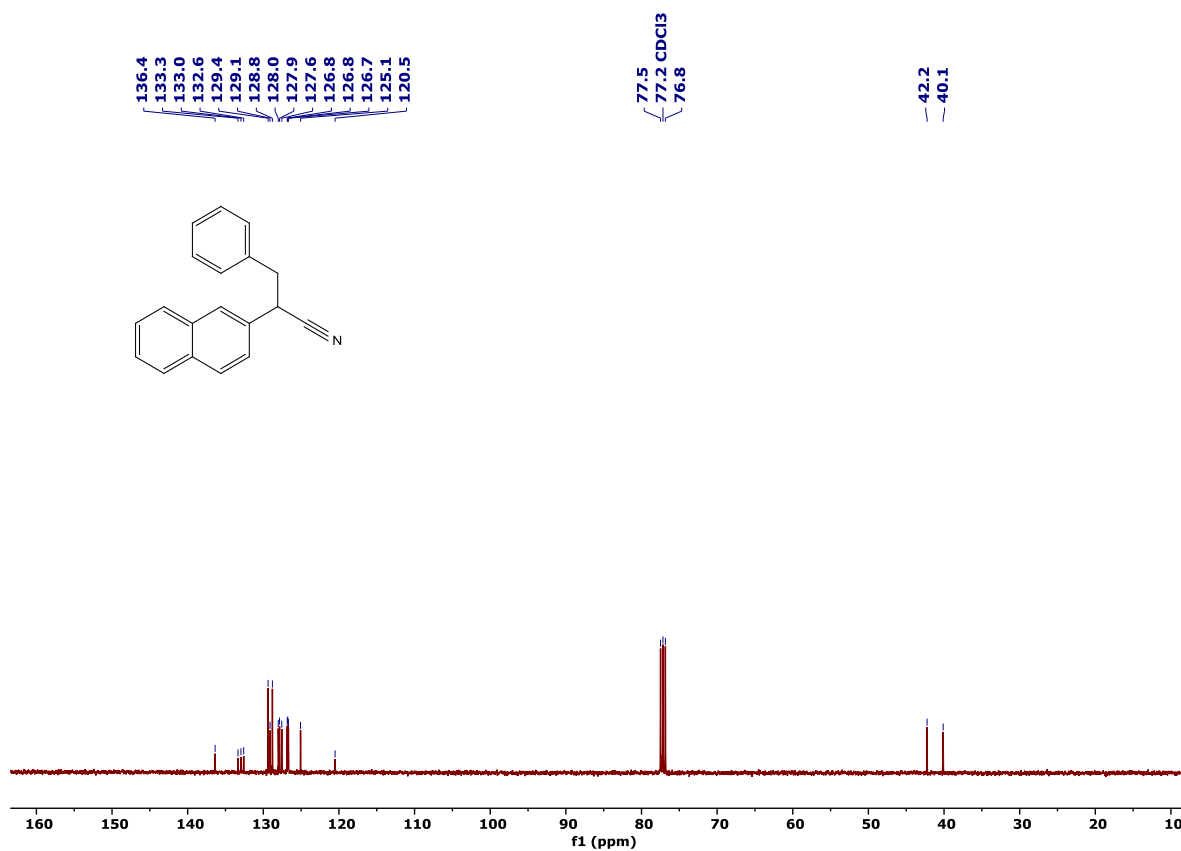


Figure S57. ¹³C{¹H} NMR spectrum of 4t in CDCl₃.

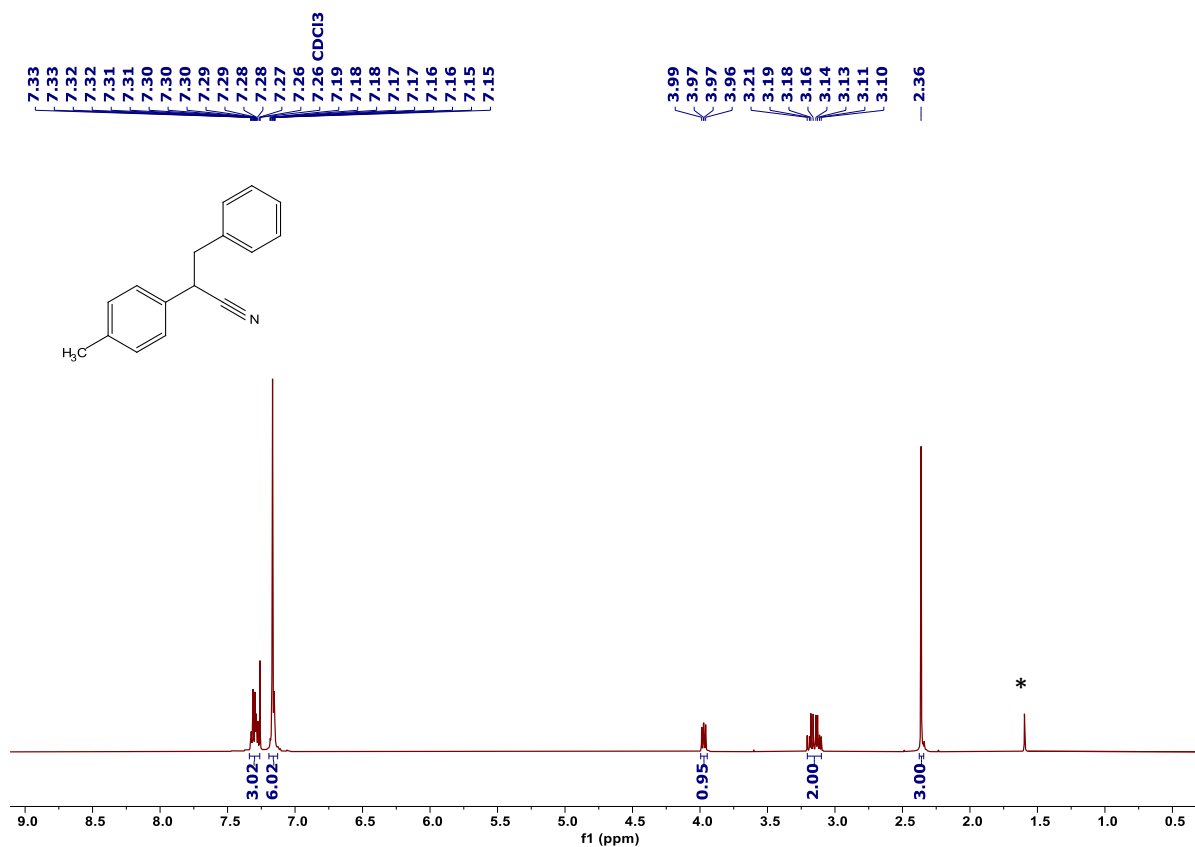


Figure S58. ¹H NMR spectrum of **4u** in CDCl₃. * indicates the solvent impurity of H₂O.

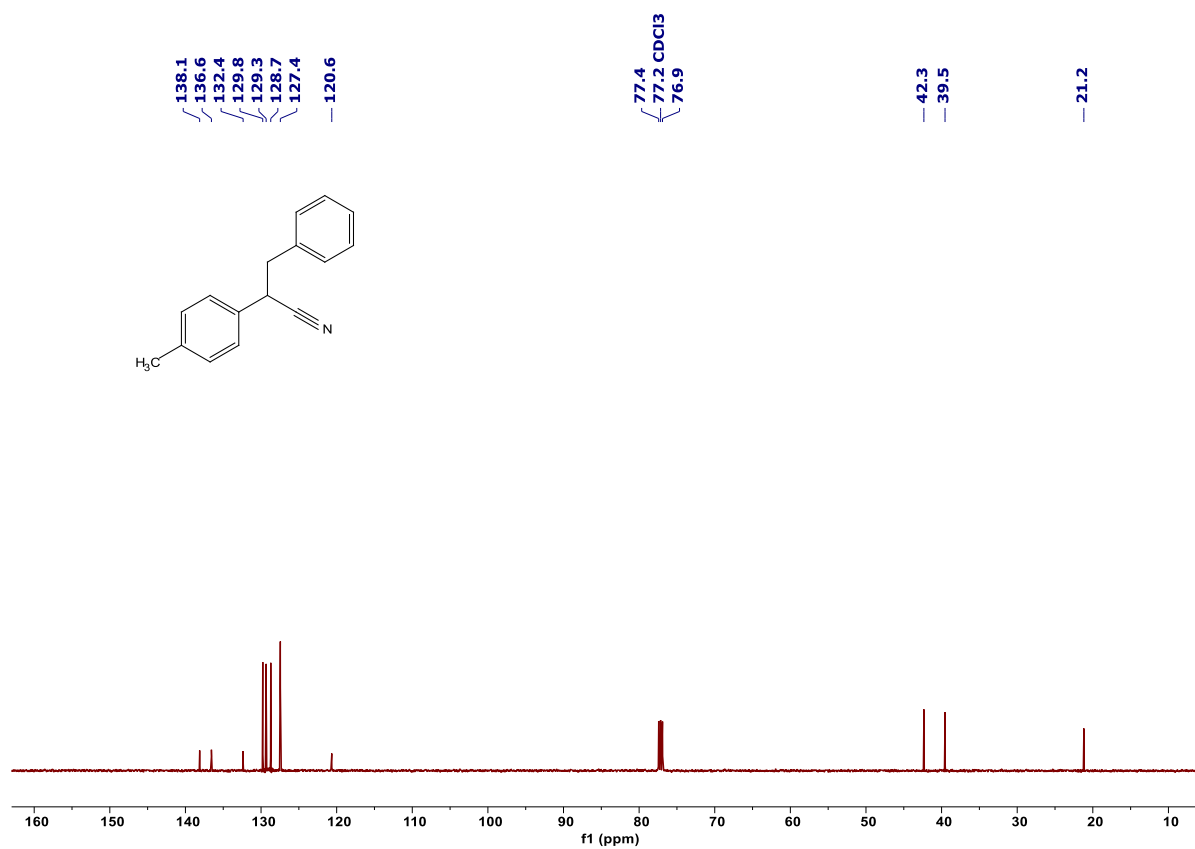


Figure S59. ¹³C{¹H} NMR spectrum of **4u** in CDCl₃.

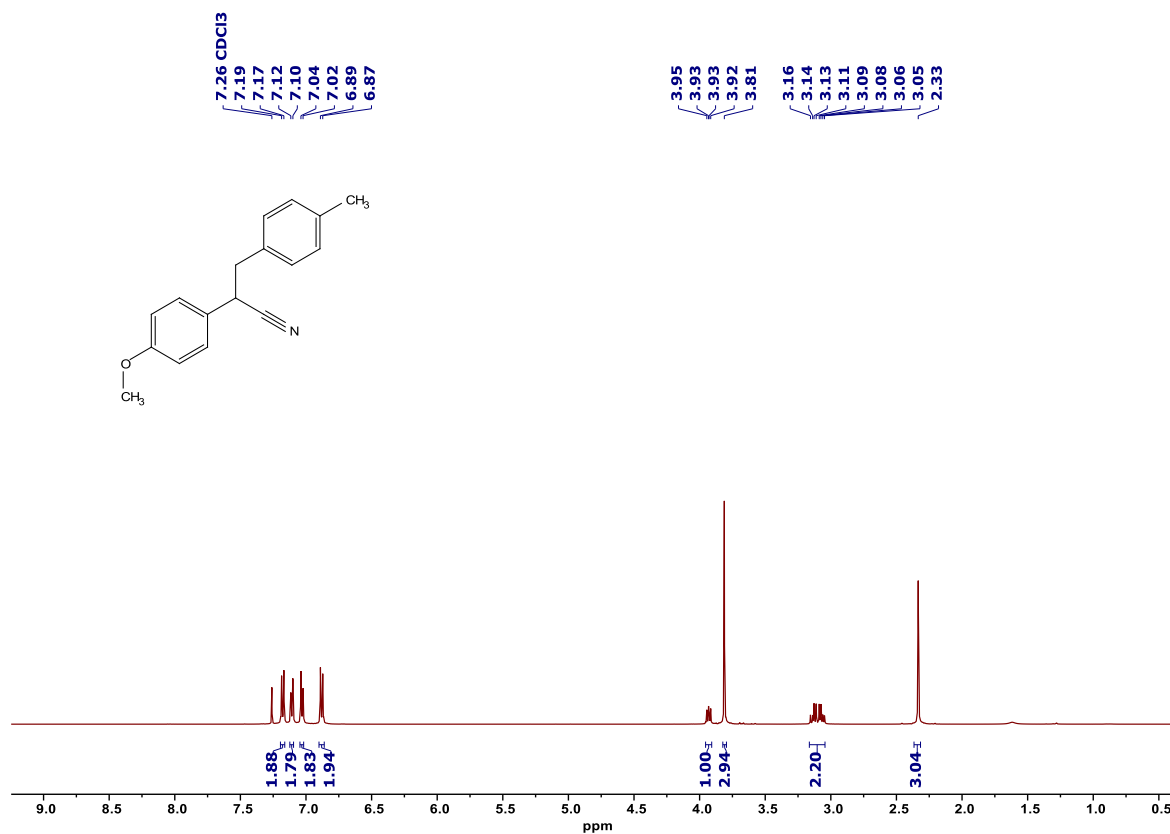


Figure S60. ^1H NMR spectrum of 4v in CDCl_3 .

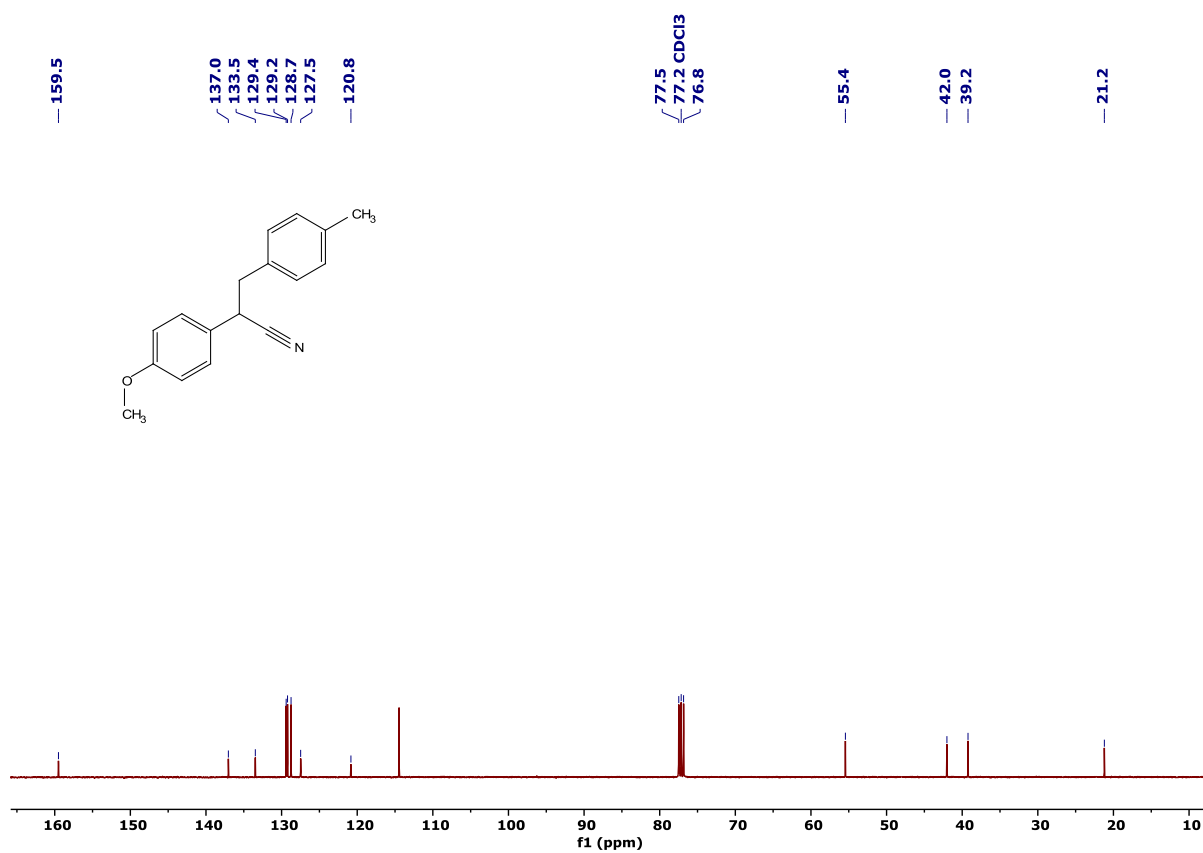


Figure S61. ^{13}C $\{^1\text{H}\}$ NMR spectrum of 4v in CDCl_3 .

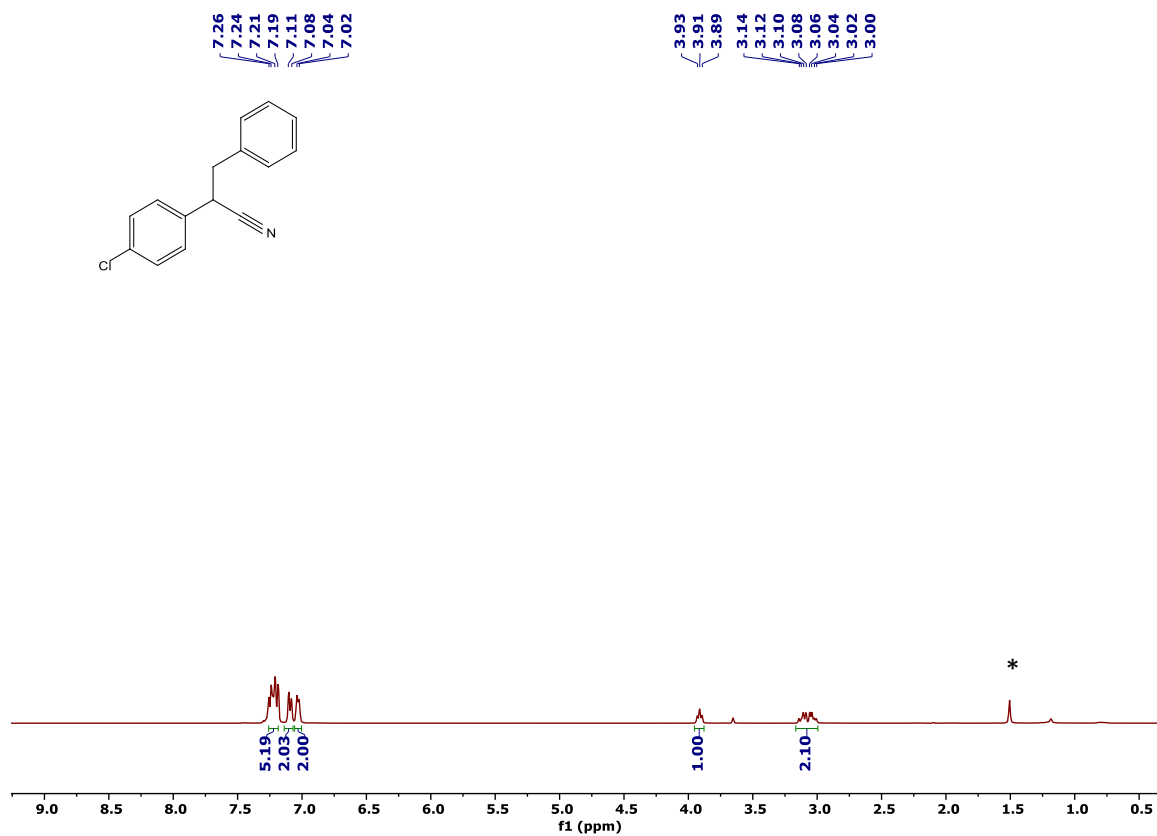


Figure S62. ¹H NMR spectrum of **4w** in CDCl₃. * indicates the solvent impurity of H₂O.

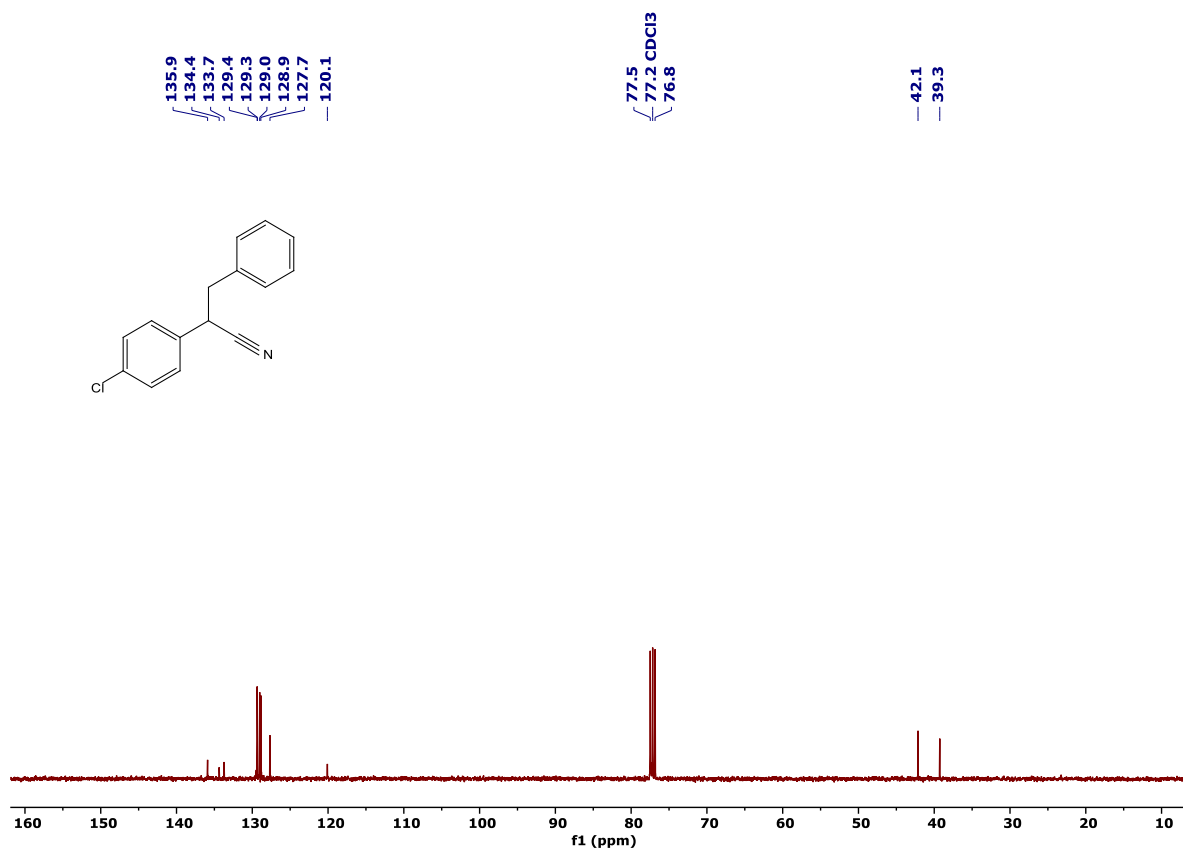


Figure S63. ¹³C {¹H} NMR spectrum of **4w** in CDCl₃.

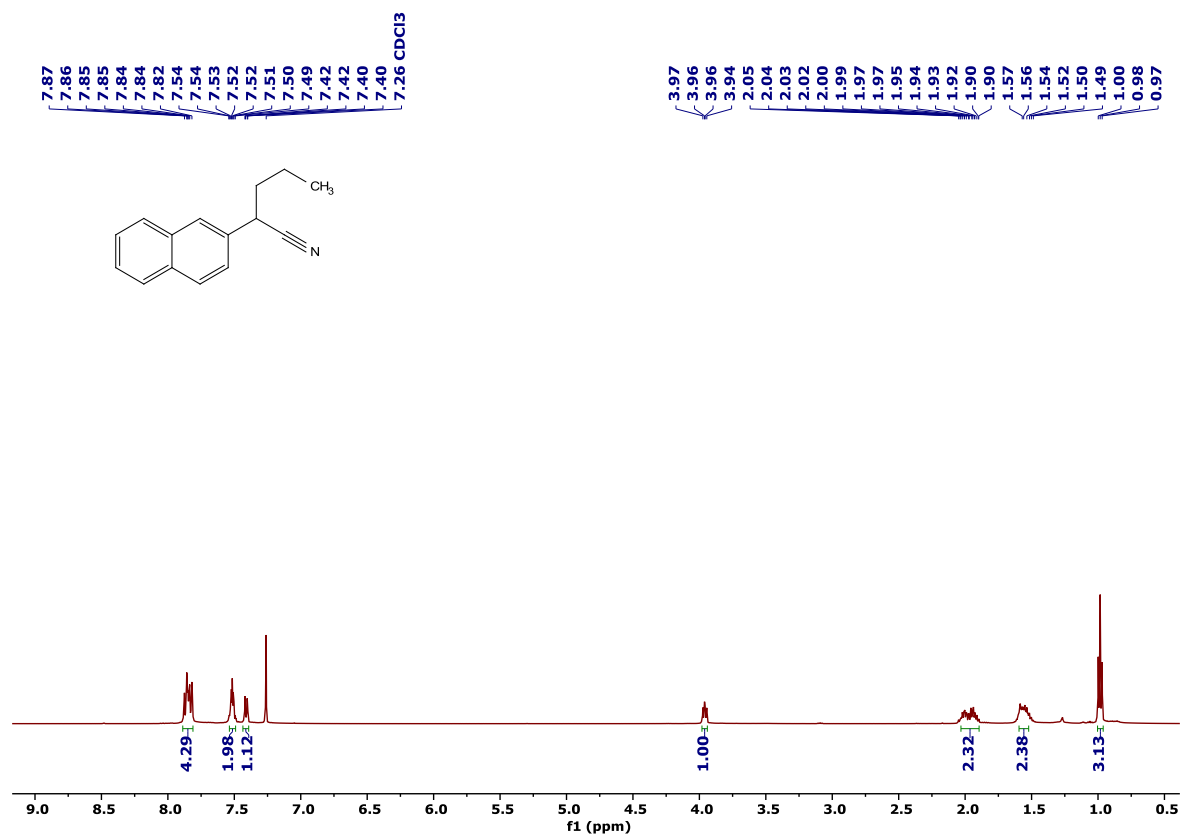


Figure S64. ¹H NMR spectrum of 6a in CDCl₃.

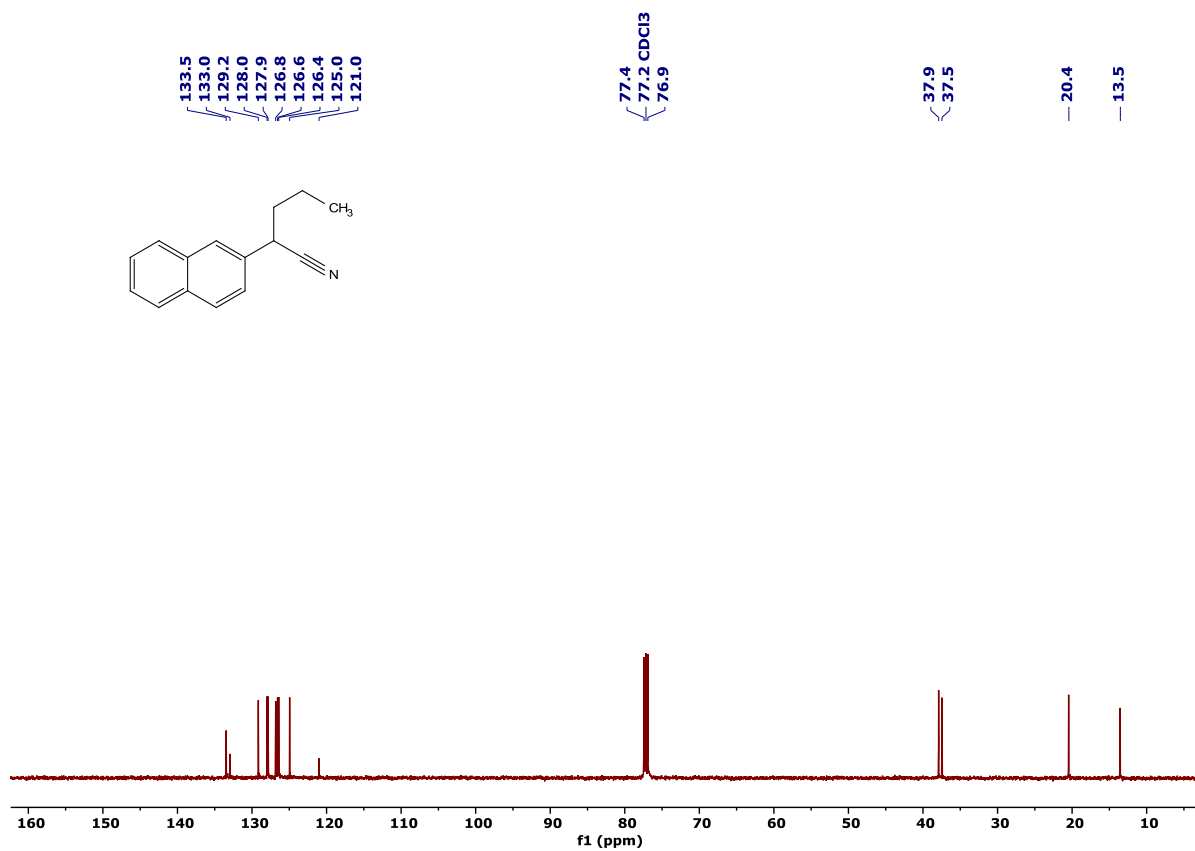


Figure S65. ¹³C {¹H} NMR spectrum of 6a in CDCl₃.

