Supporting information for….

An Intramolecular C(sp^3)−H Imination using PhI-*m*CPBA

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CONTENTS

EXPERIMENTAL SECTION

Instrumentation and Chemicals: Column chromatographic purifications of the compounds were performed using silica gel (mesh 100–200 or mesh 230–400) and hexane – ethyl acetate mixtures as eluent unless otherwise specified. NMR spectra were recorded on a 400 MHz or 700 MHz instrument at 25 °C. The chemical shift values are reported in parts per million (ppm) with respect to residual trichloromethane (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C). The peak patterns are designated as follows: s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet; dd: doublet of doublets; td: triplet of doublets; br s: broad singlet. The coupling constants (*J*) are reported in hertz (Hz). High-resolution mass spectra (HR-MS) were recorded on an ESI-TOF (time of flight) mass spectrometer. Infrared spectral data are reported in wave number (cm^{-1}). FT-IR spectra were recorded after making thin layer of the compounds on the surface of NaCl crystal using dichloromethane. Melting points of the compounds were determined using a digital melting point apparatus and are uncorrected.

Materials. $PhI(OAc)_2$ (PIDA), $PhI(OCOCF_3)_2$ (PIFA), $PhI(OPiv)_2$, mCPBA were purchased from commercial source and used without further purification. Solvents were commercially available and used without further purification.

Caution!: It has been determined that 95–100 % *m*CPBA can be detonated by shock or sparks, whereas commercial 70–85 % *m*CPBA is not shock sensitive. It should be stored in a refrigerator in tightly closed containers.[1] We used commercially available *m*CPBA for our transformation. No additional safety protocol was required to follow for our dehydrogenative coupling reaction using *m*CPBA and iodine(III) species.

Crystallographic Data collection

We recrystallized the compound **2a** and **2s'** by the slow evaporation of ethyl acetate and hexane mixture (ca. 50%). The crystals data were collected with Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an INCOATEC micro source (Cu-Kα radiation, λ = 0.71073 Å). SAINT+[2] and SADABS[3] were used to integrate the intensities and to correct the absorption respectively The structure was resolved by direct methods and refined on F^2 with SHELXL-97.[4]

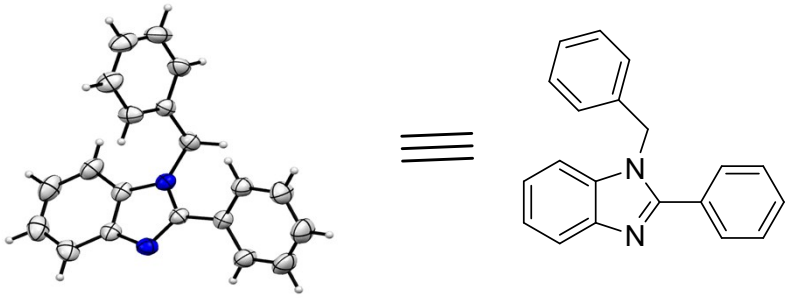


Fig. S1. Crystal structure of compound **2a.**

Table S1. Crystal data and structure refinement for **2a**

CCDC No.	**1812137**
Empirical formula	$C_{20}H_{16}N_2$
Formula weight	284.35
Temperature	296.15
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 6.0135(3) Å α = 90 °

	b = 16.9336(8) Å β = 91.429(3)
	c = 15.2048(7) Å γ = 90 °
Volume	1547.83(13)Å3
Z	4
Density (calculated)	1.220 cm^3
Absorption coefficient	0.072 mm^{-1}
F(000)	600.0
Crystal size	0.24 x 0.19 x 0.18 mm^3
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	5.36 to 57.556 °
Index ranges	$-8 \leq h \leq 7$, $-22 \leq k \leq 22$, $-20 \leq l \leq 20$
Reflections collected	27438
Independent reflections	4009 [Rint = 0.0547, Rsigma = 0.0332]
Data/restraints/parameters	4009/0/199
Goodness-of-fit on F2	1.039
Final R indexes [I>=2σ (I)]	R1 = 0.0452, wR2 = 0.1036
Final R indexes [all data]	R1 = 0.0762, wR2 = 0.1180
Largest diff. peak/hole	0.12/-0.17e $Å^{-3}$

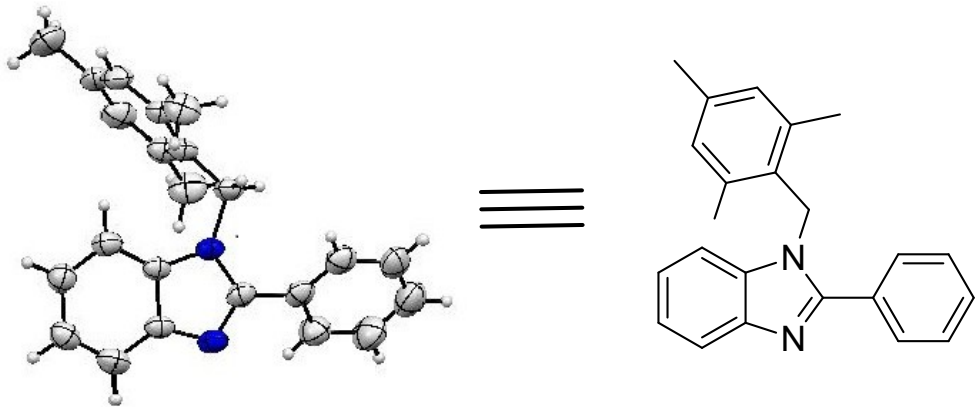


Fig. S2. Crystal structure of compound **2s'.**

Table S2. Crystal data and structure refinement for **2s'.**

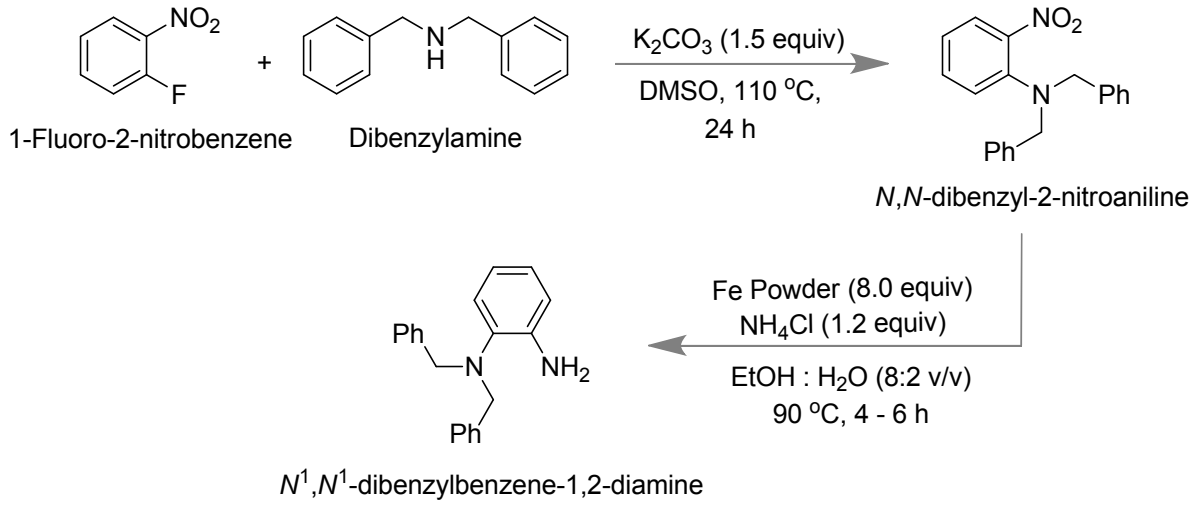
CCDC No.	**1867630**
Empirical formula	$C_{23}H_{22}N_2$
Formula weight	326.42
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	9.3816(2)
b/Å	10.7214(2)
c/Å	11.0369(2)
α/°	106.328(2)

β/°	109.830(2)
γ/°	107.983(2)
Volume/Å^3	896.17(3)
Z	2
ρ_{calc}g/cm^3	1.210
μ/mm^{-1}	0.542
F(000)	348.0
Crystal size/mm^3	0.24 × 0.19 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.442 to 155.306
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 11, -13 ≤ l ≤ 13
Reflections collected	12116
Independent reflections	3623 [R_{int} = 0.1107, R_{sigma} = 0.0704]
Data/restraints/parameters	3623/0/229
Goodness-of-fit on F^2	1.211
Final R indexes [I>=2σ (I)]	R_1 = 0.1000, wR_2 = 0.2774
Final R indexes [all data]	R_1 = 0.1075, wR_2 = 0.2917
Largest diff. peak/hole / e Å^{-3}	0.33/-0.62

Synthetic Procedures and Compound Characterisation Data

Procedures for the Synthesis of Starting Materials:

Route A:

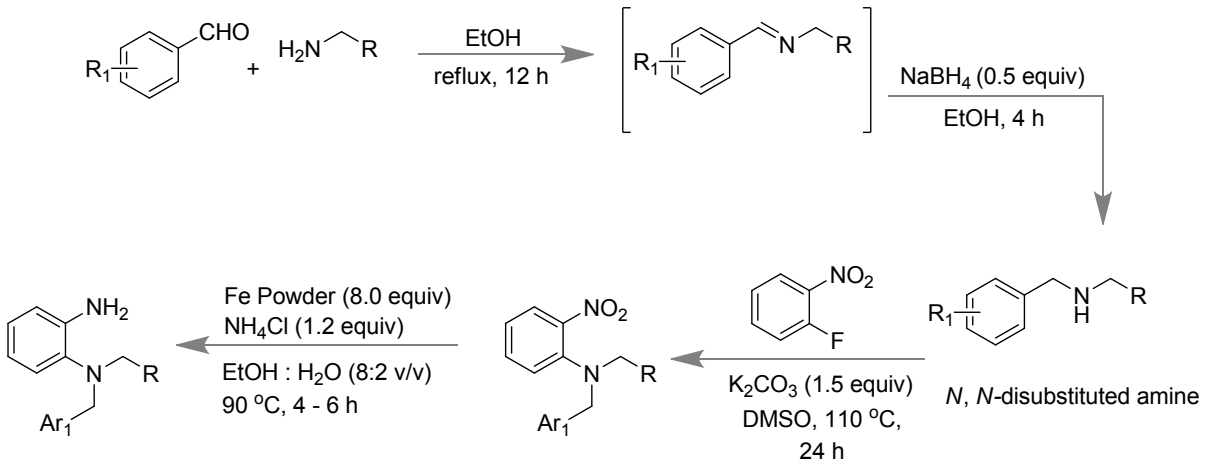


Scheme S1: Synthetic route of N^1,N^1-dibenzylbenzene-1,2-diamine from 1-Fluoro-2-nitrobenzene and Dibenzylamine.

