Supporting Information

Control over Borrowing Hydrogen and Acceptorless Dehydrogenative Coupling Process for the Co(III)-NHC Catalysed Chemoselective Alkylation and Cyclisation of 1,2-Phenylenediamine with Alcohols

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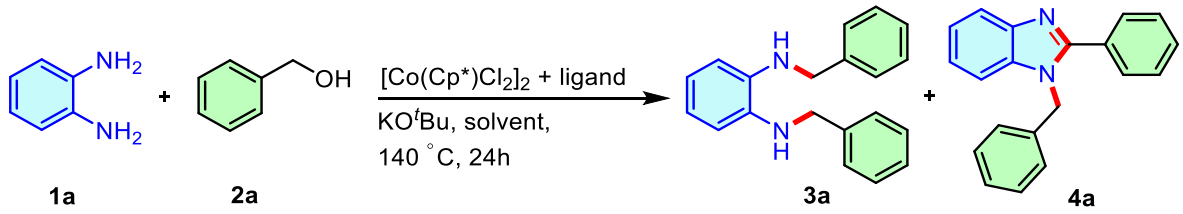
1. General Considerations

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 ^{1}H and $^{13}C\{^{1}H\}$ 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 with an Agilent 6545A Q-TOF Mass spectrometer. Chemicals e.g. cobalt precursor, $[Co(Cp^*)Cl_2]_2$ and ligands **L1-L3** were synthesized according to the literature procedures.[1] All other chemicals were procured from commercial sources and used as received.[1]

Optimization studies for the alkylation and cyclisation of 1,2-phenylene diamine[a]

Table S1: Screening of solvent

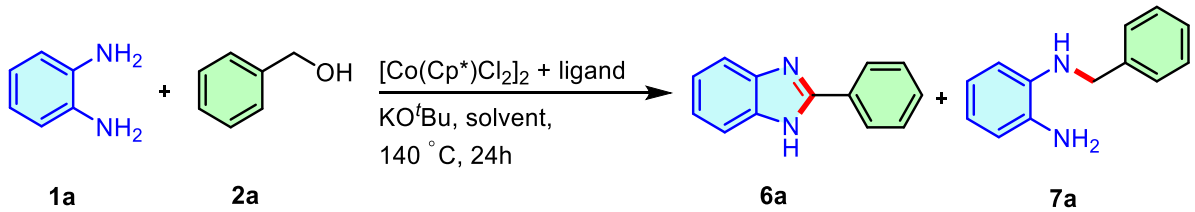


1a 2a 3a 4a

Entry	Complex	Ligand	Solvent	Yield 3a/4a (%)
1	$[Co(Cp^*)Cl_2]_2$	**L3/L1**	Xylene	38/35
2	$[Co(Cp^*)Cl_2]_2$	**L3/L1**	^{t}AmOH	40/38
3	$[Co(Cp^*)Cl_2]_2$	**L3/L1**	1,4-dioxane	52/46
4	$[Co(Cp^*)Cl_2]_2$	**L3/L1**	Toluene	80/78

[a]**Reaction conditions**: diamine **1a** (0.5 mmol), benzyl alcohol **2a** (1.25 mmol), KO^{t}Bu (1 equiv.), $[Co(Cp^*)Cl_2]_2$ (1.5 mol %), ligand (3 mol %), solvent (1 mL) at 140 °C for 24 h. Yield: All are isolated yields.

Table S2: Optimization data for the formation of **6a** and **7a**

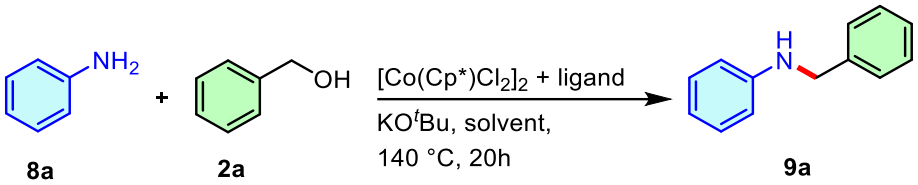


1a 2a 6a 7a

Entry	Complex	Ligand	Solvent	Yield 6a/7a (%)
1	$[Co(Cp^*)Cl_2]_2$	**L3**	Xylene	- /39
2	$[Co(Cp^*)Cl_2]_2$	**L3**	^{t}AmOH	- /46
3	$[Co(Cp^*)Cl_2]_2$	**L3**	Toluene	- /80
4	$[Co(Cp^*)Cl_2]_2$	**L1**	Xylene	35 /8
5	$[Co(Cp^*)Cl_2]_2$	**L1**	^{t}AmOH	41 /10
6	$[Co(Cp^*)Cl_2]_2$	**L1**	Toluene	78 /12

[a]**Reaction conditions**: diamine **1a** (0.5 mmol), benzyl alcohol **2a** (0.75 mmol), KO^{t}Bu (0.5 equiv.), $[Co(Cp^*)Cl_2]_2$ (1.5 mol %), ligand (3 mol %), solvent (1 mL) at 140 °C for 24 h. Yield: All are isolated yields.

Table S3: Optimization data for the formation of **9a**



Entry	Complex	Ligand	Yield 9a (%)
1	$[Co(Cp^*)Cl_2]_2$	**L1**	67
2	$[Co(Cp^*)Cl_2]_2$	**L2**	72
3	$[Co(Cp^*)Cl_2]_2$	**L3**	86

[a]**Reaction conditions**: amine **1a** (0.5 mmol), benzyl alcohol **2a** (0.75 mmol), KO^{t}Bu (0.25 equiv.), $[Co(Cp^*)Cl_2]_2$ (1.0 mol %), ligand (2 mol %), solvent (1 mL) at 140 °C for 20 h. Yield: All are isolated yields.

General procedure A for the synthesis of *N, N'*-dialkylated diamines: An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.0075 mmol), ligand **L3** (0.015 mmol), and KO^{t}Bu (0.5 mmol, 1 equiv.) followed by toluene (1 mL). Then, the tube was kept in an oil bath at 140 ˚C and heated for 1 h. After cooling to room temperature, respective diamine **1** (0.5 mmol) and alcohol **2** (1.25 mmol, 2.5 equiv.) were added and further heated at 140 ˚C for 24 h. After completion of the reaction, analytically pure products were obtained *via* column chromatography using hexane/ethyl acetate as eluent.

General procedure B for the synthesis of 1,2-disubstituted benzimidazoles: An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.0075 mmol), ligand **L1** (0.015 mmol), and KO^{t}Bu (0.5 mmol, 1 equiv.) followed by toluene (1 mL). Then, the tube was kept

in an oil bath at 140 ˚C and heated for 1 h. After cooling to room temperature, respective diamine **1** (0.5 mmol) and alcohol **2** (1.25 mmol, 2.5 equiv.) were added and further heated at 140 ˚C for 24 h. After completion of the reaction, analytically pure products were obtained *via* column chromatography using hexane/ethyl acetate as eluent.

General procedure C for the synthesis of 2-substituted benzimidazoles: An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.0075 mmol), ligand **L1** (0.015 mmol), and KO^{t}Bu (0.25 mmol, 0.5 equiv.) followed by toluene (1 mL). Then, the tube was kept in an oil bath at 140 ˚C and heated for 1 h. After cooling to room temperature, respective diamine **1** (0.5 mmol) and alcohol **2** (0.75 mmol, 1.5 equiv.) were added and further heated at 140 ˚C for 24 h. After completion of the reaction, analytically pure products were obtained *via* column chromatography using hexane/ethyl acetate.

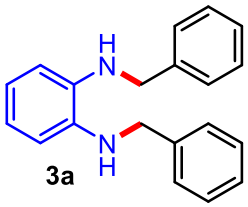
General procedure D for the cyclisation of *o*-nitro aniline: An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.0125 mmol), ligand **L1** (0.025 mmol), and KO^{t}Bu (0.5 mmol, 1.0 equiv.) followed by toluene (1 mL). Then, the tube was kept in an oil bath at 140 ˚C and heated for 1 h. After cooling to room temperature, respective *o*-nitro aniline **5** (0.5 mmol) and alcohol **2** (1.5 mmol, 3 equiv.) were added and further heated at 140 ˚C for 24 h. After completion of the reaction, analytically pure products were obtained *via* column chromatography using hexane/ethyl acetate.

General procedure E for the synthesis of mono-*N*-alkylated diamines: An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.0075 mmol), ligand **L3** (0.015 mmol), and KO^{t}Bu (0.25 mmol, 0.5 equiv.) followed by toluene (1 mL). Then, the tube was kept in an oil bath at 140 ˚C and heated for 1 h. After cooling to room temperature, respective diamine **1** (0.5 mmol) and alcohol **2** (0.75 mmol, 1.5 equiv.) were added and further heated at 140 ˚C for 24 h. After completion of the reaction, analytically pure products were obtained *via* column chromatography using hexane/ethyl acetate.

General procedure F for the synthesis of *N*-alkylated amines: An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.005 mmol), ligand **L3** (0.01 mmol), and KO^{t}Bu (0.25 mmol, 0.5 equiv.) followed by toluene (1 mL). Then, the tube was kept in an oil bath at 140 ˚C and heated for 1 h. After cooling to room temperature, respective amine **8** (0.5 mmol) and alcohol **2** (0.75 mmol, 1.5 equiv.) were added and further heated at 140 ˚C for 20 h. After

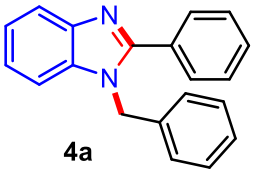
completion of the reaction, analytically pure products were obtained *via* column chromatography using hexane/ethyl acetate.

Large-scale Reaction: An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.075 mmol), ligand **L3**/**L1** (0.15 mmol), and KO^{t}Bu (5 mmol, 1 equiv.) followed by toluene (10 mL). Then, the tube was kept in an oil bath at 140 ˚C and heated for 1 h. After cooling to room temperature, respective diamine (5 mmol) and alcohol (12.5 mmol, 2.5 equiv.) were added and further heated at 140 ˚C for 24 h. After completion of the reaction, analytically pure products **3a**/**4a** were obtained *via* column chromatography using hexane/ethyl acetate.



3a

1.12 g, 78%

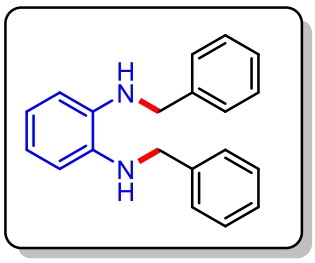


4a

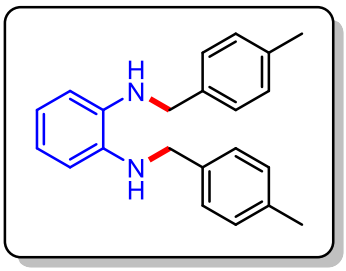
1.02 g, 72%

Analytical data of the isolated compounds

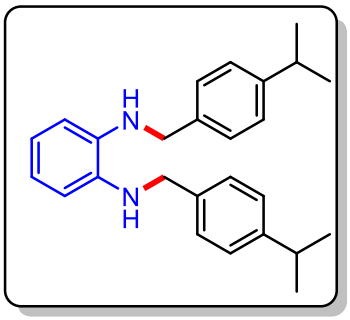
N*^{1},*N*^{2}*-dibenzylbenzene-1,2-diamine **(3a):**[2] Following the general procedure **A**, the titled compound was isolated as greenish liquid (115 mg, 0.399 mmol, 80% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.29 (m, 10H), 6.84-6.73 (m, 4H), 4.34 (s, 4H), 3.68 (s, *br*, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.6, 137.3, 128.7, 127.9, 127.4, 119.6, 112.2, 48.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{20}N_2H$ 289.1705; Found 289.1700.



N*^{1},*N*^{2}*-bis(4-methylbenzyl)benzene-1,2-diamine **(3b):**[2] Following the general procedure **A**, the titled compound was isolated as greenish liquid (123 mg, 0.389 mmol, 78% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 4H), 7.18-7.15 (m, 4H), 6.83-6.72 (m, 4H), 4.28 (s, 4H), 3.59 (s, *br*, 2H), 2.37 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.3, 137.0, 136.5, 129.4, 128.0, 127.9, 119.5, 112.0, 48.7, 21.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}N_2H$ 317.2018; Found 317.2011.

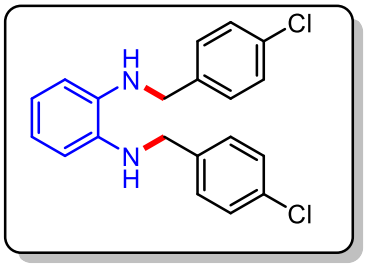


N*^{1},*N*^{2}*-bis(4-isopropylbenzyl)benzene-1,2-diamine **(3c):**[2] Following the general procedure **A**,



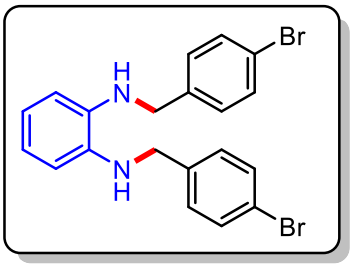
the titled compound was isolated as a white solid (155 mg, 0.414 mmol, 83% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.9 Hz, 4H), 7.21 (d, J = 8.1 Hz, 4H), 6.82-6.73 (m, 4H), 4.27 (s, 4H), 3.59 (s, *br*, 2H), 2.94-2.87 (m, 2H), 1.25 (d, J = 7.0 Hz, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.1, 137.4, 136.9, 128.1, 126.8, 119.5, 111.9, 48.7, 34.0, 24.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{32}N_2H$ 373.2644; Found 373.2633.

N*^{1},*N*^{2}*-bis(4-chlorobenzyl)benzene-1,2-diamine **(3d):**[2] Following the general procedure **A**, the



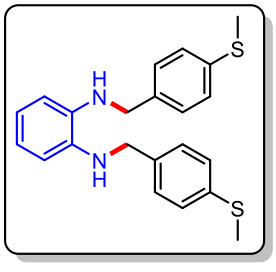
titled compound was isolated as greenish liquid (139 mg, 0.389 mmol, 78% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 8H), 6.82-6.66 (m, 4H), 4.30 (s, 4H), 3.64 (s, *br*, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.0, 137.0, 133.1, 129.2, 128.9, 119.8, 112.4, 48.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{18}Cl_2N_2H$ 357.0925; Found 357.0921.

N*^{1},*N*^{2}*-bis(4-bromobenzyl)benzene-1,2-diamine **(3e):**[3] Following the general procedure **A**, the



titled compound was isolated as greenish liquid (169.5 mg, 0.379 mmol, 76% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 8H), 6.82-6.66 (m, 4H), 4.30 (s, 4H), 3.64 (s, *br*, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.0, 137.0, 133.1, 129.2, 128.9, 119.8, 112.4, 48.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{18}Br_2N_2H$ 446.9896; Found 446.9898.

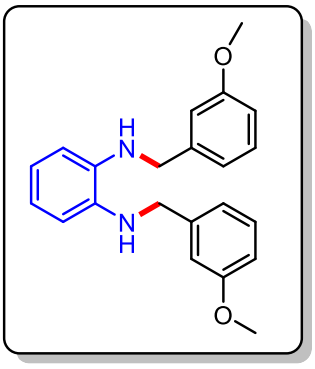
N*^{1},*N*^{2}*-bis(4-methylthiobenzyl)benzene-1,2-diamine **(3f):** Following the general procedure **A**,



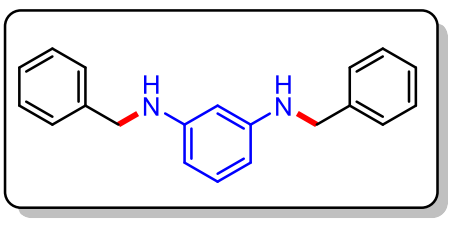
the titled compound was isolated as orange liquid (148 mg, 0.389 mmol, 78% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.30 (m, 4H), 7.26-7.24 (m, 4H), 6.82-6.80 (m, 2H), 6.73-6.70 (m, 2H), 4.28 (s, 4H), 3.65 (s, *br*, 2H), 2.49 (d, J = 2.0 Hz, 6H) ppm.^{13}C{^{1}H} NMR (126 MHz,

$CDCl_3$) δ 137.4, 137.1, 136.4, 128.5, 127.1, 119.7, 112.4, 48.5, 16.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}N_2S_2H$ 381.1459; Found 381.1458.

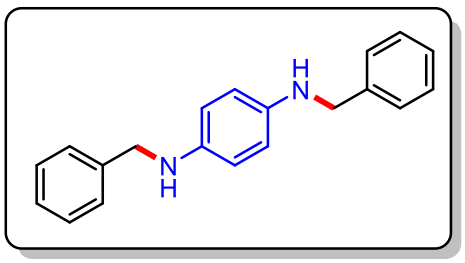
N*^{1},*N*^{2}*-bis(3-methoxybenzyl)benzene-1,2-diamine **(3g):**[2] Following the general procedure **A**, the titled compound was isolated as a greenish liquid (132 mg, 0.379 mmol, 76% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 6.99-6.95 (m, 4H), 6.83-6.70 (m, 6H), 4.29 (s, 4H), 3.79 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.0, 141.2, 137.2, 129.7, 120.2, 119.6, 113.6, 112.7, 112.2, 55.3, 48.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}N_2O_2H$ 349.1916; Found 349.1904.



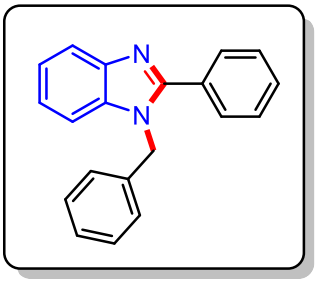
N*^{1},*N*^{3}*-dibenzylbenzene-1,3-diamine **(3h):**[2] Following the general procedure **A**, the titled compound was isolated as greenish liquid (116 mg, 0.402 mmol, 80% yield) using silica gel column chromatography (2-5% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.22 (m, 10H), 6.96 (t, J = 8.0 Hz, 1H), 6.06-6.03 (m, 2H), 5.91 (t, J = 2.3 Hz, 1H), 4.26 (s, 4H), 3.91 (s, *br*, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.5, 139.8, 130.2, 128.7, 127.6, 127.3, 103.2, 97.4, 48.5 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{20}N_2H$ 289.1705; Found 289.1703.



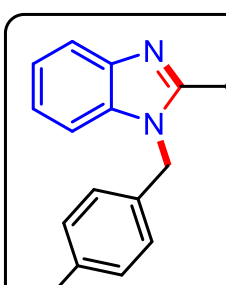
N*^{1},*N*^{4}*-dibenzylbenzene-1,4-diamine **(3i):**[2] Following the general procedure **A**, the titled compound was isolated as a brownish solid (110 mg, 0.381 mmol, 76% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 10H), 6.56 (s, 4H), 4.25 (s, 4H), 2.97 (s, *br*, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.9, 140.1, 128.7, 127.7, 127.2, 114.8, 49.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{20}N_2H$ 289.1705; Found 289.1695.



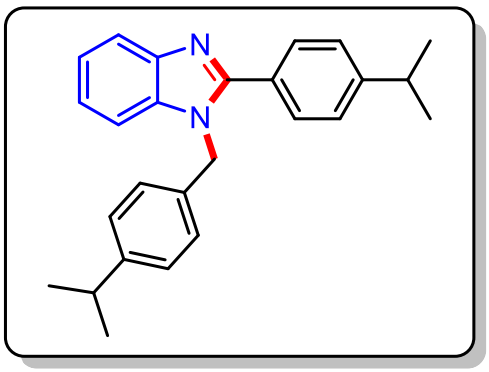
1-benzyl-2-phenyl-1H-benzo[d]imidazole **(4a):**[4] Following the general procedure **B**, the titled compound was isolated as a white solid (108 mg, 0.379 mmol, 76% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 6.9 Hz, 2H), 7.47-7.45 (m, 3H), 7.35-7.30 (m, 4H), 7.24-7.20 (m, 2H), 7.11 (d, J = 6.6 Hz, 2H), 5.46 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.3, 143.3, 136.5, 136.2, 130.2, 130.1, 129.4, 129.2, 128.9, 127.9, 126.1, 123.2, 122.8, 120.1, 110.7, 48.5 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{16}N_2H$ 285.1392; Found 285.1395.



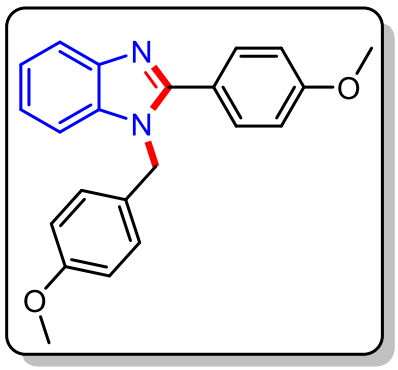
1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole **(4b):**[5] Following the general procedure **B**, the titled compound was isolated as white solid (125 mg, 0.399 mmol, 80% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 7.0 Hz, 1H), 7.28 (s, 1H), 7.25 (s, 1H), 7.22-7.19 (m, 2H), 7.13 (d, J = 7.7 Hz, 2H), 7.00 (d, J = 7.7 Hz, 2H), 5.41 (s, 2H), 2.40 (s, 3H), 2.34 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.5, 143.3, 140.3, 137.7, 136.3, 133.6, 129.9, 129.7, 129.4, 127.3, 126.1, 123.1, 122.9, 120.0, 110.7, 48.5, 21.7, 21.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{20}N_2H$ 313.1705; Found 313.1709.



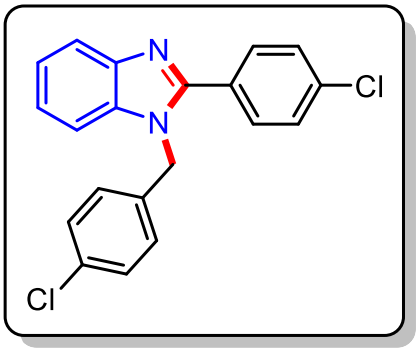
1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-1H-benzo[d]imidazole **(4c):**[4] Following the general procedure **B**, the titled compound was isolated as a white solid (129 mg, 0.349 mmol, 70% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 3H), 7.21-7.18 (m, 4H), 7.04 (d, J = 8.1 Hz, 2H), 5.44 (s, 2H), 2.99-2.93 (m, 1H), 2.91-2.84 (m, 1H), 1.28 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H), 1.23 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.5, 151.1, 148.6, 136.2, 133.9, 129.4, 127.6, 127.2, 127.0, 126.1, 123.0, 122.7, 119.9, 110.8, 48.4, 34.2, 33.9, 24.1, 24.0 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{28}N_2H$ 369.2331; Found 369.2338.



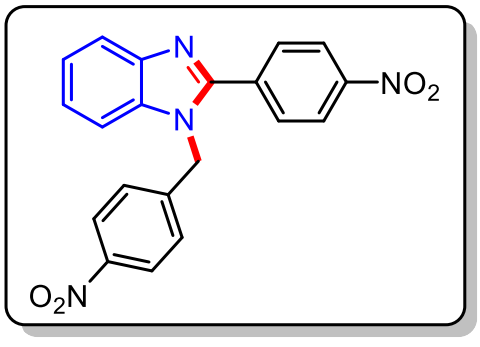
1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole **(4d):**[4] Following the general procedure **B**, the titled compound was isolated as greenish liquid (127 mg, 0.369 mmol, 74% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.7 Hz, 2H), 7.35 (s, 1H), 7.07 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 6.96 (s, 1H), 6.90 (d, J = 8.6 Hz, 2H), 5.41 (s, 2H), 3.88 (s, 3H), 3.82 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.3, 161.1, 154.3, 151.2, 130.8, 128.4, 127.4, 122.8, 122.6, 122.3, 119.7, 114.6, 114.4, 110.7, 55.5, 55.4, 48.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{20}N_2O_2H$ 345.1603; Found 345.1609.



1-(4-chlorobenzyl)-2-(4-chlorophenyl)-1H-benzo[d]imidazole **(4e):**[5] Following the general procedure **B**, the titled compound was isolated as an off-white solid (122 mg, 0.344 mmol, 69% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.26 (t, J = 8.4 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 6.94 (d, J = 8.2 Hz, 2H), 5.36 (s, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.0, 143.2, 136.1, 135.3, 132.5, 132.2, 130.8, 129.0, 127.7, 124.8, 123.6, 123.2, 122.1, 120.3, 110.4, 48.0 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{14}Cl_2N_2H$ 353.0612; Found 353.0618.

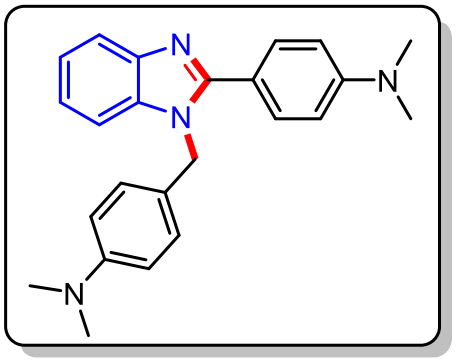


1-(4-nitrobenzyl)-2-(4-nitrophenyl)-1H-benzo[d]imidazole **(4f):**[6] Following the general procedure **B**, the titled compound was isolated as a white solid (94 mg, 0.250 mmol, 62% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.26 (t, J = 8.4 Hz, 1H), 7.18 (d, J = 7.9



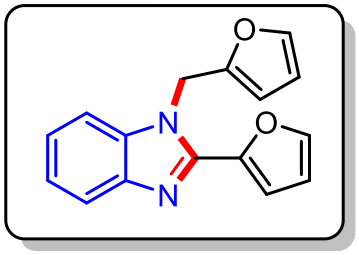
Hz, 1H), 6.94 (d, J = 8.2 Hz, 2H), 5.36 (s, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 153.0, 143.2, 136.1, 135.3, 132.5, 132.2, 130.8, 129.0, 127.7, 124.8, 123.6, 123.2, 122.1, 120.3, 110.4, 48.0 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}N_2O_2H$ 349.1916; Found 349.1919.

4-(1-(4-(diisopropyllamino)benzyl)-1H-benzo[d]imidazol-2-yl)-N, N dimethylaniline **(4g):**[6]

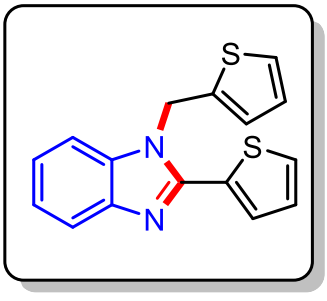


Following the general procedure **B**, the titled compound was isolated as white solid (159 mg, 0.429 mmol, 86% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.1 Hz, 2H), 7.16-7.12 (m, 1H), 7.09-7.03 (m, 2H), 6.89 (d, J = 8.6 Hz, 2H), 6.61 (d, J = 9.0 Hz, 2H), 6.54 (d, J = 8.7 Hz, 2H), 5.23 (s, 2H), 2.86 (s, 6H), 2.79 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 155.0, 151.3, 150.0, 143.4, 136.4, 130.3, 127.0, 124.4, 122.1, 119.3, 117.5, 112.8, 111.9, 110.4, 48.0, 40.5, 40.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{26}N_4H$ 371.2236; Found 371.2241.

2-(furan-2-yl)-1-(furan-2-ylmethyl)-1H-benzo[d]imidazole **(4h):**[4] Following the general procedure **B**, the titled compound was isolated as a white solid (90 mg, 0.339 mmol, 68% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.77 (m, 1H), 7.60 (d, J = 3.2 Hz, 1H), 7.45-7.44 (m, 1H), 7.28-7.25 (m, 3H), 7.20 (t, J = 3.3 Hz, 1H), 6.57 (s, 1H), 6.23 (d, J = 2.8 Hz, 1H), 6.20 (t, J = 3.0 Hz, 1H), 5.56 (s, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 149.6, 145.4, 144.0, 143.0, 142.7, 135.5, 123.3, 122.9, 119.8, 113.0, 112.1, 110.5, 110.0, 108.4, 41.7 ppm. HRMS (ESI) *m/z*: HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{12}N_2O_2H$ 265.0977; Found 265.0983.

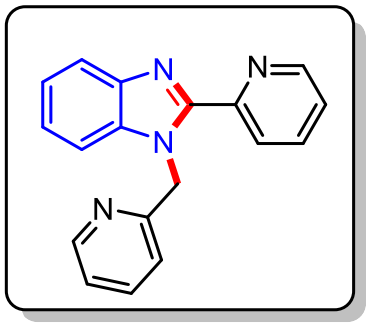


2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1H-benzo[d]imidazole **(4i):**[5] Following the general procedure **B**, the titled compound was isolated as a white solid (107 mg, 0.359 mmol, 72% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.77 (m, 1H), 7.60 (d, J = 3.2 Hz, 1H), 7.45-7.44 (m, 1H), 7.28-7.25 (m, 3H), 7.20 (t, J = 3.3 Hz, 1H), 6.57 (s, 1H), 6.23 (d, J = 2.8 Hz, 1H), 6.20 (t, J = 3.0 Hz, 1H), 5.56 (s, 2H)

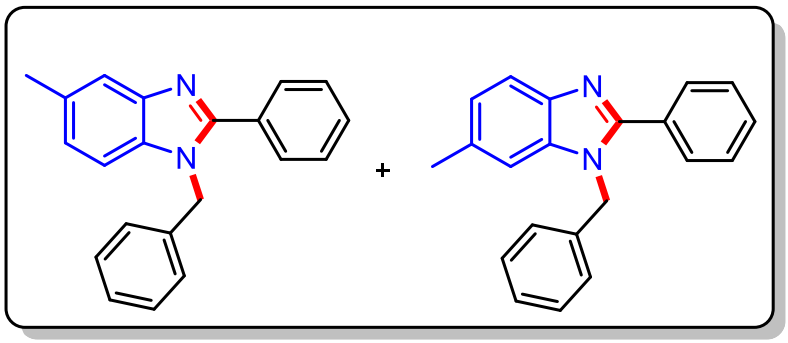


ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 149.6, 145.4, 144.0, 143.0, 142.7, 135.5, 123.3, 122.9, 119.8, 113.0, 112.1, 110.5, 110.0, 108.4, 41.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{12}N_2S_2H$ 297.0520; Found 297.0528.

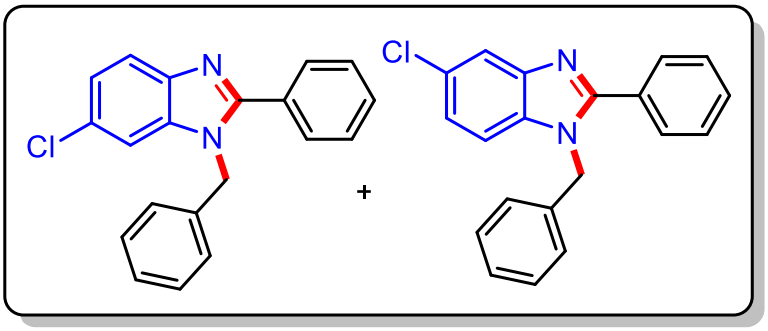
2-(pyridin-2-yl)-1-(pyridin-2-ylmethyl)-1H-benzo[d]imidazole **(4j):**[5] Following the general procedure **B**, the titled compound was isolated as brown solid (106 mg, 0.369 mmol, 74% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ 8.59-8.55 (m, 2H), 8.51 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.82-7.79 (m, 1H), 7.47-7.43 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.33-7.30 (m, 1H), 7.28-7.25 (m, 2H), 7.12-7.09 (m, 1H), 6.92 (d, J = 7.9 Hz, 1H), 6.31 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.2, 150.0, 149.6, 149.0, 148.6, 142.3, 136.9, 136.8, 136.7, 124.6, 123.9, 123.8, 123.0, 122.3, 120.9, 119.9, 110.8, 51.0 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{14}N_4H$ 287.1297; Found 287.1296.



1-benzyl-5-methyl-2-phenyl-1H-benzo[d]imidazole **(4k):**[5] Following the general procedure **B**, the titled compound was isolated as a yellow solid as a mixture of isomers in 3:1 ratio (113 mg, 0.379 mmol, 76% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 1H), 7.67-7.66 (m, 2H), 7.44-7.43 (m, 3H), 7.36-7.30 (m, 3H), 7.14 (d, J = 8.3 Hz, 1H), 7.10 (d, J = 7.1 Hz, 2H), 7.01 (s, 1H), 5.42 (s, 2H), 2.50 (s, 1H), 2.44 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 154.2, 153.8, 143.7, 141.4, 136.7, 136.5, 133.2, 132.5, 130.4, 129.8, 129.4, 129.3, 129.2, 129.1, 128.8, 127.8, 126.1, 126.0, 124.6, 124.4, 119.9, 119.6, 110.4, 110.1, 48.5, 48.4, 21.9, 21.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{18}N_2H$ 299.1548; Found 299.1546.

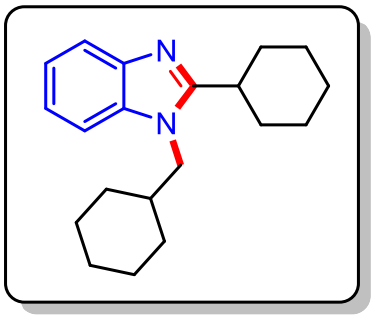


***1-benzyl-5-chloro-2-phenyl-1H-benzo[d]imidazole* (4l):**[5] Following the general procedure **B**,

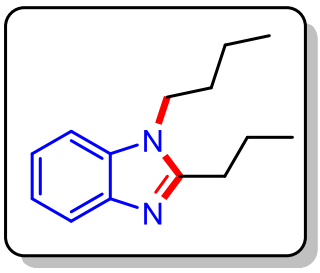


the titled compound was isolated as a yellow solid as a mixture of isomers in 2:1 ratio (111 mg, 0.350 mmol, 70% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.9 Hz, 2H), 7.72 (s, 1H), 7.66 (d, J = 8.6 Hz, 1H), 7.50 (s, 1H), 7.49 (s, 1H), 7.36 (t, J = 7.1 Hz, 1H), 7.30-7.28 (m, 2H), 7.24 (d, J = 7.7 Hz, 2H), 7.15 (s, 1H), 7.14-7.12 (m, 3H), 7.10-7.08 (m, 1H), 7.06 (s, 1H), 7.00 (d, J = 3.3 Hz, 1H), 6.99 (d, J = 3.3 Hz, 1H), 6.91 (s, 1H), 6.89-6.86 (m, 3H), 5.23 (s, 2H), 5.21 (s, 1H) ppm. ^{13}C{^{1}H} (126 MHz, $CDCl_3$) δ 155.4, 155.0, 143.5, 141.3, 136.6, 135.9, 135.8, 134.5, 133.1, 130.5, 130.1, 129.4, 129.4, 129.3, 129.3, 129.0, 128.7, 128.4, 128.2, 128.1, 126.0, 126.0, 123.8, 120.8, 119.7, 111.5, 110.7, 48.6 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{15}ClN_2H$ 319.1002; Found 319.1010.

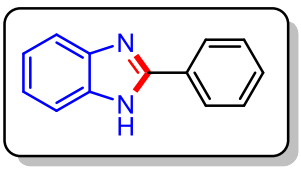
***2-cyclohexyl-1-(cyclohexylmethyl)-1H-benzo[d]imidazole* (4m):**[7] Following the general procedure **B**, the titled compound was isolated as a brown liquid (71 mg, 0.239 mmol, 48% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77-7.76 (m, 1H), 7.29-7.28 (m, 1H), 7.23-7.21 (m, 2H), 3.94 (d, J = 7.5 Hz, 2H), 2.83-2.78 (m, 1H), 1.96-1.88 (m, 6H), 1.84-1.82 (m, 1H), 1.77-1.68 (m, 6H), 1.65-1.63 (m, 2H), 1.41-1.40 (m, 2H), 1.08-1.04 (m, 2H), 0.89-0.83 (m, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.4, 122.1, 119.2, 109.9, 50.0, 38.8, 36.6, 32.2, 31.2, 26.6, 26.3, 25.9, 25.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{28}N_2H$ 297.2331; Found 297.2330.



1-butyl-2-propyl-1H-benzo[d]imidazole **(4n):**[8] Following the general procedure **B**, the titled compound was isolated as brownish liquid (69 mg, 0.319 mmol, 64% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74-7.72 (m, 1H), 7.31-7.29 (m, 1H), 7.24-7.22 (m, 2H), 4.10 (t, J = 7.5 Hz, 2H), 2.85 (t, J = 7.6 Hz, 2H), 1.98-1.91 (m, 2H), 1.82-1.76 (m, 2H), 1.44-1.40 (m, 2H), 1.08 (t, J = 6.8 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.9, 142.5, 135.1, 122.1, 121.9, 119.2, 109.3, 43.6, 32.1, 29.5, 21.4, 20.4, 14.2, 13.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{20}N_2H$ 217.1705; Found 217.1712.

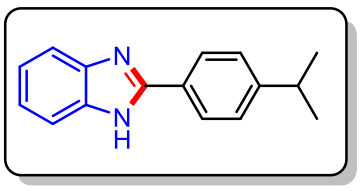


2-phenyl-1H-benzo[d]imidazole **(6a):**[4] Following the general procedure **C**/**D**, the titled compound was isolated as a yellow solid (76 mg, 0.390 mmol, 78% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 9.4 Hz, 2H), 7.65 (s, *br*, 2H), 7.51-7.46 (m, 3H), 7.30-7.27 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.7, 133.3, 130.7, 130.3, 129.2, 129.0, 128.5, 128.3, 126.9, 123.6, 115.1, 97.4, 96.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$Calcd for $C_{13}H_{10}N_2H$ 195.0922; Found 195.0930.



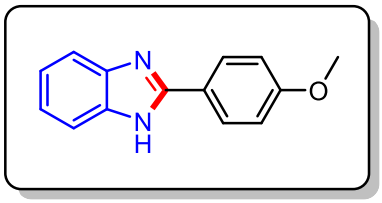
2-(p-tolyl)-1H-benzo[d]imidazole **(6b):**[4] Following the general procedure **C**/**D**, the titled compound was isolated as greenish liquid (79 mg, 0.379 mmol, 76% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.83 (s, *br*, 1H), 8.06 (d, J = 7.9 Hz, 2H), 7.57 (s, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.18 (s, 2H), 2.38 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.4, 139.6, 129.5, 127.5, 126.4, 122.1, 106.5, 103.5, 21.0 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{12}N_2H$ 209.1078; Found 209.1085.

2-(4-isopropylphenyl)-1H-benzo[d]imidazole **(6c):**[9] Following the general procedure **C**/**D**, the titled compound was isolated as a yellow solid (139 mg, 0.389 mmol, 78% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.85 (s, *br*, 1H), 8.10 (d, J = 7.9 Hz, 2H), 7.58 (dd, J = 52.0,

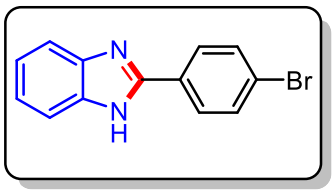


7.8 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 4.5 Hz, 2H), 2.99-2.92 (m, 1H), 1.25 (s, 3H), 1.23 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 151.4, 150.4, 143.9, 135.0, 127.9, 127.0, 126.6, 122.4, 121.6, 118.8, 111.3, 33.4, 23.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}N_2O_2H$ 349.1916; Found 349.1904.

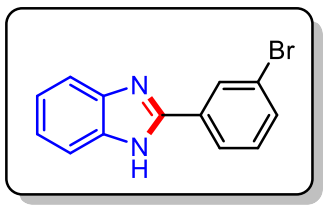
2-(4-methoxyphenyl)-1H-benzo[d]imidazole **(6d):**[5] Following the general procedure **C**/**D**, the titled compound was isolated as a yellow solid (87 mg, 0.389 mmol, 78% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^1H NMR (400 MHz, DMSO-d_6) δ 12.77 (s, *br*, 1H), 8.13 (d, J = 8.8 Hz, 2H), 7.57 (s, 2H), 7.17 (d, J = 6.0 Hz, 2H), 7.11 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 160.7, 151.4, 131.4, 130.6, 128.1, 122.7, 121.9, 114.4, 55.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{12}N_2OH$ 225.1028; Found 225.1035.



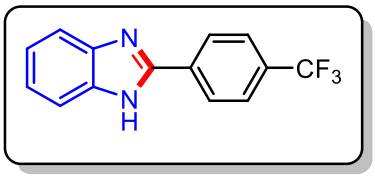
2-(4-bromophenyl)-1H-benzo[d]imidazole **(6e):**[4] Following the general procedure **C**/**D**, the titled compound was isolated as a white solid (95 mg, 0.349 mmol, 70% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^1H NMR (400 MHz, DMSO-d_6) δ 13.02 (s, *br*, 1H), 8.12 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.61 (s, 2H), 7.22 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 151.3, 150.3, 132.1, 131.7, 131.3, 129.9, 129.4, 129.0, 128.4, 126.5, 123.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_9BrN_2H$ 273.0027; Found 273.0026.



2-(3-bromophenyl)-1H-benzo[d]imidazole **(6f):**[10] Following the general procedure **C**/**D**, the titled compound was isolated as a yellow solid (94 mg, 0.344 mmol, 69% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^1H NMR (400 MHz, DMSO-d_6) δ 13.04 (s, *br*, 1H), 8.38 (s, 1H), 8.18 (s, 1H), 7.69 (s, 2H), 7.54 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 6.0 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 149.6, 143.7, 135.0, 132.5, 131.2, 128.9, 125.4, 123.0, 122.3, 122.0, 119.1, 111.6, 82.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_9BrN_2H$ 273.0027; Found 273.0026.

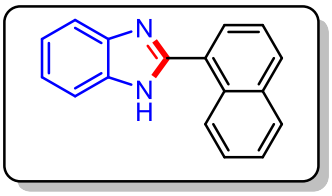


***2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole* (6g):**[4] Following the general procedure



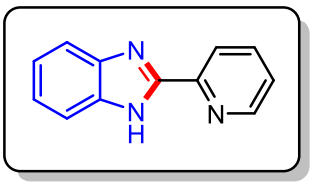
C/**D**, the titled compound was isolated as yellow solid (88 mg, 0.334 mmol, 67% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.19 (s, *br*,1H), 8.39 (d, J = 8.3 Hz, 2H), 7.93 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.29-7.21 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 149.7, 143.7, 135.1, 134.0, 129.8, 129.5, 127.1, 126.0, 125.5, 123.3, 122.8, 122.1, 119.3, 111.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_9F_3N_2H$ 263.0796 Found 263.0804.

***2-(naphthalen-1-yl)-1H-benzo[d]imidazole* (6h):**[4] Following the general procedure **C**/**D**, the



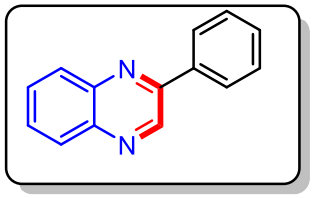
titled compound was isolated as a yellow solid (85 mg, 0.349 mmol, 70% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO-d_6) δ 8.38 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.47 (d, J = 6.7 Hz, 2H), 7.28 (s, 1H), 7.25-7.24 (m, 1H), 7.22-7.20 (m, 1H), 7.14-7.07 (m, 3H), 6.79-6.78 (m,2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$ + DMSO-d_6) δ 150.8, 132.9, 132.5, 130.2, 129.3, 129.2, 127.5, 127.3, 127.2, 127.1, 126.2, 125.4, 125.4, 124.1, 121.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}N_2H$ 245.1079; Found 245.1069.

***2-(pyridin-2-yl)-1H-benzo[d]imidazole* (6i):**[5] Following the general procedure **C**, the titled



compound was isolated as a brown solid (72 mg, 0.369 mmol, 74% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.09 (s, *br*, 1H), 8.72 (t, J = 4.2 Hz, 1H), 8.33 (d, J = 7.9 Hz, 1H), 7.99 (t, J = 6.0 Hz, 1H), 7.69 (s, 2H), 7.53-7.49 (m, 1H), 7.23 (d, J = 6.8 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 150.7, 149.4, 148.5, 137.6, 124.7, 122.6, 121.4, 119.3, 112.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_9N_3H$ 196.0875; Found 196.0865.

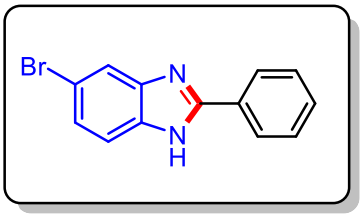
***2-phenylquinoxaline* (6j):**[12] Following the general procedure **D**, the titled compound was



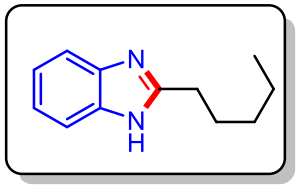
isolated as a dark brown liquid (75 mg, 0.364 mmol, 73% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.21-8.19 (m, 2H), 8.17-8.12 (m, 2H), 7.80-7.73 (m, 2H), 7.59-7.52 (m, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 152.0, 143.5, 142.4, 141.7, 136.9, 130.4, 130.3, 129.7, 129.7, 129.3, 129.2, 127.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{10}N_2H$ 207.0922; Found 207.0927.

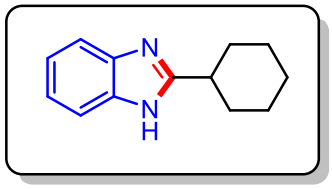
5-bromo-2-phenyl-1H-benzo[d]imidazole **(6k):**[11] Following the general procedure **D**, the titled compound was isolated as yellow solid (93 mg, 0.339 mmol, 68% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97-7.94 (m, 2H), 7.70 (d, J = 2.0 Hz, 1H), 7.49-7.45 (m, 4H), 7.28-7.25 (m, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6) δ 153.9, 147.8, 141.3, 138.6, 132.1, 130.5, 129.7, 127.7, 126.9, 118.8, 117.6, 116.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_9BrN_2H$ 273.0027; Found 273.0015.



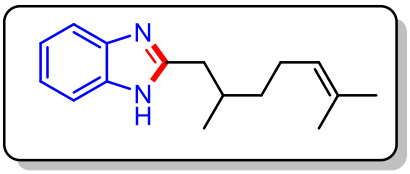
2-pentyl-1H-benzo[d]imidazole **(6l):**[4] Following the general procedure **C**, the titled compound was isolated as a brown liquid (66 mg, 0.349 mmol, 70% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.22-7.21 (m, 2H), 5.66 (s, *br*, 1H), 2.93 (t, J = 7.6 Hz, 2H), 1.87-1.83 (m, 2H), 1.33-1.25 (m, 4H), 0.85 (t, J = 6.5 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 155.3, 138.2, 122.5, 114.7, 31.6, 29.3, 28.1, 22.5, 14.0 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{16}N_2H$ 189.1392; Found 189.1394.



2-cyclohexyl-1H-benzo[d]imidazole **(6m):**[4] Following the general procedure **C**, the titled compound was isolated as orange liquid (62 mg, 0.309 mmol, 62% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.22-7.20 (m, 2H), 4.82 (s, *br*, 1H), 2.97-2.91 (m, 1H), 2.15 (d, J = 14.2 Hz, 2H), 1.88-1.84 (m, 2H), 1.75 (d, J = 14.5 Hz, 1H), 1.71-1.63 (m, 3H), 1.45-1.41 (m, 1H), 1.39-1.36 (m, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 158.9, 127.7, 122.5, 114.8, 109.9, 91.5, 38.6, 32.0, 26.1, 25.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{16}N_2H$ 201.1392; Found 201.1394.

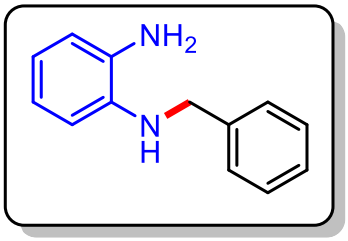


2-(2,6-dimethylhept-5-en-1-yl)-1H-benzo[d]imidazole **(6n):**[4] Following the general procedure



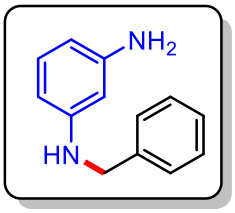
C, the titled compound was isolated as a brown liquid (85 mg, 0.349 mmol, 70% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H), 7.20-7.18 (m, 2H), 5.00 (s, *br*, 1H), 2.92-2.88 (m, 1H), 2.71-2.67 (m, 1H), 2.09-1.98 (m, 3H), 1.91 (s, 1H), 1.67 (s, 1H), 1.62 (s, 2H), 1.60 (s, 1H), 1.53-1.52 (m, 2H), 1.40 (d, J = 6.9 Hz, 1H), 1.03 (d, J = 6.3 Hz, 1H), 0.92-0.90 (m, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.6, 137.9, 131.7, 131.5, 124.6, 124.3, 122.5, 114.6, 37.1, 37.0, 36.6, 34.1, 33.0 25.7, 25.6, 19.9, 19.6, 17.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{22}N_2H$ 243.1861; Found 243.1864.

N^1-benzylbenzene-1,2-diamine **(7a):**[2] Following the general procedure **E**, the titled compound



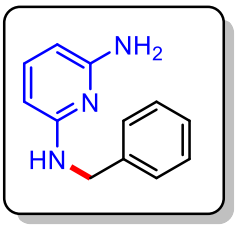
was isolated as brownish liquid (79 mg, 0.399 mmol, 80% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 4H), 7.35-7.31 (m, 1H), 6.85 (t, J = 7.5 Hz, 1H), 6.78-6.71 (m, 3H), 4.35 (s, 2H), 3.38 (s, *br*, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.5, 137.8, 134.3, 128.7, 127.9, 127.4, 120.8, 118.9, 116.6, 112.1, 48.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{14}N_2H$ 199.1235; Found 199.1238.

N^1-benzylbenzene-1,3-diamine **(7b):**[2] Following the general procedure **E**, the titled compound



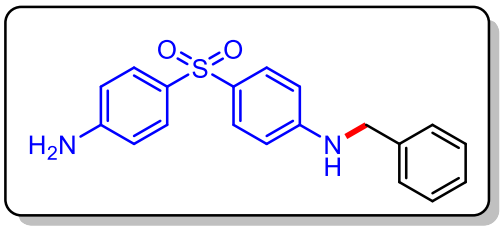
was isolated as brownish liquid (139 mg, 0.389 mmol, 78% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 4H), 7.20-7.15 (m, 1H), 6.86 (t, J = 7.9 Hz, 1H), 6.00-5.99 (m, 2H), 5.89 (s, 1H), 4.19 (s, 2H), 3.41 (s, *br*, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.4, 147.5, 139.7, 130.2, 128.7, 127.6, 127.3, 105.3, 104.3, 99.7, 48.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{14}N_2H$ 199.1235; Found 199.1238.

***N*²-benzylpyridine-2,6-diamine (7c):**[2] Following the general procedure **E**, the titled compound



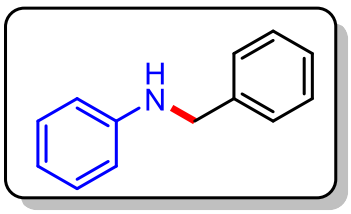
was isolated as a greenish solid (77.7 mg, 0.389 mmol, 78% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 4H), 7.28 (s, 1H), 7.24-7.20 (m, 1H), 5.85 (d, J = 7.8 Hz, 1H), 5.76 (d, J = 8.0 Hz, 1H), 4.83 (s, *br*, 1H, NH), 4.42 (d, J = 5.8 Hz, 2H), 4.28 (s, *br*, 2H, NH_2) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.1, 157.7, 139.7, 139.5, 128.7, 127.4, 127.2, 97.3, 95.7, 46.5 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{13}N_3H$ 200.1188; Found 200.1183.

***4-((4-aminophenyl)sulfonyl)-N-benzylaniline* (7d):**[2] Following the general procedure **E**, the



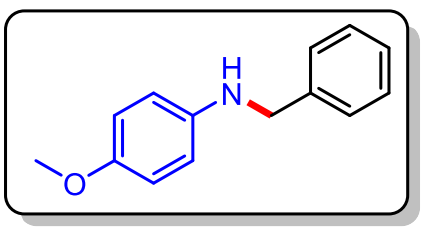
titled compound was isolated as a yellow solid (100 mg, 0.295 mmol, 65% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 4H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 2H), 6.63-6.57 (m, 4H), 4.34 (d, J = 5.2 Hz, 2H), 4.06 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.4, 150.5, 138.1, 131.6, 130.2, 129.3, 129.0, 127.8, 127.5, 114.3, 112.2, 47.8 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{18}N_2O_2SH$ 339.1167; Found 339.1160.

***N-benzylaniline* (9a):**[13] Following the general procedure **F**, the titled compound was isolated



as a yellow liquid (79 mg, 0.429 mmol, 86% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 4H), 7.31-7.28 (m, 1H), 7.21-7.17 (m, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.66 (d, J = 7.5 Hz, 2H), 4.35 (s, 2H), 4.04 (s, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.3, 139.6, 129.4, 128.8, 127.6, 127.4, 117.7, 113.0, 48.5 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{13}NH$ 184.1126; Found 184.1129.

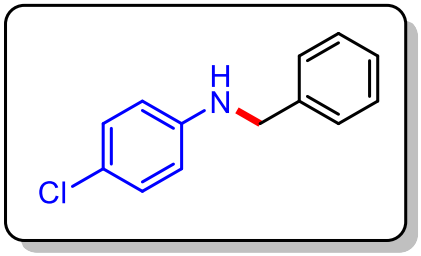
***N-benzyl-4-methoxyaniline* (9b):**[13] Following the general procedure **F**, the titled compound



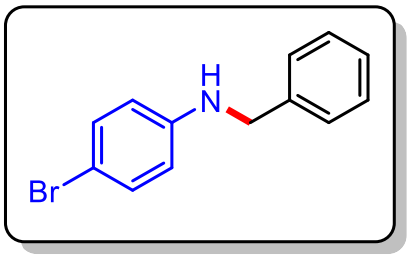
was isolated as a yellow liquid (85 mg, 0.400 mmol, 80% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 4H), 7.19-7.12 (m, 1H), 6.68 (d, J = 8.9 Hz, 2H), 6.50 (d, J = 8.9 Hz, 2H), 4.17 (s, 2H), 3.63 (s, 3H)

ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.3, 142.6, 139.8, 128.7, 127.7, 127.2, 114.9, 114.0, 55.9, 49.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}NOH$ 214.1232; Found 214.1238.

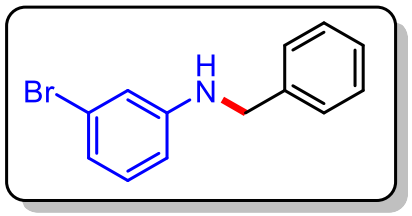
N-benzyl-4-chloroaniline **(9c):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (91 mg, 0.400 mmol, 84% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 2.7 Hz, 4H), 7.23-7.19 (m, 1H), 7.04-7.02 (m, 2H), 6.44 (d, J = 8.9 Hz, 2H), 4.19 (s, 2H), 3.95 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.7, 139.0, 129.1, 128.8, 127.5, 127.4, 122.1, 114.0, 48.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{12}ClNH$ 218.0737; Found 218.0740.



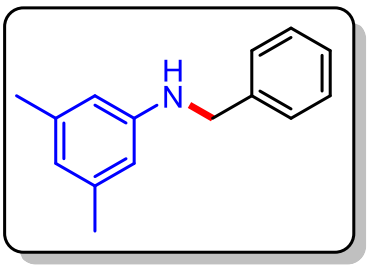
N-benzyl-4-bromoaniline **(9d):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (105 mg, 0.400 mmol, 80% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 4H), 7.38-7.35 (m,1H), 7.18 (d, J = 8.9 Hz, 2H), 6.59 (d, J = 8.9 Hz, 2H), 4.34 (s, 2H), 4.10 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.7, 139.0, 129.1, 128.8, 127.5, 127.4, 122.1, 114.0, 48.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{12}BrNH$ 262.0231; Found 262.0237.



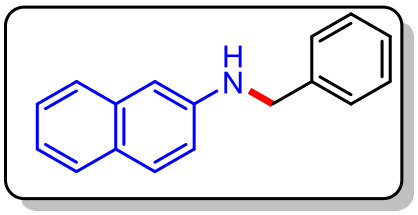
N-benzyl-3-bromoaniline **(9e):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (102 mg, 0.389 mmol, 78% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (m, 4H), 7.33-7.29 (m, 1H), 7.02 (t, J = 8.1 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 6.79 (s, 1H), 6.55 (d, J= 8.2Hz, 1H), 4.31 (s, 2H), 4.10 (s, *br*, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.5, 138.8, 130.6, 128.9, 127.6, 127.6, 123.4, 120.4, 115.5, 111.6, 48.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{12}BrNH$ 262.0231; Found 262.0237.



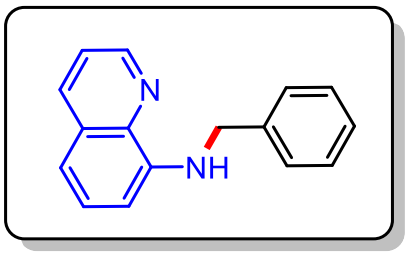
***N-benzyl-3,5-dimethylaniline* (9f):**[13] Following the general procedure **F**, the titled compound was isolated as an orange liquid (72 mg, 0.339 mmol, 68% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 6.5 Hz, 1H), 7.15 (s, 1H), 6.29 (s, 1H), 6.19 (s, 2H), 4.21 (s, 2H), 3.80 (s, *br*, 1H), 2.13 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.5, 139.8, 139.1, 128.7, 127.7, 127.3, 119.8, 110.9, 48.5, 21.6 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}NH$ 212.1439; Found 212.1444.



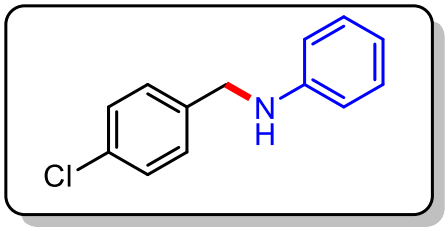
***N-benzylnaphthalen-2-amine* (9g):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (82 mg, 0.349 mmol, 70% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, J = 8.5 Hz, 2H), 7.48-7.44 (m, 4H), 7.41-7.37 (m, 3H), 7.34 (d, J = 7.0 Hz, 2H), 7.28 (s, 1H), 6.65 (d, J = 7.5 Hz, 1H), 4.52 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.3, 139.2, 134.4, 128.9, 128.8, 127.9, 127.5, 126.7, 125.9, 124.9, 123.5, 120.0, 117.8, 104.9, 48.8 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{15}NH$ 234.1283; Found 234.1289.



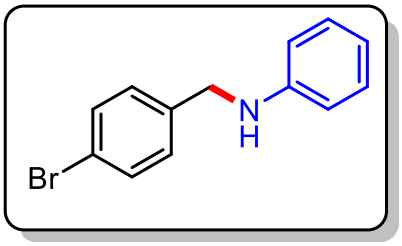
***N-benzylquinolin-8-amine* (9h):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (82 mg, 0.349 mmol, 70% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 4.2 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 7.2 Hz, 2H), 7.40-7.33 (m, 4H), 7.31-7.28 (m, 1H), 7.08 (d, J = 8.2 Hz, 1H), 6.67 (d, J = 7.7 Hz, 1H), 6.64 (s, *br*, 1H), 4.58 (d, J = 4.8 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.0, 144.7, 139.4, 138.3, 136.1, 128.8, 128.7, 127.9, 127.5, 127.2, 121.5, 114.2, 105.2, 47.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{14}N_2H$ 235.1235; Found 235.1241.



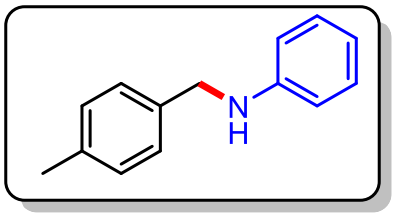
***N-(4-chlorobenzyl)aniline* (9i):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (83 mg, 0.379 mmol, 76% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 4H), 7.20 (t, J = 7.2 Hz, 2H), 6.76 (t, J = 7.6 Hz, 1H), 6.64 (d, J = 8.7 Hz, 2H), 4.33 (s, 2H), 4.07 (s, *br*, 1H) ppm .^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.9, 138.1, 133.0, 129.5, 128.9, 128.7, 118.0, 113.1, 47.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{12}ClNH$ 218.0737; Found 218.0742.



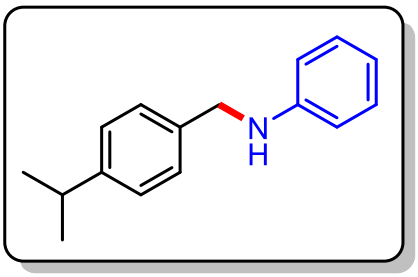
***N-(4-bromobenzyl)aniline* (9j):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (92 mg, 0.349 mmol, 70% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 4H), 7.38-7.36 (m, 1H), 7.18 (d, J= 9.0 Hz, 2H), 6.59 (d, J = 8.9 Hz, 2H), 4.34 (s, 2H), 4.10 (s, *br*, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.7, 139.0, 129.1, 128.8, 127.5, 127.4, 122.1, 114.0, 48.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{12}BrNH$ 262.0231; Found 262.0237.



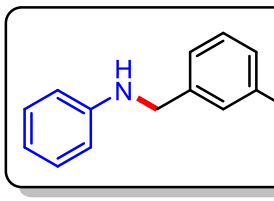
***N-(4-methylbenzyl)aniline* (9k):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (77 mg, 0.389 mmol, 78% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 2H), 7.18-7.13 (m, 4H), 6.70 (t, J = 7.4 Hz, 1H), 6.62 (d, J = 7.9 Hz, 2H), 4.27 (s, 2H), 3.97 (s, *br*, 1H), 2.33 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.4, 137.0, 136.5, 129.4, 129.4,127.7, 117.6, 112.9, 48.2, 21.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}NH$ 198.1283; Found 198.1289.



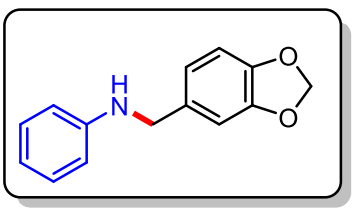
N-(4-isopropylbenzyl)aniline **(9l):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (84 mg, 0.374 mmol, 75% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2H), 7.21 (s, 1H), 7.19-7.13 (m, 4H), 6.68 (t, J = 7.4 Hz, 1H), 6.61 (d, J = 7.7 Hz, 2H), 4.25 (s, 2H), 2.91-2.84 (m, 1H), 1.23 (s, 3H), 1.21 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.4, 148.1, 136.9, 129.4, 127.8, 126.8, 117.6, 113.0, 48.2, 33.9, 24.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{19}NH$ 226.1596; Found 226.1599.



N-(3-methylbenzyl)aniline **(9m):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (67 mg, 0.339 mmol, 68% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (m, 1H), 7.44-7.41 (m, 5H), 7.00-6.94 (m, 1H), 6.85-6.82 (m, 2H), 4.46 (s, 2H), 3.98 (s, *br*, 1H), 2.61 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.3, 137.0, 136.3, 130.4, 129.3, 128.2, 127.4, 126.2, 117.4, 112.7, 46.3, 18.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}NH$ 198.1283; Found 198.1289.



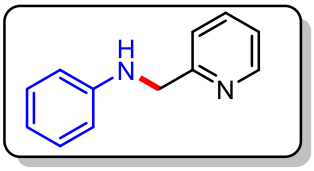
N-benzylpyridin-2-amine **(9n):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (59 mg, 0.319 mmol, 64% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 5.1 Hz, 1H), 7.31-7.22 (m, 5H), 7.19-7.16 (m, 1H), 6.48 (t, J = 6.5 Hz, 1H), 6.27 (d, J = 8.3 Hz, 1H), 5.05 (s, *br*, 1H), 4.40 (d, J = 5.7 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.8, 148.3, 139.3, 137.6, 128.7, 127.5, 127.2, 113.1, 106.9, 46.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{12}N_2H$ 185.1079; Found 185.1072.



N-(benzo[d][1,3]dioxol-5-ylmethyl)aniline **(9o):**[13] Following the general procedure **F**, the titled compound was isolated as a yellow liquid (84 mg, 0.369 mmol, 74% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 7.6 Hz, 2H), 6.90 (s, 1H), 6.87-6.80 (m, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.66 (d, J = 8.1 Hz, 2H), 5.96 (s, 2H), 4.25 (s,

2H), 3.99 (s, *br*, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.1, 148.0, 146.8, 133.4, 129.3, 120.7, 117.7, 112.9, 108.5, 108.1, 101.1, 48.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}NO_2H$ 228.1025; Found 228.1029.

N-(pyridin-2-ylmethyl)aniline **(9p):**[13] Following the general procedure **F**, the titled compound



was isolated as a yellow liquid (73 mg, 0.394 mmol, 79% yield) using silica gel column chromatography (5-10% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, J = 4.7 Hz, 1H), 7.66-7.62 (m, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.9 Hz, 3H), 6.73 (t, J = 7.2 Hz, 1H), 6.68 (d, J = 8.5 Hz, 2H), 4.47 (s, 2H), 4.14 (s, *br*, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 158.7, 149.3, 148.1, 136.8, 129.4, 122.2, 121.8, 117.8, 113.2, 49.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{12}N_2H$ 185.1079; Found 185.1072.

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

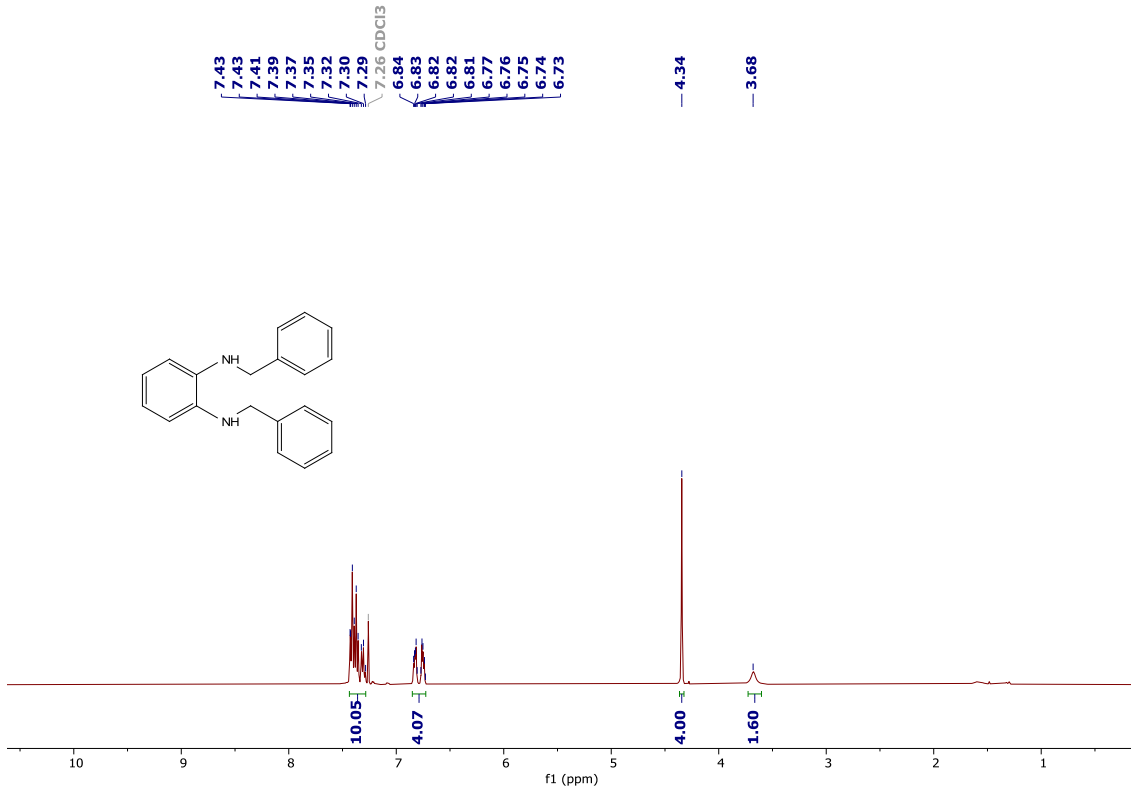


Figure S1. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

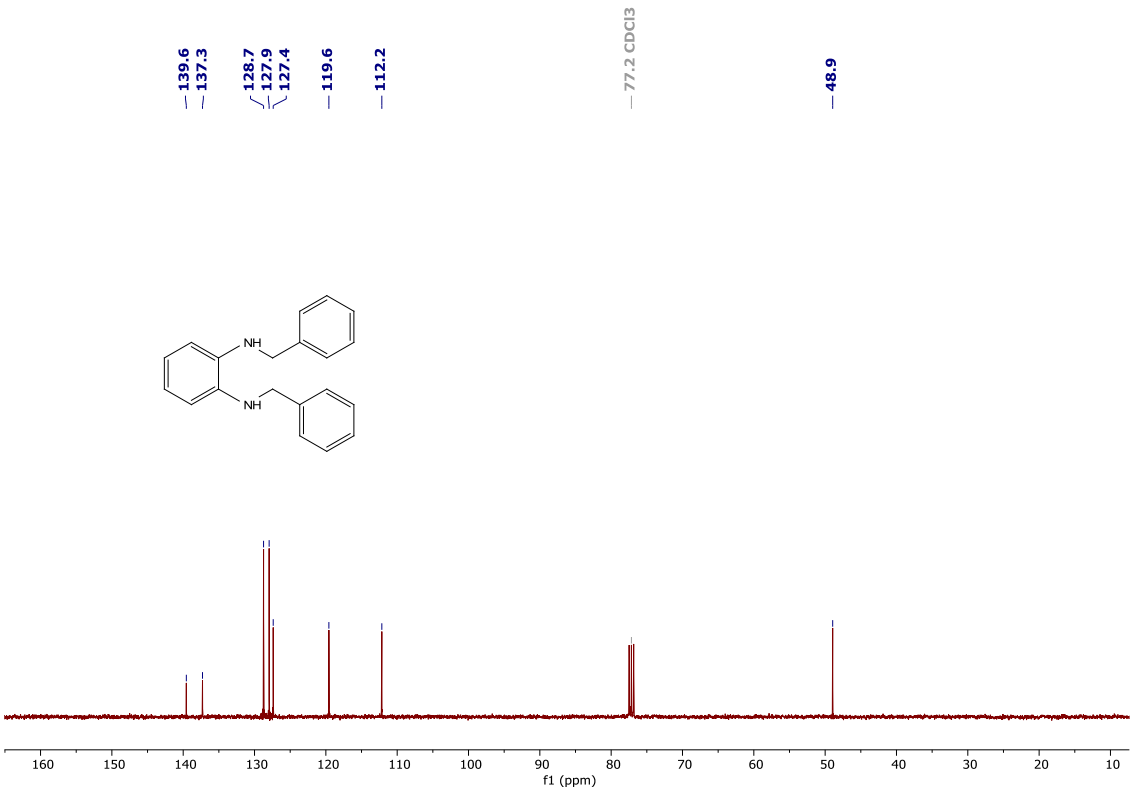


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$.