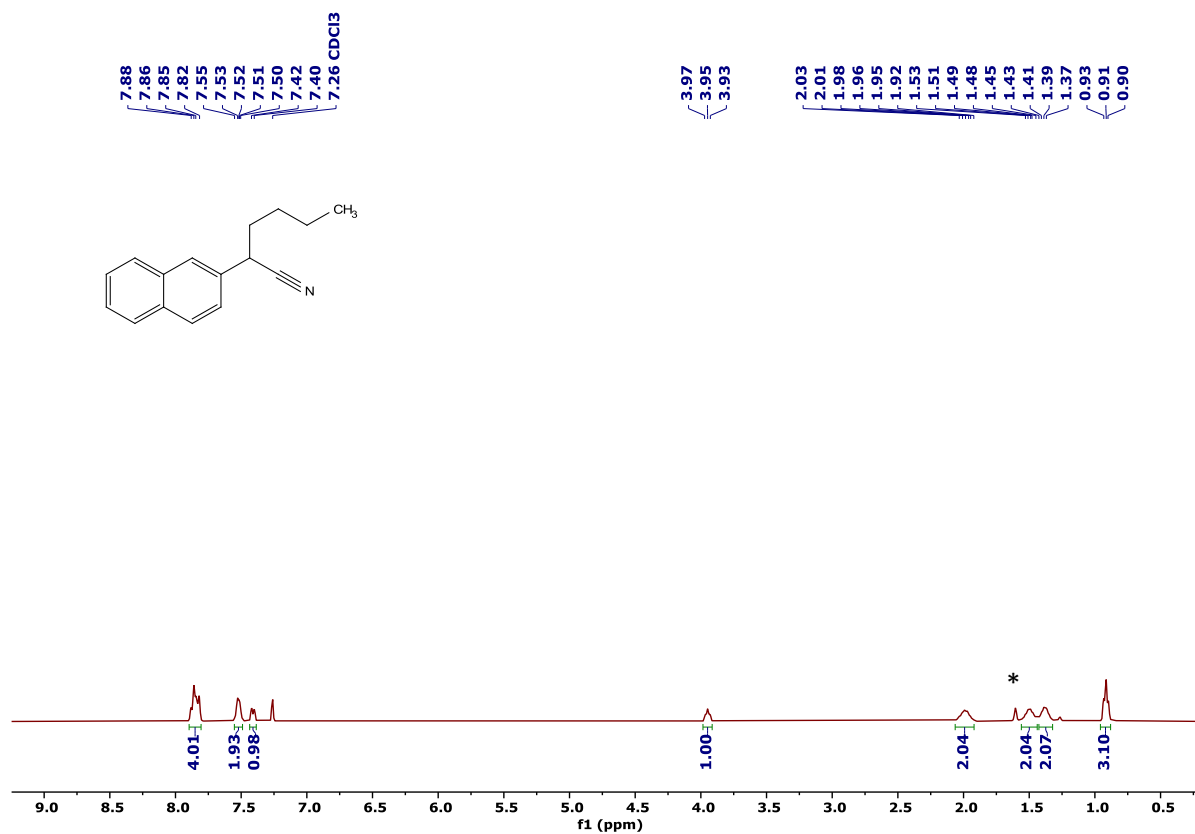


Figure S66. ¹H NMR spectrum of **6b** in CDCl₃. * indicates the solvent impurity of H₂O.

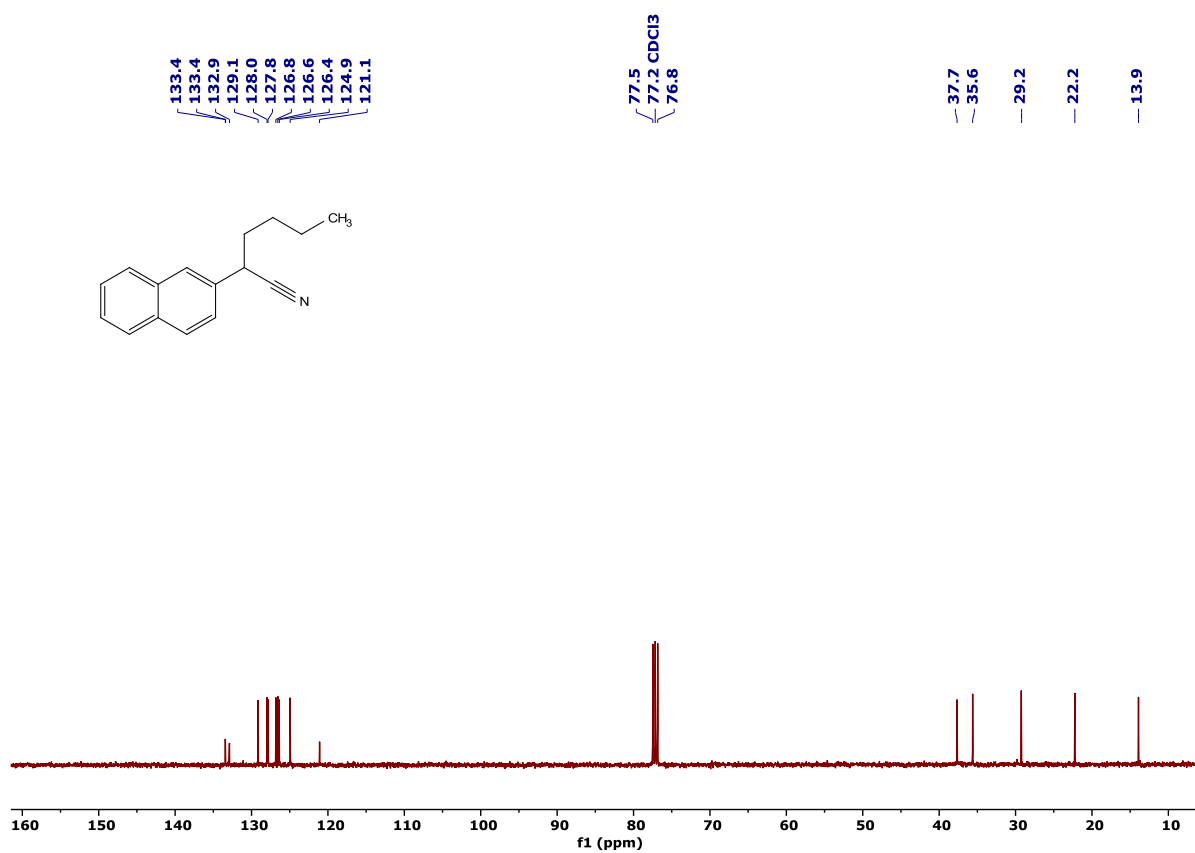


Figure S67. ¹³C {¹H} NMR spectrum of **6b** in CDCl₃.

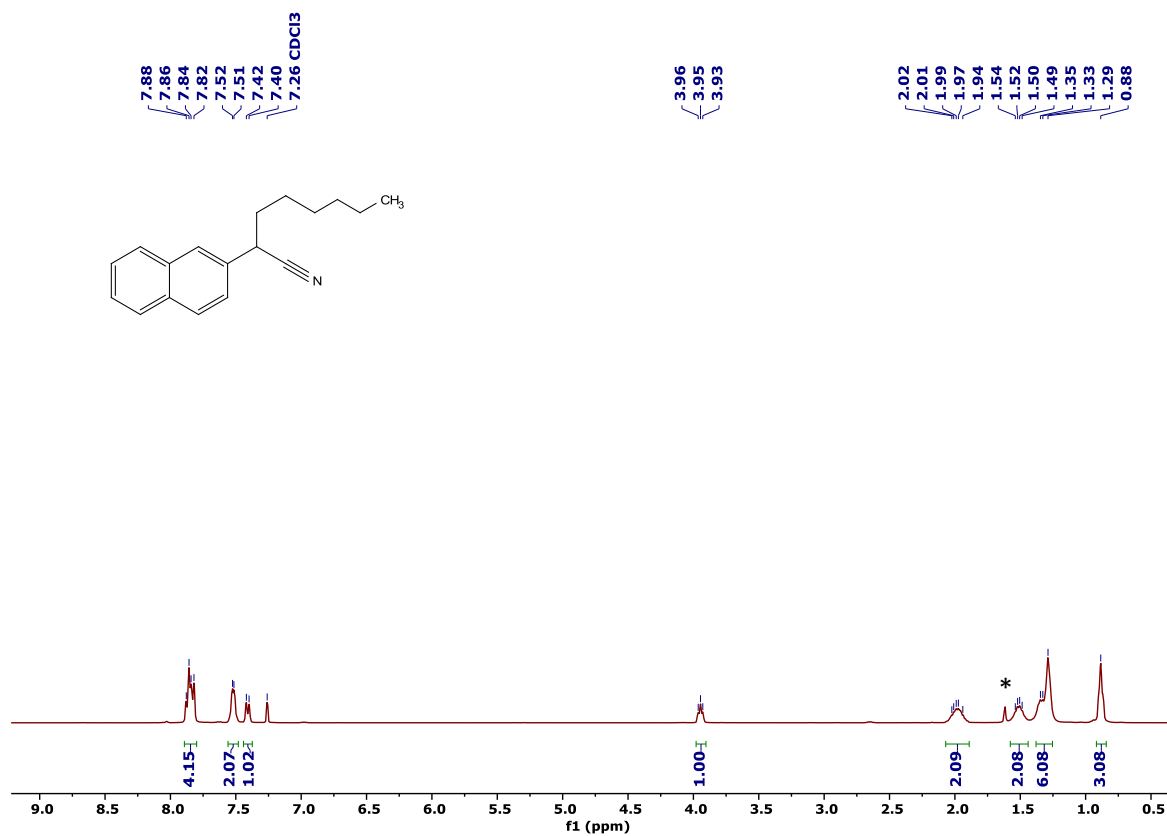


Figure S68. ¹H NMR spectrum of **6c** in CDCl₃. * indicates the solvent impurity of H₂O.

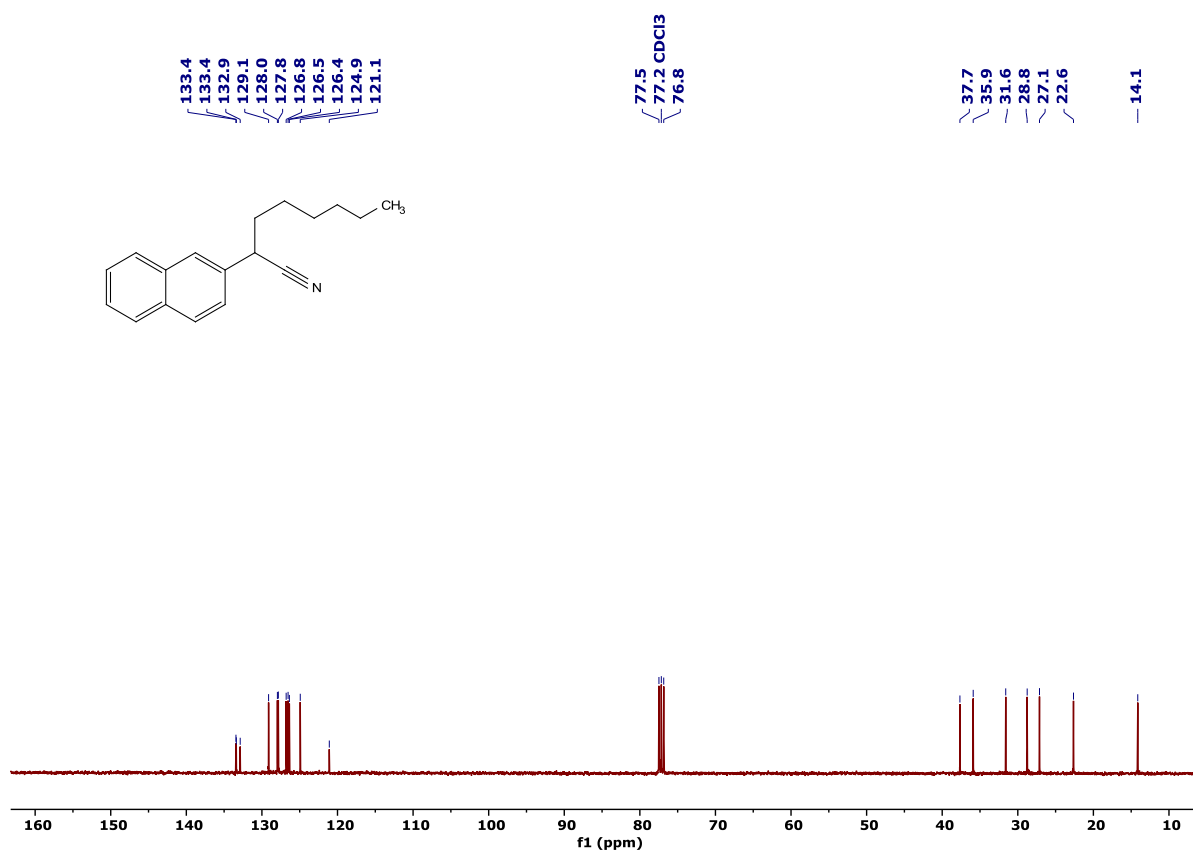


Figure S69. ¹³C {¹H} NMR spectrum of **6c** in CDCl₃.

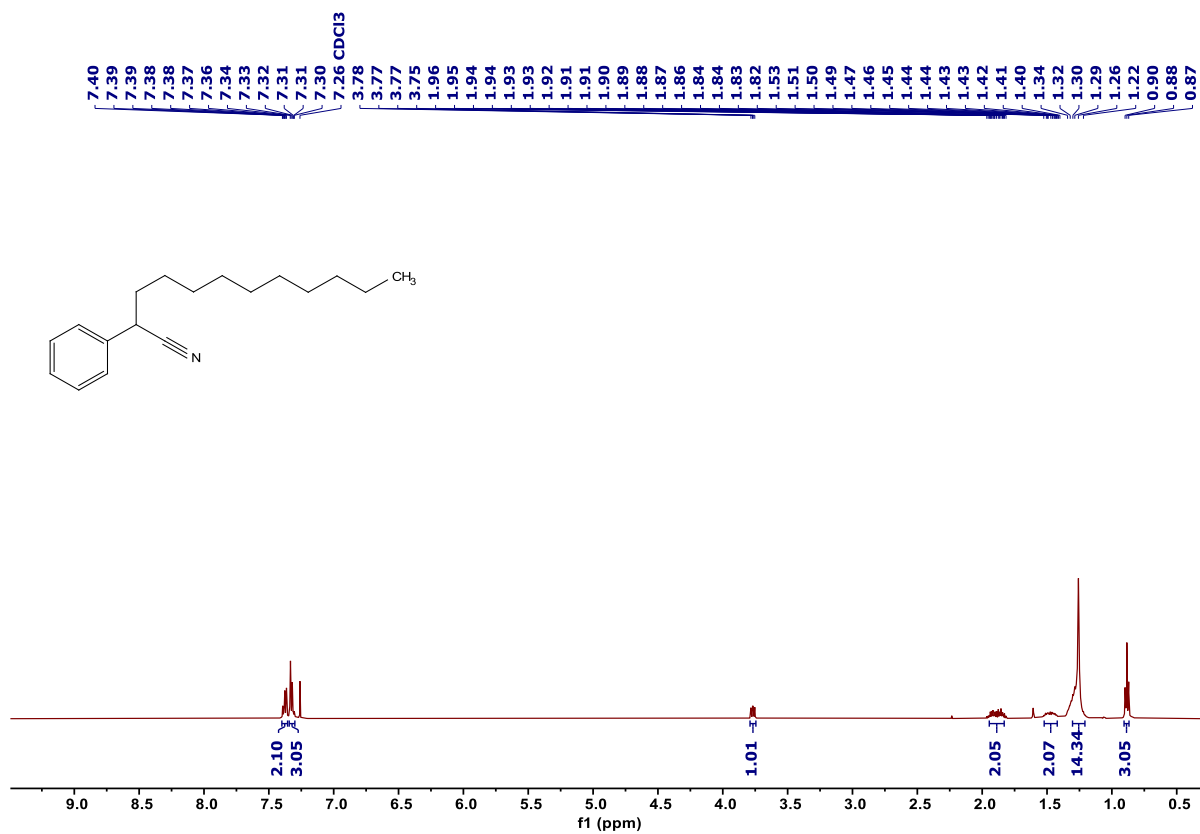


Figure S70. ¹H NMR spectrum of 6d in CDCl₃.

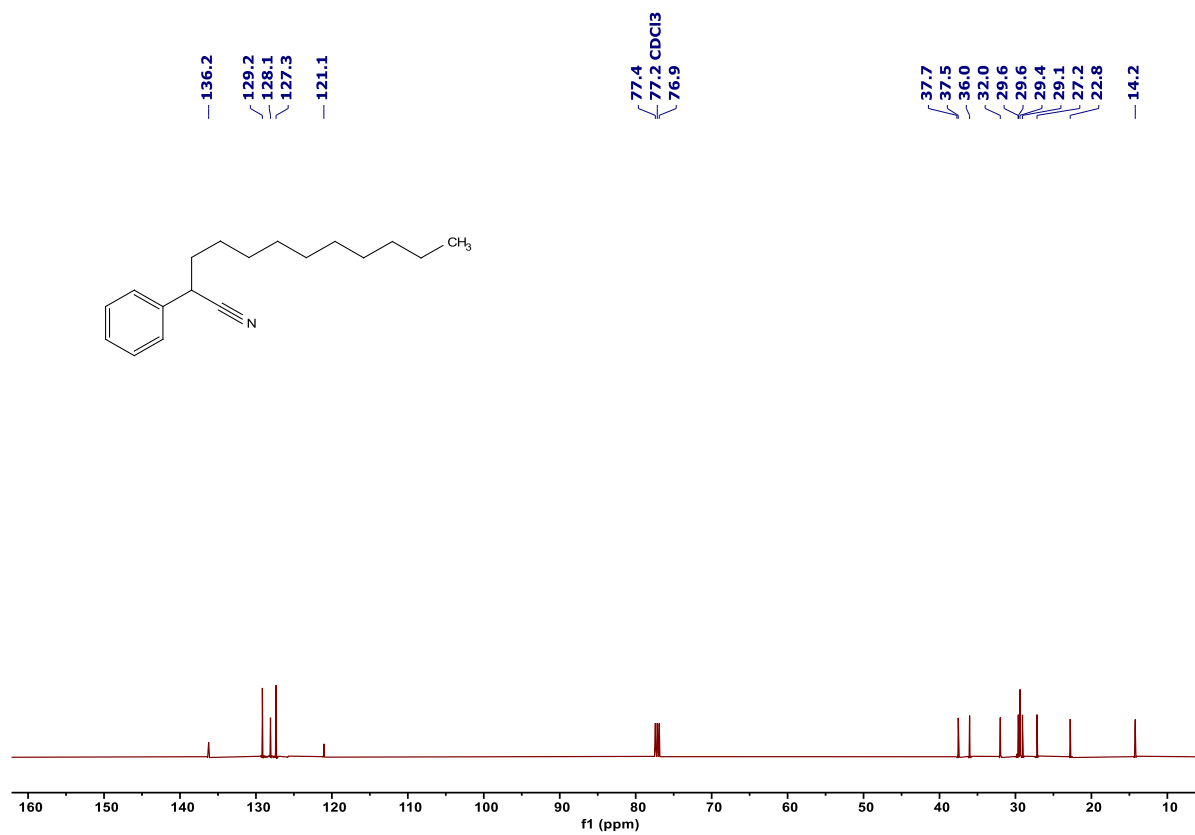


Figure S71. ¹³C{¹H} NMR spectrum of 6d in CDCl₃.

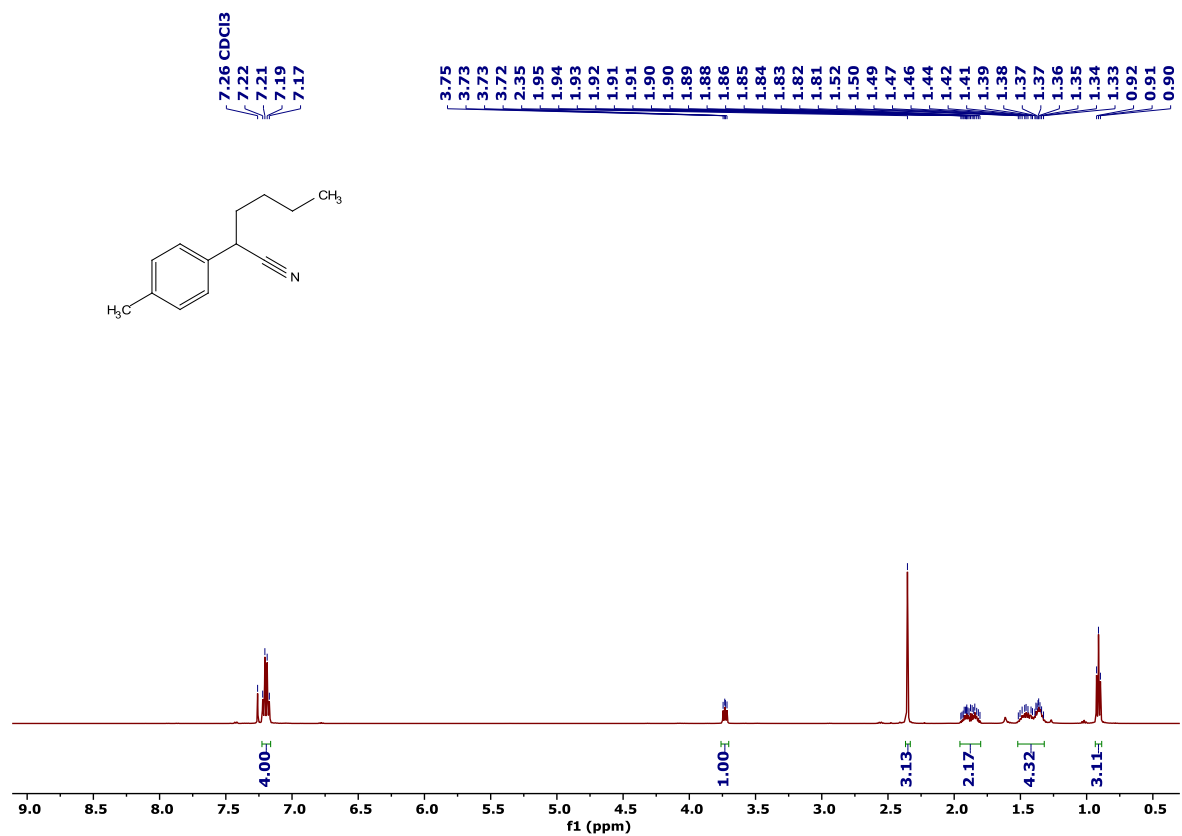


Figure S72. ¹H NMR spectrum of 6e in CDCl₃.

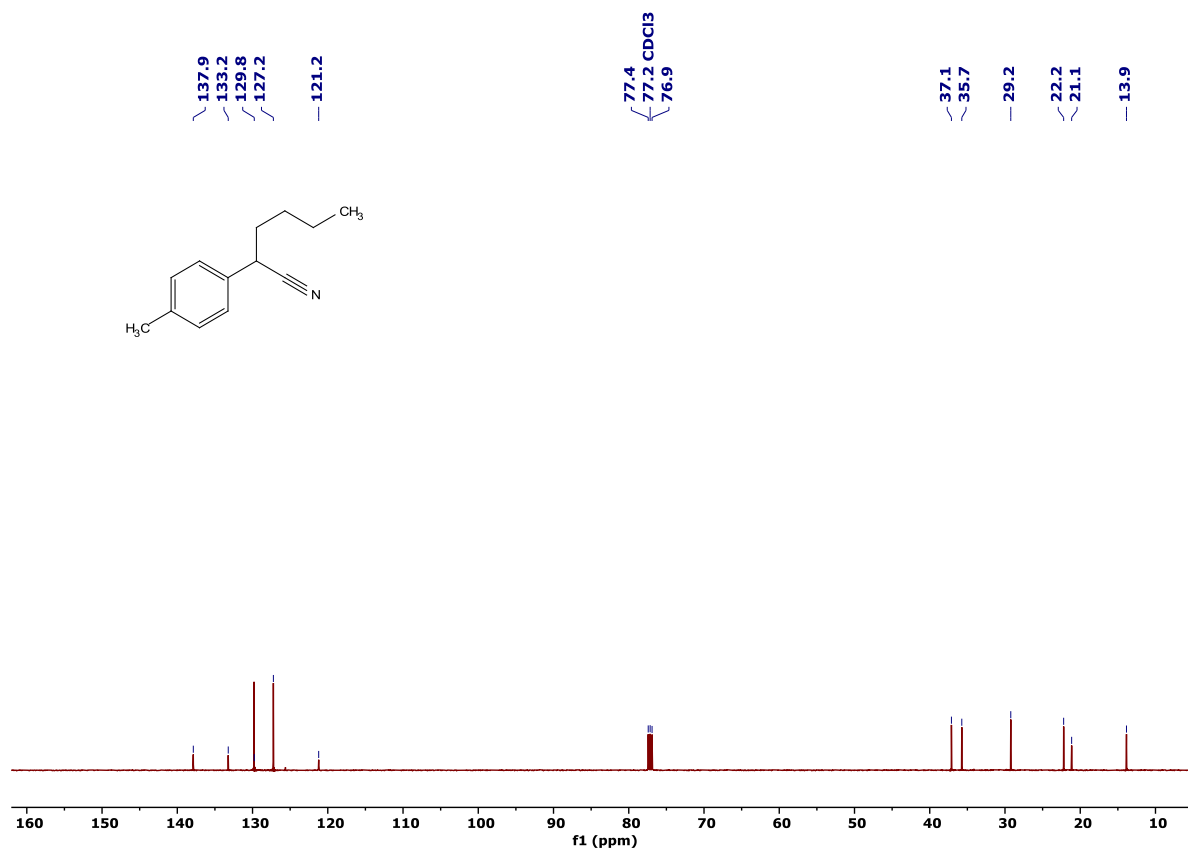


Figure S73. ¹³C {¹H} NMR spectrum of 6e in CDCl₃.

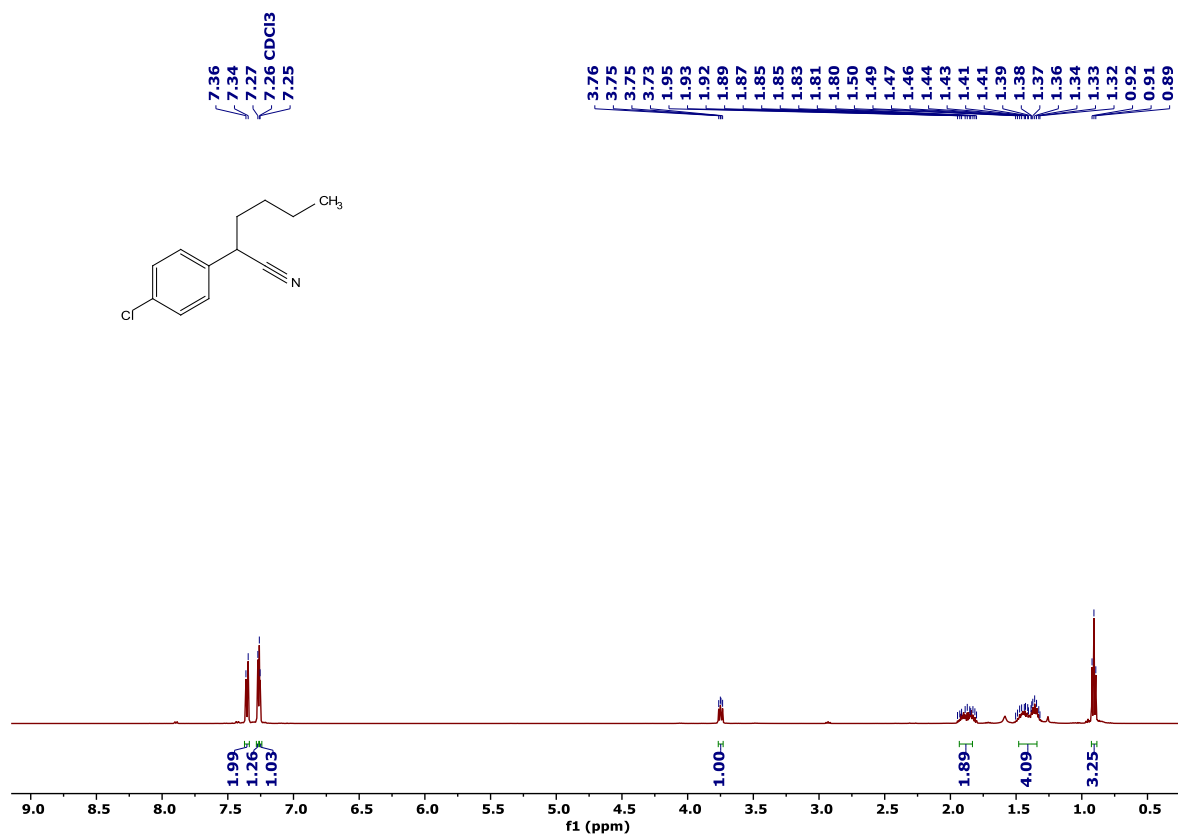


Figure S74. ¹H NMR spectrum of **6f** in CDCl₃.