Representative procedure for the synthesis of *N, N*-dibenzyl-2-nitroaniline: To an oven-dried sealed tube charged with a magnetic stirring bar and 1-Fluoro-2-nitrobenzene[5] (327.0 µl, 3.54 mmol, 1 equiv), Dibenzylamine (680.0 µl, 3.54 mmol, 1 equiv), and K_2CO_3 (605 mg, 4.7 mmol, 1.5 equiv) in 10 ml DMSO mixture were stirred at 110 °C for 24 h and completion of reaction was confirmed by thin layer chromatography (TLC). The reaction mixture was cooled to room temperature and washed with brine solution. The organic layer was extracted with ethyl acetate and were dried over Na_2SO_4, and concentrated under reduced pressure. The yellow crude product of *N,N*-dibenzyl-2-nitroaniline was dried in vacuum and used directly for the next step.

Representative procedure for the synthesis of *N*^{1},*N*^{1}-dibenzylbenzene-1,2-diamine: The crude *N*,*N*-dibenzyl-2-nitroaniline (~790 mg, 2.48 mmol, 1 equiv) from the previous step was dissolved in EtOH and H_2O (8:2 v/v) in a sealed tube charged with magnetic stirring bar. To it Fe powder (1.1 g, 20 mmol, 8 equiv)[6] and NH_4Cl (160 mg, 3.0 mmol, 1.2 equiv) equivalent was added and the resulting mixture was stirred in a preheated oil bath of 90 ^oC for 4 – 6 h. Completion of the reaction was confirmed by TLC and reaction mixture was cooled to room temperature and washed with water. The organic layer was extracted with ethyl acetate and were dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography using 5% ethyl acetate/hexane as eluent to get *N*^{1},*N*^{1}-dibenzylbenzene-1,2-diamine as brown oily liquid. By following similar synthetic procedure compound **1a, 1c, 1e, 1f, 1i** were prepared.

Route B:



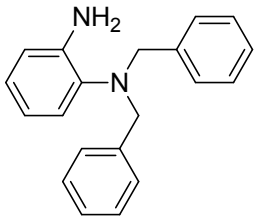
Scheme S2: Synthetic route of *N*^{1},*N*^{1}-dibenzylbenzene-1,2-diamine from benzaldehyde and benzyl amine derivatives.

Representative procedure for the synthesis of *N*, *N*-disubstituted amine[7]: To an oven-dried sealed tube charged with a magnetic stirring bar and 4-Methoxy benzaldehyde (450 µl, 3.6 mmol, 1 equiv), 4-methoxy benzylamine (515 µl, 4.0 mmol, 1.1 equiv) was added and dissolved in 10 ml EtOH. The resulting solution was stirred at 90 ^oC for 12 h. Then the reaction

mixture was cooled to room temperature and further kept in ice bath to maintain 0 °C. After 2 h the precipitate was dissolved further in EtOH and $NaBH_4$ (63 mg, 1.8 mmol, 0.5 equiv) was added portion wise at 0 °C. After 4 h reaction completion was confirmed by TLC and resulting reaction mixture was quenched with 1N HCl and washed with water. Organic layer was extracted with ethyl acetate and were dried over Na_2SO_4, and concentrated under reduced pressure. The oily crude product was dried in vacuum and used directly for the next step. Then similar procedure like route A was followed. By adopting this route compound **1b, 1d, 1g, 1h**, and **1j – 1v** were synthesized.

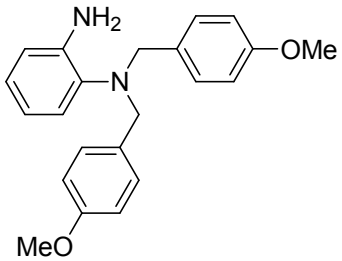
Compound Characterization Data for Starting Material

***N*^{1},*N*^{1}-dibenzylbenzene-1,2-diamine (1a)[5]:** R_f = 0.7 (5% ethyl acetate/hexane); brown oily



liquid; yield 315 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 10H), 6.92 – 6.87 (m, 2H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.64 (t, *J* = 7.6 Hz, 1H), 4.09 (br s, 2H), 4.05 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 138.4, 137.3, 129.1, 128.3, 127.1, 125.0, 123.4, 118.3, 115.4, 56.4; IR (neat) $\tilde{\nu}$ 3703, 2972, 1611, 1499, 1263, 1156, 775 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{20}N_2Na$ $[M+Na]^+$ 311.1524, found 311.1519.

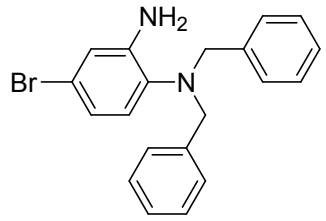
***N*^{1},*N*^{1}-bis(4-methoxybenzyl)benzene-1,2-diamine (1b):** R_f = 0.7 (6% ethyl acetate/hexane);



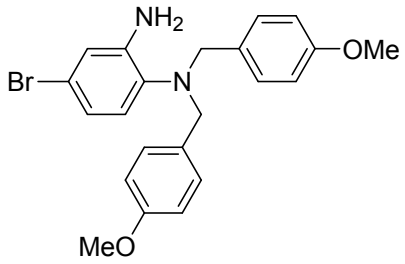
brown oily liquid; yield 345 mg (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.4 Hz, 4H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 4H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.64 (t, *J* = 7.6 Hz, 1H), 4.08 (br s, 2H), 3.96 (s, 4H), 3.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 142.5, 137.4, 130.5, 130.3, 124.9, 123.6, 118.2,

115.4, 113.6, 55.5, 55.3; IR (neat) $\tilde{\nu}$ 3691, 2976, 1608, 1411, 1172, 755 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{24}N_2O_2Na$ $[M+Na]^+$ 371.1735, found 371.1730.

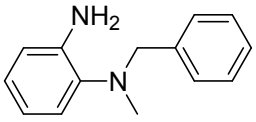
***N*^{1},*N*^{1}-dibenzyl-4-bromobenzene-1,2-diamine (1c):** R_f = 0.7 (4% ethyl acetate/hexane); pale yellow oily liquid; yield 265 mg (64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 10H), 6.83 (s, 1H), 6.71 (s, 2H), 4.13 (br s, 2H), 4.02 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 137.9, 136.0, 129.0, 128.4, 127.3, 124.9, 120.9, 118.0, 117.9, 56.4; IR (neat) $\tilde{\nu}$ 3756, 3035, 2966, 2305, 1603, 1494, 1156, 737 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{20}BrN_2$ $[M+H]^+$ 367.0810, found 367.0750.



4-Bromo-*N*^{1},*N*^{1}-bis(4-methoxybenzyl)benzene-1,2-diamine (1d): R_f = 0.7 (6% ethyl acetate/hexane); brown oily liquid; yield 345 mg (71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.4 Hz, 4H), 6.82 (d, *J* = 8.8 Hz, 5H), 6.73 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 4.14 (br s, 2H), 3.93 (s, 4H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 144.0, 136.1, 130.2, 129.9, 125.1, 120.8, 117.9, 117.8, 113.7, 55.5, 55.3; IR (neat) $\tilde{\nu}$ 3456, 3364, 3053, 2837, 1511, 1493, 1262, 896, 749 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{23}BrN_2O_2Na$ $[M+Na]^+$ 449.0841, found 449.0830.

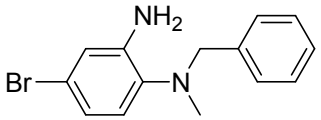


***N*^{1}-benzyl-*N*^{1}-methylbenzene-1,2-diamine (1e):** R_f = 0.6 (5% ethyl acetate/hexane); brown oily liquid; yield 255 mg (68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 4H), 7.28 – 7.26 (m, 1H), 7.03 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.94 (dt, *J* = 8.0, 1.2 Hz, 1H), 6.77 – 6.72 (m, 2H), 4.08 (br s, 2H), 4.01 (s, 2H), 2.57 (s, 3H); ^{13}C



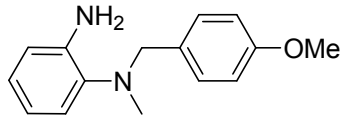
NMR (100 MHz, $CDCl_3$) δ 141.7, 139.9, 138.8, 128.7, 128.3, 127.1, 124.6, 120.9, 118.5, 115.2, 60.0, 40.5; IR (neat) $\tilde{\nu}$ 3690, 2946, 2360, 1500, 1264, 746, 704 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{17}N_2$ $[M+H]^+$ 213.1393, found 213.1386.

***N*¹-benzyl-4-bromo-*N*¹-methylbenzene-1,2-diamine (1f):** R_f = 0.7 (4% ethyl acetate/hexane);



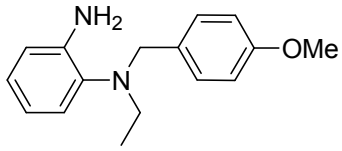
brown oily liquid; yield 250 mg (75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 5H), 6.87 (d, *J* = 1.6 Hz, 1H), 6.84 – 6.80 (m, 2H), 4.12 (br s, 2H), 3.97 (s, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 138.9, 138.4, 128.8, 128.5, 127.3, 122.6, 121.1, 117.8, 117.6, 59.9, 40.7; IR (neat) $\tilde{\nu}$ 3400, 2936, 1618, 1550, 1427, 1157, 896, 746 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{16}BrN_2$ $[M+H]^+$ 291.0497, found 291.0492.