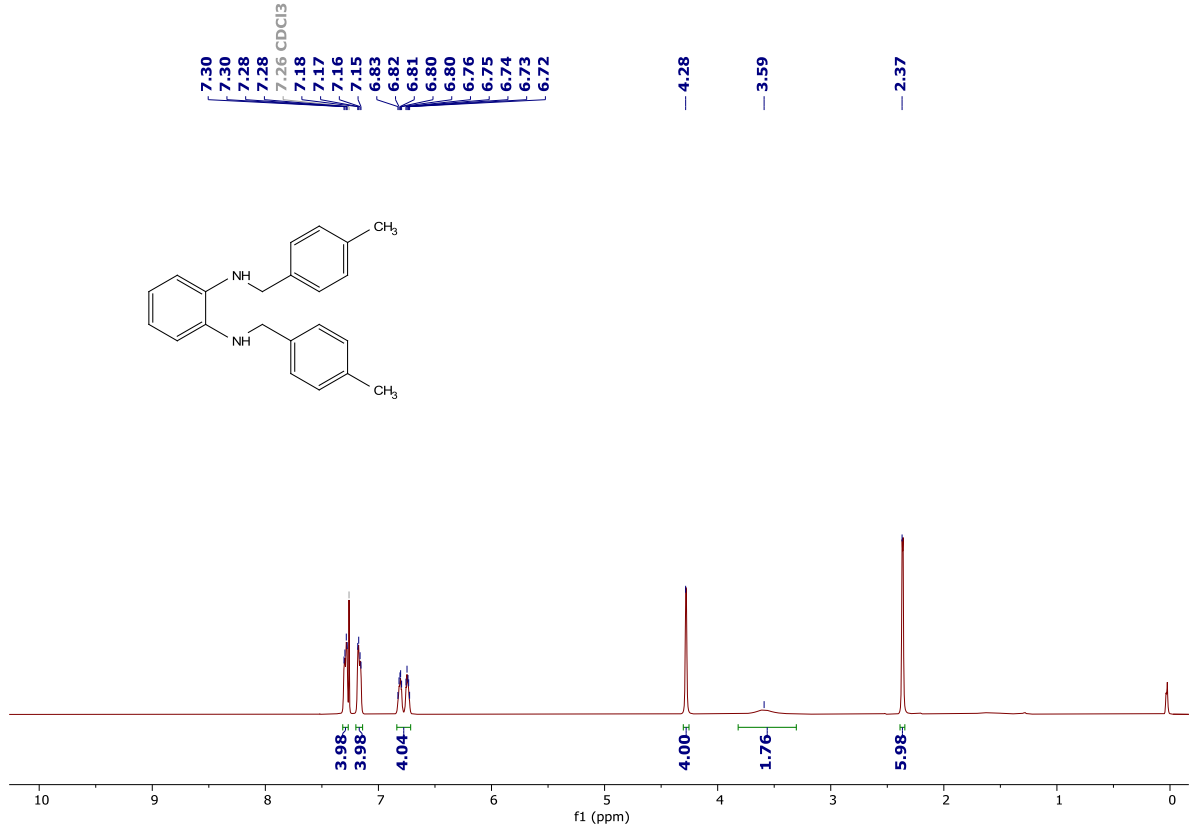


Figure S3. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

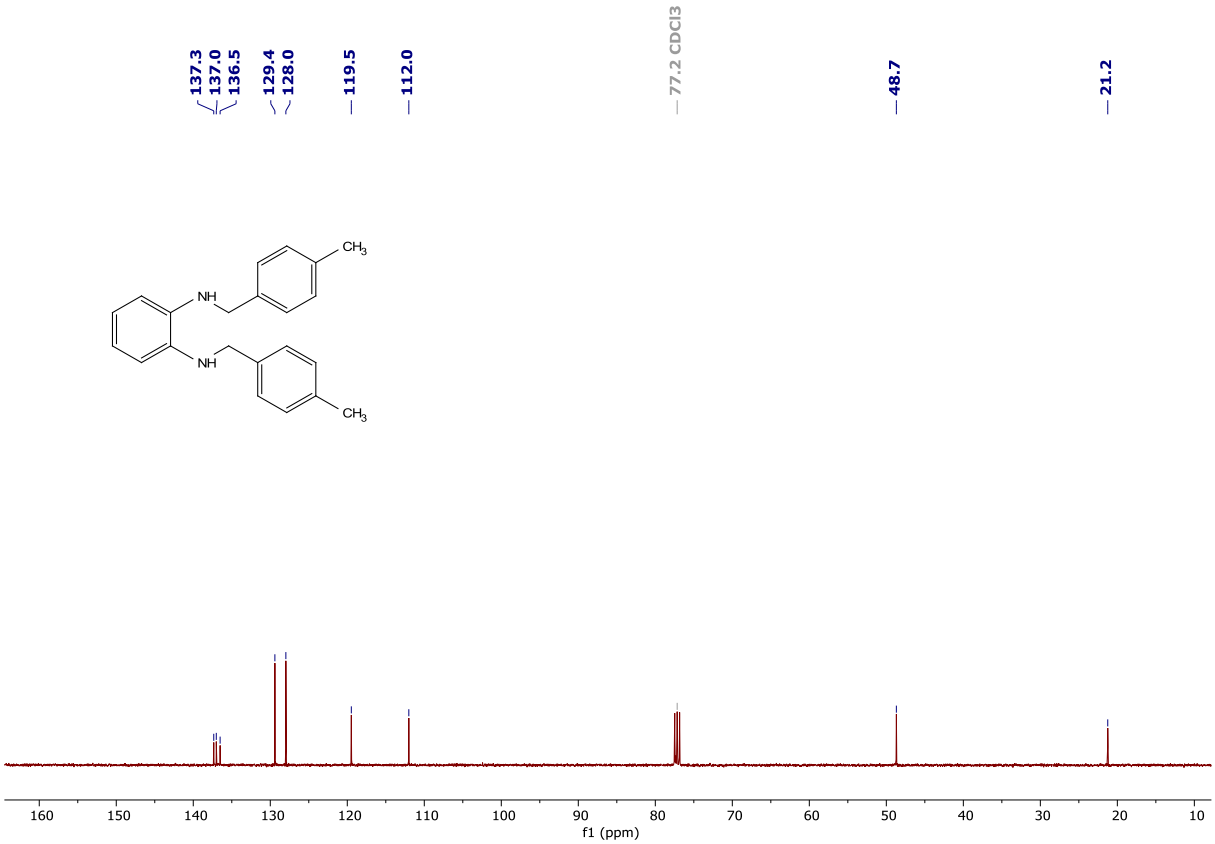


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$.

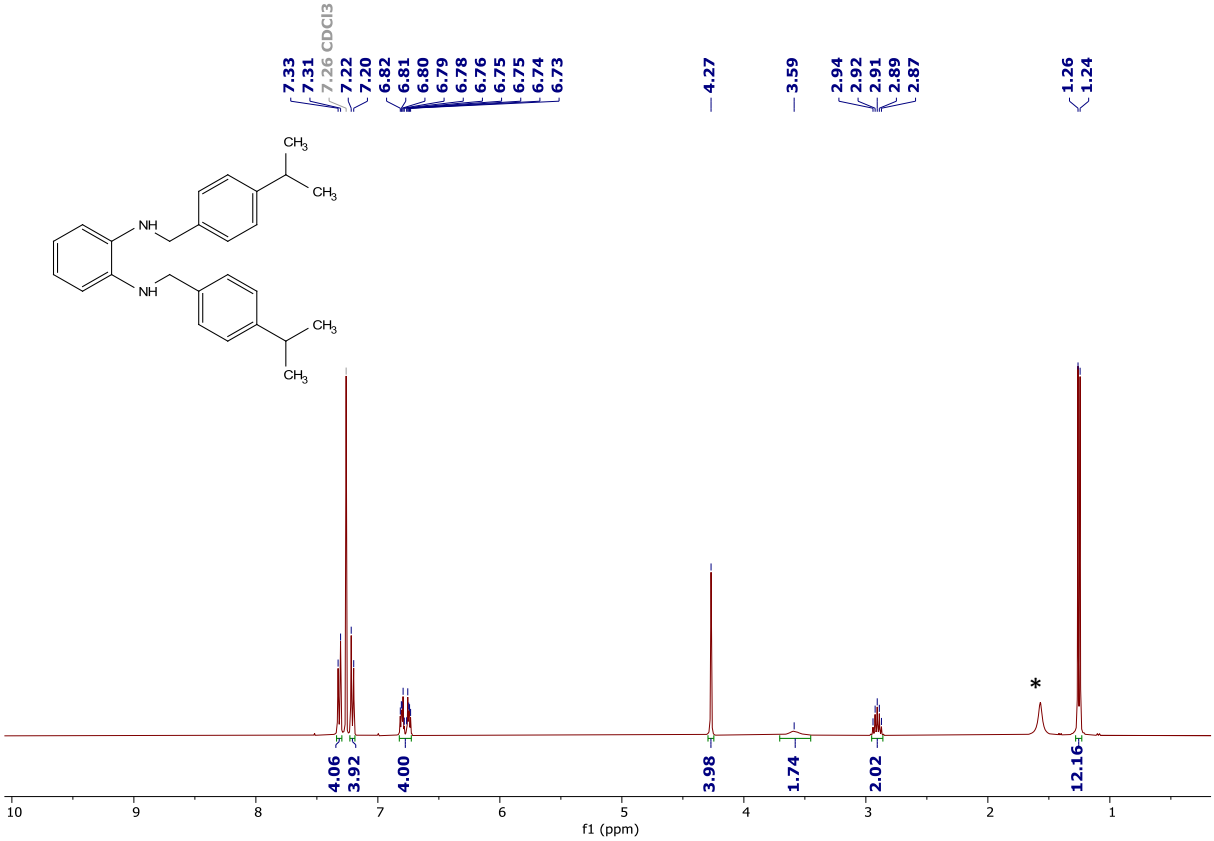


Figure S5. ^{1}H NMR spectrum of **3c** in $CDCl_3$. * indicates the solvent impurity of H_2O.

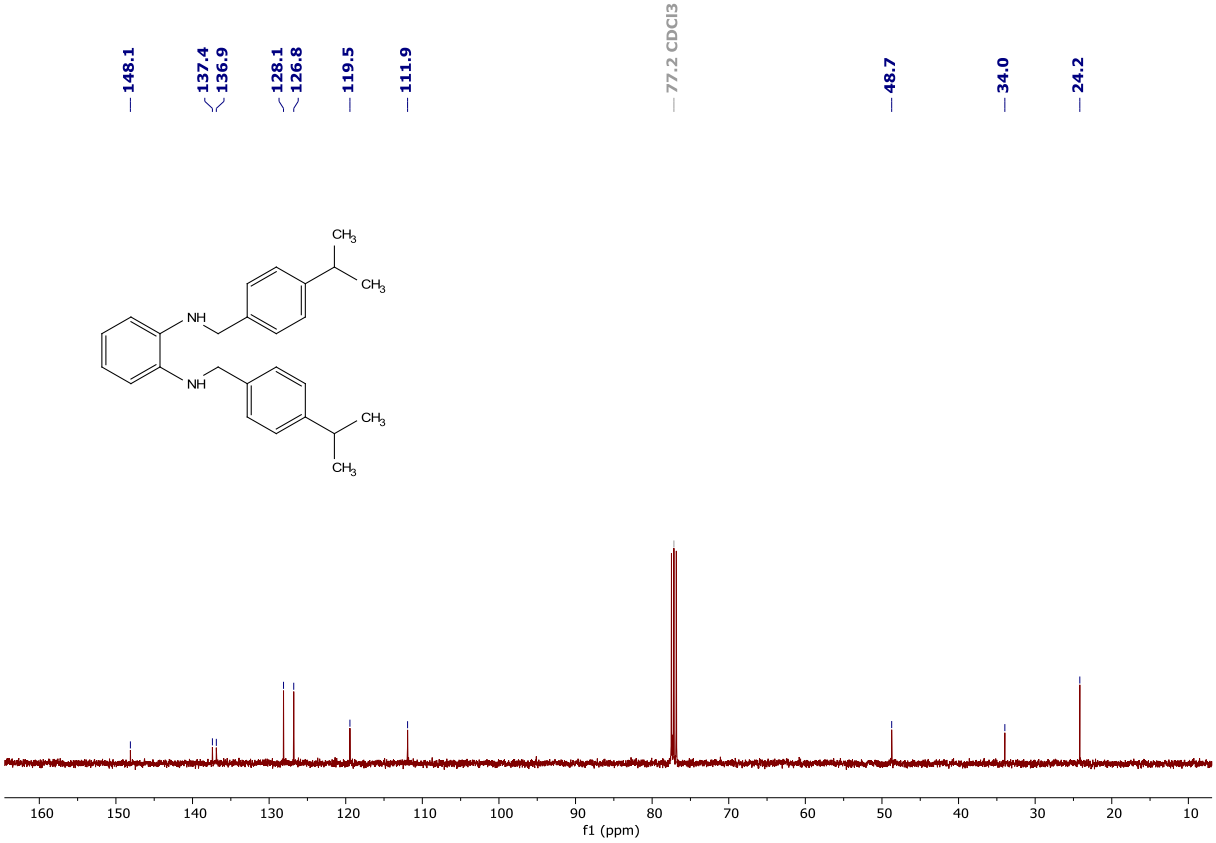


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **3c** in $CDCl_3$.

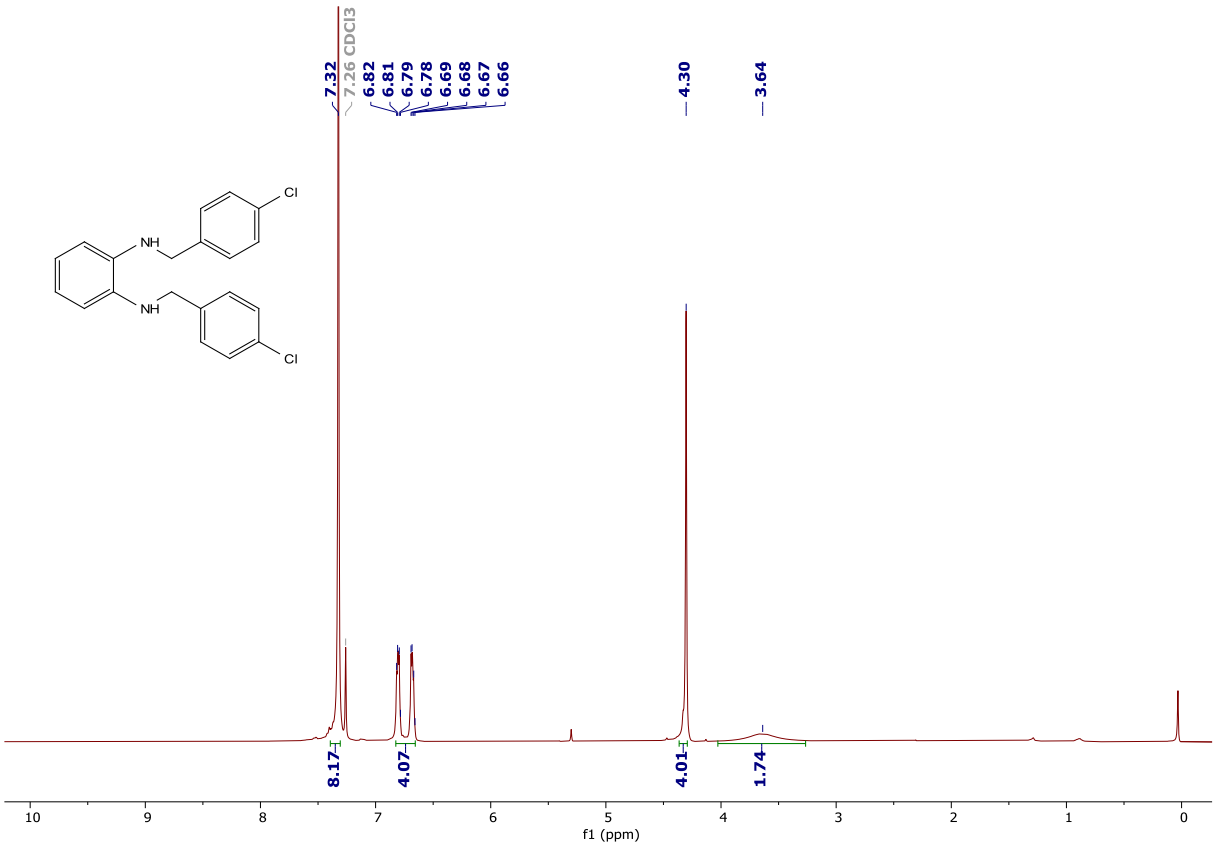


Figure S7. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

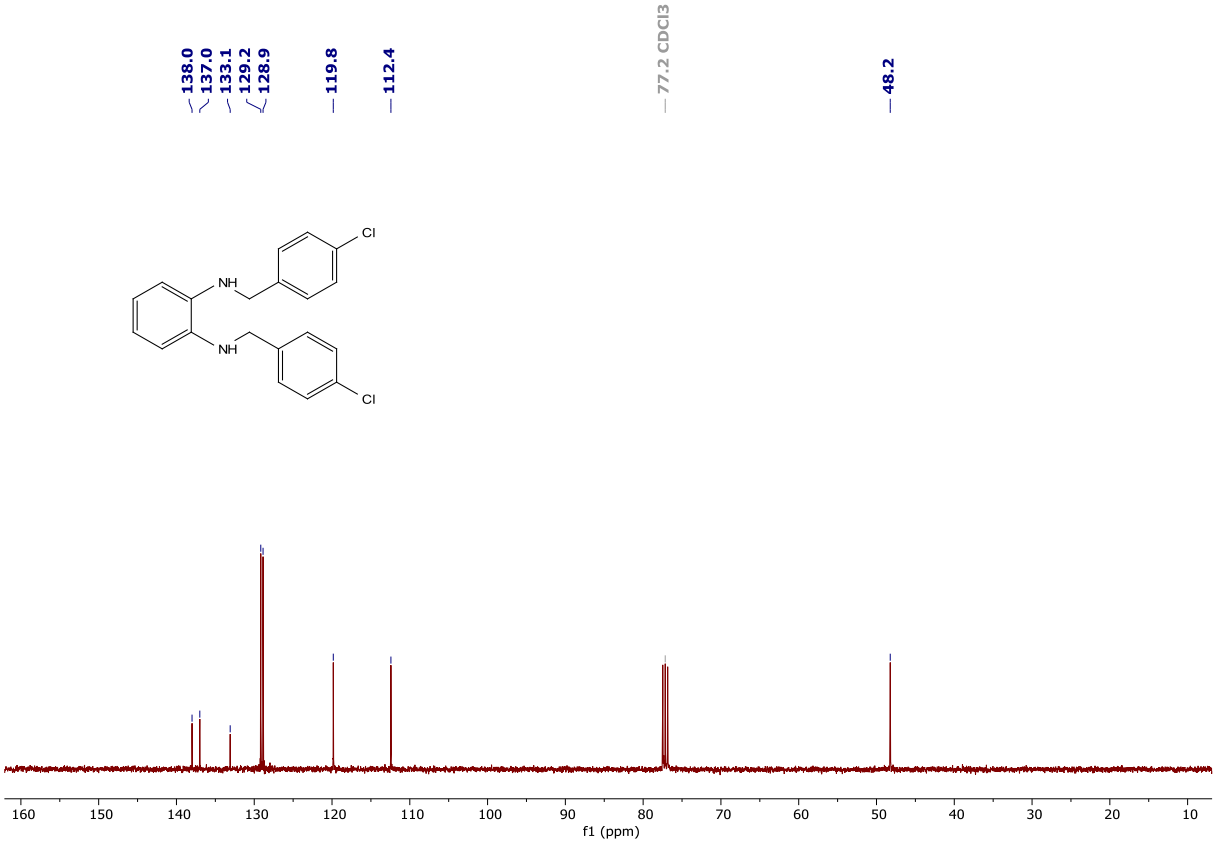


Figure S8. ^{13}C{^{1}H} NMR spectrum of **3d** in $CDCl_3$.

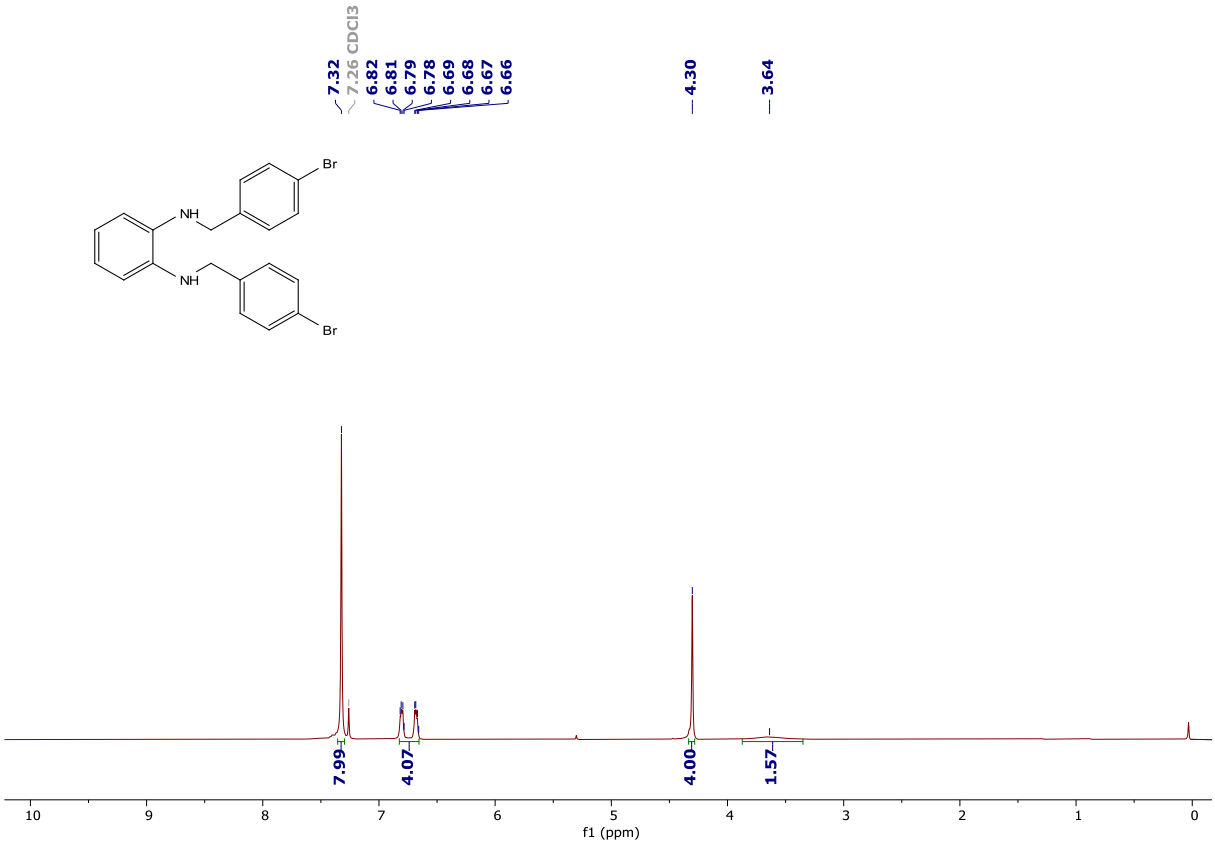


Figure S9. ^{1}H NMR spectrum of **3e** in $CDCl_3$.

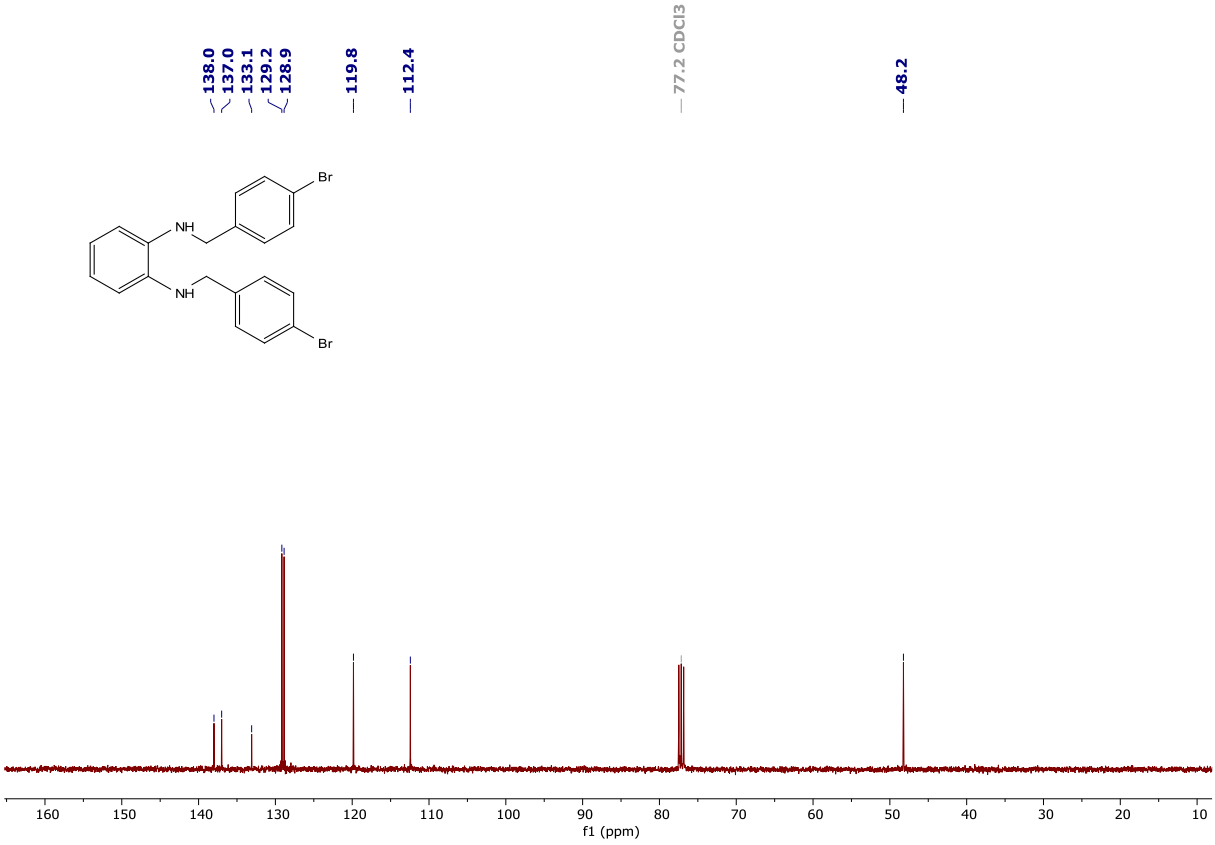


Figure S10. ^{13}C{^{1}H} NMR spectrum of **3e** in $CDCl_3$.

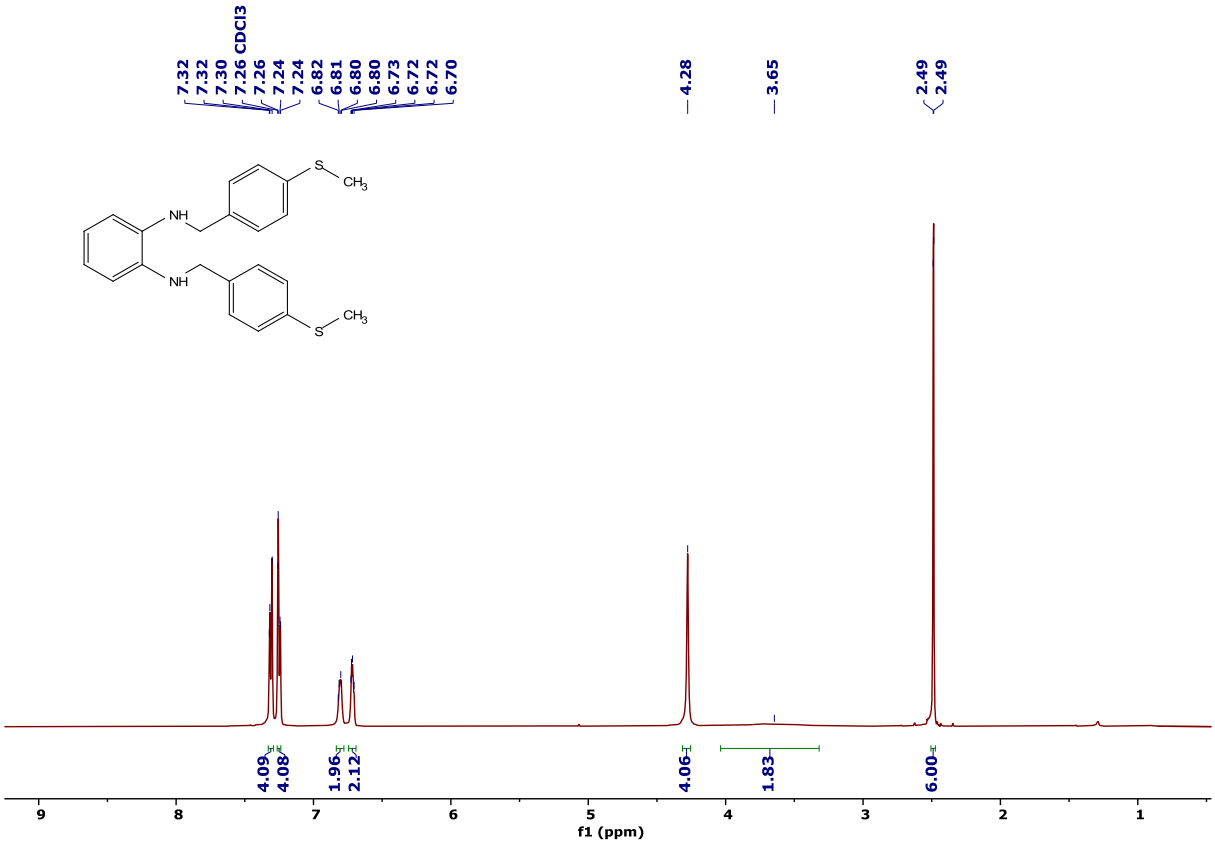


Figure S11. ^{1}H NMR spectrum of **3f** in $CDCl_3$.

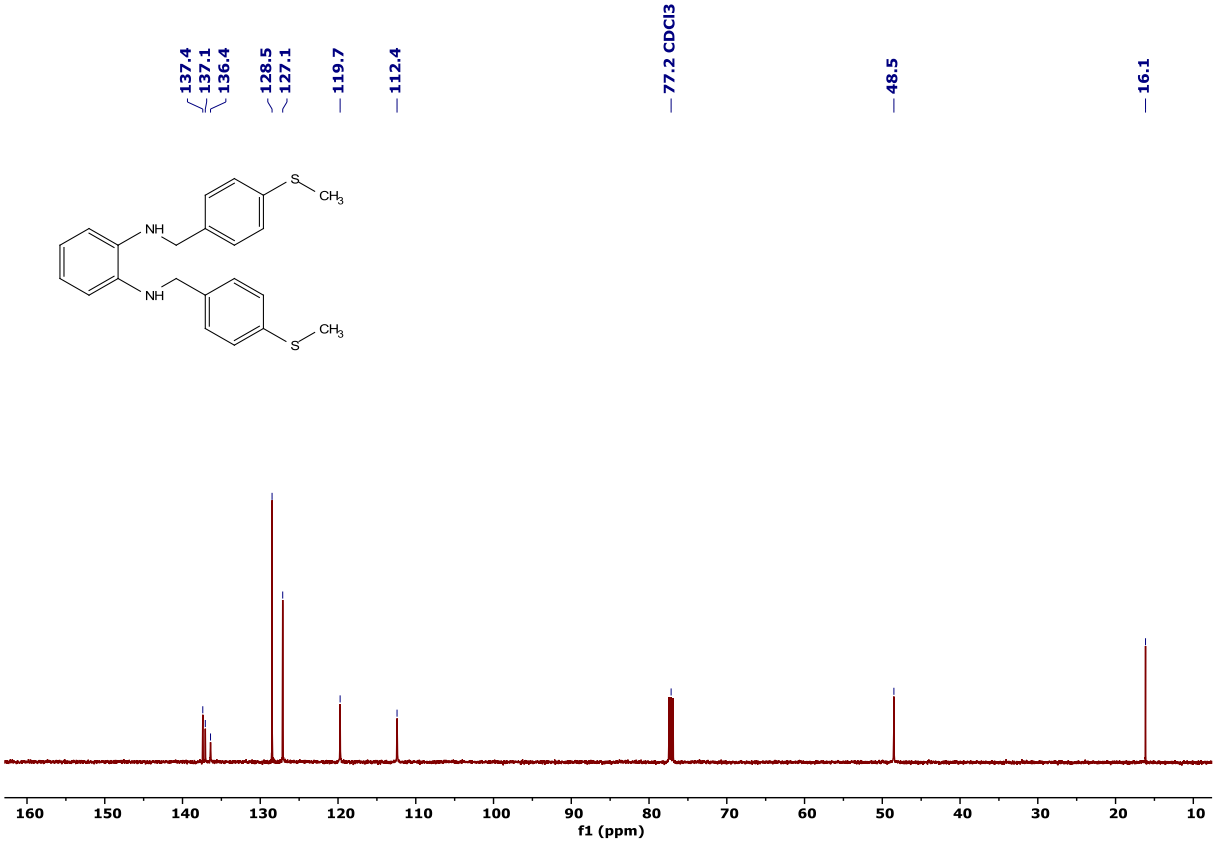


Figure S12. ^{13}C{^{1}H} NMR spectrum of **3f** in $CDCl_3$.

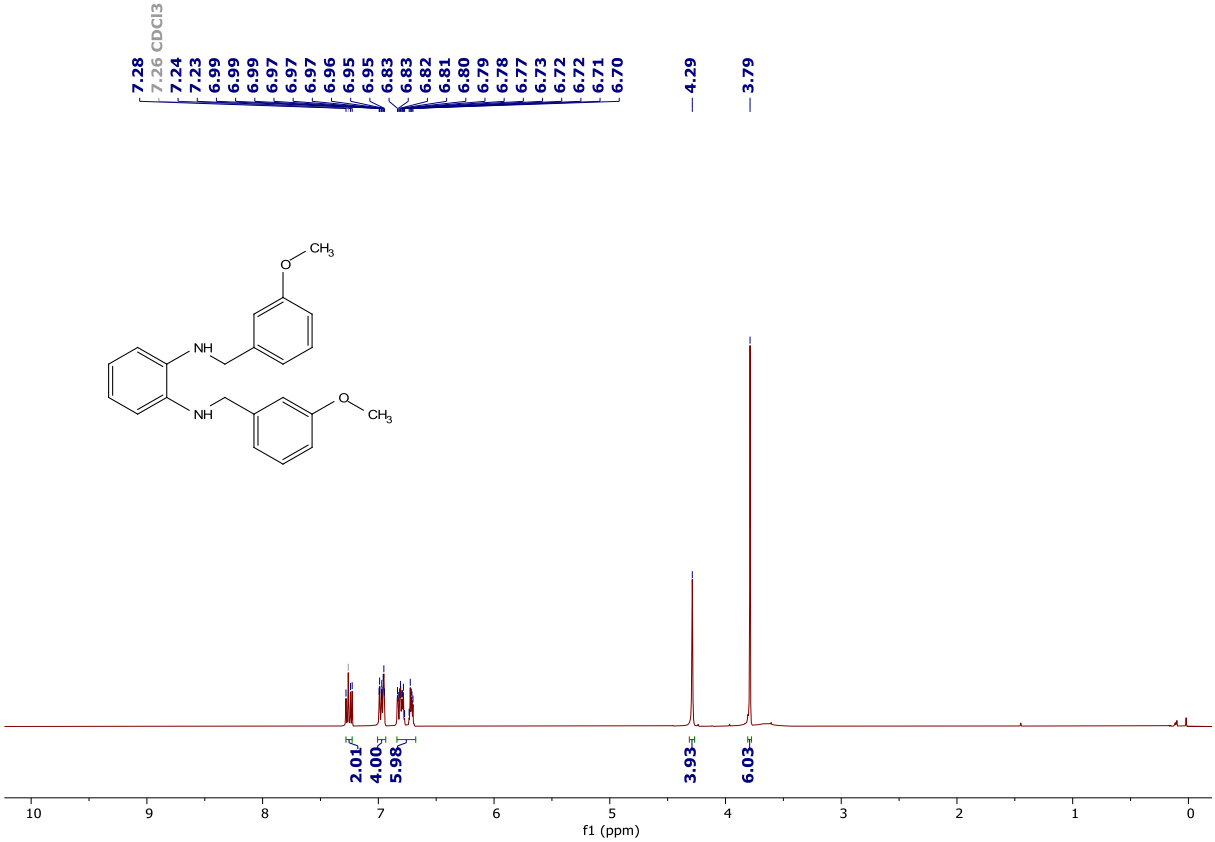


Figure S13. ^{1}H NMR spectrum of **3g** in $CDCl_3$.

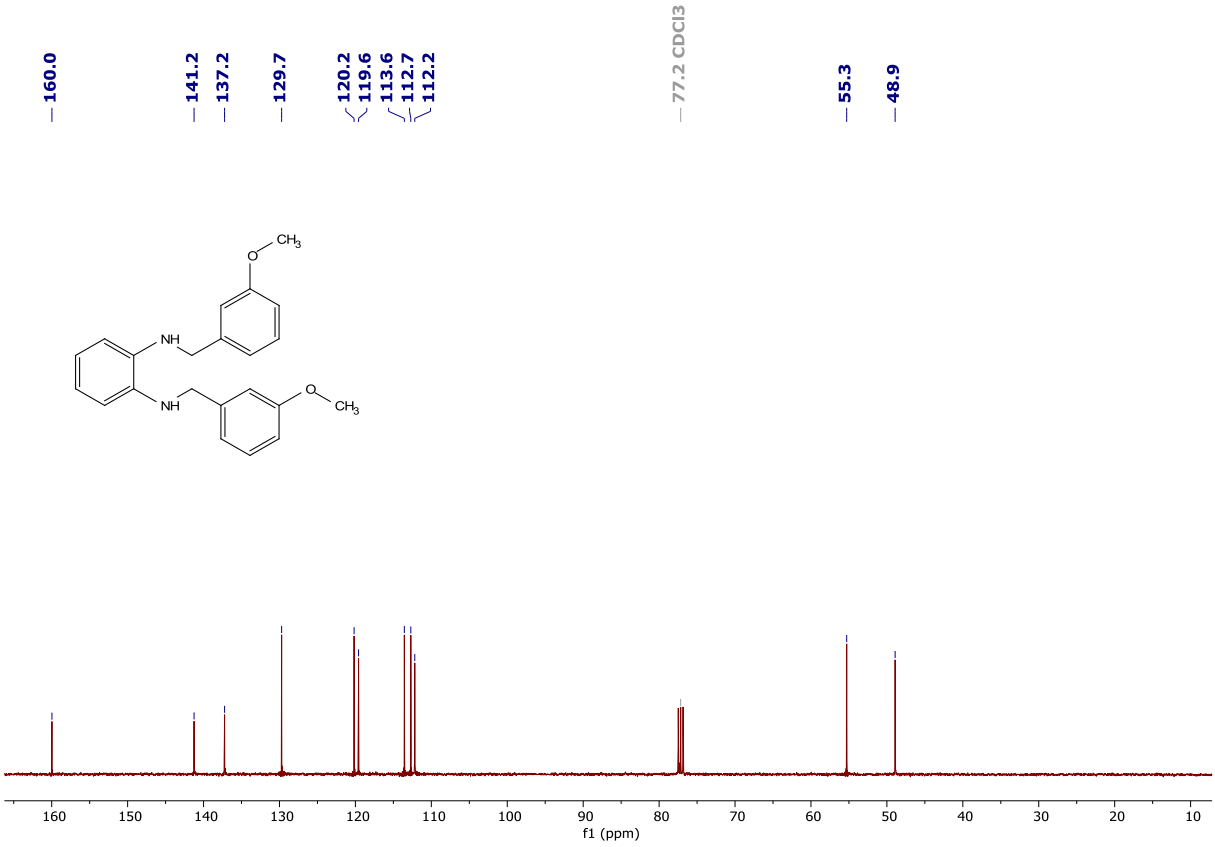


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **3g** in $CDCl_3$.

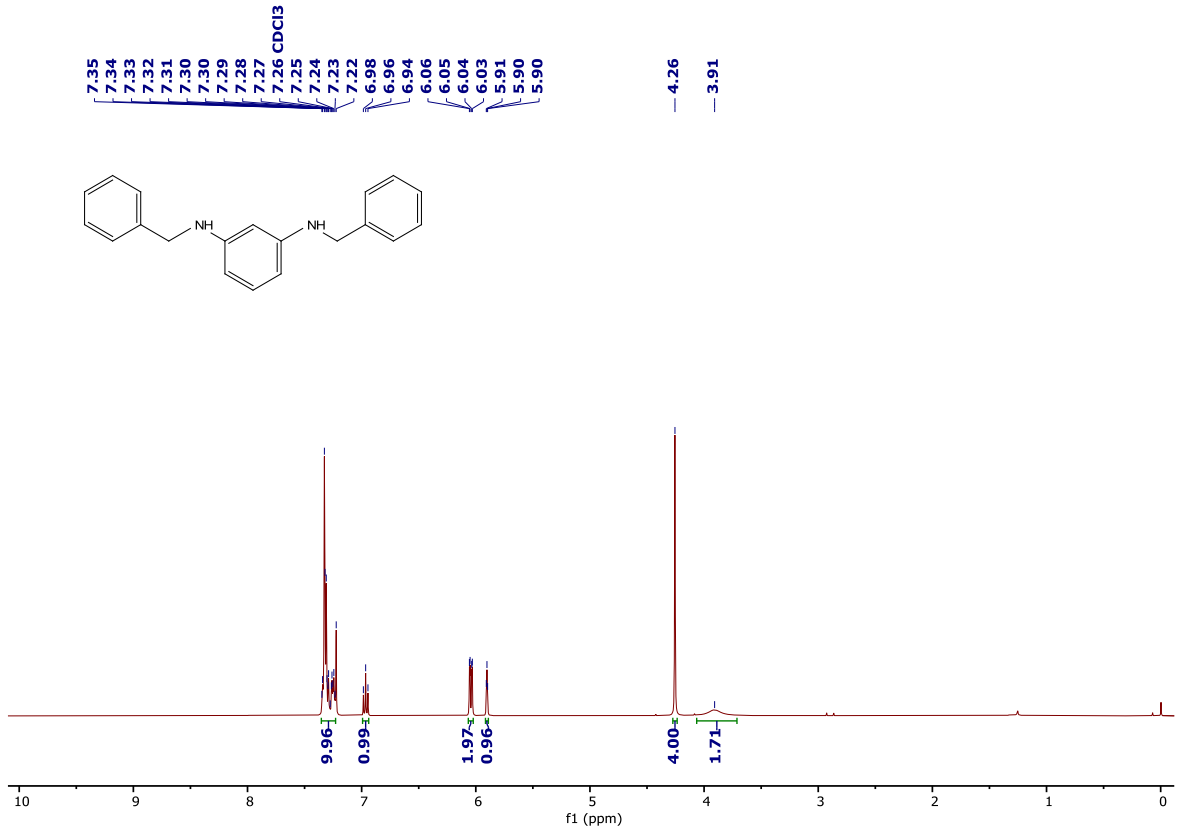


Figure S15. ^{1}H NMR spectrum of **3h** in $CDCl_3$.

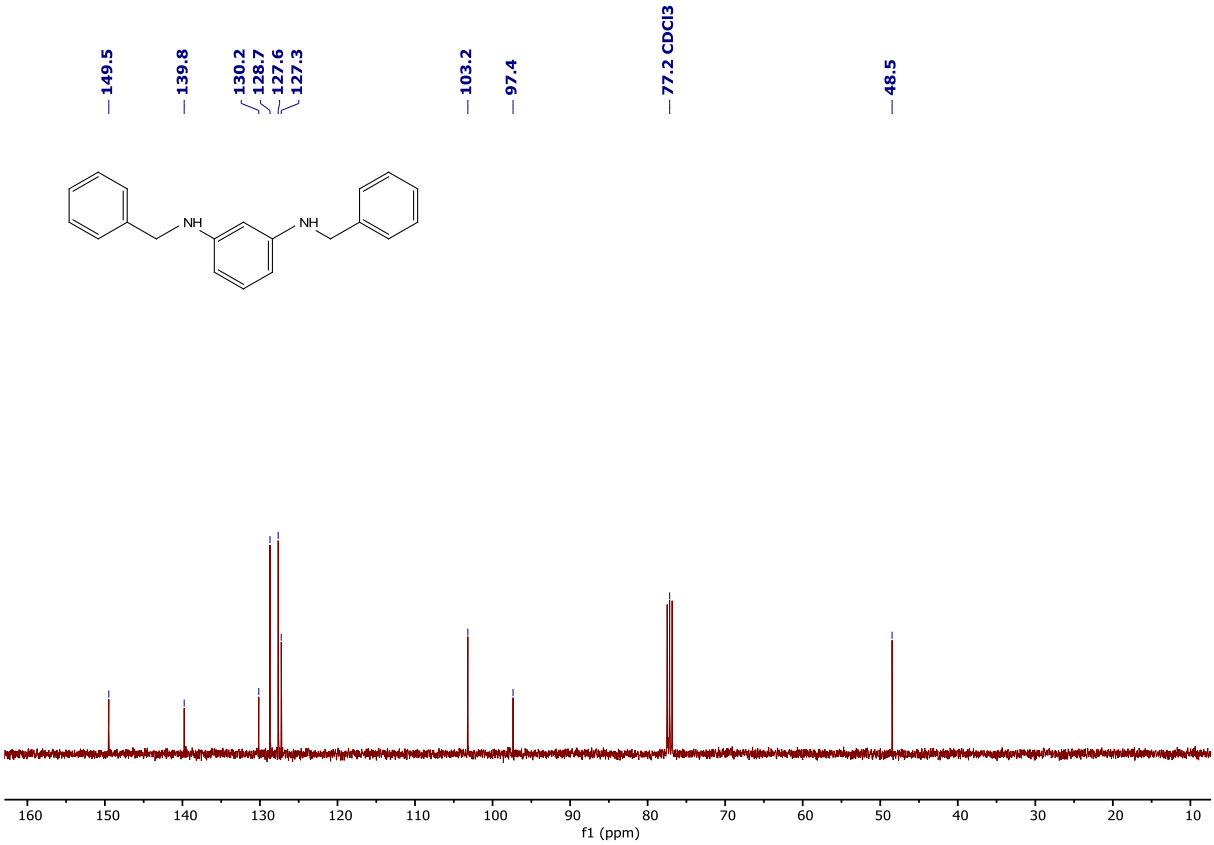


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **3h** in $CDCl_3$.

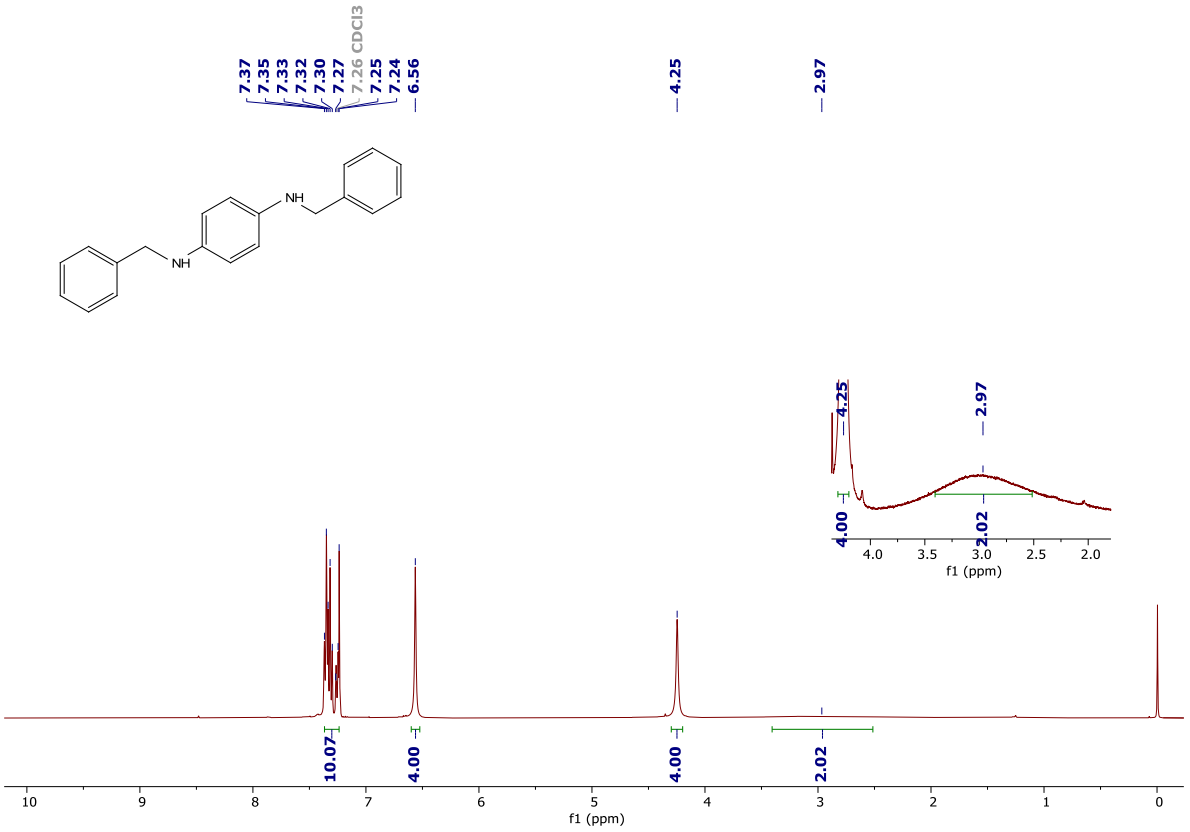


Figure S17. ^{1}H NMR spectrum of **3i** in $CDCl_3$.

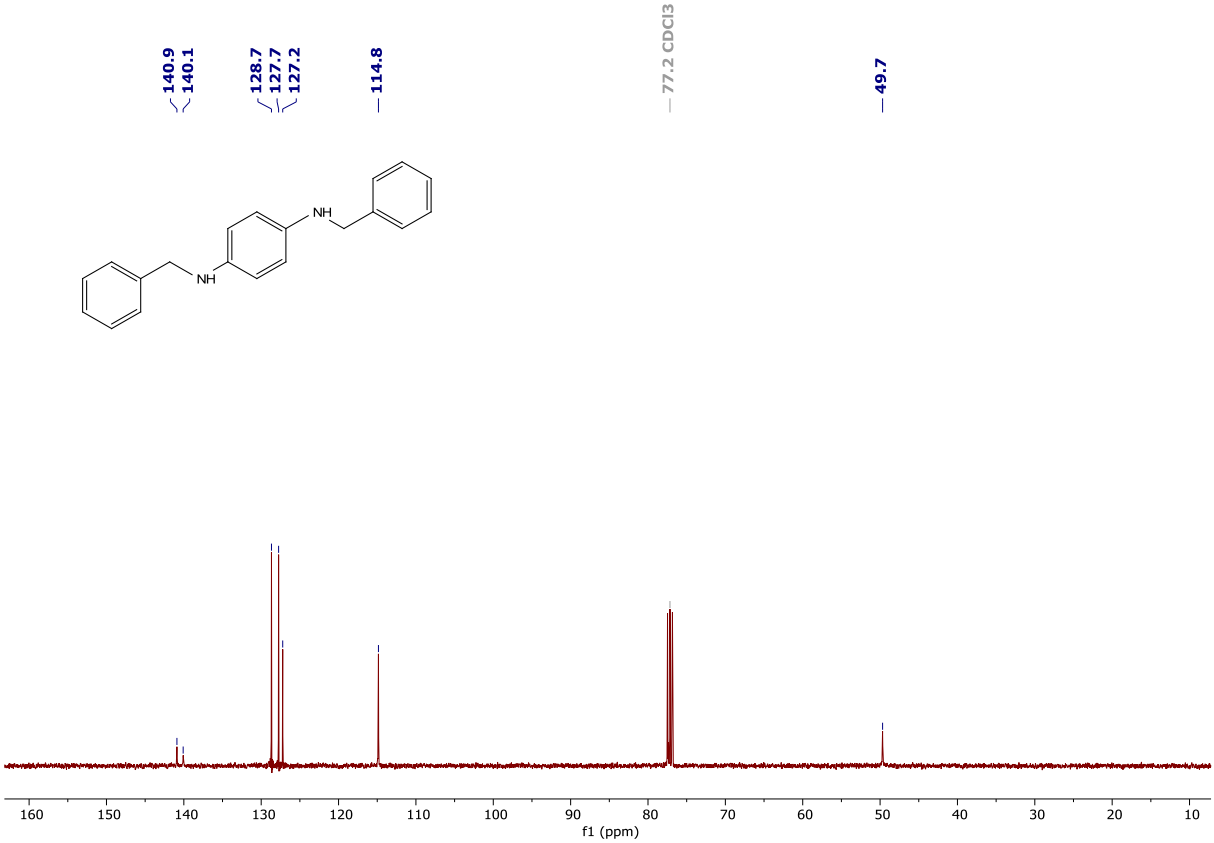


Figure S18. ^{13}C{^{1}H} NMR spectrum of **3i** in $CDCl_3$.

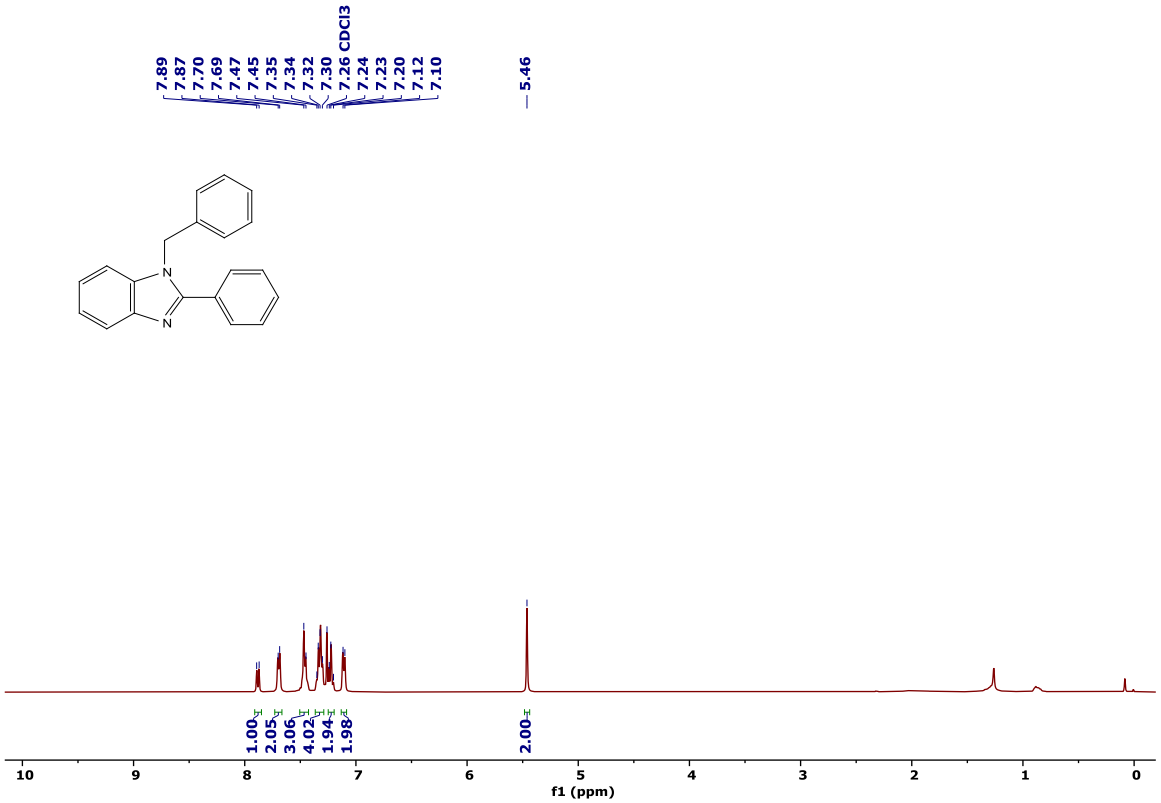


Figure S19. ^{1}H NMR spectrum of **4a** in $CDCl_3$.

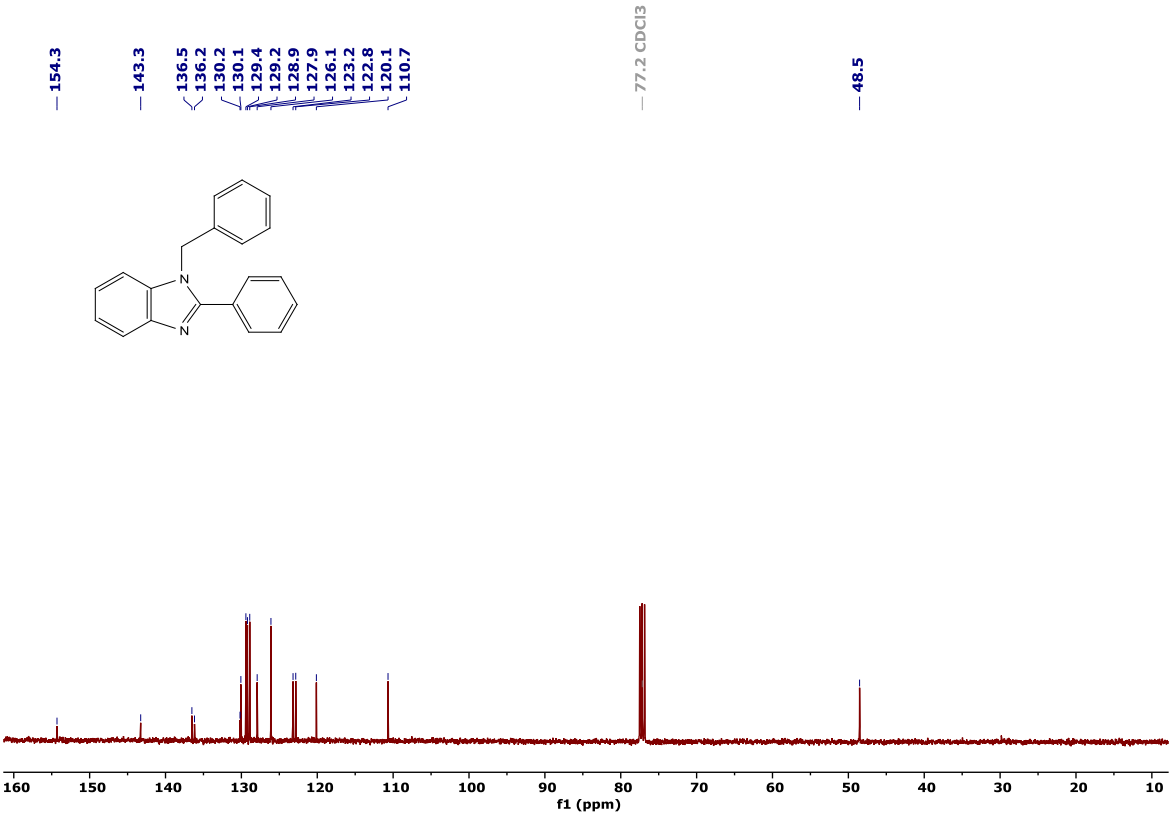


Figure S20. ^{13}C{^{1}H} NMR spectrum of **4a** in $CDCl_3$.

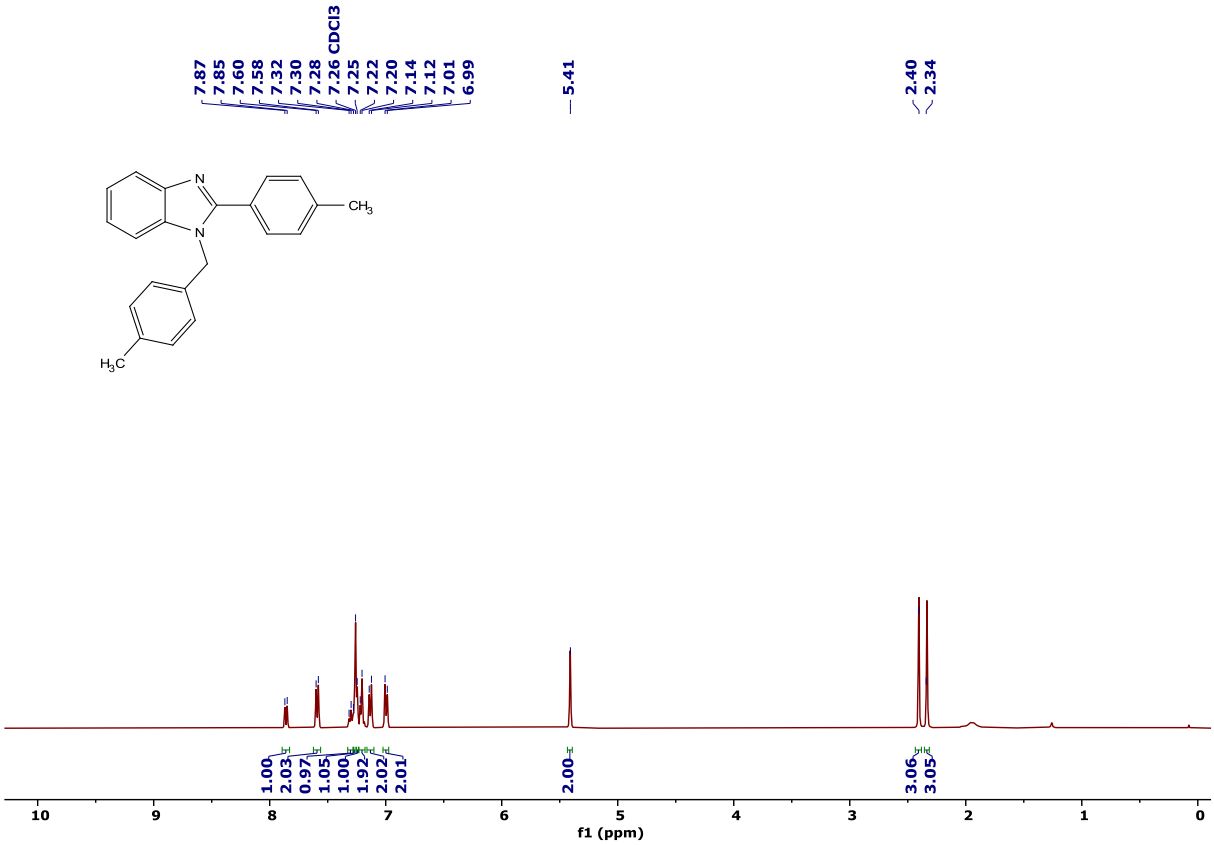


Figure S21. ^{1}H NMR spectrum of **4b** in $CDCl_3$.

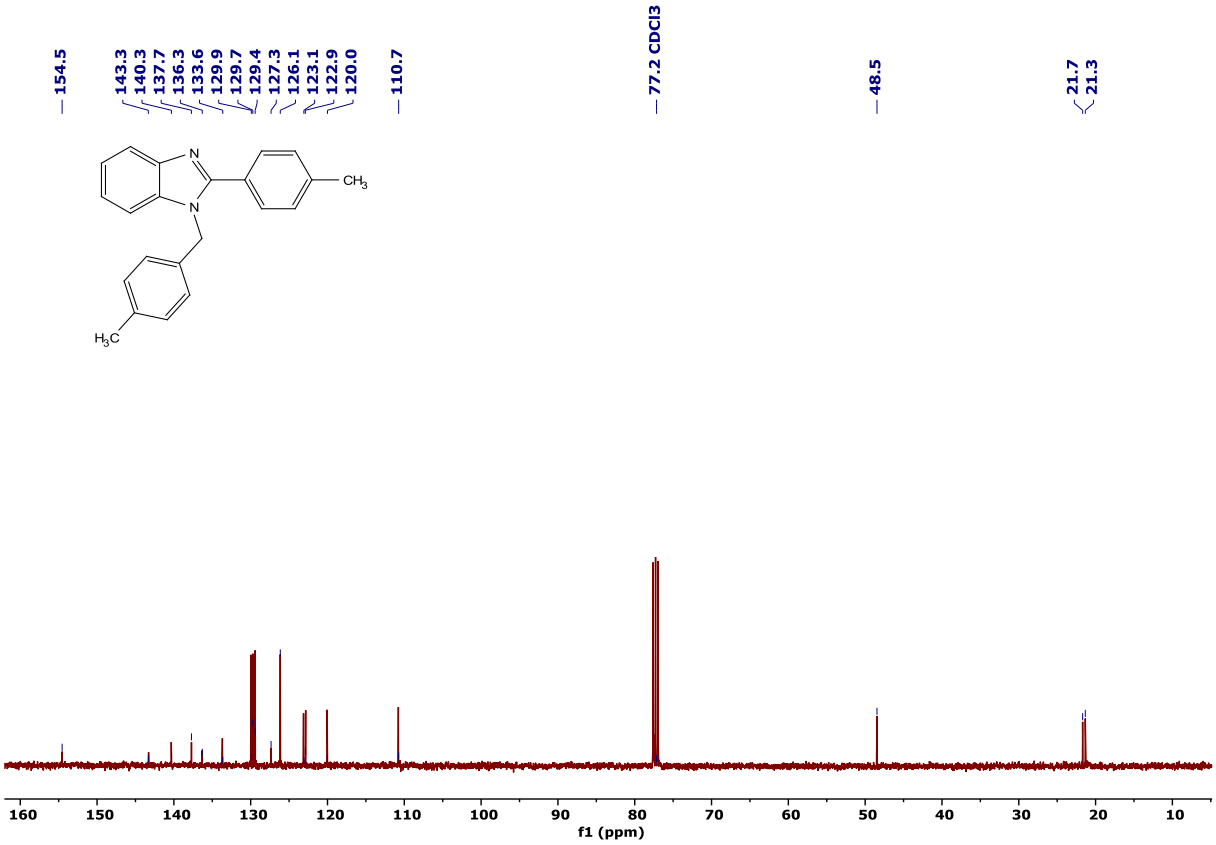


Figure S22. ^{13}C{^{1}H} NMR spectrum of **4b** in $CDCl_3$.