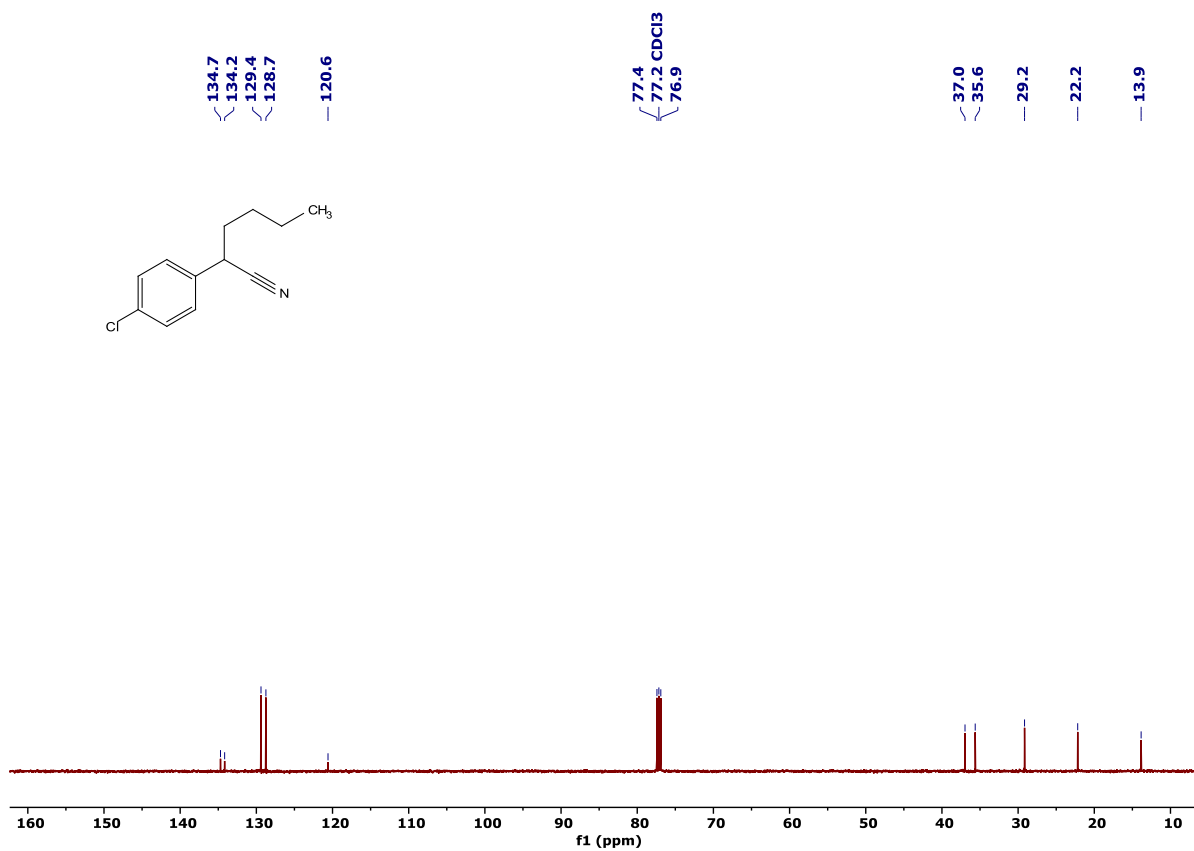


Figure S75. ¹³C {¹H} NMR spectrum of **6f** in CDCl₃.

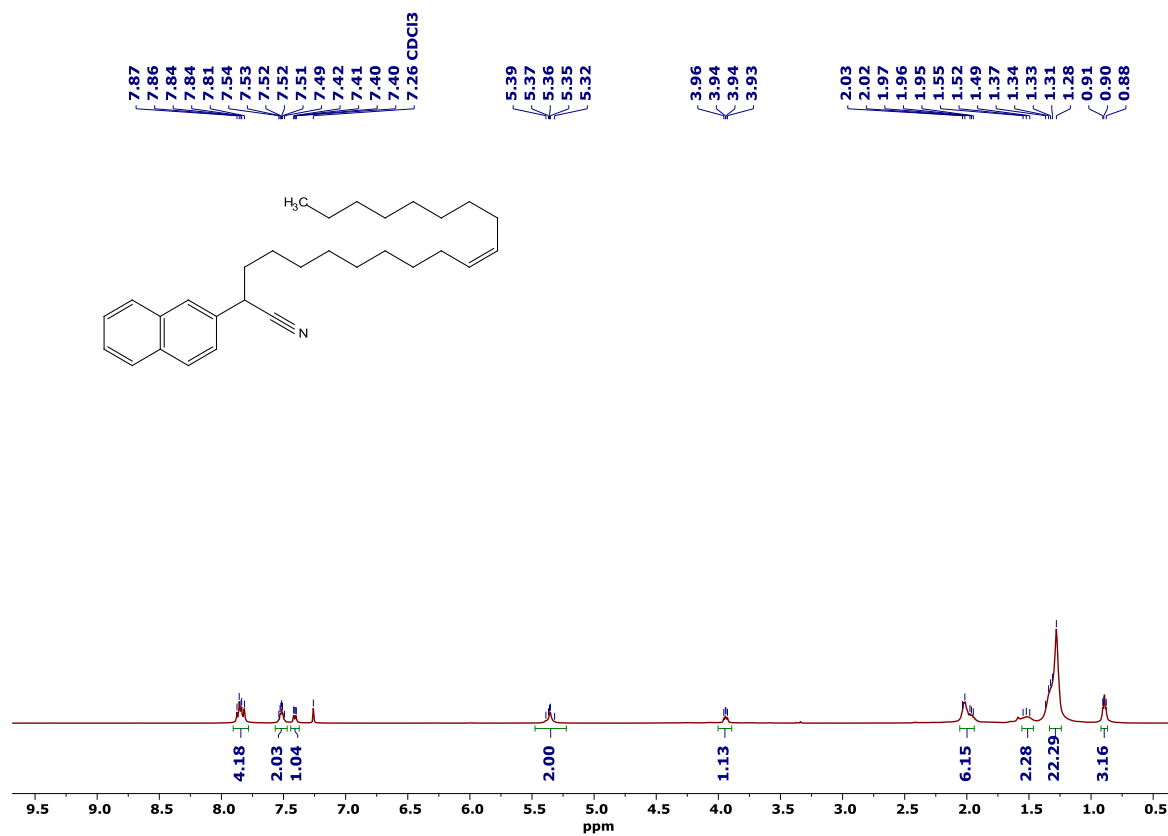


Figure S76. ^1H NMR spectrum of **6g** in CDCl_3 .

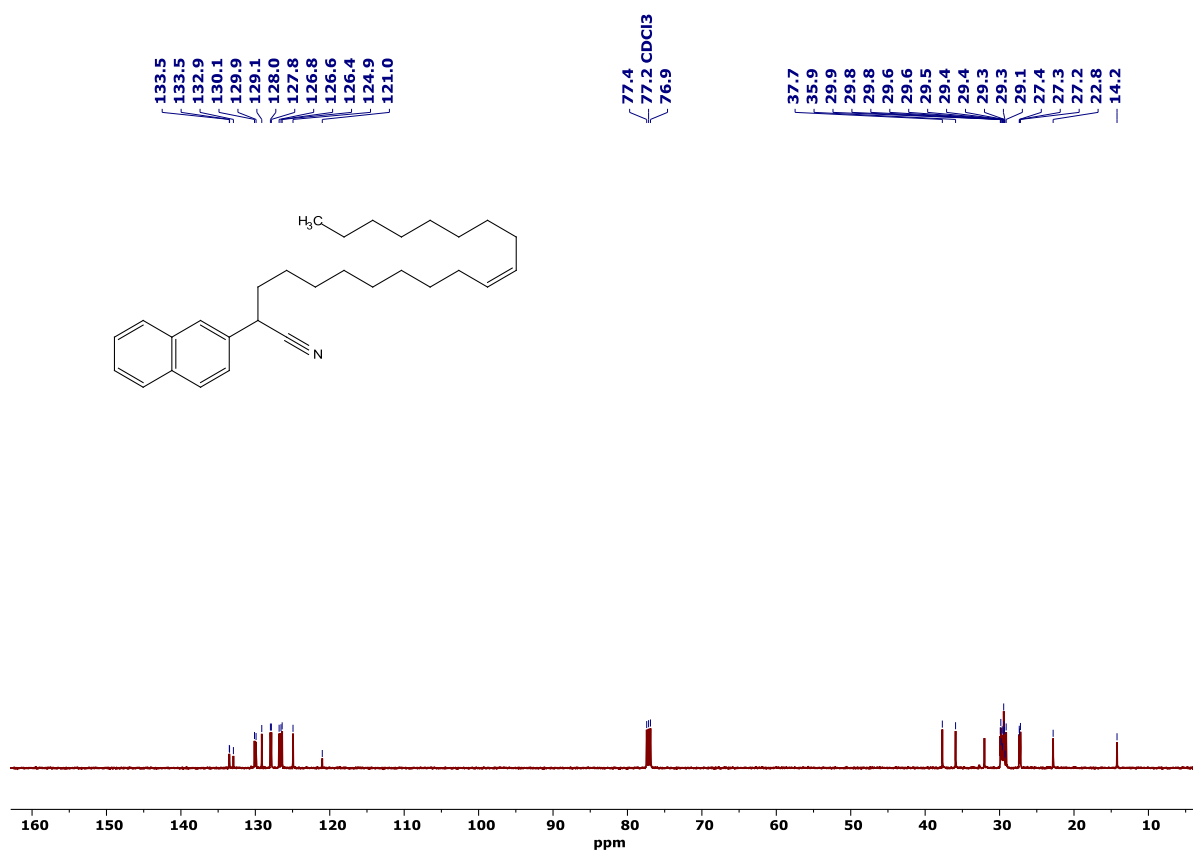


Figure S77. ^{13}C $\{^1\text{H}\}$ NMR spectrum of **6g** in CDCl_3 .

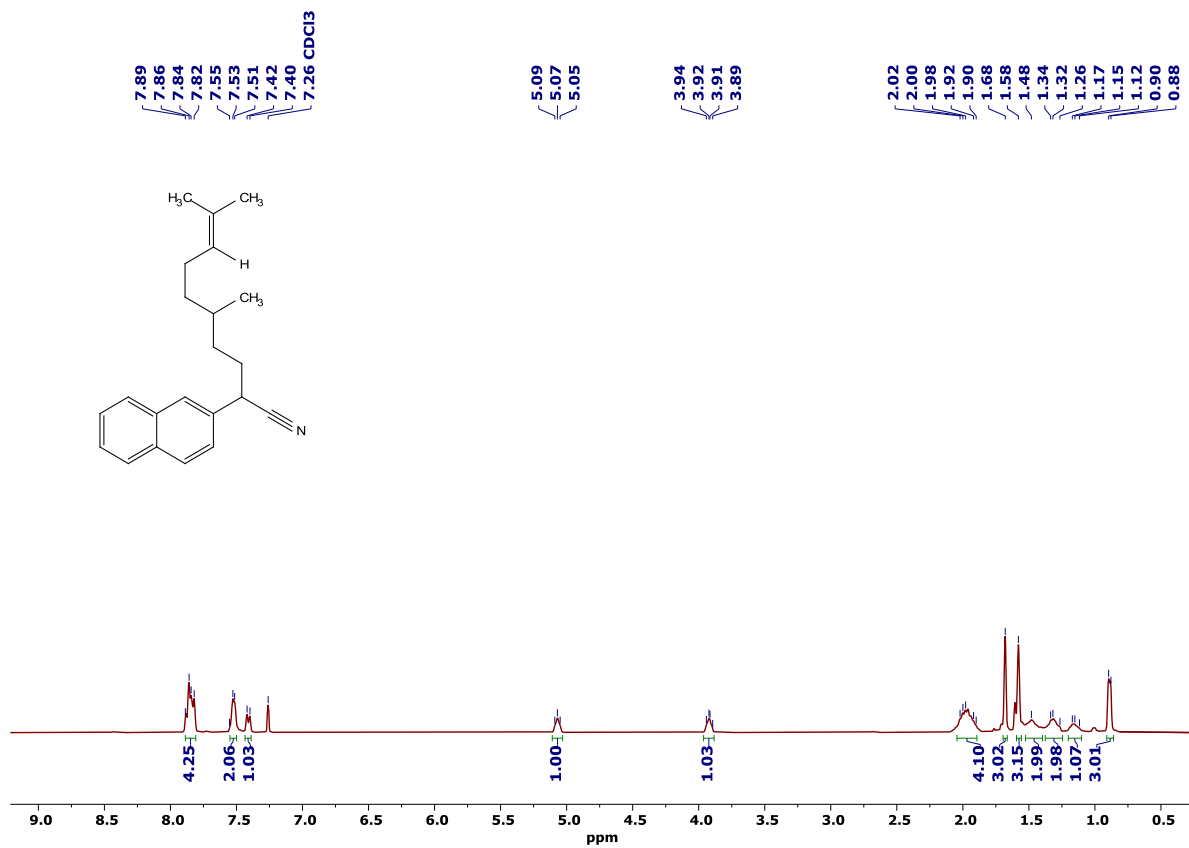


Figure S78. ¹H NMR spectrum of **6h** in CDCl₃.

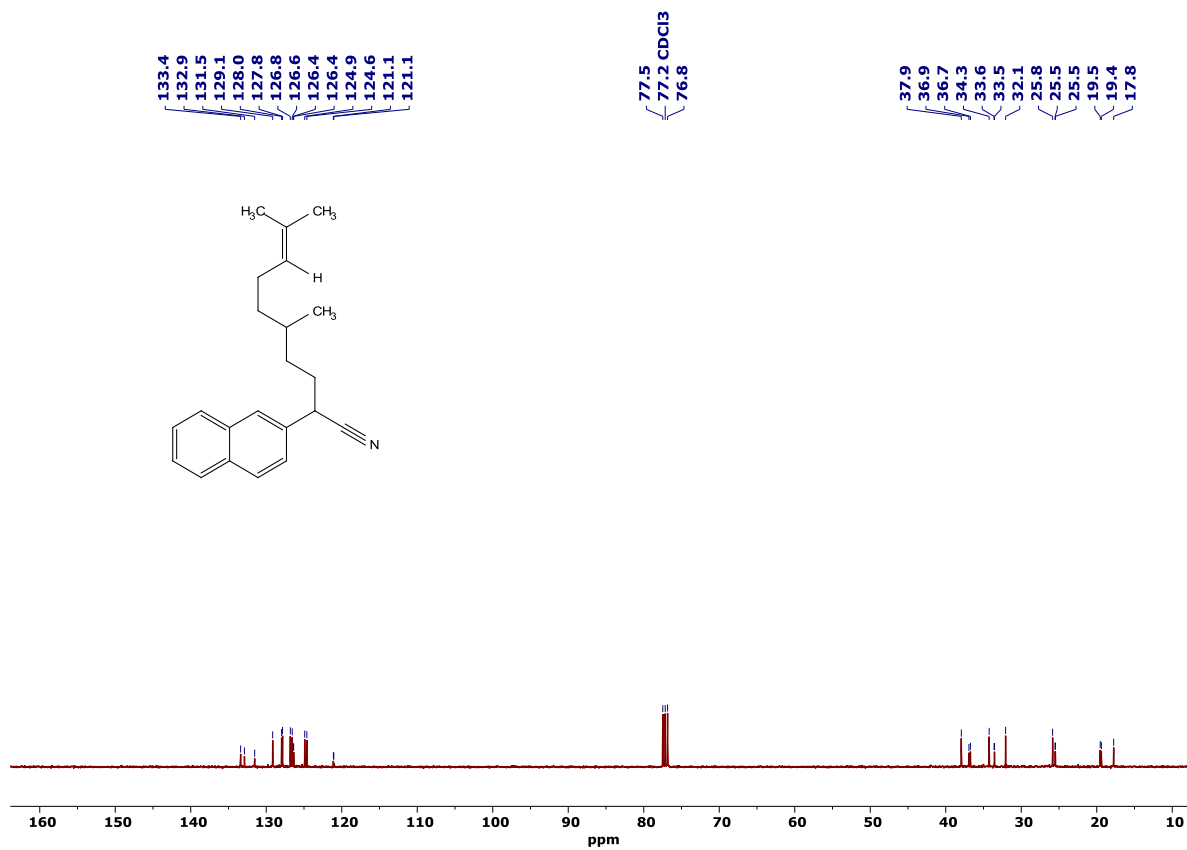


Figure S79. ¹³C{¹H} NMR spectrum of **6h** in CDCl₃.

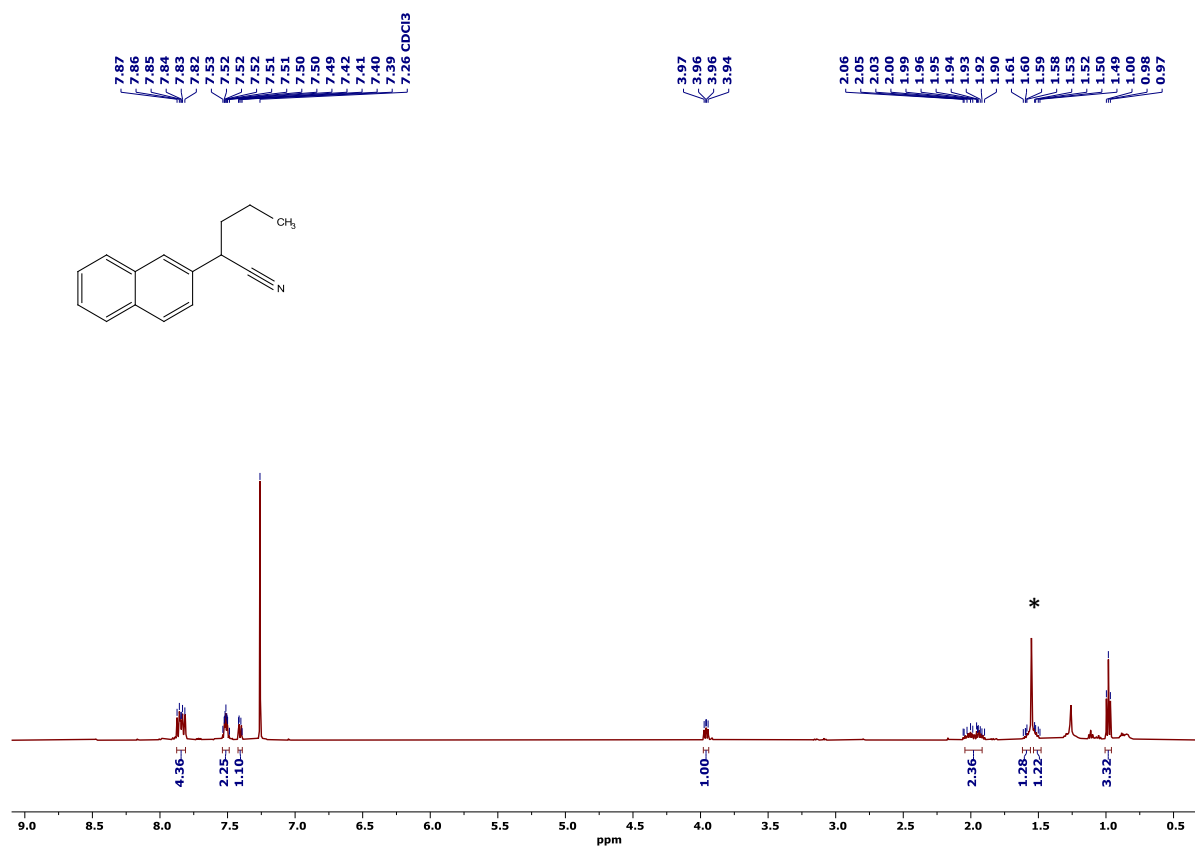


Figure S80. ¹H NMR spectrum of **6i** in CDCl₃. * indicates the solvent impurity of H₂O.

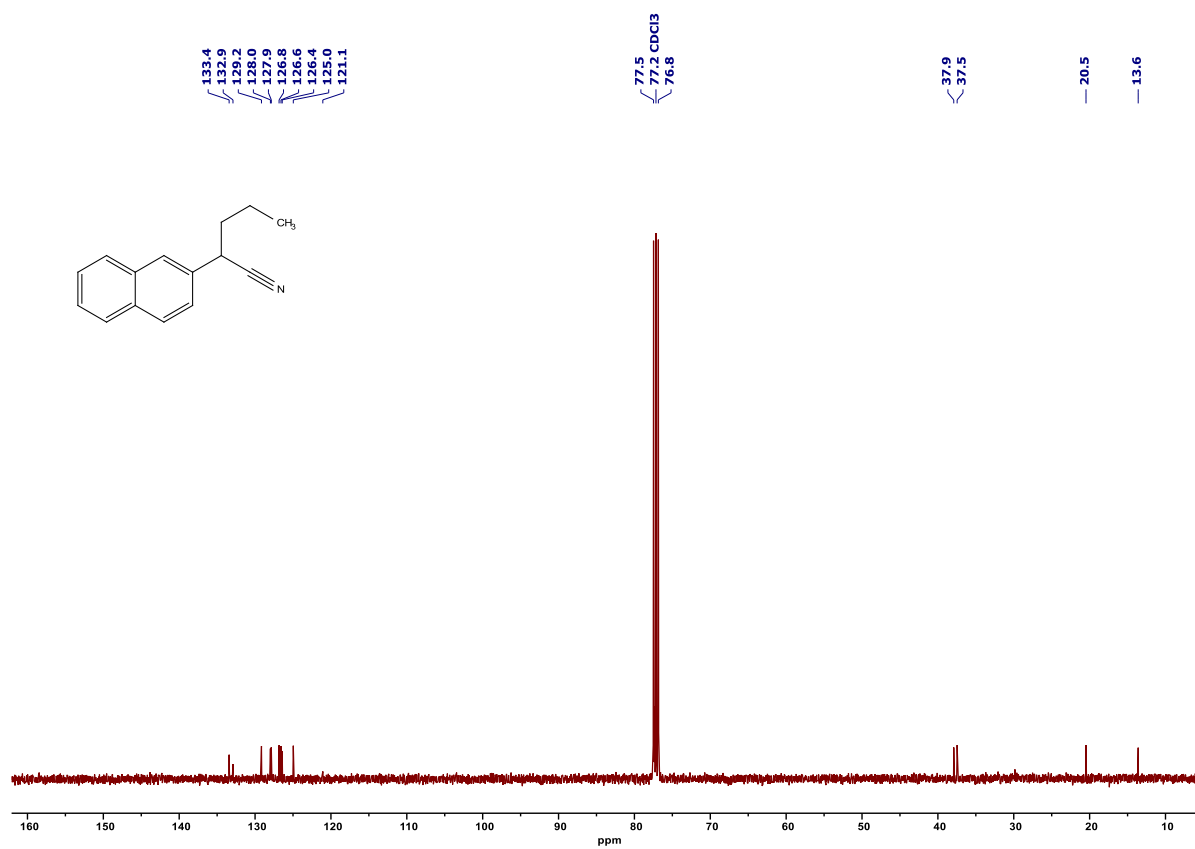


Figure S81. ¹³C{¹H} NMR spectrum of **6i** in CDCl₃.

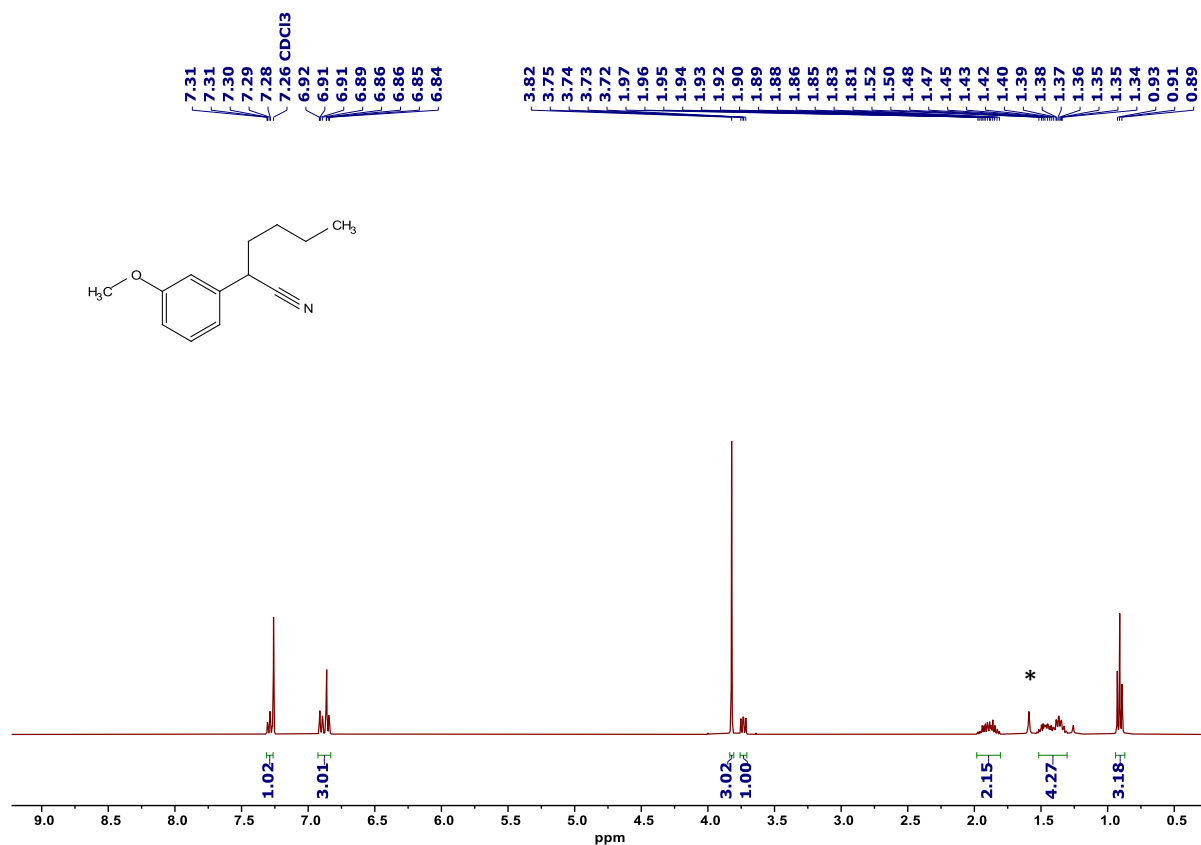


Figure S82. ¹H NMR spectrum of **6j** in CDCl₃. * indicates the solvent impurity of H₂O.