***N*¹-(4-methoxybenzyl)-*N*¹-methylbenzene-1,2-diamine (1g):** R_f = 0.6 (6% ethyl



acetate/hexane); colorless liquid; yield 295 mg (69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.76 – 6.72 (m, 2H), 4.07 (br s, 2H), 3.94 (s, 2H), 3.80 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 141.8, 140.1, 130.9, 130.0, 124.6, 121.1, 118.6, 115.3, 113.7, 59.4, 55.4, 40.5; IR (neat) $\tilde{\nu}$ 3443, 3048, 2972, 1608, 1511, 1172, 1034, 749 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{18}N_2NaO$ $[M+Na]^+$ 265.1317, found 265.1313.

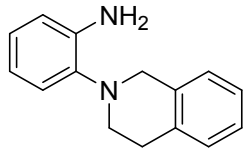
***N*¹-ethyl-*N*¹-(4-methoxybenzyl)benzene-1,2-diamine (1h):** R_f = 0.7 (6% ethyl



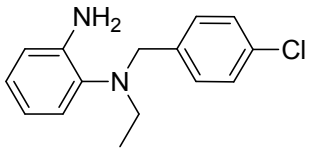
acetate/hexane); brown oily liquid; yield 192 mg (66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2H), 7.00 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.93 (td, *J* = 7.6, 1.2 Hz, 1H), 6.82 (d, *J* = 8.4

Hz, 2H), 6.71 (m, 2H), 4.08 (br s, 2H), 3.97 (s, 2H), 3.79 (s, 3H), 2.92 (q, J = 6.8 Hz, 2H), 0.97 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 143.3, 137.3, 131.1, 129.9, 124.9, 123.1, 118.1, 115.2, 113.5, 57.4, 55.2, 46.0, 12.2; IR (neat) $\tilde{\nu}$ 3600, 2976, 2836, 1607, 1499, 1247, 732 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{20}N_2NaO$ $[M+Na]^+$ 279.1473, found 279.1467.

2-(3,4-Dihydroisoquinolin-2-yl)aniline (1i)[5]: R_f = 0.5 (5% ethyl acetate/hexane); pale yellow

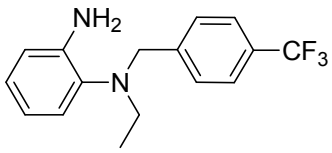


solid; yield 302 mg (76%); mp: 124 - 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.14 (m, 3H), 7.09 – 7.06 (m, 2H), 6.99 – 6.95 (m, 1H), 6.79 – 6.76 (m, 2H), 4.10 (s, 2H), 4.02 (br s, 2H), 3.25 (t, J = 5.6 Hz, 2H), 3.02 (t, J = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 139.4, 135.6, 134.5, 129.1, 126.6, 126.4, 125.8, 124.9, 120.3, 118.8, 115.3, 53.9, 49.5, 30.0; IR (neat) $\tilde{\nu}$ 3689, 3054, 2986, 2305, 1421, 1264, 896, 745 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{17}N_2$ $[M+H]^+$ 225.1392, found 225.1387.



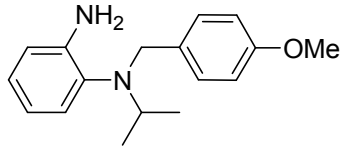
***N*^{1}-(4-chlorobenzyl)-*N*^{1}-ethylbenzene-1,2-diamine (1j):** R_f = 0.6 (5% ethyl acetate/hexane); colorless oily liquid; yield 325 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 9.6 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.93 (t, J = 7.2 Hz, 1H), 6.74 – 6.68 (m, 2H), 4.06 (br s, 2H), 4.01 (s, 2H), 2.92 (q, J = 6.8 Hz, 2H), 0.98 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.6, 136.8, 132.7, 130.2, 128.4, 125.2, 123.1, 118.3, 115.4, 57.4, 46.6, 12.3; IR (neat) $\tilde{\nu}$ 3690, 3054, 2886, 2359, 1498, 1156, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{18}ClN_2$ $[M+H]^+$ 261.1159, found 261.1150.

***N*^{1}-ethyl-*N*^{1}-(4-(trifluoromethyl)benzyl)benzene-1,2-diamine (1k):** R_f = 0.7 (6% ethyl



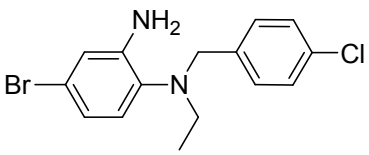
acetate/hexane); brown oily liquid; yield 330 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.00 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.95 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.76 – 6.68 (m, 2H), 4.11 (s, 2H), 4.08 (br s, 2H), 2.94 (q, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 143.3, 136.8, 129.0 (x2), 125.4, 125.28 (q, *J* = 7.6, 3.8 Hz), 123.1, 118.4, 115.5, 57.7, 46.9, 12.4; IR (neat) $\tilde{\nu}$ 3690, 3104, 2948, 1609, 1499, 1325, 1124, 1066, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{18}F_3N_2$ $[M+H]^+$ 295.1422, found 295.1415.

***N*^{1}-isopropyl-*N*^{1}-(4-methoxybenzyl)benzene-1,2-diamine (1l):** R_f = 0.6 (5% ethyl



acetate/hexane); brown oily liquid; yield 278 mg (58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.86 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.66 – 6.62 (m, 2H), 4.08 (s, 2H), 4.00 (br s, 2H), 3.73 (s, 3H), 3.27 (sept, *J* = 6.8 Hz, 1H), 1.15 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 144.2, 136.4, 132.1, 129.6, 124.96, 124.92, 117.9, 115.3, 113.5, 55.3, 52.4, 50.8, 19.8; IR (neat) $\tilde{\nu}$ 3693, 2987, 1606, 1512, 1417, 1195, 749 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{22}N_2NaO$ $[M+Na]^+$ 293.1630, found 293.1621.

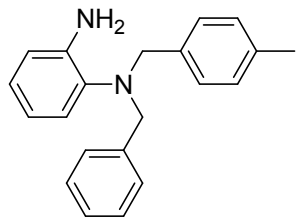
4-Bromo-*N*^{1}-(4-chlorobenzyl)-*N*^{1}-ethylbenzene-1,2-diamine (1m): R_f = 0.7 (5% ethyl



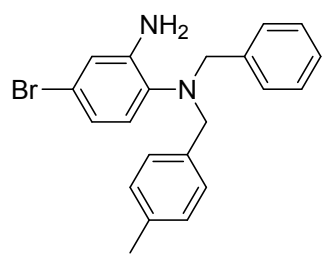
acetate/hexane); brown oily liquid; yield 250 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 1H), 6.81 – 6.77 (m, 2H), 4.11 (br s, 2H), 3.97 (s, 2H), 2.90 (q, *J* = 7.2 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 144.8, 136.9, 135.6, 132.9, 130.2, 128.5, 124.7, 120.9, 118.2, 117.8, 57.2, 46.7, 12.3; IR (neat) $\tilde{\nu}$ 3564, 2949, 1612, 1493, 1287, 1154, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{16}BrClN_2Na$ $[M+Na]^+$ 361.0083, found 361.0067.

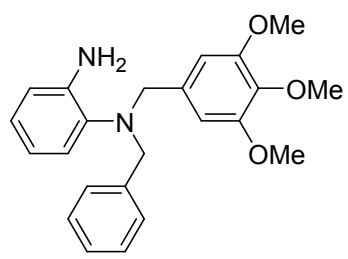
***N*¹-benzyl-*N*¹-(4-methylbenzyl)benzene-1,2-diamine (1n):** R_f = 0.4 (3% ethyl acetate/hexane); brown oily liquid; yield 385 mg (72%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 5H), 7.09 (dd, *J* = 8.0, 4.0 Hz, 4H), 6.92 – 6.86 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.63 (t, *J* = 6.8 Hz, 1H), 4.09 (br s, 2H), 4.04 (s, 2H), 4.00 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 138.5, 137.4, 136.7, 135.3, 129.1, 129.0, 128.9, 128.3, 127.1, 124.9, 123.4, 118.3, 115.4, 56.2, 56.1, 21.3; IR (neat) $\tilde{\nu}$ 3500, 3054, 2986, 1421, 1265, 892, 740 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{23}N_2$ $[M+H]^+$ 303.1861, found 303.1854.



***N*¹-benzyl-4-bromo-*N*¹-(4-methylbenzyl)benzene-1,2-diamine (1o):** R_f = 0.6 (4% ethyl acetate/hexane); pale yellow solid; yield 325 mg (76%); mp: 107 - 109 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 3H), 7.22 (d, *J* = 6.8 Hz, 2H), 7.11 (s, 4H), 6.85 (d, *J* = 2.0 Hz, 1H), 6.75 – 6.69 (m, 2H), 4.16 (br s, 2H), 4.02 (s, 2H), 3.99 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 137.9, 136.8, 136.1, 134.7, 129.05, 129.0, 128.98, 128.3, 127.2, 124.9, 120.8, 117.9, 117.8, 56.2, 56.0, 21.2; IR (neat) $\tilde{\nu}$ 3680, 2926, 2831, 1621, 1493, 1272, 1188, 1028, 775 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{21}BrN_2Na$ $[M+Na]^+$ 403.0786, found 403.0780.