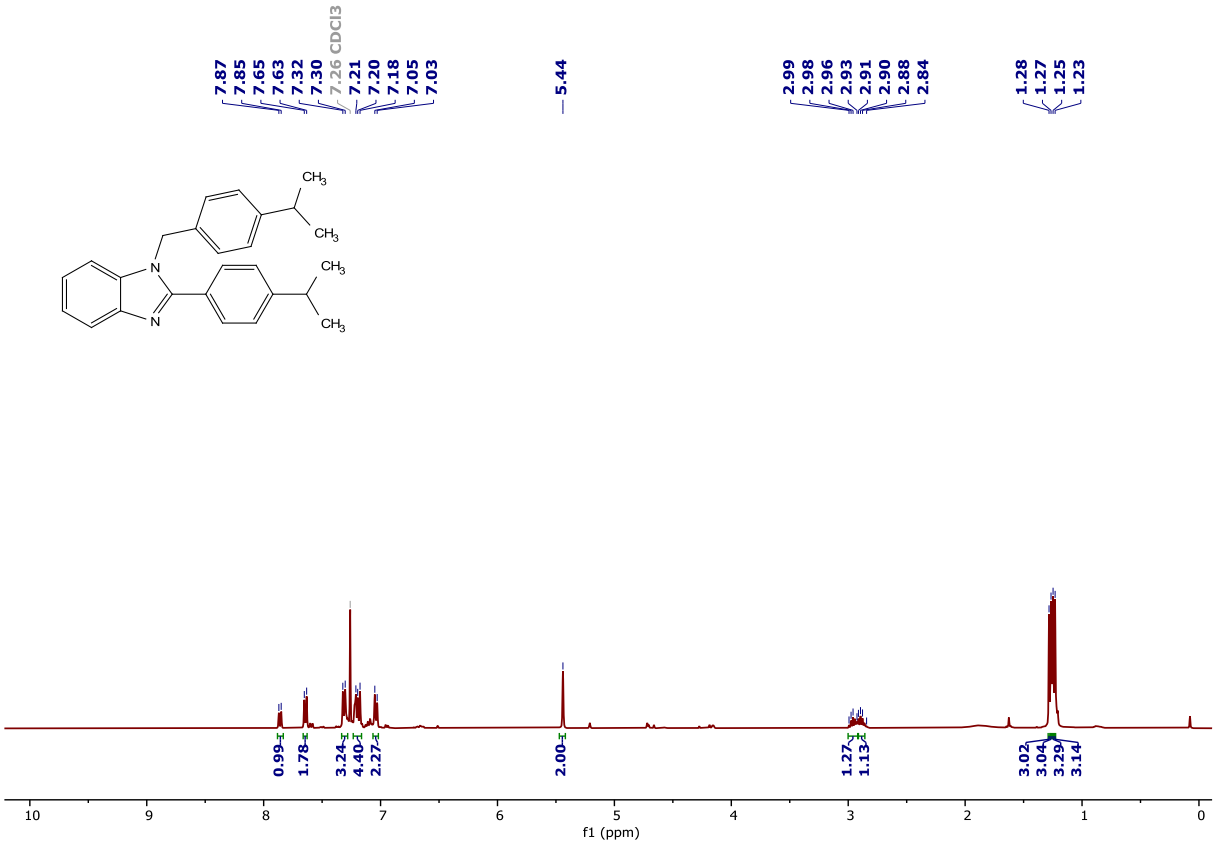


Figure S23. ^{1}H NMR spectrum of **4c** in $CDCl_3$.

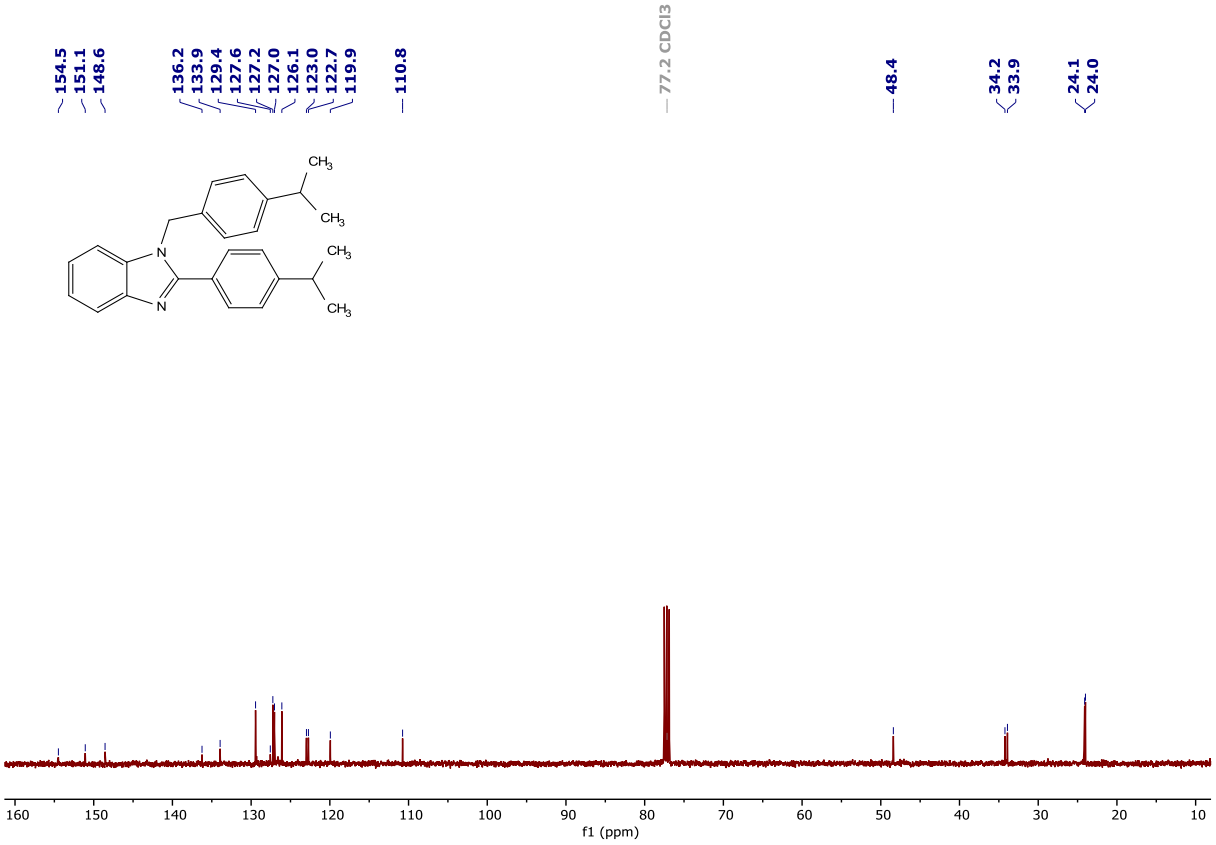


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **4c** in $CDCl_3$.

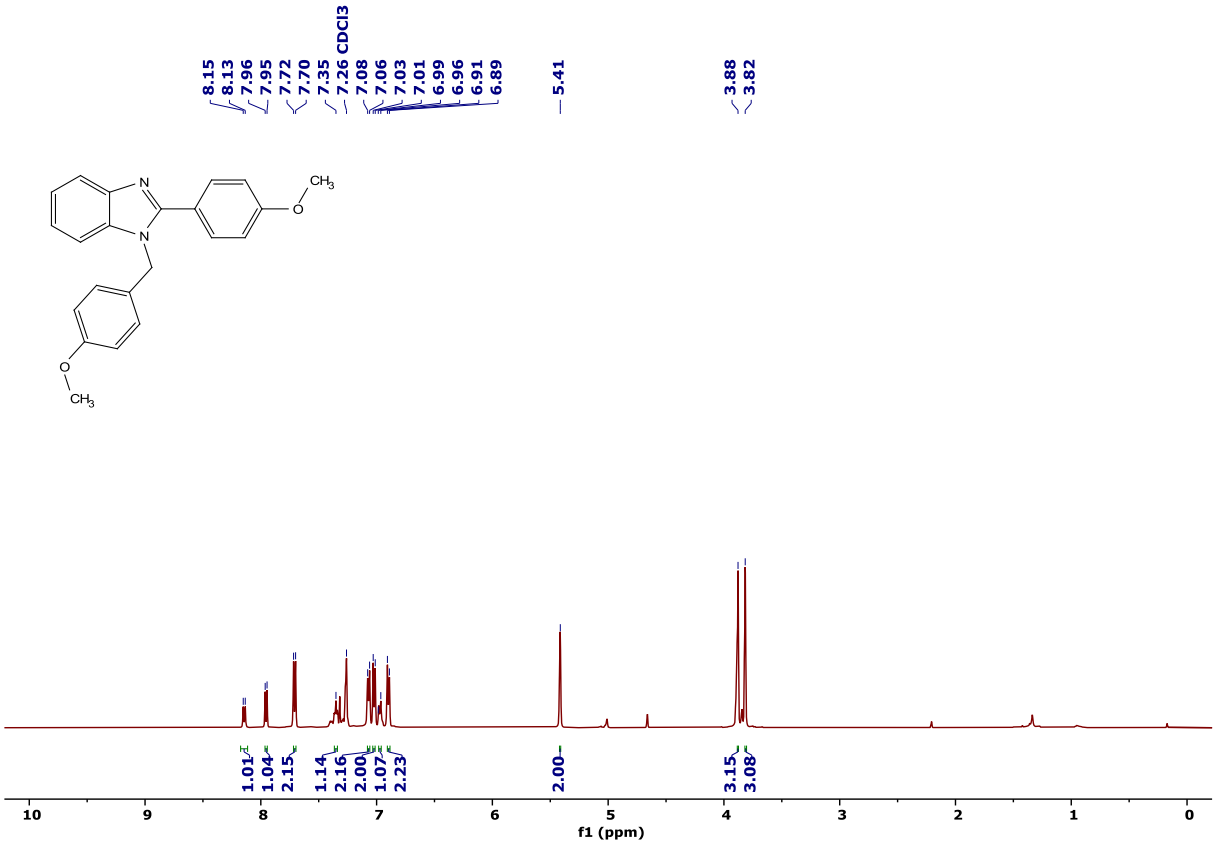


Figure S25. ^{1}H NMR spectrum of **4d** in $CDCl_3$.

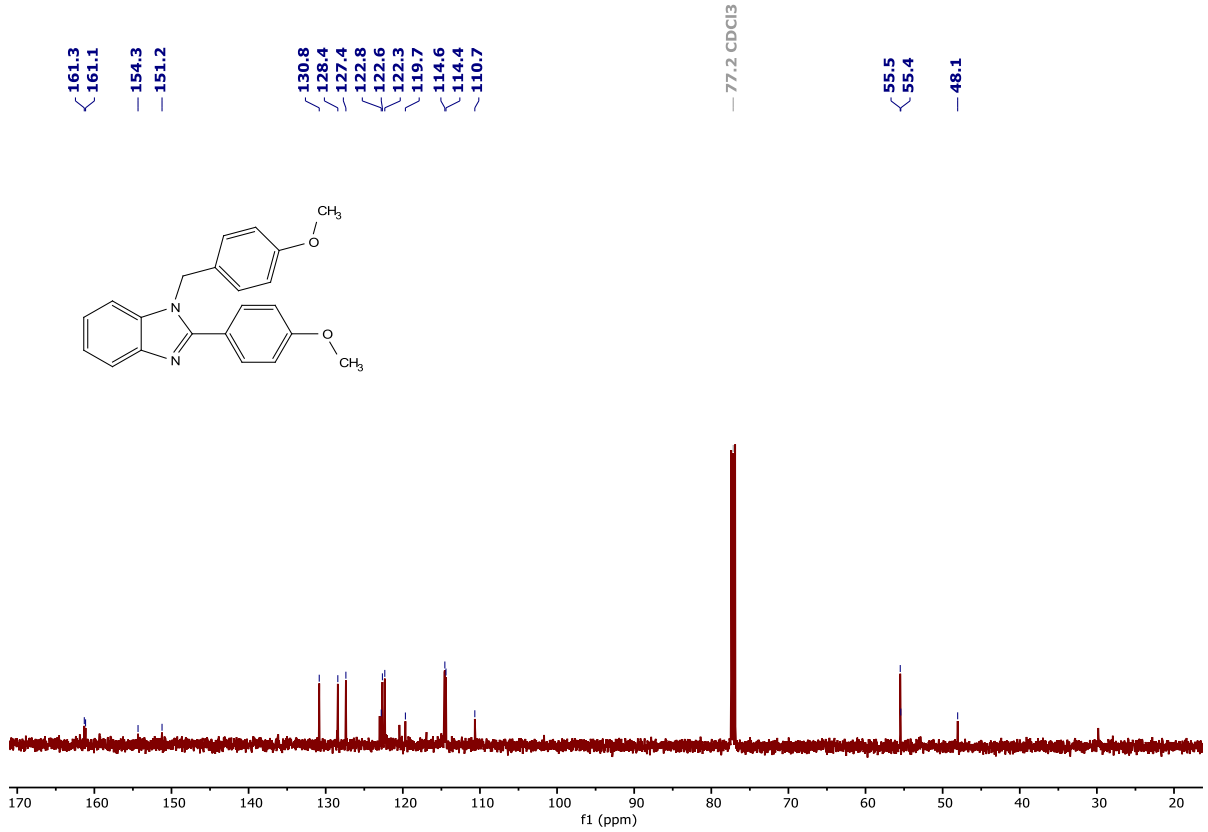


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **4d** in $CDCl_3$.

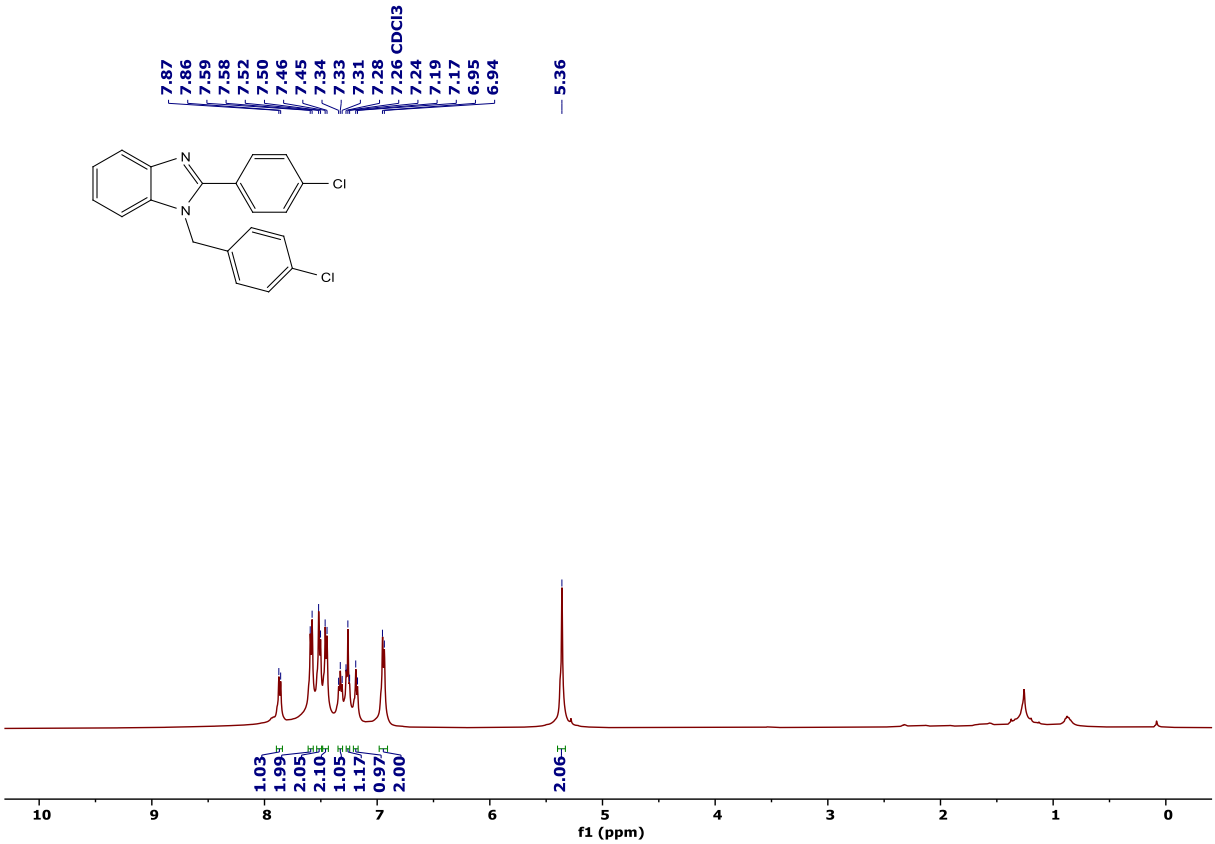


Figure S27. ^{1}H NMR spectrum of **4e** in $CDCl_3$.

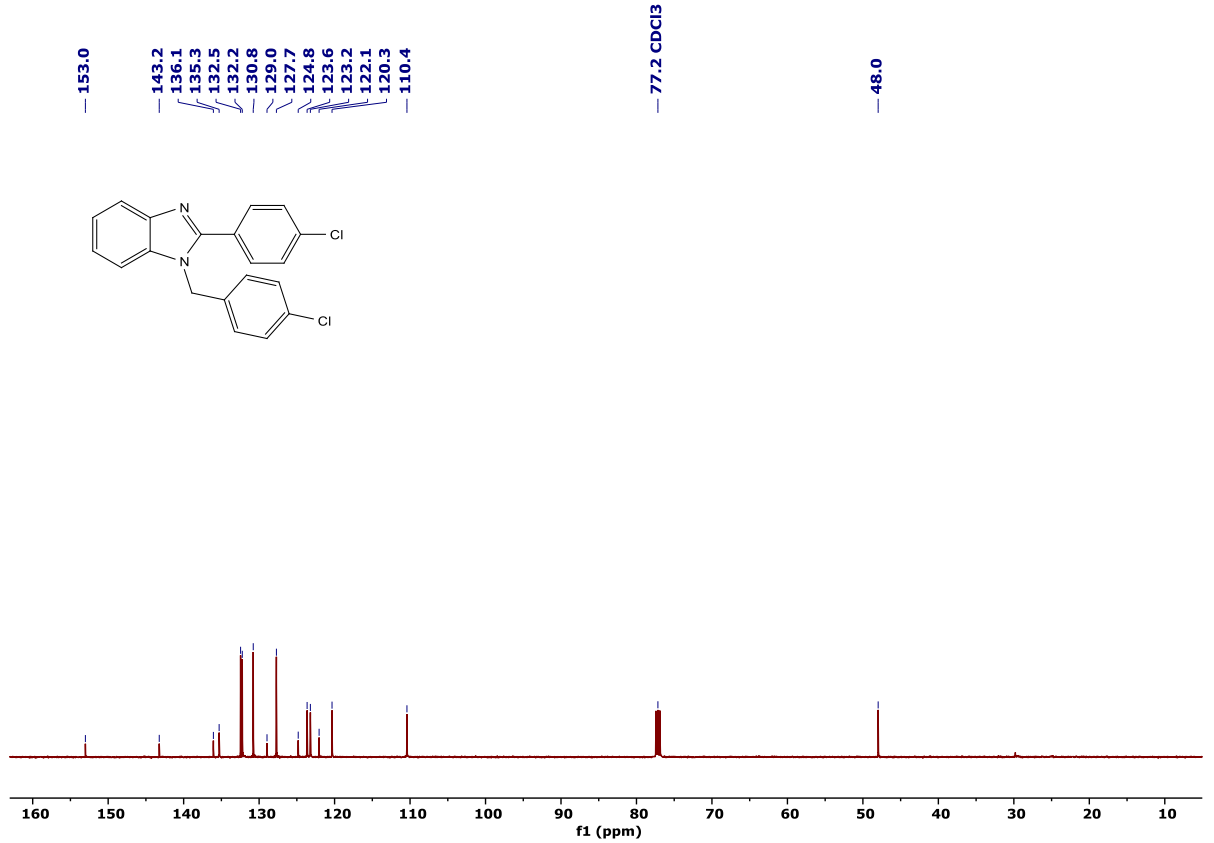


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **4e** in $CDCl_3$.

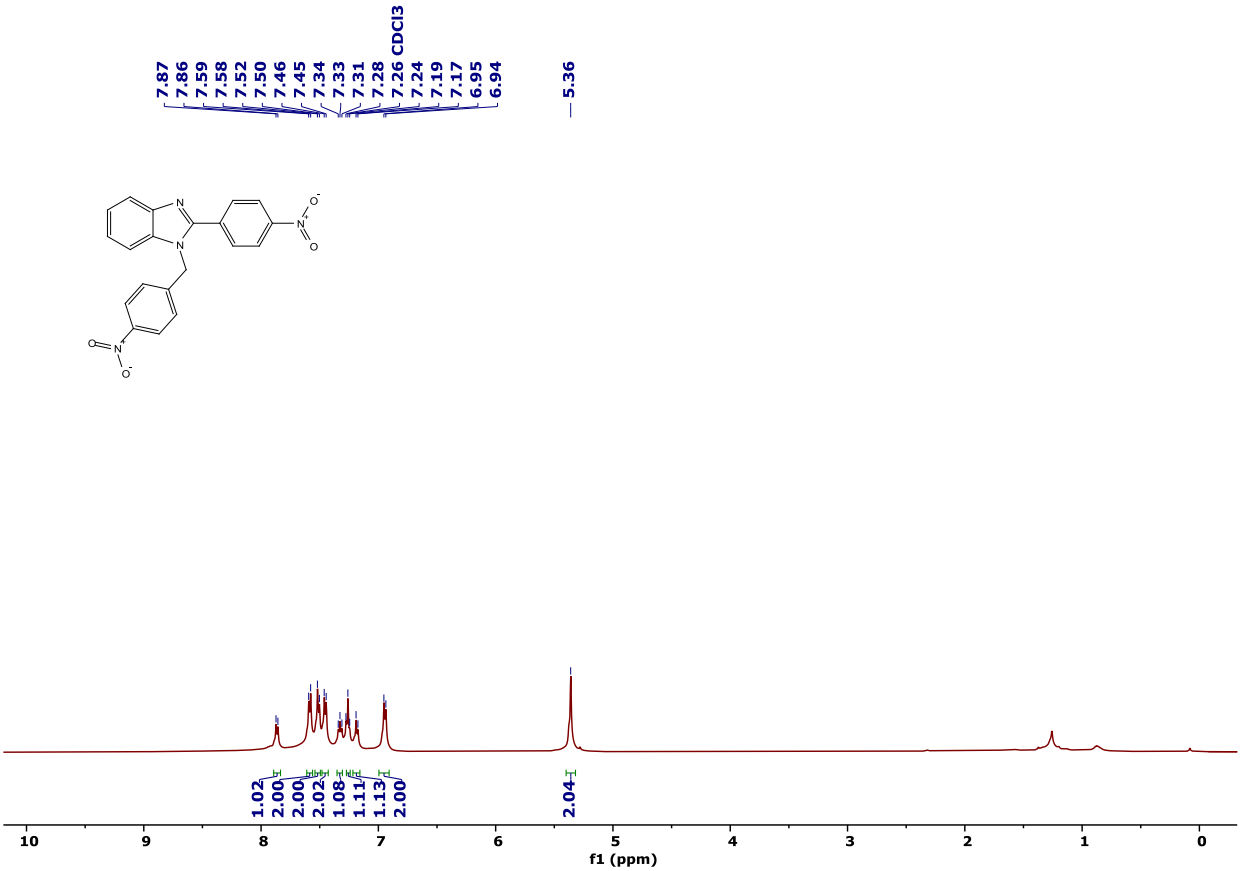


Figure S29. ^{1}H NMR spectrum of **4f** in $CDCl_3$.

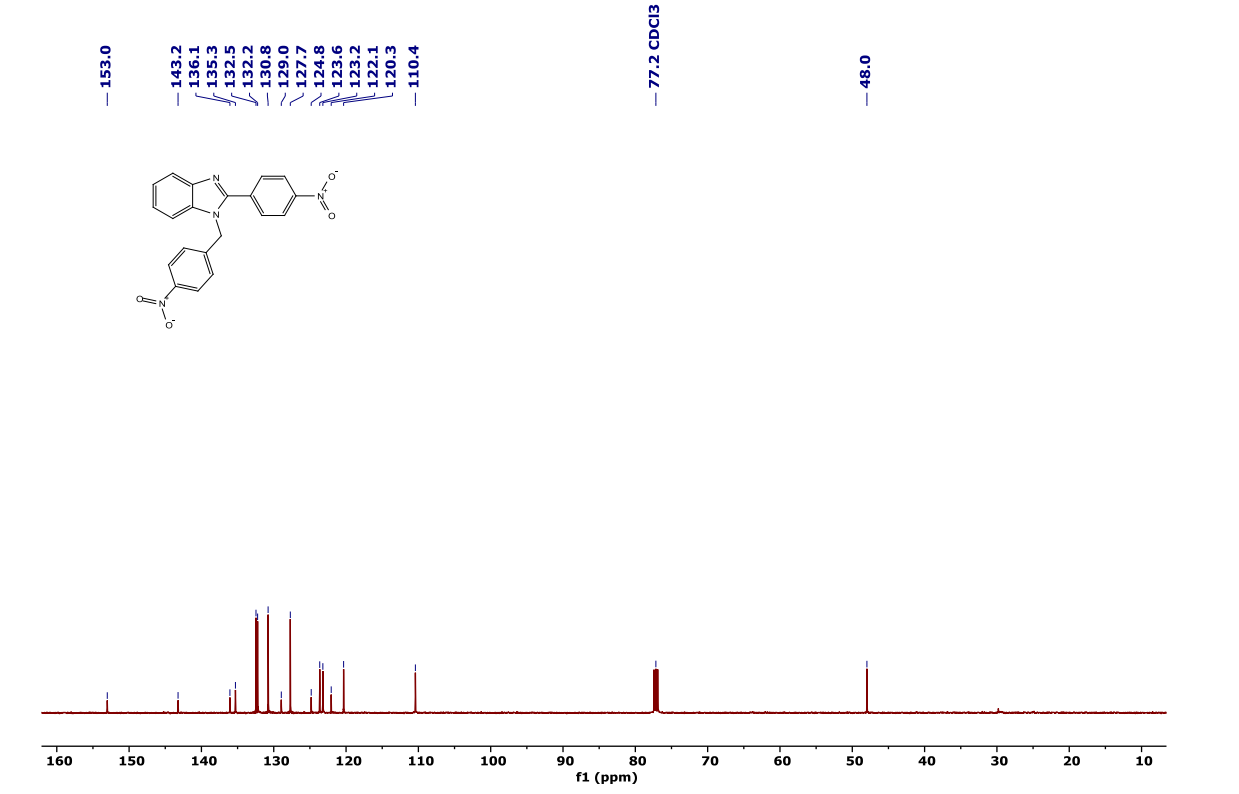


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **4f** in $CDCl_3$.

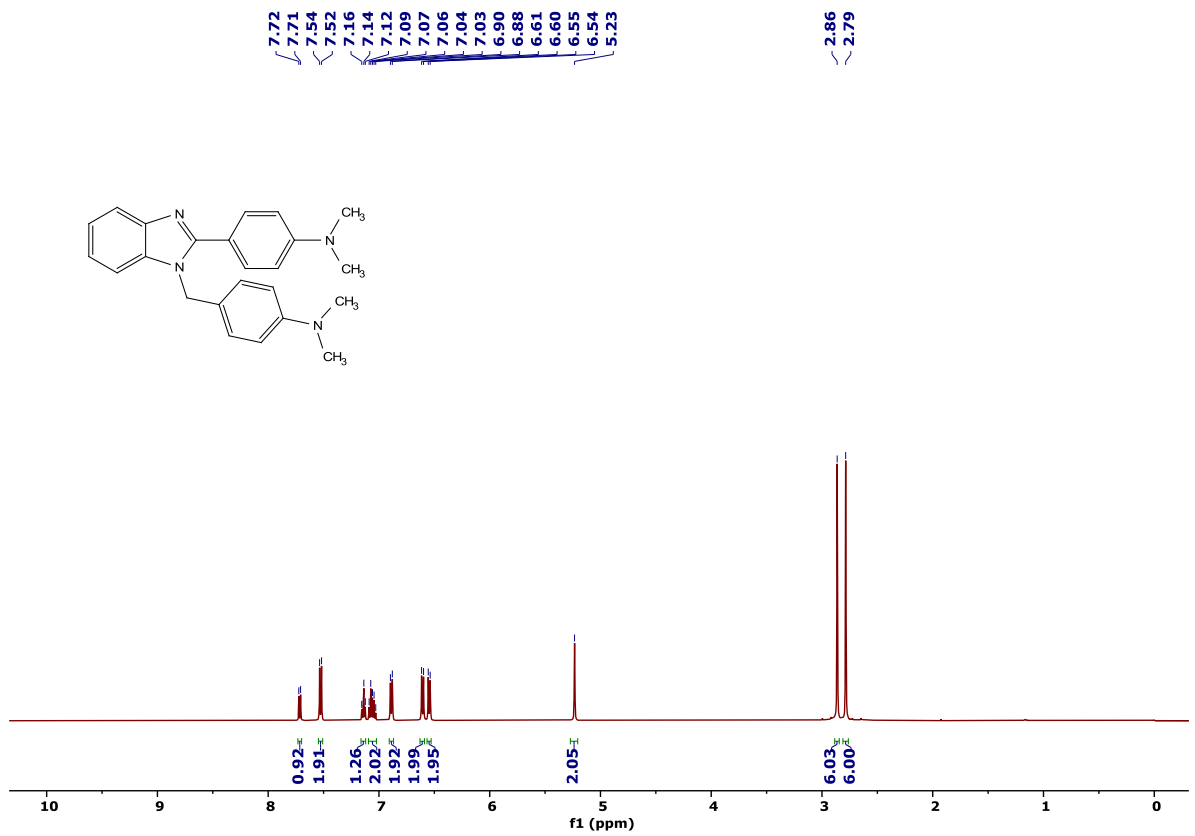


Figure S31. ^{1}H NMR spectrum of **4g** in $CDCl_3$.

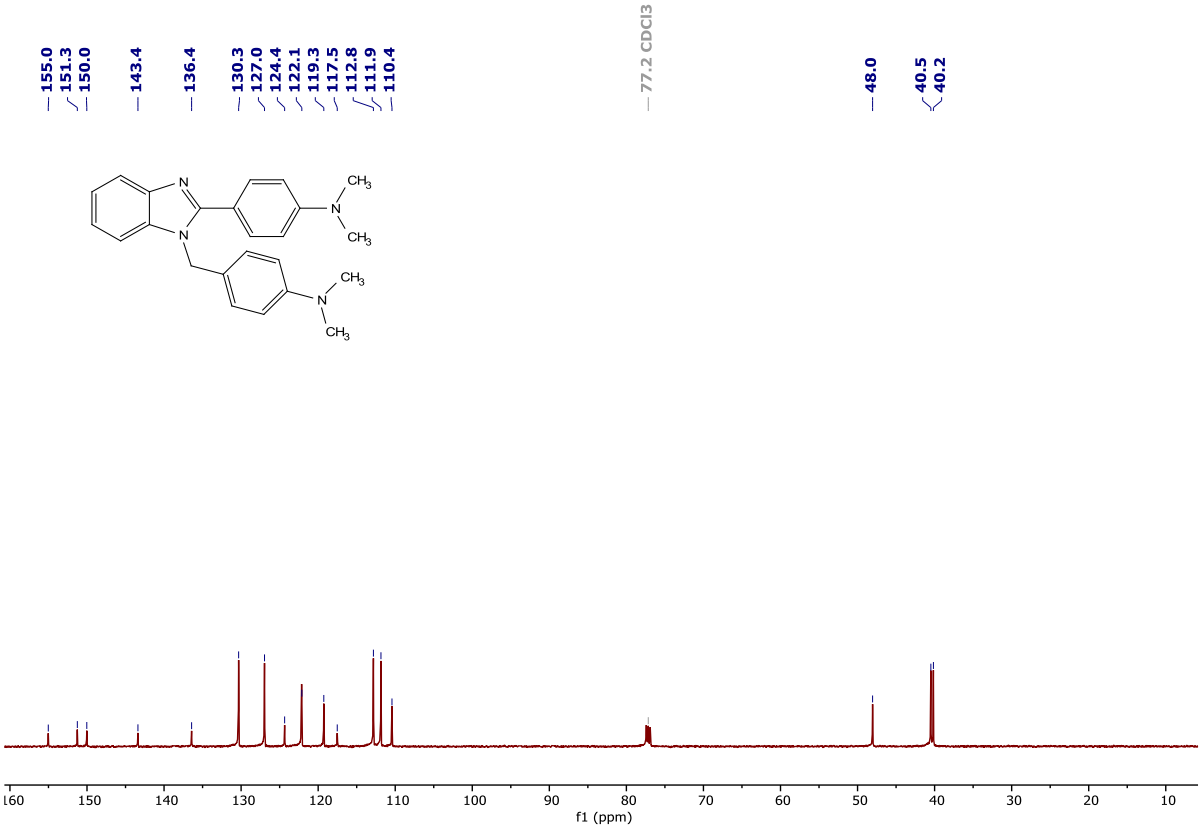


Figure S32. ^{13}C{^{1}H} NMR spectrum of **4g** in $CDCl_3$

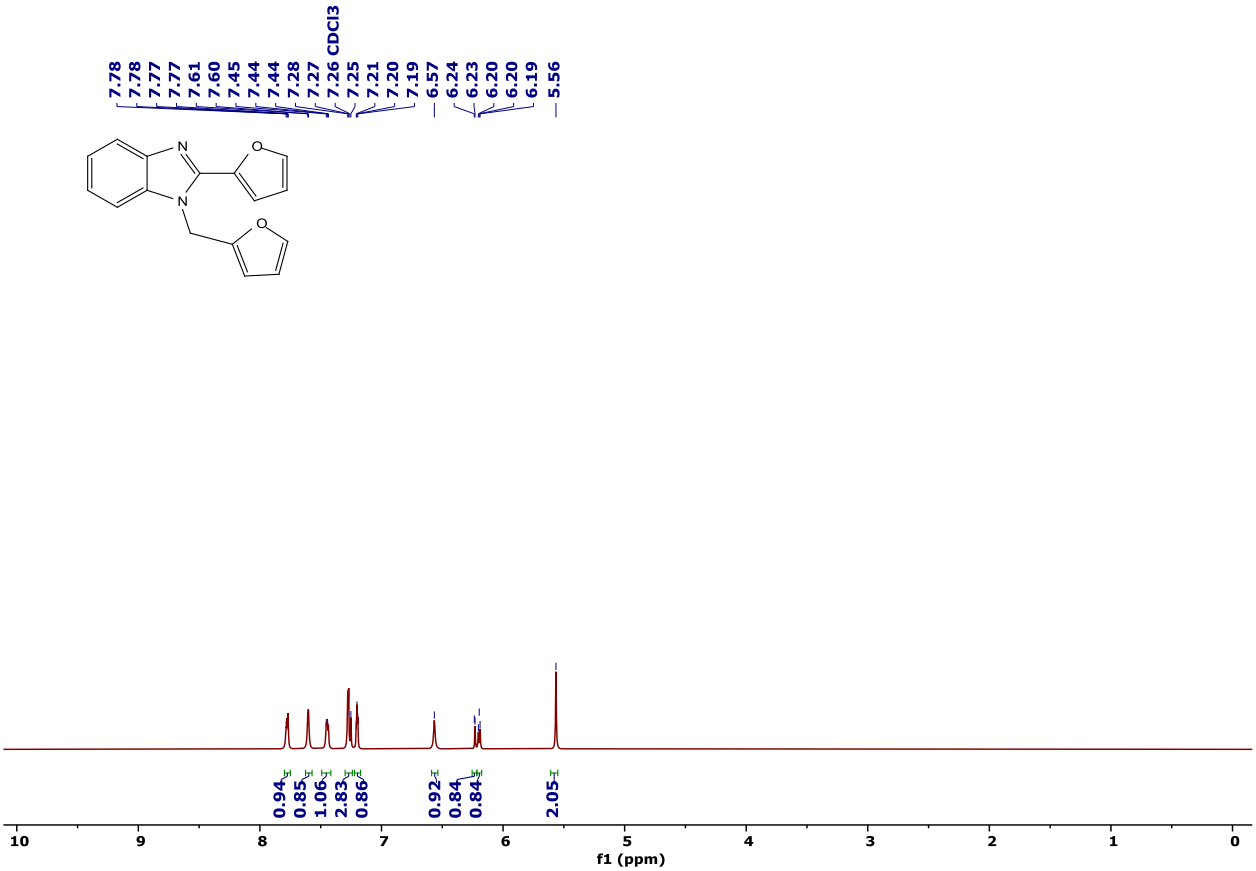


Figure S33. ^{1}H NMR spectrum of **4h** in $CDCl_3$.

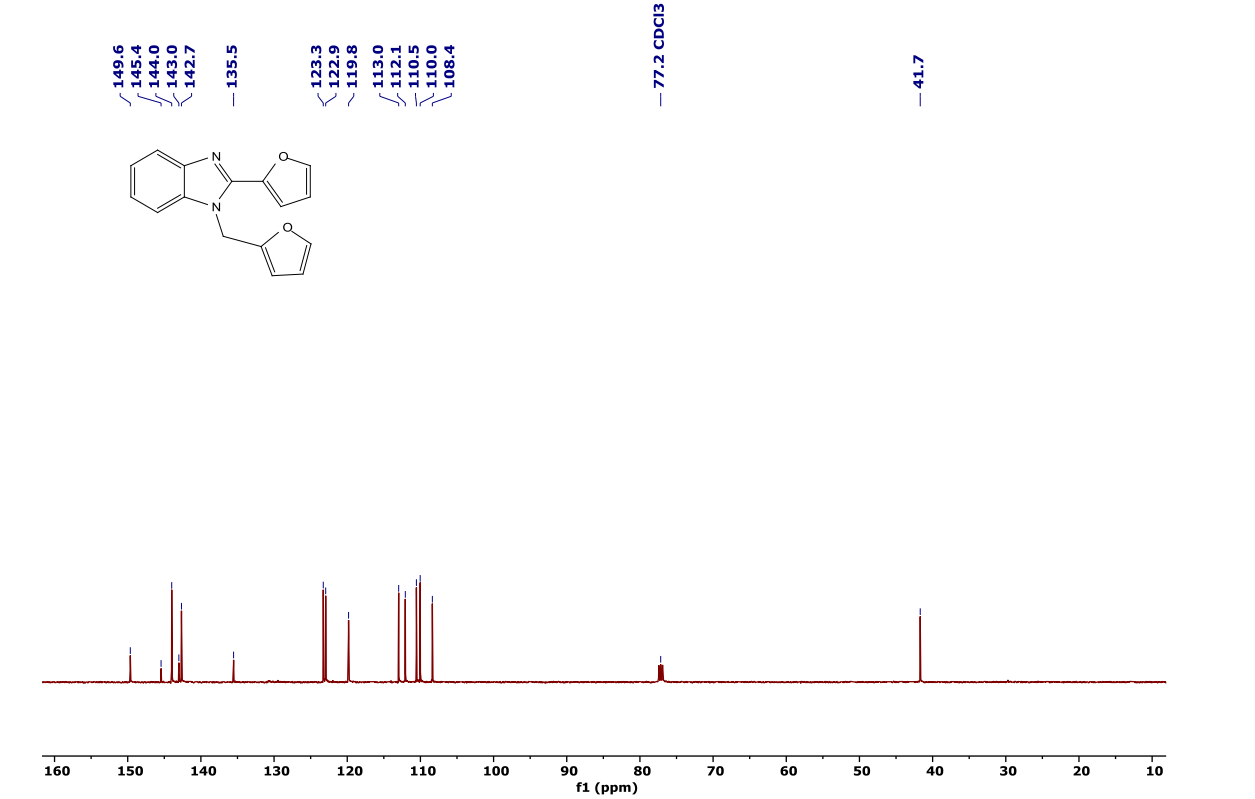


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **4h** in $CDCl_3$.

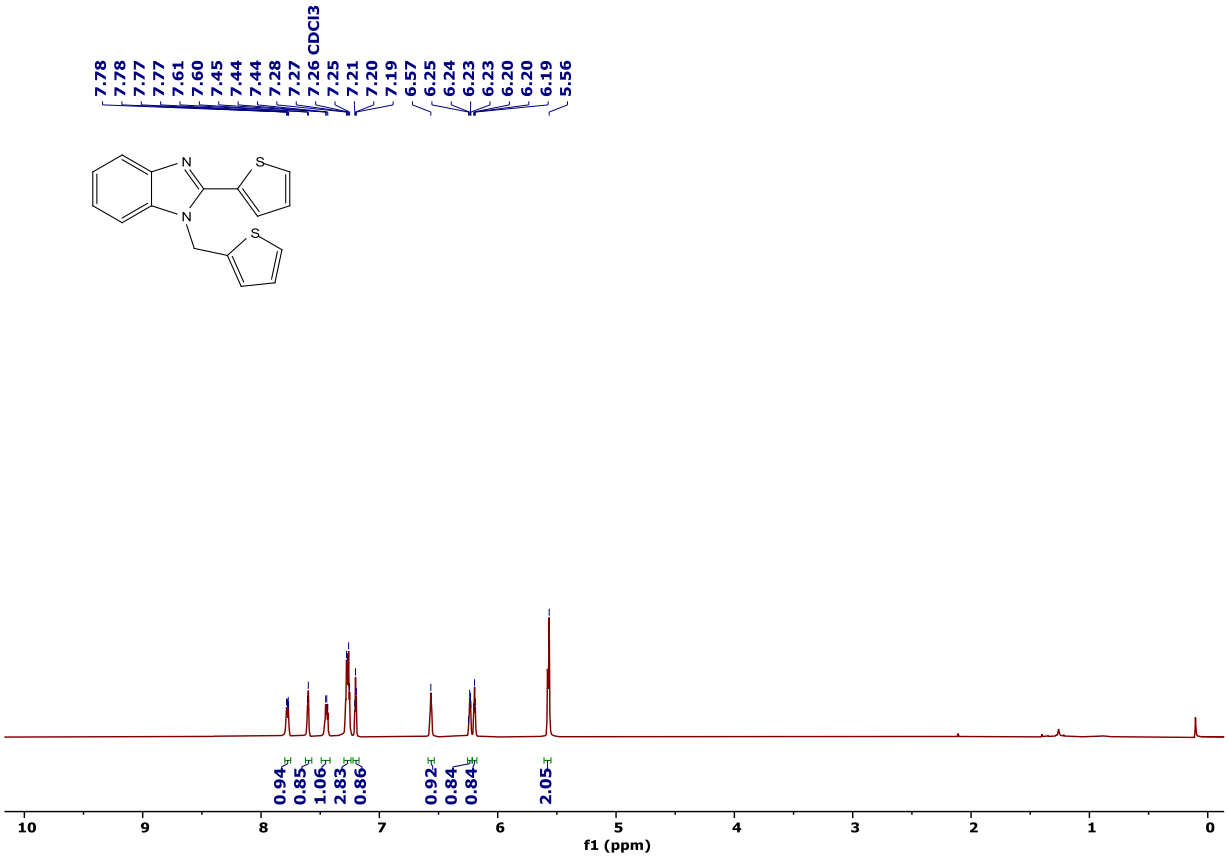


Figure S35. ^{1}H NMR spectrum of **4i** in $CDCl_3$.

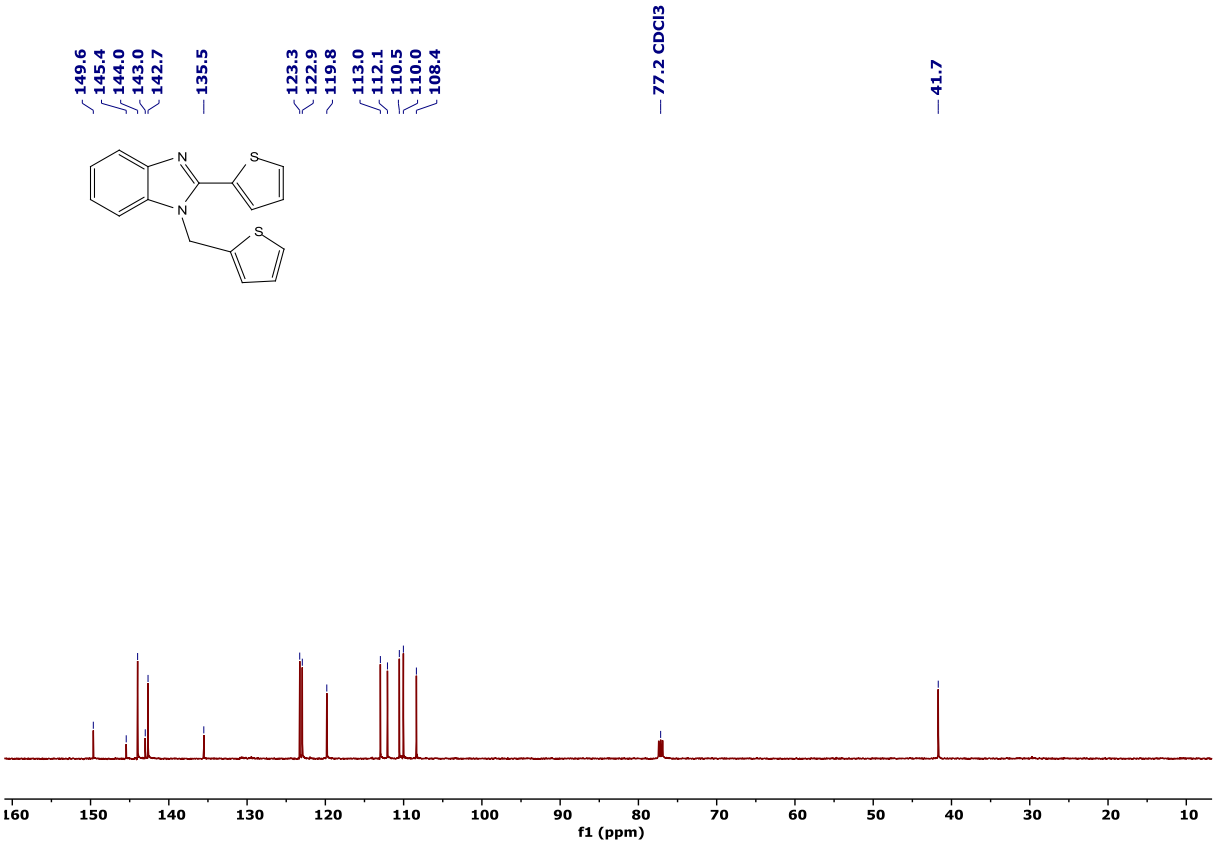


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of **4i** in $CDCl_3$.

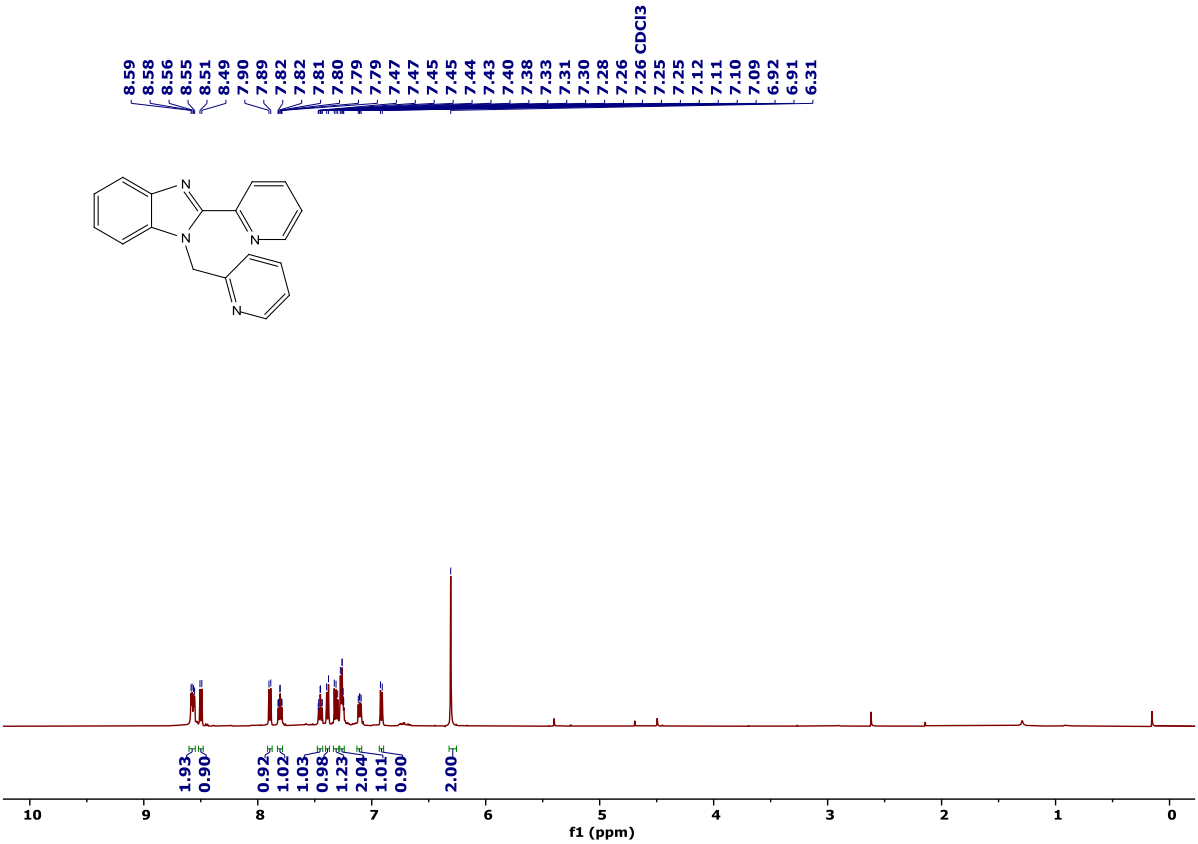


Figure S37. ^{1}H NMR spectrum of **4j** in $CDCl_3$.

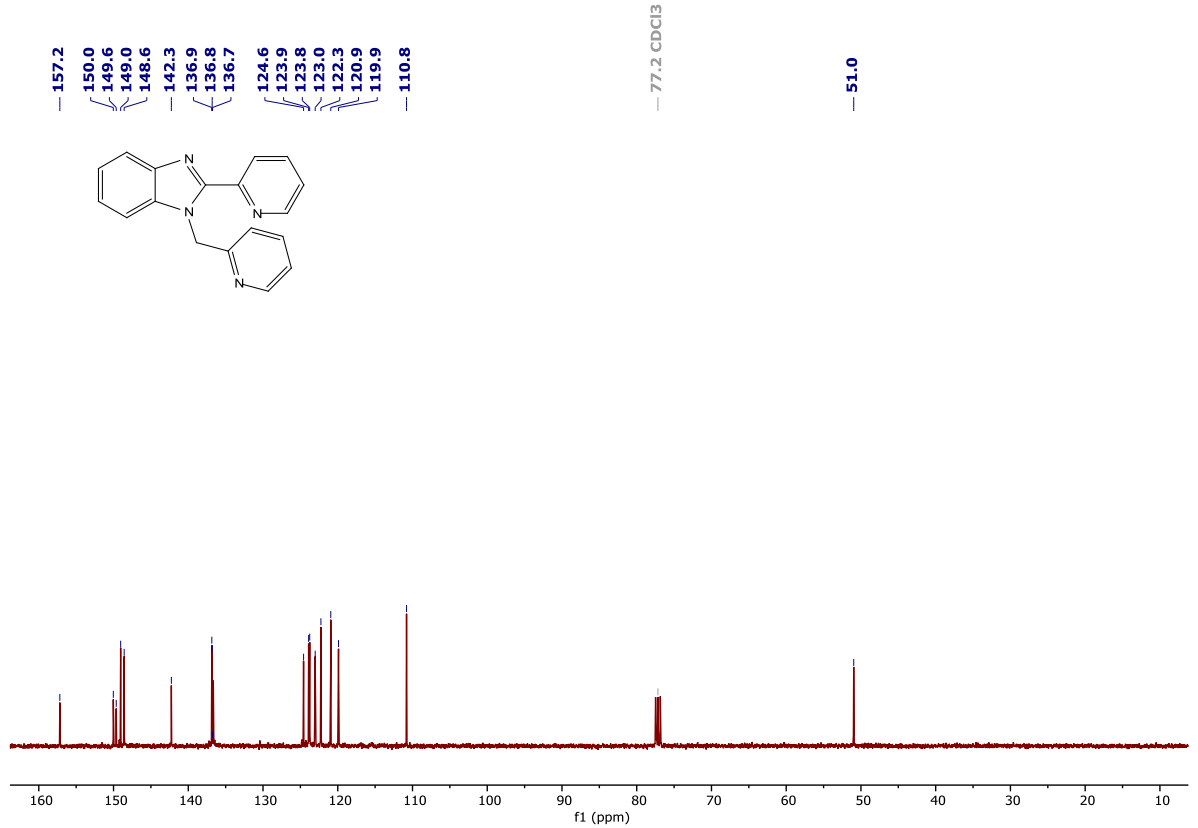


Figure S38. ^{13}C{^{1}H} NMR spectrum of **4j** in $CDCl_3$.

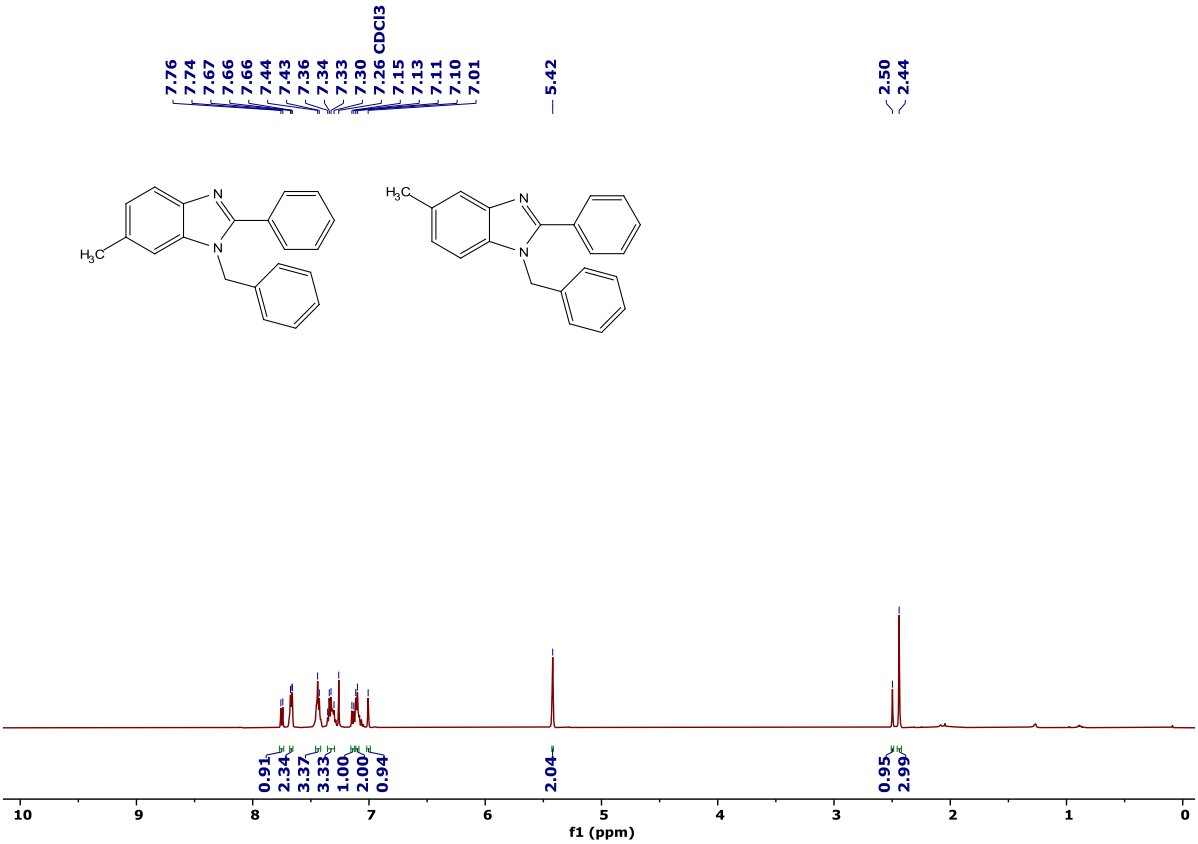


Figure S39. ^{1}H NMR spectrum of **4k** in $CDCl_3$.

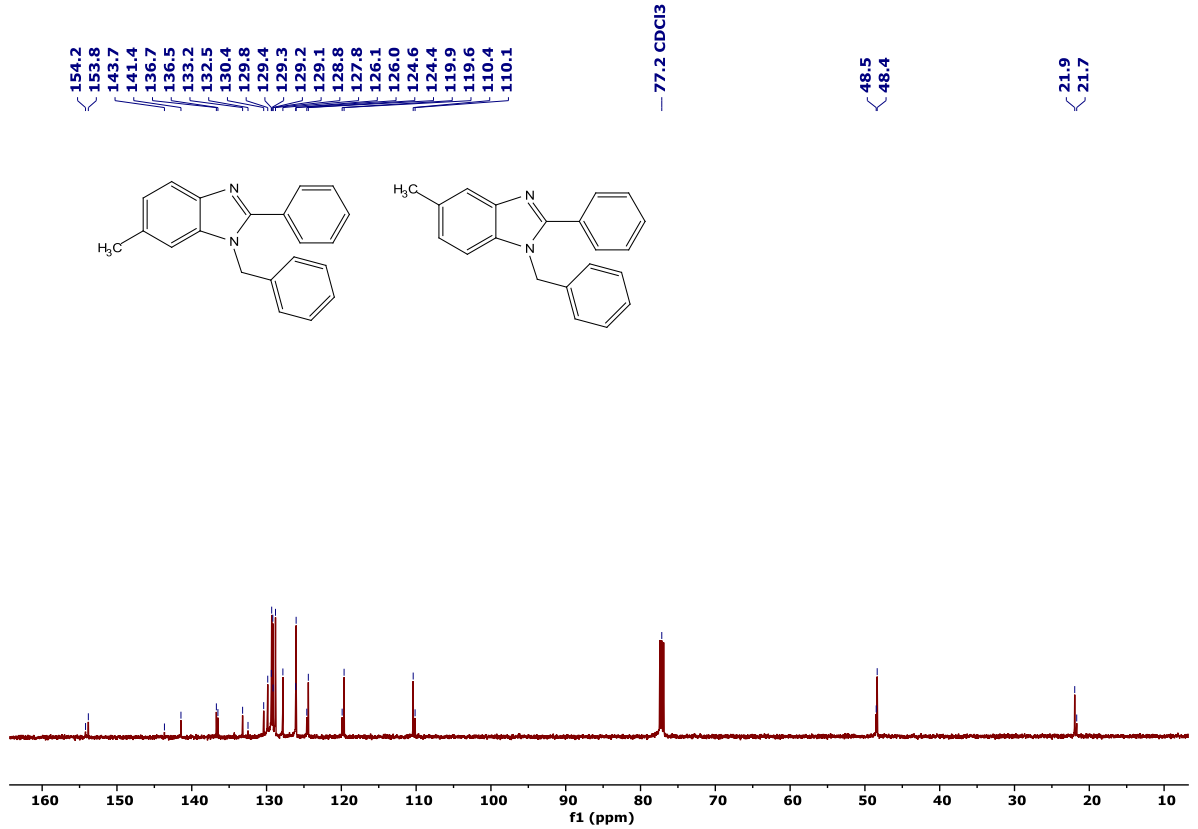


Figure S40. ^{13}C{^{1}H} NMR spectrum of **4k** in $CDCl_3$.

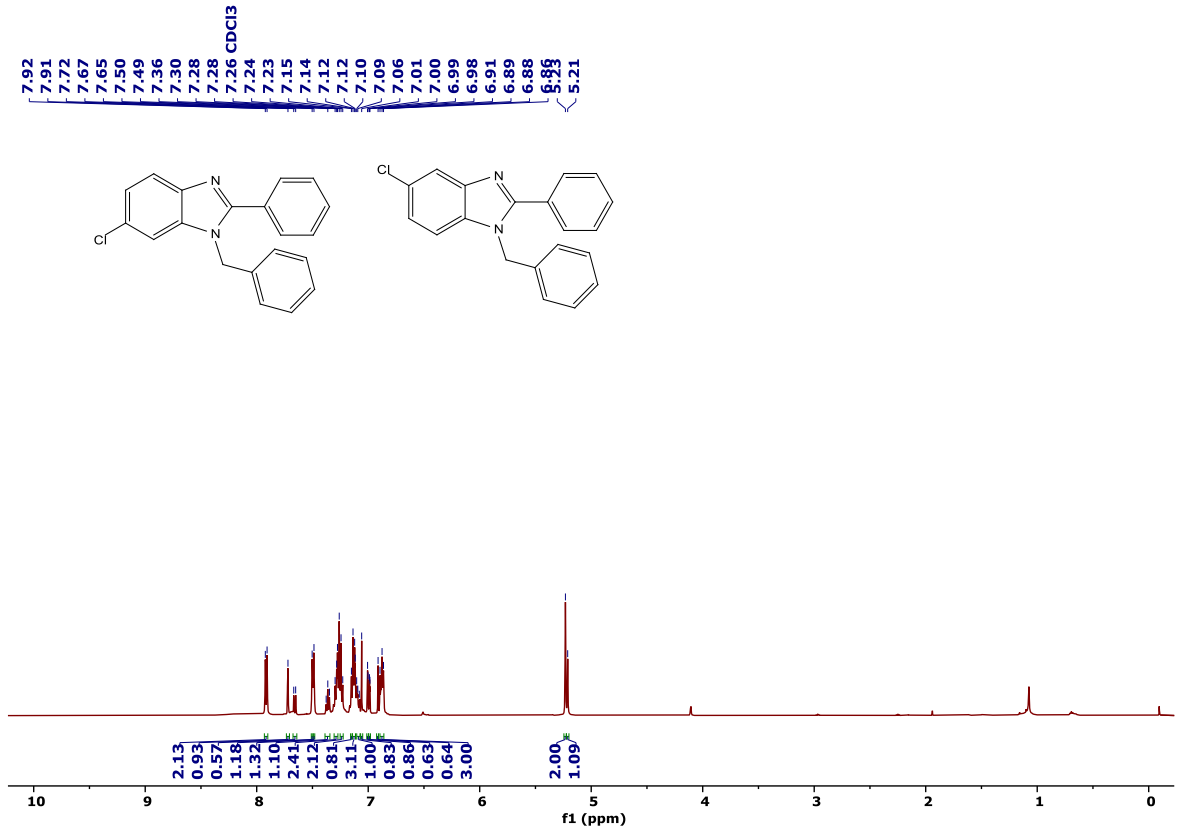


Figure S41. ^{1}H NMR spectrum of **4l** in $CDCl_3$.

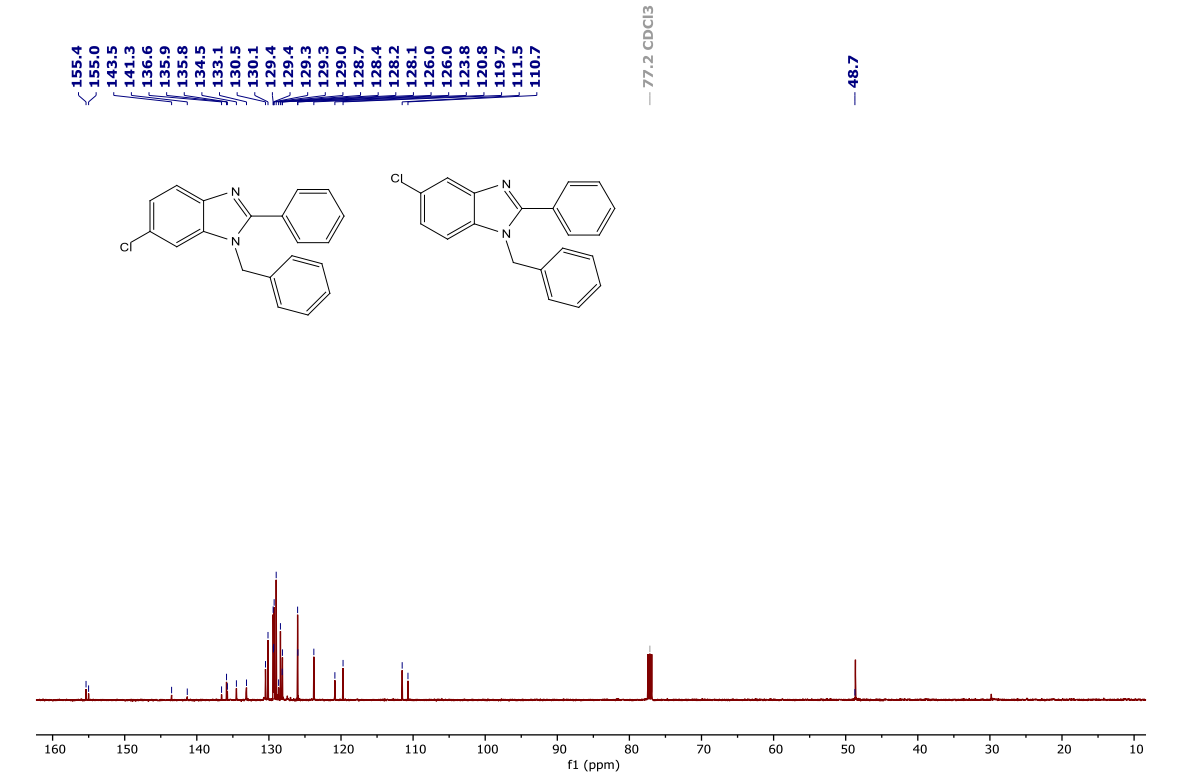


Figure S42. ^{13}C{^{1}H} NMR spectrum of **4l** in $CDCl_3$.

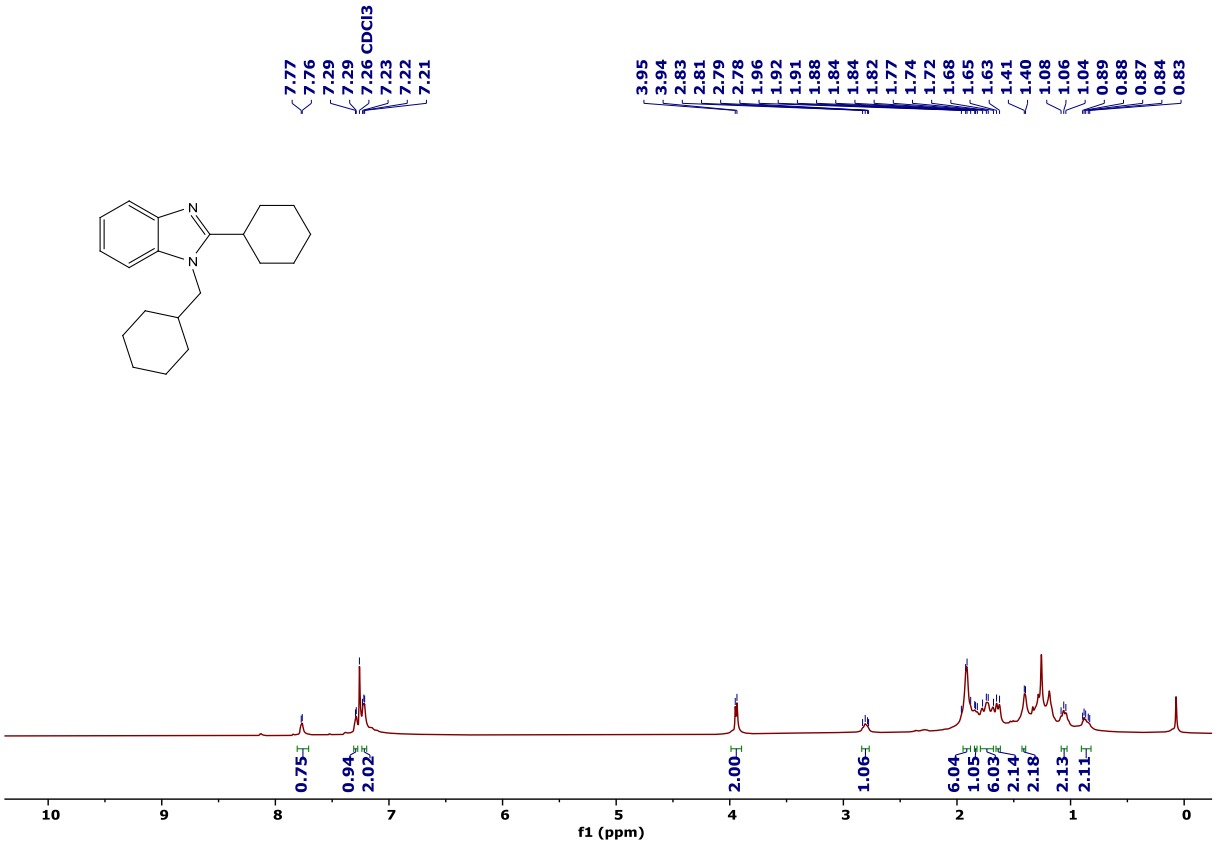


Figure S43. ^{1}H NMR spectrum of **4m** in $CDCl_3$.