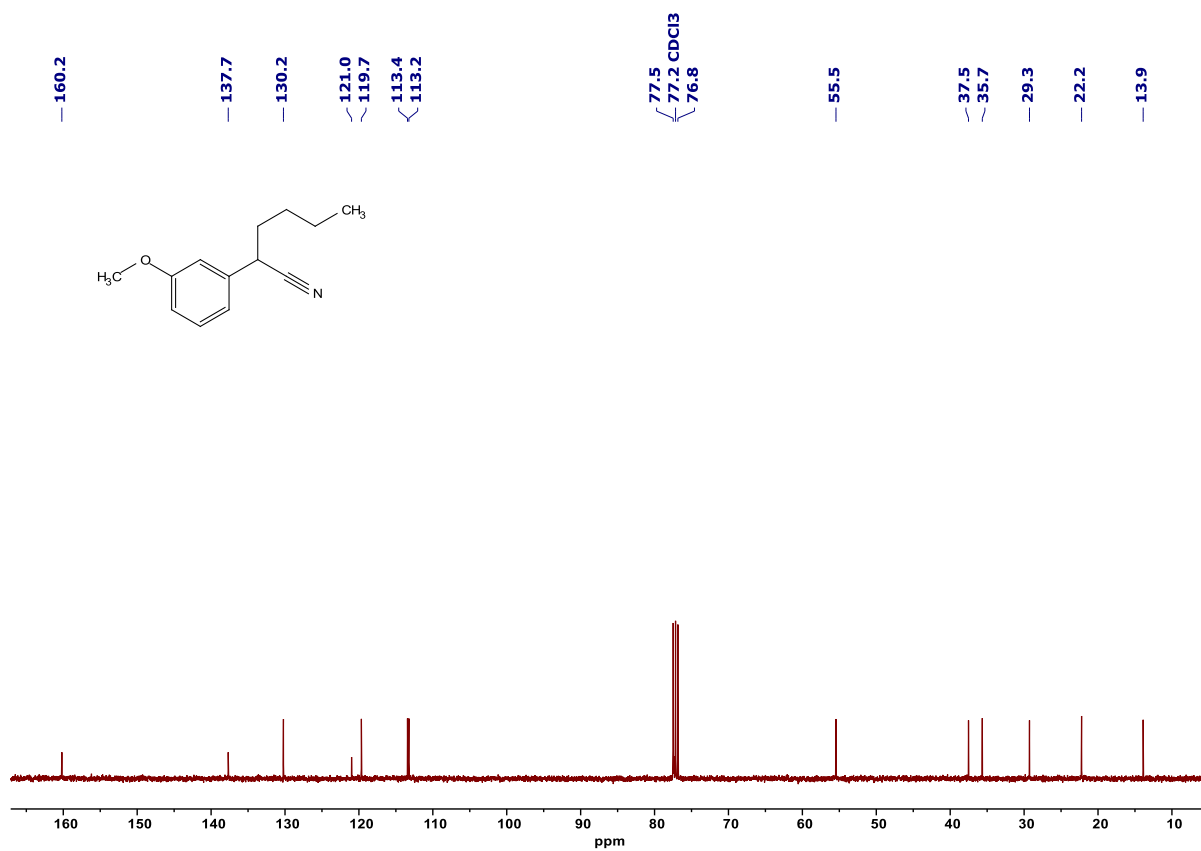


Figure S83. ¹³C{¹H} NMR spectrum of **6j** in CDCl₃.

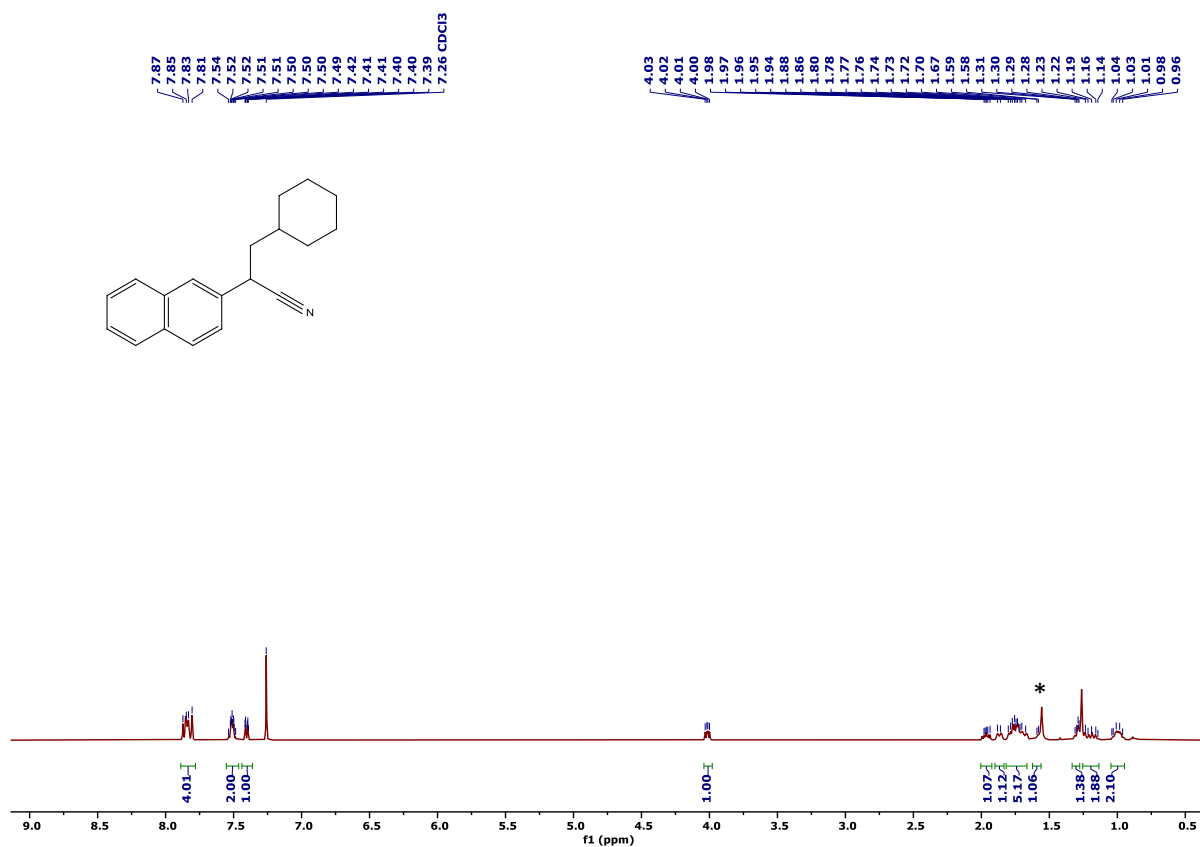


Figure S84. ¹H NMR spectrum of **6k** in CDCl₃. * indicates the solvent impurity of H₂O.

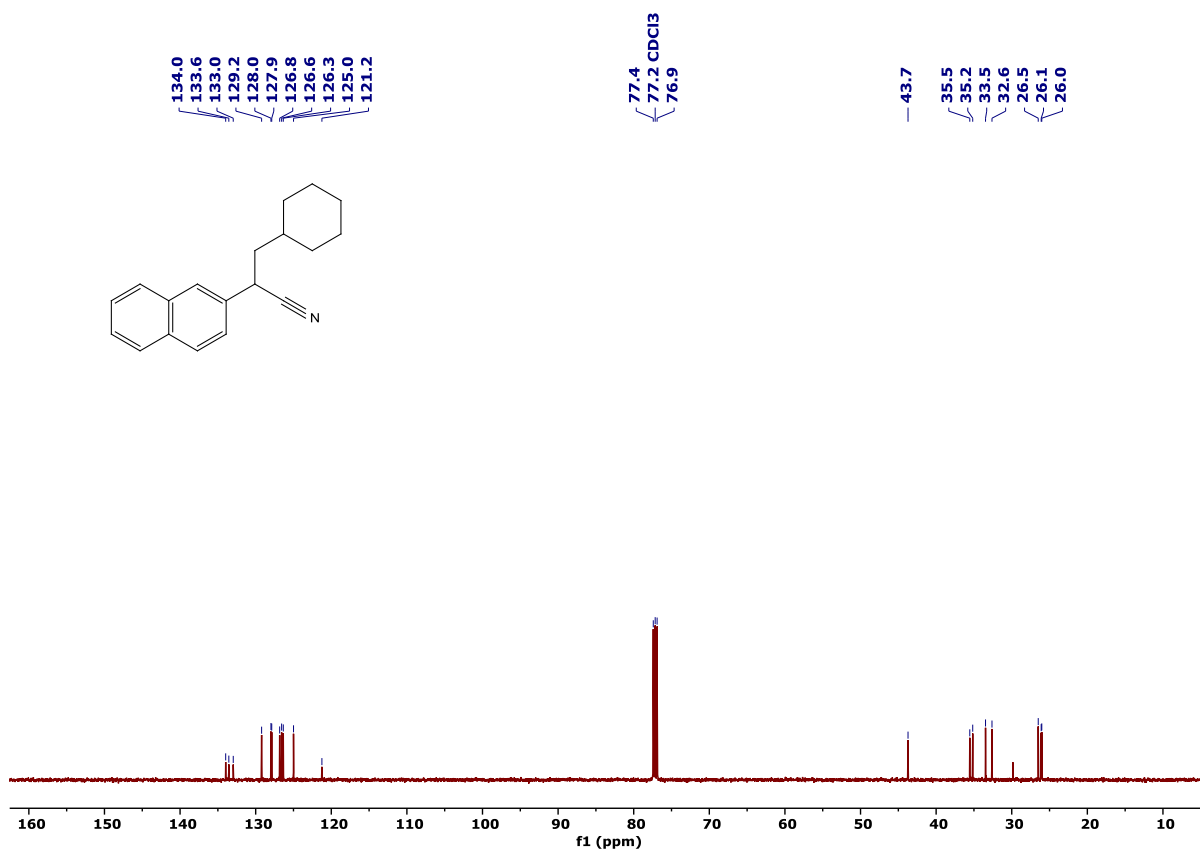


Figure S85. ¹³C{¹H} NMR spectrum of **6k** in CDCl₃.

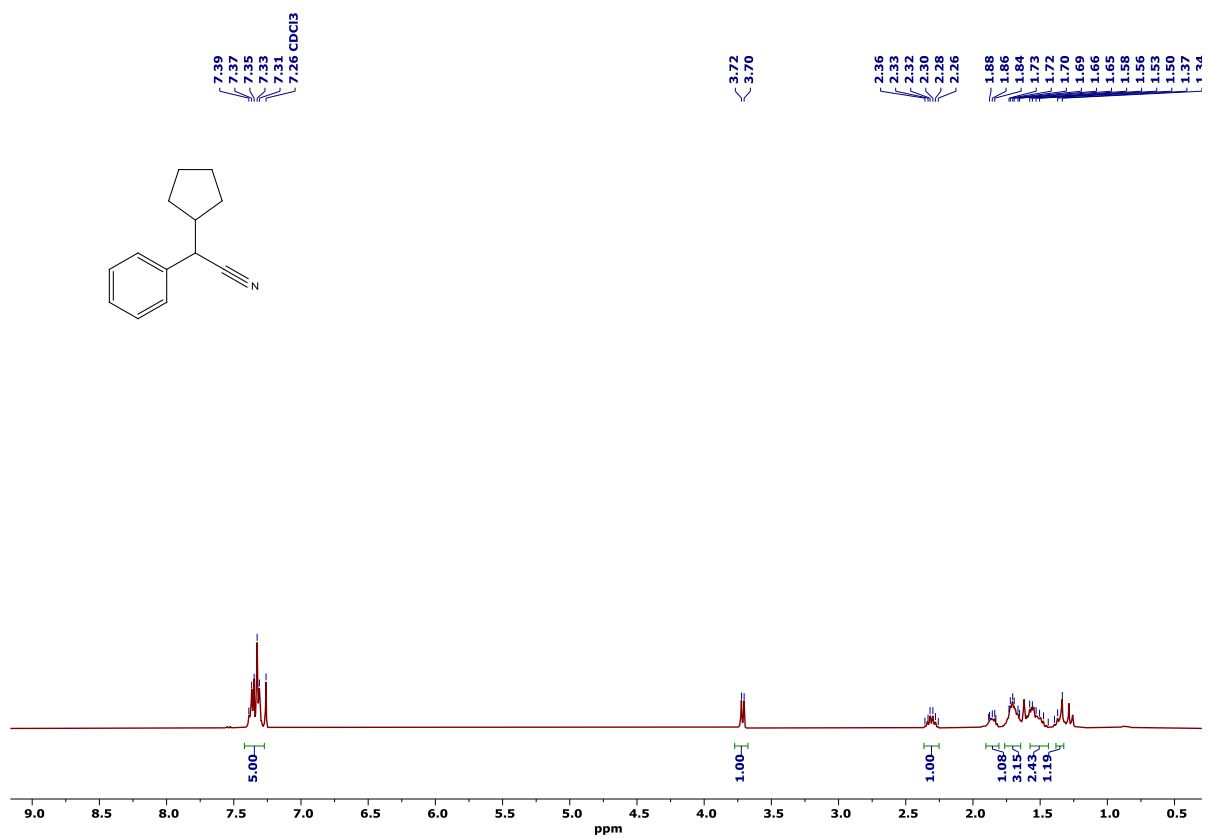


Figure S86. ¹H NMR spectrum of **6l** in CDCl₃.

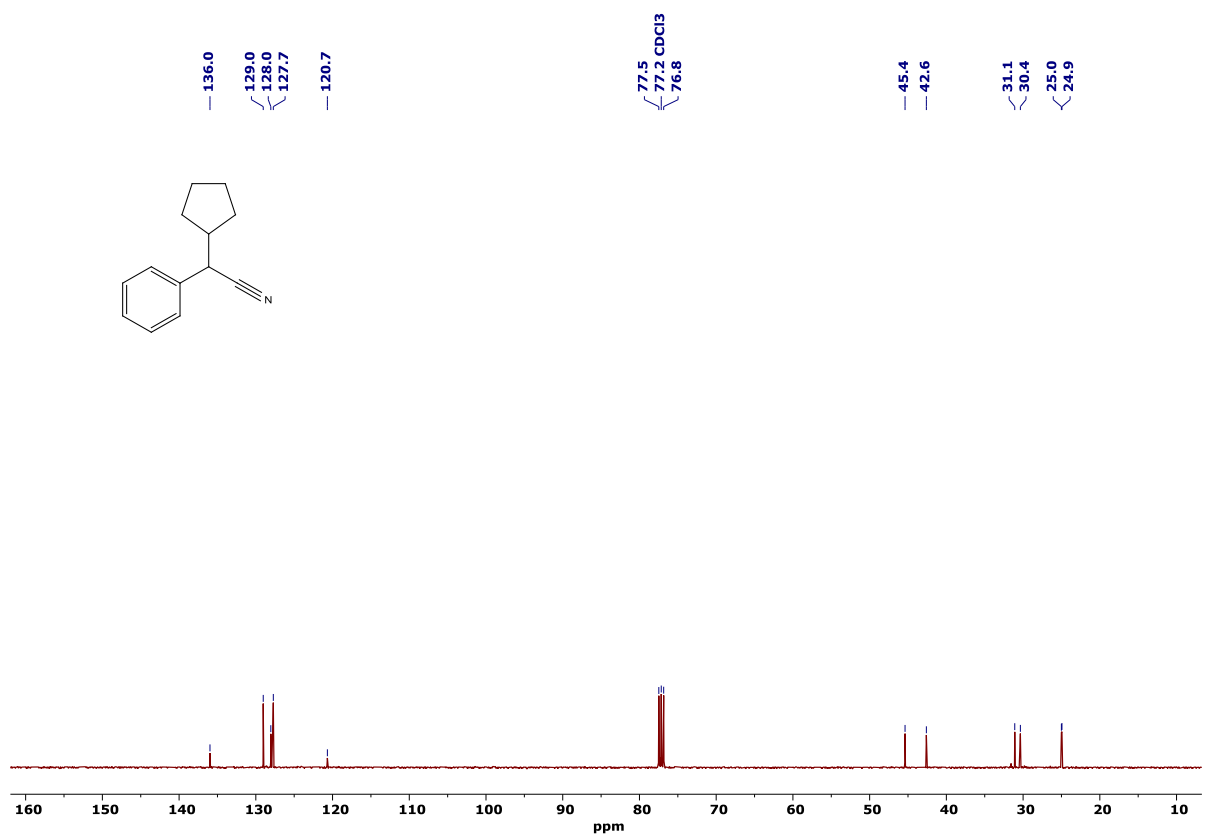


Figure S87. ¹³C{¹H} NMR spectrum of **6l** in CDCl₃.

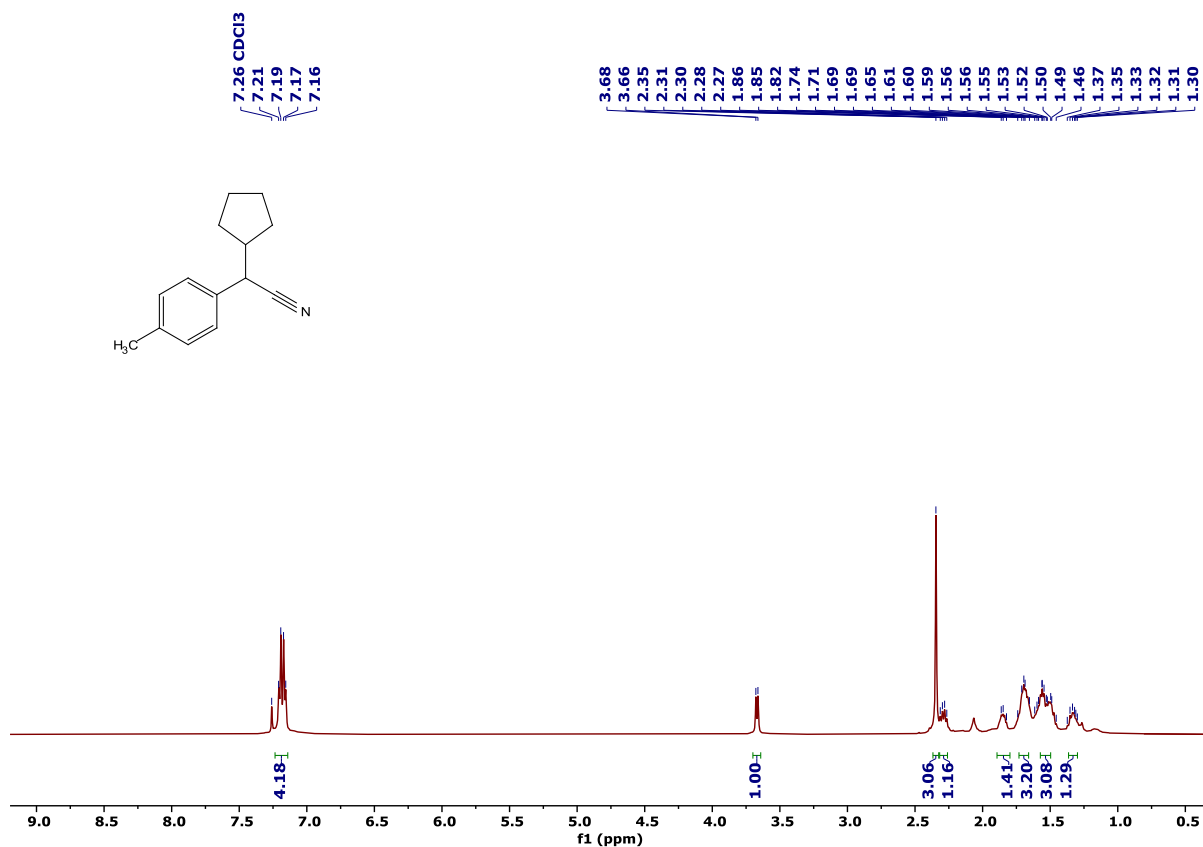


Figure S88. ¹H NMR spectrum of **6m** in CDCl₃.

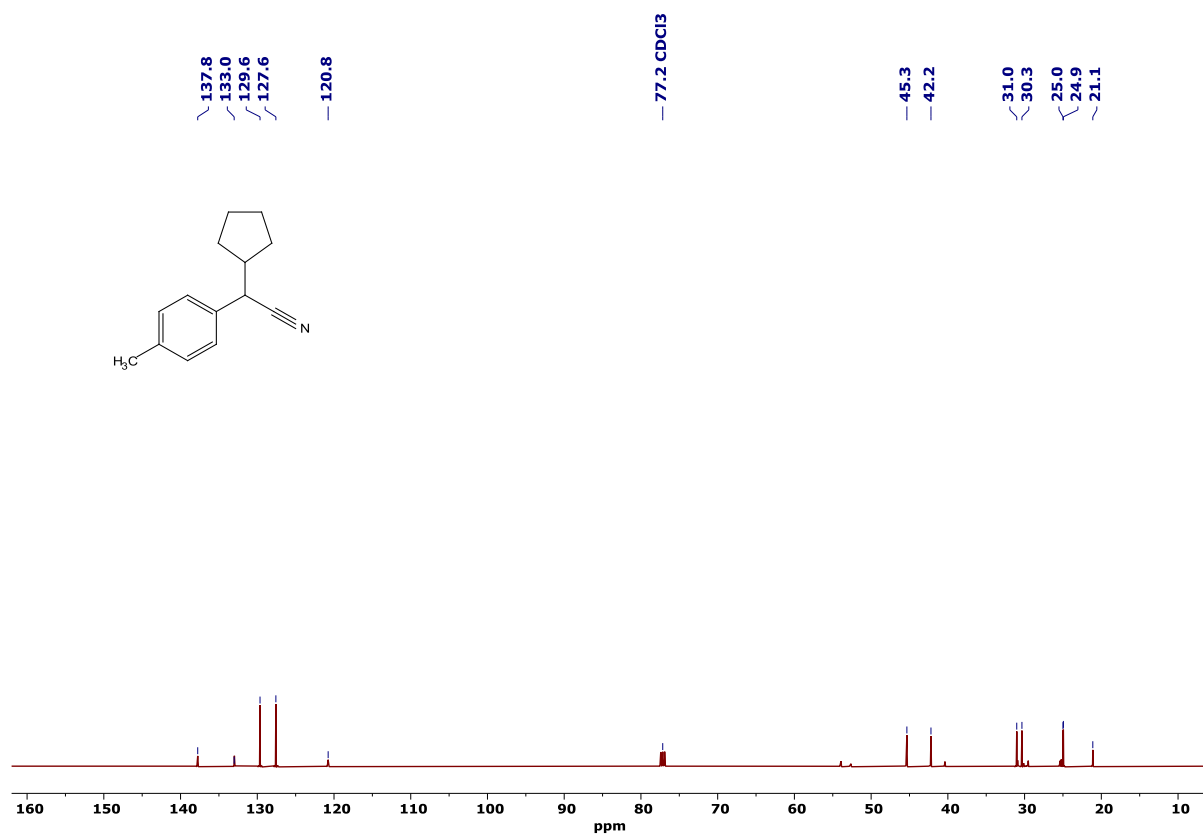


Figure S89. ¹³C {¹H} NMR spectrum of **6m** in CDCl₃.

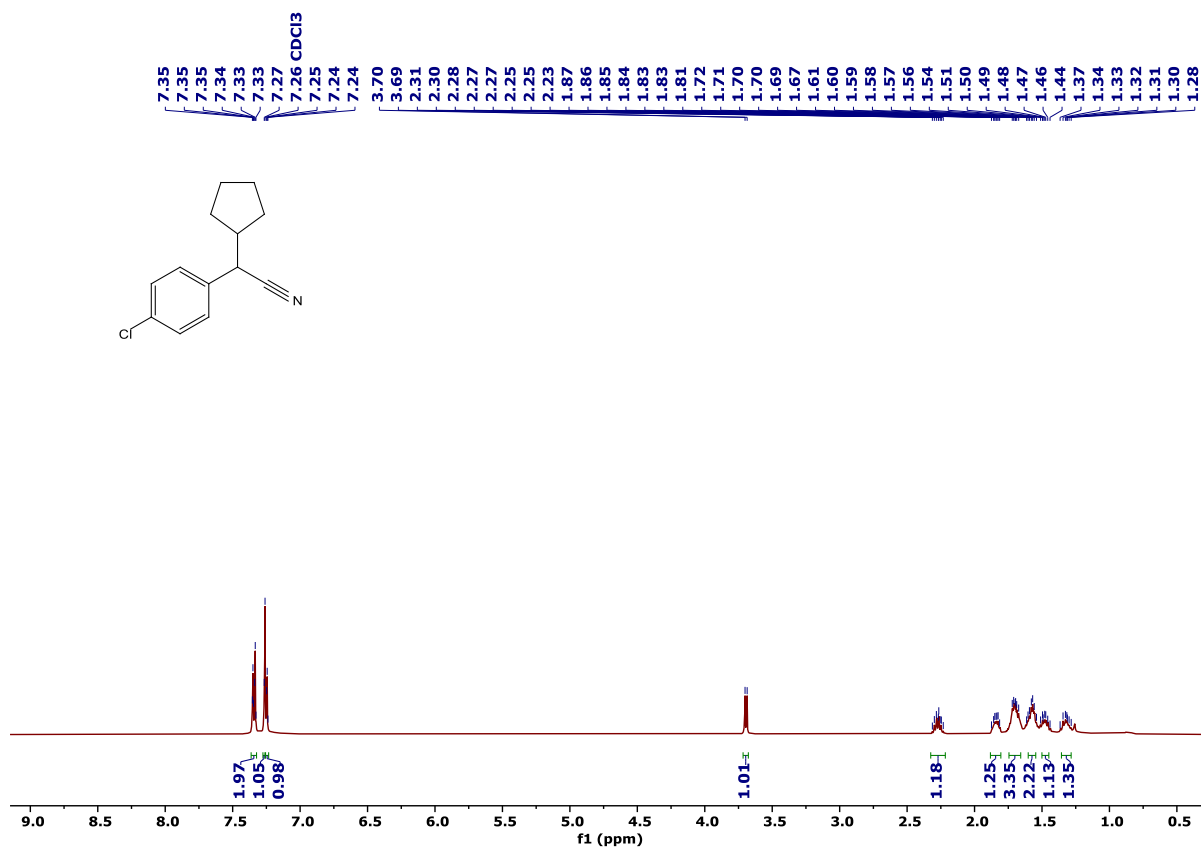


Figure S90. ^1H NMR spectrum of 6n in CDCl_3 .

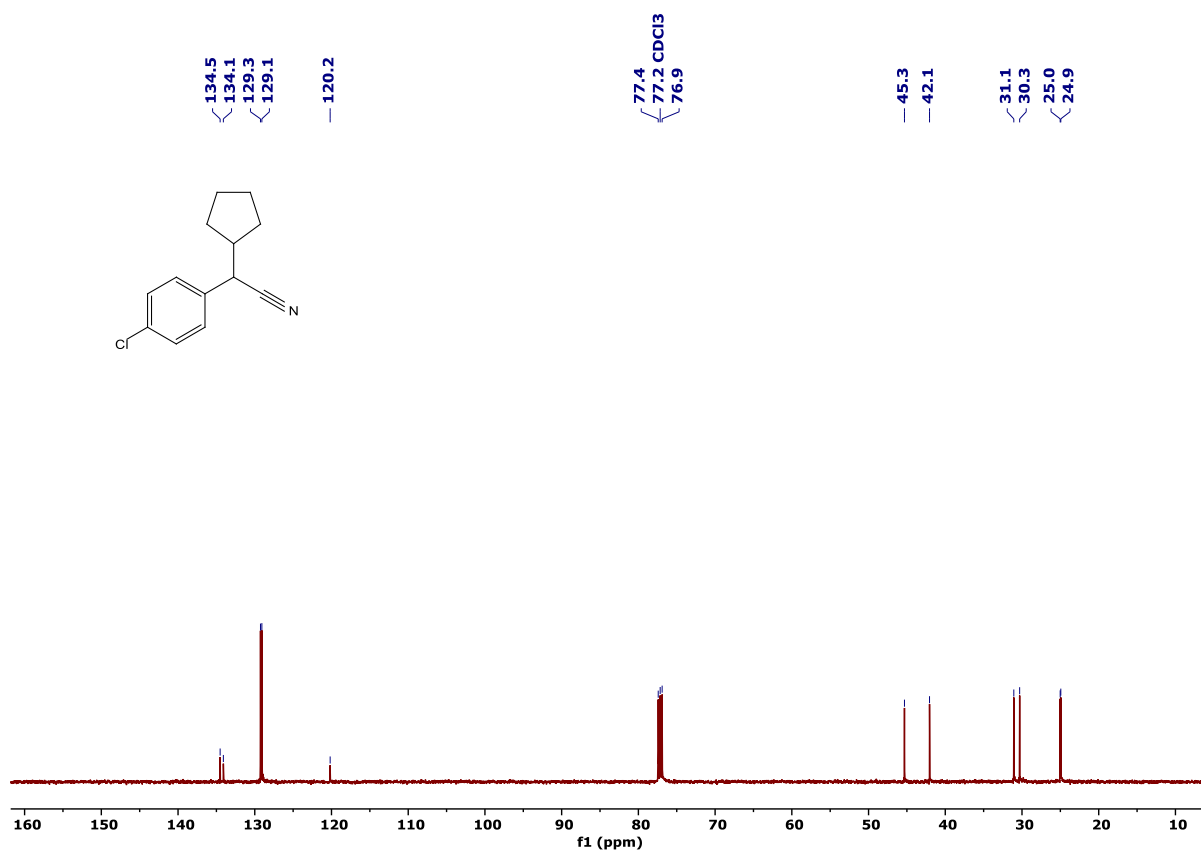


Figure S91. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 6n in CDCl_3 .