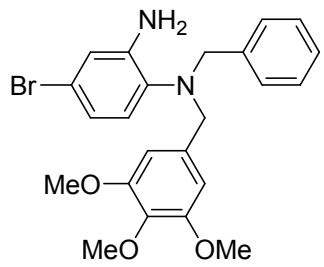


***N*¹-benzyl-*N*¹-(3,4,5-trimethoxybenzyl)benzene-1,2-diamine (1p):** R_f = 0.5 (8% ethyl acetate/hexane); orange sticky liquid; yield 410 mg (61%); ^1H

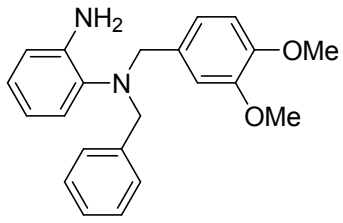


NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 5H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.36 (s, 2H), 4.07 (br s, 4H), 3.99 (s, 2H), 3.82 (s, 3H), 3.76 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 142.1, 138.4, 137.2, 136.9, 133.5, 128.9, 128.2, 127.1, 124.9, 123.4, 118.2, 115.3, 106.0, 60.9, 56.2, 56.0, 55.9; IR (neat) $\tilde{\nu}$ 3690, 3050, 2988, 1550, 1423, 1129, 746 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{26}N_2O_3Na$ $[M+Na]^+$ 401.1841, found 401.1853.

***N*^{1}-benzyl-4-bromo-*N*^{1}-(3,4,5-trimethoxybenzyl)benzene-1,2-diamine (1q):** R_f = 0.6 (8% ethyl acetate/hexane); yellow sticky liquid; yield 295 mg (57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 5H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.34 (s, 2H), 4.15 (br s, 2H), 4.03 (s, 2H), 3.95 (s, 2H), 3.82 (s, 3H), 3.77 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 143.7, 138.0, 137.1, 136.0, 133.2, 128.9, 128.4, 127.4, 125.0, 120.8, 118.0, 117.9, 106.0, 60.9, 56.3, 56.2, 56.1; IR (neat) $\tilde{\nu}$ 3692, 2996, 2305, 1602, 1256, 1129, 887 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{25}BrN_2O_3Na$ $[M+Na]^+$ 479.0946, found 479.0925.

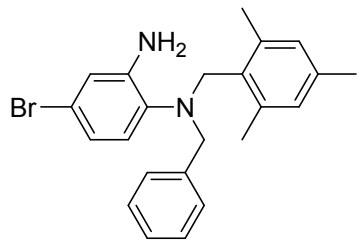


***N*^{1}-benzyl-*N*^{1}-(3,4-dimethoxybenzyl)benzene-1,2-diamine (1r):** R_f = 0.5 (6% ethyl acetate/hexane); yellow oily liquid; yield 405 mg (66%); mp: 128 - 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.81 – 6.74 (m, 3H), 6.67 (t, *J* = 7.6 Hz, 1H), 6.62 (s, 1H), 4.07 (s, 2H), 4.02 (s, 2H), 3.87 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 148.0, 142.2, 138.5, 137.2, 130.4, 129.0, 128.2, 127.1, 124.9, 123.5, 121.3, 118.2, 115.3, 112.5, 110.7, 56.1, 55.8,



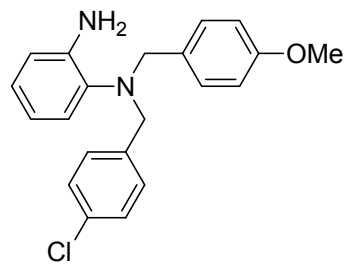
55.7, 55.5; IR (neat) $\tilde{\nu}$ 3692, 2978, 2831, 1625, 1513, 1155, 1027, 749 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{24}N_2O_2Na$ $[M+Na]^+$ 371.1735, found 371.1742.

***N*^{1}-benzyl-*N*^{1}-(2,4,6-trimethylbenzyl)benzene-1,2-diamine (1s):** R_f = 0.6 (5% ethyl acetate/hexane); brown oily liquid; yield 425 mg (73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.20 – 7.15 (m, 5H), 6.89 (dt, *J* = 8.0, 2.0 Hz, 1H), 6.76 – 6.72 (m, 3H), 6.52 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.06 (s, 2H), 4.04 (s, 2H), 3.63 (br s, 2H), 2.22 (s, 3H), 2.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 139.1, 138.2, 138.1, 136.6, 131.9, 129.7, 129.1, 128.0, 127.1, 126.0, 124.9, 118.6, 115.7, 59.5, 53.8, 21.0; IR (neat) $\tilde{\nu}$ 3576, 2966, 1605, 1423, 1287, 896, 776 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{26}N_2Na$ $[M+Na]^+$ 353.1994, found 353.1989.



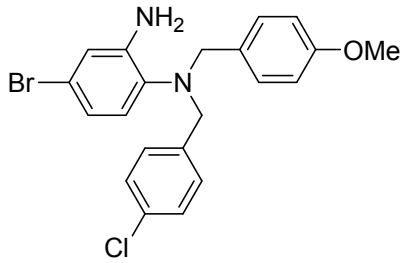
***N*^{1}-benzyl-4-bromo-*N*^{1}-(2,4,6-trimethylbenzyl)benzene-1,2-diamine (1t):** R_f = 0.6 (3% ethyl acetate/hexane); brown oily liquid; yield 240 mg (52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.2 Hz, 3H), 7.16 (d, *J* = 8.0 Hz, 3H), 6.83 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.78 (s, 2H), 6.63 (d, *J* = 2.0 Hz, 1H), 4.04 (s, 2H), 4.03 (s, 2H), 3.69 (br s, 2H), 2.24 (s, 3H), 2.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 138.6, 137.9, 137.0, 136.8, 131.6, 129.6, 129.2, 128.1, 127.8, 127.2, 126.5, 121.1, 118.0, 59.5, 53.8, 21.0, 20.1; IR (neat) $\tilde{\nu}$ 3442, 3053, 2986, 1635, 1491, 1265, 737 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{26}BrN_2$ $[M+H]^+$ 409.1279, found 409.1261.

***N*^{1}-(4-chlorobenzyl)-*N*^{1}-(4-methoxybenzyl)benzene-1,2-diamine (1u):** R_f = 0.5 (8% ethyl acetate/hexane); yellow oily liquid; yield 450 mg (72%); ^{1}H

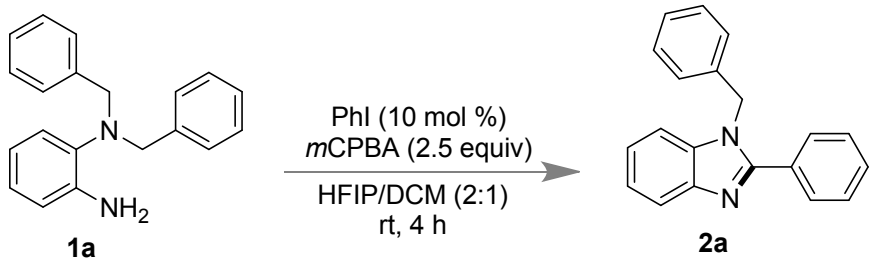


NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.11 (dd, *J* = 8.0, 1.6 Hz, 3H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.85 – 6.80 (m, 3H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 4.04 (br s, 2H), 4.00 (s, 2H), 3.96 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 142.4, 136.9, 132.8, 130.4, 130.3, 130.1, 130.0, 128.4, 125.2, 123.4, 118.3, 115.5, 113.7, 56.0, 55.4, 55.2; IR (neat) $\tilde{\nu}$ 3690, 2956, 2831, 1608, 1532, 1156, 1034, 775 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{21}ClN_2ONa$ $[M+Na]^+$ 375.1240, found 375.1233.

4-Bromo-*N*^{1}-(4-chlorobenzyl)-*N*^{1}-(4-methoxybenzyl)benzene-1,2-diamine (1v): R_f = 0.5 (7% ethyl acetate/hexane); light orange oily liquid; yield 332 mg (68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.09 (dd, *J* = 8.4, 2.0 Hz, 4H), 6.83 – 6.81 (m, 3H), 6.72 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 4.10 (br s, 2H), 3.96 (s, 2H), 3.92 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 143.9, 136.4, 135.7, 133.0, 130.4, 130.3, 129.6, 128.5, 125.0, 120.9, 118.2, 117.9, 113.8, 56.0, 55.4, 55.3; IR (neat) $\tilde{\nu}$ 3690, 3053, 2986, 2410, 1422, 1264, 896, 749 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{20}BrClN_2ONa$ $[M+Na]^+$ 453.0345, found 453.0361.



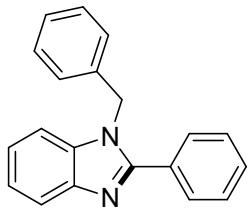
Representative procedure for the synthesis of 1-Benzyl-2-phenyl-benzo[d]imidazole (2a):



Scheme S3: Synthetic route of 1-Benzyl-2-phenyl-benzo[d]imidazole (**2a**)

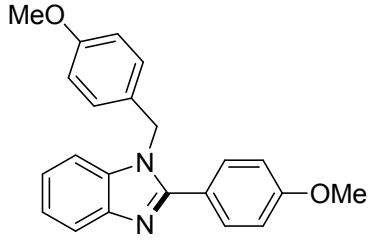
To a round bottom flask charged with a magnetic stirring bar and N^1,N^1-dibenzylbenzene-1,2-diamine (1a) (60 mg, 0.208 mmol, 1.0 equiv), PhI (3 µl, 0.0208 mmol, 10 mol %) was added and mCPBA (90 mg, 0.52 mmol, 2.5 equiv) dissolved in 1,1,1,3,3,3-Hexafluoro-2-propanol and dichloromethane (1.5 ml, 2:1 v/v). The mixture was stirred under room temperature for 4 h. The completion of reaction was confirmed by TLC and afterwards it was evaporated to dryness under reduced pressure. The crude reaction mixture was purified by 230 – 400 mesh silica gel column chromatography using 18% ethyl acetate/hexane as eluent to get 1-Benzyl-2-phenyl-benzo[d]imidazole (**2a**) as white solid with 89% yield.