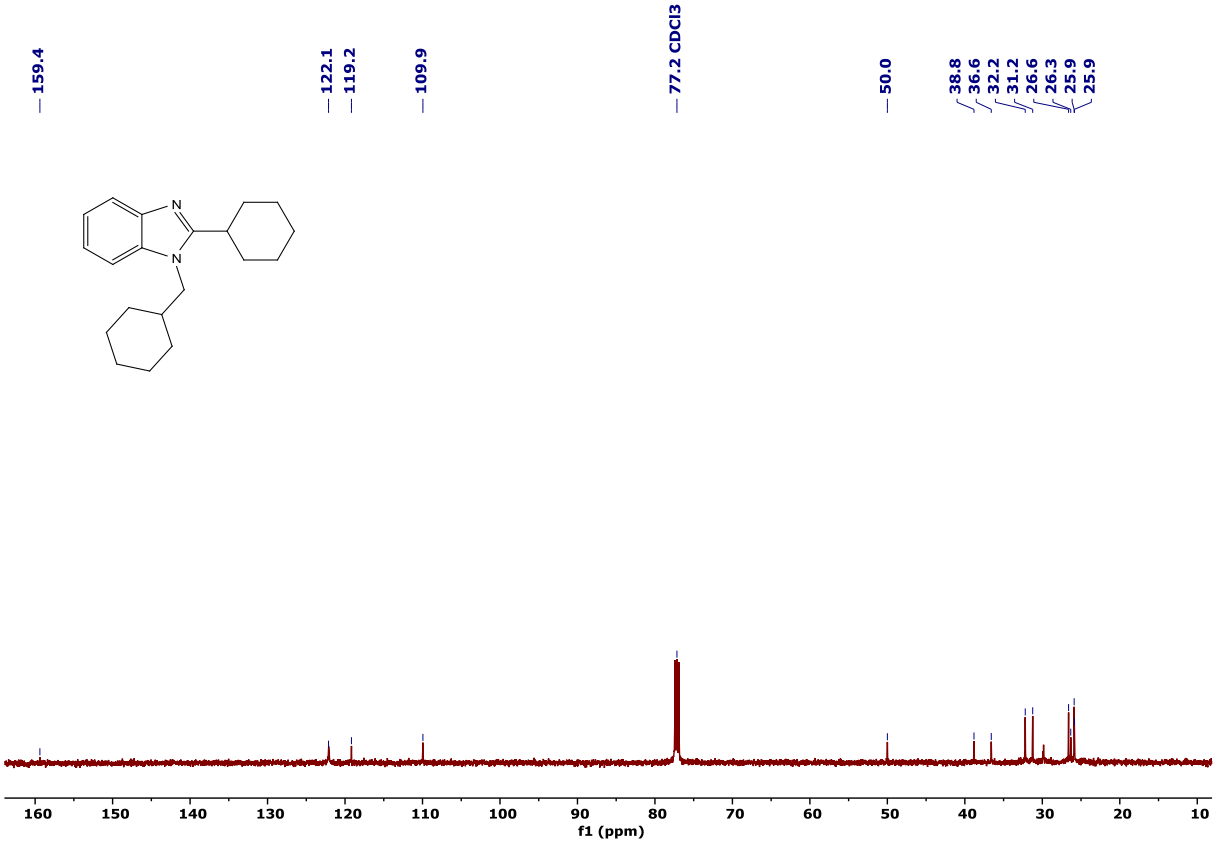


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of **4m** in $CDCl_3$.

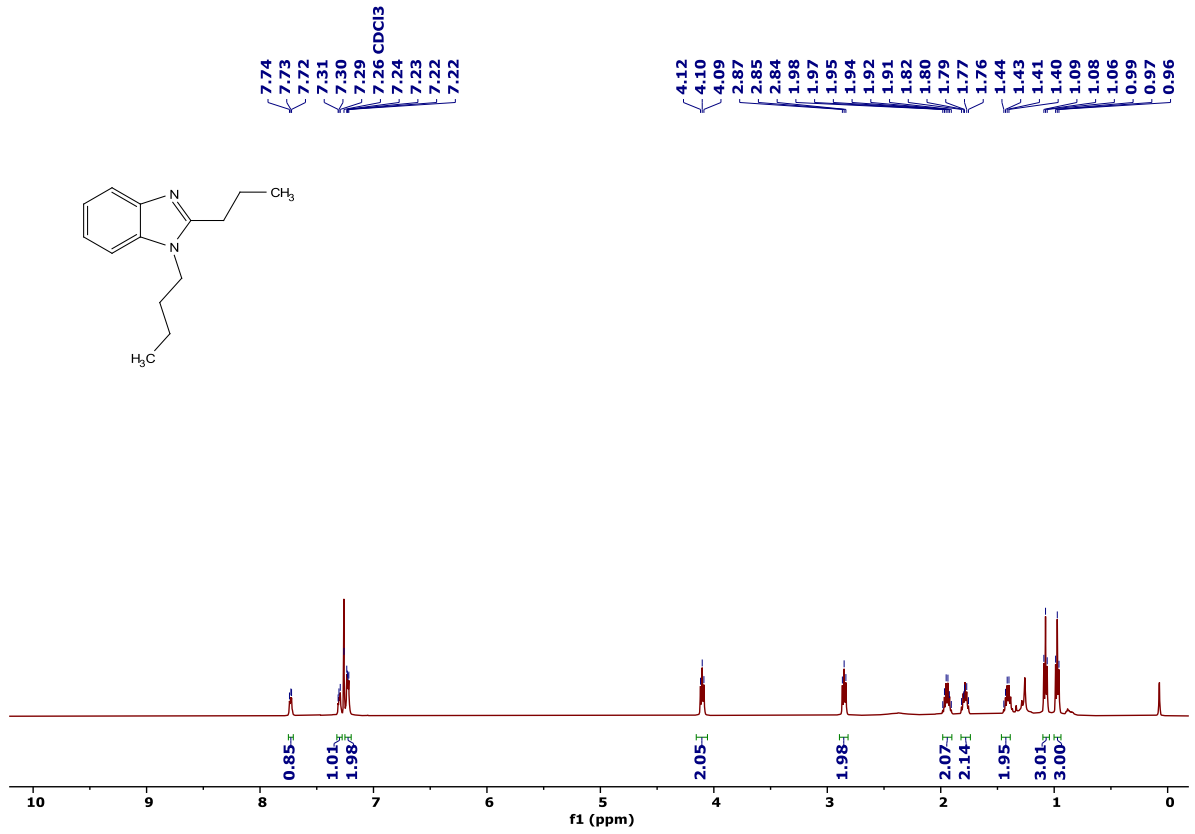


Figure S45. ^{1}H NMR spectrum of **4n** in $CDCl_3$.

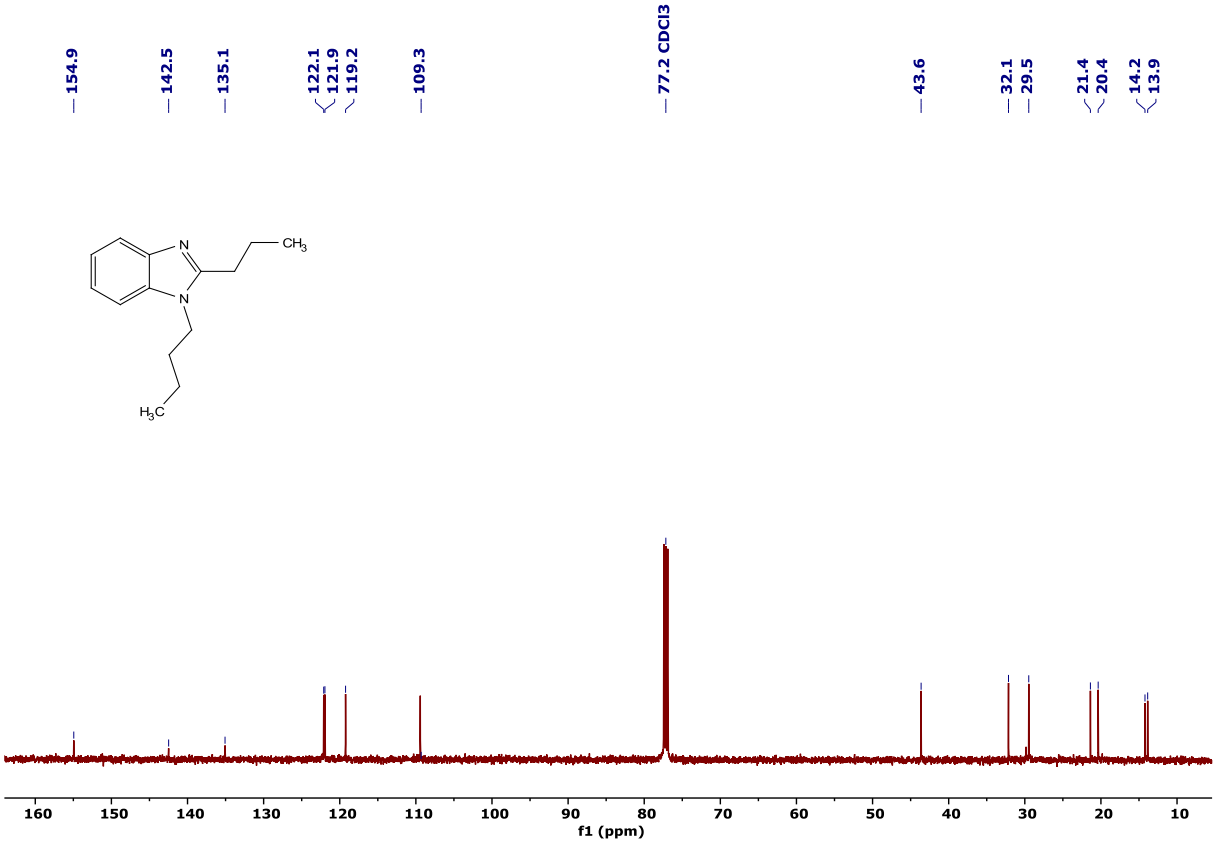


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of **4n** in $CDCl_3$.

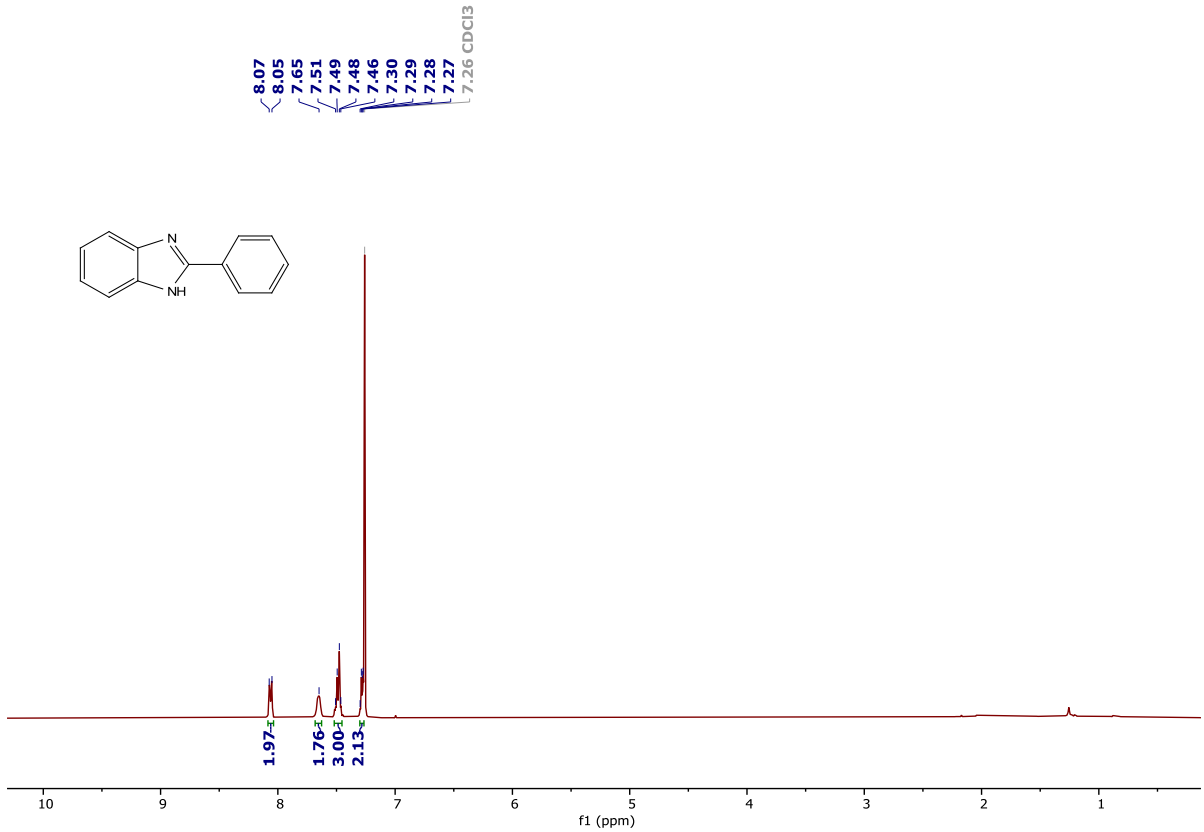


Figure S47. ^{1}H NMR spectrum of **6a** in $CDCl_3$.

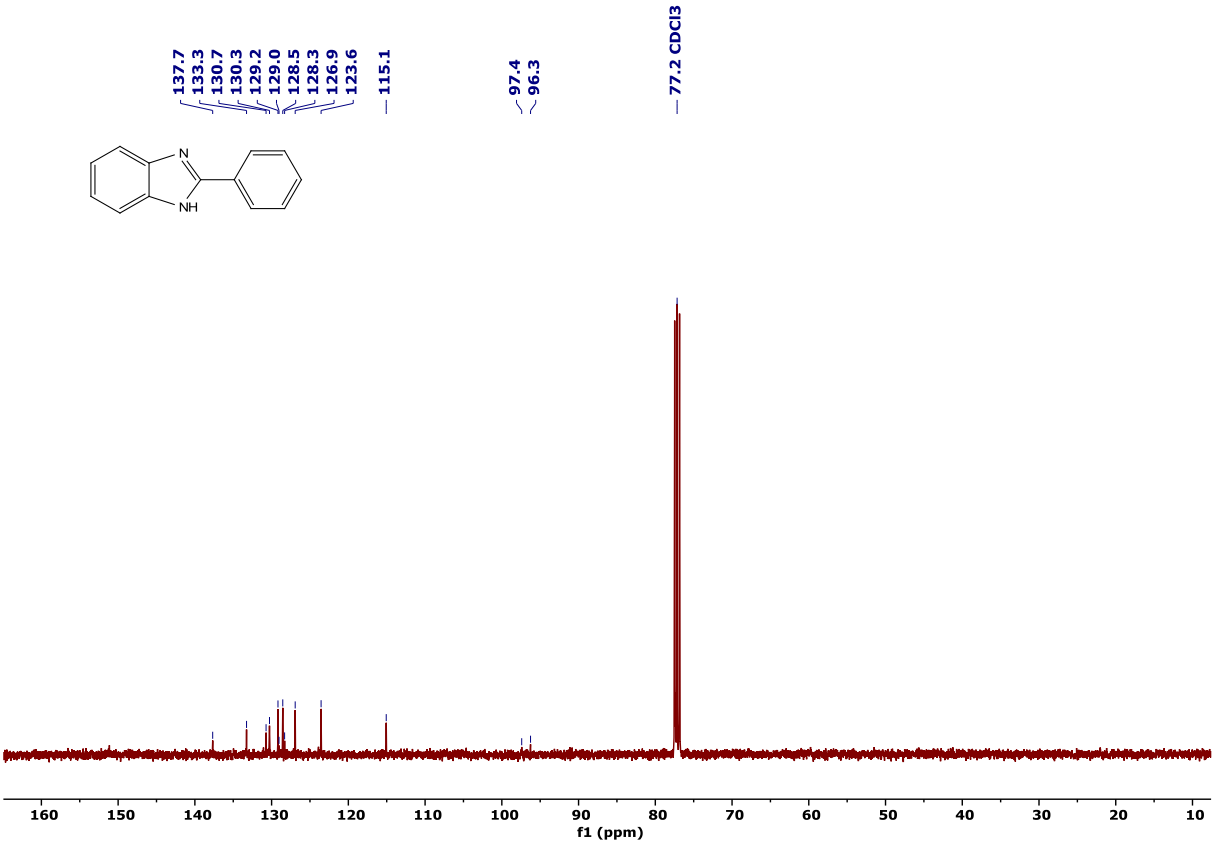


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of **6a** in $CDCl_3$.

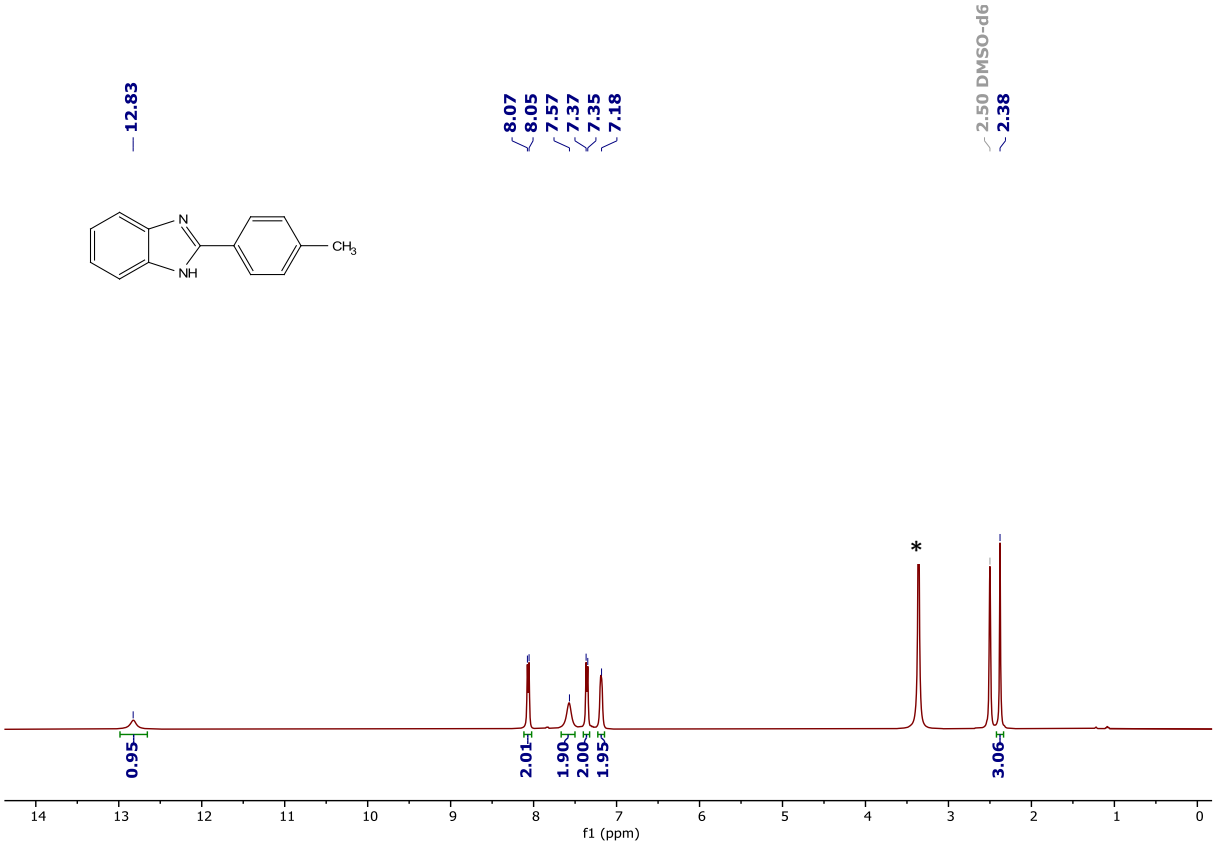


Figure S49. ^{1}H NMR spectrum of **6b** in DMSO-d_6. * indicates the solvent impurity of H_2O.

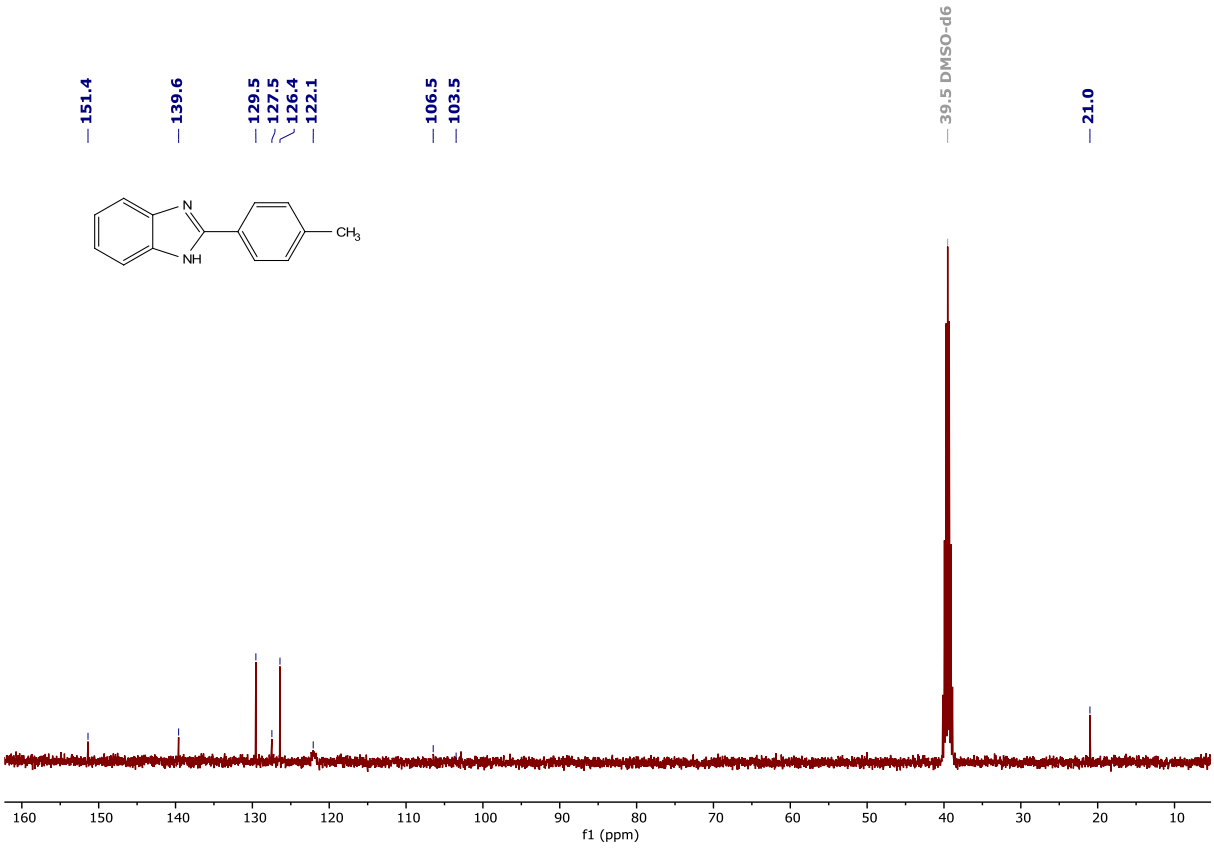


Figure S50. ^{13}C{^{1}H} NMR spectrum of **6b** in DMSO-d_6.

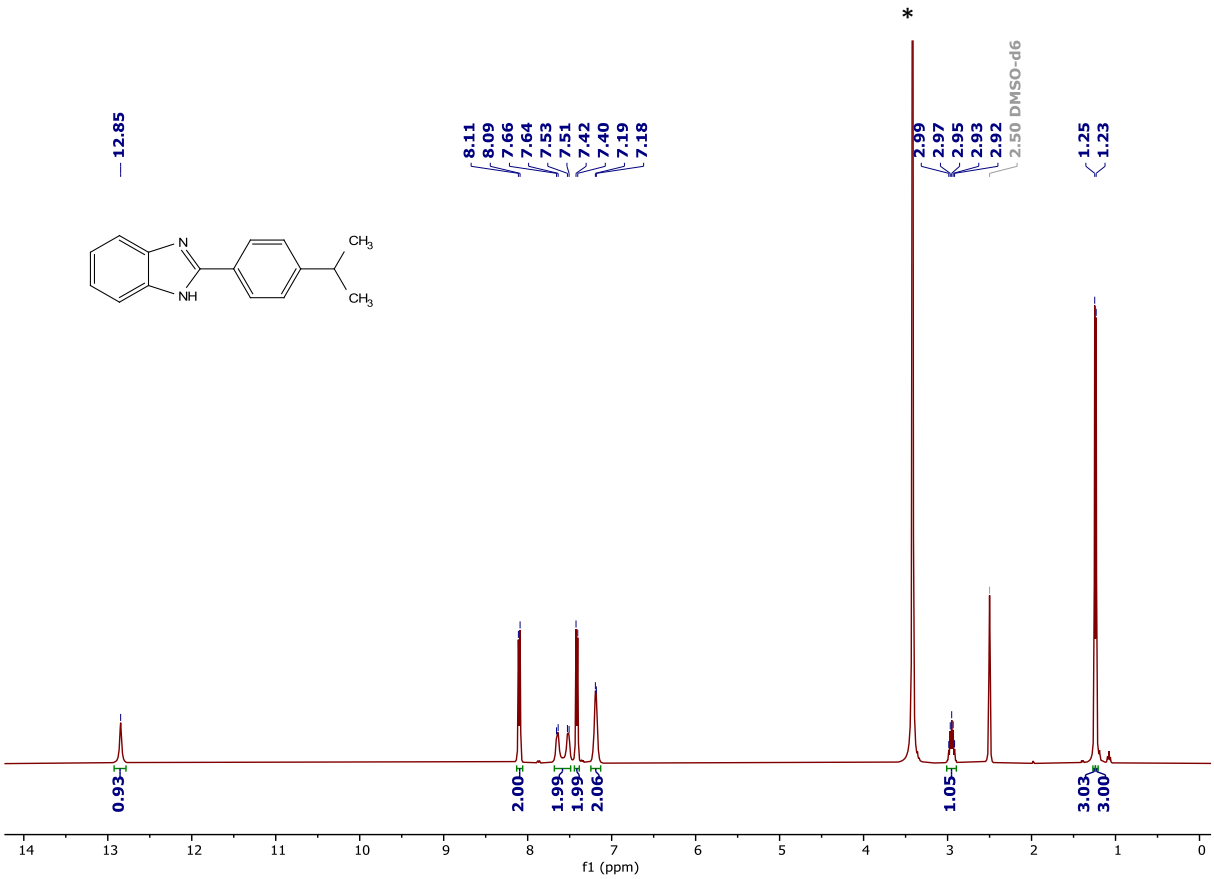


Figure S51. ^{1}H NMR spectrum of **6c** in DMSO-d_6. * indicates the solvent impurity of H_2O.

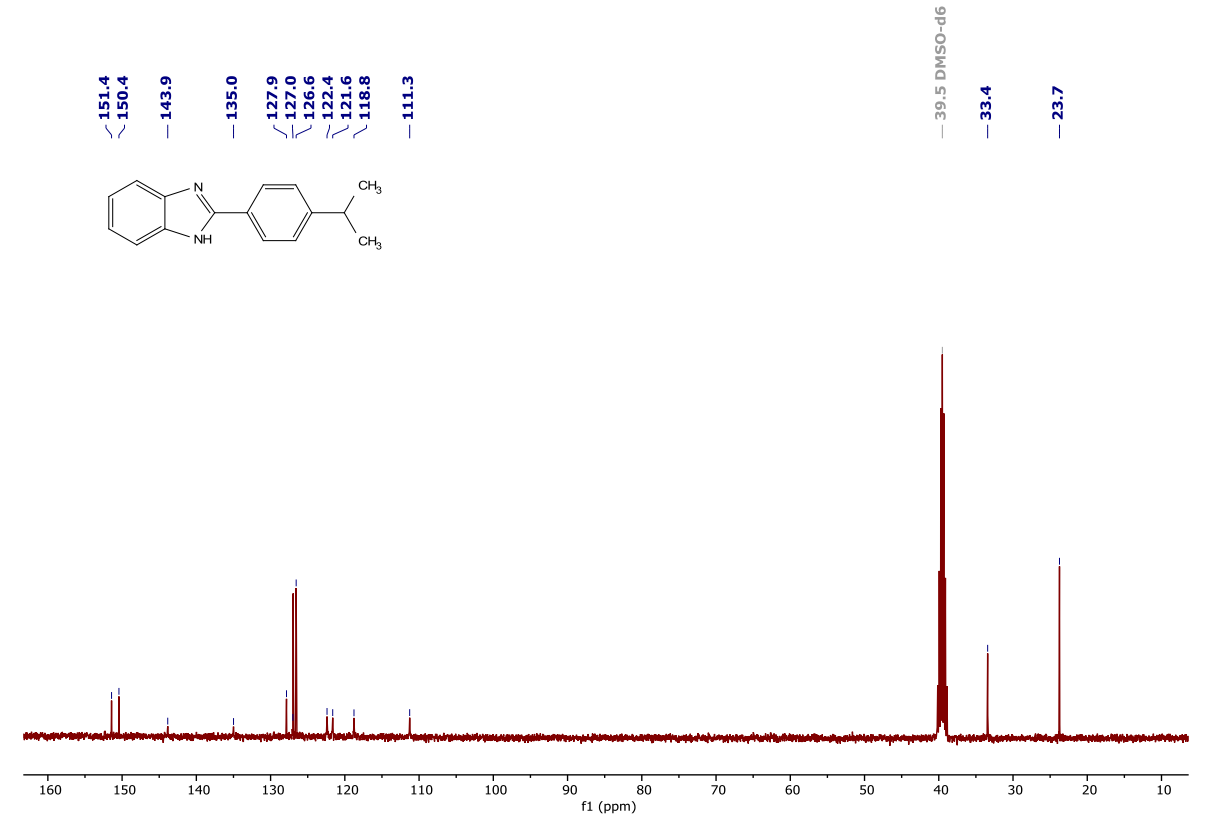


Figure S52. ^{13}C{^{1}H} NMR spectrum of **6c** in DMSO-d_6.

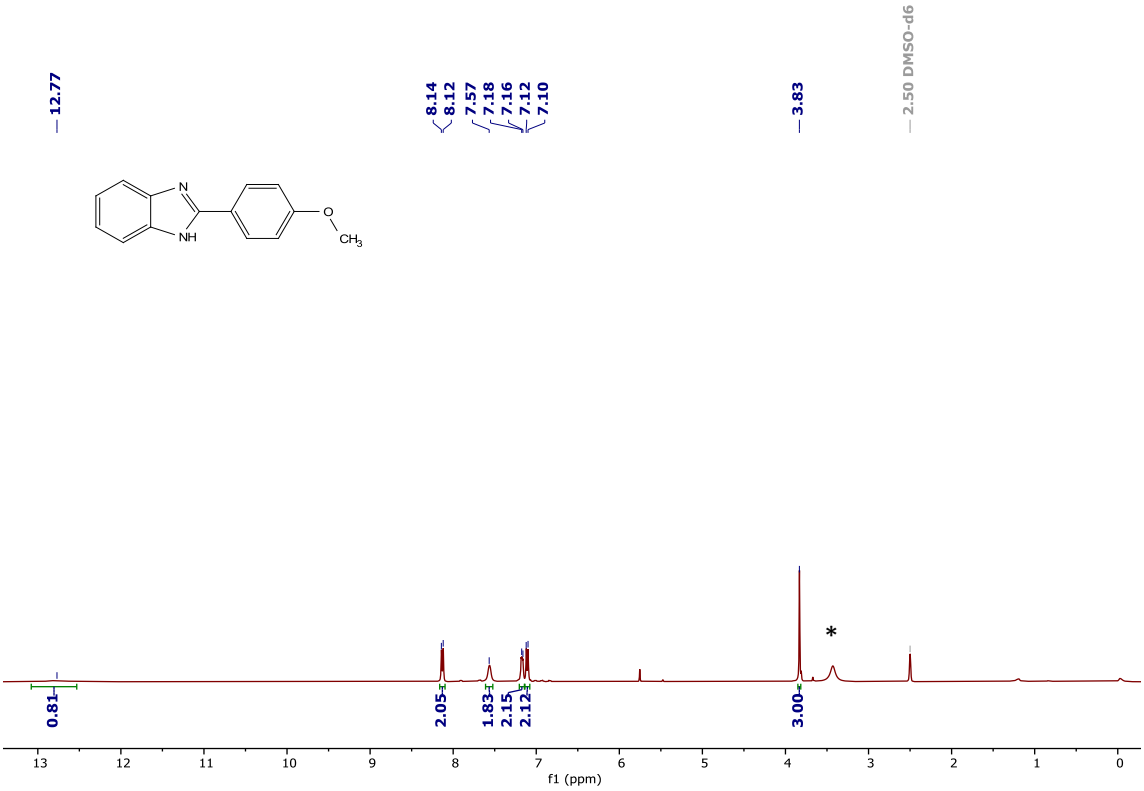


Figure S53. ^{1}H NMR spectrum of **6d** in DMSO-d_6. * indicates the solvent impurity of H_2O.

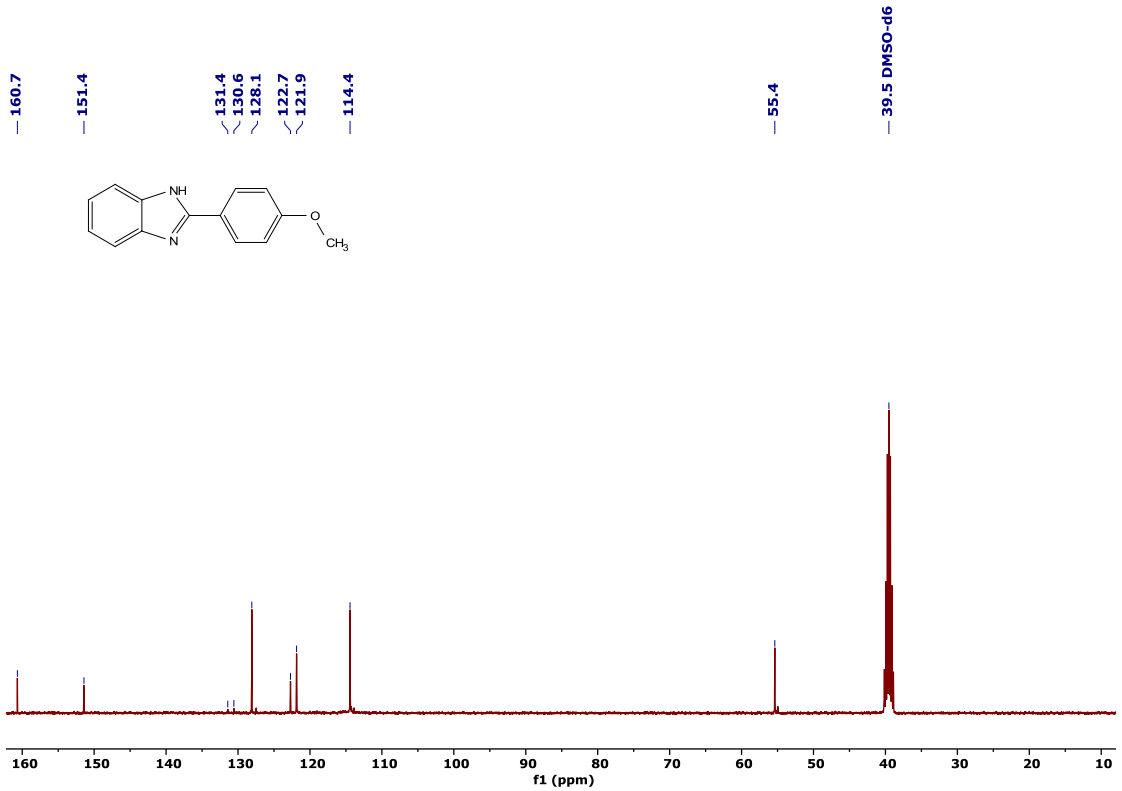


Figure S54. ^{13}C{^{1}H} NMR spectrum of **6d** in DMSO-d_6.

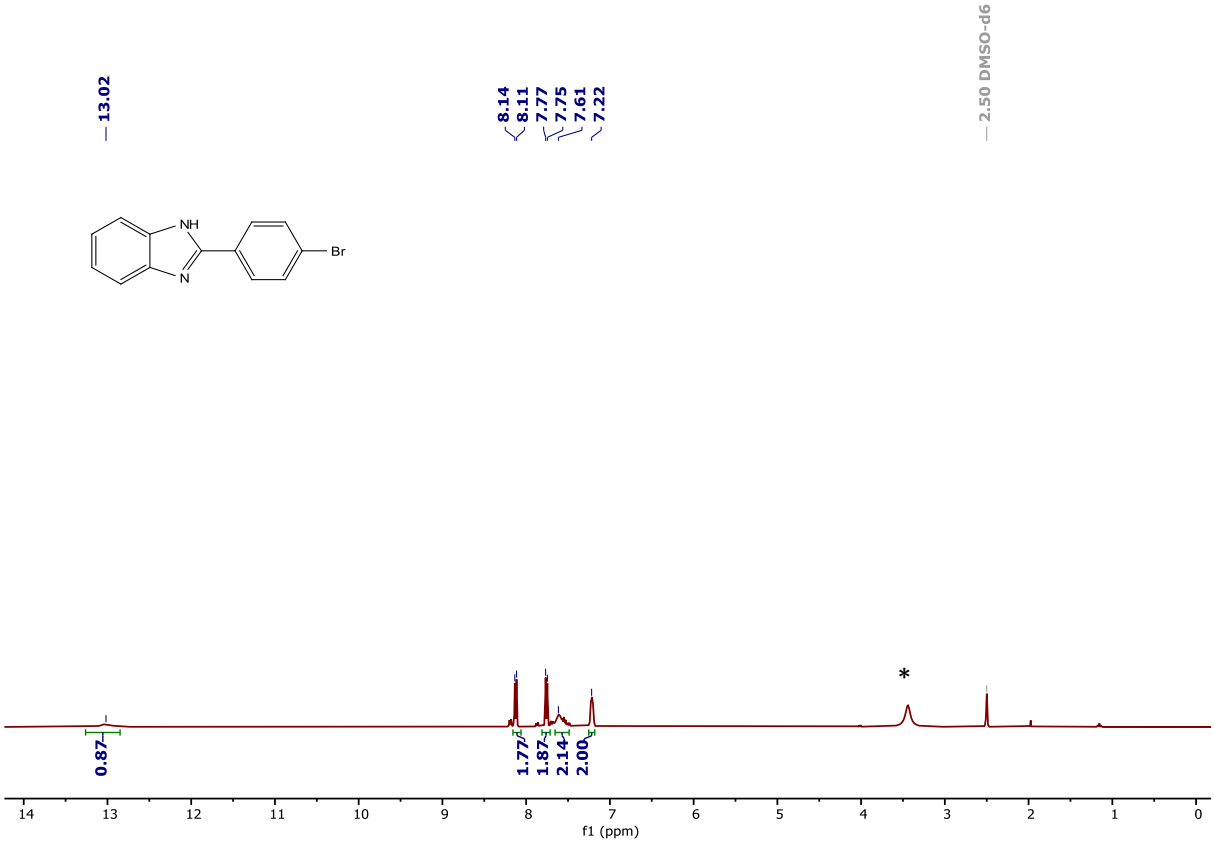


Figure S55. ^{1}H NMR spectrum of **6e** in DMSO-d_6. * indicates the solvent impurity of H_2O.

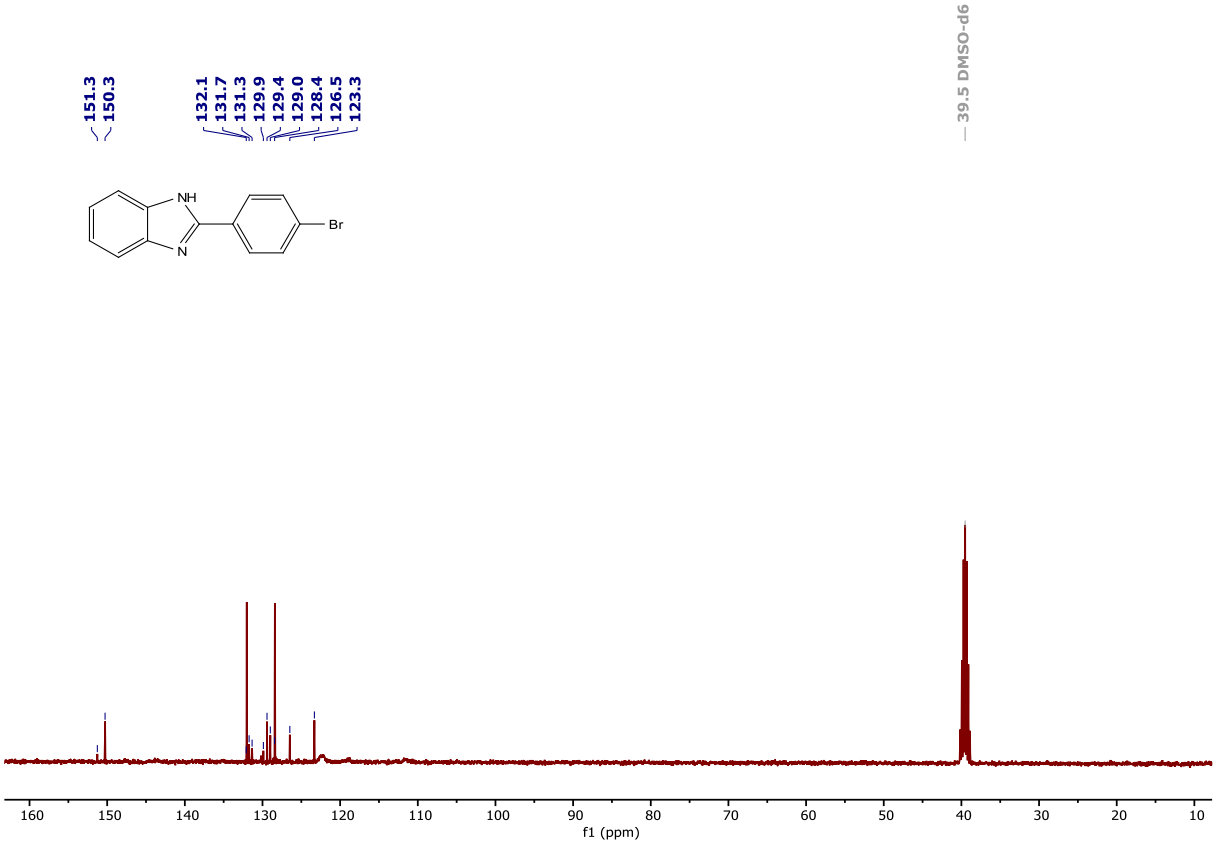


Figure S56. ^{13}C{^{1}H} NMR spectrum of **6e** in DMSO-d_6.

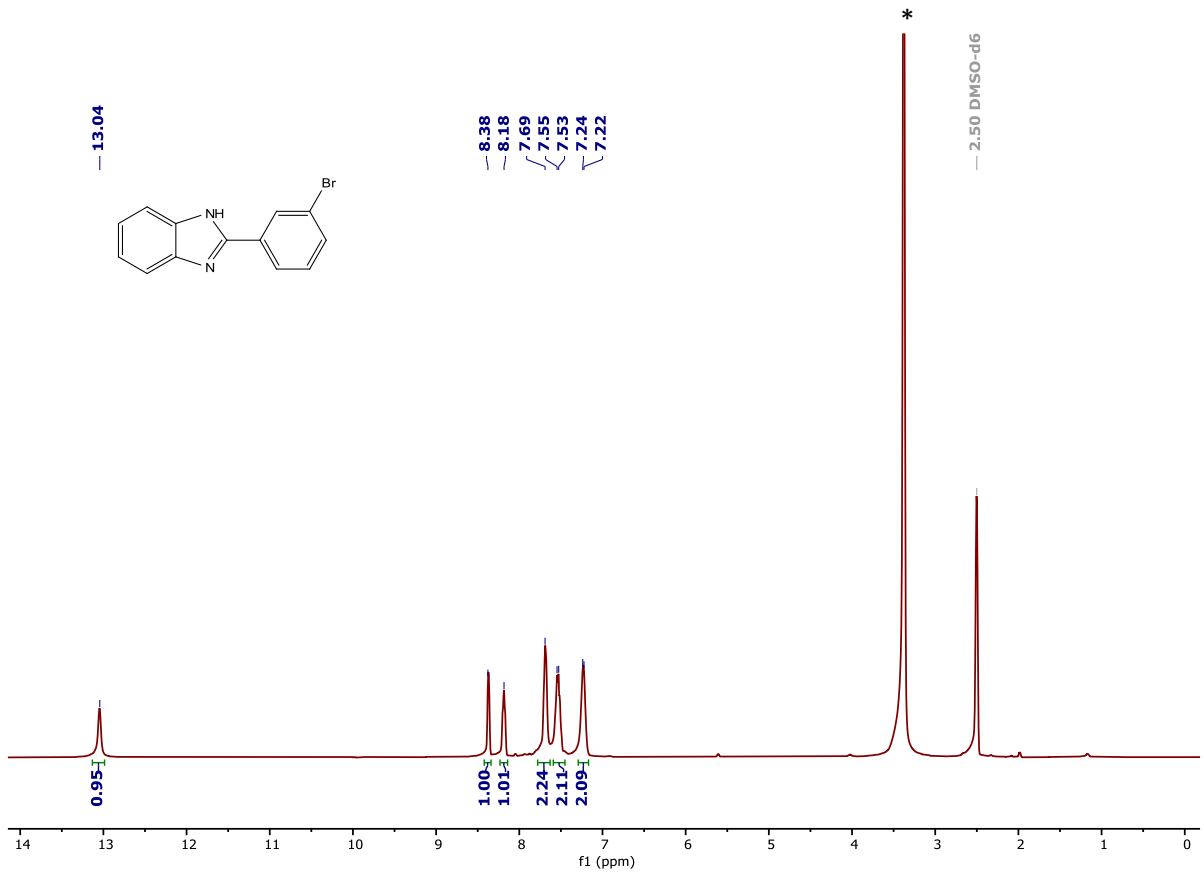


Figure S57. ^{1}H NMR spectrum of **6f** in DMSO-d_6. * indicates the solvent impurity of H_2O.

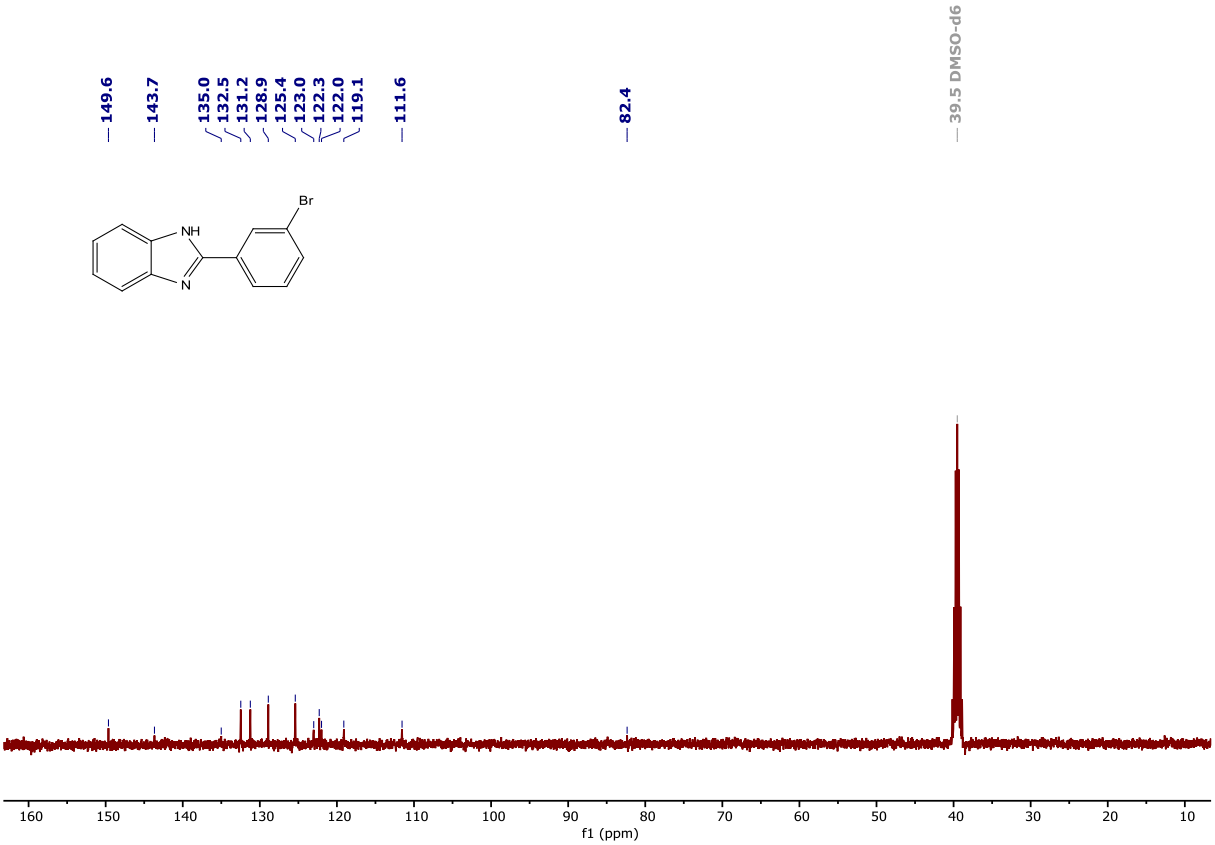


Figure S58. ^{13}C{^{1}H} NMR spectrum of **6f** in DMSO-d_6.

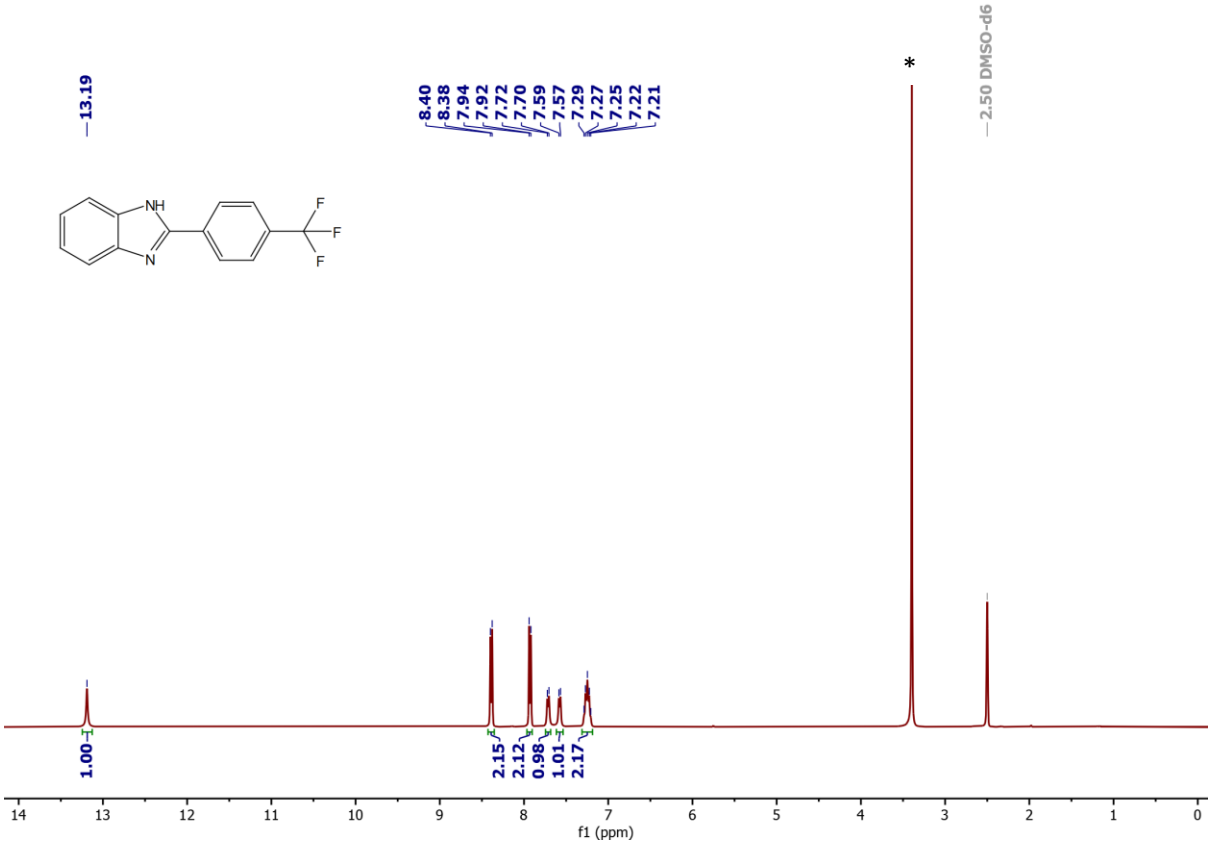


Figure S59. ^{1}H NMR spectrum of **6g** in DMSO-d_6. * indicates the solvent impurity of H_2O.

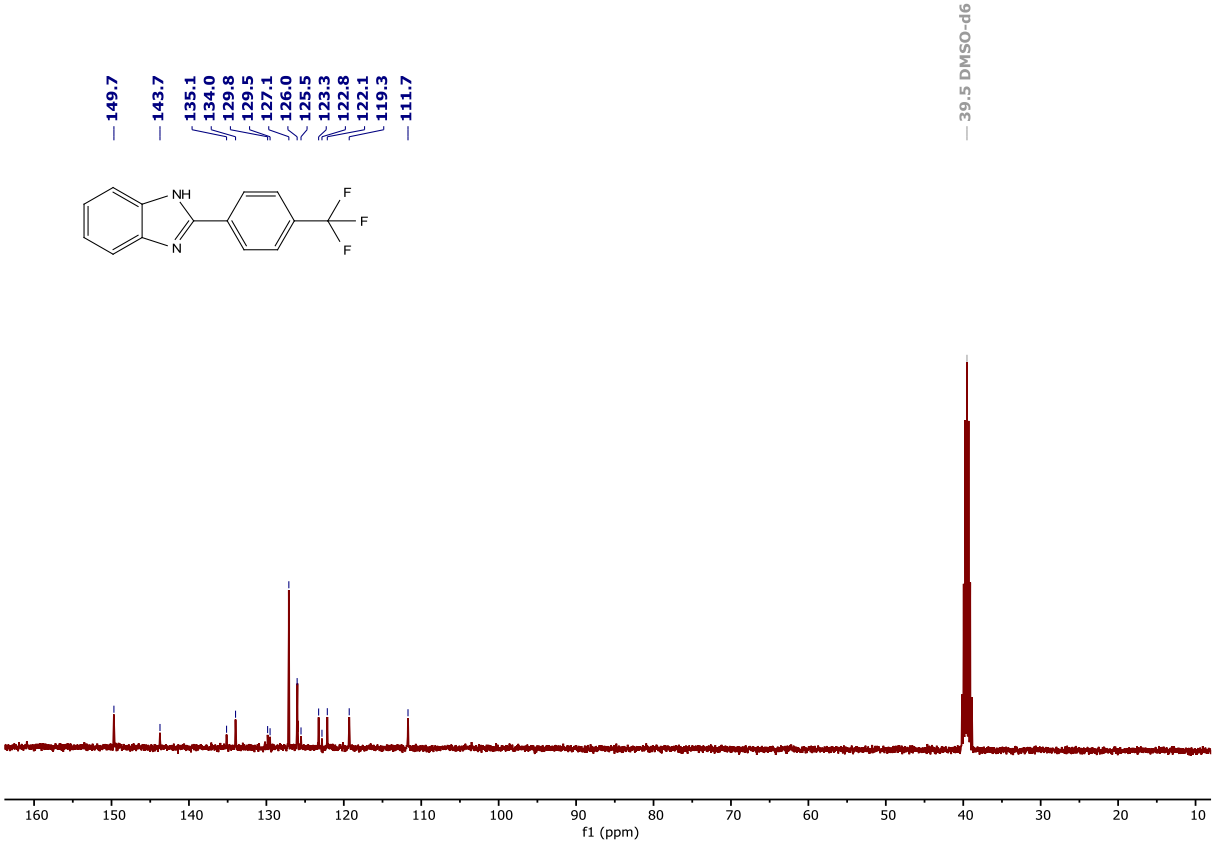


Figure S60. ^{13}C{^{1}H} NMR spectrum of **6g** in DMSO-d_6.

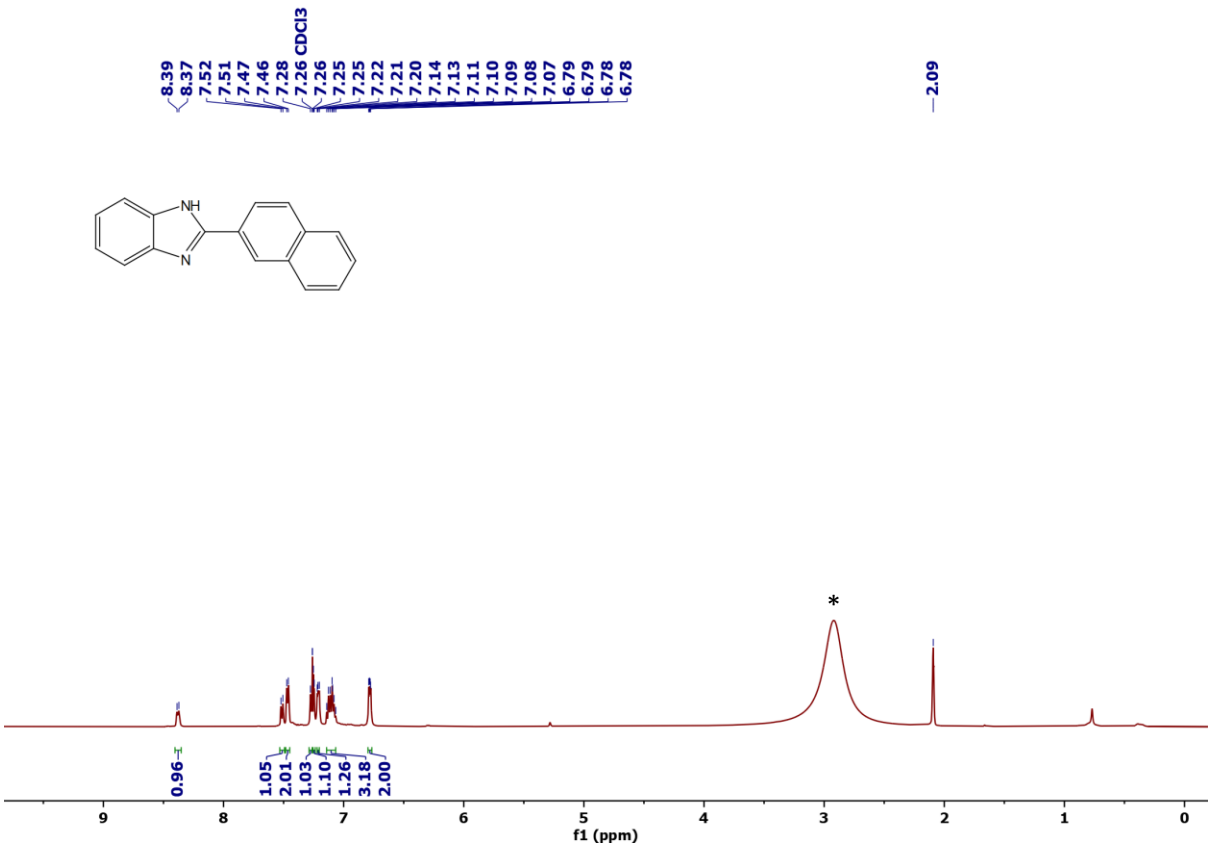


Figure S61. ^{1}H NMR spectrum of **6h** in $CDCl_3$ * indicates the solvent impurity of H_2O.

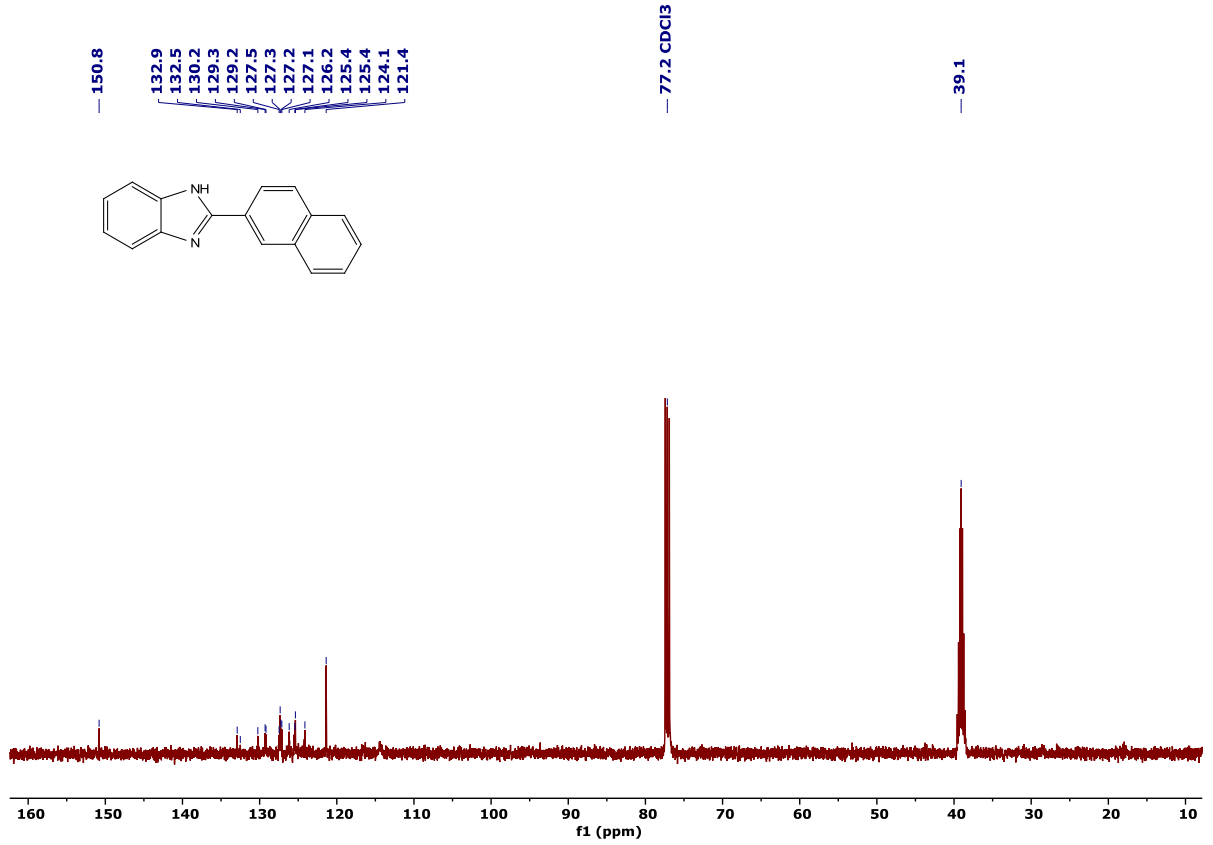


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of **6h** in $CDCl_3$.

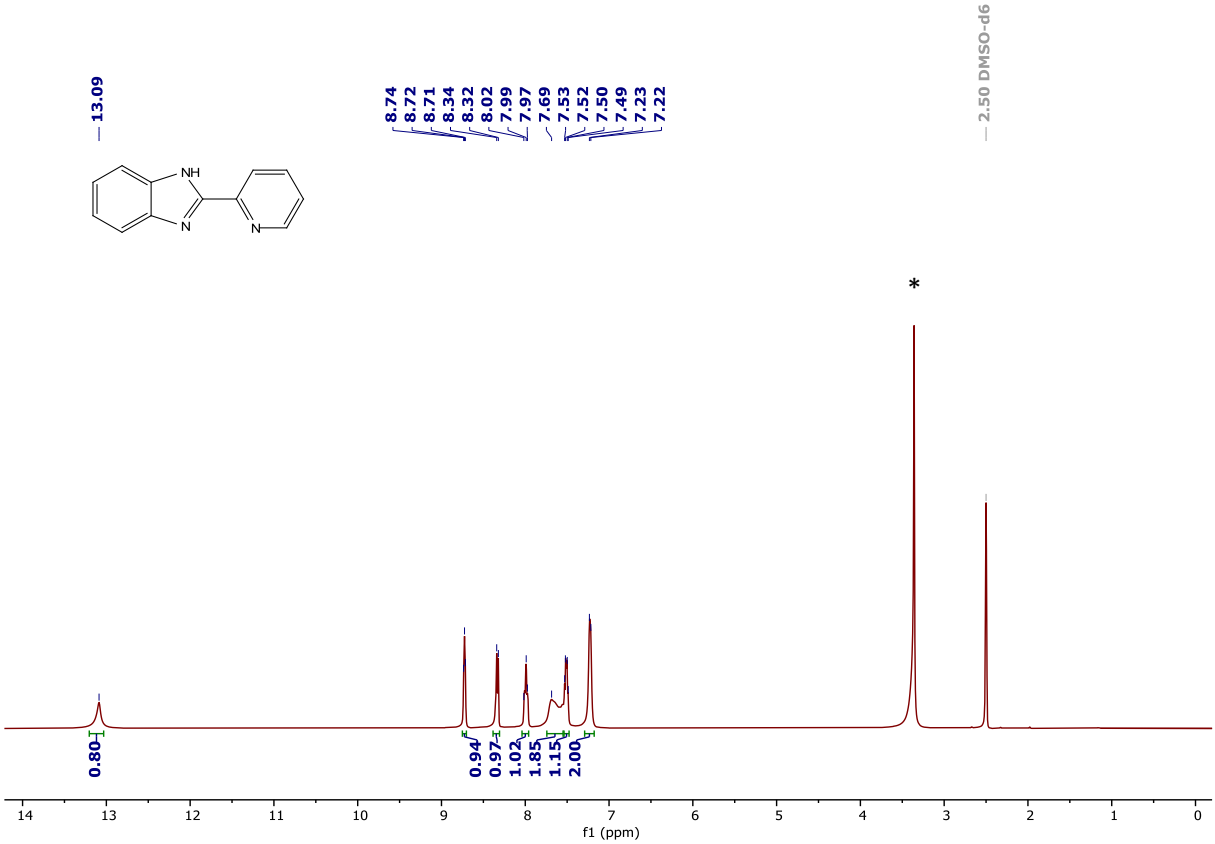


Figure S63. ^{1}H NMR spectrum of **6i** in DMSO-d_6. * indicates the solvent impurity of H_2O.

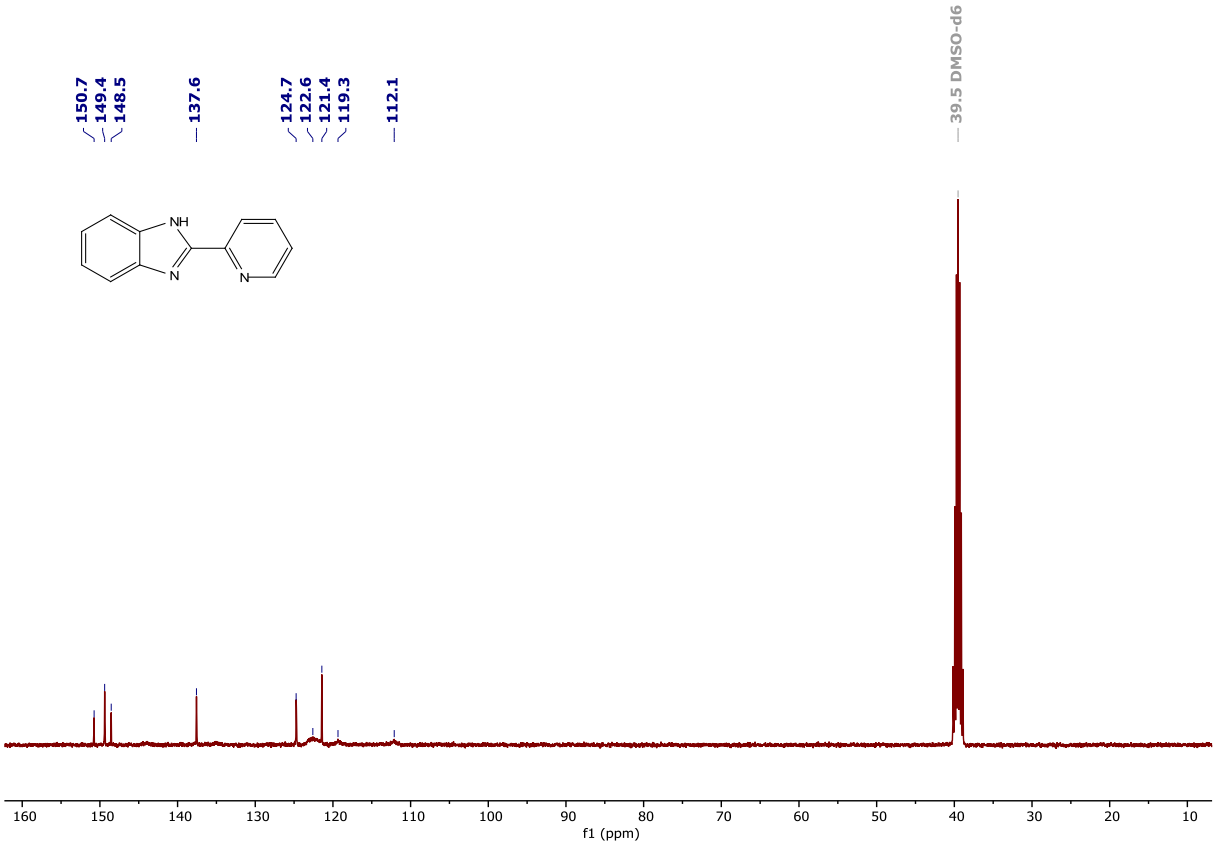


Figure S64. ^{13}C{^{1}H} NMR spectrum of **6i** in DMSO-d_6.