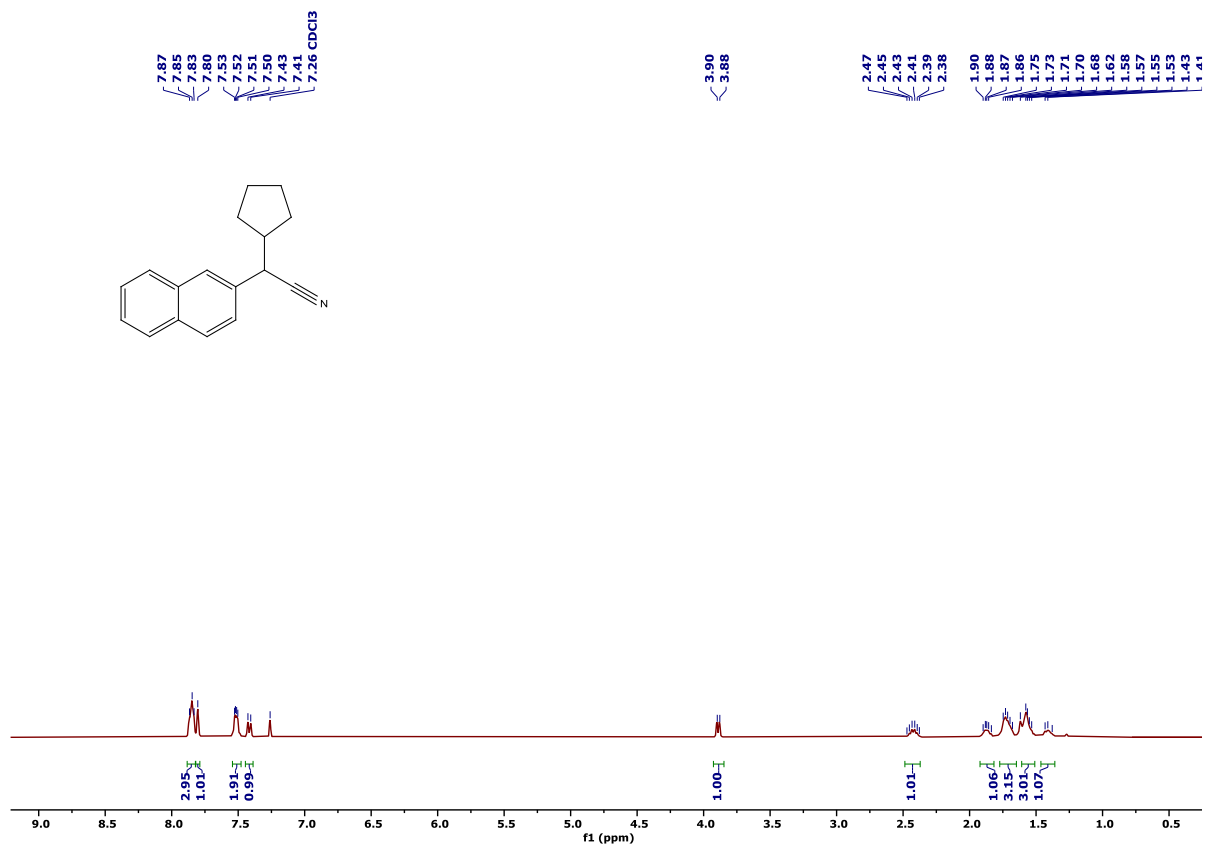


Figure S92. $^1\text{H NMR}$ spectrum of **60** in CDCl_3 .

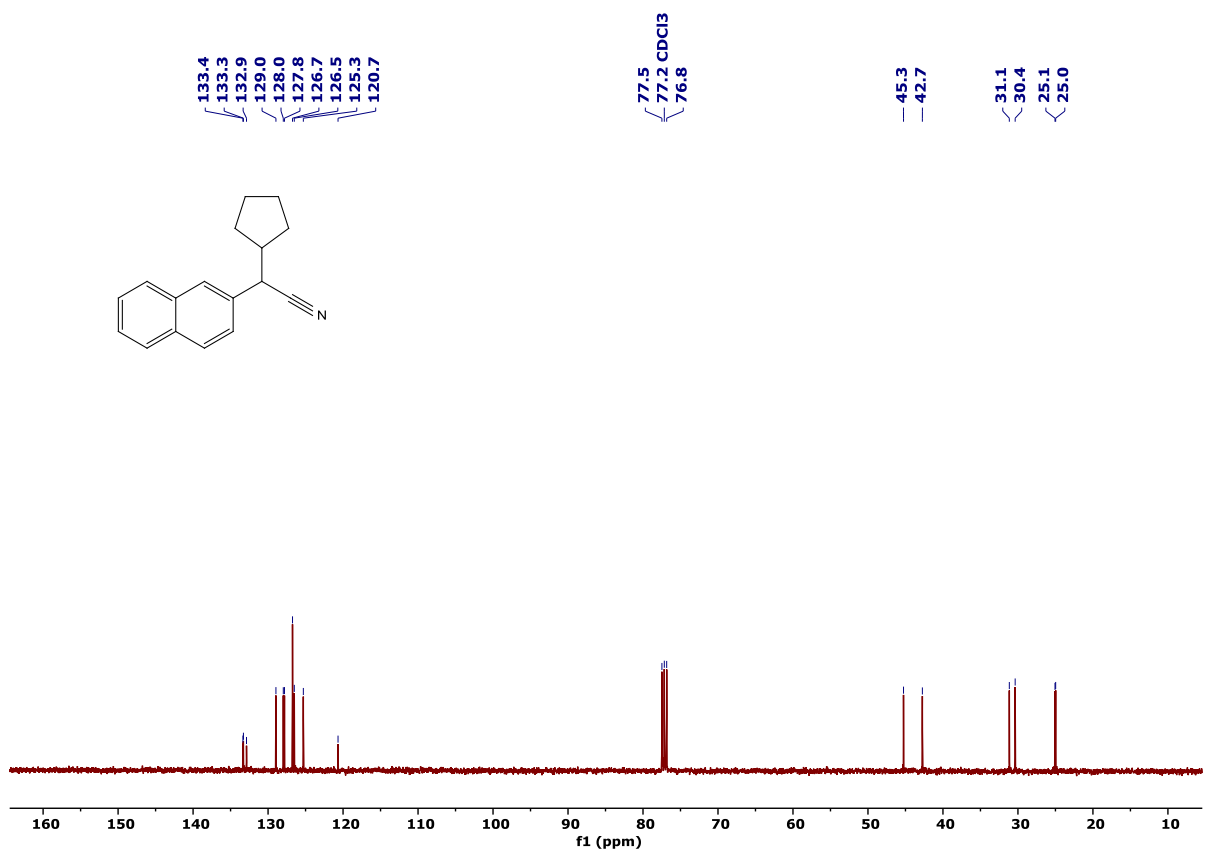


Figure S93. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **60** in CDCl_3 .

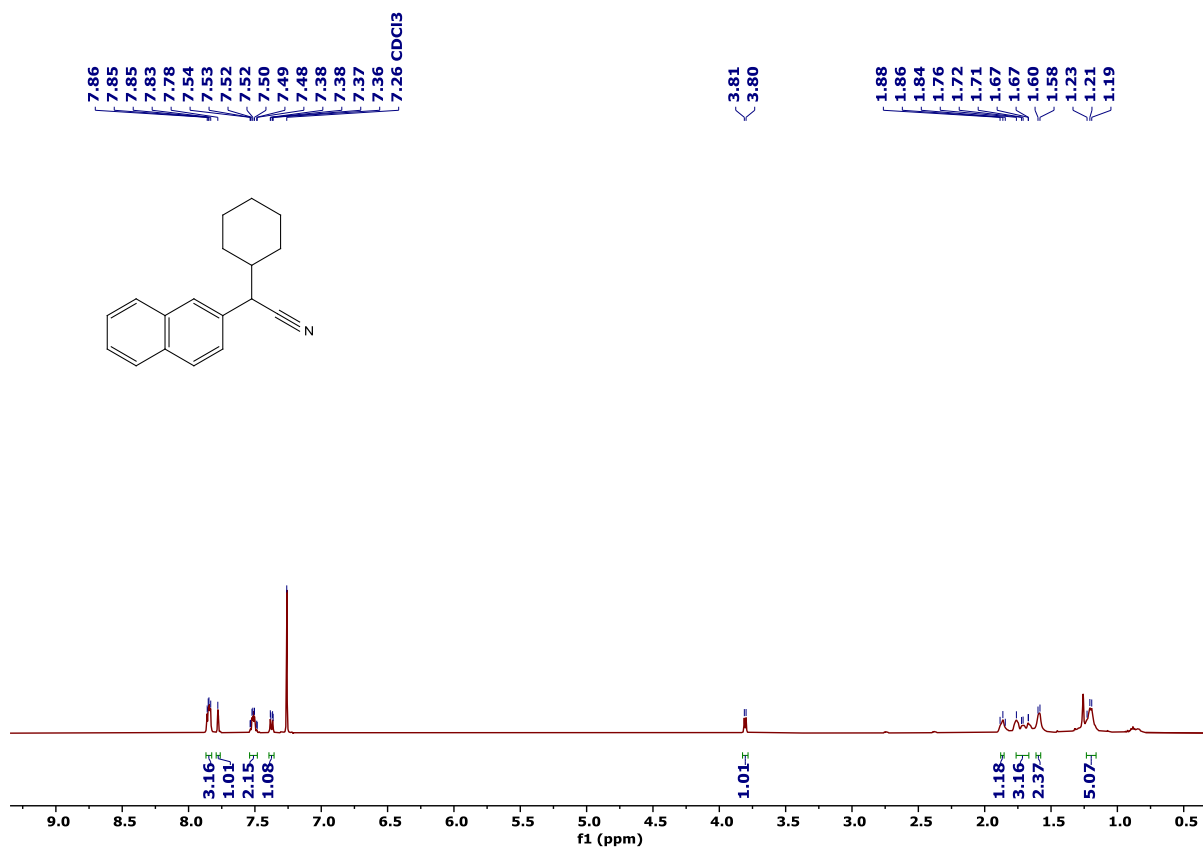


Figure S94. ¹H NMR spectrum of **6p** in CDCl₃.

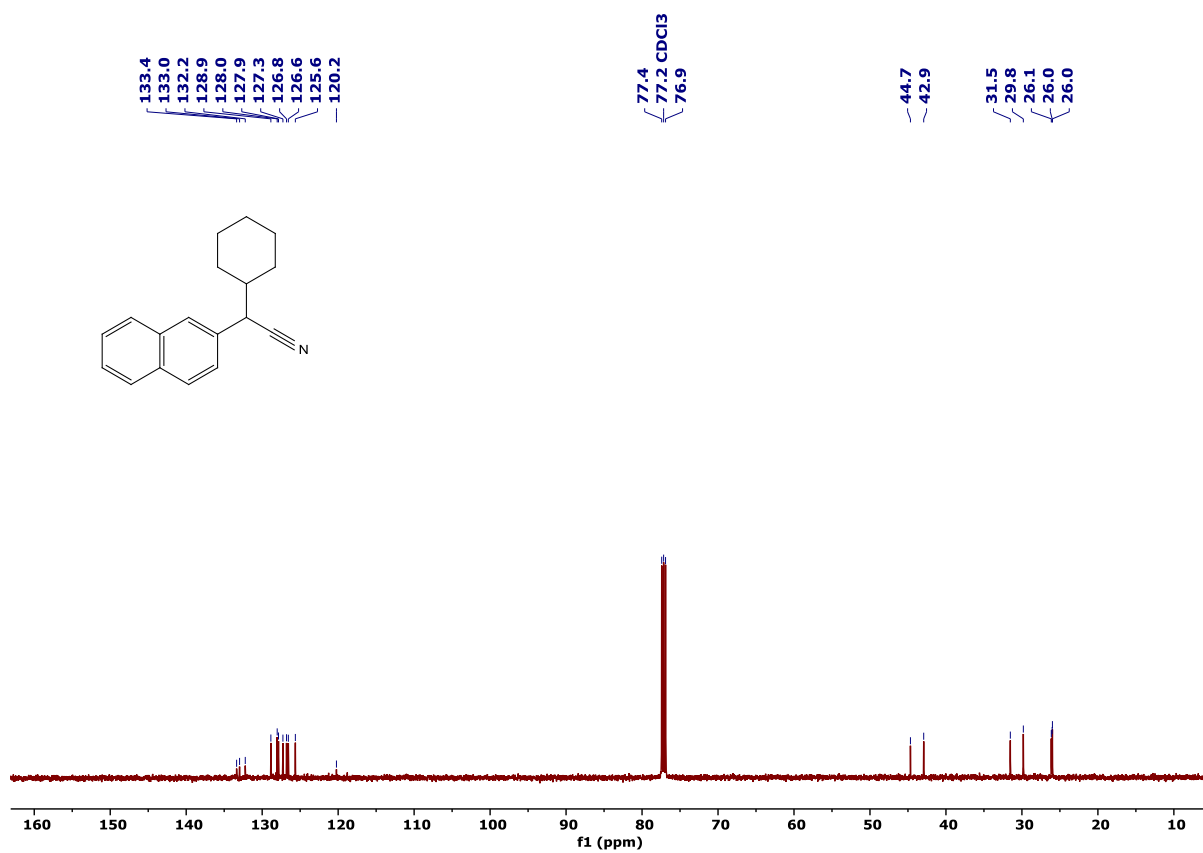


Figure S95. ¹³C{¹H} NMR spectrum of **6p** in CDCl₃.

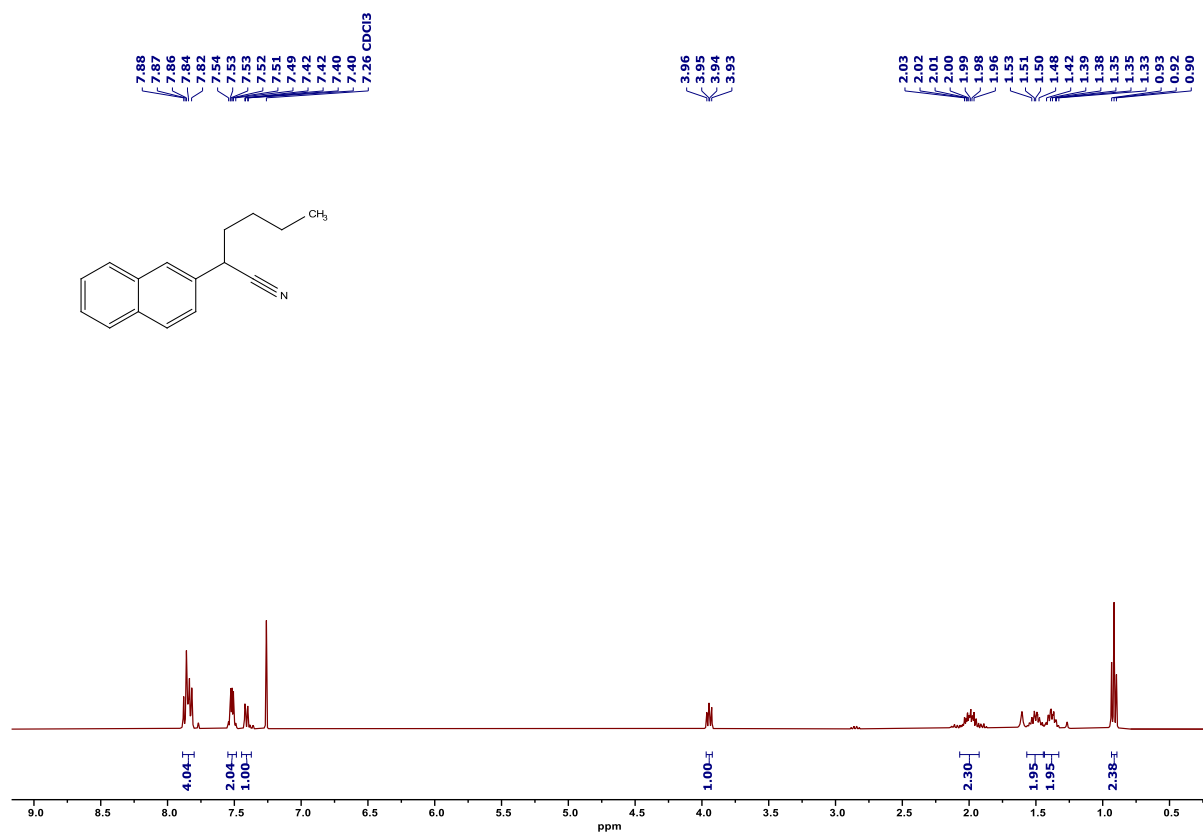


Figure S96. ^1H NMR spectrum of **6q** in CDCl_3 .

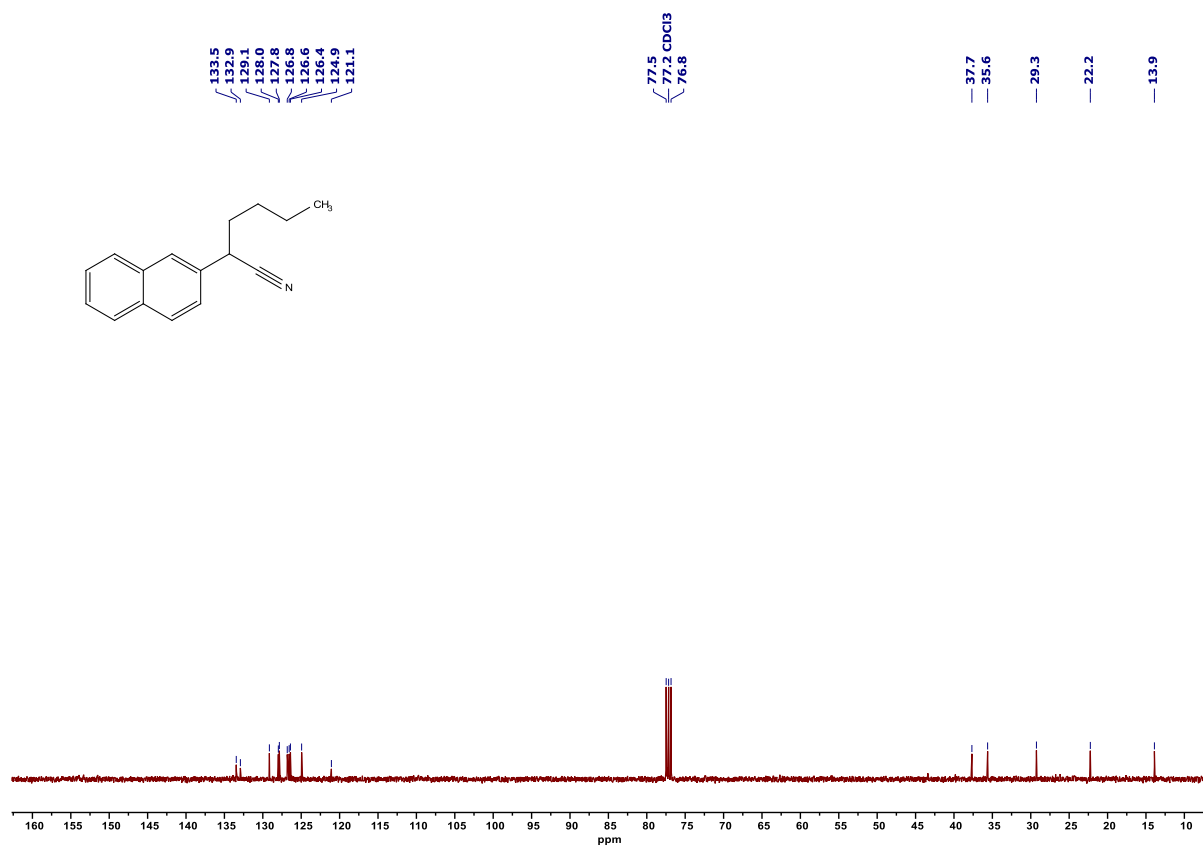


Figure S97. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6q** in CDCl_3 .

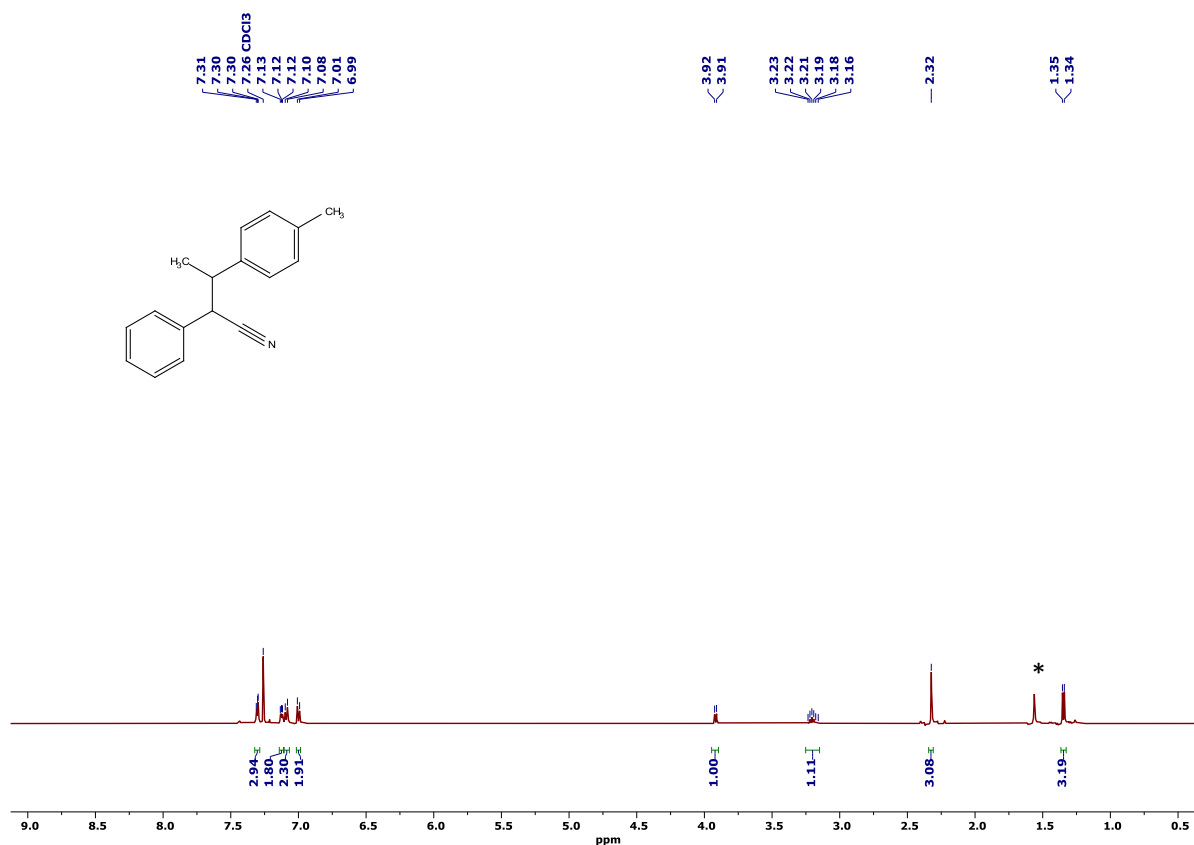


Figure S98. ¹H NMR spectrum of **6r** in CDCl₃. * indicates the solvent impurity of H₂O.

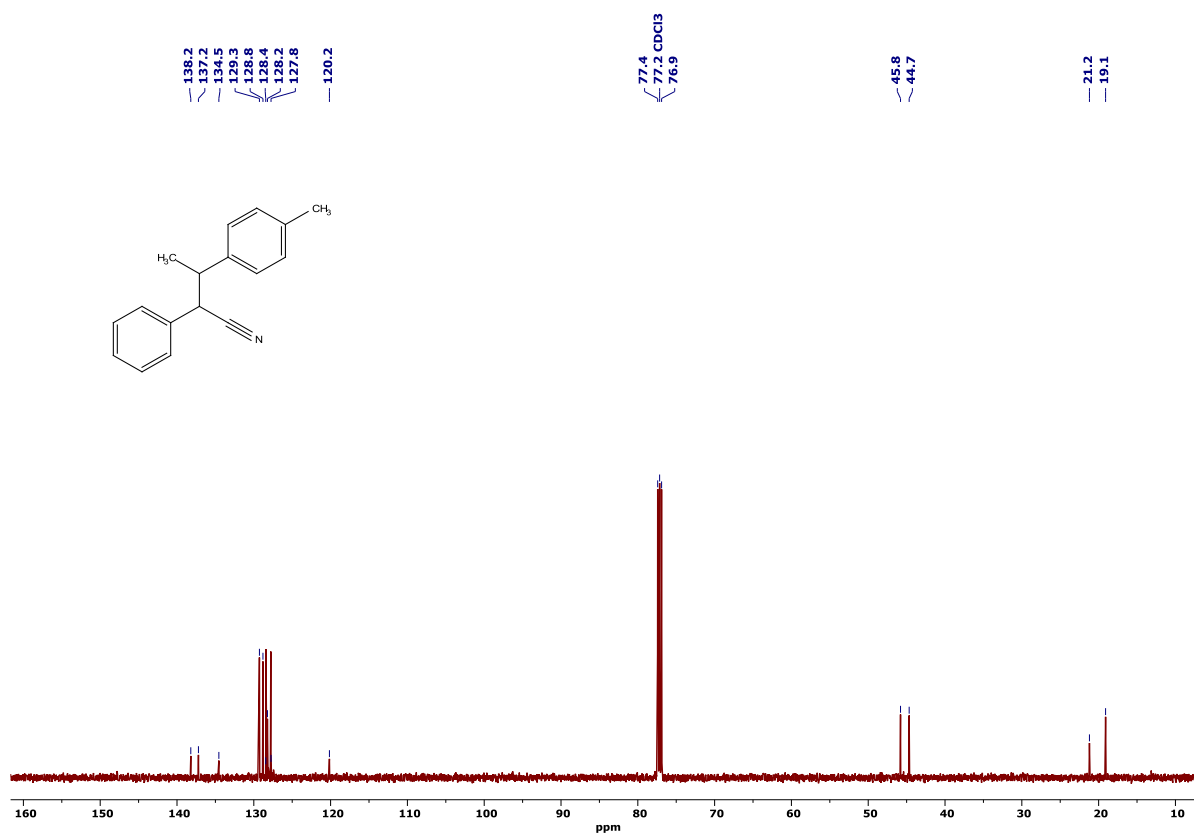


Figure S99. ¹³C{¹H} NMR spectrum of **6r** in CDCl₃.