Compound Characterization Data:



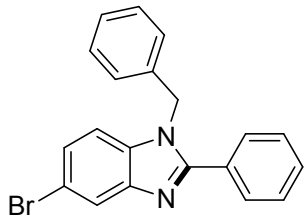
1-Benzyl-2-phenyl-benzo[d]imidazole (2a)[8]: R_f = 0.5 (18% ethyl acetate/hexane); white solid; yield 52 mg (89%); mp: 139 - 141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 6.0 Hz, 2H), 7.46 (d, J = 6.8 Hz, 3H), 7.35 – 7.30 (m, 4H), 7.22 (t, J = 8.0 Hz, 2H), 7.11 (d, J = 7.2 Hz, 2H), 5.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 134.7, 133.5, 130.3, 129.9, 129.5, 129.2, 129.0, 128.4, 128.0, 126.1, 123.5, 123.2, 119.9, 110.8, 48.6; IR (KBr) ῡ 2927, 2854, 1605, 1453, 1160, 1028, 970, 737 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1386, found 285.1366.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (2b)[9]: R_f = 0.5 (30% ethyl acetate/hexane); white solid; yield 53 mg (90%); mp: 128 - 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.8 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.21 (d, J = 2.0 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 5.38 (s, 2H), 3.85 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$)



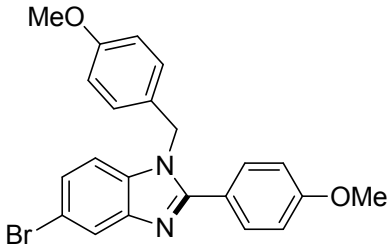
δ 161.0, 159.2, 154.2, 143.2, 136.2, 130.8, 128.6, 127.3, 122.9, 122.6, 122.5, 119.8, 114.5, 114.3, 110.5, 55.5, 55.4, 48.0; IR (KBr) ῡ 2912, 2839, 1696, 1514, 1265, 970, 748 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{21}N_2O_2$ $[M+H]^+$ 345.1598, found 345.1615.

1-Benzyl-5-bromo-2-phenyl-benzo[d]imidazole (2c)[10]: R_f = 0.5 (15% ethyl acetate/hexane);



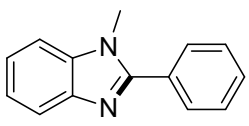
white solid; yield 48 mg (82%); mp: 156 - 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.6 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.52 – 7.44 (m, 3H), 7.36 – 7.29 (m, 4H), 7.06 (d, *J* = 8.4 Hz, 3H), 5.44 (s, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.3, 144.6, 136.0, 135.1, 130.4, 129.7, 129.4, 129.3, 129.0, 128.1, 126.2, 126.0, 122.9, 115.8, 111.9, 48.6; IR (KBr) ῡ 2916, 2851, 1516, 1455, 1384, 1160, 923 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{16}BrN_2$ $[M+H]^+$ 363.0491, found 363.0506.

5-Bromo-1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (2d): R_f = 0.5



(30% ethyl acetate/hexane); white solid; yield 54 mg (92%); mp: 136 - 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.6 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.30 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 4H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.35 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 159.4, 155.2, 144.5, 135.1, 130.8, 128.0, 127.3, 125.8, 122.6, 121.9, 115.6, 114.6, 114.4, 111.8, 55.5, 55.4, 48.1; IR (KBr) ῡ 2927, 2831, 1611, 1461, 1293, 1173, 1028, 735 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{20}BrN_2O_2$ $[M+H]^+$ 423.0703, found 423.0712.

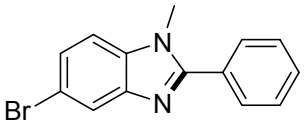
1-Methyl-2-phenyl-benzo[d]imidazole (2e)[11]: R_f = 0.5 (12% ethyl acetate/hexane); white



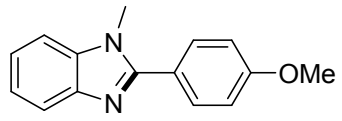
solid; yield 53 mg (90%), (372 mg (83%) from 2.2 mmol of **1e**); mp:

100 - 102 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 1H), 7.77 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.55 – 7.50 (m, 3H), 7.41 – 7.39 (m, 1H), 7.34 – 7.30 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 153.9, 143.0, 136.7, 130.3, 129.9, 129.6, 128.8, 122.9, 122.6, 119.9, 109.7, 31.8; IR (KBr) ῡ 3009, 2981, 1612, 1384, 1175, 1027, 893 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1073, found 209.1096.

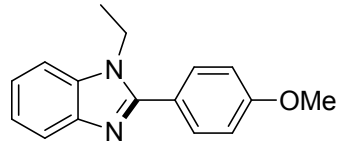
5-Bromo-1-methyl-2-phenyl-benzo[d]imidazole (2f): R_f = 0.5 (10% ethyl acetate/hexane); white solid; yield 52 mg (89%); mp: 150 - 152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.2 Hz, 1H), 7.73 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.53 – 7.51 (m, 3H), 7.41 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.24 (d, *J* = 3.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.9, 144.3, 135.7, 130.2, 129.8, 129.6, 128.9, 125.9, 122.8, 115.6, 111.0, 31.9; IR (KBr) ῡ 3046, 2985, 1492, 1421, 1261, 895 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{12}BrN_2$ $[M+H]^+$ 287.0178, found 287.0155.



2-(4-Methoxyphenyl)-1-methyl-benzo[d]imidazole (2g): R_f = 0.5 (15% ethyl acetate/hexane); white solid; yield 53 mg (90%); mp: 122 - 124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.35 (m, 1H), 7.31 – 7.28 (m, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 153.9, 143.0, 136.7, 130.9, 122.64, 122.60, 122.4, 119.7, 114.2, 109.6, 55.5, 31.8; IR (KBr) ῡ 2925, 2843, 1610, 1462, 1379, 1250, 1179, 1023, 835 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{15}N_2O$ $[M+H]^+$ 239.1179, found 239.1162.

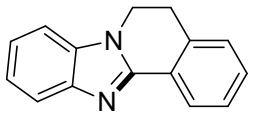


1-Ethyl-2-(4-methoxyphenyl)-benzo[d]imidazole (2h): R_f = 0.5 (15% ethyl acetate/hexane); white solid; yield 52 mg (88%); mp: 112 - 114 °C; ^{1}H NMR (400



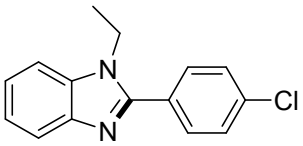
MHz, $CDCl_3$) δ 7.80 (dd, *J* = 6.4, 2.8 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.41 (dd, *J* = 6.4, 2.8 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 160.9, 153.5, 143.2, 135.5, 130.8, 122.9, 122.6, 122.4, 119.8, 114.3, 109.9, 55.5, 39.7, 15.4; IR (KBr) ῡ 2939, 2838, 1614, 1455, 1249, 1028, 839 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{17}N_2O$ $[M+H]^+$ 253.1335, found 253.1341.

5,6-Dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (2i)[12]: R_f = 0.5 (10% ethyl acetate/hexane); white solid; yield 46 mg (78%); mp: 148 - 150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.29 (m, 1H), 7.84 – 7.80 (m, 1H), 7.44 – 7.36 (m, 3H), 7.33 – 7.27 (m, 3H),



4.33 (t, *J* = 6.8 Hz, 2H), 3.29 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.2, 144.0, 134.8, 134.4, 130.3, 128.2, 127.9, 126.8, 125.8, 122.8, 122.6, 119.9, 109.2, 40.5, 28.4; IR (KBr) ῡ 3058, 2992, 1615, 1433, 1268, 1037, 738 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{13}N_2$ $[M+H]^+$ 221.1073, found 221.1056.

2-(4-Chlorophenyl)-1-ethyl-benzo[d]imidazole (2j): R_f = 0.5 (14% ethyl acetate/hexane);



white solid; yield 45 mg (77%); mp: 126 - 128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 5.6, 3.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 152.4, 143.2, 136.2, 135.5, 130.7, 129.2, 129.1, 123.1, 122.7, 120.2, 110.1, 39.8, 15.4; IR (KBr) ῡ 3053, 2986, 1607, 1421, 1264, 1094, 895, 747 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{14}ClN_2$ $[M+H]^+$ 257.0840, found 257.0816.

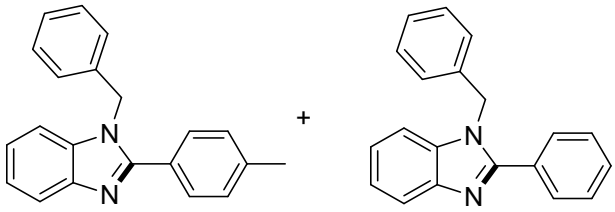
1-Ethyl-2-(4-(trifluoromethyl)phenyl)-benzo[d]imidazole (2k): R_f = 0.5 (20% ethyl acetate/hexane); white solid; yield 47 mg (80%); mp: 127 - 130 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.32 (m, 2H), 4.30 (q, *J* = 7.0 Hz, 2H), 1.49 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 151.9, 143.3, 135.6, 134.3, 131.8 (q, *J* = 32.8 Hz), 129.8, 125.9 (q, *J* = 3.6 Hz), 123.4, 122.9, 120.4, 110.2, 39.9, 15.5; IR (KBr) ῡ 2981, 2937, 1619, 1452, 325, 1115, 1071, 854 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{14}F_3N_2$ $[M+H]^+$ 291.1104, found 291.1099.