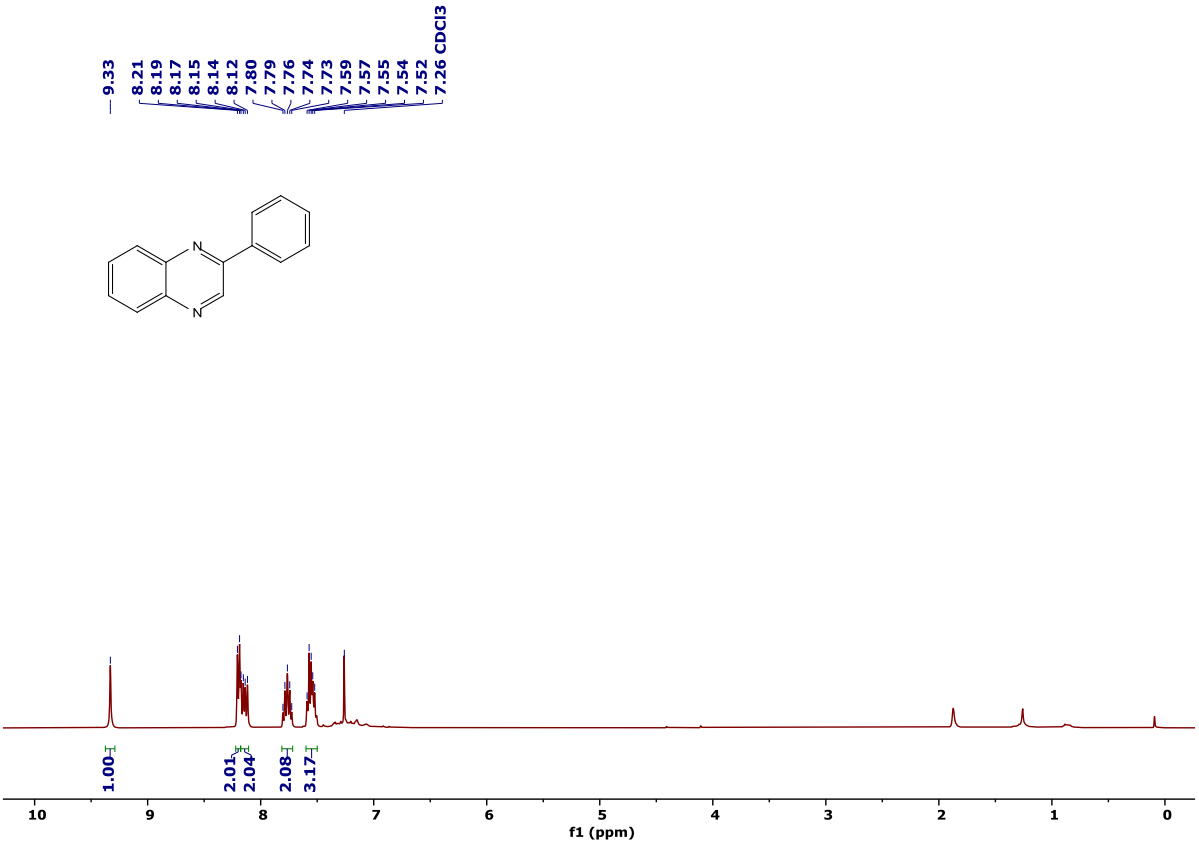


Figure S65. ^{1}H NMR spectrum of **6j** in $CDCl_3$.

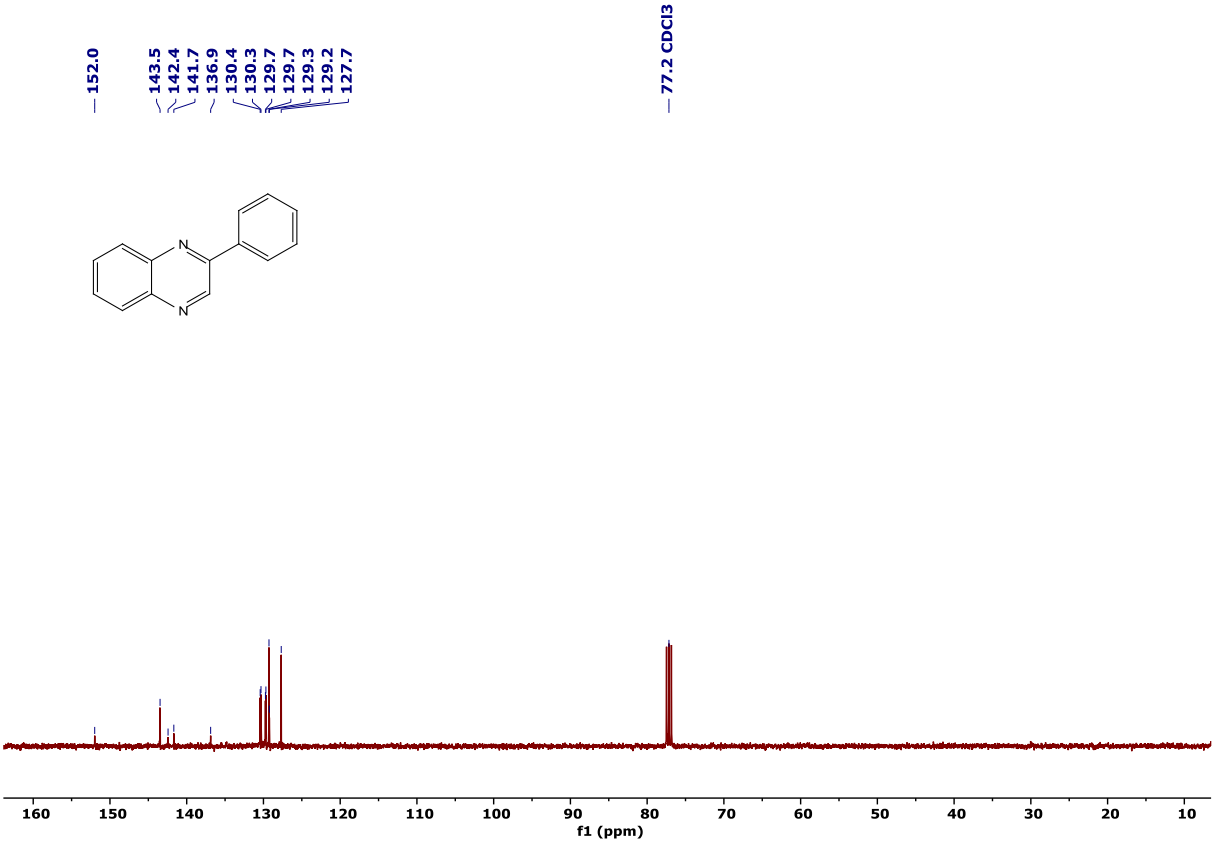


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of **6j** in $CDCl_3$.

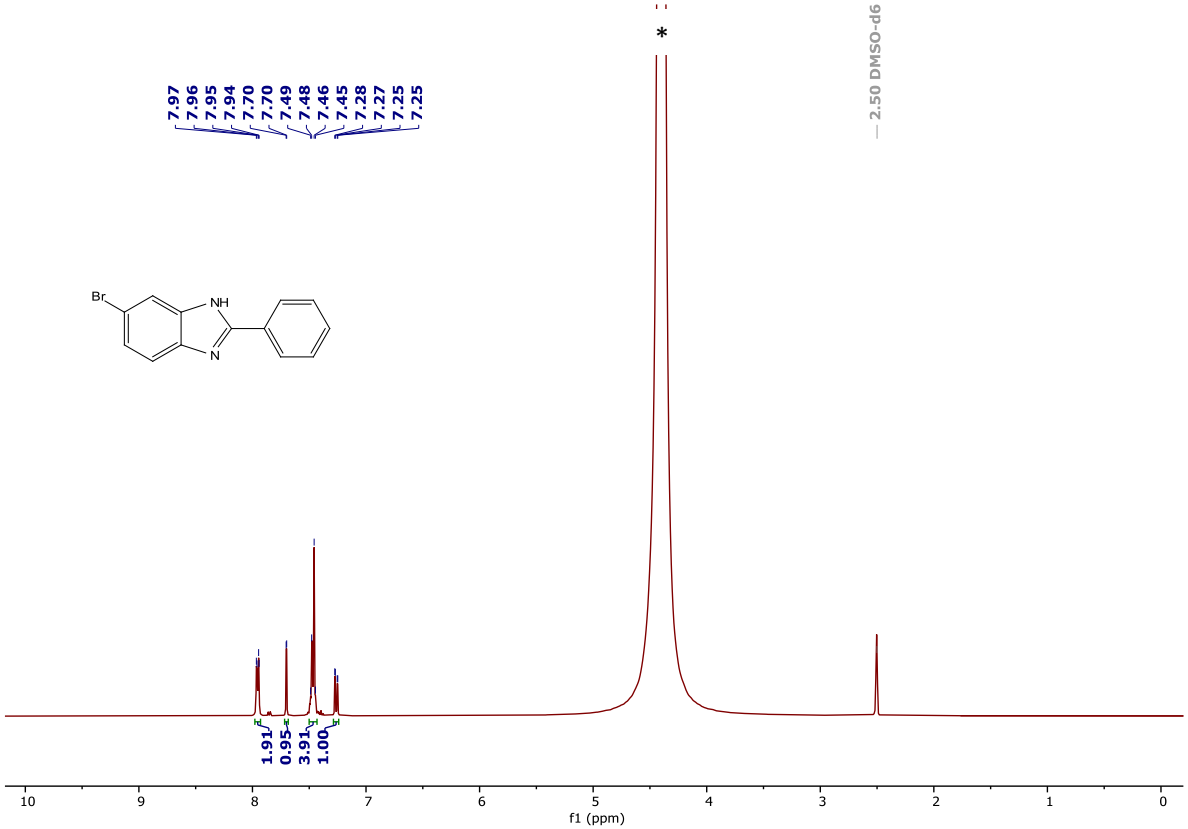


Figure S67. ^{1}H NMR spectrum of **6k** in DMSO-d_6. * indicates the solvent impurity of H_2O.

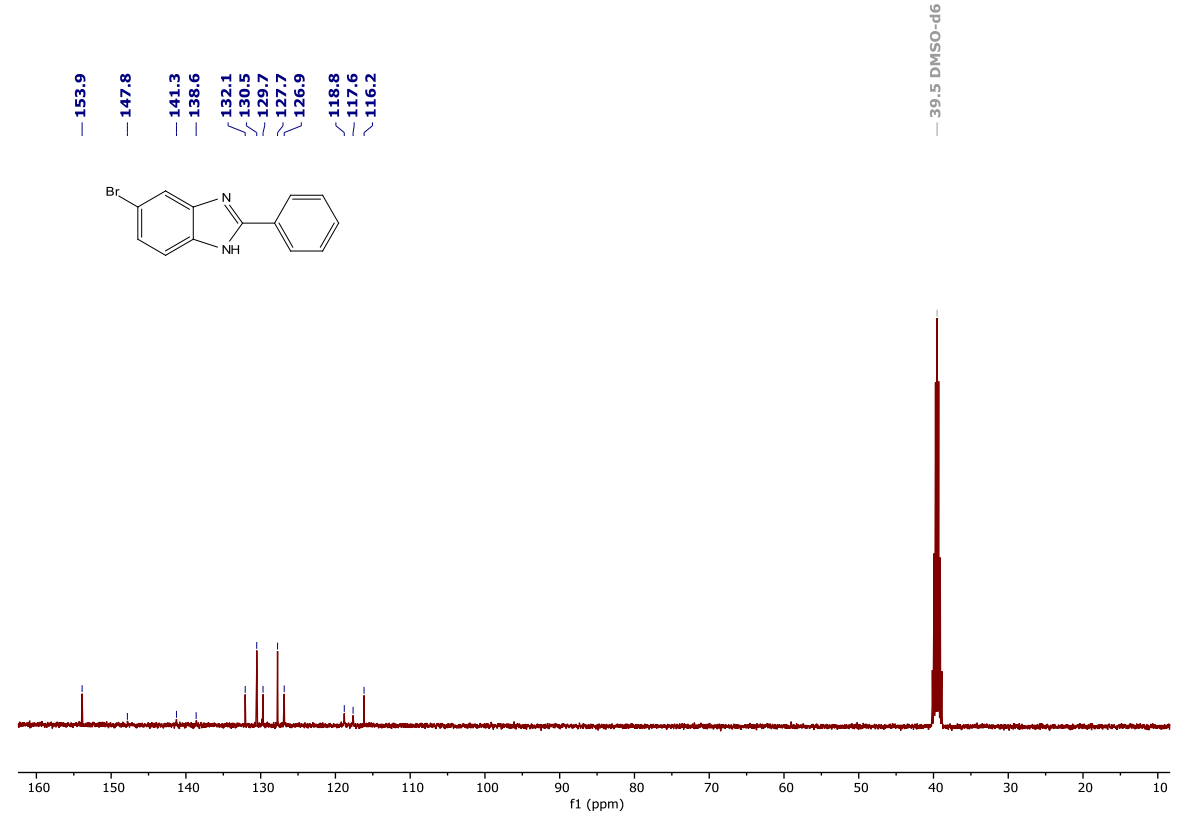


Figure S68. ^{13}C{^{1}H} NMR spectrum of **6k** in DMSO-d_6.

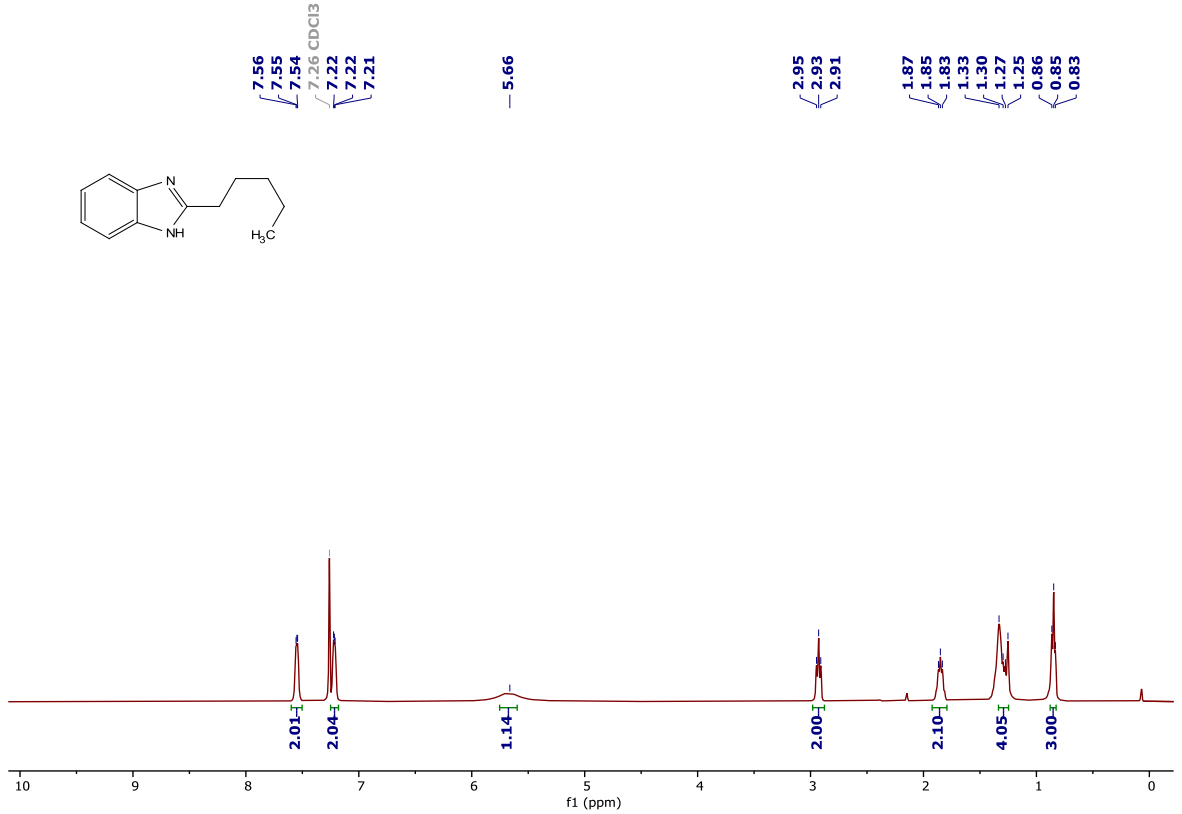


Figure S69. ^{1}H NMR spectrum of **6l** in $CDCl_3$.

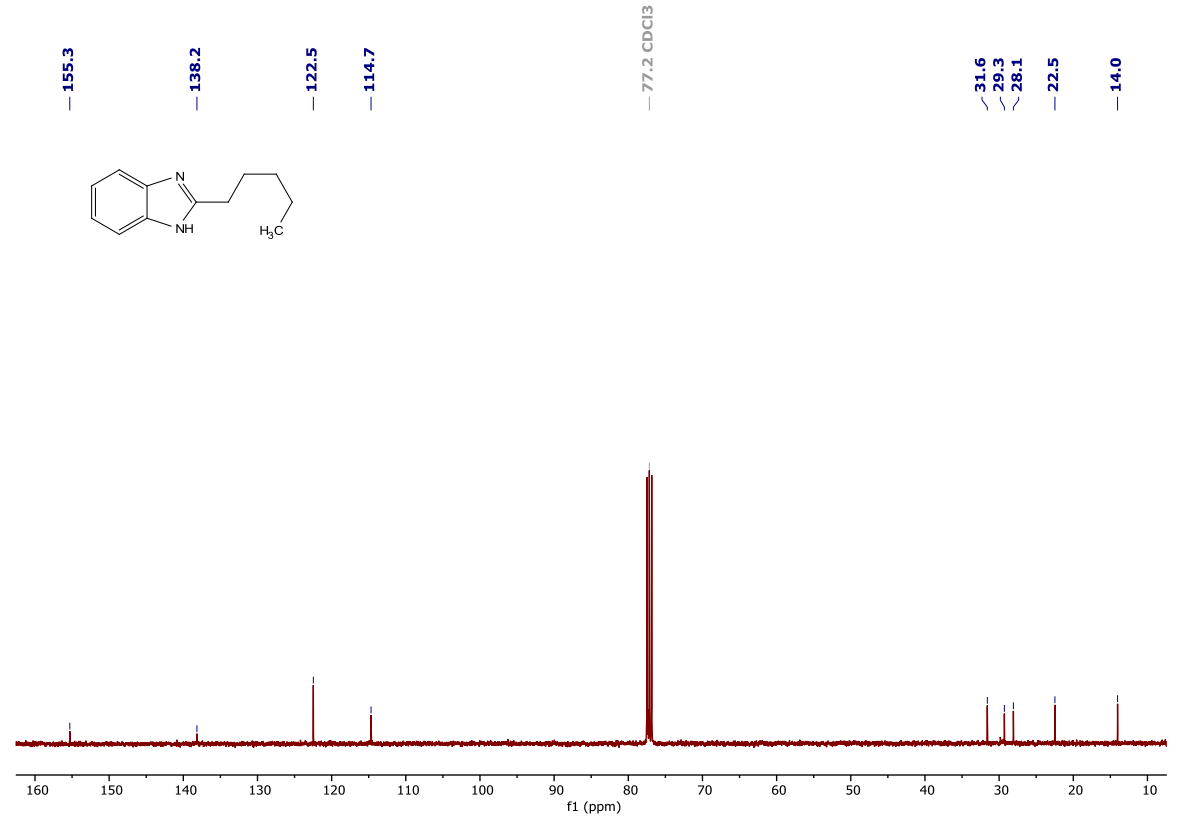


Figure S70. ^{13}C{^{1}H} NMR spectrum of **6l** in $CDCl_3$.

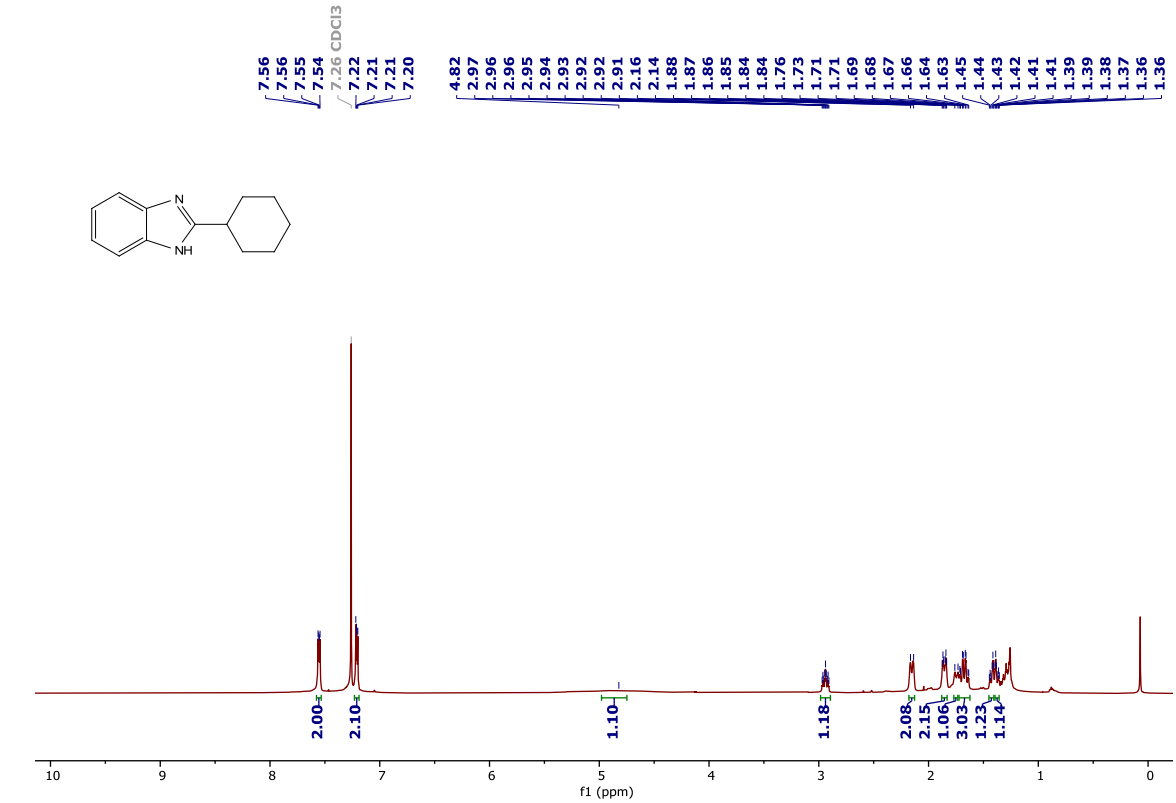


Figure S71. ^{1}H NMR spectrum of **6m** in $CDCl_3$.

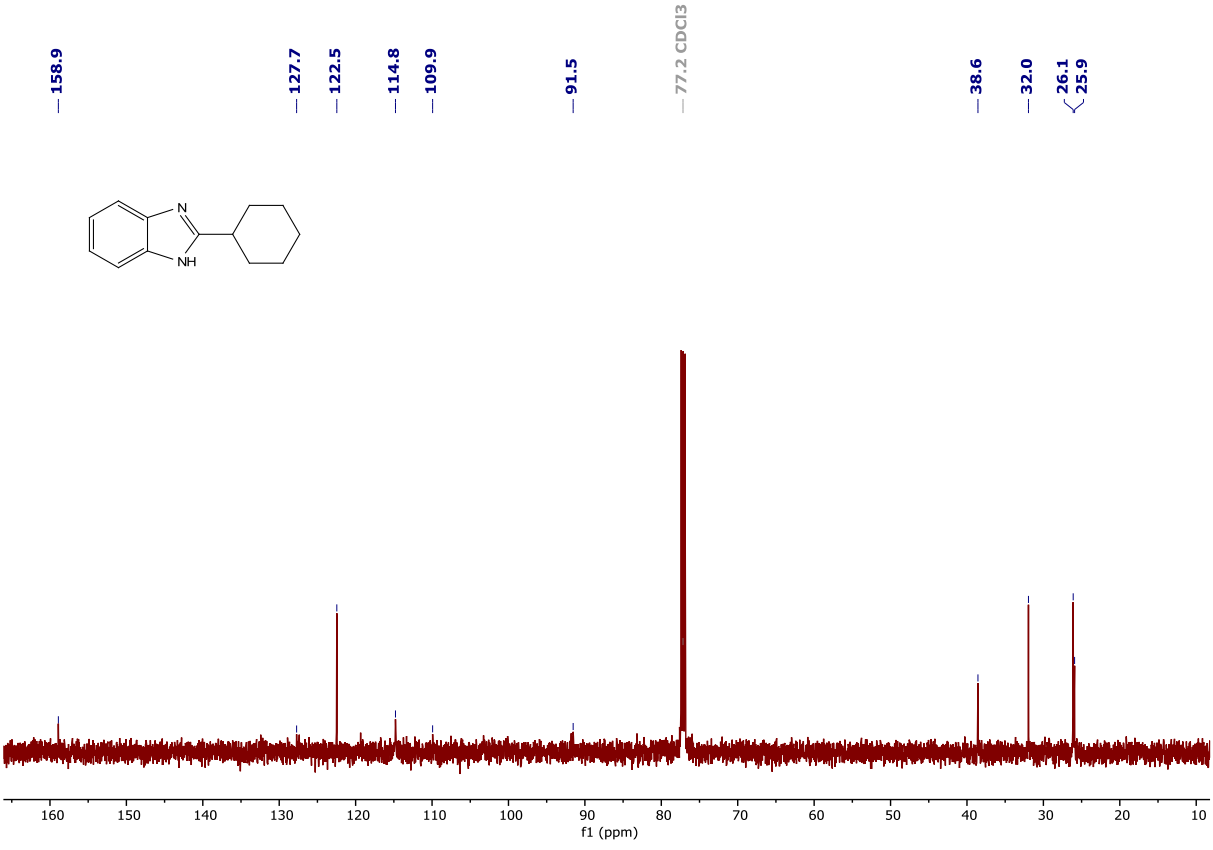


Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum of **6m** in $CDCl_3$.

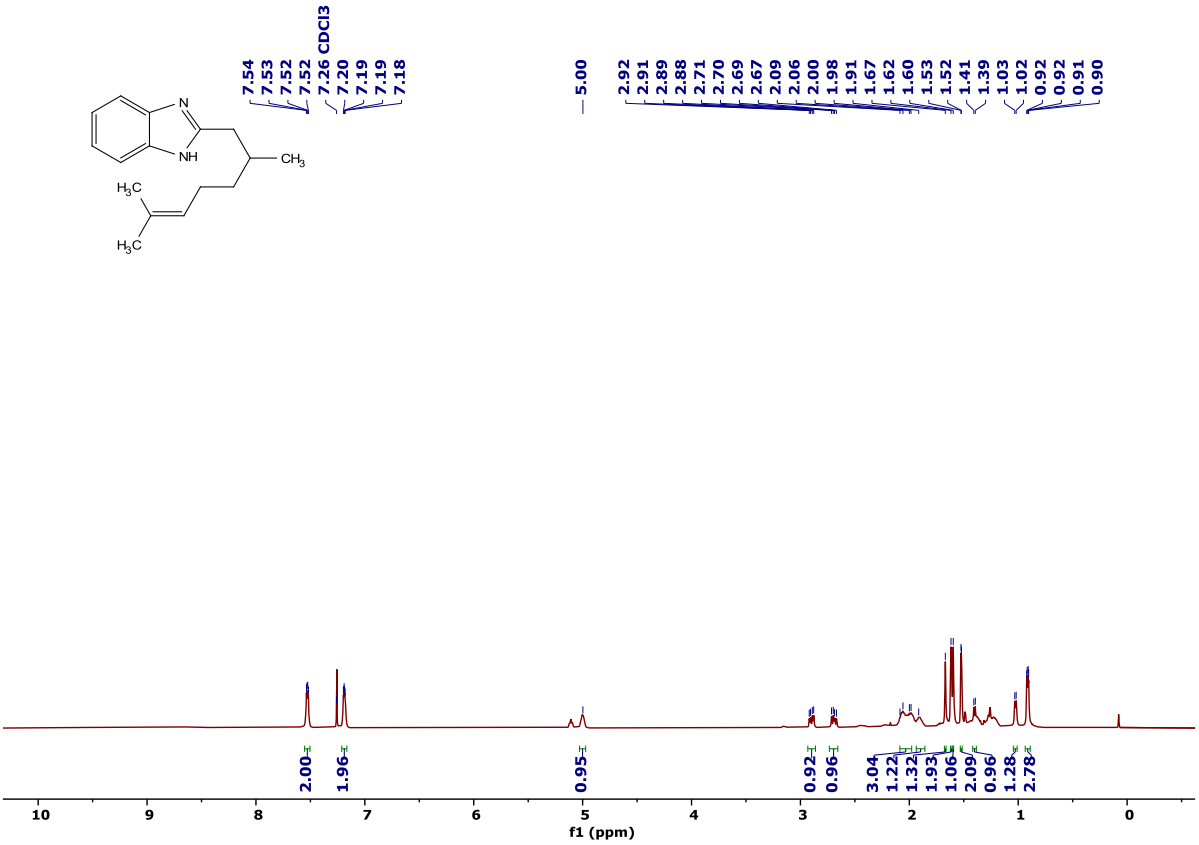


Figure S73. ^{1}H NMR spectrum of **6n** in $CDCl_3$.

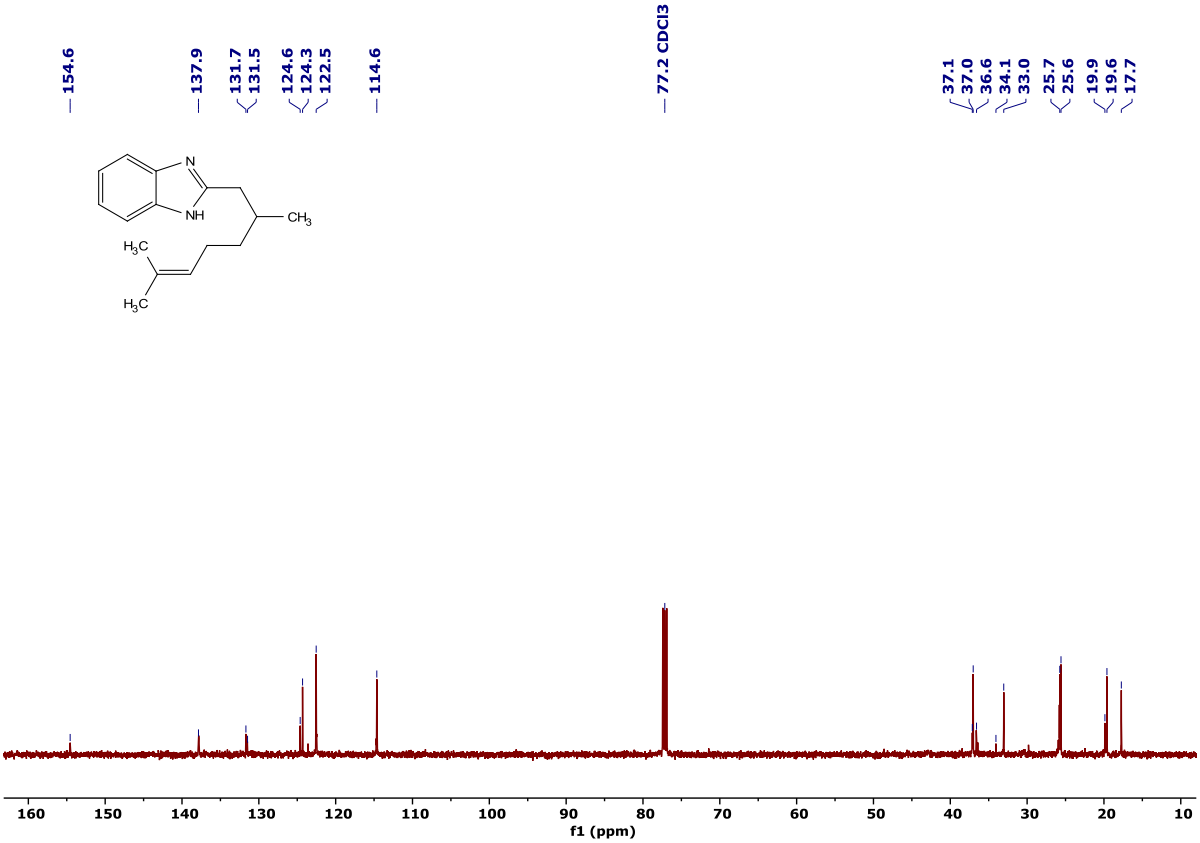


Figure S74. ^{13}C{^{1}H} NMR spectrum of **6n** in $CDCl_3$.

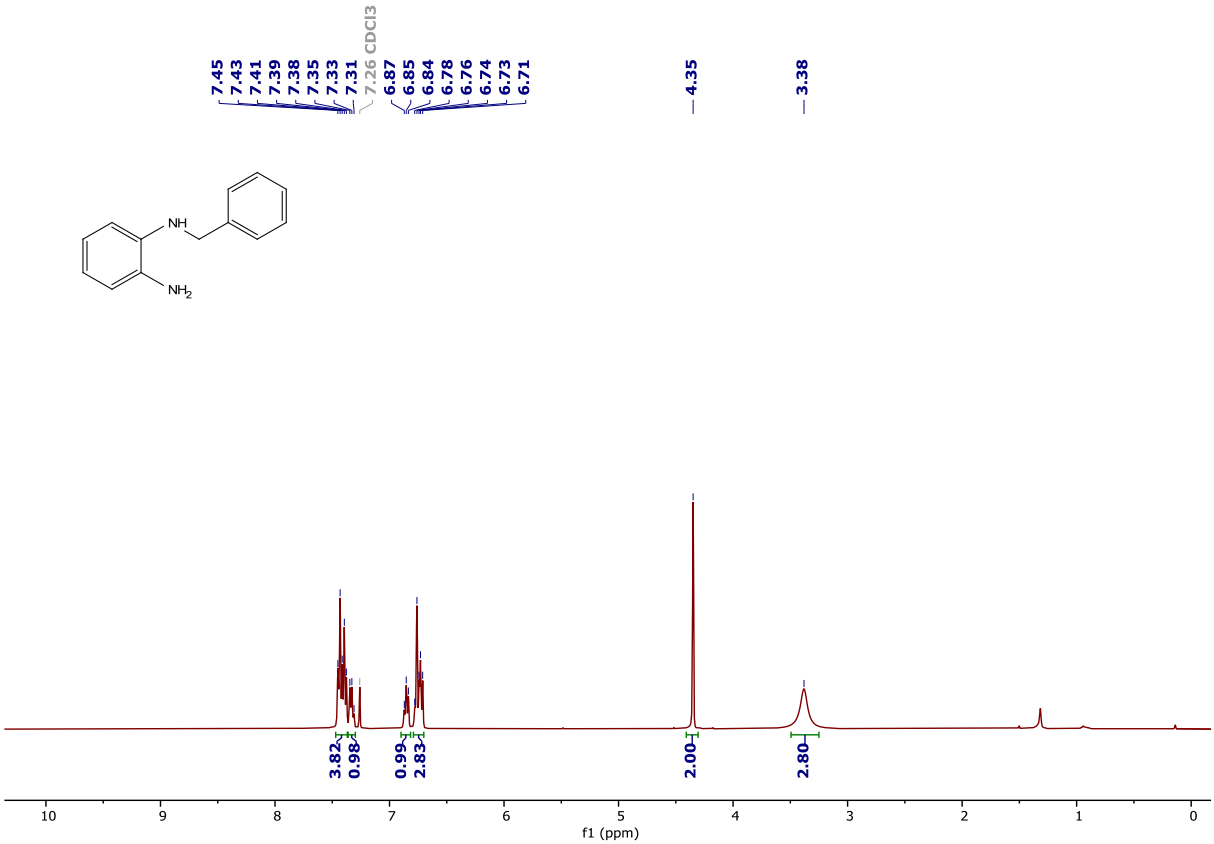


Figure S75. ^{1}H NMR spectrum of **7a** in $CDCl_3$.

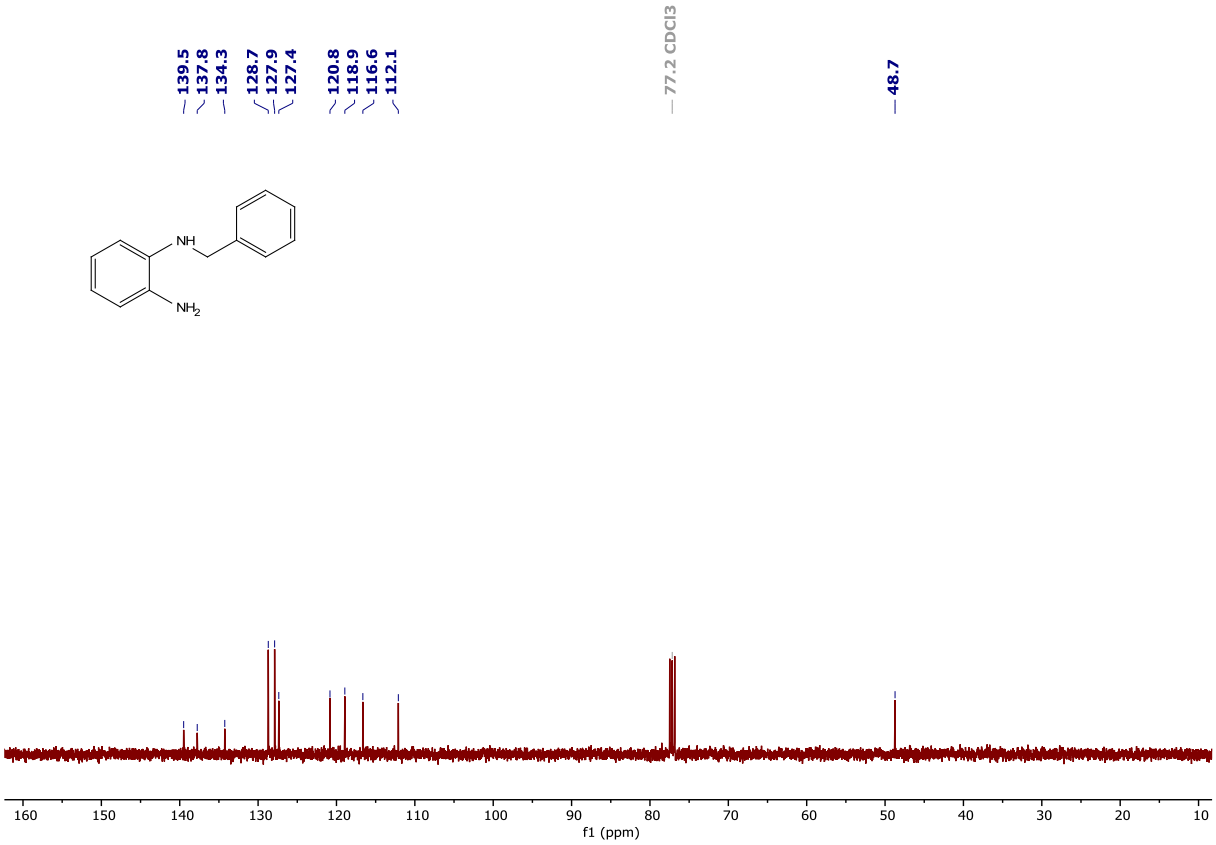


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of **7a** in $CDCl_3$.

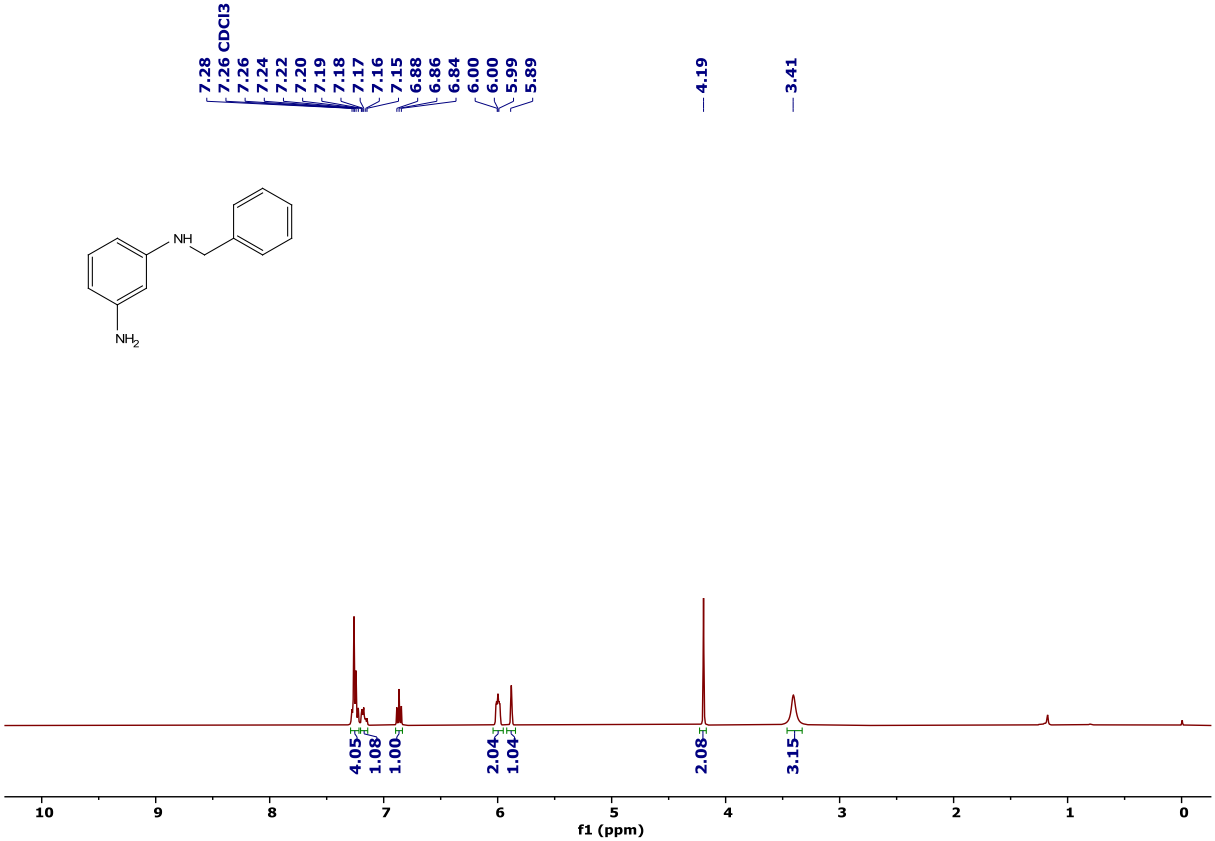


Figure S77. ^{1}H NMR spectrum of **7b** in $CDCl_3$.

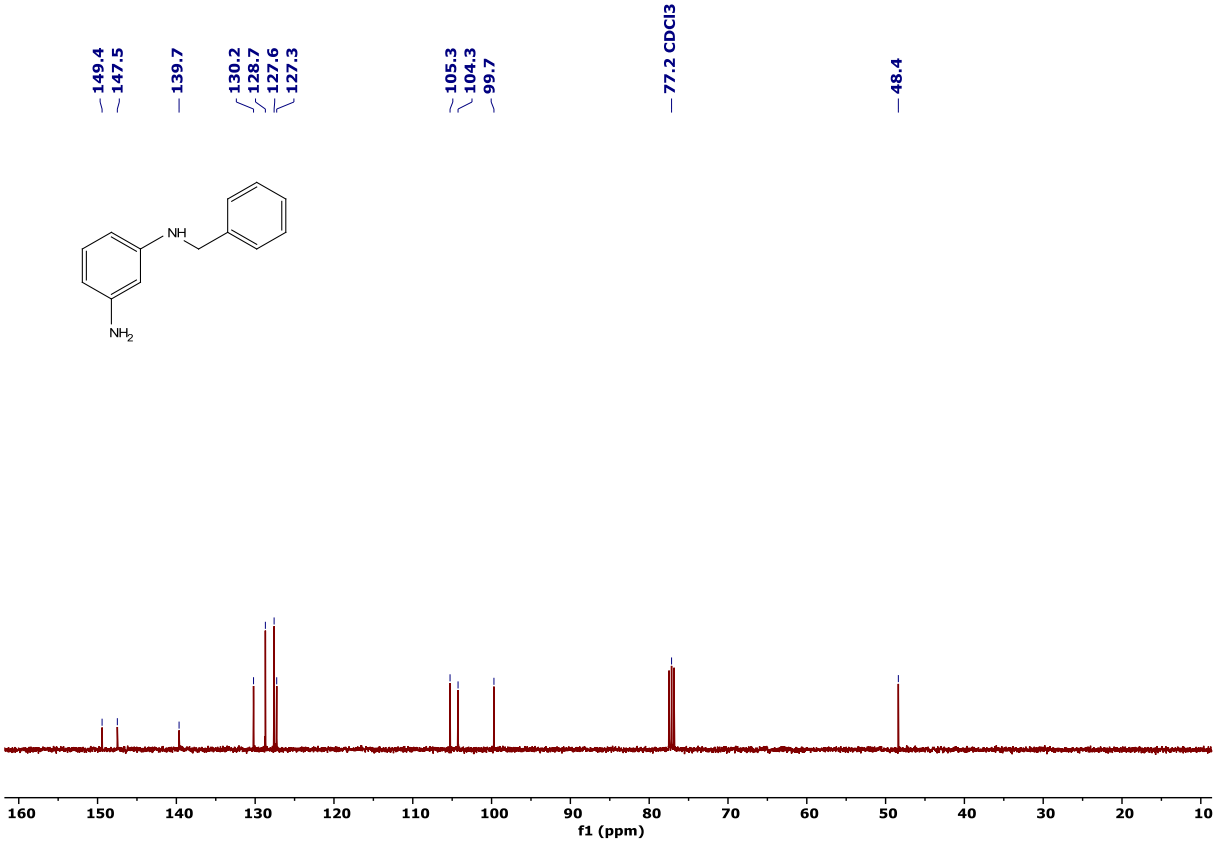


Figure S78. ^{13}C{^{1}H} NMR spectrum of **7b** in $CDCl_3$.

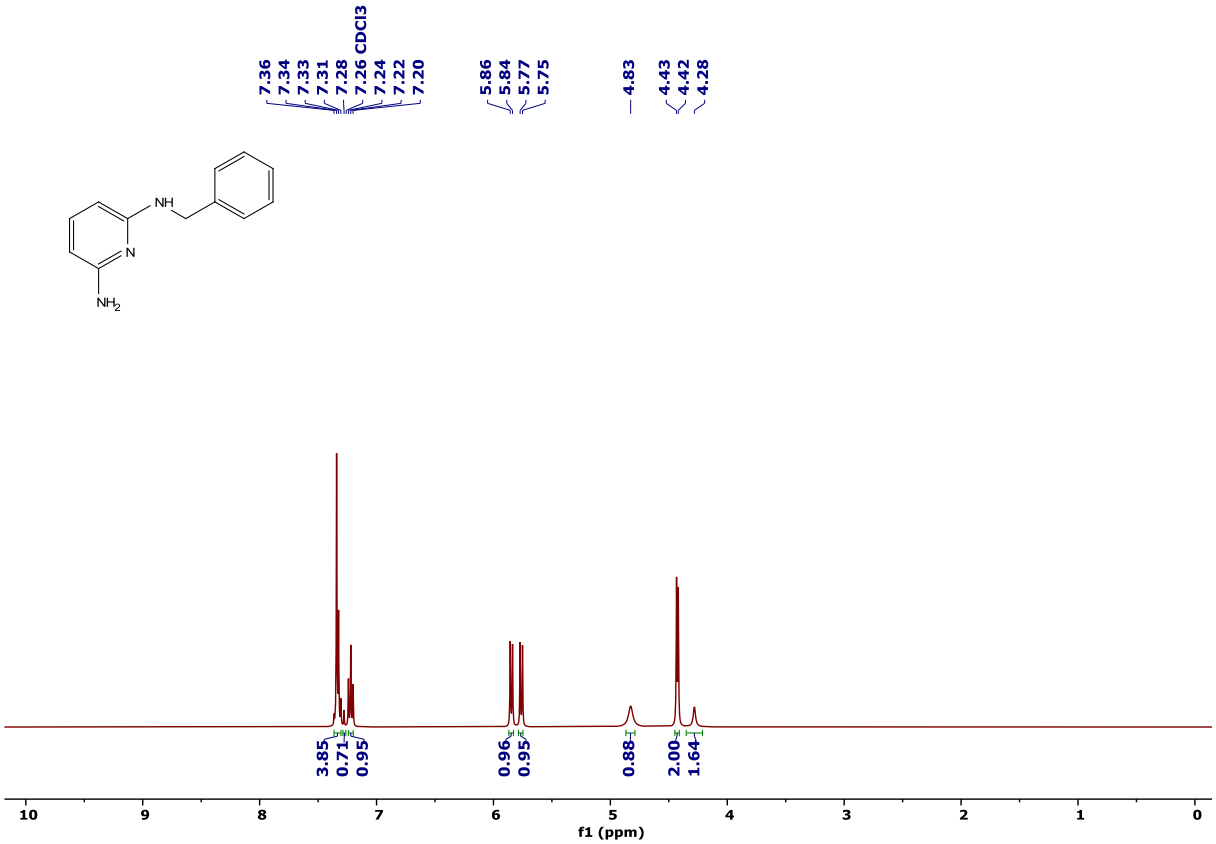


Figure S79. ^{1}H NMR spectrum of **7c** in $CDCl_3$.

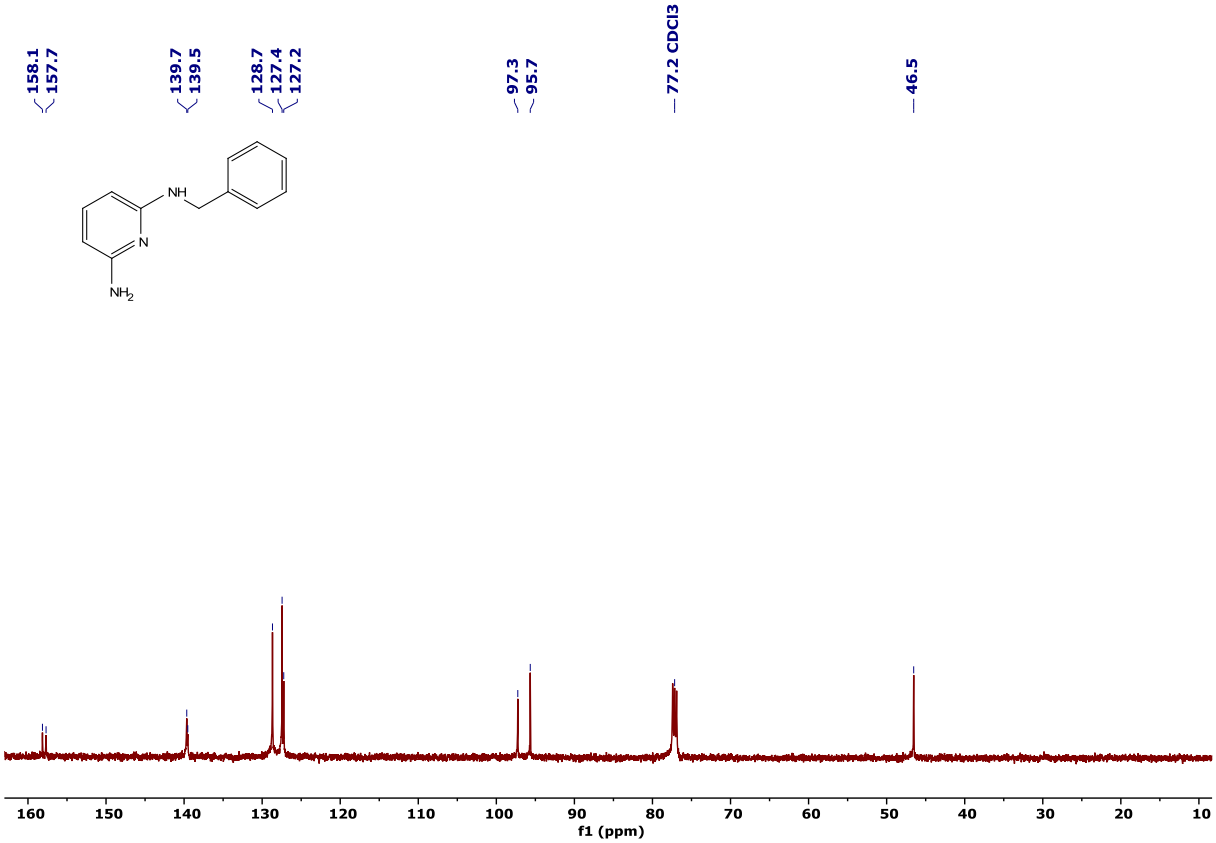


Figure S80. $^{13}C\{^{1}H\}$ NMR spectrum of **7c** in $CDCl_3$.

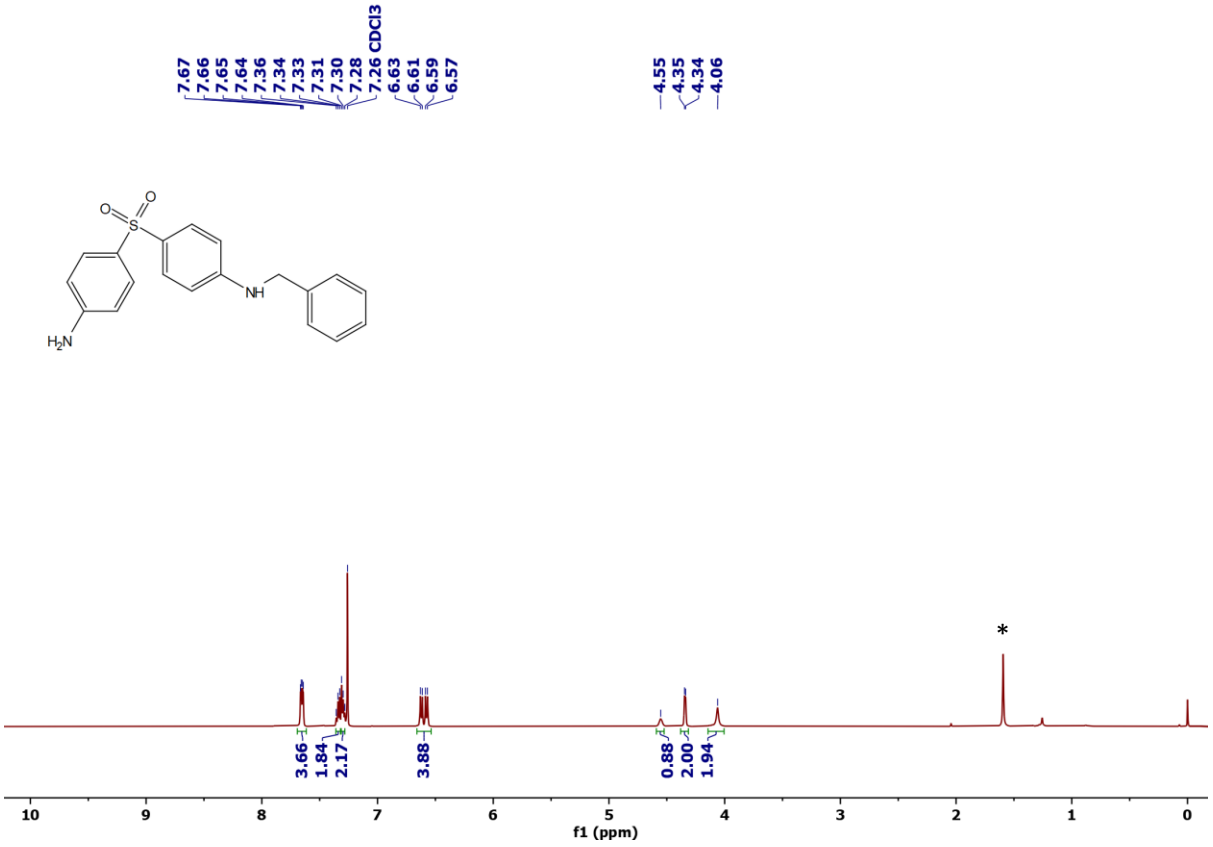


Figure S81. ^{1}H NMR spectrum of **7d** in $CDCl_3$. * indicates the solvent impurity of H_2O.

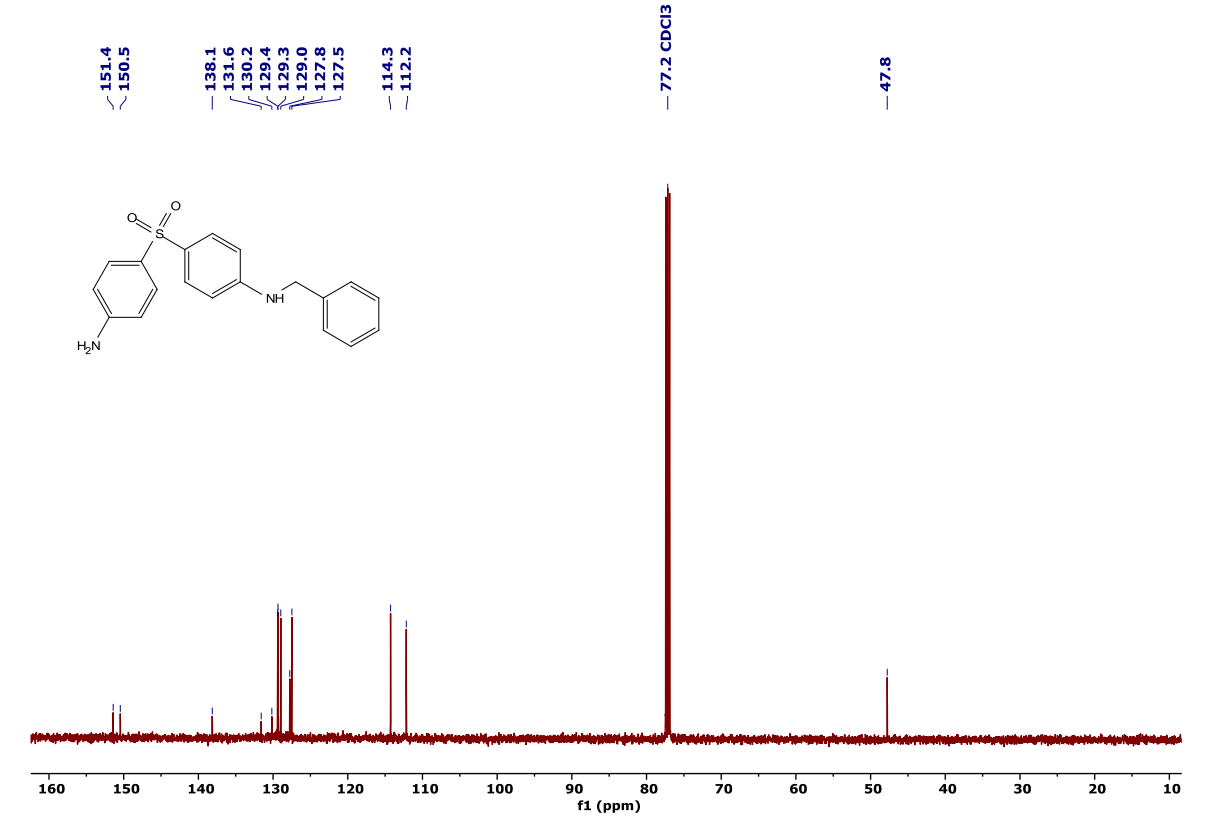


Figure S82. $^{13}C\{^{1}H\}$ NMR spectrum of **7d** in $CDCl_3$.

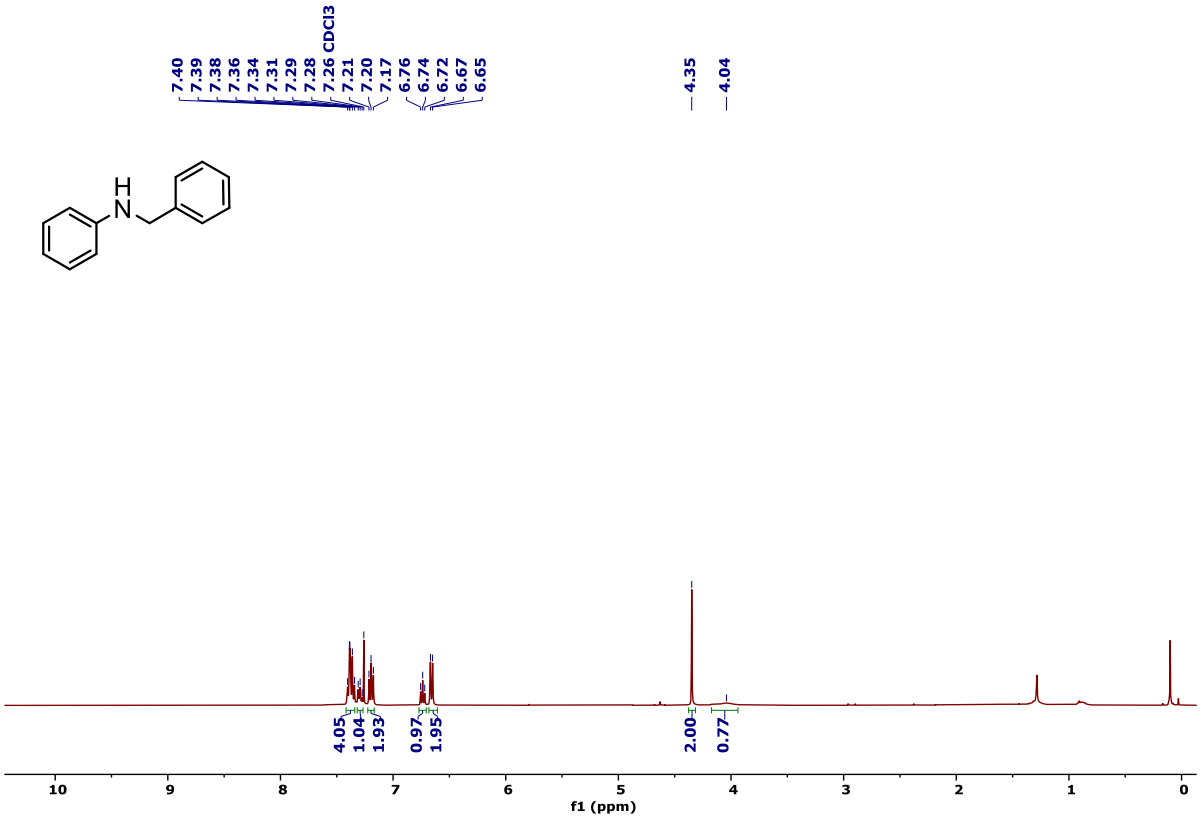


Figure S83. ^{1}H NMR spectrum of **9a** in $CDCl_3$.

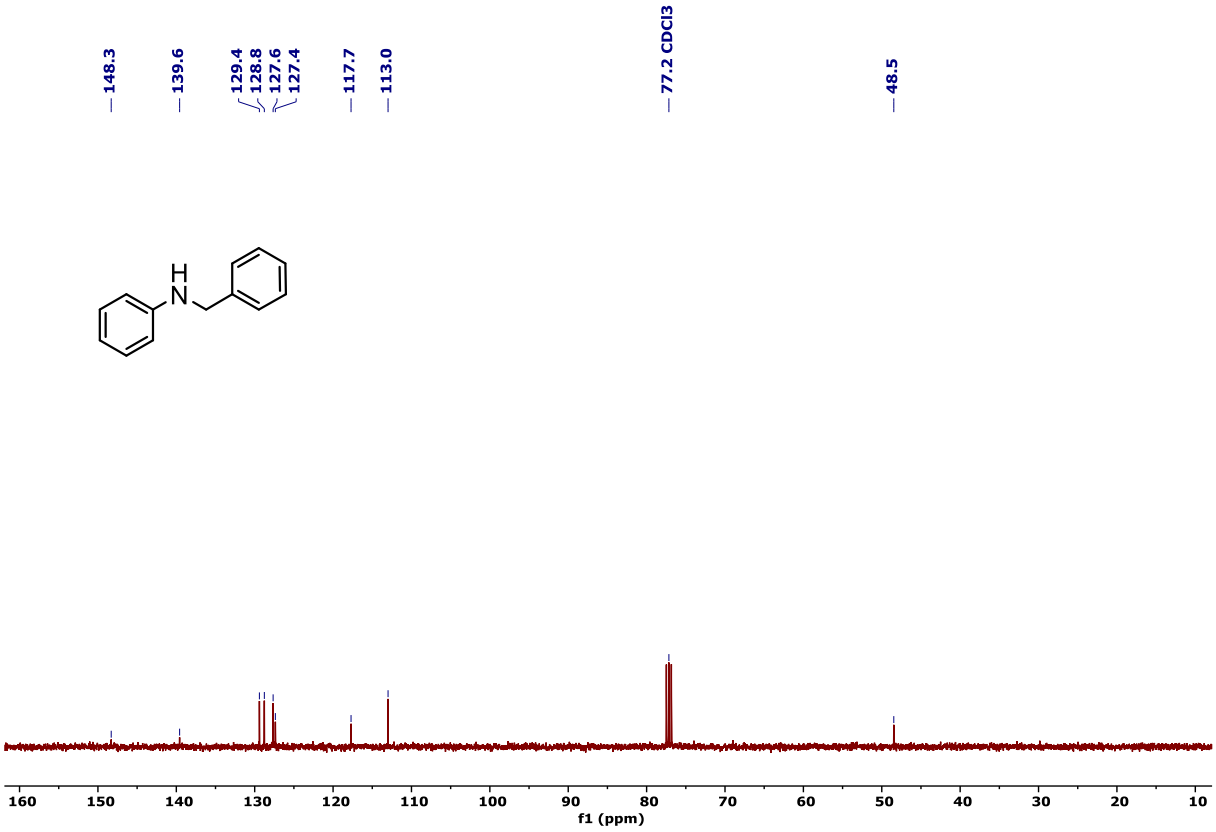


Figure S84. ^{13}C{^{1}H} NMR spectrum of **9a** in $CDCl_3$.

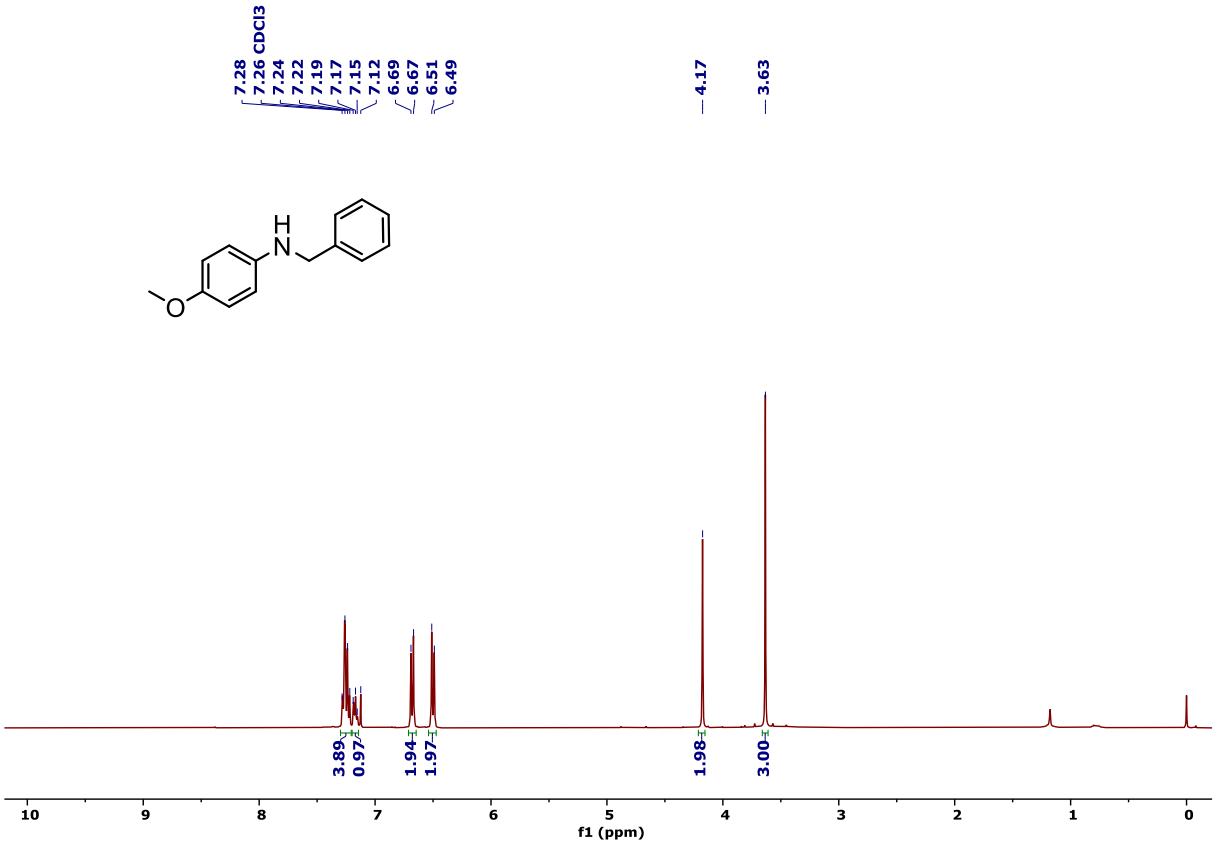


Figure S85. ^{1}H NMR spectrum of **9b** in $CDCl_3$.