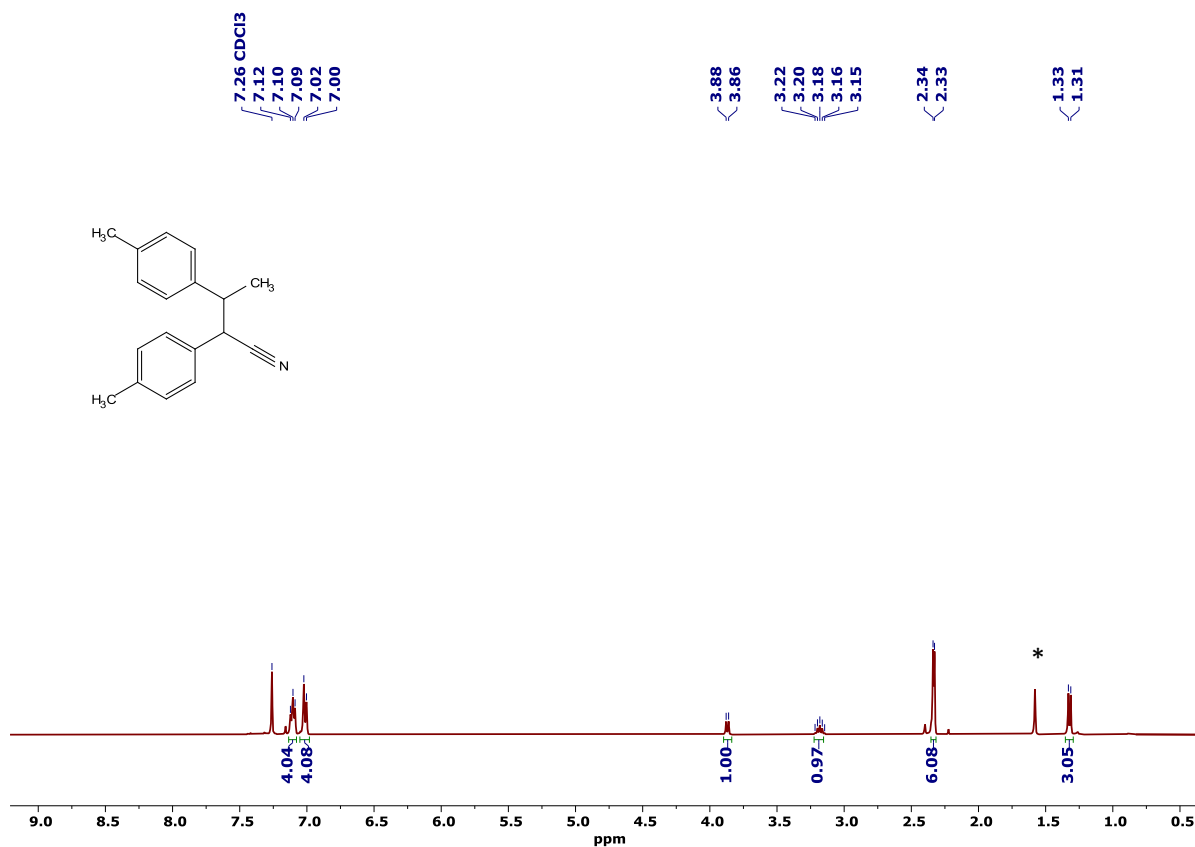


Figure S100. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6s** in CDCl_3 . * indicates the solvent impurity of H_2O .

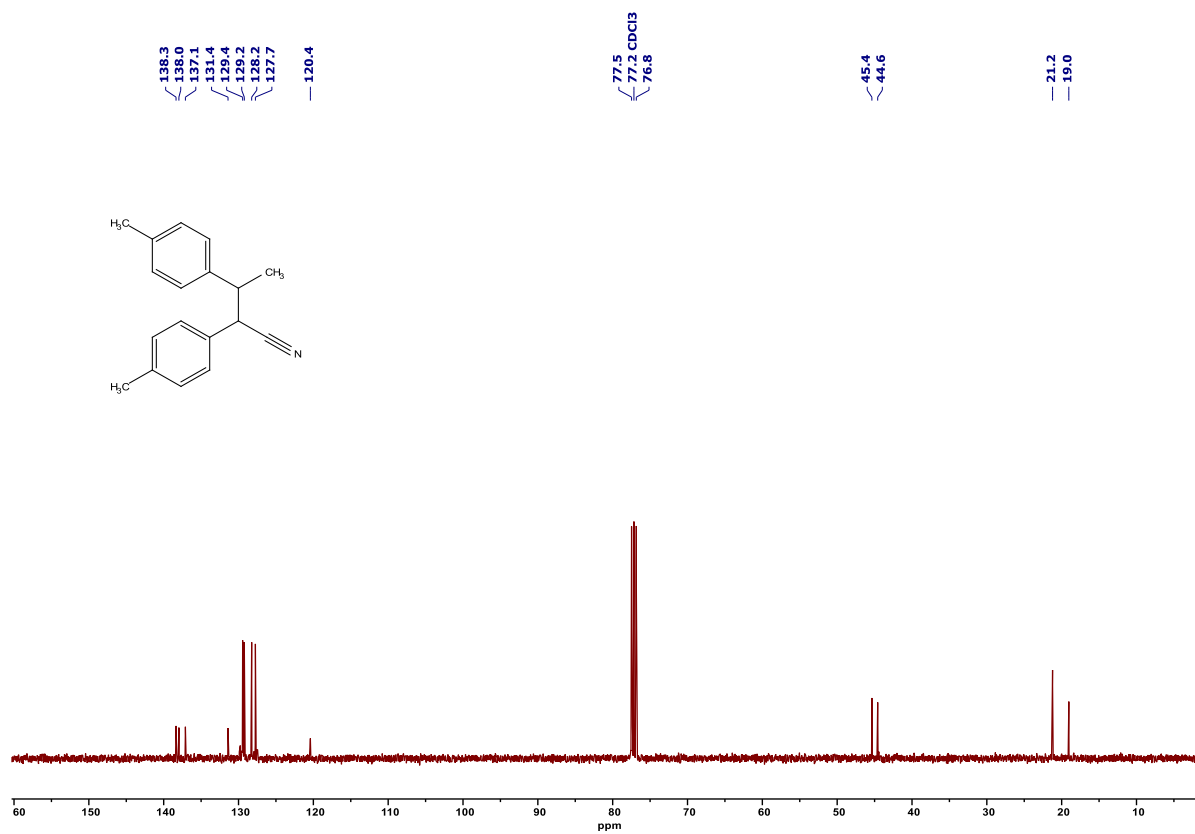


Figure S101. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6s** in CDCl_3 .

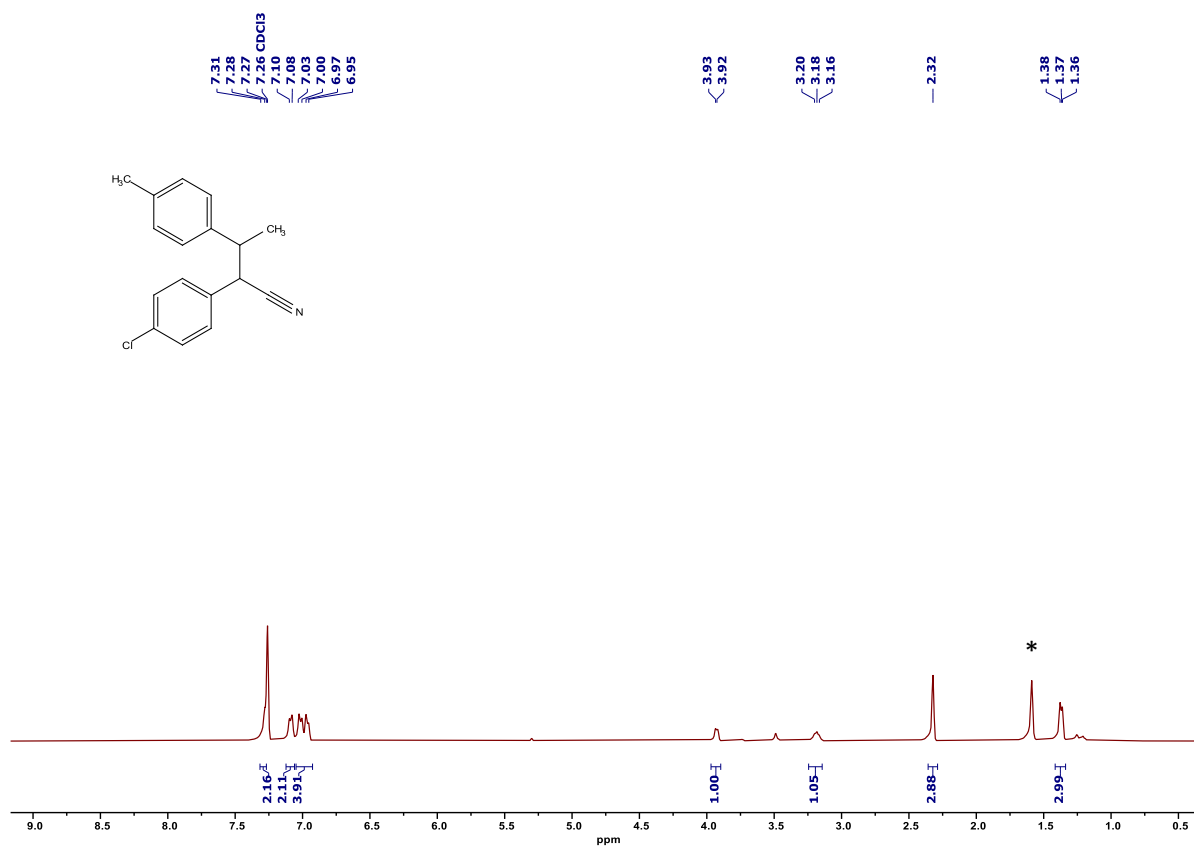


Figure S102. ¹H NMR spectrum of **6t** in CDCl₃. * indicates the solvent impurity of H₂O.

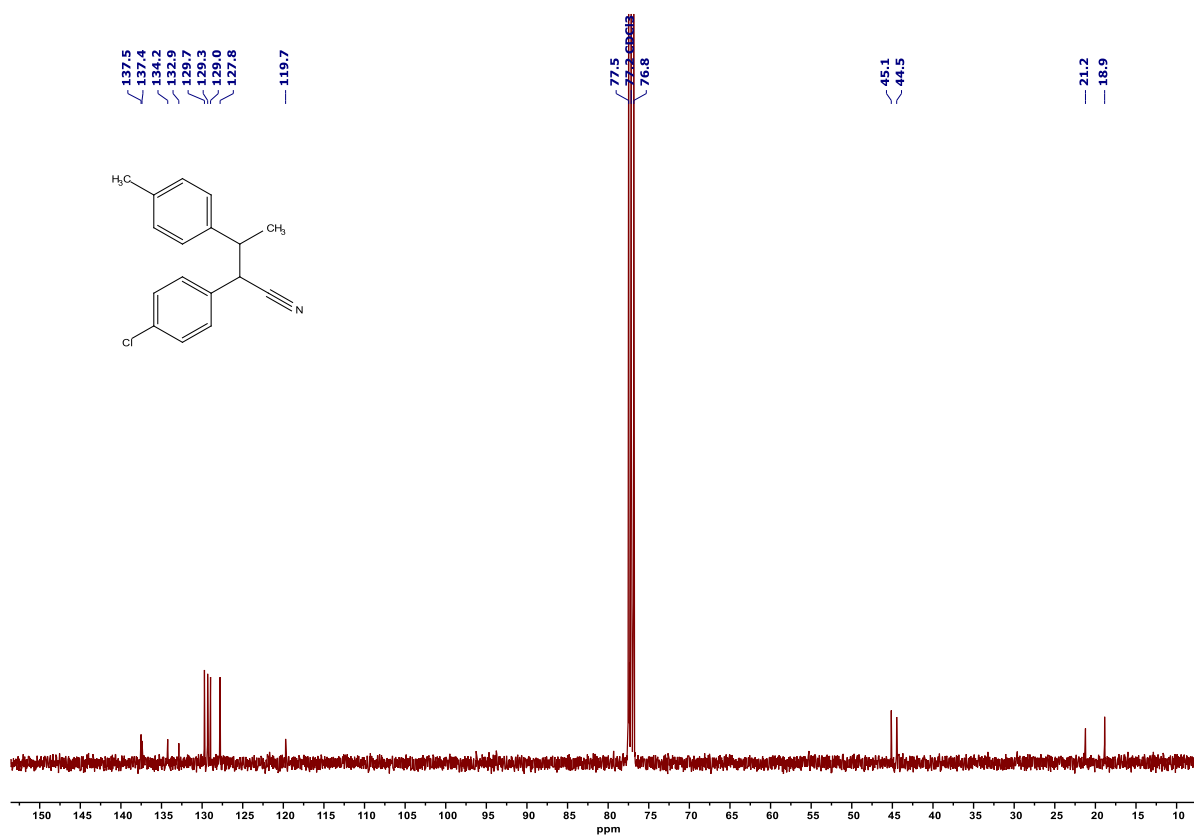


Figure S103. ¹³C {¹H} NMR spectrum of **6t** in CDCl₃.

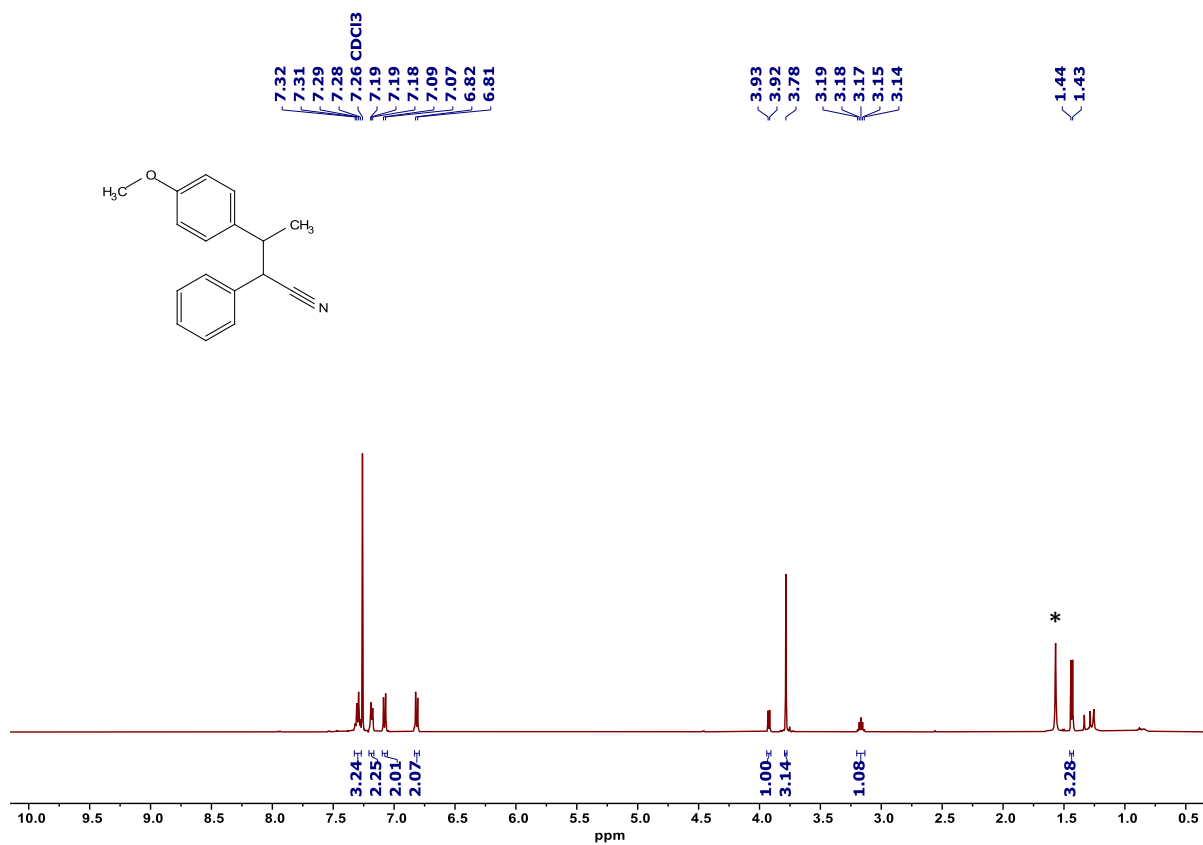


Figure S104. ¹H NMR spectrum of **6u** in CDCl₃. * indicates the solvent impurity of H₂O.

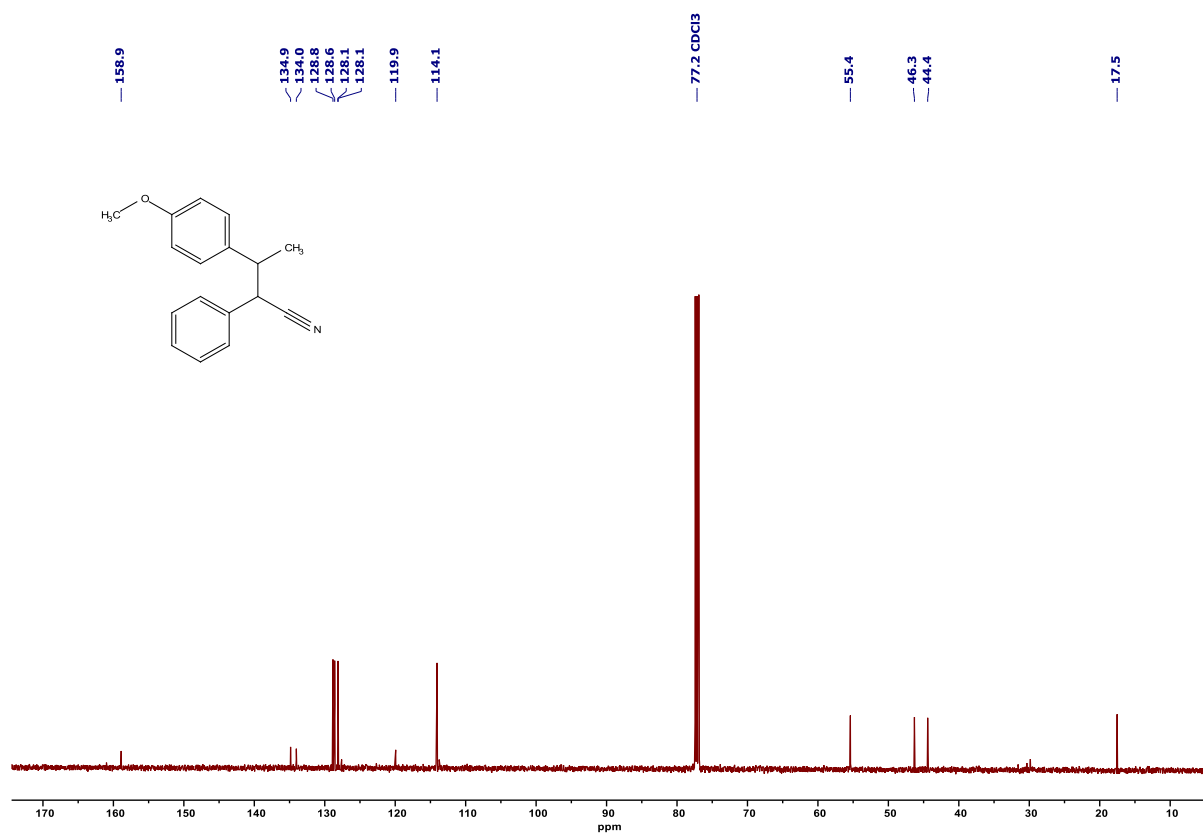


Figure S105. ¹³C{¹H} NMR spectrum of **6u** in CDCl₃.

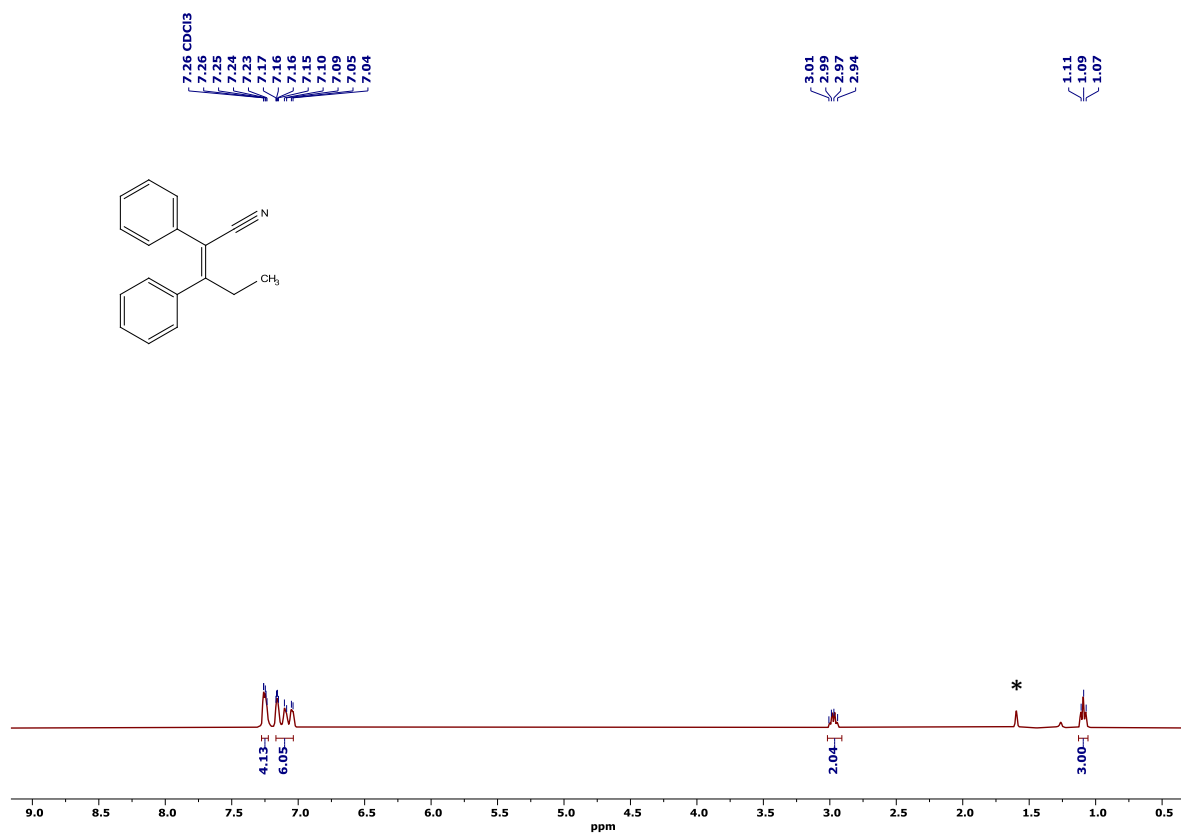


Figure S106. ¹H NMR spectrum of **6v** in CDCl₃. * indicates the solvent impurity of H₂O.

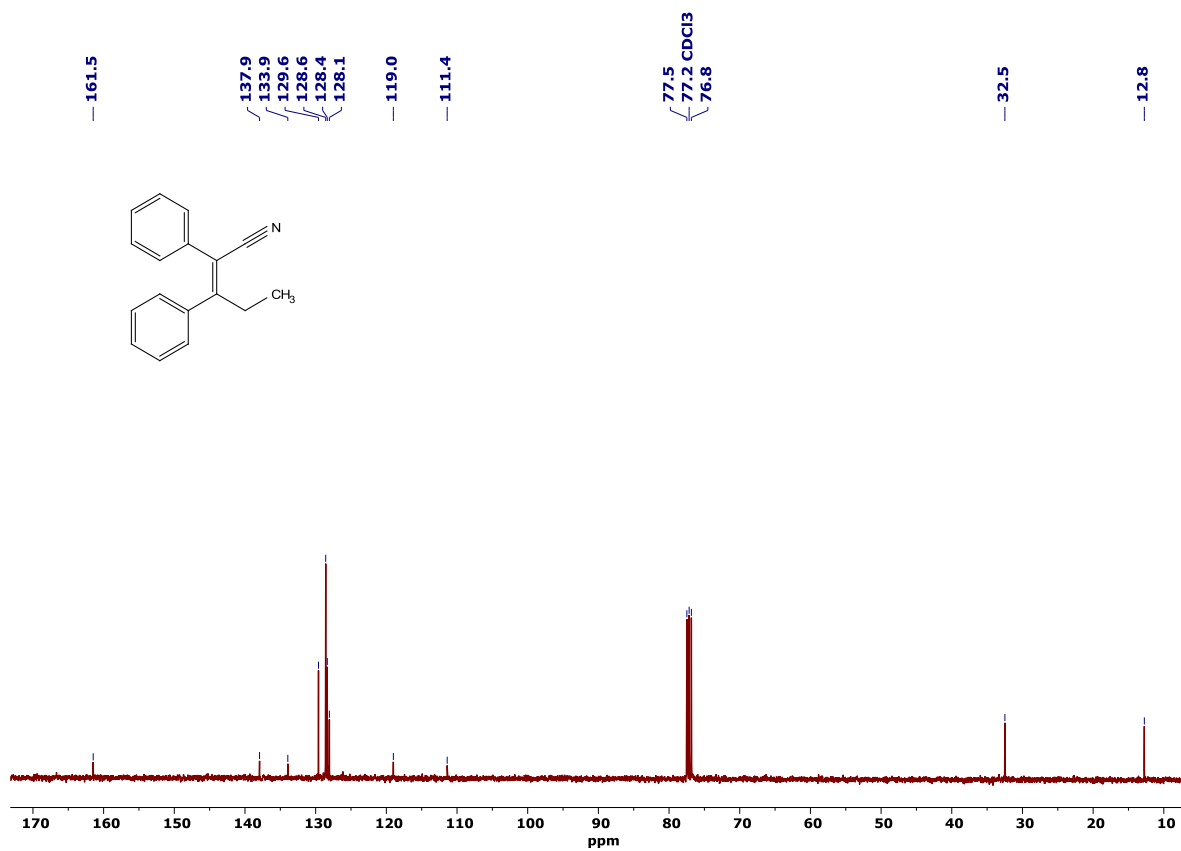


Figure S107. ¹³C {¹H} NMR spectrum of **6v** in CDCl₃.

Kinetics study of the reaction with respect to nitrile and catalyst:

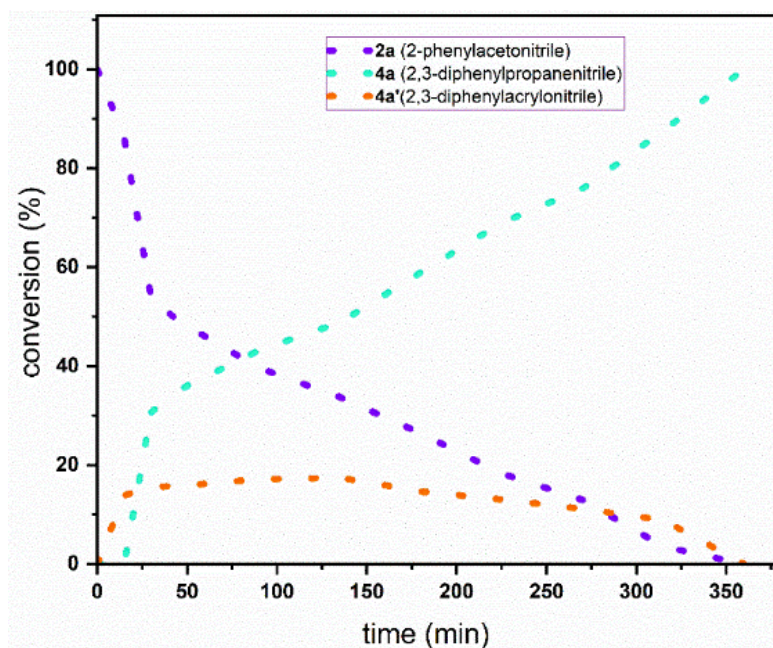


Figure S108. Time-dependent reaction profile for the present α -alkylation of nitriles

Rate and order determination with respect to phenylacetonitrile (**1a**):

To determine the order of the reaction on **1a**, the initial rates at different initial concentrations of **1a** were recorded. To an oven dried pressure tube (25 mL), **3a** (0.4 mmol, 2 eq.), **Co-1a** catalyst (2 mol%), KO^tBu (30 mol%), specific amount of **2a** and toluene (2 mL) were added. The reaction mixture was then kept for stirring at 140 °C. At regular intervals (30 min, 45 min, 60 min, 75 min, and 90 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with methanol and subjected to gas chromatographic analysis. The concentration of the products was determined from the conversion obtained from GC analysis. The data was used to plot the concentration of the product (M) vs time (min.) plot (Figure S109, a). The rate of reaction at different initial concentration of **2a** is given in (Table S1) and used to plot the log(rate) vs log(conc.) plot (Figure S109, b) to determine the order of reaction with respect to phenylacetonitrile **2a**.

Table S1. Rate of the reaction at different initial concentration of (**2a**).