1-Isopropyl-2-(4-methoxyphenyl)-benzo[d]imidazole (2l): R_f = 0.4 (15% ethyl acetate/hexane); white solid; yield 43 mg (73%); mp: 150 - 152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 1H), 7.62 – 7.57 (m, 3H), 7.29 – 7.23 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.82 (sept, *J* = 6.8 Hz, 1H), 3.88 (s, 3H), 1.64 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 160.8, 153.7, 143.8, 133.6, 130.9, 123.4, 122.1, 122.0, 120.2, 114.2, 112.3, 55.5, 48.8, 21.5; IR (KBr) ῡ 2976, 2839, 1608, 1454, 1371, 1251,1176 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{19}N_2O$ $[M+H]^+$ 267.1492, found 267.1472.

5-Bromo-2-(4-chlorophenyl)-1-ethyl-benzo[d]imidazole (2m): R_f = 0.5 (15% ethyl acetate/hexane); white solid; yield 44 mg (75%); mp: 160 - 162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.41 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 153.4, 144.5, 136.5, 134.5, 130.6, 129.3, 128.6, 126.1, 122.9, 115.6,

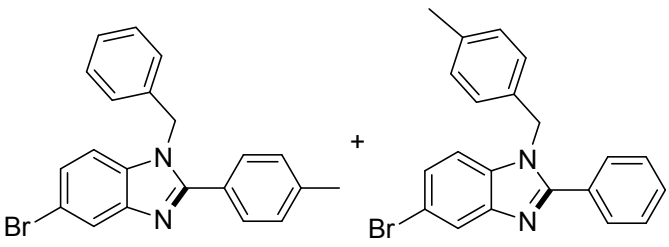
111.3, 39.9, 15.4; IR (KBr) ῡ 2981, 2933, 1599, 1405, 1326, 1087, 992 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{13}BrClN_2$ $[M+H]^+$ 334.9945, found 334.9944.

1-Benzyl-2-(p-tolyl)-benzo[d]imidazole and 1-(4-Methylbenzyl)-2-phenyl-benzo[d]imidazole (2n): R_f = 0.6 (10% ethyl acetate/hexane); white solid; yield 44 mg (75%);



Two regio isomers with 82:18 Ratio; ^1H NMR (700 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 1H), 7.70 (d, *J* = 7.0 Hz, 2H x 0.22), 7.58 (d, *J* = 8.4 Hz, 2H), 7.48 - 7.44 (m, 1H), 7.34 – 7.28 (m, 4H), 7.25 (d, *J* = 7.0 Hz, 3H), 7.23 – 7.19 (m, 2H), 7.13 (d, *J* = 7.7 Hz, 2H x 0.22), 7.11 (d, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 2H x 0.22), 5.45 (s, 2H, major isomer), 5.42 (s, 2H x 0.22, minor isomer), 2.40 (s, 3H, major isomer), 2.33 (s, 3H x 0.22, minor isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 143.3, 140.2, 136.6, 136.2, 129.8, 129.6, 129.4, 129.3, 129.2, 128.9, 127.9, 127.3, 126.1, 126.0, 123.1, 123.0, 122.8, 122.7, 120.1, 120.0, 110.7, 110.6, 48.5, 48.3, 21.6, 21.2; HRMS (ESI-TOF) calcd for $C_{21}H_{19}N_2$ $[M+H]^+$ 299.1543, found 299.1523.

1-Benzyl-5-bromo-2-(p-tolyl)-benzo[d]imidazole and 5-Bromo-1-(4-methylbenzyl)-2-phenyl-benzo[d]imidazole (2o): R_f = 0.6 (12% ethyl acetate/hexane); white solid; yield 43 mg



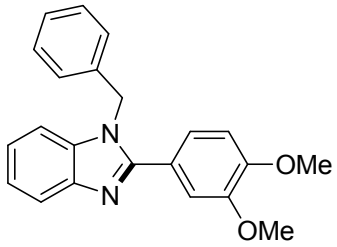
(73%); Two regio isomers with 52:48 Ratio; ^1H NMR (700 MHz, $CDCl_3$) δ 7.98 (d, *J* = 3.5 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.49 – 7.44 (m, 3H), 7.33 – 7.28 (m, 5H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.06 – 7.02 (m, 4H), 6.95 (d, *J* = 7.7 Hz, 2H), 5.41 (s, 2H, major isomer), 5.38 (s, 2H, minor isomer),

2.40 (s, 4H, major isomer), 2.33 (s, 3H, minor isomer); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.5, 155.2, 144.51, 144.49, 140.6, 137.8, 136.1, 135.1, 132.9, 130.3, 129.9, 129.7, 129.3, 129.2, 128.9, 128.0, 126.7, 126.1, 125.98, 125.96, 125.92, 122.8, 122.7, 115.72, 115.70, 111.9, 111.8, 48.6, 48.4, 21.5, 21.2; HRMS (ESI-TOF) calcd for $C_{21}H_{18}BrN_2$ $[M+H]^+$ 377.0648, found 377.0656.

1-Benzyl-2-(3,4,5-trimethoxyphenyl)-benzo[d]imidazole[8] and 2-Phenyl-1-(3,4,5-trimethoxybenzyl)-benzo[d]imidazole (2p): R_f = 0.5 (35% ethyl acetate/hexane); white solid; yield 52 mg (88%); Two regio isomers with 70:30 Ratio; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.72 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.49 – 7.47 (m, 2H), 7.37 – 7.27 (m, 7H), 7.15 (d, *J* = 7.2 Hz, 2H), 6.86 (s, 2H, major isomer), 6.29 (s, 2H x 0.43, minor isomer), 5.48 (s, 2H, major isomer), 5.38 (s, 2H x 0.43, minor isomer), 3.87 (s, 3H, major isomer), 3.82 (s, 3H x 0.43, minor isomer), 3.70 (s, 6H x 0.43, minor isomer), 3.64 (s, 6H, major isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 154.2, 153.9, 153.4, 143.2, 143.0, 139.5, 137.5, 136.9, 136.5, 136.2, 132.2, 130.1, 129.4, 129.3, 128.9, 127.9, 125.8, 125.2, 123.4, 123.3, 123.0, 122.9, 120.1, 120.0, 110.6, 110.3, 106.5, 103.2, 61.1, 61.0, 56.2, 56.0, 48.6, 48.5; HRMS (ESI-TOF) calcd for $C_{23}H_{23}N_2O_3$ $[M+H]^+$ 375.1703, found 375.1675.

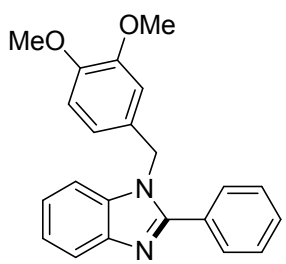
1-Benzyl-5-bromo-2-(3,4,5-trimethoxyphenyl)-benzo[d]imidazole and 5-Bromo-2-phenyl-1-(3,4,5-trimethoxybenzyl)-benzo[d]imidazole (2q): R_f = 0.4 (30% ethyl acetate/hexane); white solid; yield 54 mg (91%); Two regio isomers with 87:13 Ratio; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.00 (d, *J* = 1.6 Hz, 1H), 7.70 – 7.68 (m, 2H x 0.15), 7.49 (d, *J* = 7.2 Hz, 3H x 0.15), 7.38 – 7.34 (m, 3H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 8.8 Hz, 3H), 6.84 (s, 2H, major isomer), 6.25 (s, 2H x 0.15, minor isomer), 5.45 (s, 2H, major isomer), 5.36 (s, 2H x 0.15, minor isomer), 3.87 (s, 3H, major isomer), 3.83 (s, 3H x 0.15, minor isomer), 3.70 (s, 6H x 0.15, minor isomer), 3.65 (s, 6H, major isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 155.2, 153.9, 153.5, 144.5, 144.3, 139.7, 137.6, 136.4, 135.5, 135.2, 131.6, 130.4, 129.7, 129.3, 129.0, 128.1, 126.25, 126.20, 125.7, 124.7, 122.9, 122.8, 115.8, 111.8, 111.5, 106.4, 103.0, 61.0, 60.9, 56.2, 56.0, 48.7, 48.6; HRMS (ESI-TOF) calcd for $C_{23}H_{22}BrN_2O_3$ $[M+H]^+$ 453.0808, found 453.0793.



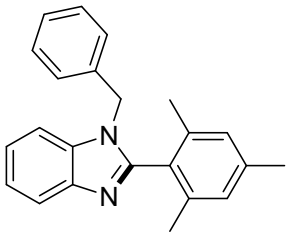
1-Benzyl-2-(3,4-dimethoxyphenyl)-benzo[d]imidazole (2r)[8]: R_f = 0.4 (25% ethyl acetate/hexane); white solid; yield 34 mg (58%); mp: 144 - 146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.28 (m, 4H), 7.25 – 7.21 (m, 4H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.47 (s, 2H), 3.91 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 150.5, 149.1, 143.1, 136.8, 136.4, 129.2, 127.8, 125.9, 123.0, 122.8, 122.6, 121.9, 119.8, 112.3, 111.1, 110.3, 56.0, 55.8, 48.5; IR (KBr) ῡ 3016, 2856, 1643, 1417, 1134, 895, 670 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{21}N_2O_2$ $[M+H]^+$ 345.1598, found 345.1613.

1-(3,4-Dimethoxybenzyl)-2-phenyl-benzo[d]imidazole (2r'): R_f = 0.4 (22% ethyl acetate/hexane); white solid; yield 14 mg (24%); mp: 150 - 152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 7.2, 2.4 Hz, 2H), 7.49 – 7.45 (m, 3H), 7.33 – 7.29 (m, 1H), 7.28 – 7.25 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.63 – 6.61 (m, 2H), 5.40 (s,



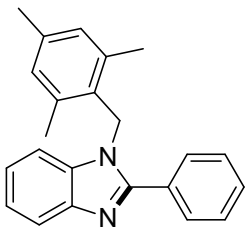
2H), 3.85 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 149.5, 148.7, 143.3, 136.2, 130.3, 130.0, 129.40, 128.9, 128.8, 123.1, 122.8, 120.1, 118.4, 111.6, 110.6, 109.3, 56.0, 55.9, 48.2; IR (KBr) ῡ 2933, 2830, 1592, 1515, 1460, 1237, 1139, 1025 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{21}N_2O_2$ $[M+H]^+$ 345.1598, found 345.1573.