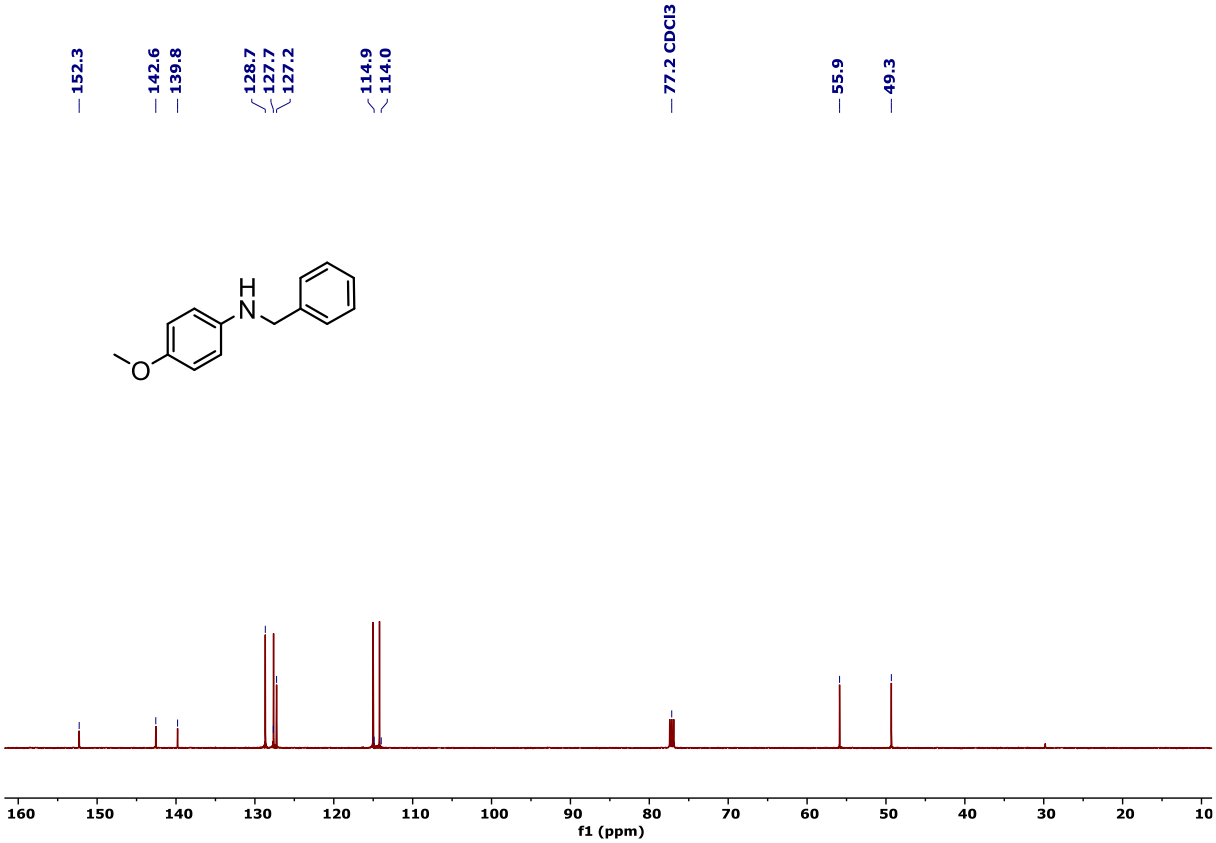


Figure S86. $^{13}C\{^{1}H\}$ NMR spectrum of **9b** in $CDCl_3$.

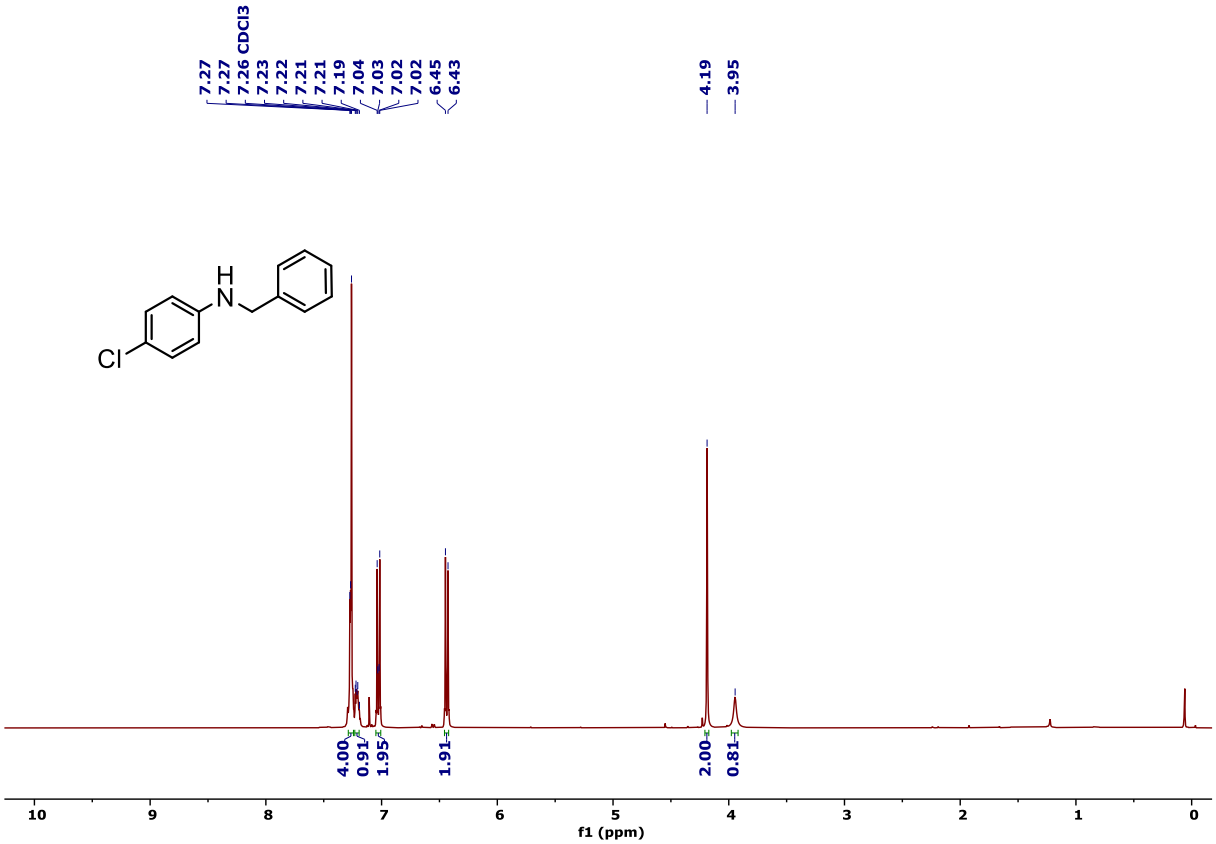


Figure S87. ^{1}H NMR spectrum of **9c** in $CDCl_3$.

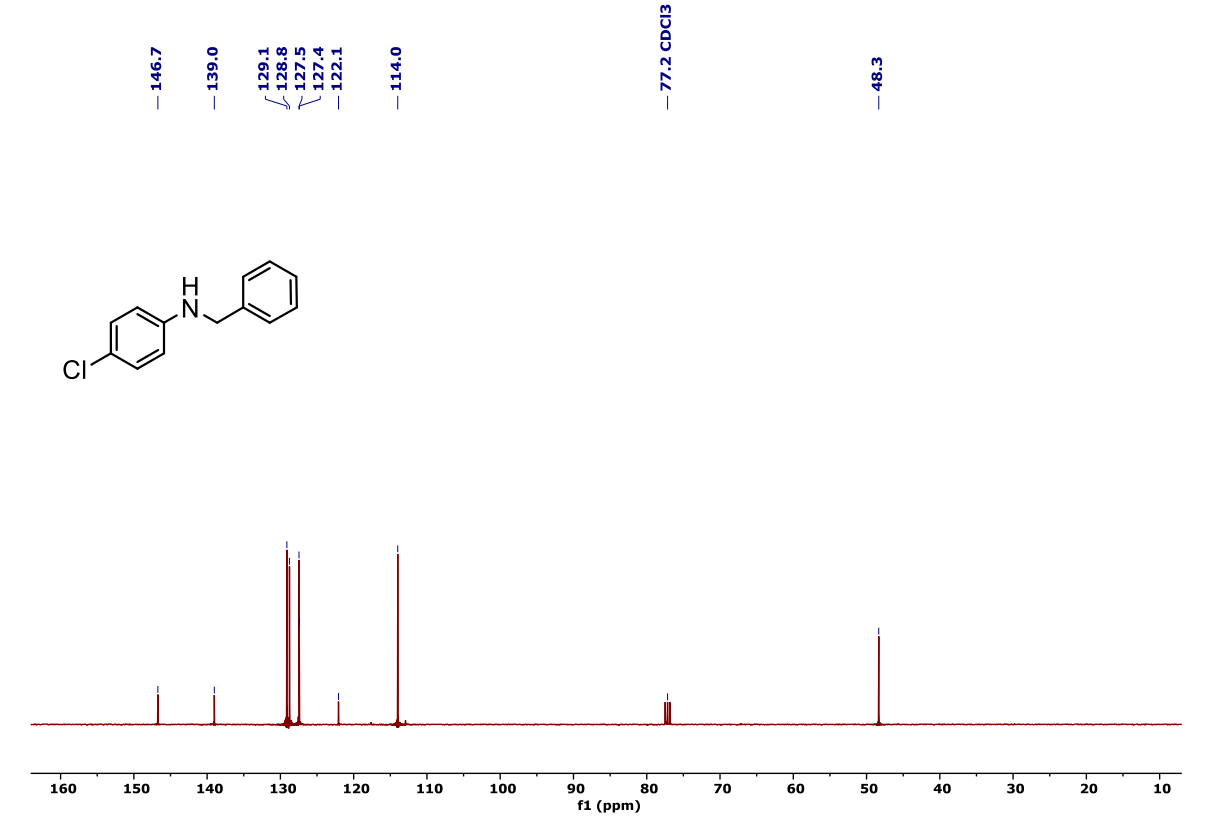


Figure S88. ^{13}C{^{1}H} NMR spectrum of **9c** in $CDCl_3$.

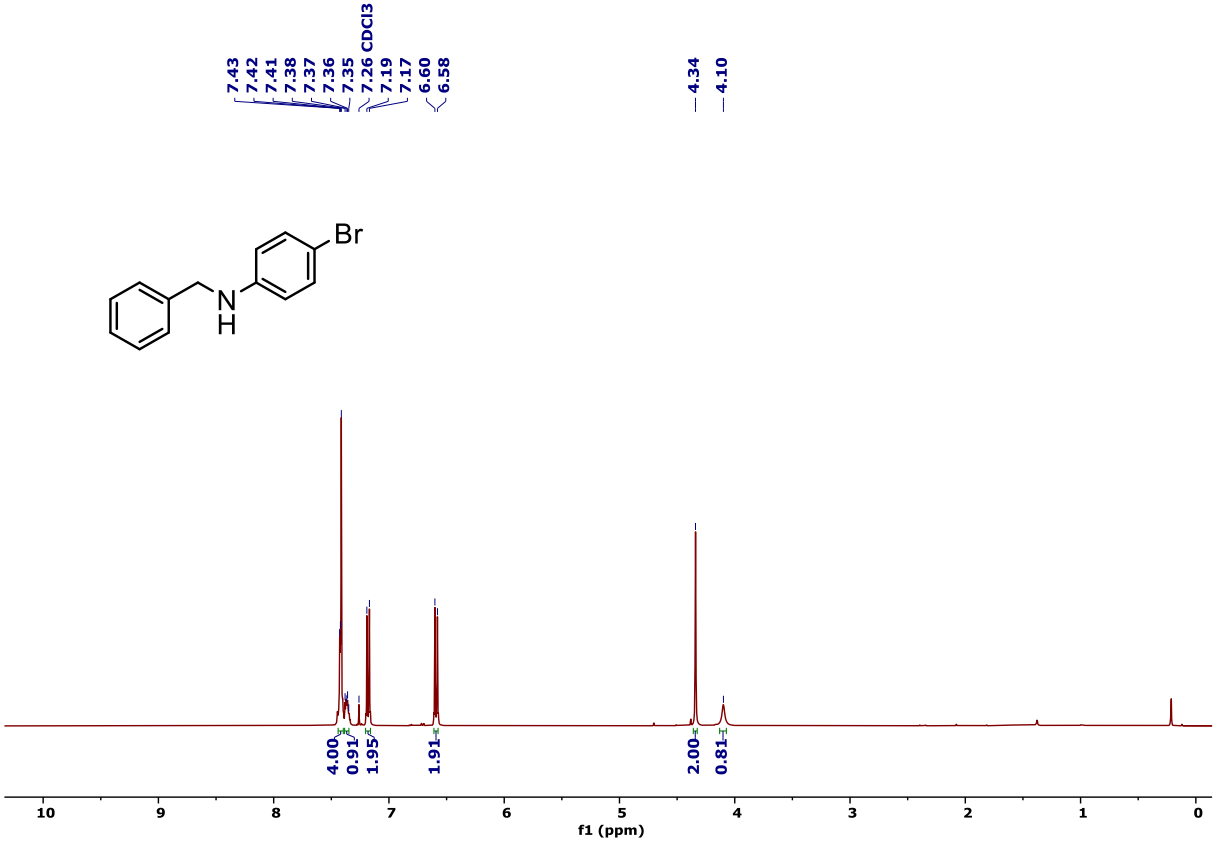


Figure S89. ^{1}H NMR spectrum of **9d** in $CDCl_3$.

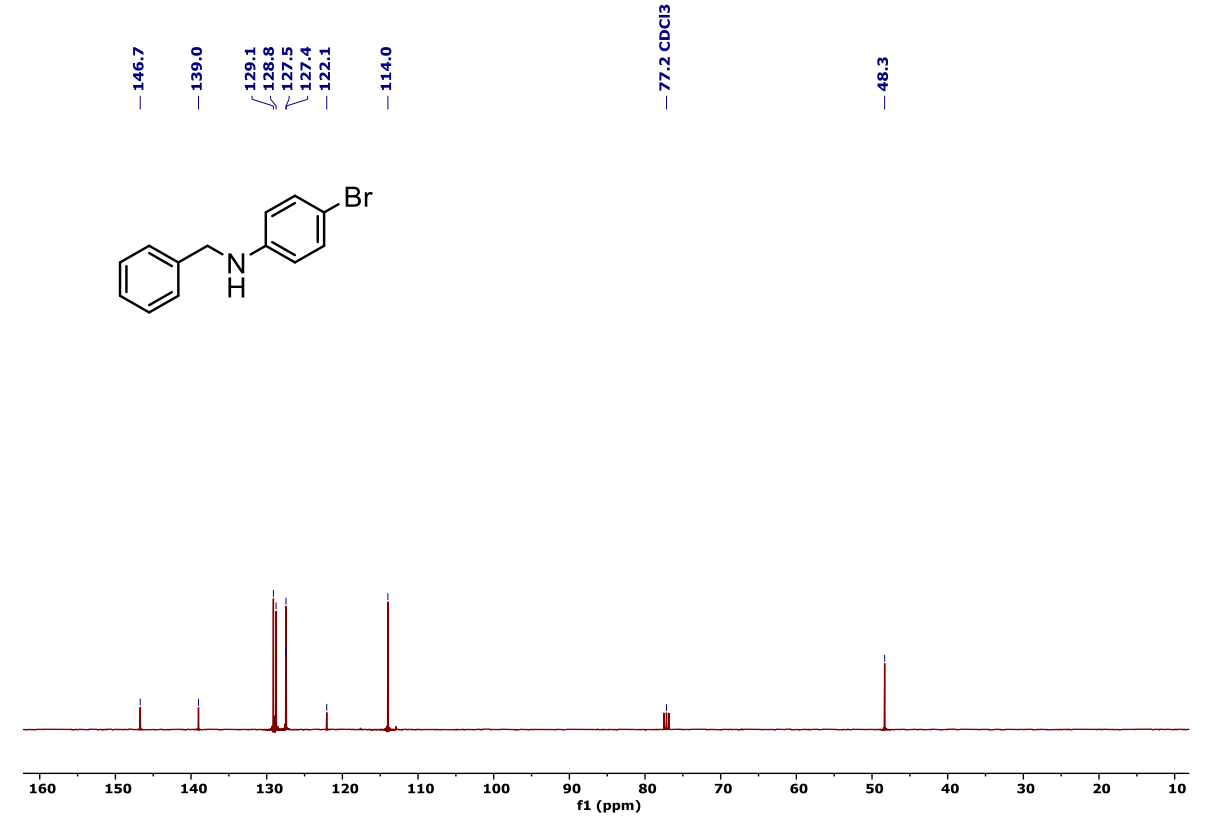


Figure S90. $^{13}C\{^{1}H\}$ NMR spectrum of **9d** in $CDCl_3$.

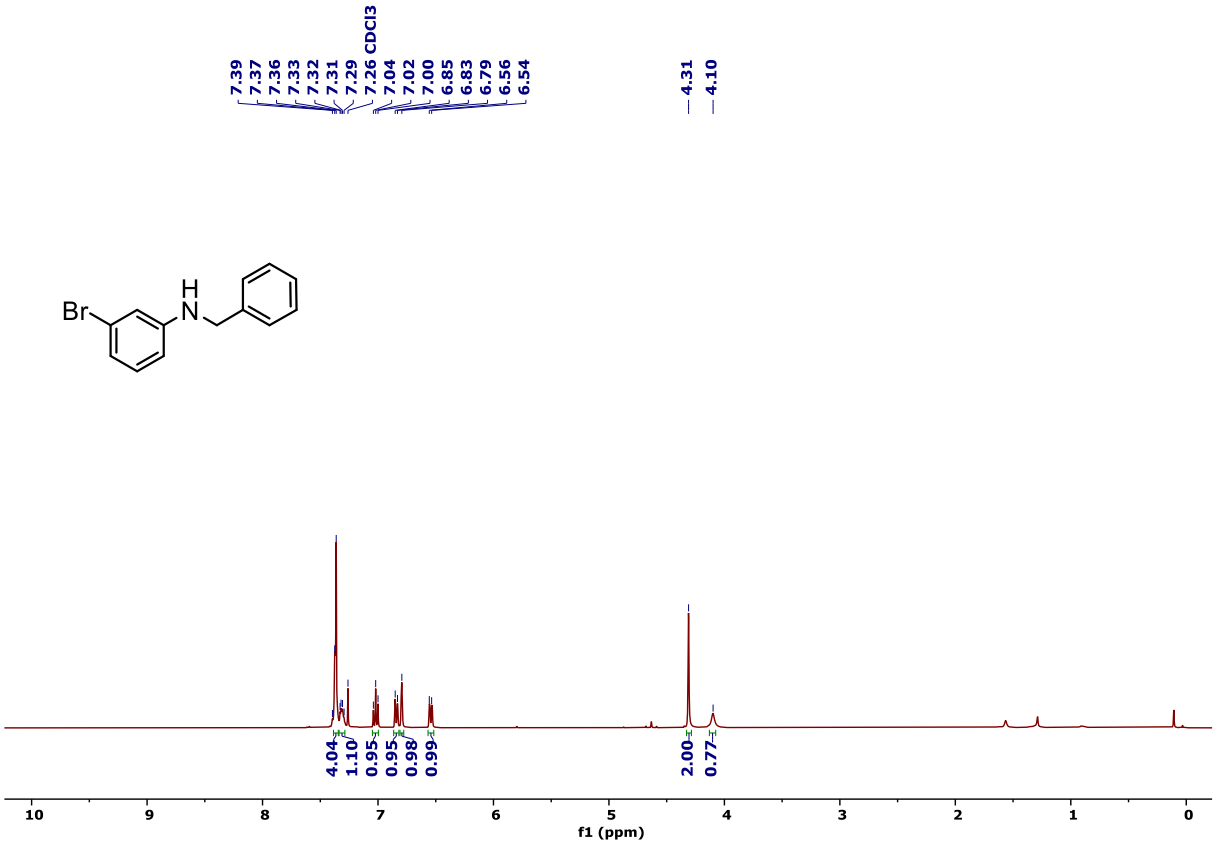


Figure S91. ^{1}H NMR spectrum of **9e** in $CDCl_3$.

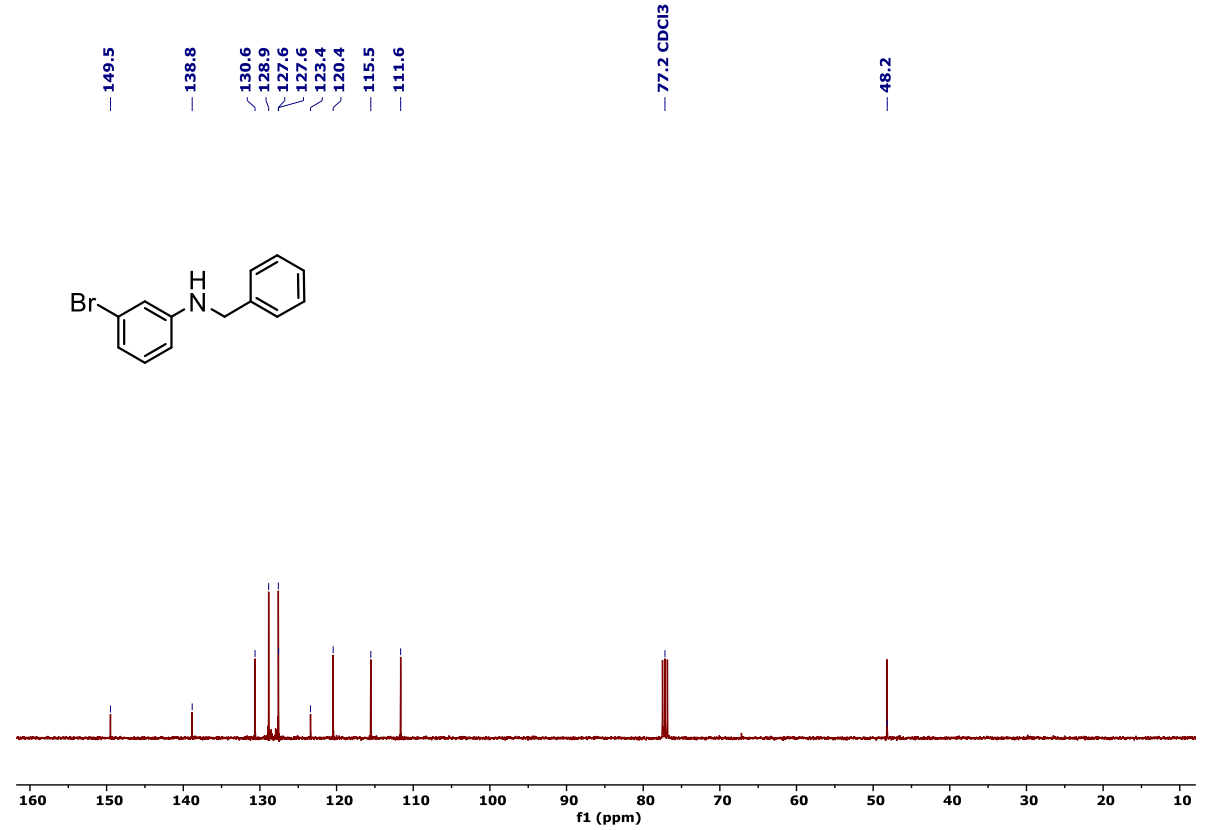


Figure S92. $^{13}C\{^{1}H\}$ NMR spectrum of **9e** in $CDCl_3$.

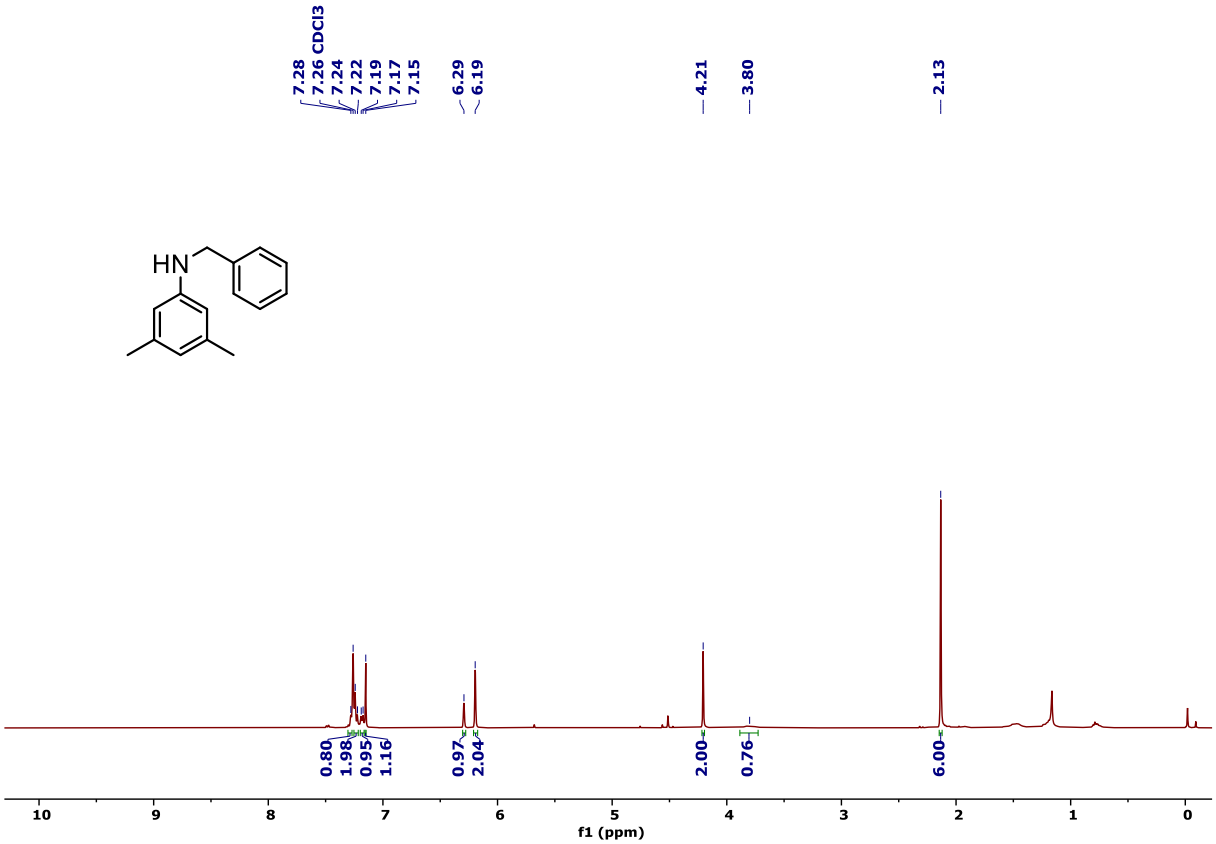


Figure S93. ^{1}H NMR spectrum of **9f** in $CDCl_3$.

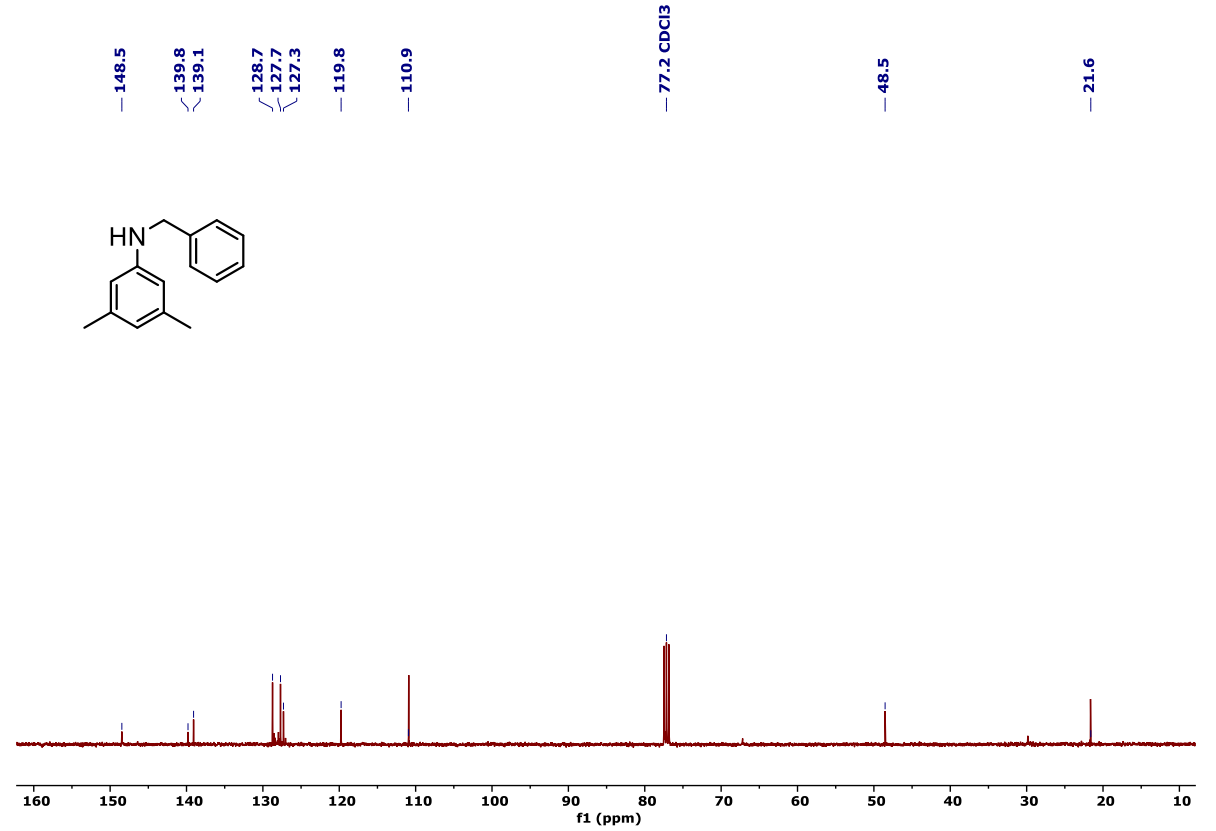


Figure S94. $^{13}C\{^{1}H\}$ NMR spectrum of **9f** in $CDCl_3$.

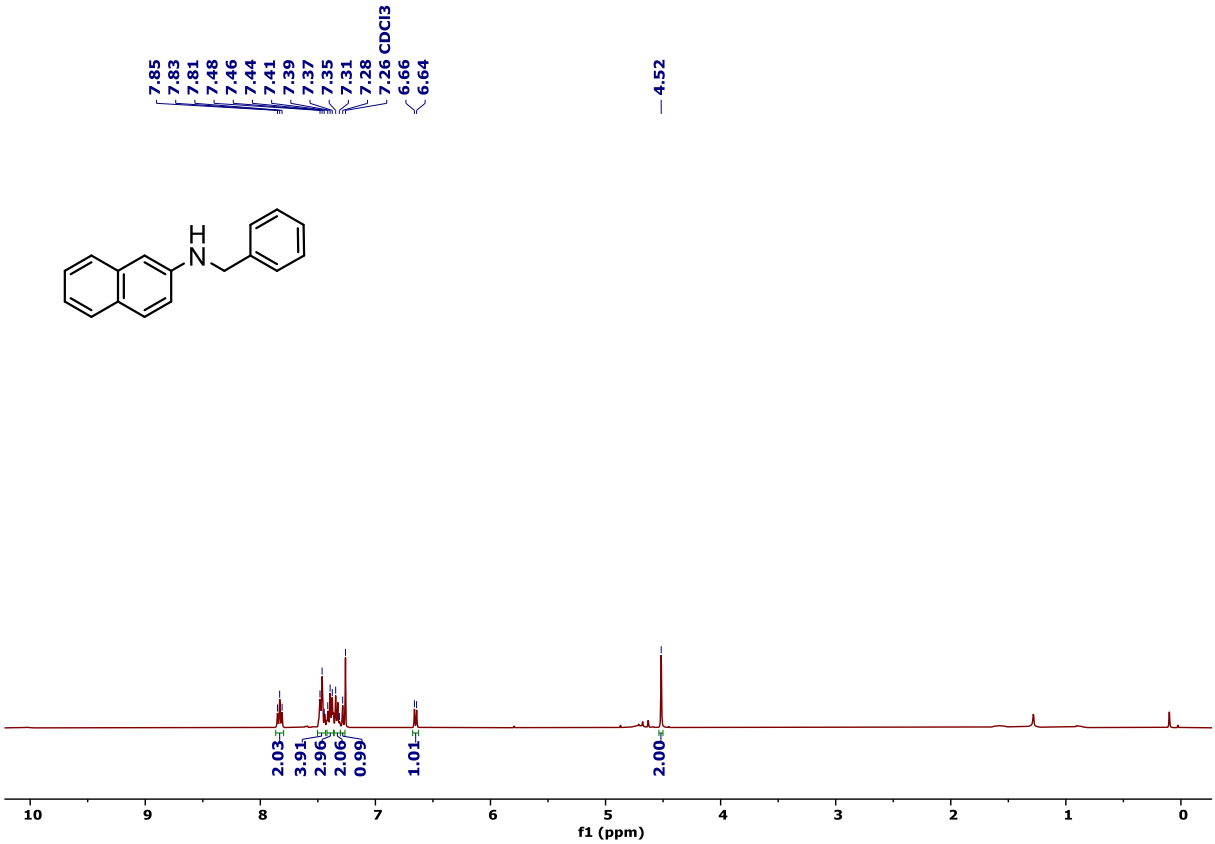


Figure S95. ^{1}H NMR spectrum of **9g** in $CDCl_3$.

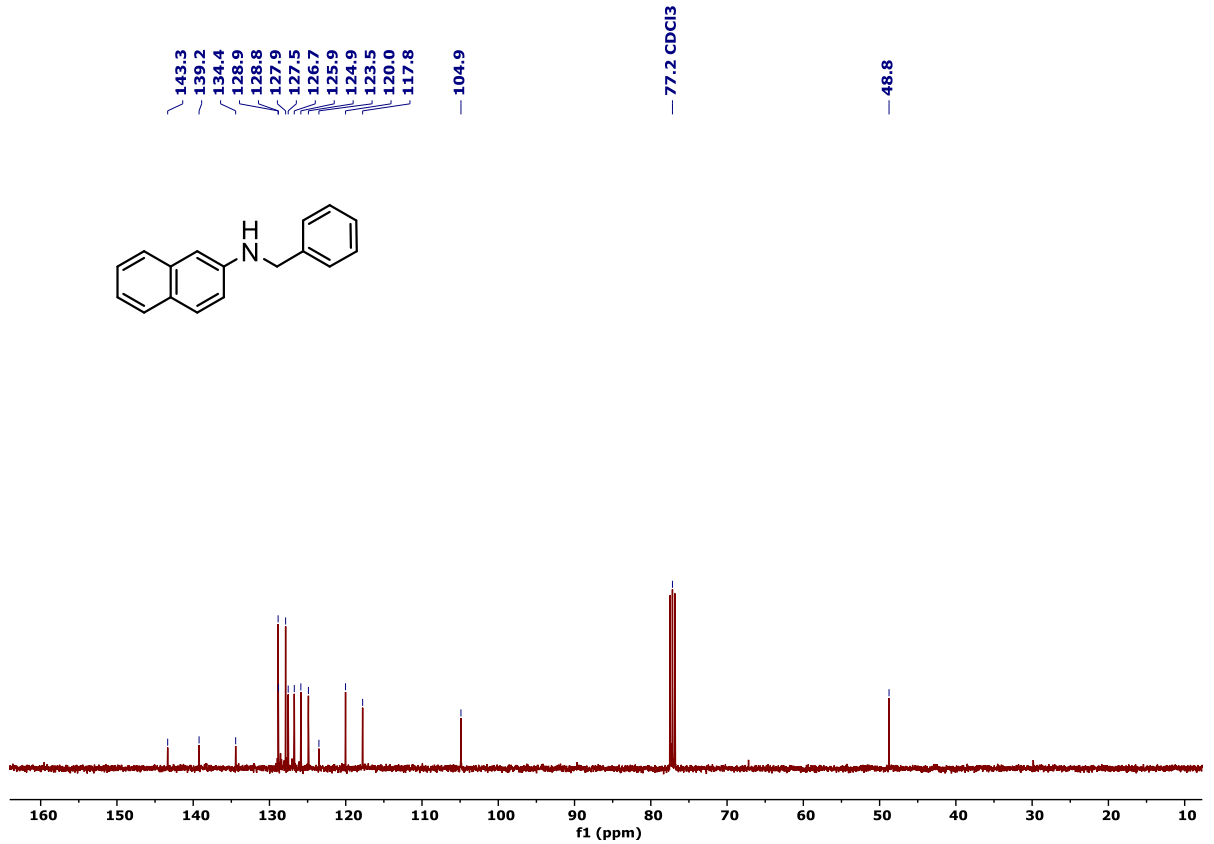


Figure S96. $^{13}C\{^{1}H\}$ NMR spectrum of **9g** in $CDCl_3$.

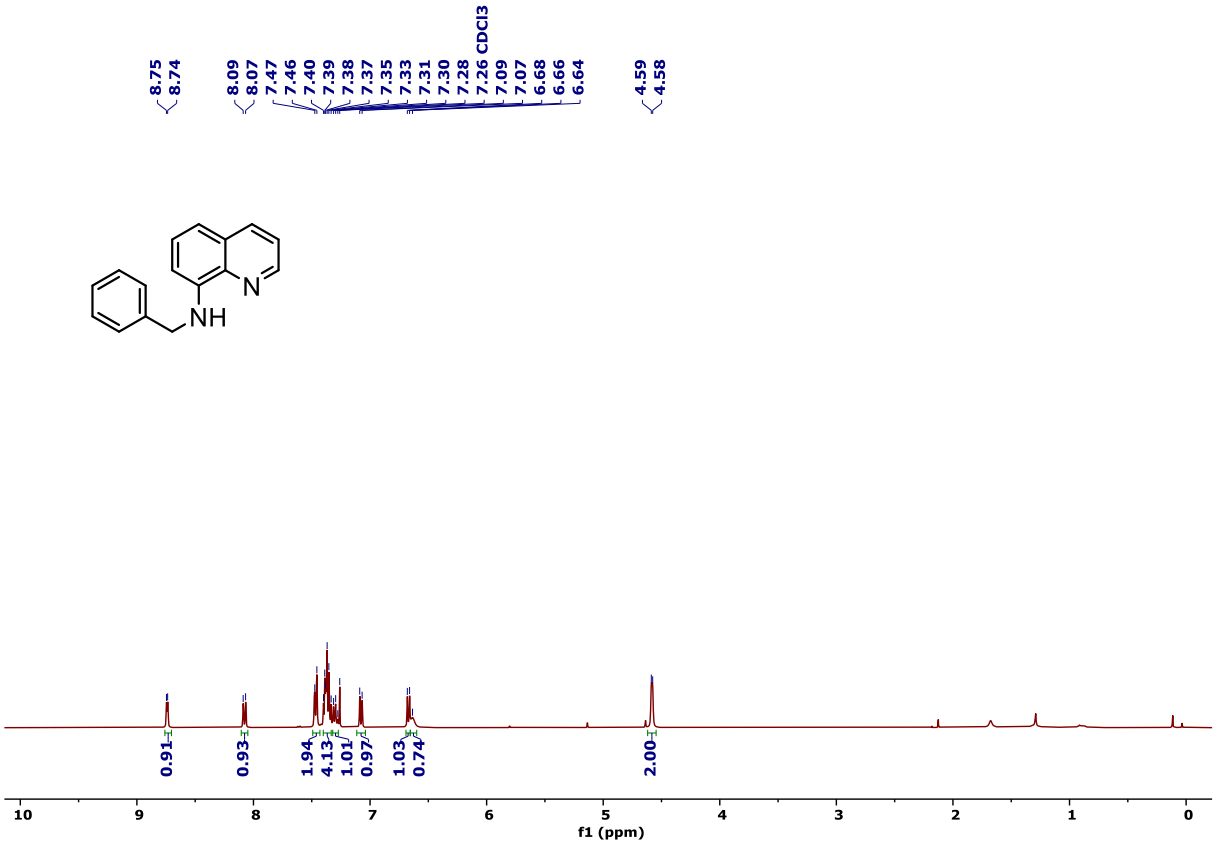


Figure S97. ^{1}H NMR spectrum of **9h** in $CDCl_3$.

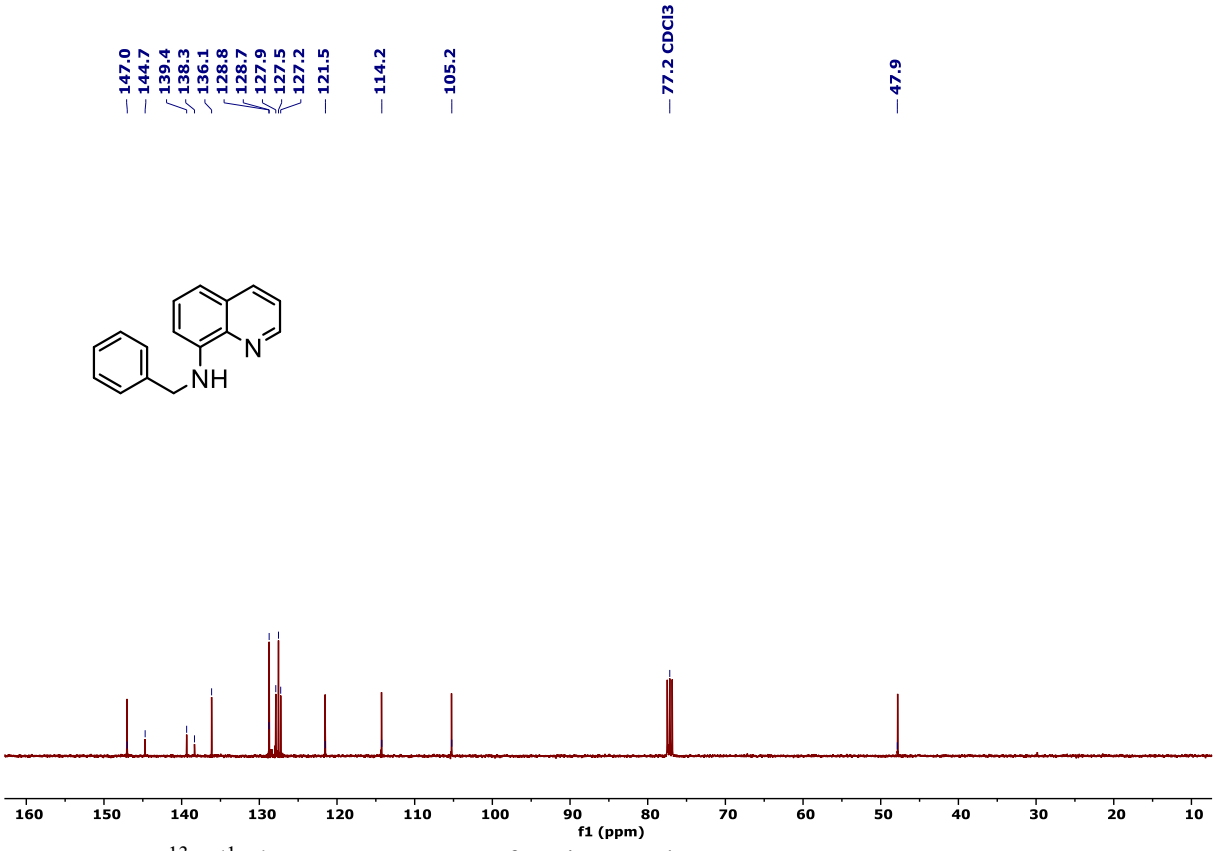


Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum of **9h** in $CDCl_3$.

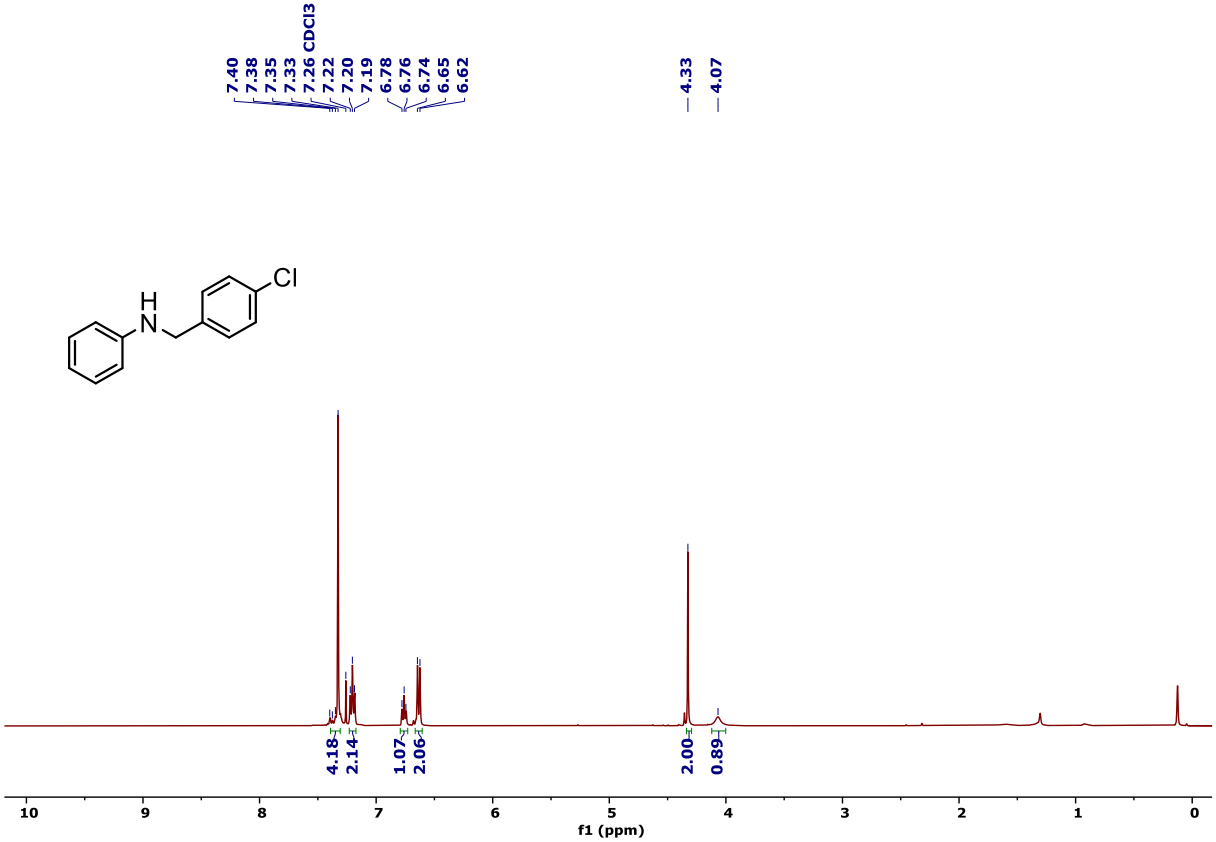


Figure S99. ^{1}H NMR spectrum of **9i** in $CDCl_3$.

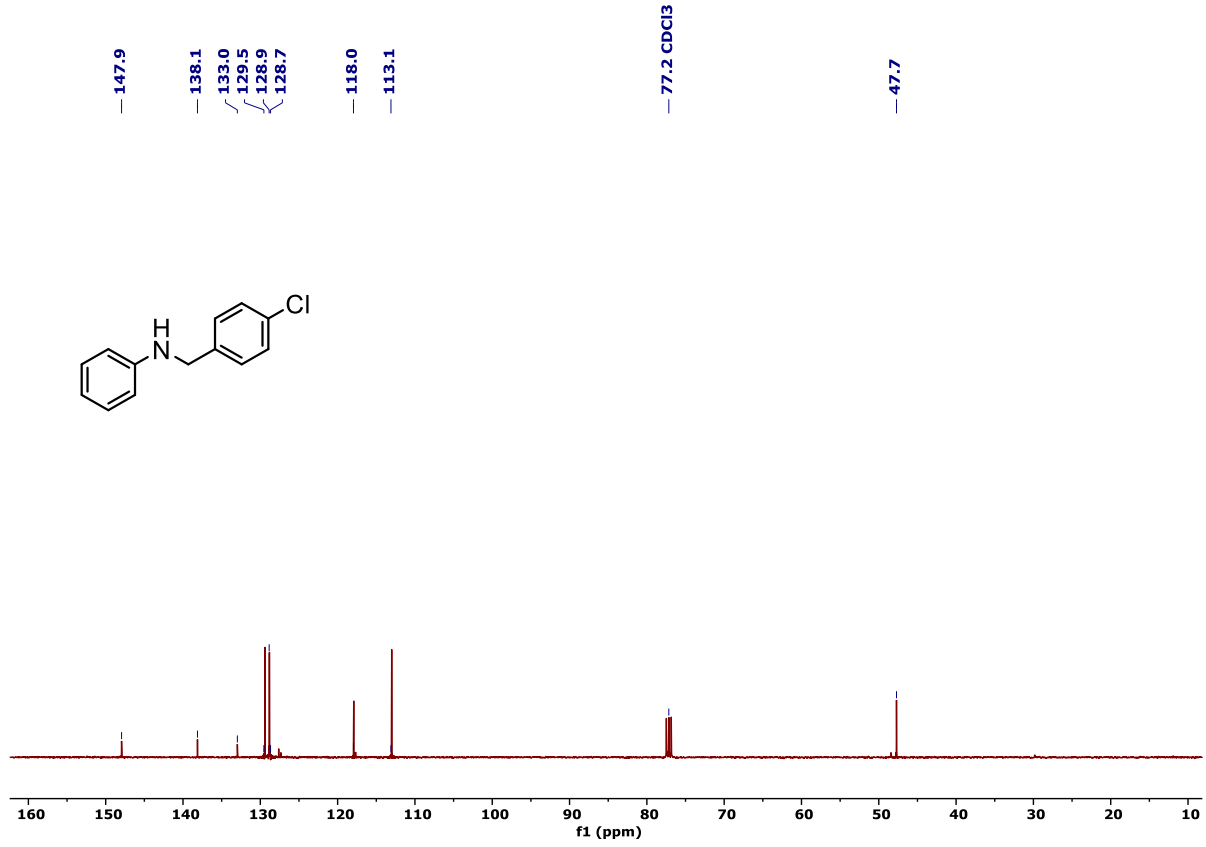


Figure S100. $^{13}C\{^{1}H\}$ NMR spectrum of **9i** in $CDCl_3$.

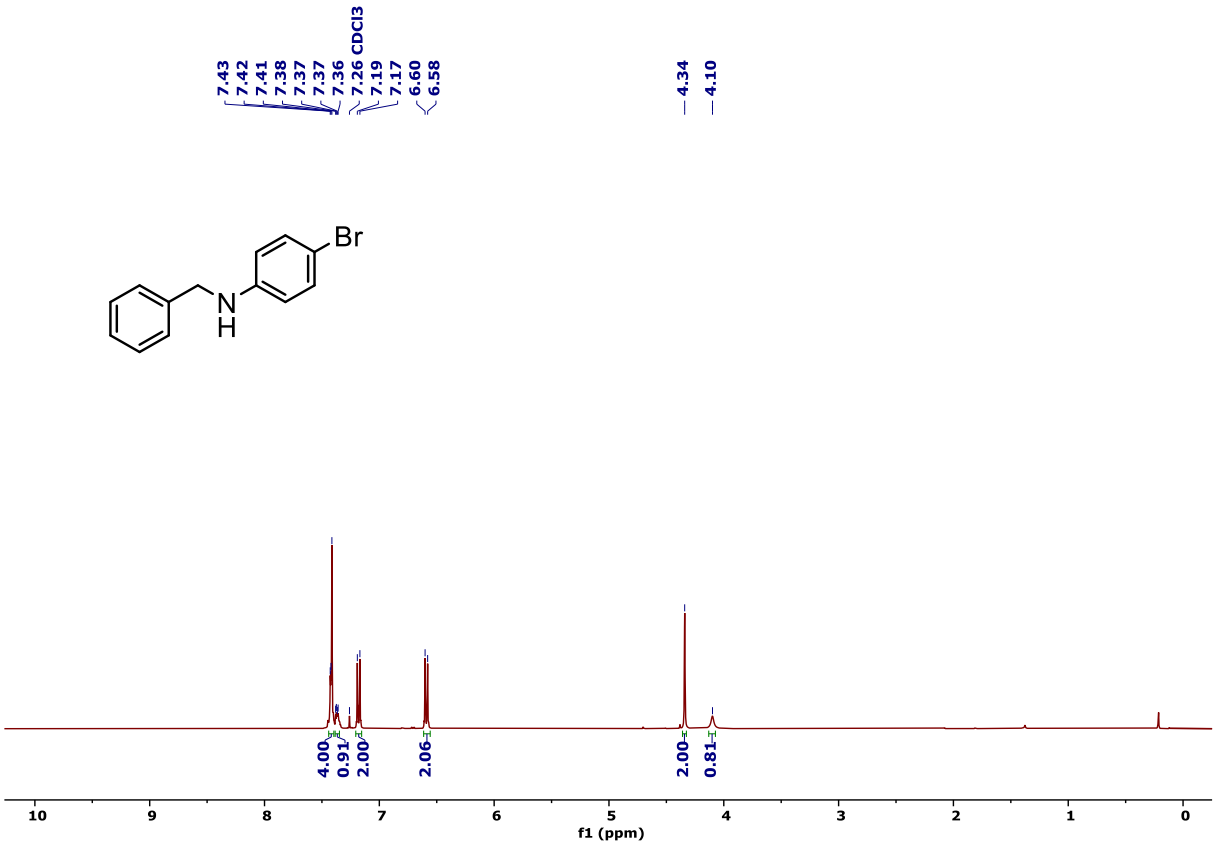


Figure S101. ^{1}H NMR spectrum of **9j** in $CDCl_3$.

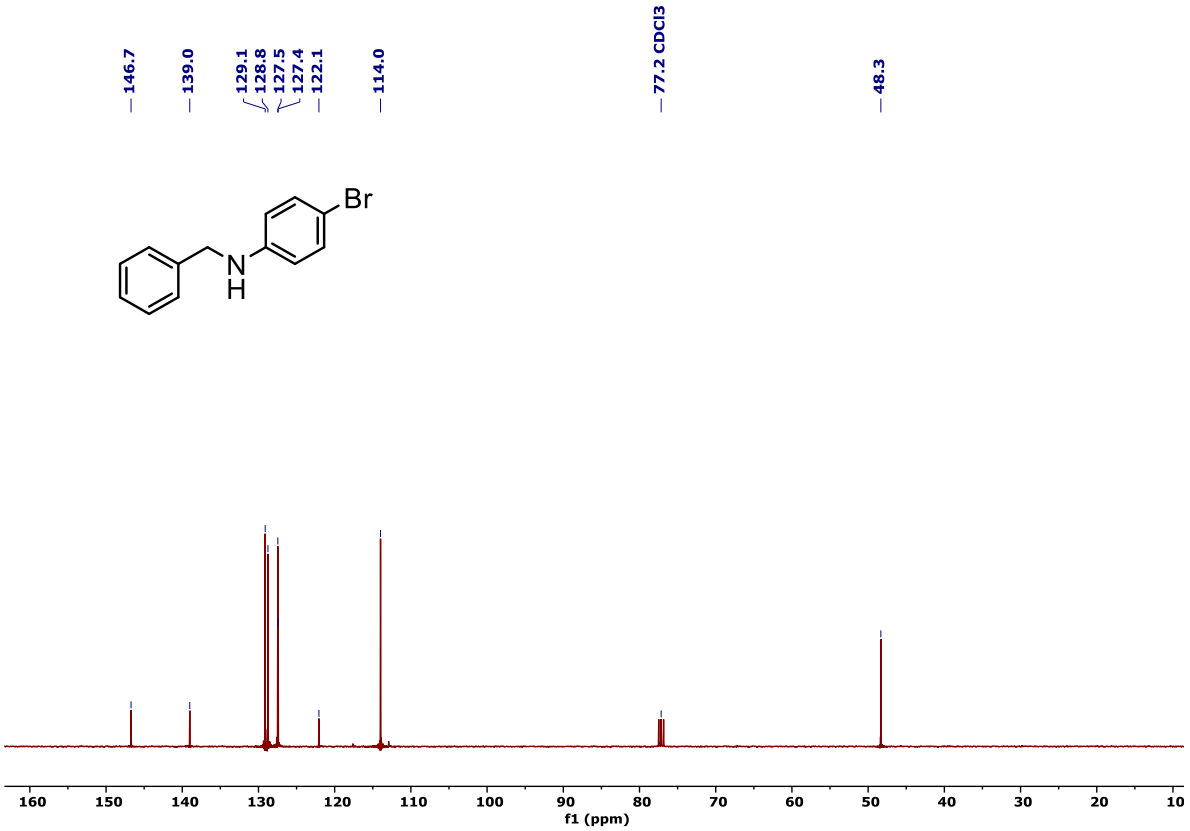


Figure S102. $^{13}C\{^{1}H\}$ NMR spectrum of **9j** in $CDCl_3$.

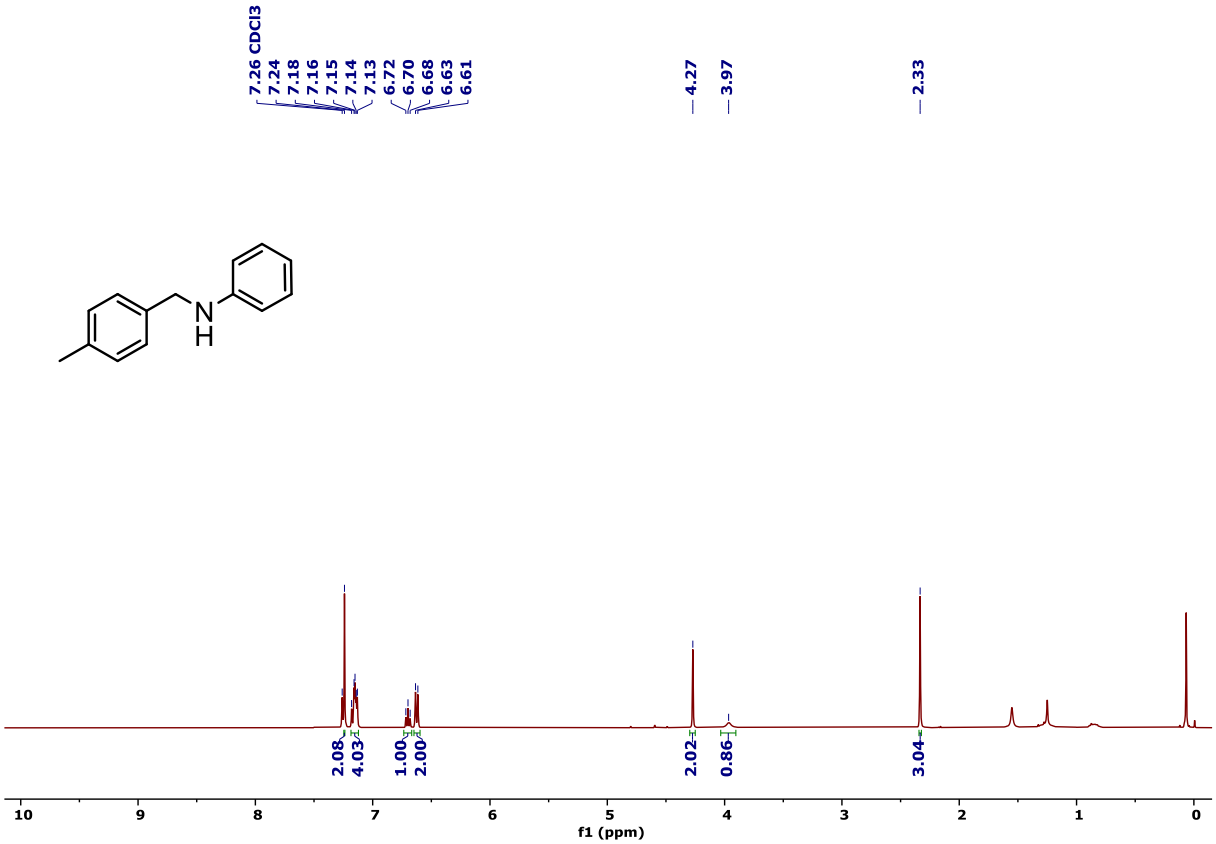


Figure S103. ^{1}H NMR spectrum of **9k** in $CDCl_3$.

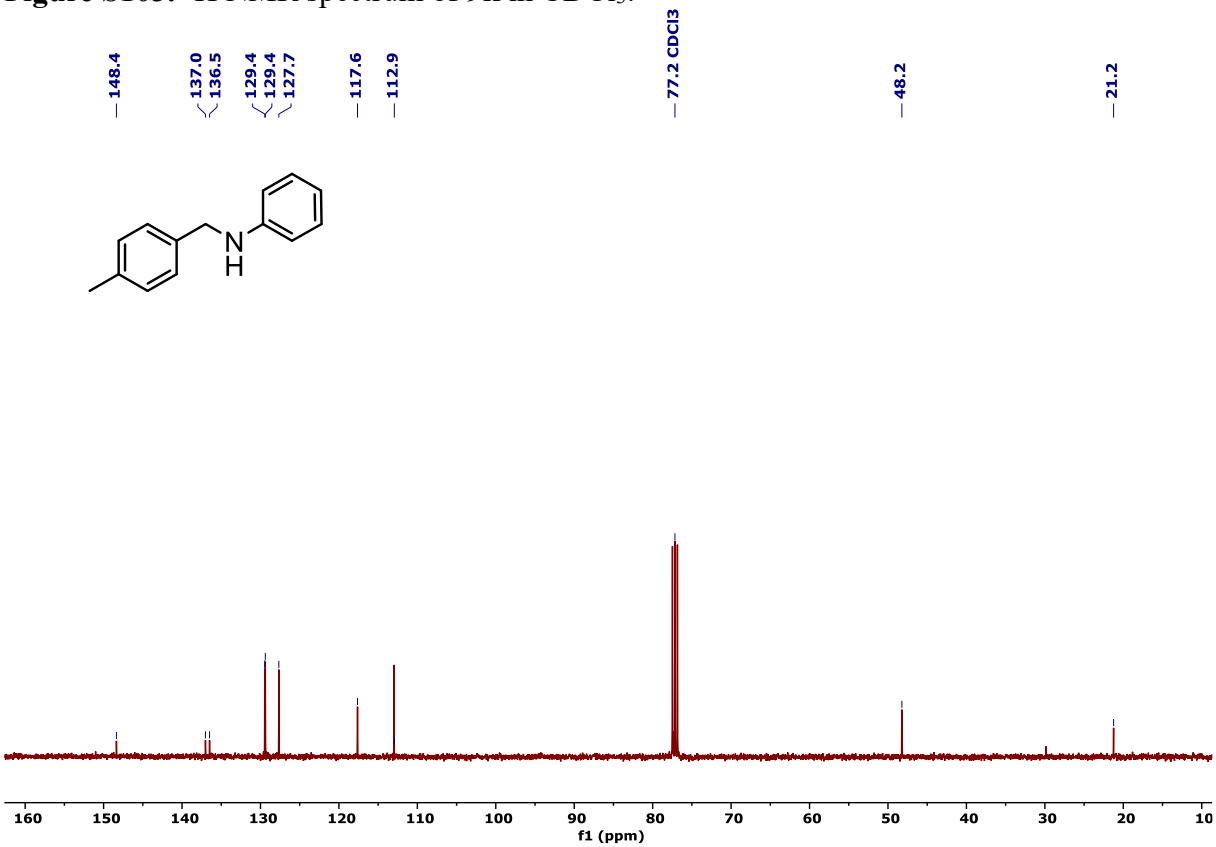


Figure S104. $^{13}C\{^{1}H\}$ NMR spectrum of **9k** in $CDCl_3$.

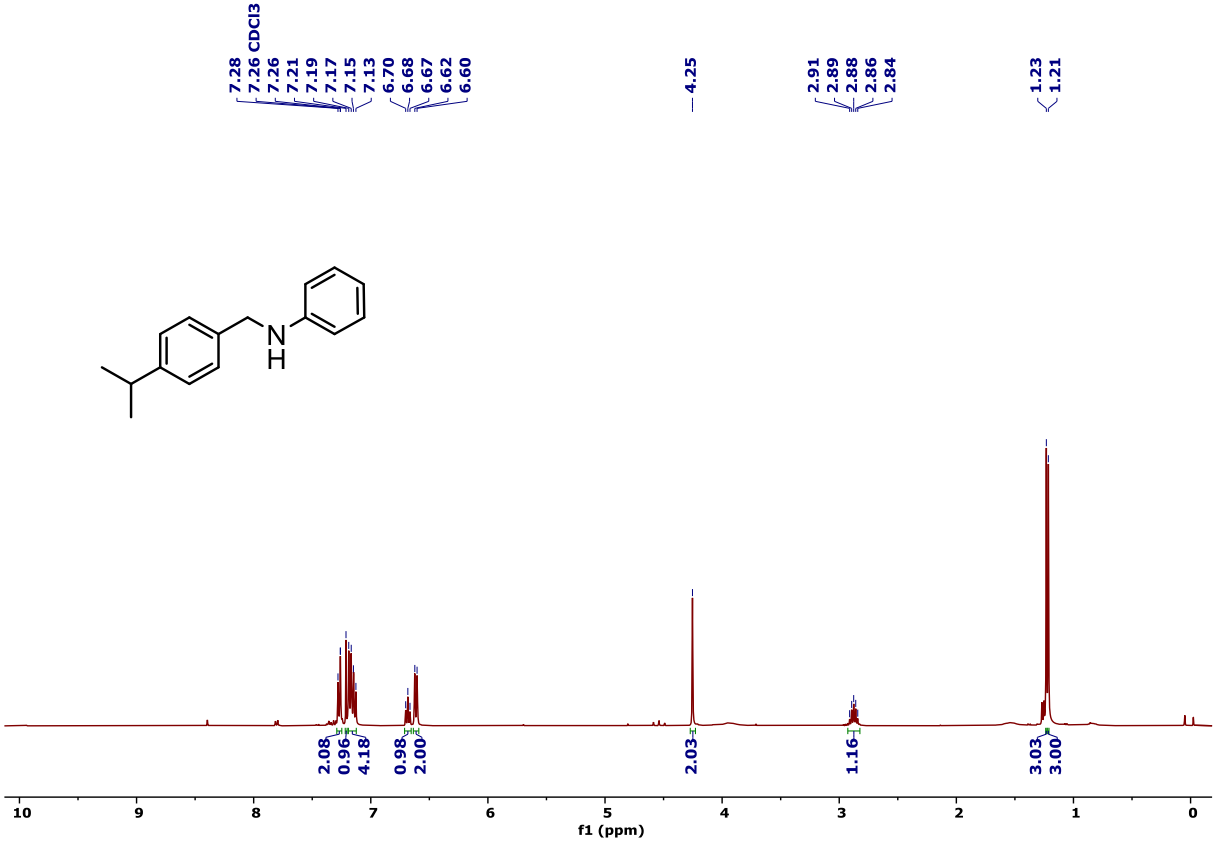


Figure S105. ^{1}H NMR spectrum of **9l** in $CDCl_3$.