Experiment	Initial conc. of 2a (M)	Initial rate [M/min]
1	0.0001	6.284×10^{-7}
2	0.00015	9.228×10^{-7}
3	0.0002	1.546×10^{-6}
4	0.00025	1.786×10^{-6}
5	0.0003	2.050×10^{-6}

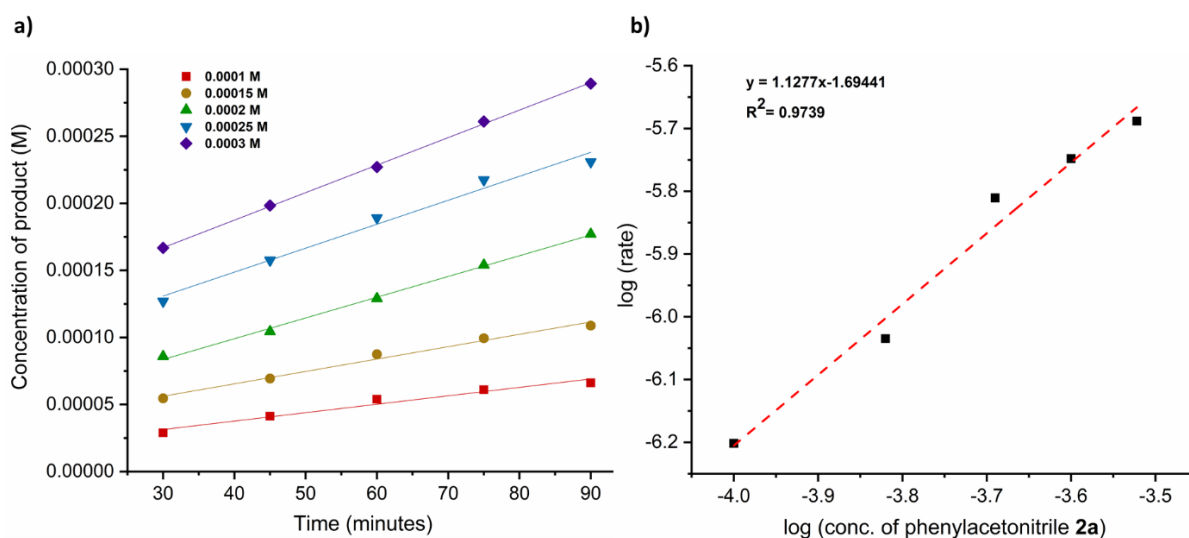


Figure S109. (a) Concentration versus time plot at various concentrations of (**2a**). (b) log(rate) versus log(conc.) graph of (**1a**).

Rate order determination with respect to catalyst **1a**

To determine the order of the reaction with respect to catalyst, the initial rates at different initial concentrations of catalyst were recorded. To an oven dried pressure tube (25 mL), **2a** (0.4 mmol, 1 eq.), benzyl alcohol **3a** (0.8 mmol, 2 eq.), KO^tBu (20 mol %), specific amount of catalyst **1a** and toluene (2 mL) were added under inert condition. The reaction mixture was kept for stirring at 140 °C. At regular intervals (30 min, 45 min, 60 min, 75 min, and 90 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with methanol and subjected to gas chromatographic analysis. The conversion of the products was determined. The data was used to plot the

concentration of the product (M) vs time (min.) plot (Figure S110, a). The rate of reaction at different initial concentration of catalyst is given in (Table S2) and used to plot the log(rate) vs log(conc.) plot (Figure S110, b) to determine the order of reaction with respect to catalyst.

Table S2. Rate of the reaction at different initial concentration of catalyst.

Experiment	Initial conc. of catalyst 1a (M)	Initial rate [M/min]
1	0.000004	2.600×10^{-6}
2	0.000006	2.630×10^{-6}
3	0.000008	2.806×10^{-6}
4	0.00001	2.846×10^{-6}
5	0.000012	2.960×10^{-6}

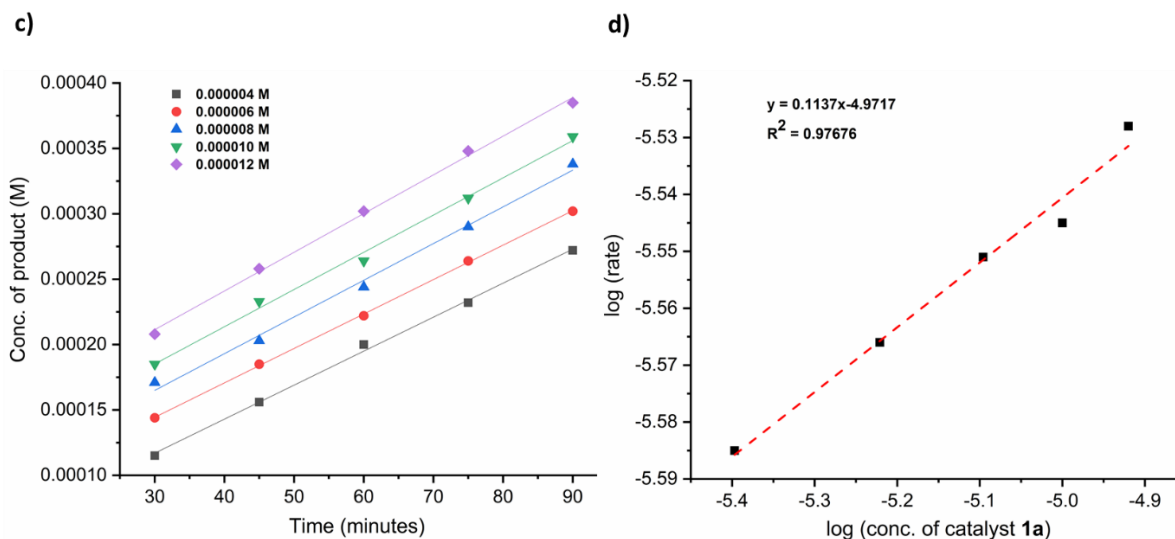


Figure S110. (a) Concentration versus time plot at various concentrations of catalyst. (b) log(rate) versus log(conc.) graph of catalyst.

Post-modification of 4a and 4f (Scheme S3)

Procedure for synthesis of the compound 7 from 4a^{13b}

To a reaction tube, **4a** (0.25mmol, 52 mg), hydrogen peroxide (56.0 μ L, 0.55 mmol; 30% (w/w) solution in water) and potassium carbonate (5.2 mg, 0.04 mmol) were taken in dry dimethyl sulfoxide (0.5 mL) at 0 °C under an atmosphere of nitrogen. The resulting solution was allowed to warm slowly to room temperature and stirred for 12 hours. After the completion, the reaction mixture was quenched by the addition of water and extracted with ethyl acetate. The organic layers were dried (MgSO₄), filtered and concentrated. The pure products **7** (white solid, 48 mg, 0.21 mmol) were isolated using column chromatography with ethyl acetate and hexane as eluents.

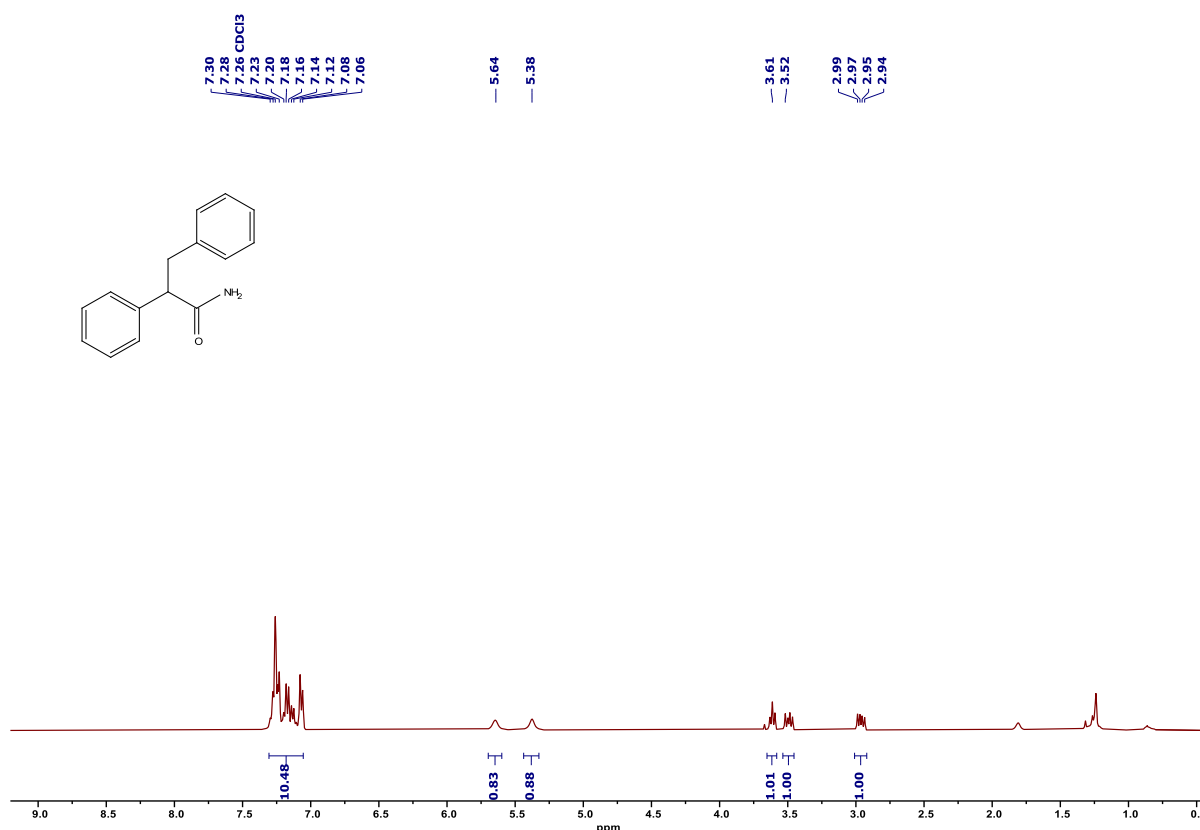
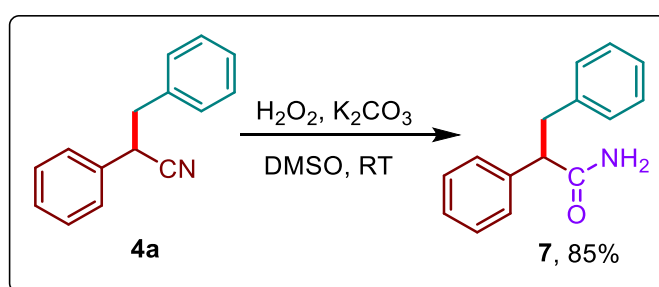


Figure S111. ¹H NMR spectrum of **7** in CDCl₃.

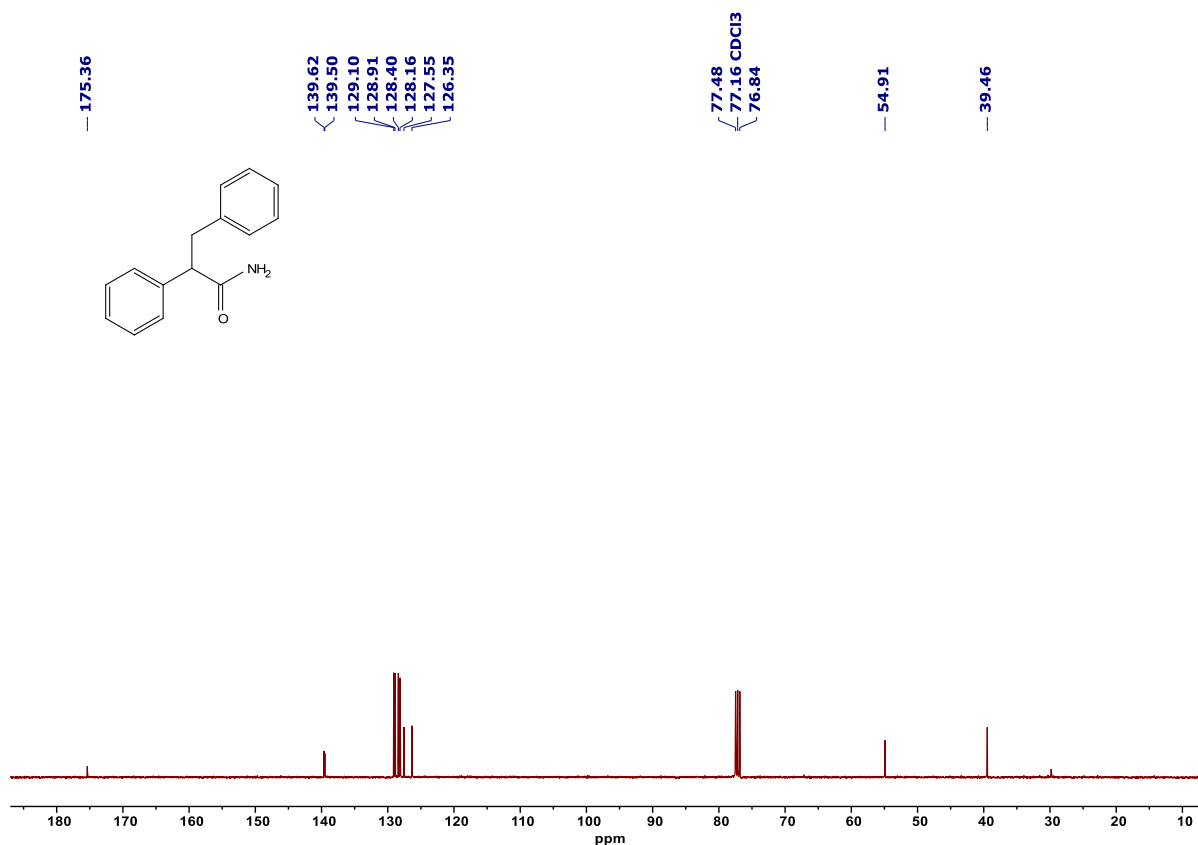
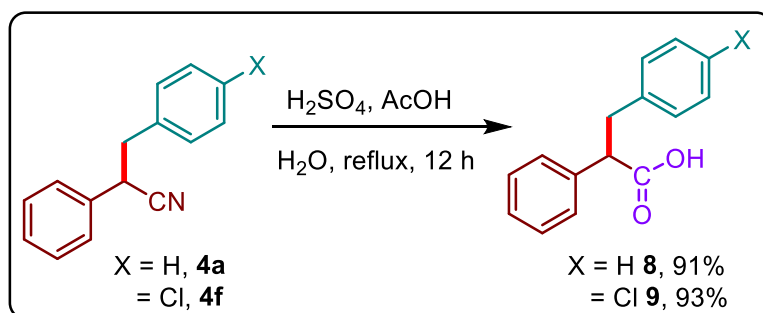


Figure S112. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** in CDCl_3 .

Procedure for synthesis of the compound **8** from **4a**^{13b}

To a reaction tube, **4a** and **4f** (0.25mmol), concentrated H_2SO_4 (1.0 mL), H_2O (1.0 mL) and acetic acid (0.5mL) was refluxed for 12 h. Then the mixture was quenched with 2.0mL of H_2O and diluted with DCM (4 mL). The mixture was stirred another 30 min at room temperature, then it was extracted with ethyl acetate and water work up, dried (MgSO_4), filtered, and concentrated. The pure products **8** and **9** were isolated respectively using column chromatography with ethyl acetate and hexane as eluents.



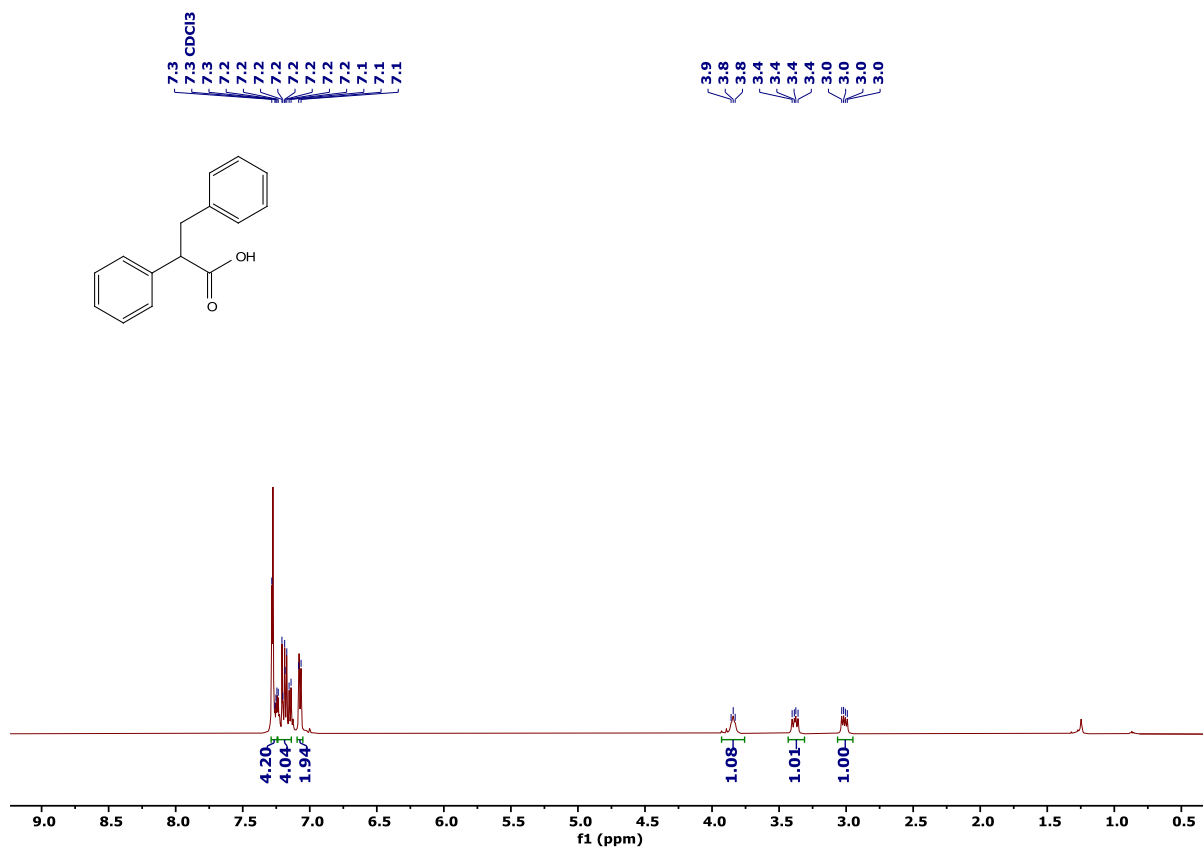


Figure S113. ¹H NMR spectrum of **8** in CDCl₃.

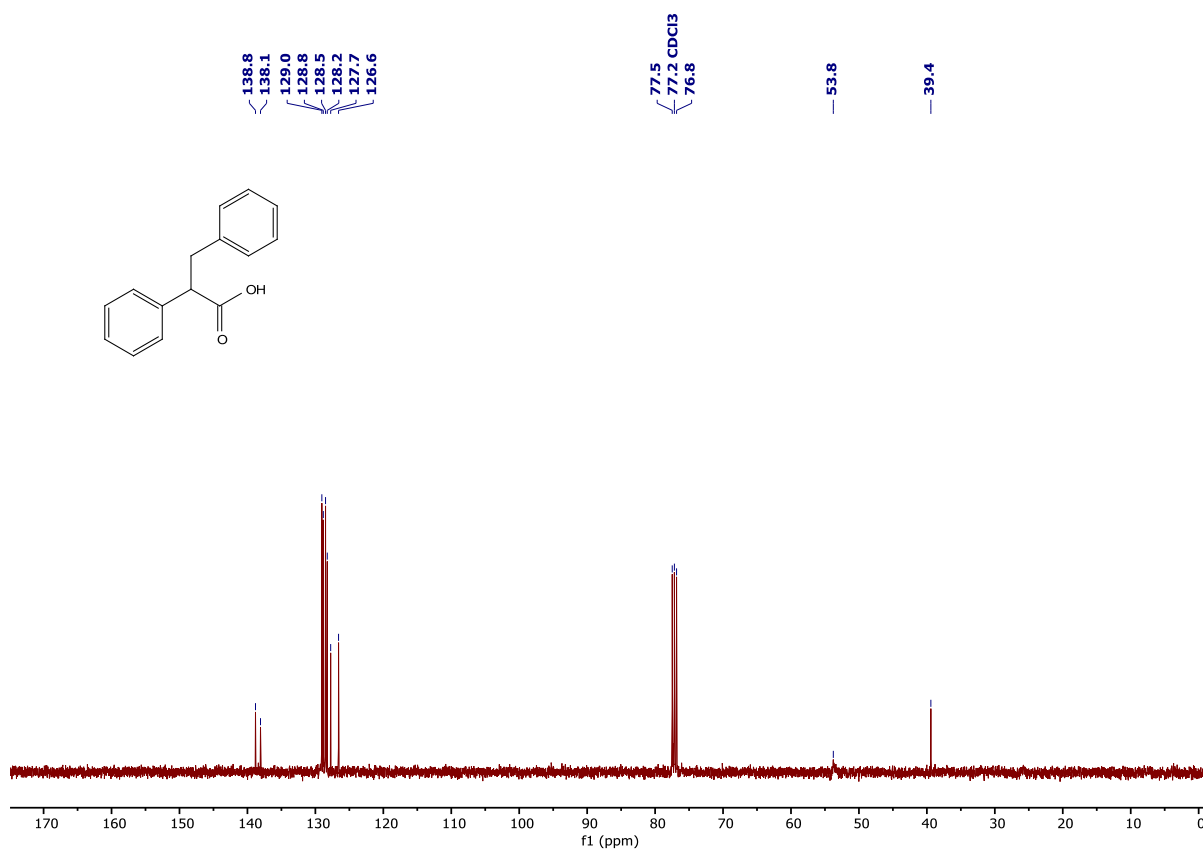


Figure S114. ¹³C{¹H} NMR spectrum of **8** in CDCl₃.

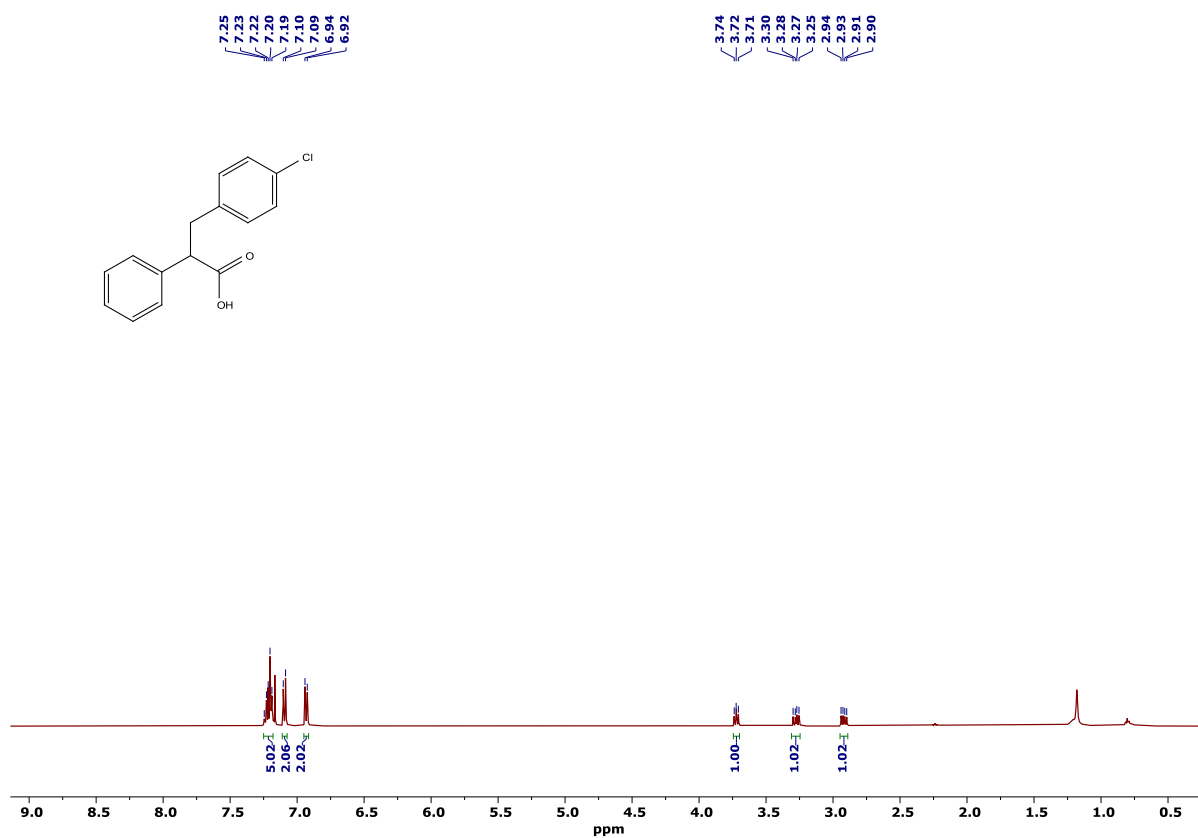


Figure S115. ¹H NMR spectrum of **9** in CDCl₃.

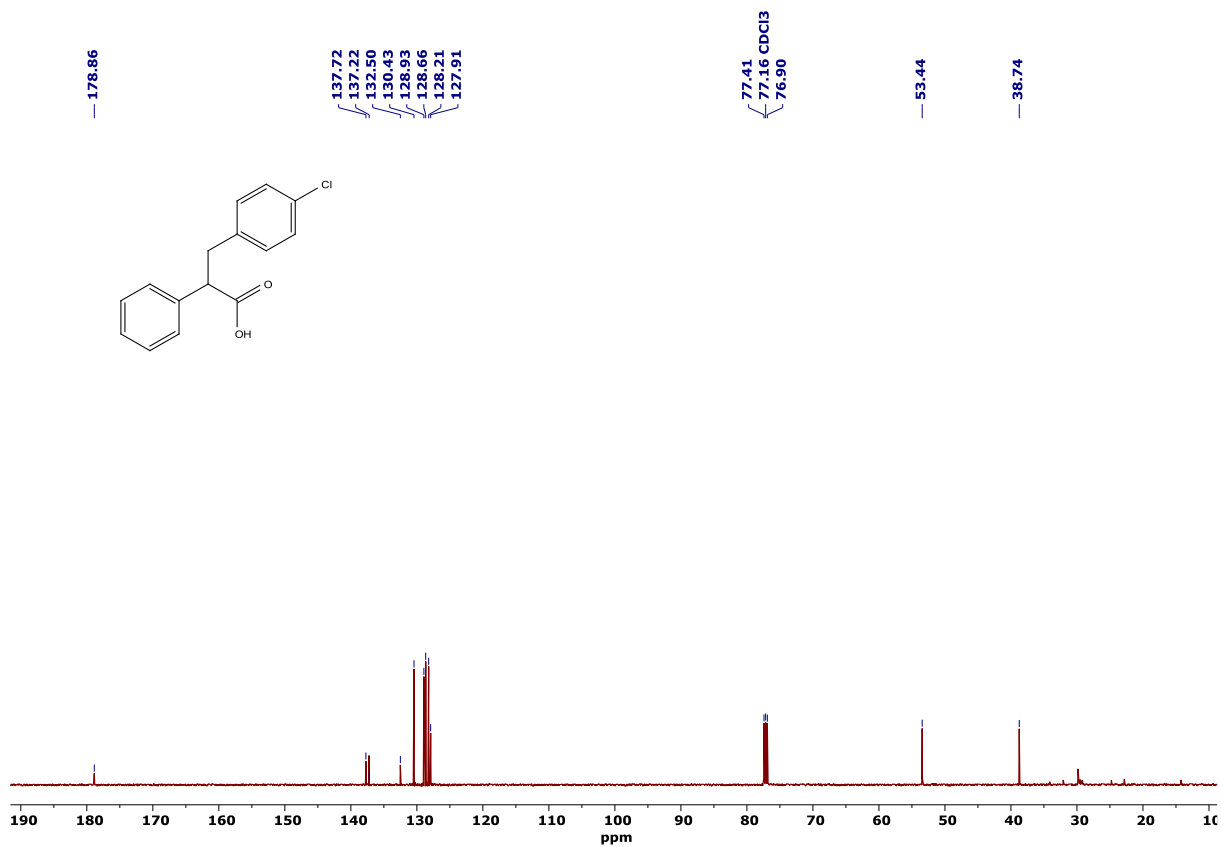
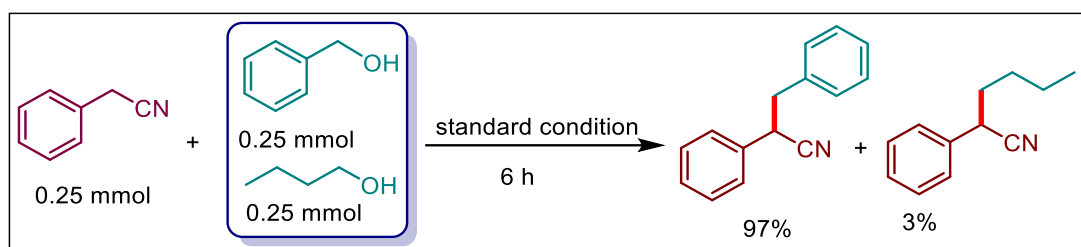


Figure S116. ¹³C{¹H} NMR spectrum of **9** in CDCl₃.