1-Benzyl-2-mesityl-benzo[d]imidazole (2s): R_f = 0.6 (8% ethyl acetate/hexane); white solid;



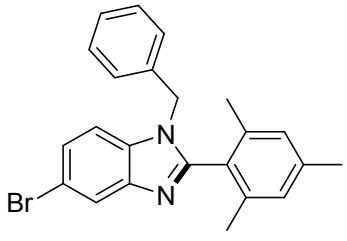
yield 31 mg (52%); mp: 140 - 142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.25 (m, 3H), 7.23 – 7.21 (m, 3H), 6.97 (dd, *J* = 6.4, 2.8 Hz, 2H), 6.92 (s, 2H), 5.07 (s, 2H), 2.34 (s, 3H), 1.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 143.5, 139.6, 138.2, 135.9, 134.8, 128.8, 128.4, 127.9, 127.3, 126.9, 122.6, 122.2, 120.1, 110.6, 47.9, 21.4, 19.8; IR (KBr) ῡ 2916, 2851, 1613, 1449, 1374, 1170, 852 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{23}N_2$ $[M+H]^+$ 327.1856, found 327.1862.

2-Phenyl-1-(2,4,6-trimethylbenzyl)-benzo[d]imidazole (2s'): R_f = 0.6 (10% ethyl



acetate/hexane); white solid; yield 12 mg (20%); mp: 204 - 206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 3H), 7.55 – 7.52 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.80 (s, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.45 (s, 2H), 2.24 (s, 3H), 2.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 143.3, 138.0, 137.3, 135.1, 131.0, 129.9, 129.8, 128.8, 128.4, 122.7, 122.2, 119.9, 111.4, 45.5, 21.1, 20.2; IR (KBr) ῡ 2912, 2847, 1692, 1518, 1423, 1015, 895 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{23}N_2$ $[M+H]^+$ 327.1856, found 327.1875.

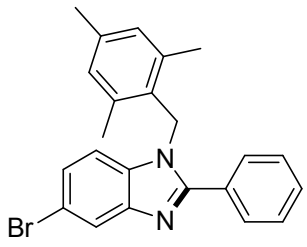
1-Benzyl-5-bromo-2-mesityl-benzo[d]imidazole (2t): R_f = 0.6 (6% ethyl acetate/hexane);



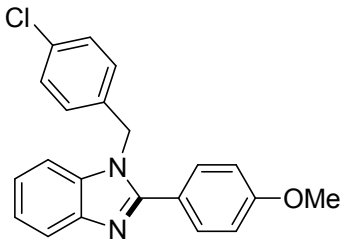
oily liquid; yield 32 mg (53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.97 (d, *J* = 1.6 Hz, 1H), 7.35 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.23 (dd, *J* = 5.2, 1.2 Hz, 3H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 4H), 5.04 (s, 2H), 2.34 (s, 3H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 144.8, 139.9, 138.1, 135.5, 133.8, 128.9, 128.5, 128.1, 127.2, 126.5, 125.7, 123.0, 115.3, 111.8, 48.0, 21.4, 19.8; IR (KBr) ῡ 2920, 2853, 1610, 1454, 1372, 1045, 853 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{22}BrN_2$ $[M+H]^+$ 405.0961, found 405. 0949.

5-Bromo-2-phenyl-1-(2,4,6-trimethylbenzyl)-benzo[d]imidazole (2t'): R_f = 0.6 (8% ethyl acetate/hexane); white solid; yield 11 mg (18%); mp: 190 - 192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 1.6 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.55 – 7.54 (m, 3H), 7.08 (dd, *J* = 8.8, 1.6 Hz, 1H), 6.81 (s, 2H), 6.50 (d, *J* = 8.8 Hz, 1H), 5.42 (s, 2H), 2.25 (s, 3H), 2.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 144.7, 138.4, 137.3, 134.1, 130.5, 130.2, 129.9, 129.8, 128.9, 127.9, 125.8, 122.7, 115.3, 112.6, 45.7, 21.1, 20.2; IR (KBr) ῡ 2916, 2843, 1609, 1455, 1372, 1172, 1013, 844 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{22}BrN_2$ $[M+H]^+$ 405.0961, found 405. 0984.

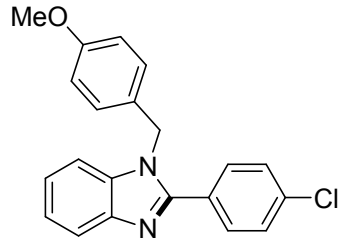


1-(4-Chlorobenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (2u): R_f = 0.5 (14% ethyl acetate/hexane); white solid; yield 38 mg (62%); mp: 147 - 150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.33-7.30 (m, 3H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 5.40 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 154.2, 143.3, 136.0, 135.1, 133.7, 130.7, 129.4, 127.4, 123.0, 122.8, 122.3, 119.9, 114.4, 110.3, 55.5, 47.9;

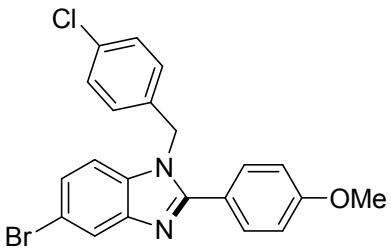


IR (KBr) ῡ 2935, 2825, 1612, 1513, 1248, 1094, 1033, 839 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{18}ClN_2O$ $[M+H]^+$ 349.1102, found 349.1083.

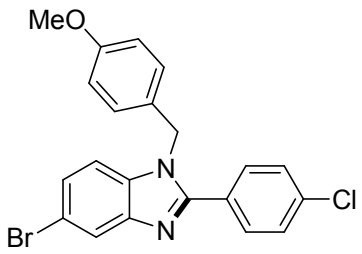
2-(4-Chlorophenyl)-1-(4-methoxybenzyl)-benzo[d]imidazole (2u'): R_f = 0.6 (16% ethyl acetate/hexane); white solid; yield 11 mg (14%); mp: 130 - 132 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.30 (m, 1H), 7.25 (s, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.38 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 153.0, 143.2, 136.3, 136.2, 130.8, 129.2, 128.8, 128.3, 127.3, 123.4, 122.9, 120.2, 114.6, 110.7, 55.4, 48.0; IR (KBr) ῡ 2929, 2835, 1614, 1483, 1249, 1176, 1029, 837 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{18}ClN_2O$ $[M+H]^+$ 349.1102, found 349.1112.



5-Bromo-1-(4-chlorobenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (2v): R_f = 0.6 (10% ethyl acetate/hexane); white solid; yield 37 mg (65%); mp: 150 - 152 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.0 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.33 - 7.30 (m, 3H), 7.03 – 6.96 (m, 5H), 5.38 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 155.3, 144.6, 134.9, 134.6, 133.9, 130.7, 129.5, 127.4, 126.0, 122.8, 121.7, 115.9, 114.5, 111.5, 55.5, 48.0; IR (KBr) ῡ 2929, 2839, 1613, 1469, 1247, 1176, 1034, 836 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{17}BrClN_2O$ $[M+H]^+$ 427.0207, found 427.0206.

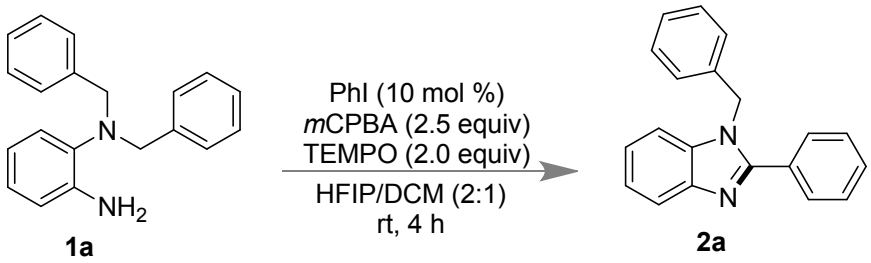


5-Bromo-2-(4-chlorophenyl)-1-(4-methoxybenzyl)-benzo[d]imidazole (2v'): R_f = 0.6 (13% ethyl acetate/hexane); white solid; yield 13 mg (18%); mp: 123 - 125 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.0 Hz,



1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.34 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.35 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 154.1, 144.5, 136.7, 135.2, 130.6, 129.3, 128.2, 127.7, 127.2, 126.4, 122.9, 115.9, 114.7, 111.9, 55.5, 48.2; IR (KBr) ῡ 3051, 2977, 2916, 1606,1469, 1264, 1176, 738 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{17}BrClN_2O$ $[M+H]^+$ 427.0207, found 427.0231.

Procedure for the radical scavenger experiment with 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl radical (TEMPO):

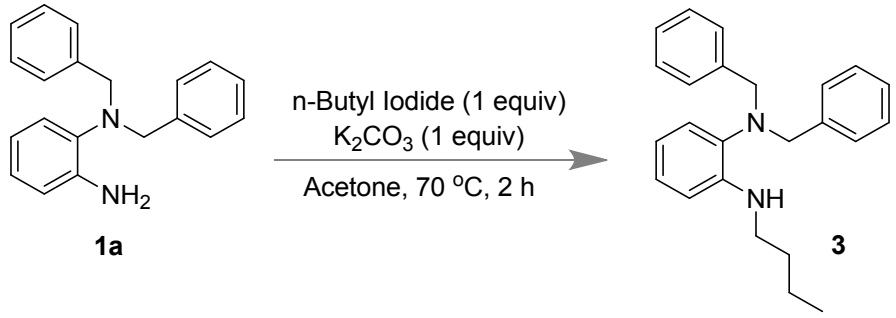


Scheme S4: Radical Scavenger experiment for route 1-Benzyl-2-phenyl-benzo[d]imidazole (**2a**) with TEMPO.