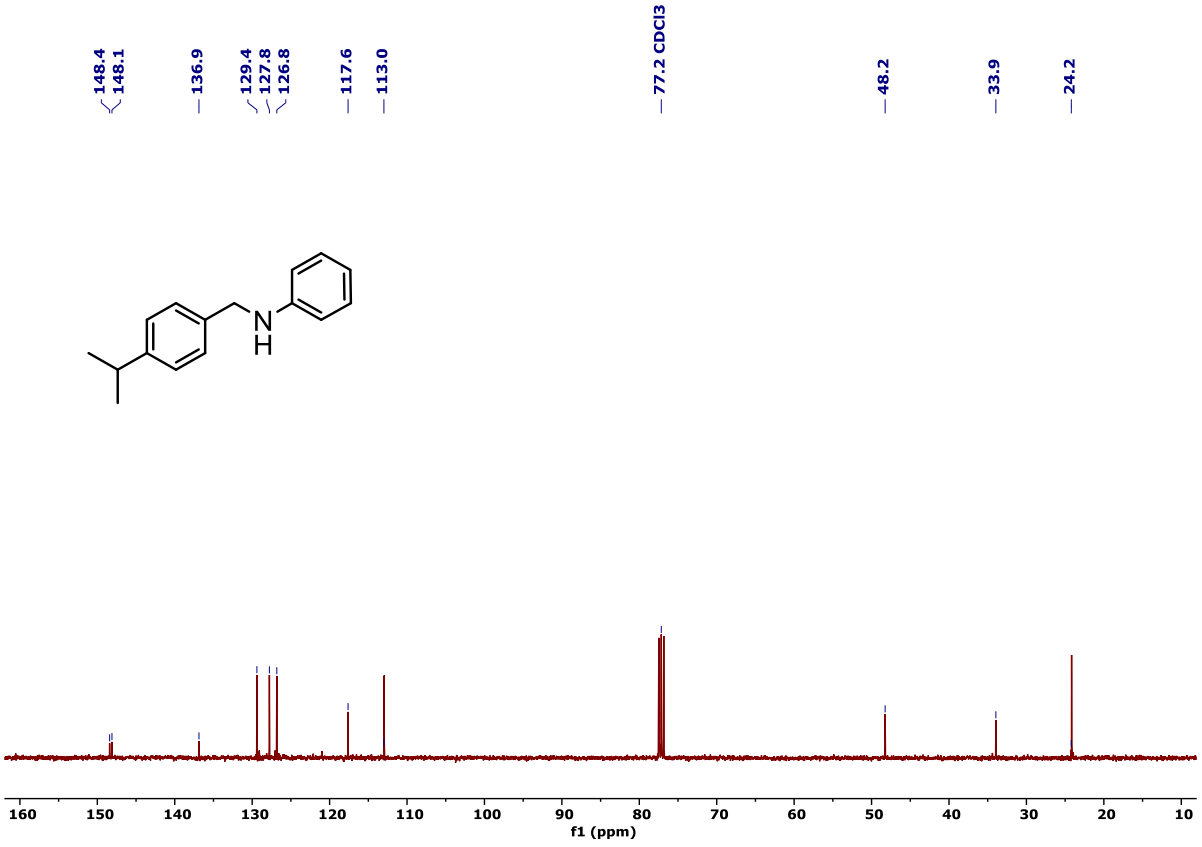


Figure S106. $^{13}C\{^{1}H\}$ NMR spectrum of **9l** in $CDCl_3$.

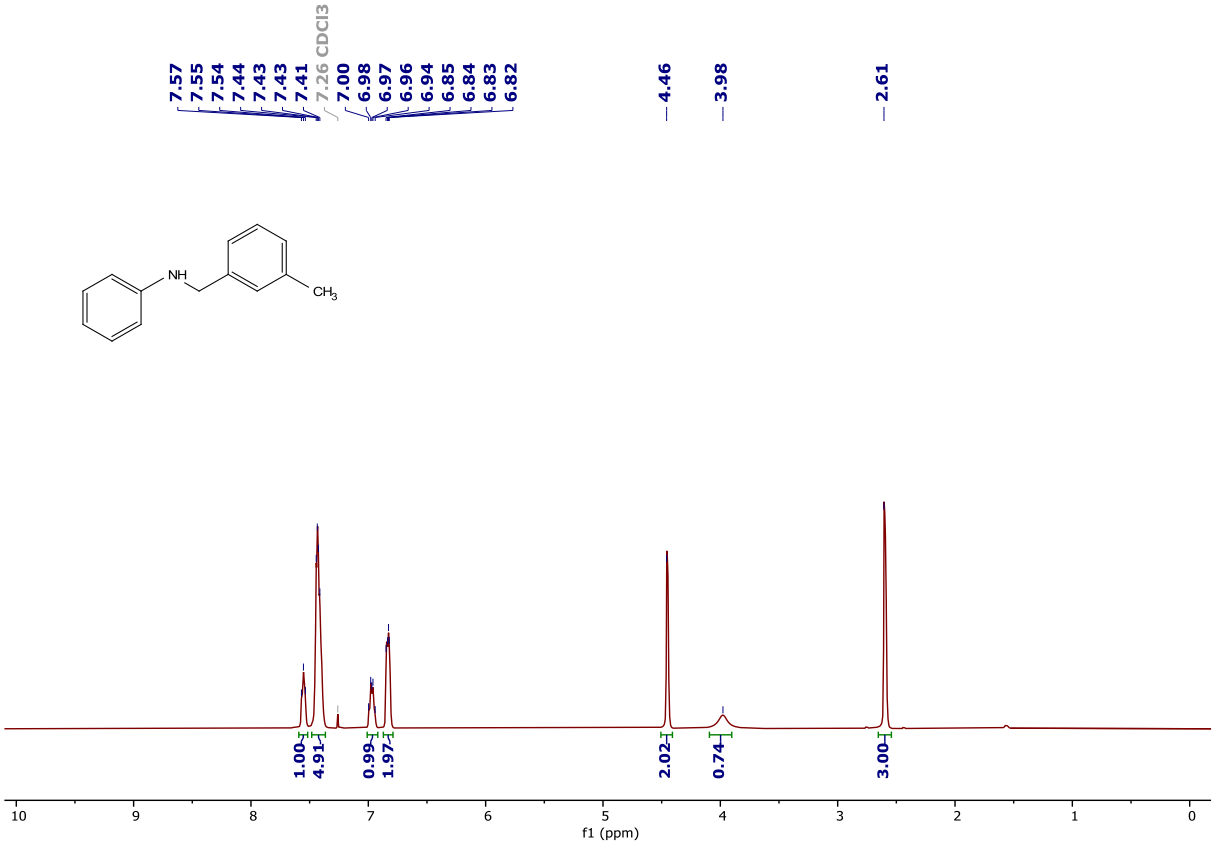


Figure S107. ^{1}H NMR spectrum of **9m** in $CDCl_3$.

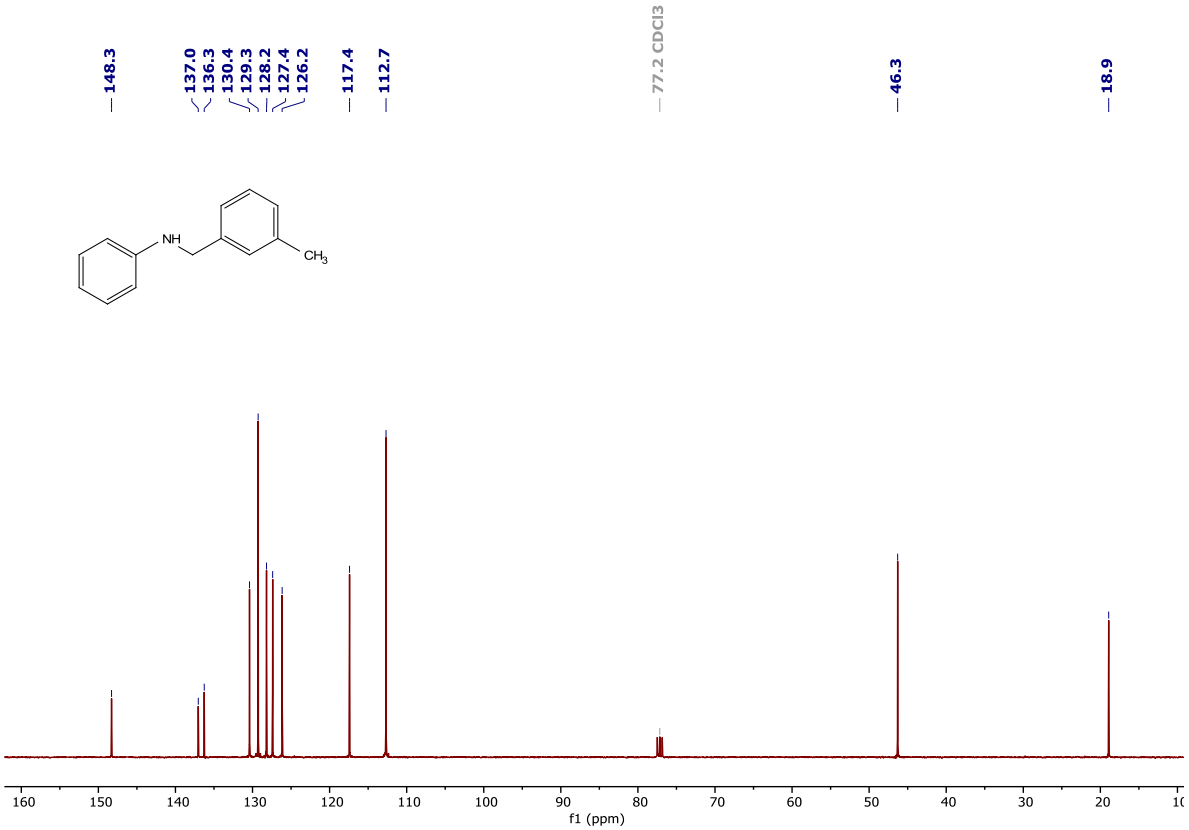


Figure S108. $^{13}C\{^{1}H\}$ NMR spectrum of **9m** in $CDCl_3$.

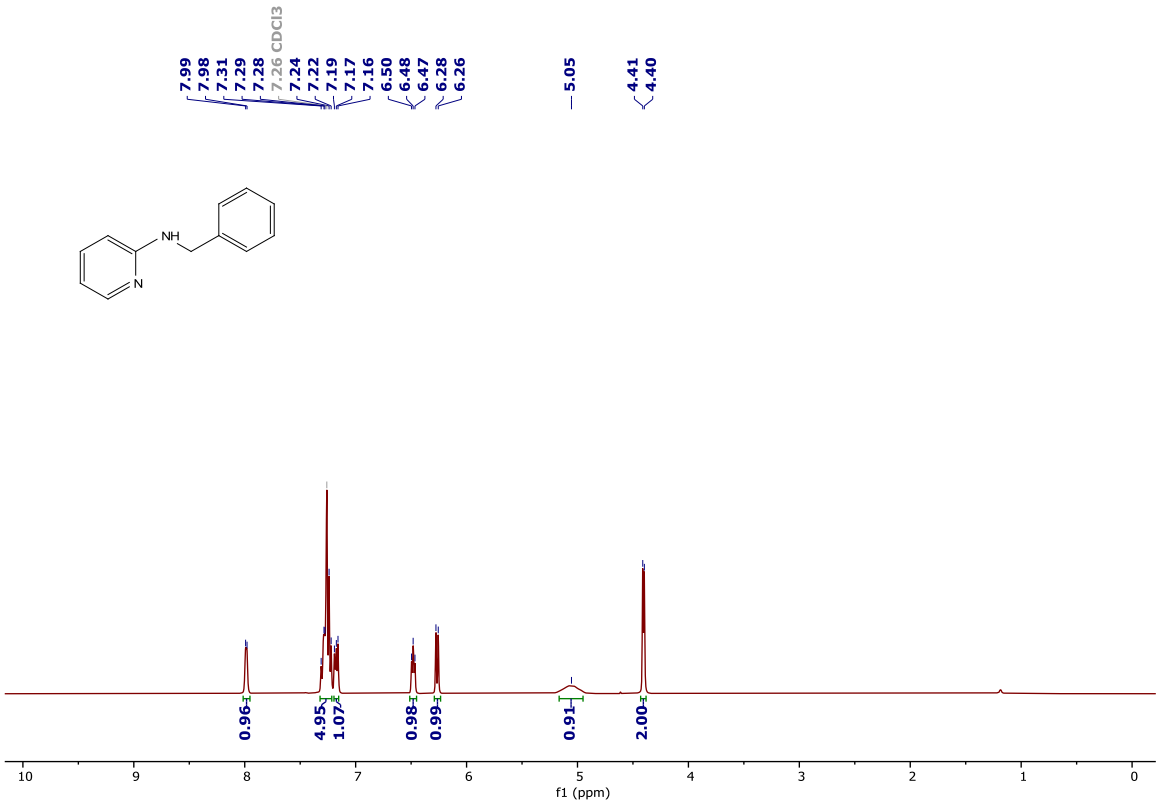


Figure S109. ^{1}H NMR spectrum of **9n** in $CDCl_3$.

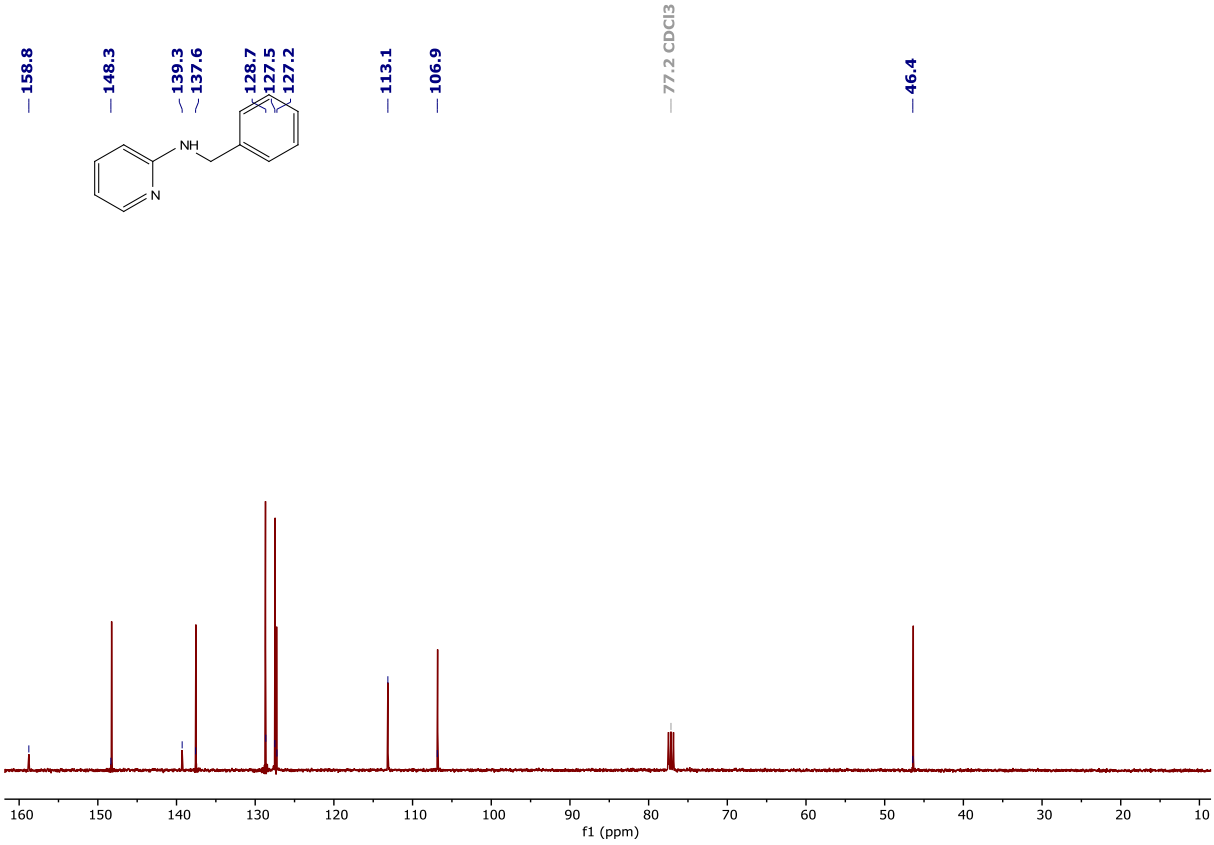


Figure S110. $^{13}C\{^{1}H\}$ NMR spectrum of **9n** in $CDCl_3$.

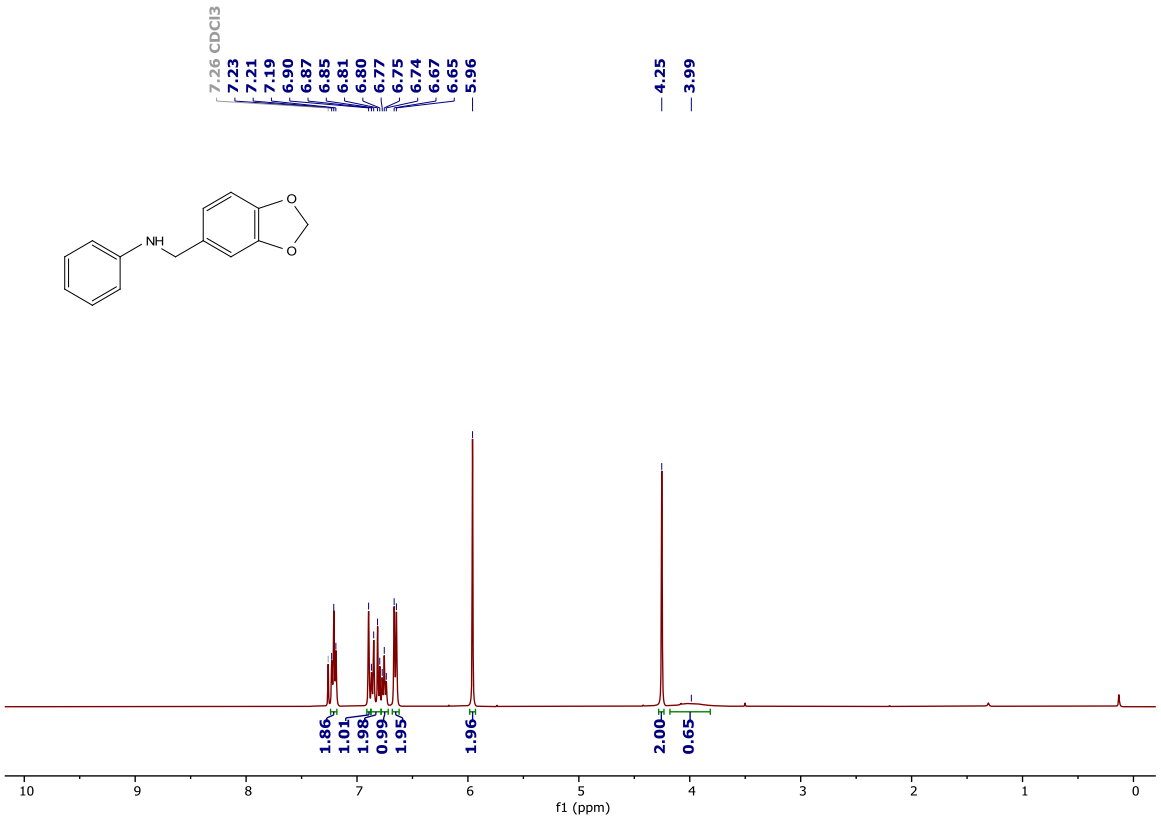


Figure S111. ^{1}H NMR spectrum of **9o** in $CDCl_3$.

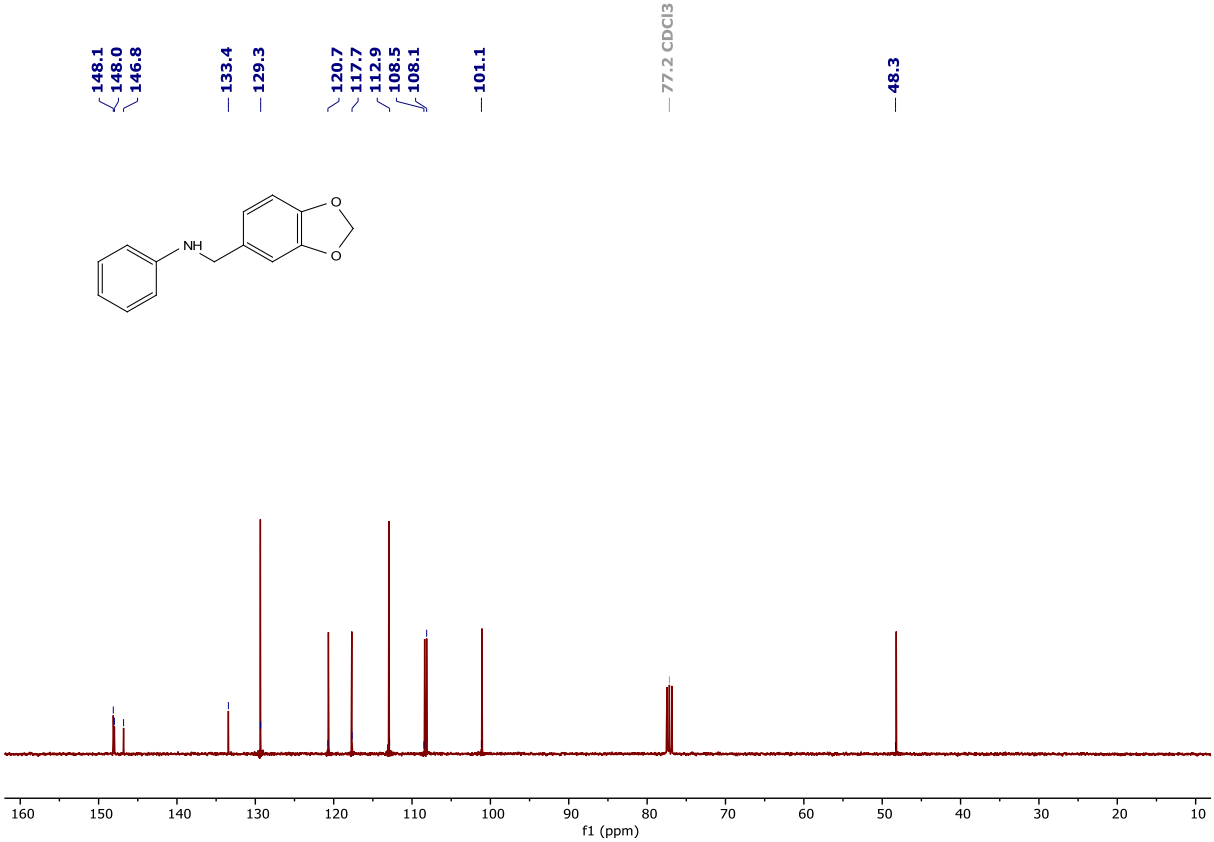


Figure S112. $^{13}C\{^{1}H\}$ NMR spectrum of **9o** in $CDCl_3$.

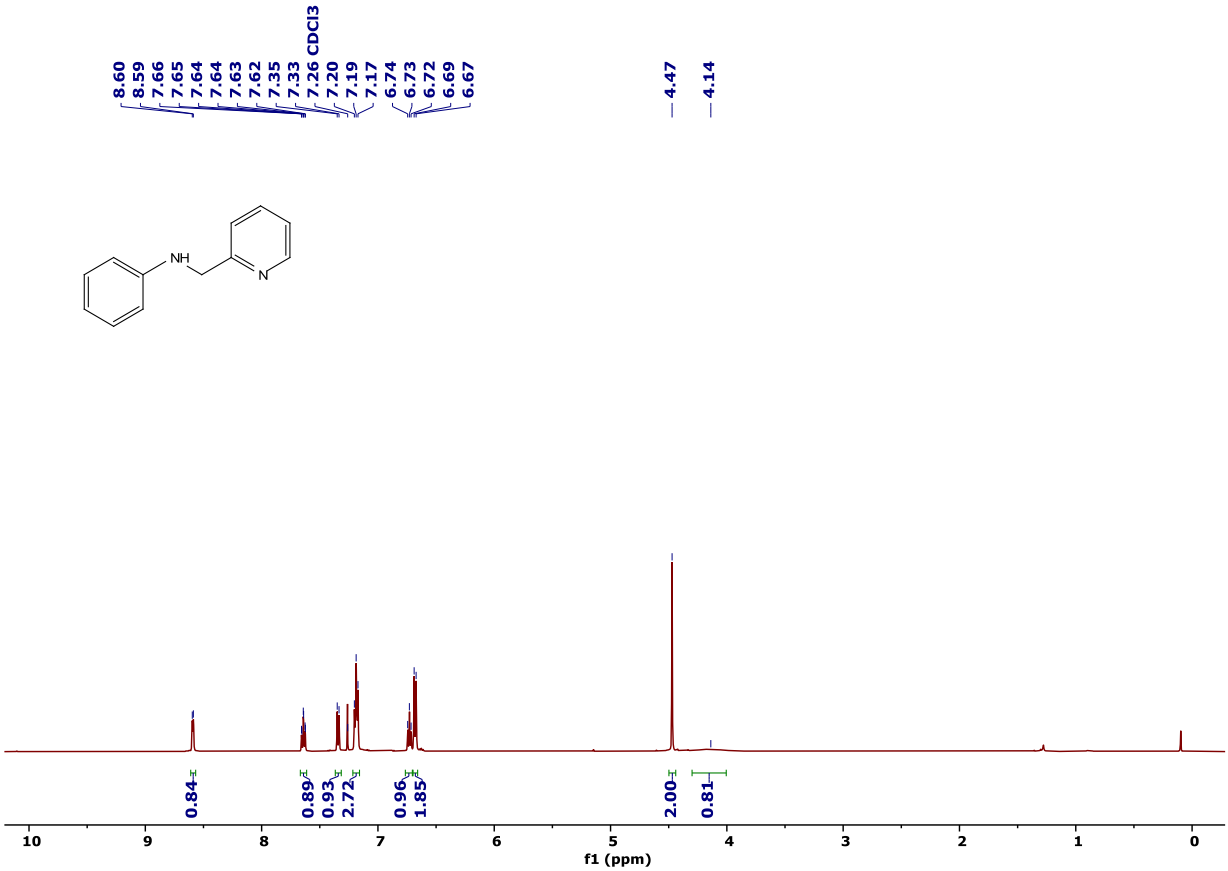


Figure S113. ^{1}H NMR spectrum of **9p** in $CDCl_3$.

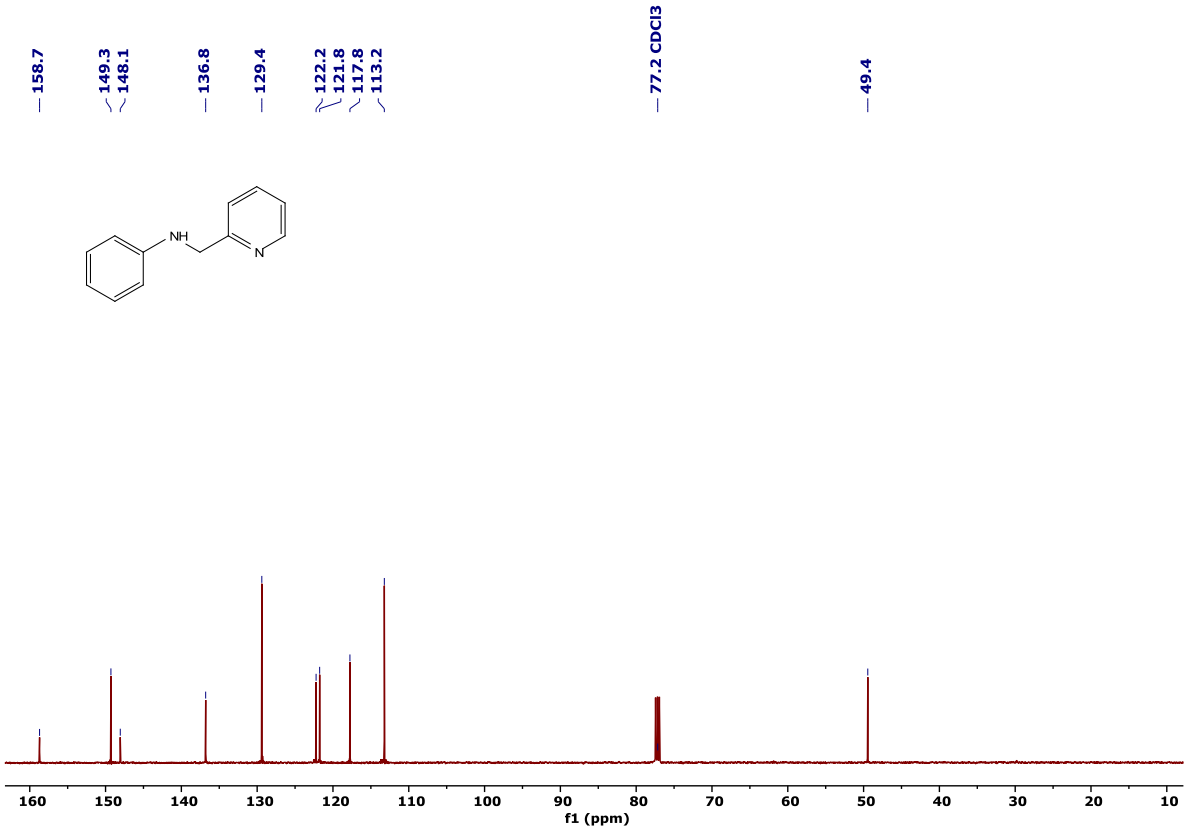


Figure S114. $^{13}C\{^{1}H\}$ NMR spectrum of **9p** in $CDCl_3$.

General procedure for the post modification of isolated compounds

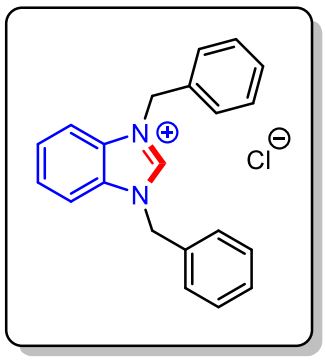
i) Synthesis of benzimidazolium salt 10a-b: Following the previous report,[2] an oven-dried Schlenk tube (25 mL) was charged with **3a**/**3d** (1.8 mmol), followed by the addition of triethyl orthoformate (220 µL, 3.3 equiv.) and con. HCl (220 µL, 18 equiv.). After that, the reaction mixture was stirred at 120 °C for 6 h and following that the reaction mixture was allowed to cool to room temperature and ether was added to the precipitate white colour products **10a-b** in 86-90% yield.

ii) Synthesis of Complex 11a-b: Following the previous report,[3] an oven-dried Schlenk tube (25 mL) was charged with **6k** (0.256 mmol, 1 equiv.) followed by the addition of dry methanol (3 mL). To this, an appropriate metal salt {$[Ru(p\text{-}cym)Cl_2]_2$, 0.5 equiv./ $[Mn(CO)_5Br]$, 1 equiv.} dissolved in DCM was added and the reaction mixture was stirred at room temperature for 12 h. Following that NH_4PF_6 (1 equiv.) was added for complex **11a** and the reaction was then stirred for two hours. The resulting precipitates generated for both cases were filtered and washed with diethyl ether giving the corresponding products **11a-b** in 78-90% yield.

iii) Unsymmetrical *N*-alkylation of 7c-d: An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (1.5 mol%), ligand **L3** (3 mol%), and KO^{t}Bu (0.5 mmol, 1 equiv.) followed by the addition of toluene (1 mL). Then, the tube was kept in an oil bath at 140 °C and heated for 1 h. After cooling to room temperature, respective alkylated diamines **7c-d** (0.5 mmol) and substituted benzyl alcohols (0.75 mmol, 1.5 equiv.) were added and further heated at 140 ˚C for 24-36 h. After completion of the reaction, analytically pure unsymmetrically dialkylated diamines were obtained *via* column chromatography using hexane/ethyl acetate.

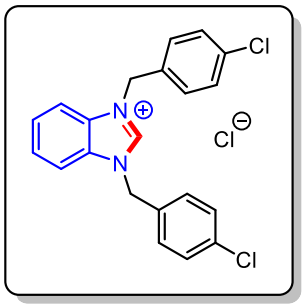
Analytical data of compounds obtained *via* post-synthetic modifications

1,3-bis(4-c-1H-benzo[d]imidazol-3-ium chloride **(10a):**[14] Following the general procedure (**i**),

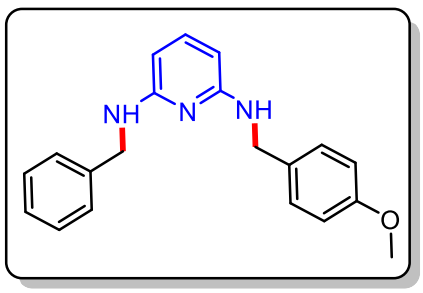


the titled compound was isolated as a white solid (566 mg, 1.69 mmol, 90% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.46 (s, 1H), 8.00-7.98 (m, 2H), 7.63-7.61 (m, 2H), 7.56 (d, J = 7.9 Hz, 4H), 7.42 (d, J = 8.2 Hz, 3H), 7.40-7.35 (m, 3H), 5.84 (s, 4H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 142.9, 134.1, 131.1, 129.0, 128.8, 128.4, 126.8, 114.1, 50.0 ppm. HRMS (ESI) *m/z*: $[M - Cl]^+$ Calcd for $C_{21}H_{19}N_2$ 299.1548; Found 299.1552.

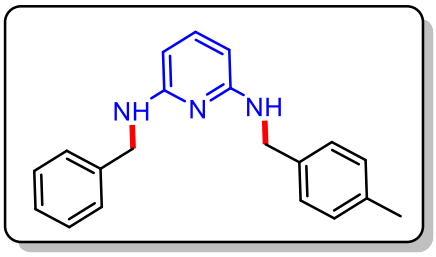
1,3-bis(4-chlorobenzyl)-1H-benzo[d]imidazol-3-ium chloride **(10b):**[15] Following the general procedure (**i**), the titled compound was isolated as a yellow solid (653 mg, 1.62 mmol, 86% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.36 (s, 1H), 7.98-7.97 (m, 2H), 7.61 (d, J = 7.6 Hz, 6H), 7.49 (d, J = 7.7 Hz, 4H), 5.83 (s, 4H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 143.1, 133.5, 132.9, 131.0, 130.5, 129.0, 126.8, 114.0, 49.3 ppm. HRMS (ESI) *m/z*: $[M - Cl]^+$ Calcd for $C_{21}H_{17}Cl_2N_2$ 367.0769; Found 367.0775.



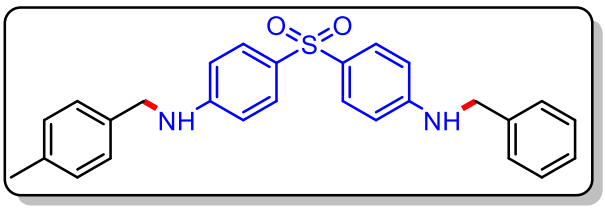
N²-benzyl-N⁶-(4-methoxybenzyl)pyridine-2,6-diamine **(12a):**[2] Following the general procedure (**iii**), the titled compound was isolated as greenish liquid (136 mg, 0.42 mmol, 85% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.21 (m, 4H), 7.18-7.16 (m, 3H), 7.11 (t, J = 7.8 Hz, 1H), 6.76 (d, J = 8.6 Hz, 2H), 5.64 (d, J = 7.8 Hz, 2H), 4.59 (t, J = 6.4 Hz, 1H), 4.52 (t, J = 5.7 Hz, 1H), 4.35 (d, J = 5.8 Hz, 2H), 4.26 (d, J = 5.6 Hz, 2H), 3.70 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.8, 158.1, 139.9, 139.2, 131.8, 128.9, 128.6, 127.6, 127.1, 114.0, 95.2, 55.4, 46.4, 45.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{21}N_3OH$ 320.1763; Found 320.1755.



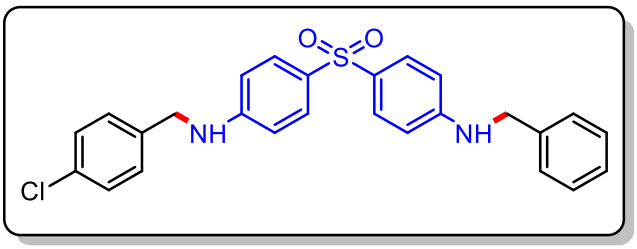
N²-benzyl-N⁶-(4-methylbenzyl)pyridine-2,6-diamine **(12b):**[2] Following the general procedure (**iii**), the titled compound was isolated as greenish liquid (124 mg, 0.41 mmol, 82% yield) using silica gel column chromatography (10-15% ethyl acetate in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 4H), 7.27-7.25 (m, 1H), 7.24-7.11 (m, 5H), 5.73 (d, J = 7.9 Hz, 2H), 4.64-4.59 (m, 2H,), 4.43 (d, J = 5.8 Hz, 2H), 4.38 (d, J = 5.7 Hz, 2H), 2.33 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.2, 158.2, 139.9, 139.3, 136.8, 129.3, 128.7, 127.6, 127.2, 95.3, 95.2, 46.5, 46.3, 21.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{21}N_3H$ 304.1814; Found 304.1806.



N-benzyl-4-({4-[(4-methylbenzyl)amino]phenyl}sulfonyl)-aniline **(12c):**[2] Following the general procedure (**iii**), the titled compound was isolated as greenish liquid (159 mg, 0.34 mmol, 72% yield) using silica gel column chromatography (30-40% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.65 (m, 4H), 7.36-7.29 (m, 5H), 7.20-7.14 (m, 4H), 6.58-6.56 (m, 4H), 4.34 (s, 2H), 4.29 (s, 2H), 2.34 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.4, 151.3, 138.2, 137.5, 135.1, 130.5, 130.3, 129.6, 129.3, 129.0, 127.8, 127.5, 112.2, 112.1, 47.8, 47.6, 21.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{26}N_2O_2SH$ 443.1793; Found 443.1783.



N-benzyl-4-({4-[(4-chlorolbenzyl)amino]phenyl}sulfonyl)-aniline **(12d):**[2] Following the general procedure (**iii**), the titled compound was isolated as greenish liquid (190 mg, 0,41 mmol, 82% yield) using silica gel column chromatography (30-40% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 4H), 7.36-7.28 (m, 8H), 7.22 (d, J = 8.4 Hz, 1H), 6.57-6.52 (m, 4H), 4.60 (s, 2H), 4.32 (d, J = 9.5 Hz, 4H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.3, 151.1, 138.2, 136.8, 133.4, 129.3, 129.2, 129.0, 128.9, 128.7, 127.7, 127.4, 112.2, 112.1, 47.7, 47.0 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{23}ClN_2O_2SH$ 463.1247; Found 463.1230.



^{1}H and $^{13}C\{^{1}H\}$ NMR spectra compounds obtained *via* post-synthetic modifications

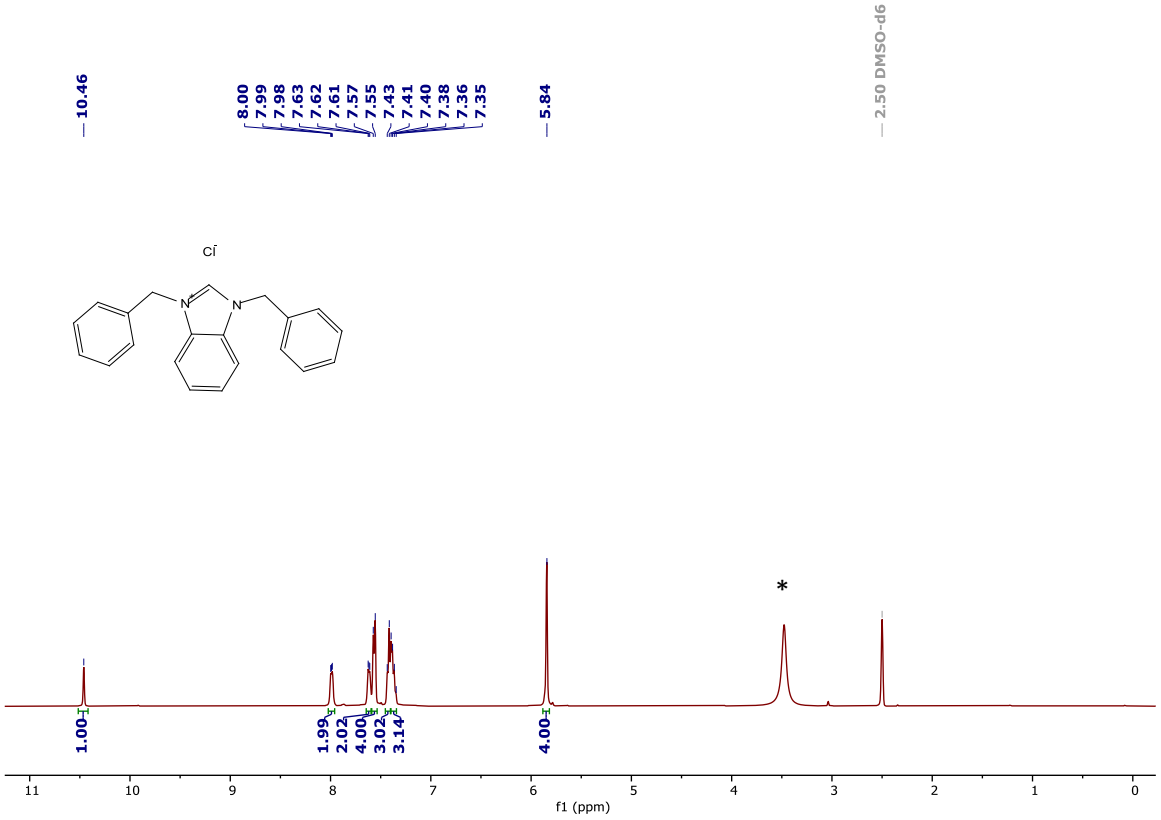


Figure S115. ^{1}H NMR spectrum of **10a** in DMSO-d_6. * indicates the solvent impurity of H_2O.

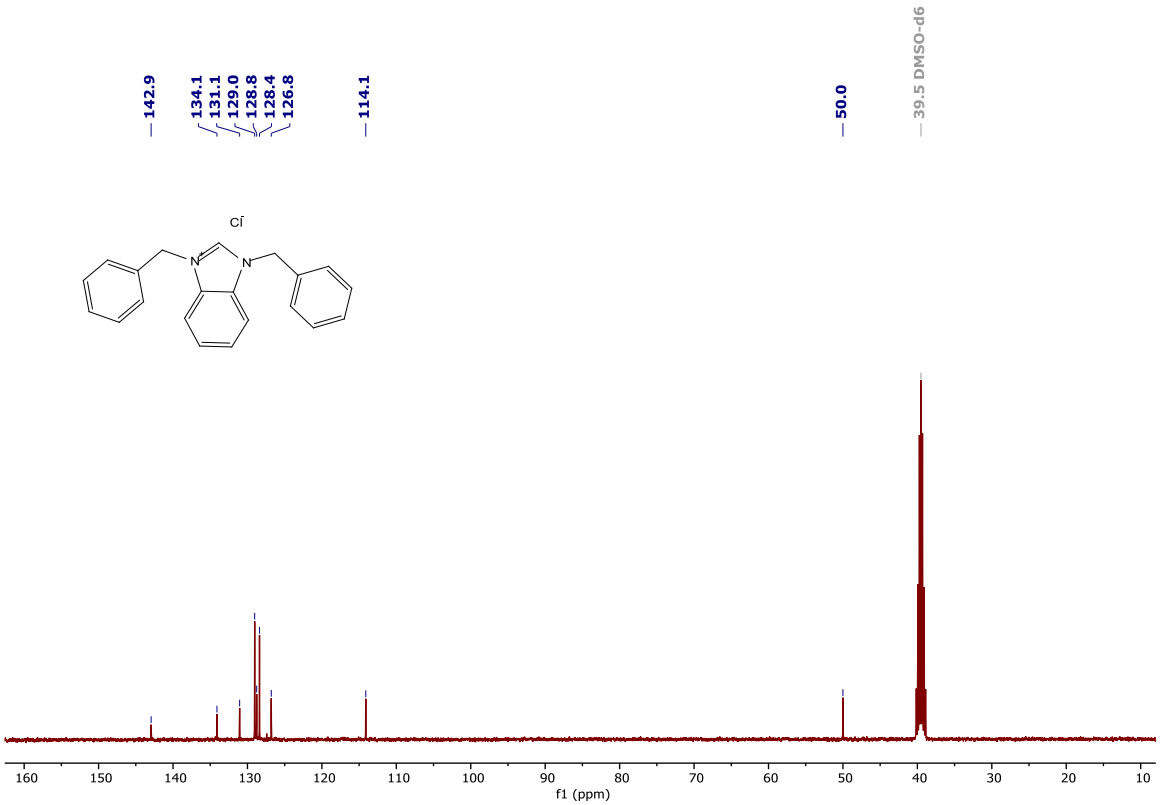


Figure S116. $^{13}C\{^{1}H\}$ NMR spectrum of **10a** in DMSO-d_6.

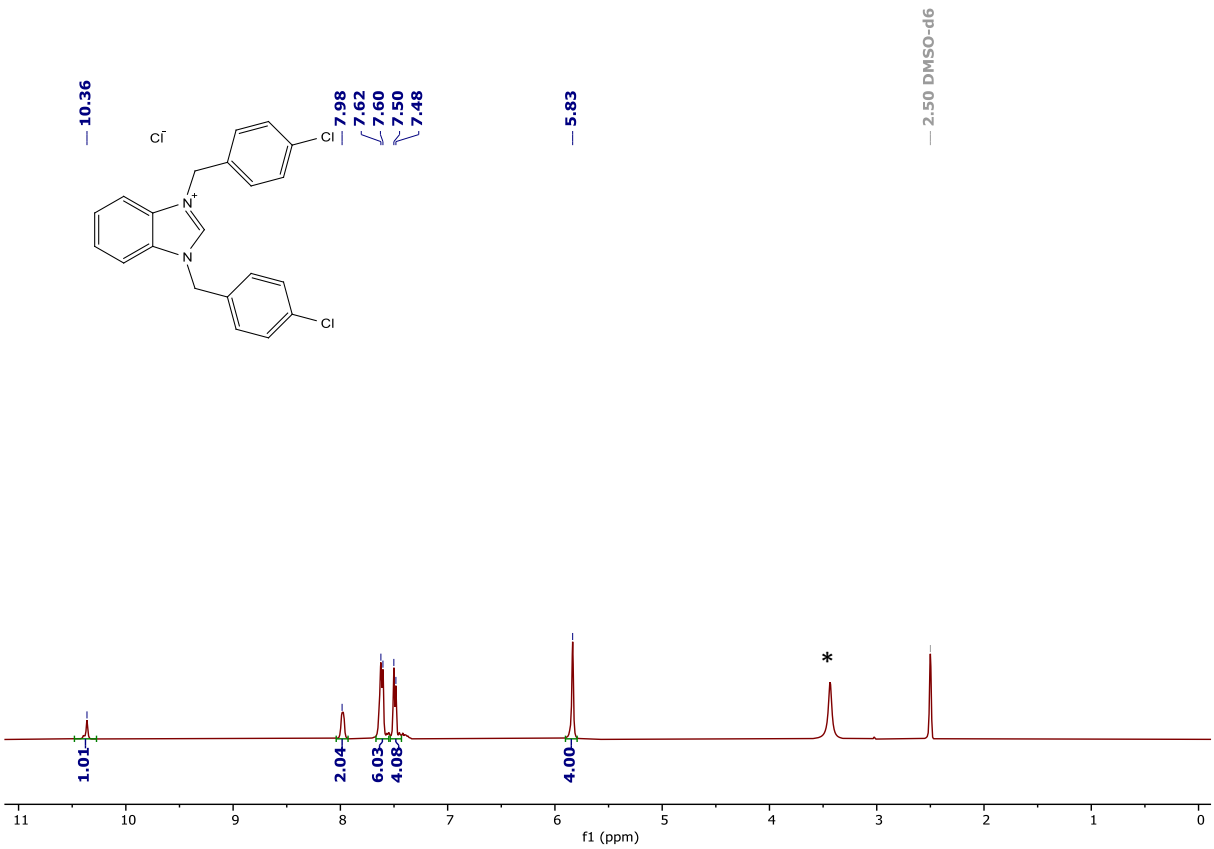


Figure S117. ^{1}H NMR spectrum of **10b** in DMSO-d_6. * indicates the solvent impurity of H_2O.

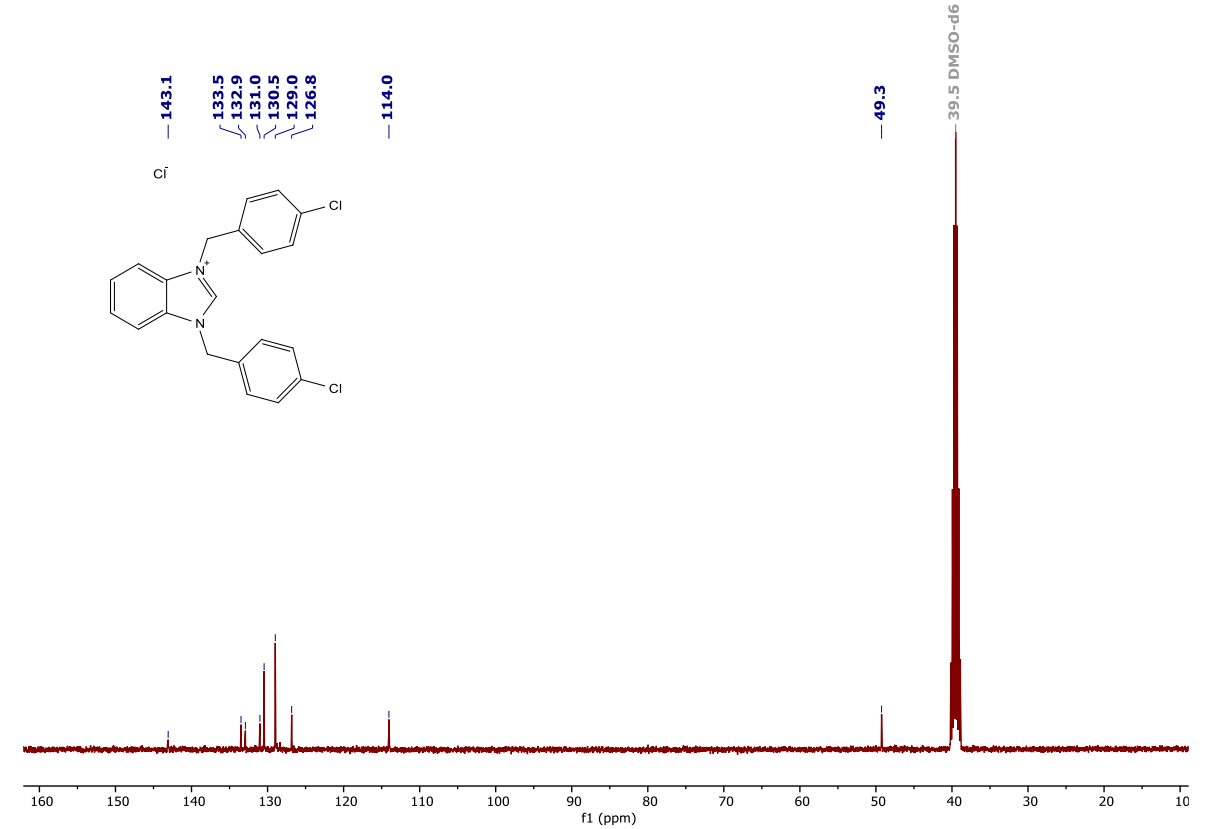


Figure S118. ^{13}C{^{1}H} NMR spectrum of **10b** in DMSO-d_6.

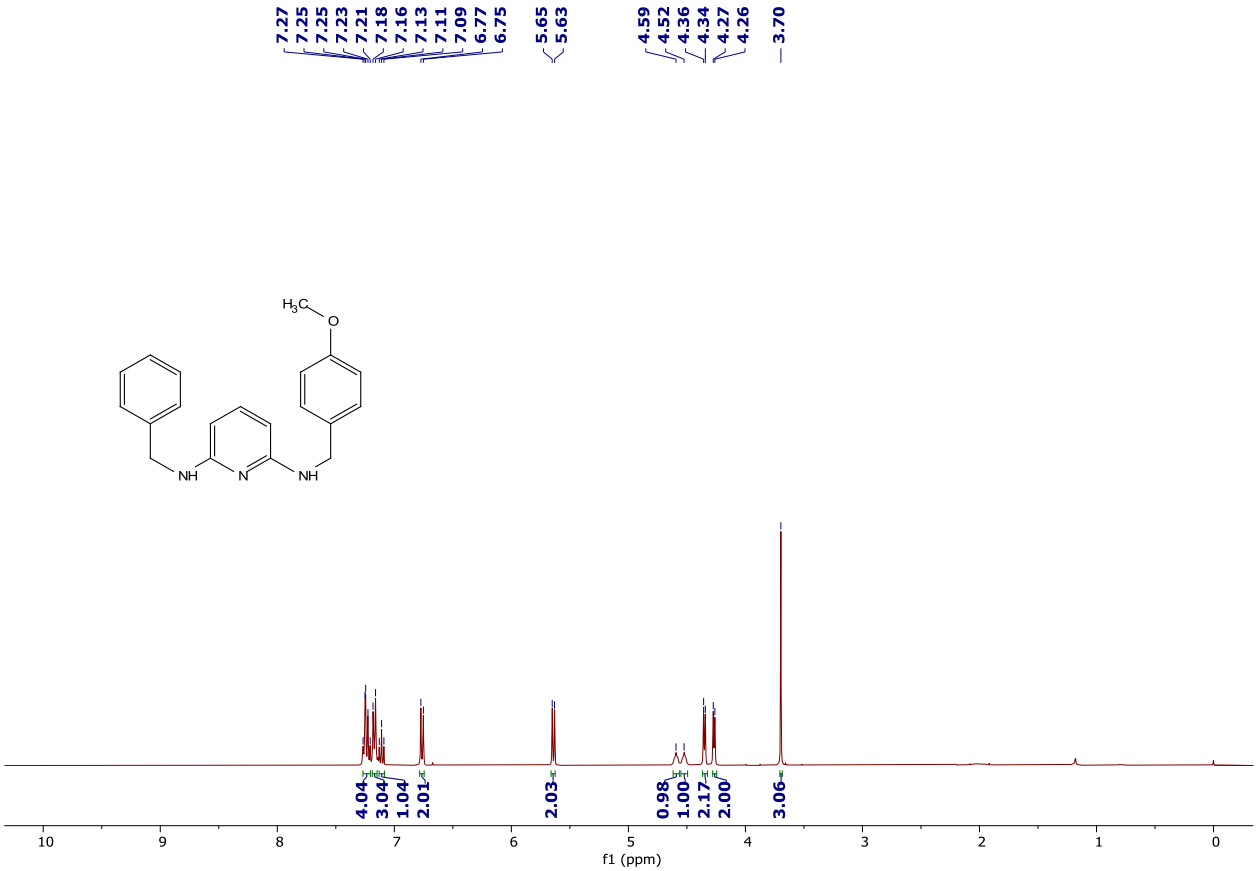


Figure S119. ^{1}H NMR spectrum of **12a** in $CDCl_3$.

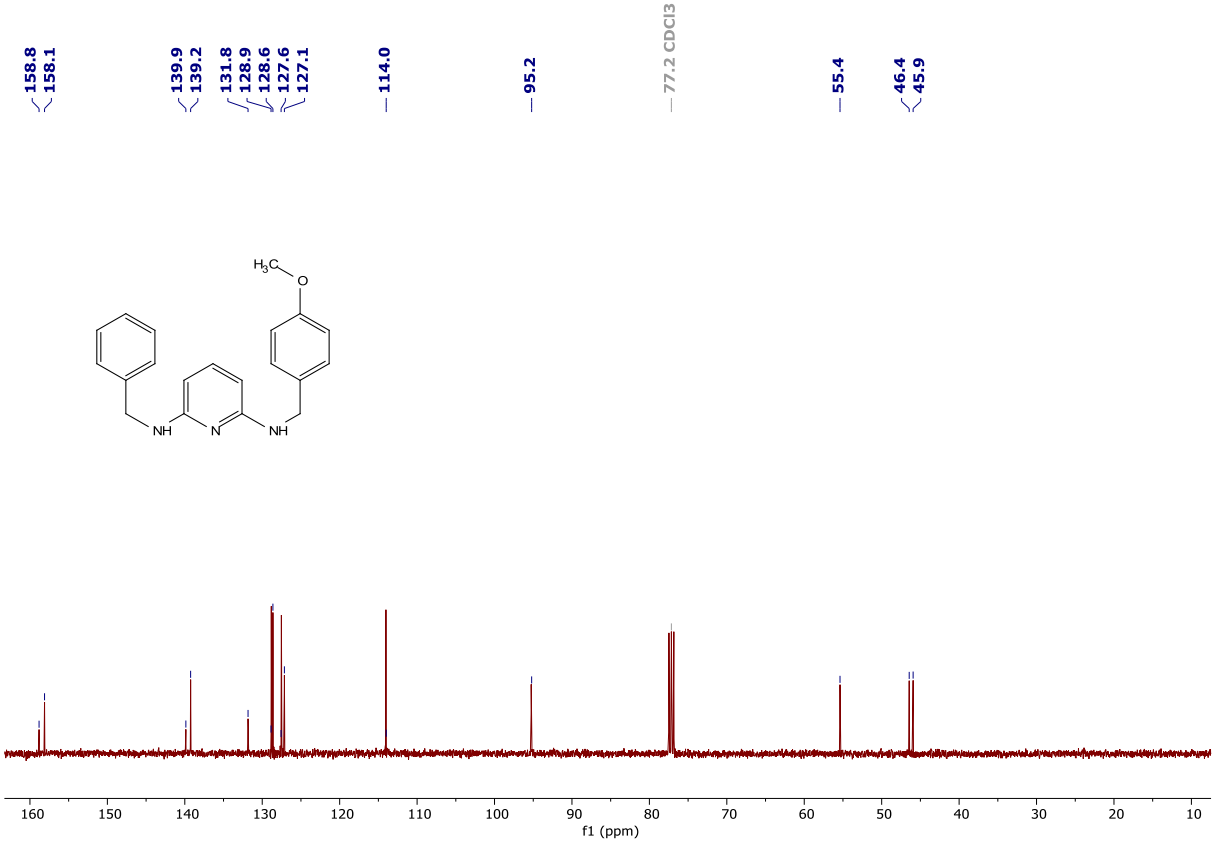


Figure S120. $^{13}C\{^{1}H\}$ NMR spectrum of **12a** in $CDCl_3$.

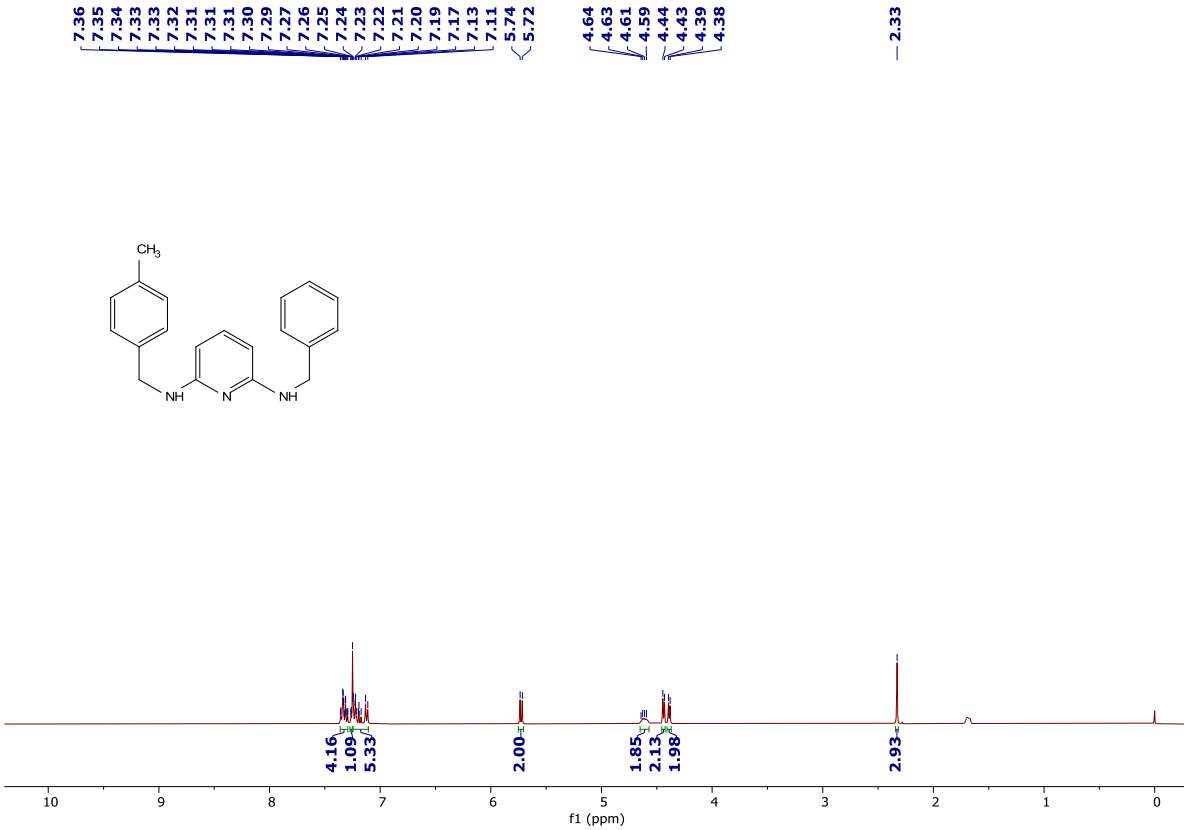


Figure S121. ^{1}H NMR spectrum of **12b** in $CDCl_3$.

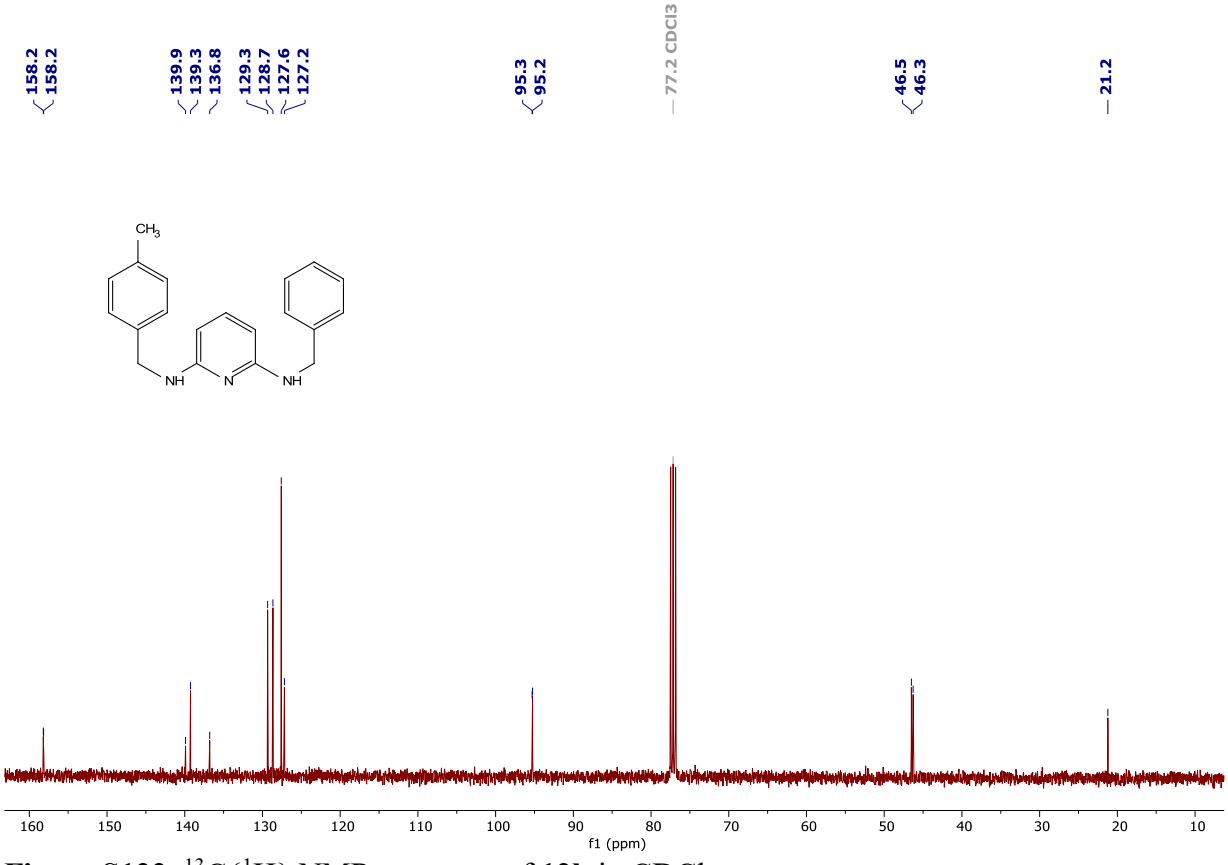


Figure S122. $^{13}C\{^{1}H\}$ NMR spectrum of **12b** in $CDCl_3$.

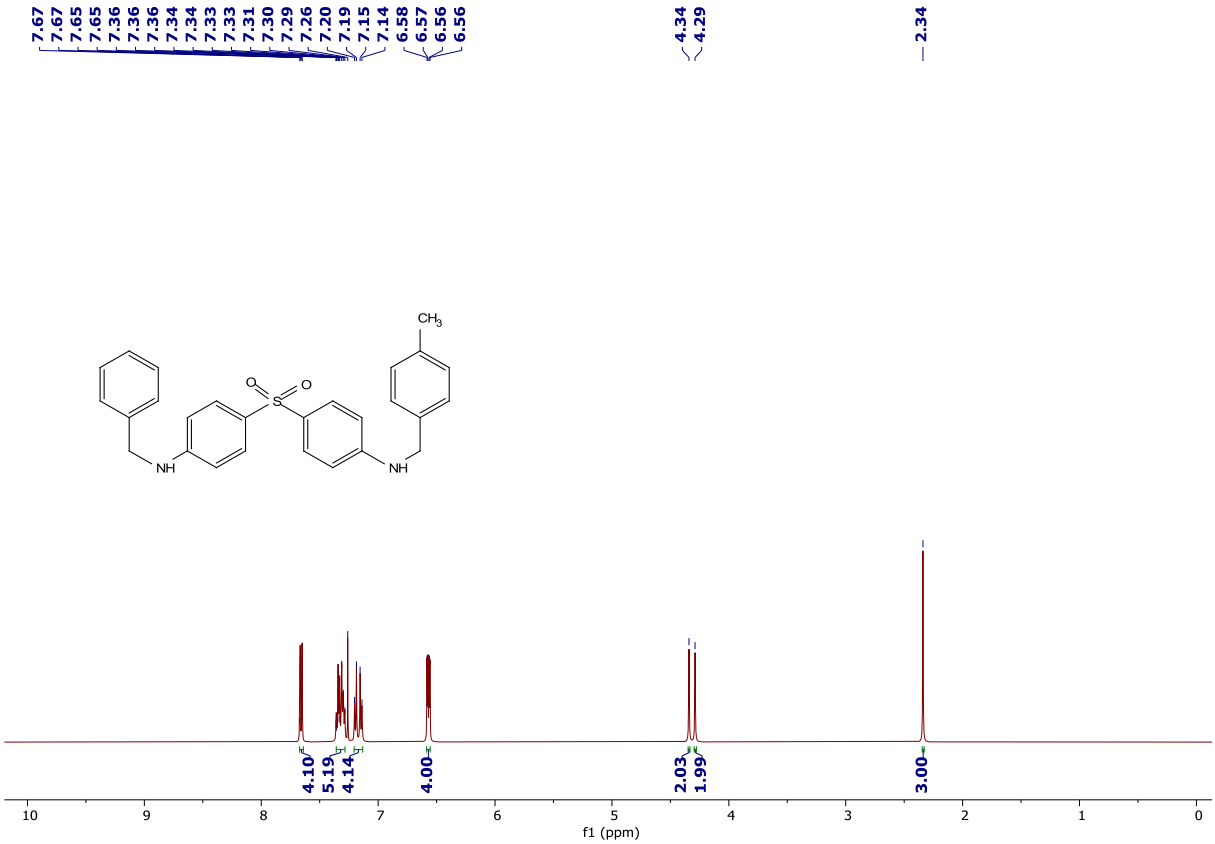


Figure S123. ^{1}H NMR spectrum of **12c** in $CDCl_3$.