General procedure for competitive experiments (Scheme S4):

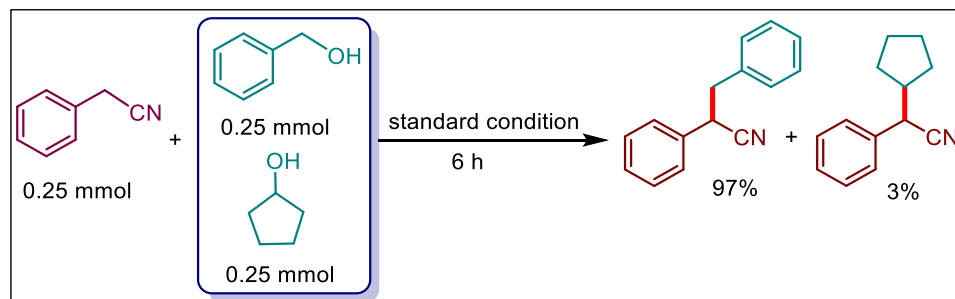
(a) α -alkylation of phenyleneacetonitrile (**3a**) with primary aromatic and primary aliphatic alcohol:

An oven-dried pressure tube (25 mL) was charged with phenyleneacetonitrile **3a** (0.25 mmol), benzyl alcohol (0.25 mmol), n-butanol (0.25 mmol), KO^tBu (0.05 mmol, 20 mol%), and catalyst **1a** (0.005 mmol, 2 mol%), followed by the addition of toluene (1 mL). Then, the tube was kept in a preheated oil bath at 140 °C and heated for 6 h. After that, the pressure tube was taken out and cooled to room temperature. The progress of the reaction was monitored using GC-MS analysis.



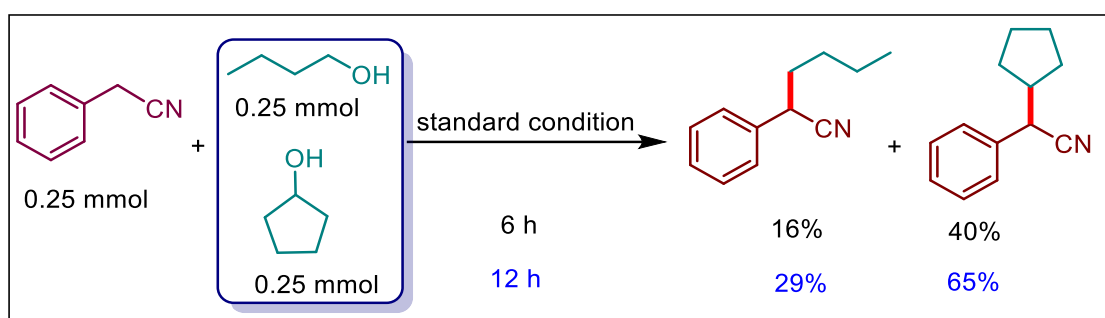
(b) α -alkylation of phenyleneacetonitrile (**3a**) with primary aromatic and secondary alcohol:

An oven-dried pressure tube (25 mL) was charged with phenyleneacetonitrile **3a** (0.25 mmol), benzyl alcohol (0.25 mmol), cyclobutanol (0.25 mmol), KO^tBu (0.05 mmol, 20 mol%), and catalyst **1a** (0.005 mmol, 2 mol%), followed by the addition of toluene (1 mL). Then, the tube was kept in a preheated oil bath at 140 °C and heated for 6 h. After that, the pressure tube was taken out and cooled to room temperature. The progress of the reaction was monitored using GC-MS analysis.



(c) α -alkylation of phenylacetonitrile (3a**) with primary aliphatic and secondary alcohol:**

An oven-dried pressure tube (25 mL) was charged with phenylacetonitrile **3a** (0.25 mmol), n-butanol (0.25 mmol), cyclobutanol (0.25 mmol), KO^tBu (0.05 mmol, 20 mol%), and catalyst **1a** (0.005 mmol, 2 mol%), followed by the addition of toluene (1 mL). Then, the tube was kept in a preheated oil bath at 140 °C and heated for 6 h/12h. After that, the pressure tube was taken out and cooled to room temperature. The progress of the reaction was monitored using GC-MS analysis.



Control experiments

Comparison of catalytic activity of **1a vs **1c/1d** towards secondary alcohol:**

Three oven-dried pressure tubes (25 mL) were charged with phenylacetonitrile **3a** (0.2 mmol), cyclopentanol (0.4 mmol), KO^tBu (0.04 mmol, 20 mol%), and catalyst **1a/1c/1d** (0.004 mmol, 2 mol%) separately, followed by the addition of toluene (1 mL). Then, the tubes were kept parallelly in a preheated oil bath at 140 °C and heated for 6 h. After that, the pressure tubes were taken out and cooled to room temperature. The progress of the reaction was monitored using GC-MS.

Metal hydride trapping experiment:

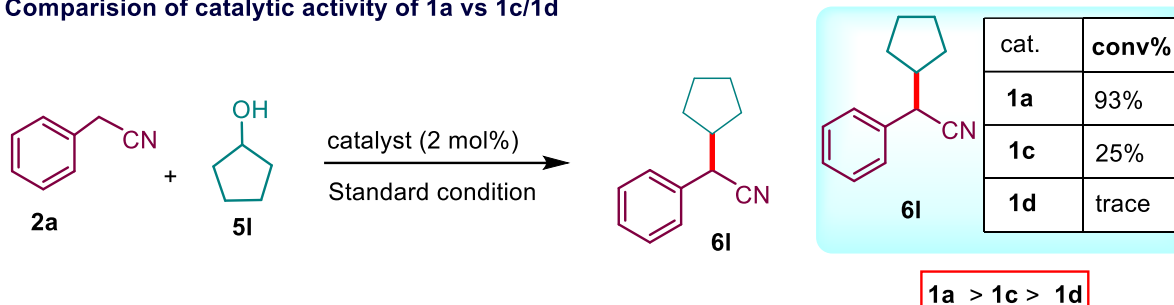
An oven-dried pressure tube was charged with catalyst **1a** (0.005 mmol, 2 mol%), KO^tBu (0.05 mmol, 20 mol%), nitrile (0.25 mmol), alcohol (0.5 mmol), and trityl PF₆ (0.01 mmol) in toluene (1 mL). Then the reaction mixture was kept in a preheated oil bath at 140 °C for 6 h. After that, the pressure tube was taken out and cooled to room temperature. The progress of the reaction was monitored using GC-MS analysis.

Radical scavenger experiment: An oven-dried pressure tube was charged with catalyst **1a** (0.005 mmol, 2 mol%), KO^tBu (0.05 mmol, 20 mol%), nitrile (0.25 mmol), alcohol (0.5 mmol), and TEMPO/BHT (0.75 mmol) in toluene (1 mL). Then the reaction mixture was kept

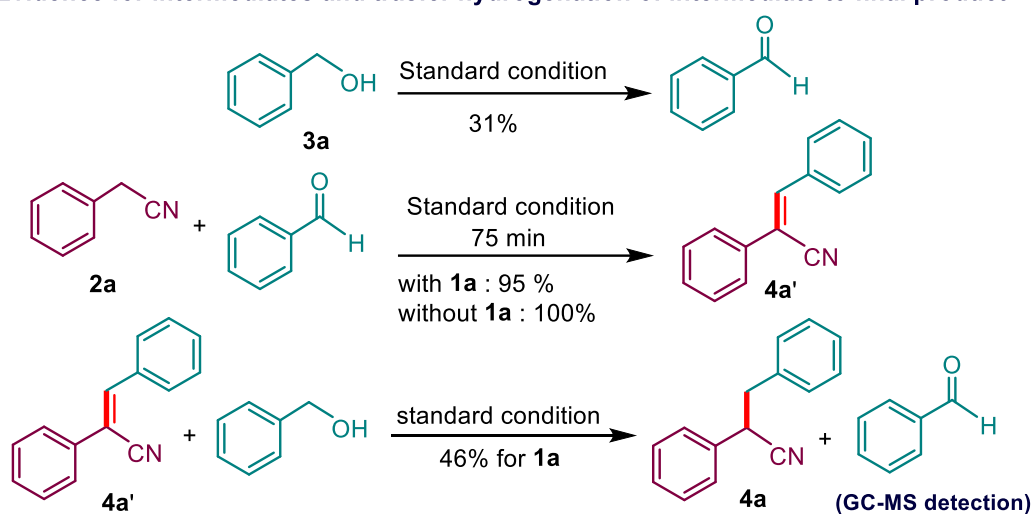
in a preheated oil bath at 140 °C for 6 h. After that, the pressure tube was taken out and cooled to room temperature. The progress of the reaction was monitored using GC-MS analysis.

Control experiments (Scheme S5):

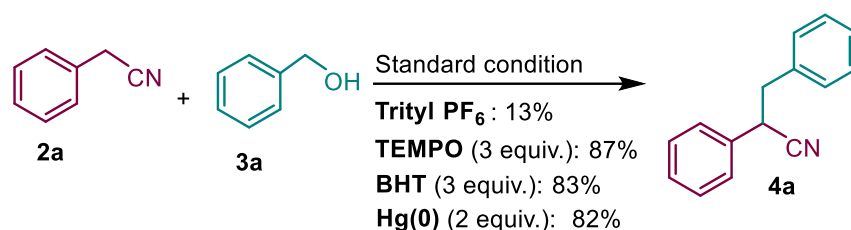
Comparison of catalytic activity of 1a vs 1c/1d



Evidence for intermediates and transfer hydrogenation of intermediate to final product



Hydride quencher, radical trapping and Hg(0) poisoning experiment



Mercury dropping experiment: An oven-dried pressure tube was charged with catalyst **1a** (0.005 mmol, 2 mol %), KO^tBu (0.05 mmol, 20 mol%), nitrile (0.25 mmol), alcohol (0.5 mmol), and mercury (0.5 mmol) in toluene (1 mL). After that, the pressure tube was taken out and cooled to room temperature. The progress of the reaction was monitored using GC-MS analysis.

Detection of Cobalt amido complex A

In an inert condition J Young® NMR tube was charged with complex **1a** followed by C₆D₆. It was found that the complex **1a** is insoluble in C₆D₆. However, after adding 2 equiv. of base KO^tBu and sonicated for 10 min, the colourless solution turned to dark brown which was further subjected to ¹H NMR and ESI-MS analysis.

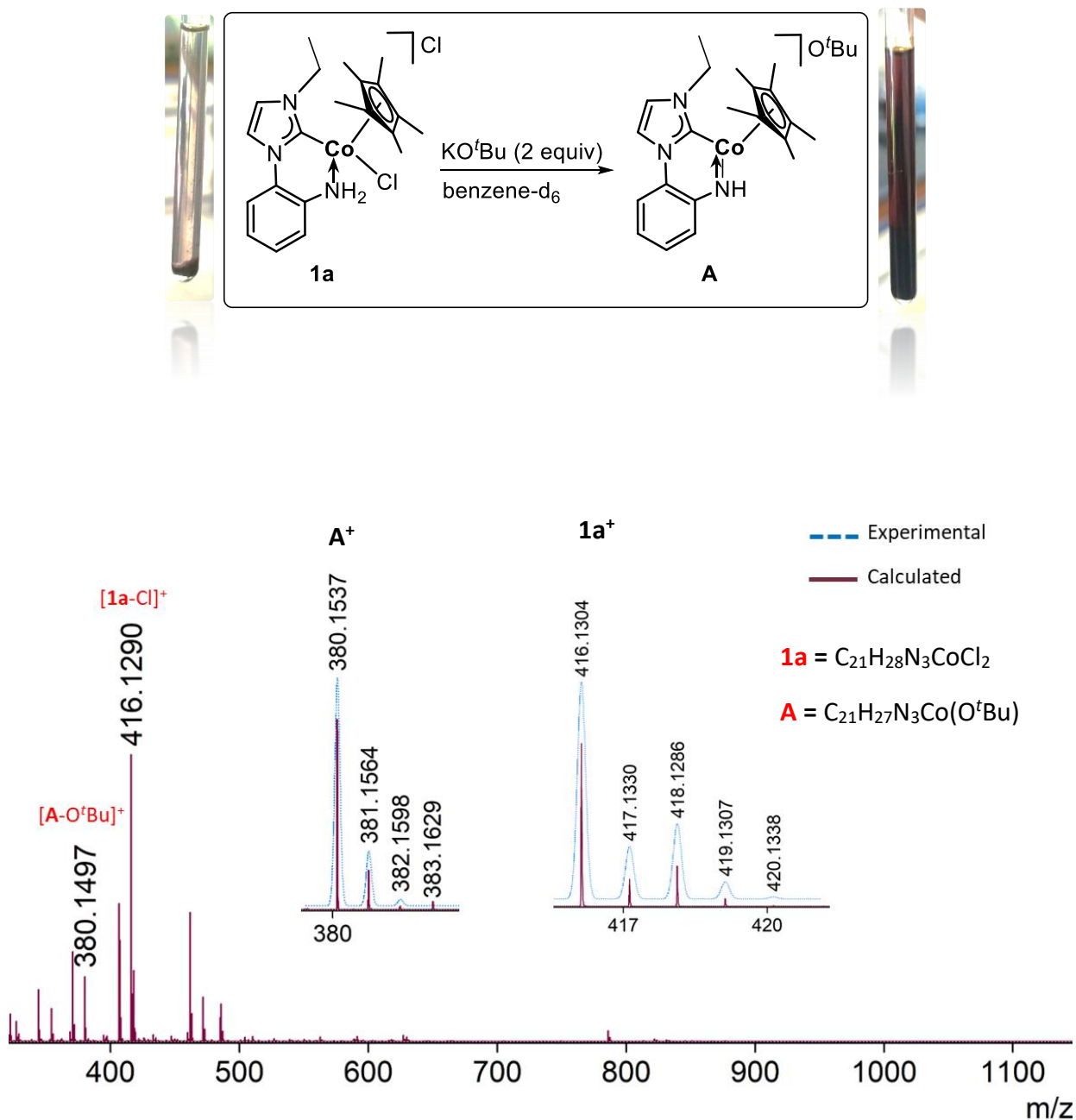


Figure S117. ESI-MS (positive ions) spectrum of the above reaction mixture.

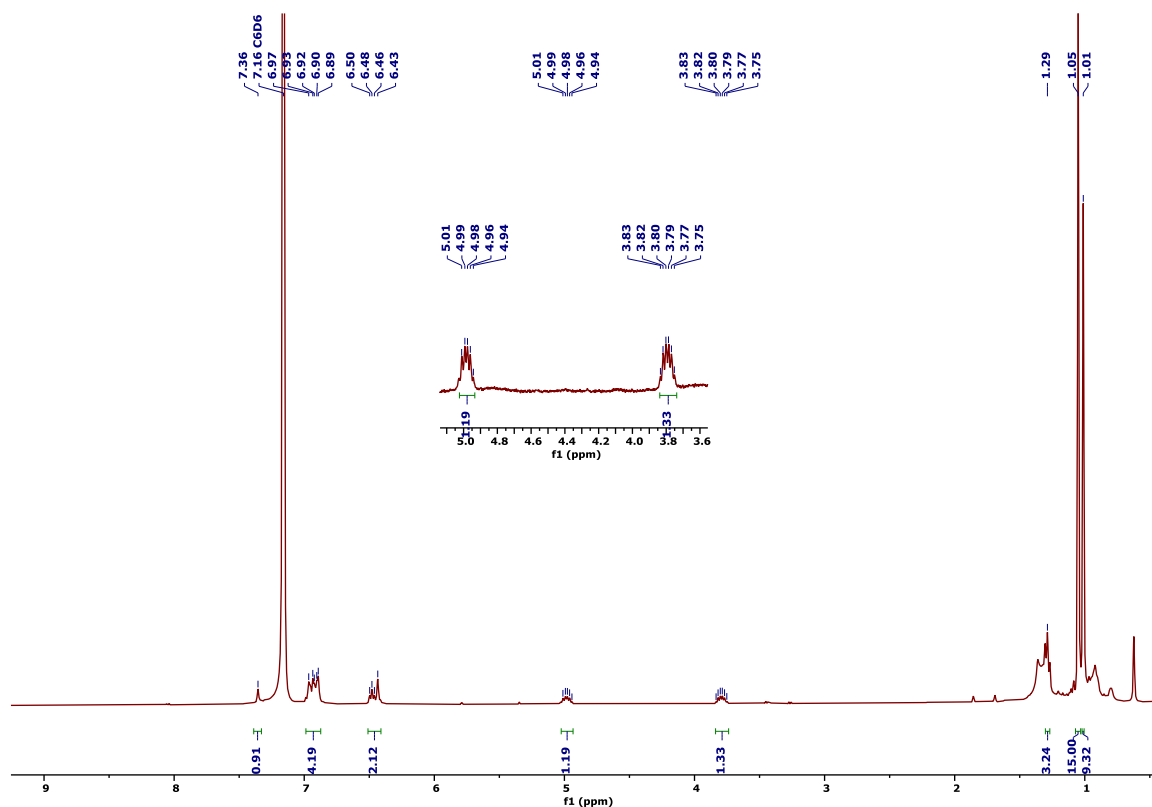
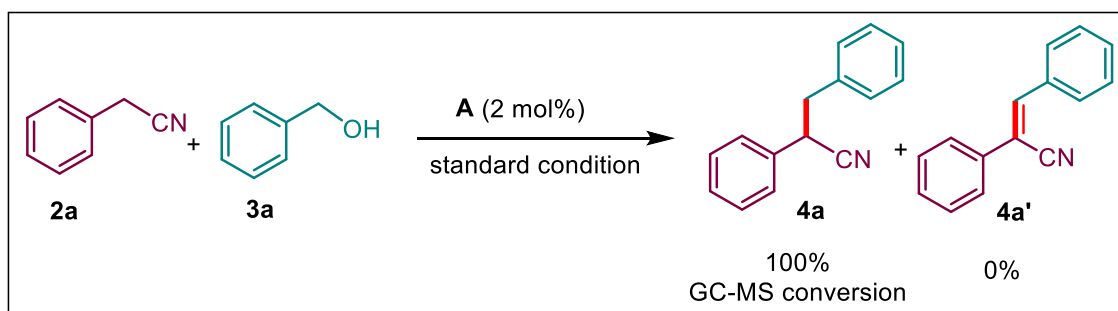


Figure S118. ^1H NMR spectrum of the above reaction mixture in C_6D_6 .

Catalytic activity of A (Scheme S6)

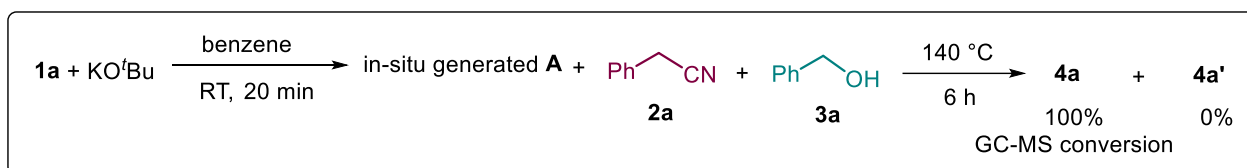
Using isolated catalyst, **A**: complex **1a** (1 equiv.) was taken in an oven dried Schlenk tube and toluene was added to it. Complex **1a** was insoluble in toluene. After that KO^tBu (2 equiv.) was added which generated the cobalt amido complex **A**, accompanied by the change of a colourless solution to a dark brown solution. The reaction mixture was then stirred for 30 min at room temperature. Finally, all the volatiles were removed in high vacuum and complex **A** was isolated as solid after work up with dry hexane (formation was confirmed with NMR analysis). The active catalyst **A** was then used for the α -alkylation of nitrile under our standard reaction conditions which showed 100% conversion of **2a** to **4a**.



Reaction conditions: **2a** (0.2 mmol), **3a** (0.4 mmol), KO^tBu (20 mol%), **A** (2 mol%) in toluene at 140 $^\circ\text{C}$ for 6 h. Conversion of **2a** was determined by GC-MS using mesitylene as an internal standard.

***In-situ* generated A (in benzene solvent):**

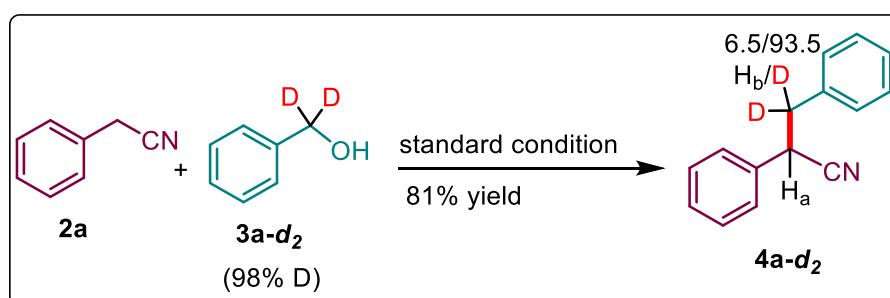
An oven-dried pressure tube was charged with catalyst **1a** (0.004 mmol, 2 mol %), KO^tBu (0.04 mmol, 20 mol%) in benzene (1 mL) and stirred 20 min at room temperature to generate the active catalyst **A** (we have previously confirmed its formation with NMR and mass analysis, page S83-S84). After that nitrile **2a** (0.2 mmol), and alcohol **3a** (0.4 mmol) were added to the reaction mixture and kept in a preheated oil bath at 140 °C for 6 h. After completion of the reaction, a small portion of aliquot was taken for GC-MS analysis.



Reaction conditions: **2a** (0.2 mmol), **3a** (0.4 mmol), KO^tBu (20 mol%), **1a** (2 mol%) in benzene at 140 °C for 6 h. Conversion of **2a** was determined by GC-MS using mesitylene as an internal standard.

Deuterium incorporation experiment

The deuterium incorporation experiment was carried out following the general procedure of α -alkylation of nitrile using **2a** (0.1 mmol) and (98% D) benzyl alcohol (0.2 mmol). After the completion of the reaction, the reaction mixture was filtered over a short pad of silica and the pad was washed with methanol. Then the obtained filtrate was concentrated and dissolved in CDCl₃. An equivalent amount of internal standard mesitylene (0.1 mmol) was added to this and resultant solution was subjected to ¹H NMR analysis. Conversion was calculated by ¹H-NMR integration value.



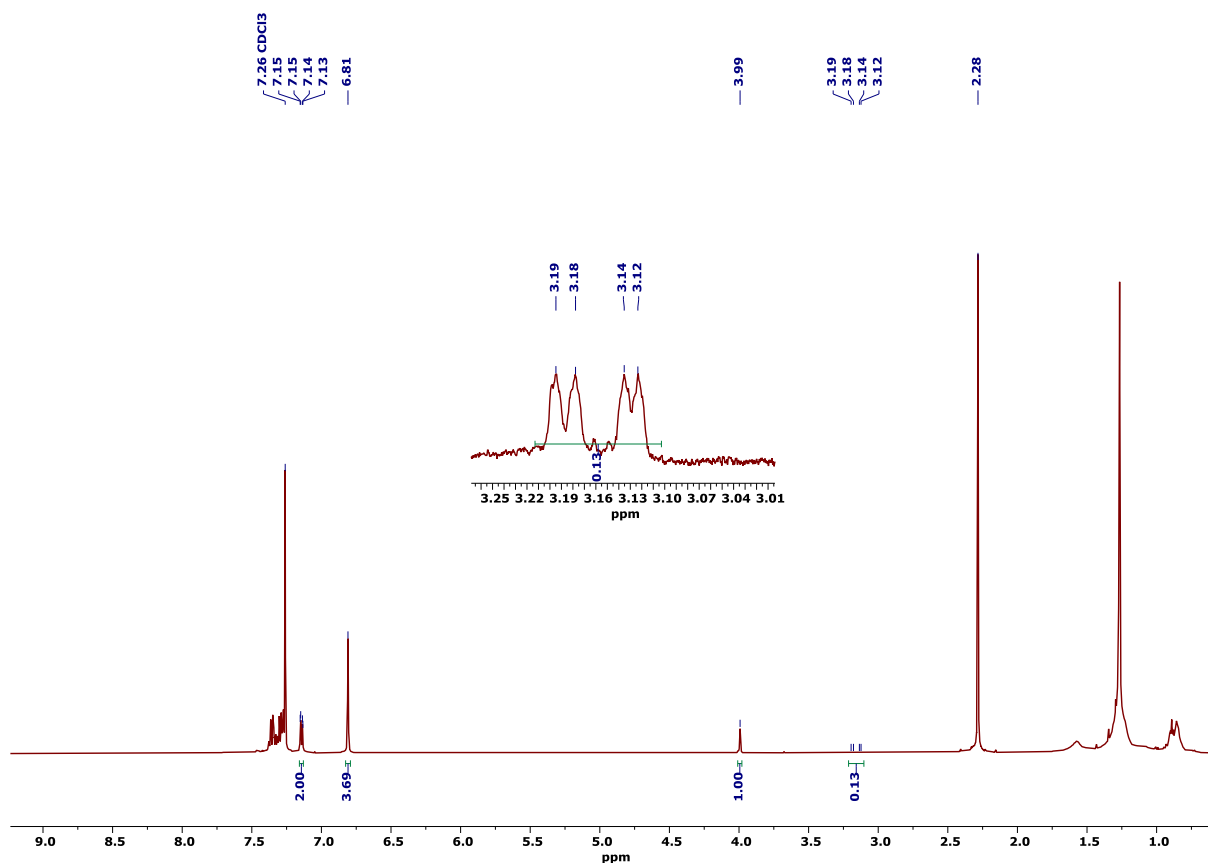


Figure S119. ^1H NMR spectrum of the reaction mixture in CDCl_3 .

Conversion was calculated by ^1H -NMR integration value

		H_a	H_b
Signal δ	7.13 [2H]	3.99 [1H]	3.14 [2H]
Integral Value	2.00	1.00	0.13
Calculated ratio	-	-	$\{(2-0.13)/2\} \times 100 = 93.5\%$

Calculation of P_H/P_D :

By considering individual reaction for the formation of (**4a-d₂**) deuterated and (**4a**) non-deuterated product, P_H/P_D was calculated.

Deuterium incorporation in the product using 98% of **3a-d₂** = 93.5%

Deuterium incorporation in the product for 100% of **3a-d₂** = $(93.5/98) \times 100\% = 95.4\%$

Total product (deuterated **4a-d₂** + non deuterated **4a**) yield = 81%

Therefore, yield of the total deuterated product = $(95.4 \times 81)/100 = 77.2\%$

Yield of product for non-deuterated reaction = 100% (GC-MS yield)

Hence, $P_H/P_D = 100/77.2 = 1.29$

Single crystal X-ray Crystallography

Single crystal X-ray diffraction data were collected on a Bruker AXS Kappa Apex II equipped with a CCD detector (for **1a**). The compound was measured using MoK α radiation ($\lambda = 0.71073$ Å). Crystals were selected using a polarizing optical microscope and then mounted in a crystal-mounting loop using Paratone oil. The mounted crystal was then placed on a goniometer head and the crystal was centered with the help of a video microscope. The automatic cell determination routine, with 24/36 frames (10 sec exposure time per frame) at two/three different orientations of the detector, respectively was employed to collect reflections for unit cell determination. The collected reflections were indexed using inbuilt APEX software^{14a} to obtain unit cell parameters. Further, intensity data for structure determination were collected through an optimized strategy, which gave an average 4-fold redundancy for the reflections. The program Bruker-S SAINT^{14b} was used for integrating the frames and multi-scan absorption correction was applied using the program SADABS.^{14c} The structure was solved by SHELXS-97^{14d} and refined by full-matrix least squares techniques on F^2 using SHELXL^{14e} computer program incorporated in WinGX^{14f} system. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed at chemically meaningful positions and riding model refinement was applied. The graphical representations were performed using the program Mercury.^{14g} The crystal data (CCDC No. 2298764) and refinement details are summarized in Table S3.

Table S3. Crystallographic data for the complex **1a**

Compound	Complex 1a
CCDC No.	2298764
Empirical formula	C ₂₁ H ₂₈ Cl ₂ CoN ₃
Formula weight	452.29
Temperature	296(2) K
Crystal system	Monoclinic
Space group	P2 ₁ /n
a (Å)	10.4791(3)
b (Å)	15.9525(4)
c (Å)	12.9626(3)
α (°)	90
β (°)	99.6049(14)
γ (°)	90
V (Å ³)	2136.55(10)
Z	4
D calc (Mg/m ³)	1.406
F (000)	944
μ (mm ⁻¹)	1.064
θ Range (°)	2.042 to 24.998
Crystal size (mm)	0.160 x 0.120 x 0.100
No. of total reflns collected	16720
No. of unique reflns [I > 2σ(I)]	3765
Data/restraints/ parameters	3765 / 0 / 258
Goodness-of-fit on F ²	1.022
Final R indices [I > 2σ(I)]	0.0314, 0.0726
R indices (all data)	0.0457, 0.0802

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