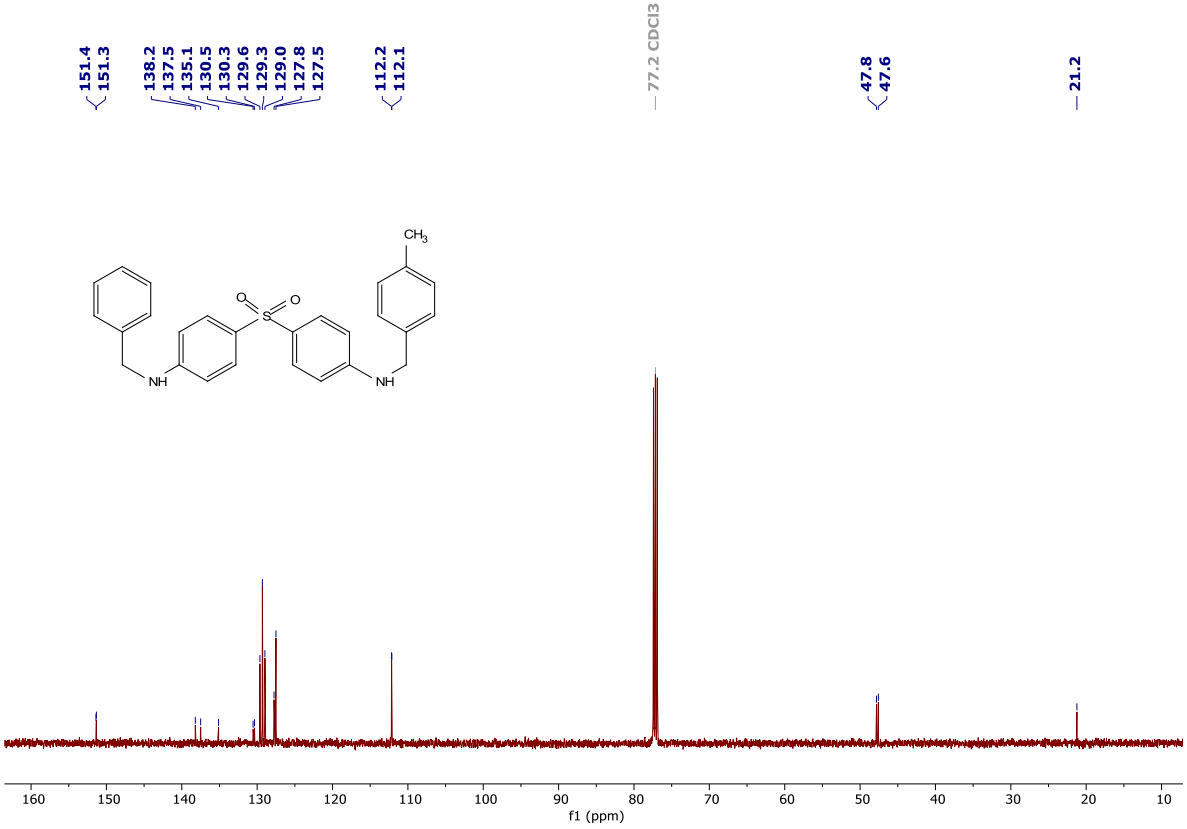


Figure S124. $^{13}C\{^{1}H\}$ NMR spectrum of **12c** in $CDCl_3$.

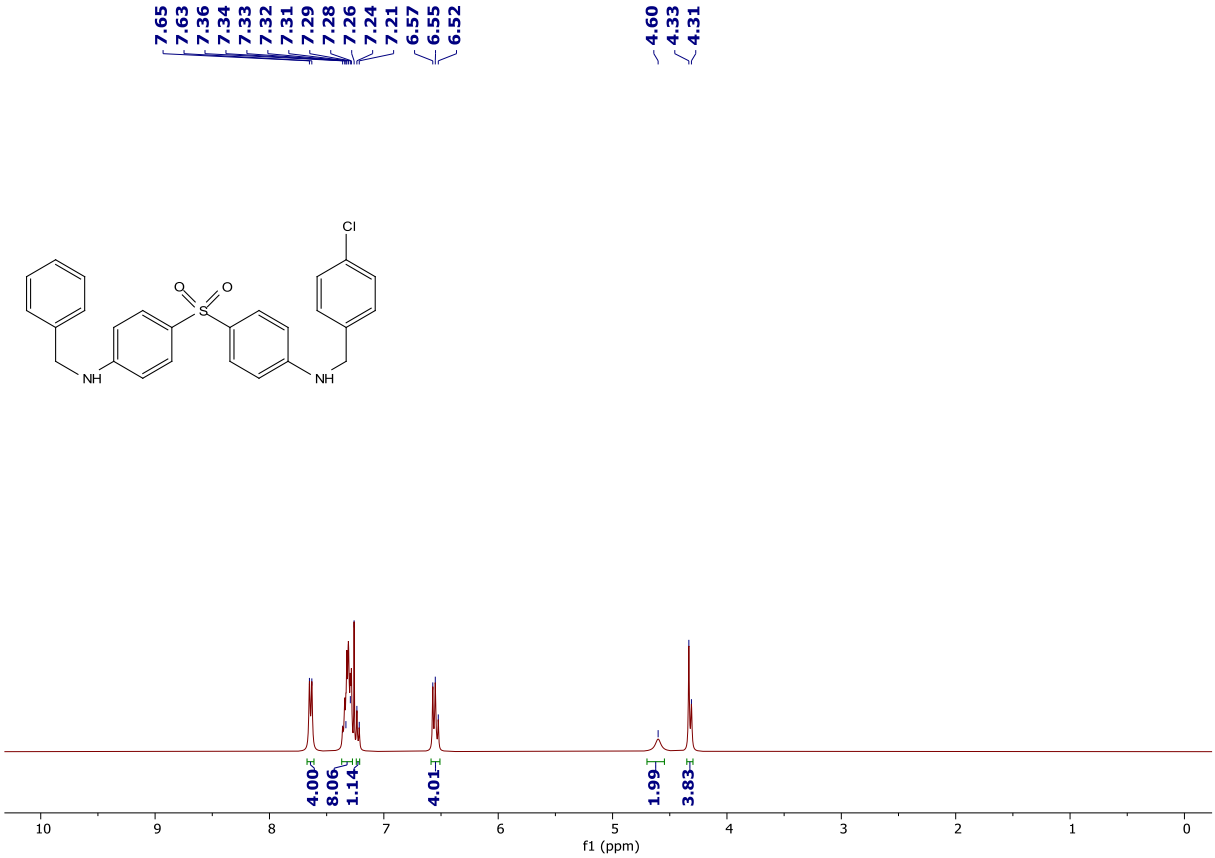


Figure S125. ^{1}H NMR spectrum of **12d** in $CDCl_3$.

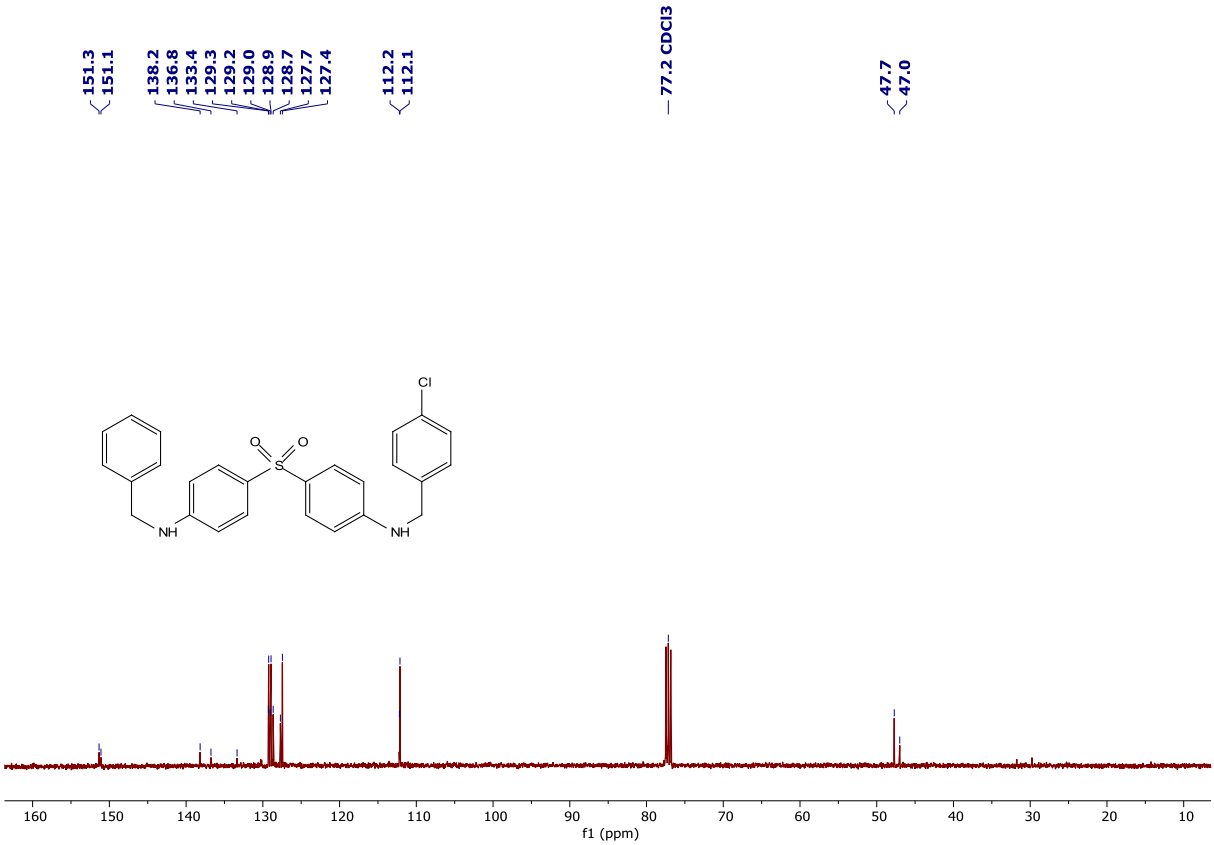


Figure S126. $^{13}C\{^{1}H\}$ NMR spectrum of **12d** in $CDCl_3$.

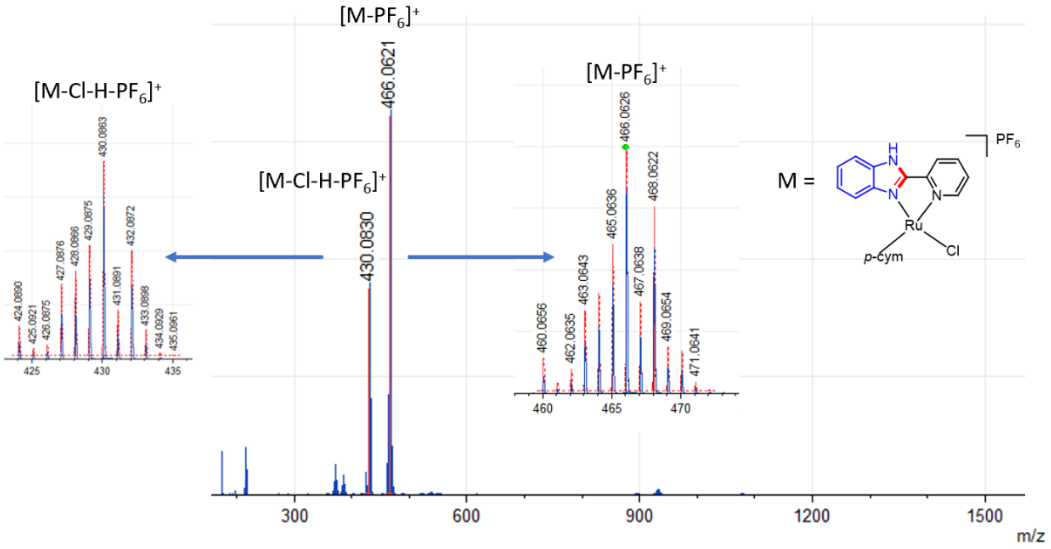


Figure S127. ESI-Mass of Ru-complex (**11a**).

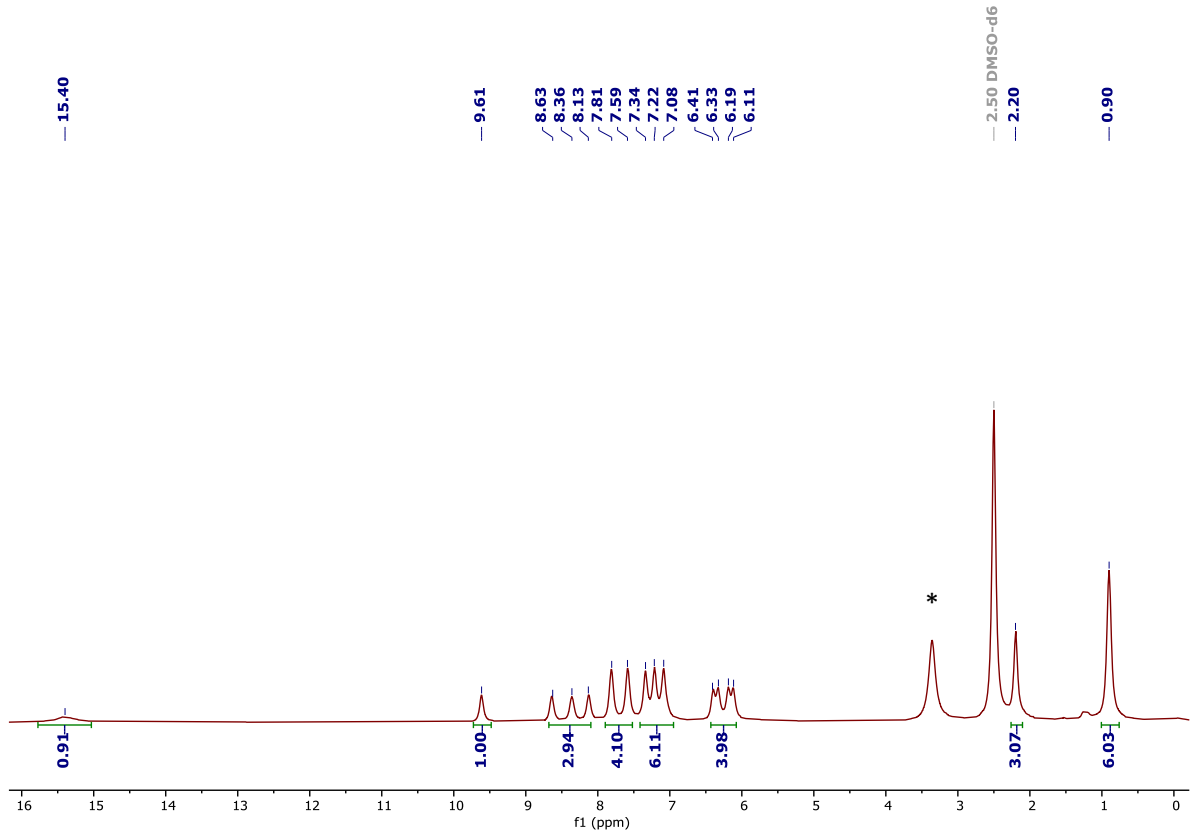


Figure S128. ^{1}H NMR spectrum of the Ru-complex (**11a**) in DMSO-d_6. * indicates the solvent impurity of H_2O.

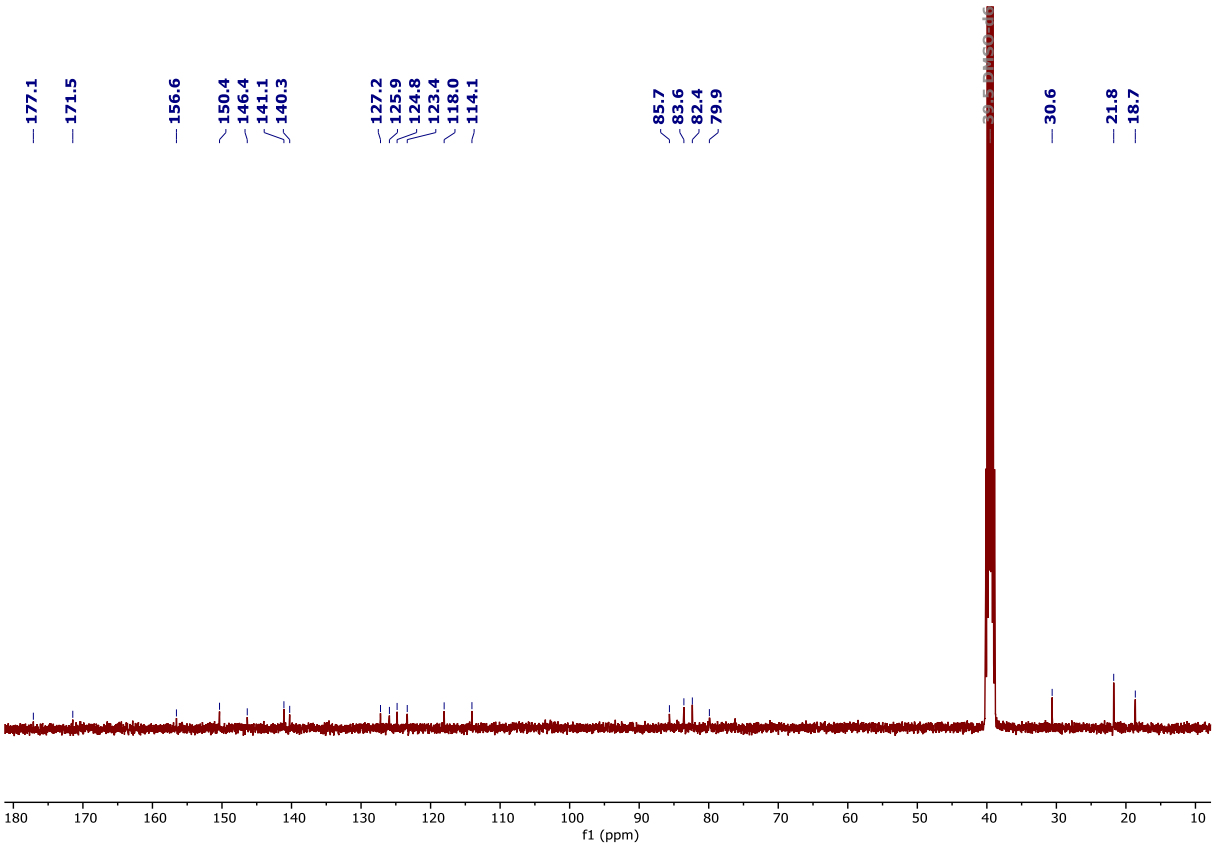


Figure S129. $^{13}C\{^{1}H\}$ NMR spectrum of **11a** in DMSO-*d*$_6$.

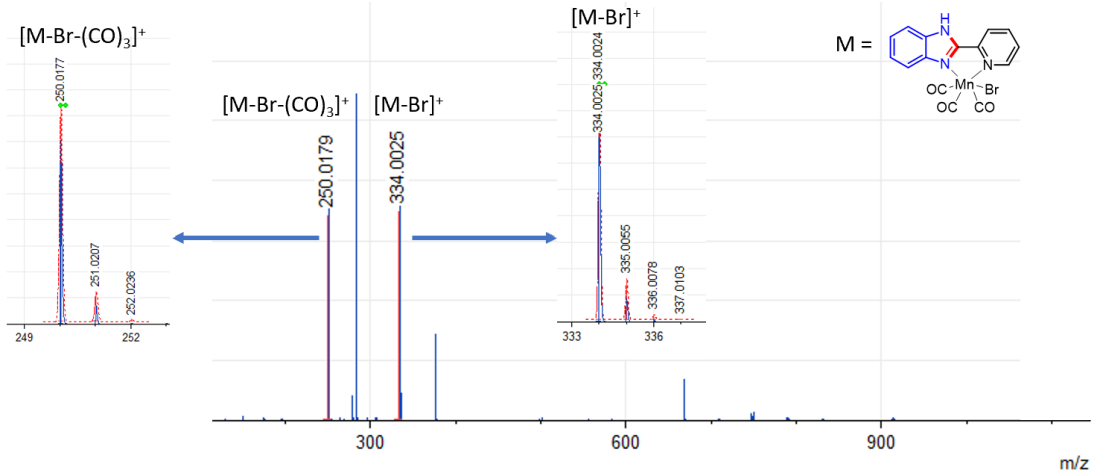


Figure S130. ESI-Mass of Mn-complex (**11b**).

General procedure for control experiments:

i) Effect of catalyst loading (Scheme 1a-b): Different sets of reactions were carried out by charging oven-dried Schlenk tubes (25 mL) with different loadings of $[Co(Cp^*)Cl_2]_2$ (0.5 to 2.5 mol%), ligand **L3/L1** (1 to 5 mol%), and KO^{t}Bu (0.5 mmol, 1 equiv.) followed by toluene (1 mL). Then, the tube was kept in an oil bath at 140 ˚C and heated for 1 h. After cooling to room temperature, *o*-phenylene diamine (0.5 mmol) and alcohol (1.25 mmol) were added and further heated at 140 ˚C for 24 h. After completion of the reaction, analytically pure products were obtained *via* column chromatography and the yield of the isolated product was noted for each case.

ii) Metal hydride trapping experiment (Scheme 2f): An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.0075 mmol), ligand **L3** (0.015 mmol), and KO^{t}Bu (0.5 mmol). Then, the tube was kept in an oil bath at 140 °C for 1 h. After cooling to room temperature, diamine (0.5 mmol), benzyl alcohol (1.25 mmol), and trityl PF_6 (3-5 mol%) were added and further heated at 140 ˚C for 24 h (standard conditions for our catalytic reactions). After completion of the reaction, product **3a** was obtained after column chromatography using hexane/ethyl acetate as eluent in maximum 22% yield.

iii) Radical scavenger experiment (Scheme 2f): An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.0075 mmol), ligand **L3/L1** (0.015 mmol), and KO^{t}Bu (0.5 mmol). Then, the tube was kept in an oil bath at 140 °C for 1 h. After cooling to room temperature, diamine (0.5 mmol), benzyl alcohol (1.25 mmol), and TEMPO/BHT (0.5 mmol) were added and further heated at 140 °C for 24 h (standard conditions for our catalytic reactions). After completion of the reaction, analytically pure **3a/4a** was obtained in ~74-79% yield after column chromatography.

iv) Mercury dropping experiment (Scheme 2e): An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.0075 mmol), ligand **L3** (0.015 mmol), and KO^{t}Bu (0.5 mmol). Then, the tube was kept in an oil bath at 140 °C for 1 h. After cooling to room temperature, diamine (0.5 mmol), benzyl alcohol (1.25 mmol), and elemental mercury (1.0 mmol) were added and further heated at 140 ˚C for 24 h (standard conditions for our catalytic reactions). After completion of the reaction, the reaction mixture was decanted, and product **3a** obtained in 73% yield after purification *via* column chromatography.

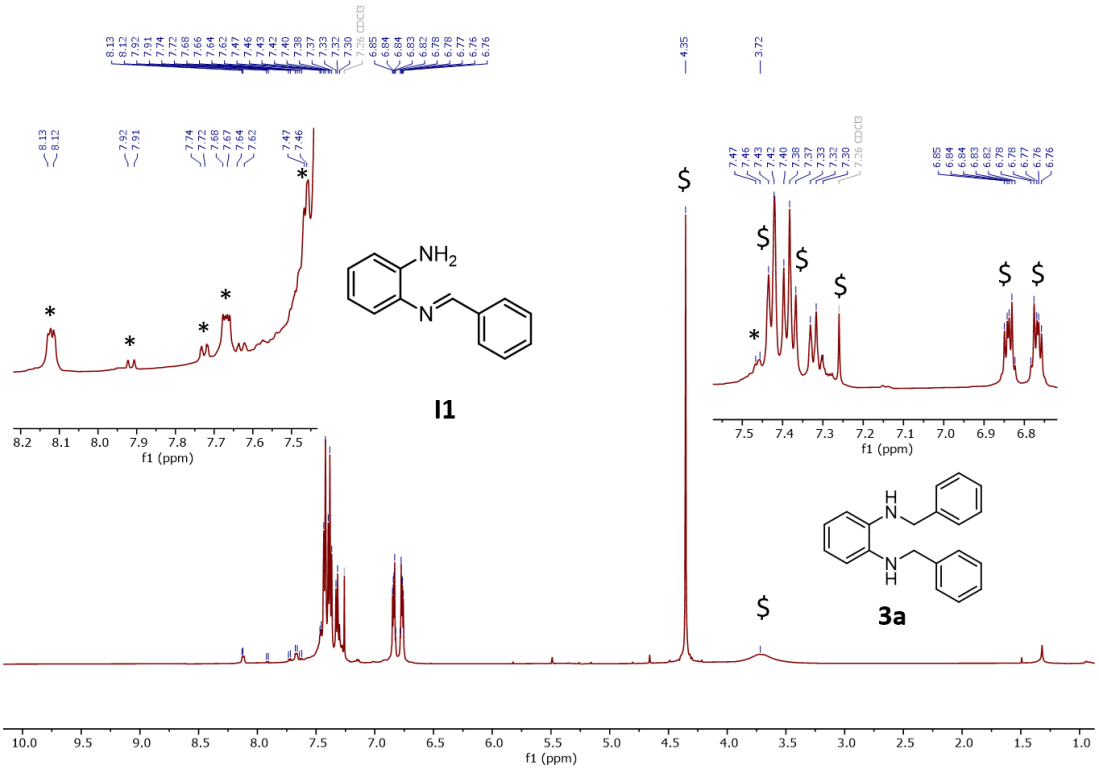


Figure S131. ^{1}H NMR spectrum of a reaction mixture (~ 4 h) of diamine dialkylation catalysed by **CoL3** in $CDCl_3$. * peaks are for **I1**, **$** peaks for **3a**.

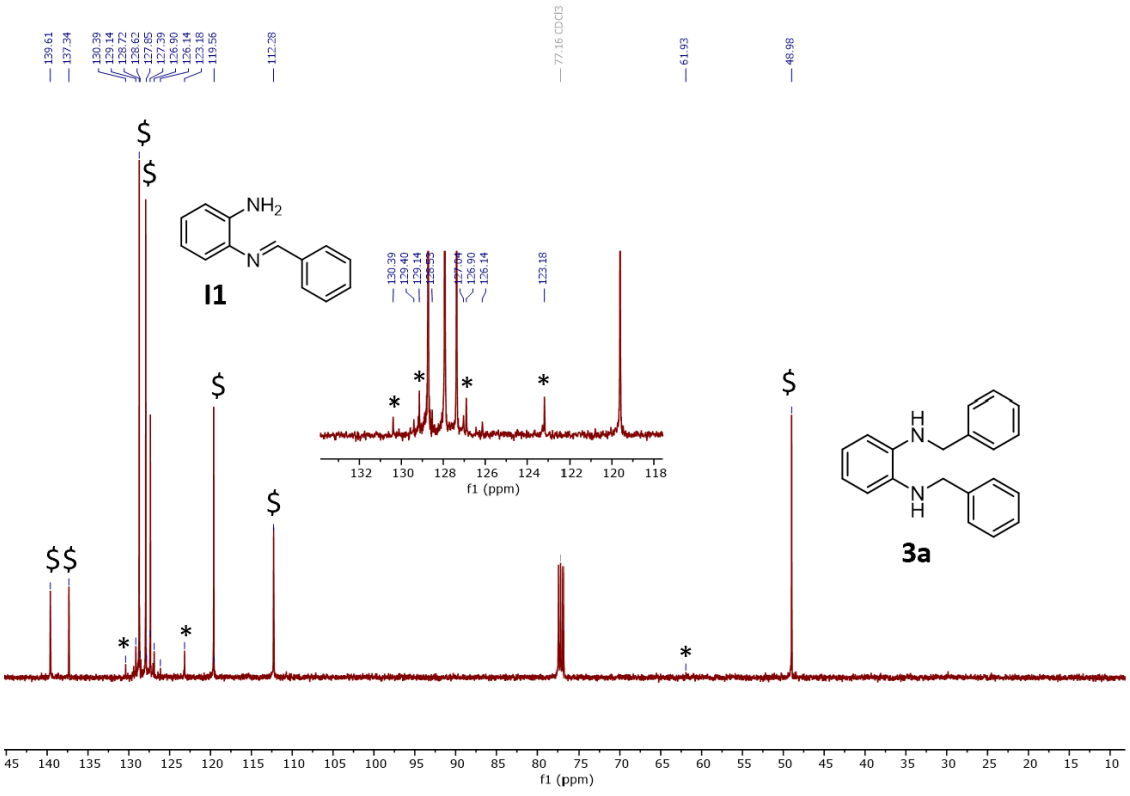


Figure S132. $^{13}C\{^{1}H\}$ NMR spectrum of a reaction mixture (~ 4 h) of diamine dialkylation catalysed by **CoL3** in $CDCl_3$. * peaks are for **I1**, **$** peaks for **3a**.

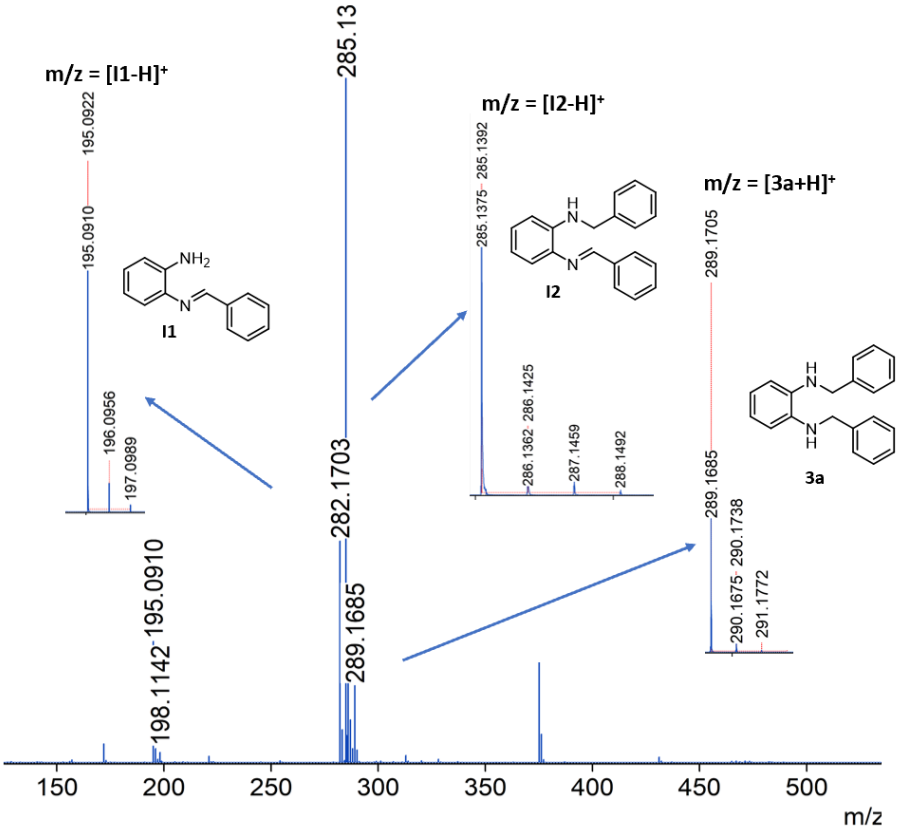


Figure S133. ESI-MS of a reaction mixture of diamine dialkylation catalysed by **CoL3**.

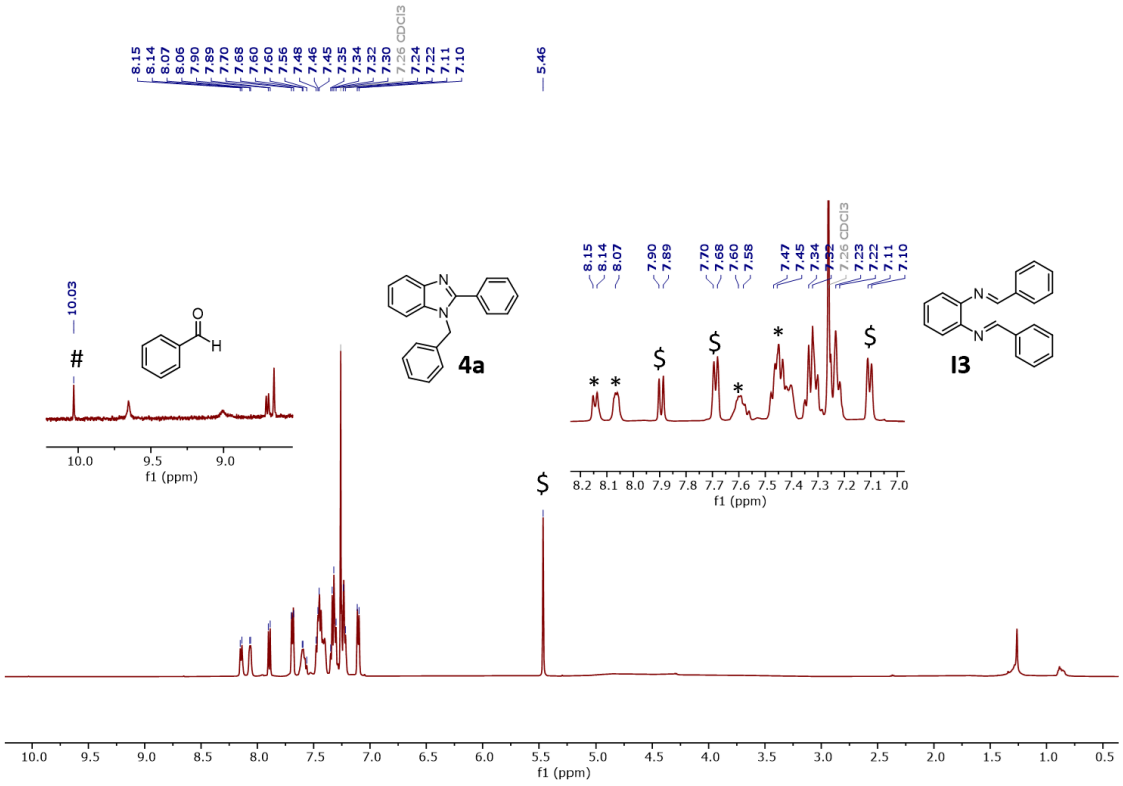


Figure S134. ^{1}H NMR spectrum of a reaction mixture (~ 4 h) of diamine cyclisation catalysed by **CoL1** in $CDCl_3$. ***** peaks are for **I3**, **$** peaks for **4a**, and # for benzaldehyde.

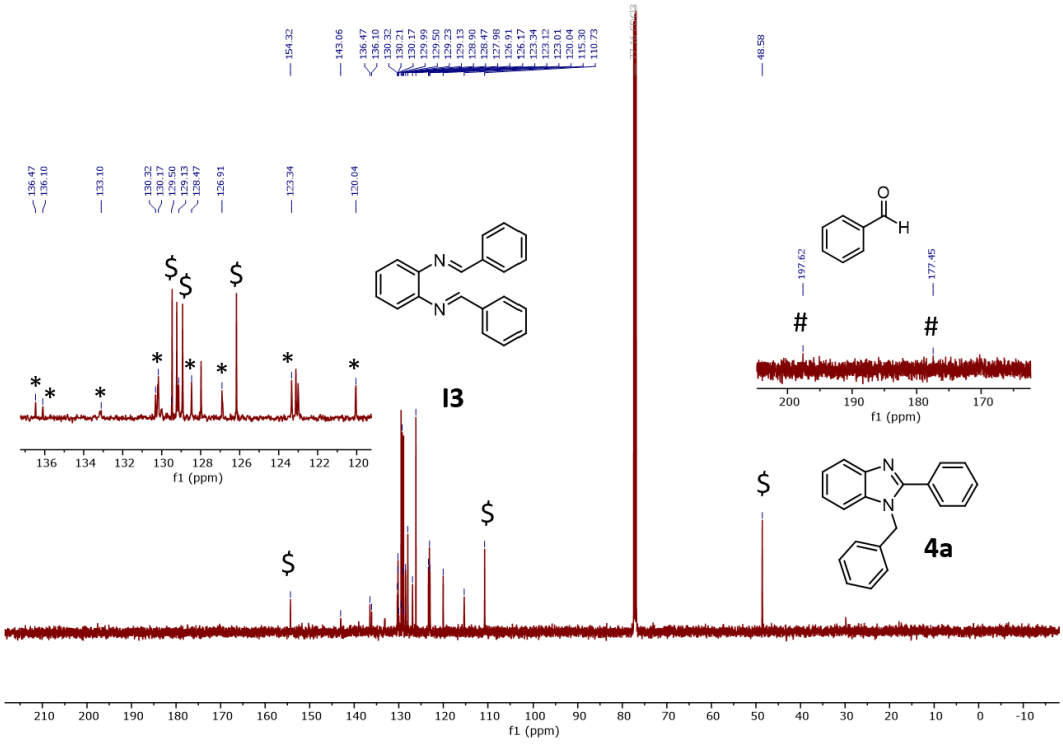


Figure S135. $^{13}C\{^{1}H\}$ NMR spectrum of a reaction mixture (~ 4 h) of diamine cyclisation catalysed by **CoL1** in $CDCl_3$. ***** peaks are for **I3**, **$** peaks for **4a** and # for benzaldehyde.

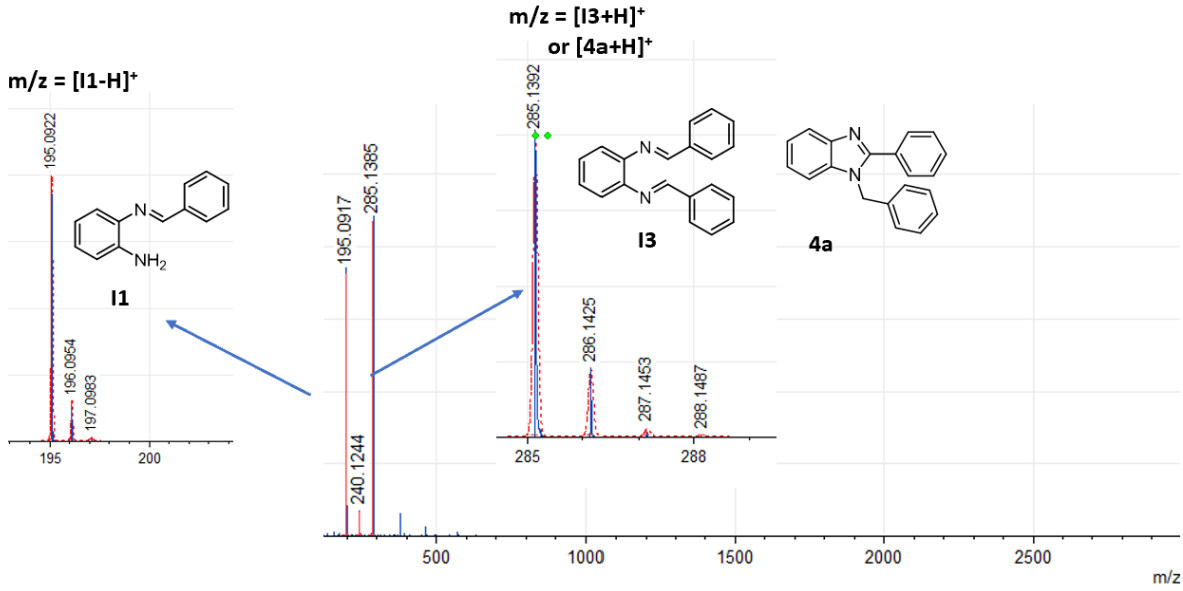
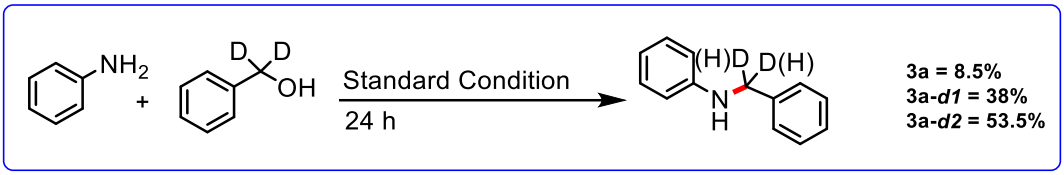


Figure S136. ESI-MS of a reaction mixture a reaction mixture of diamine cyclisation catalysed by **CoL1**.

General procedure for deuterium labelling experiment

The metal precursor $[(Cp^*)CoCl_2]_2$ (1 mol%), ligand (**L3**) (2 mol%) and KO^{t}Bu (0.25 mmol) were taken in a pre-dried Schlenk tube under inert atmosphere followed by the addition of toluene. The closed Schlenk tube was stirred at 140 °C for 1 h. After that, it was charged with aniline (0.25 mmol) and benzyl alcohol-d_2 (0.375 mmol) in an inert atmosphere at room temperature and again stirred at 140 °C for 20 h. The resultant solution was concentrated and purified by silica gel column chromatography and the percentage of deuterium incorporation was analysed from ^{1}H-NMR.



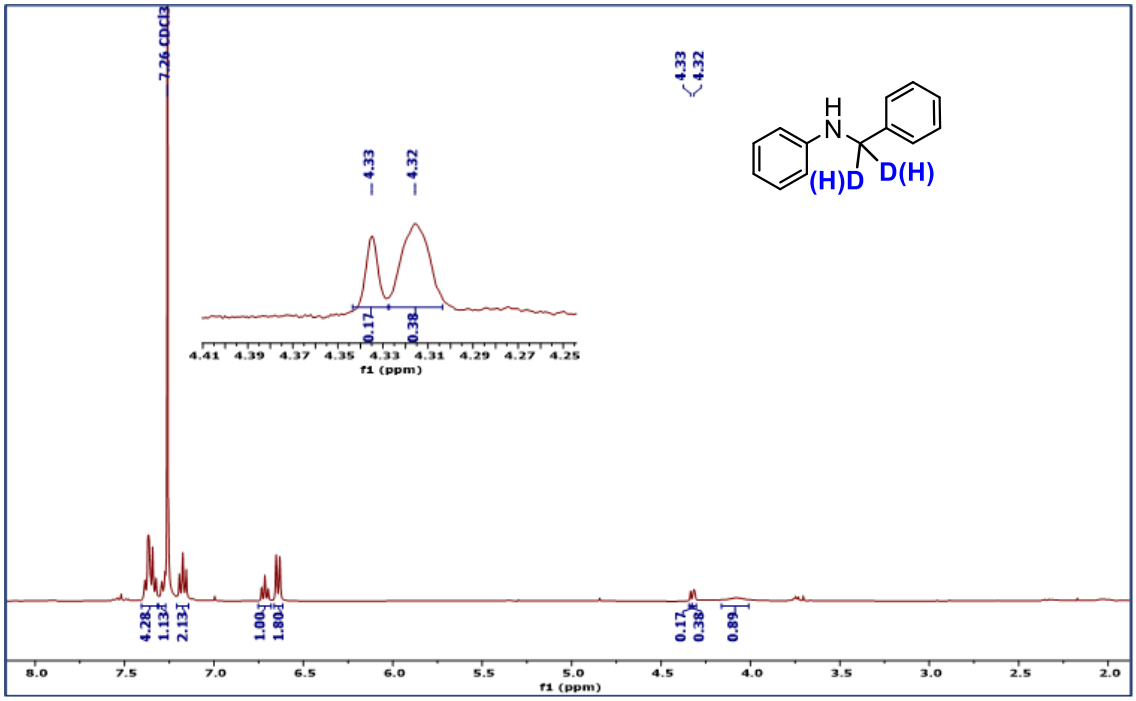


Figure S137. ^{1}H NMR spectrum of **9a-*d*$_1$/*d*$_2$** in $CDCl_3$.

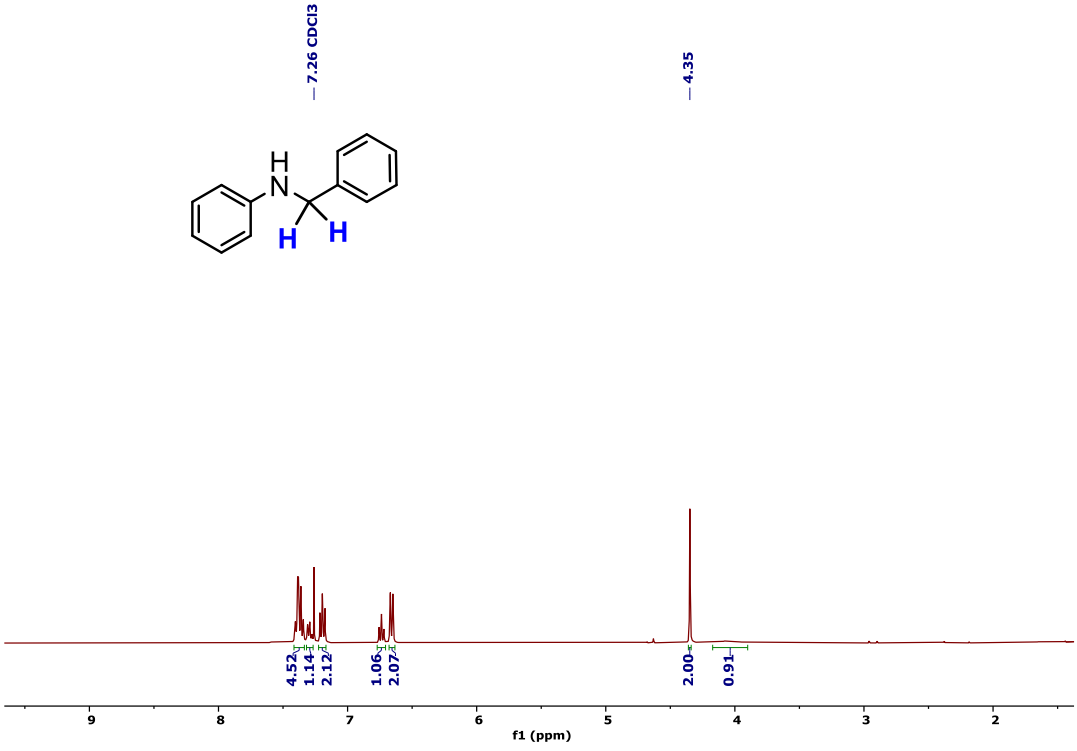


Figure S138. ^{1}H NMR spectrum of **9a** in $CDCl_3$.

Product distribution by ^{1}H NMR integration

	9a	9a-d_1	9a-d_2
Signal	4.33 [benzyl-H(2H)]	4.32 [benzyl-H(1H)]	-
Integral Value	0.17	0.38	-
Calculated ratio	**8.5%**	**38%**	**53.5%**

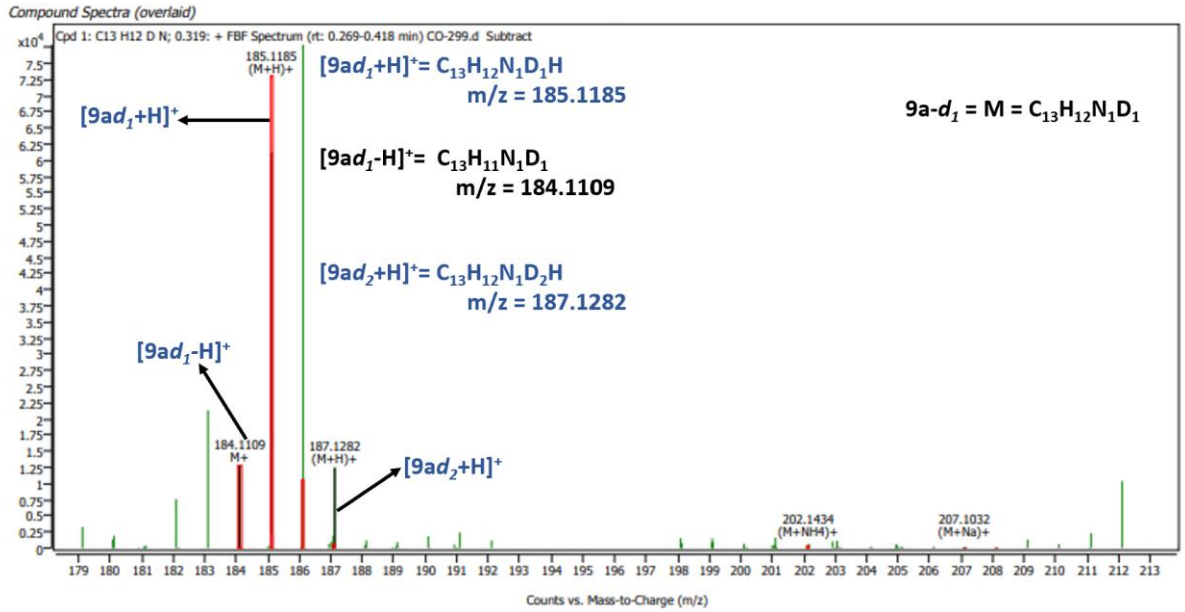


Figure S139. HRMS of deuterated product **9a-d_1/d_2**.

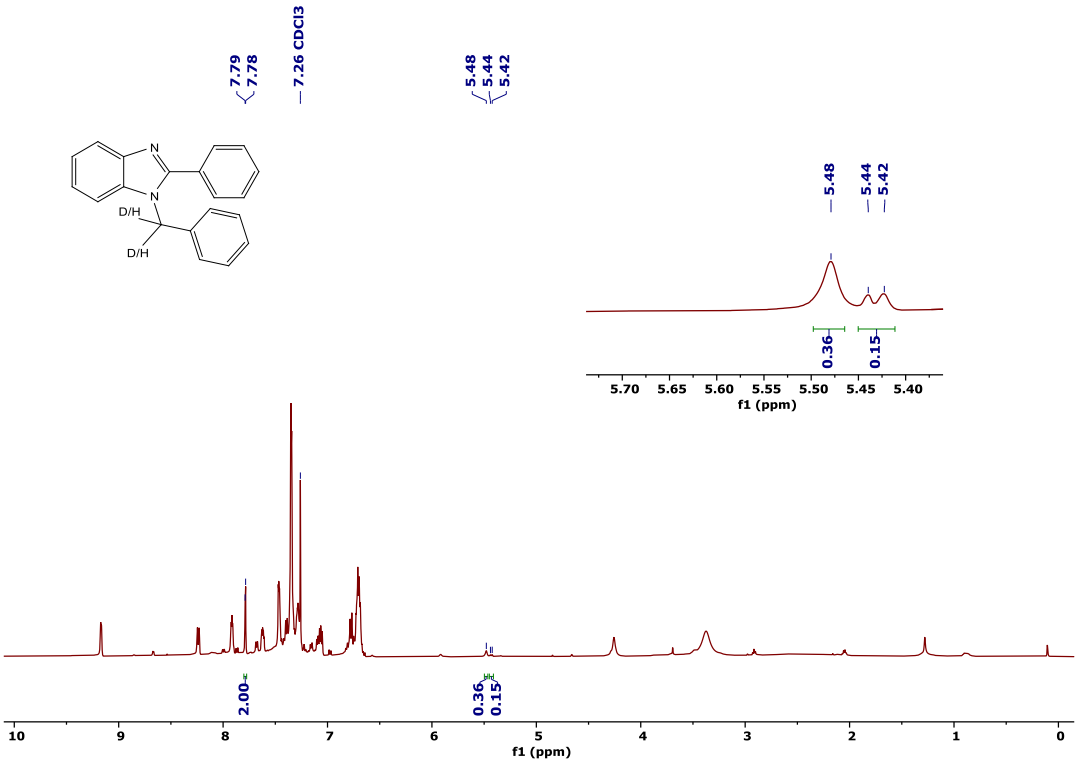


Figure S140. ^{1}H NMR spectrum of a reaction mixture for **4a-d_1/d_2** in $CDCl_3$.

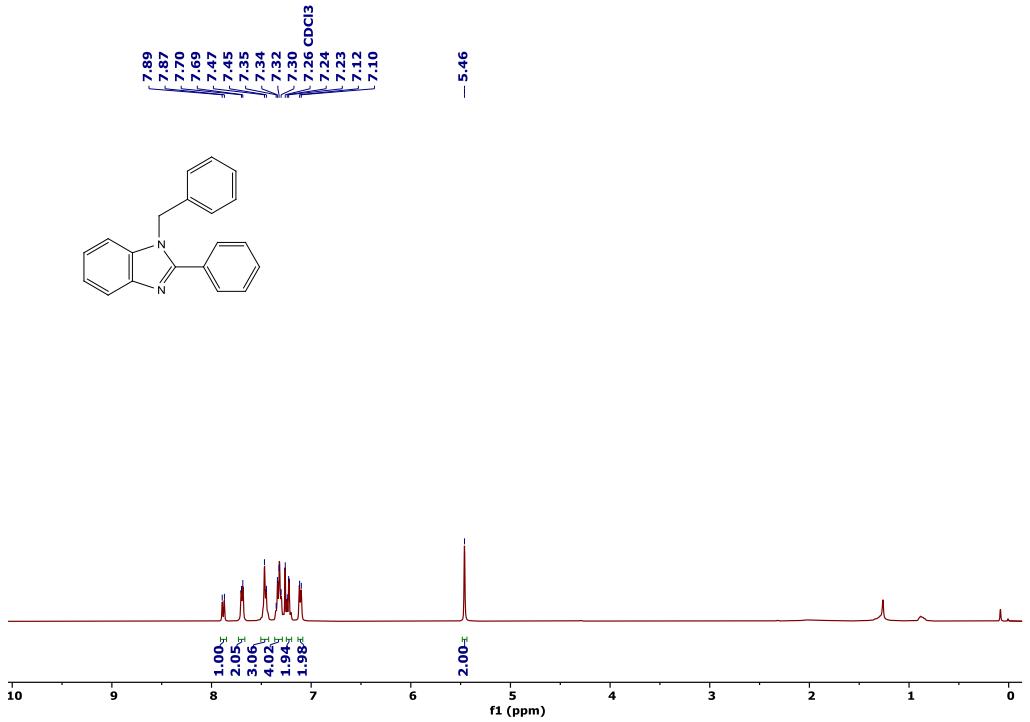


Figure S141. ^{1}H NMR spectrum of **4a** in $CDCl_3$.

Product distribution by ^{1}H NMR integration

	4a	**4a-*d*$_1$**	**4a-*d*$_2$**
Signal	5.48 [benzyl-H(2H)]	5.43 [benzyl-H(1H)]	-
Integral Value	0.36	0.15	-
Calculated ratio	**18%**	**15%**	**67%**

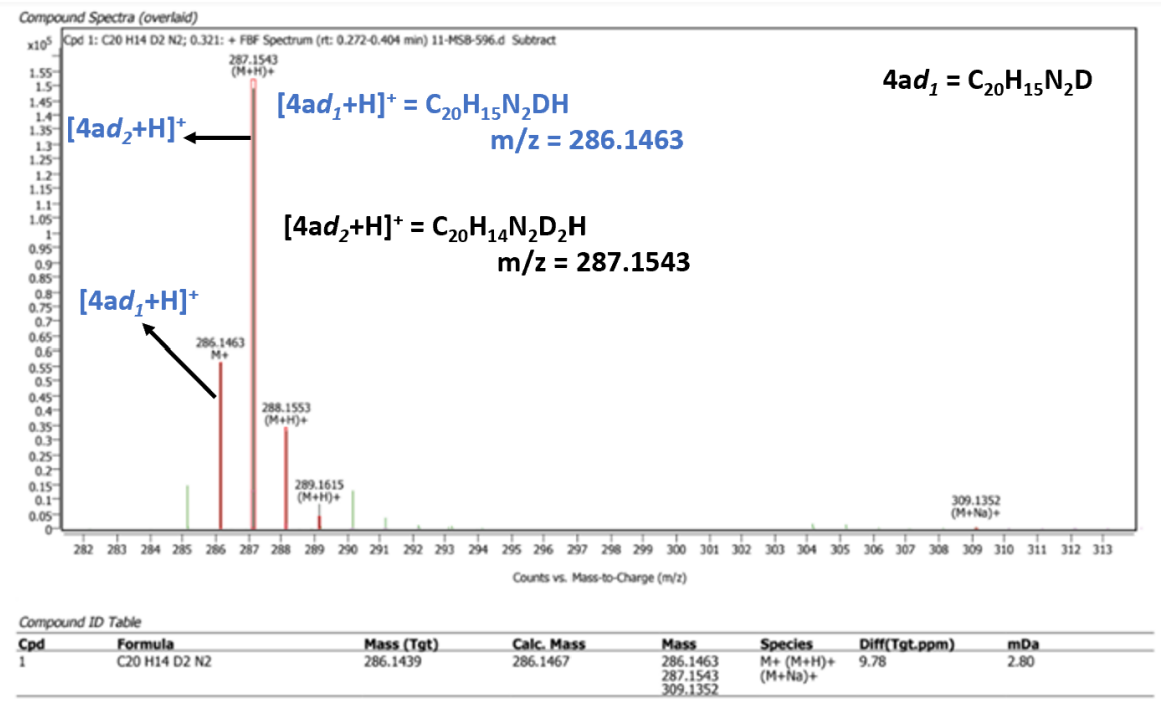


Figure S142. HRMS of deuterated product **4a-*d*₂**.

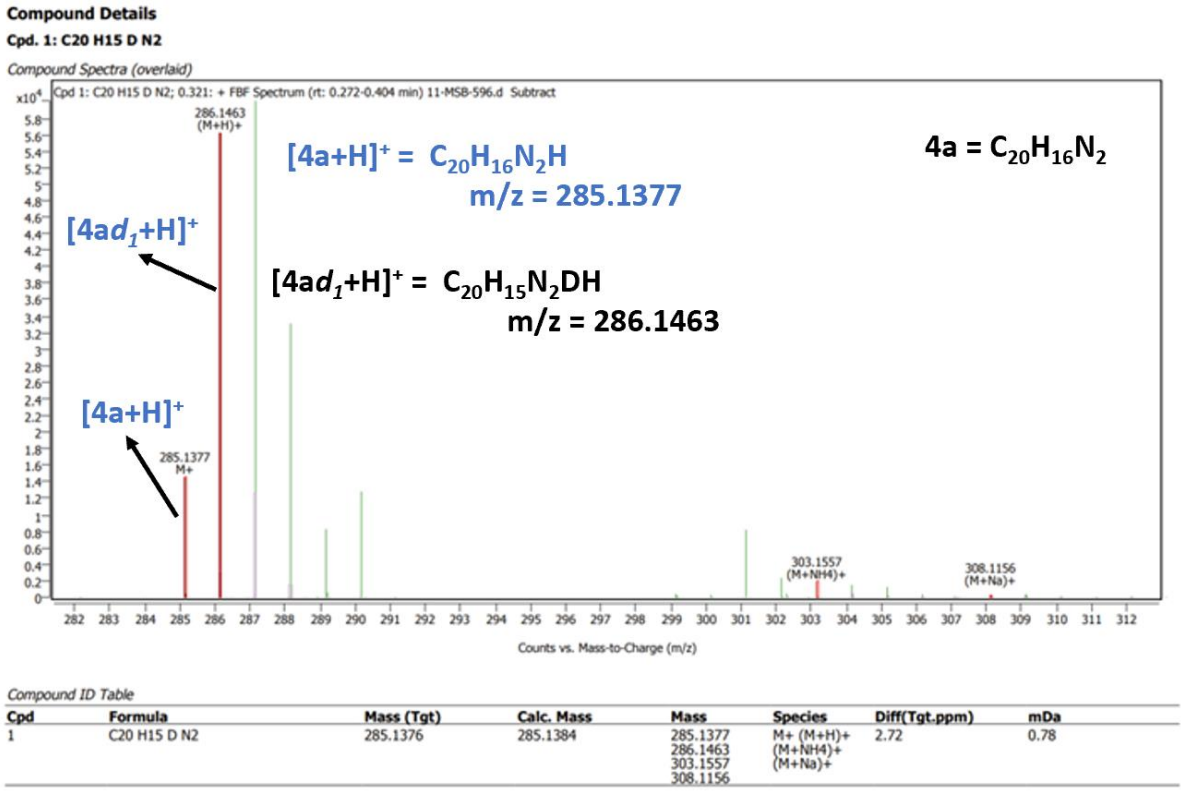


Figure S143. HRMS of deuterated product **4a-*d*₁**.

***In situ* NMR monitoring experiment for dehydrogenation of alcohol:**

An oven-dried Schlenk tube (25 mL) was charged with $[Co(Cp^*)Cl_2]_2$ (0.0075 mmol), ligand **L3** (0.015 mmol), and KO^{t}Bu (0.5 mmol) followed by toluene (1 mL). Then, the tube was kept in an oil bath at 140 ˚C and heated for 1 h. After cooling to room temperature, alcohol **2** (1.25 mmol) were added and further heated at 140 ˚C and progress of the reaction was monitored over the interval of 6 h, 12 h, and 24 h using ^{1}H NMR analysis.

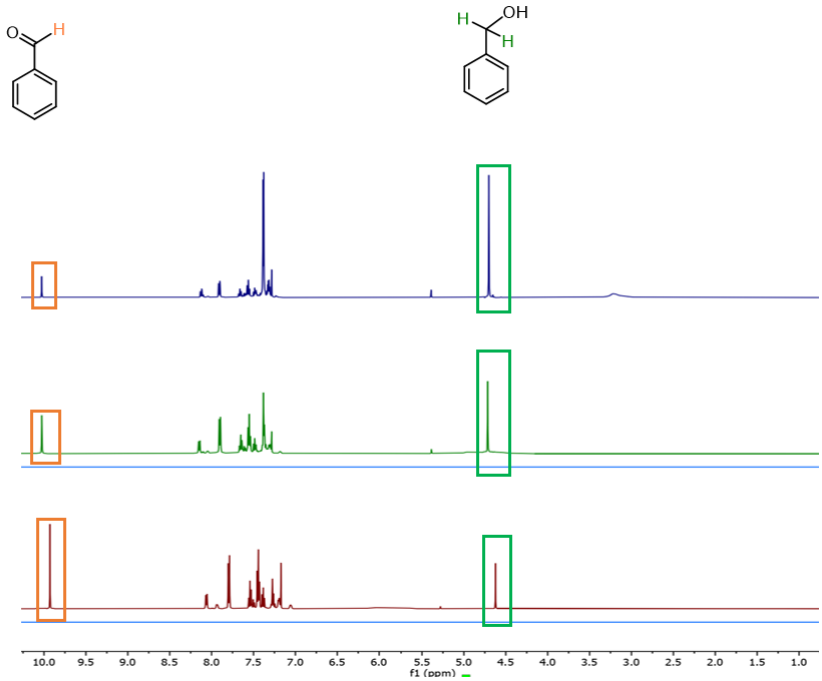


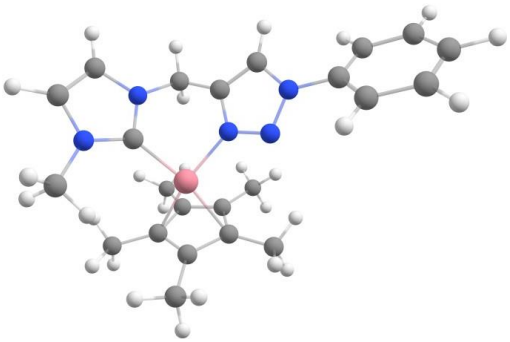
Figure S144. ^{1}H NMR spectra of reaction mixture for alcohol dehydrogenation under optimized conditions of table 2 catalyzed by **CoL3** catalyst in $CDCl_3$.

Computational data

All the calculations were performed using the Gaussian 16, Revision B.01 program.[16] All structures cationic complexes $[\mathbf{CoL1}]^{2+}$ and $[\mathbf{CoL3}]^{2+}$ were optimized with B3LYP[17] functional. Metal (Co) was treated with LANL2DZ[18] basis set with an effective core potential, while the other atoms were treated using using 6-31G**[19], a double-ζ Pople type basis set.

Cartesian Coordinates of all the optimized geometries:

Cationic complex of [CoL1]$^{2+}$

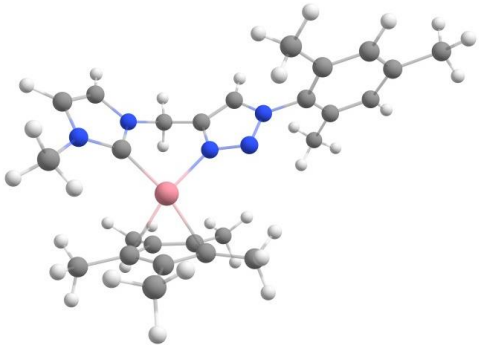


6	-2.271034529	1.648781754	0.865684946
6	-0.904766263	1.495176024	0.845874841
6	0.205527796	2.307792641	1.441693588
6	1.795392301	3.792175232	0.138823280
6	2.684965937	3.575196495	-0.862054700
6	1.797464183	1.559011718	-0.313072985
6	3.428938417	1.601057475	-2.214763561
6	1.160417247	-1.973728182	1.306489547
6	0.966224125	-2.438180799	-0.063700221
6	2.155428763	-2.165636730	-0.797009587
6	3.016196684	-1.405897149	0.057138691
6	2.410996969	-1.340598042	1.385128895
6	0.169437751	-2.174021030	2.414970979
6	-0.202719867	-3.255053218	-0.535213447
6	2.439783444	-2.587127663	-2.211617878
6	4.438576942	-1.013419454	-0.223374712

6	3.075347222	-0.759534773	2.600063189
27	1.192168427	-0.303020304	-0.155068557
7	-2.752267250	0.583987772	0.164375180
7	-1.754742227	-0.193988897	-0.277552782
7	-0.640095478	0.359070778	0.136416583
7	1.261123821	2.551666612	0.455756074
7	2.667144655	2.212308126	-1.128287325
1	-0.283217880	-3.250968636	-1.625225032
1	-0.097264868	-4.300468914	-0.218536116
1	-1.148106759	-2.881587856	-0.134622956
1	-0.857312277	-2.011569504	2.073337576
1	0.219999904	-3.201774927	2.794982697
1	0.357510759	-1.505915226	3.259427487
1	2.356956435	-0.553887974	3.398207062
1	3.820711221	-1.453116836	3.009658545
1	3.599258115	0.173830392	2.371767091
1	4.683630459	-0.029679522	0.188163486
1	5.123003599	-1.734192020	0.241295118
1	4.664068015	-1.004081370	-1.291821584
1	1.536364593	-2.586804055	-2.827956319
1	3.172802865	-1.936316684	-2.696551045
1	2.849180618	-3.604580374	-2.237998432
1	-0.172803554	3.271242464	1.787862045

1	0.634706295	1.785879212	2.304181938
1	3.313849028	4.261834038	-1.406600786
1	1.505710535	4.700830218	0.642817857
1	-2.911392119	2.410055483	1.280855947
1	3.210697147	2.118536176	-3.152028144
1	4.500706516	1.657803782	-2.010698987
1	3.127907991	0.559244095	-2.300933334
6	-5.104465789	0.531934569	0.816744554
1	-4.842964163	0.949350509	1.783834048
6	-6.431581654	0.228640027	0.514921276
1	-7.206180781	0.434665750	1.246287612
6	-6.758694688	-0.351837326	-0.712125117
1	-7.792542723	-0.590287357	-0.939932562
6	-5.756418796	-0.629200729	-1.644870637
1	-6.009284187	-1.079208627	-2.599355637
6	-4.426594237	-0.320148309	-1.364669267
1	-3.639939077	-0.517028166	-2.083584135
6	-4.117213256	0.259356360	-0.1325510916

Cationic complex of [CoL3]$^{2+}$



6	-6.287962896	-0.115246316	-0.551296271
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6	-4.131860713	0.921005358	-1.065669045
6	-3.611272746	0.302001756	0.081939828
6	-4.375413552	-0.526405768	0.918342977
6	-5.716924869	-0.716960908	0.575930742
6	-3.785105022	-1.199752956	2.134557869
6	-7.747135134	-0.316371704	-0.878825470
6	-3.278637134	1.787452260	-1.960484394
6	-1.707281690	1.403456420	1.315392795
6	-0.343945176	1.244863596	1.229601918
6	0.795604547	1.894062209	1.955980170
6	2.346615539	3.638203164	0.963033334
6	3.191235706	3.656755367	-0.098414708
6	2.311499496	1.566788375	0.015128069
6	3.859374864	2.044971278	-1.897127193
6	1.741443807	-2.239021226	0.832544797
6	1.466826909	-2.389529745	-0.593208273
6	2.615420437	-1.955975090	-1.313943267
6	3.528406510	-1.399911842	-0.363236043
6	2.998733628	-1.632320743	0.978400531
6	0.814906198	-2.686916850	1.924020732
6	0.266734947	-3.087073282	-1.166905908

6	2.816441951	-2.051025568	-2.800658911
6	4.936941459	-0.951223072	-0.629243566
6	3.733881427	-1.328665841	2.252145378
27	1.702109184	-0.285621685	-0.224173044
7	-2.221505618	0.525183222	0.411825062
7	-1.246917958	-0.147543268	-0.215852229
7	-0.114417490	0.287786168	0.282075974
7	1.816558602	2.357220717	1.012084684
7	3.151020892	2.390378096	-0.667063256
1	-3.886503395	2.247027535	-2.742256365
1	-2.789458531	2.593015199	-1.401310474
1	-2.489783539	1.203042628	-2.445920746
1	-7.922456637	-0.288644275	-1.957739816
1	-8.115715608	-1.271717474	-0.496061953
1	-8.358640933	0.474891207	-0.428440378
1	-3.523213630	-0.477714348	2.916741154
1	-4.499083804	-1.903809506	2.566290054
1	-2.874710917	-1.755400905	1.886105934
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1	-5.905681177	1.159538861	-2.242319069
1	0.128997870	-2.847951821	-2.224350951
1	0.377675812	-4.176078182	-1.088577890
1	-0.653079292	-2.808953326	-0.647073622

1	-0.228565462	-2.458583106	1.686191807
1	0.879811084	-3.773101224	2.062964093
1	1.055054274	-2.221371794	2.883387323
1	3.062551568	-1.305707338	3.114863740
1	4.495612545	-2.091500558	2.457728918
1	4.251233331	-0.365394852	2.204670246
1	5.214225850	-0.082611093	-0.024413161
1	5.638935044	-1.755276257	-0.375023568
1	5.103056950	-0.704687261	-1.680041979
1	1.878874806	-1.922985974	-3.348846641
1	3.521969868	-1.301467236	-3.170156772
1	3.220620660	-3.033194958	-3.075517914
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1	1.251934008	1.185728097	2.656152210
1	3.802379680	4.450379092	-0.498616542
1	2.086089149	4.407406391	1.672995164
1	-2.333521022	2.043204186	1.917049113
1	3.609459282	2.766356981	-2.678829614
1	4.939376654	2.049252830	-1.732462023
1	3.541194422	1.052552228	-2.209042171

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