To a round bottom flask charged with a magnetic stirring bar and *N*^{1},*N*^{1}-dibenzylbenzene-1,2-diamine (1a) (50 mg, 0.173 mmol, 1.0 equiv), PhI (3 µl, 0.0173 mmol, 10 mol %) was added and mCPBA (75 mg, 0.43 mmol, 2.5 equiv) dissolved in 1,1,1,3,3,3-Hexafluoro-2-propanol and dichloromethane (1.5 ml, 2:1 v/v). To it TEMPO (54 mg, 0.35 mmol, 2.0 equiv) was added.

The mixture was stirred under room temperature for 4 h. The completion of reaction was confirmed by TLC and afterwards it was evaporated to dryness under reduced pressure. The crude reaction mixture was purified by 230 – 400 mesh silica gel column chromatography using 18% ethyl acetate/hexane as eluent to get 1-Benzyl-2-phenyl-benzo[d]imidazole (2a) as white solid with 74% yield.

Procedure for the synthesis of *N*^{1},*N*^{1}-dibenzyl-*N*^{2}-butylbenzene-1,2-diamine (3):

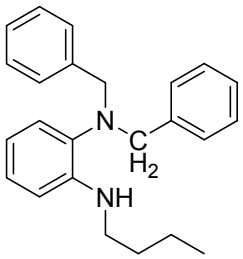


Scheme S5: Synthetic route of *N*^{1},*N*^{1}-dibenzyl-*N*^{2}-butylbenzene-1,2-diamine (**4**)

To an oven-dried sealed tube charged with a magnetic stirring bar and *N*^{1},*N*^{1}-dibenzylbenzene-1,2-diamine (1a) (100 mg, 0.35 mmol, 1.0 equiv), K_2CO_3 (48 mg, 0.35 mmol, 1.0 equiv) was added[13]. To it 4 ml acetone was further added and n-Butyl Iodide (40 µl, 0.35 mmol, 1.0 equiv) was added drop wise. The resulting mixture was stirred at 70 °C for 2 h. After completion of the reaction the whole solution was transferred in to a round bottom flask and evaporated to dryness. Then the crude material was washed with water and organic layer was extracted with

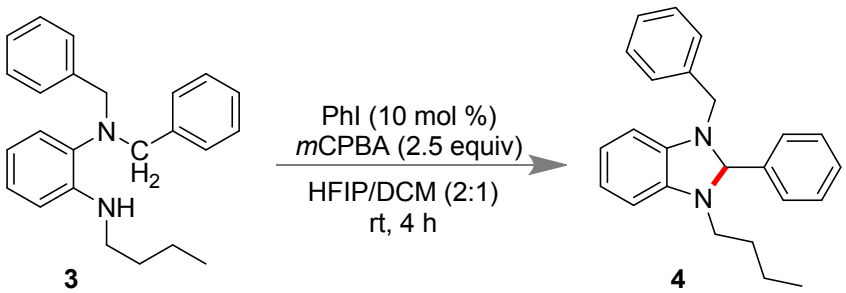
dichloromethane. It was collected together and dried over Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by 230 – 400 mesh silica gel column chromatography using 1% ethyl acetate/hexane as eluent to get N^1,N^1-dibenzyl-N^2-butylbenzene-1,2-diamine **(3)** as colorless oily liquid with 54% yield.

***N*^{1},*N*^{1}-dibenzyl-*N*^{2}-butylbenzene-1,2-diamine (3):** R_f = 0.9 (1% ethyl acetate/hexane);



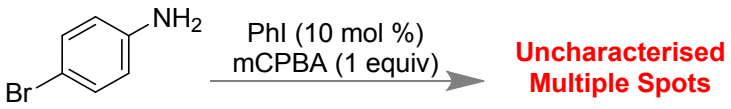
colorless liquid; yield 64 mg (54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 4H), 7.23 – 7.19 (m, 6H), 6.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.90 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.60 – 6.55 (m, 2H), 4.87 (s, 1H), 4.00 (s, 4H), 1.62 – 1.57 (m, 2H), 1.46 – 1.41 (m, 2H), 1.33 – 1.26 (m, 2H), 0.98 – 0.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.6, 136.7, 129.0, 128.3, 127.1, 125.4, 122.9, 116.0, 110.3, 56.8, 43.6, 31.9, 20.5, 14.1; IR (neat) $\tilde{\nu}$ 3433, 2962, 1601, 1454, 1146, 765 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{29}N_2$ $[M+H]^+$ 345.2331, found 345.2326.

Identification of Intermediate of the reaction pathway (1-Benzyl-3-butyl-2-phenyl-2,3-dihydro-benzo[d]imidazole, 4): Under standard condition when the model substrate N^1,N^1-dibenzyl-N^2-butylbenzene-1,2-diamine **3** was treated with PhI (10 mol %) and 2.5 equivalent mCPBA, intermediate **4** was observed (**Figure S103**) in ESI – TOF Mass spectrometer although it was not isolable through silica gel column chromatography.

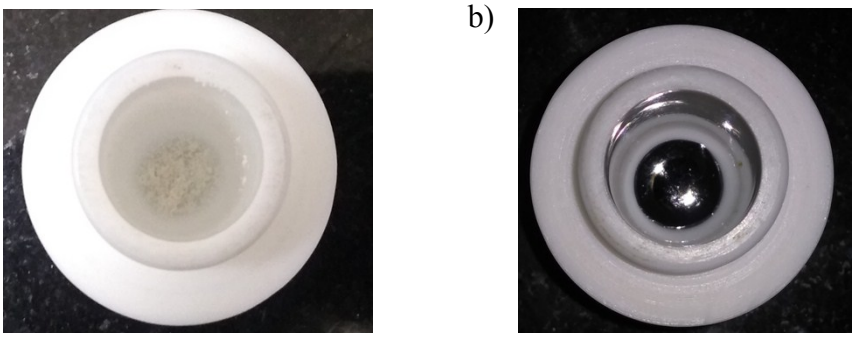


Scheme S6: Understanding reaction mechanism with N^1,N^1-dibenzyl-N^2-butylbenzene-1,2-diamine (**4**).

Pictorial Presentation of Reactivity of Aniline Derivative with PhI and mCPBA:

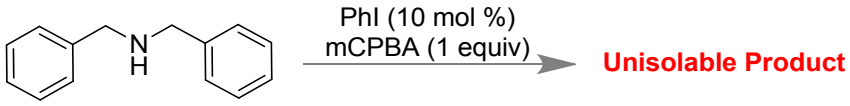


a) b)

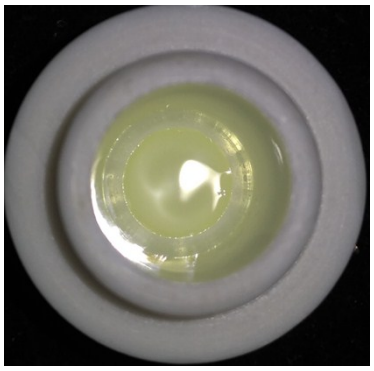


Scheme S7: a) *p*-Bromoaniline before treatment with PhI and mCPBA. b) Color of reaction mixture of *p*-Bromoaniline and 10 mol % PhI and 1 equiv *m*CPBA.

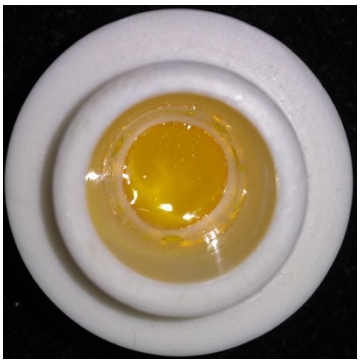
Pictorial Presentation of Reactivity of Dibenzylamine with PhI and mCPBA:



c)

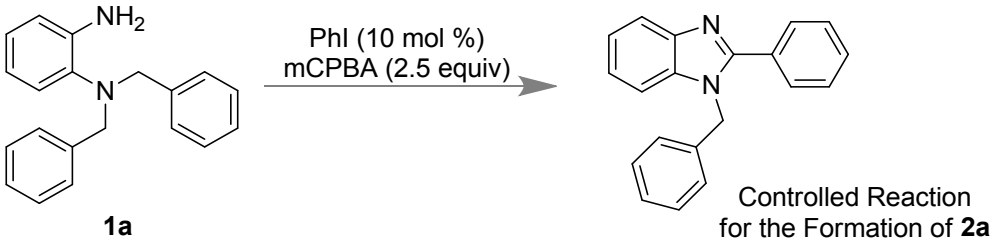


d)

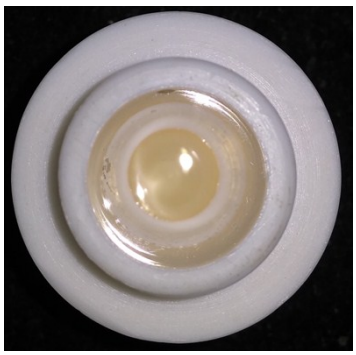


Scheme S8: c) Dibenzylamine before treatment with PhI and mCPBA. d) Color of reaction mixture of dibenzylamine and 10 mol % PhI and 1 equiv *m*CPBA.

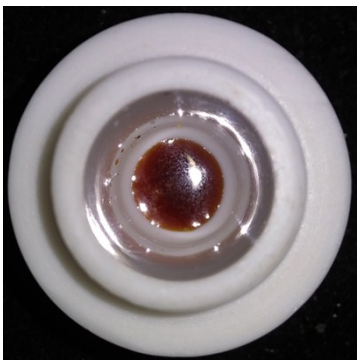
Pictorial Presentation of Reactivity of Substrate 1a with PhI and mCPBA:



e)



f)



Scheme S9: e) Substrate **1a** before treatment with PhI and mCPBA. f) Color of reaction mixture of **1a** and 10 mol % PhI and 1 equiv *m*CPBA.

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Copies of ^{1}H and ^{13}C NMR Spectra of Compounds

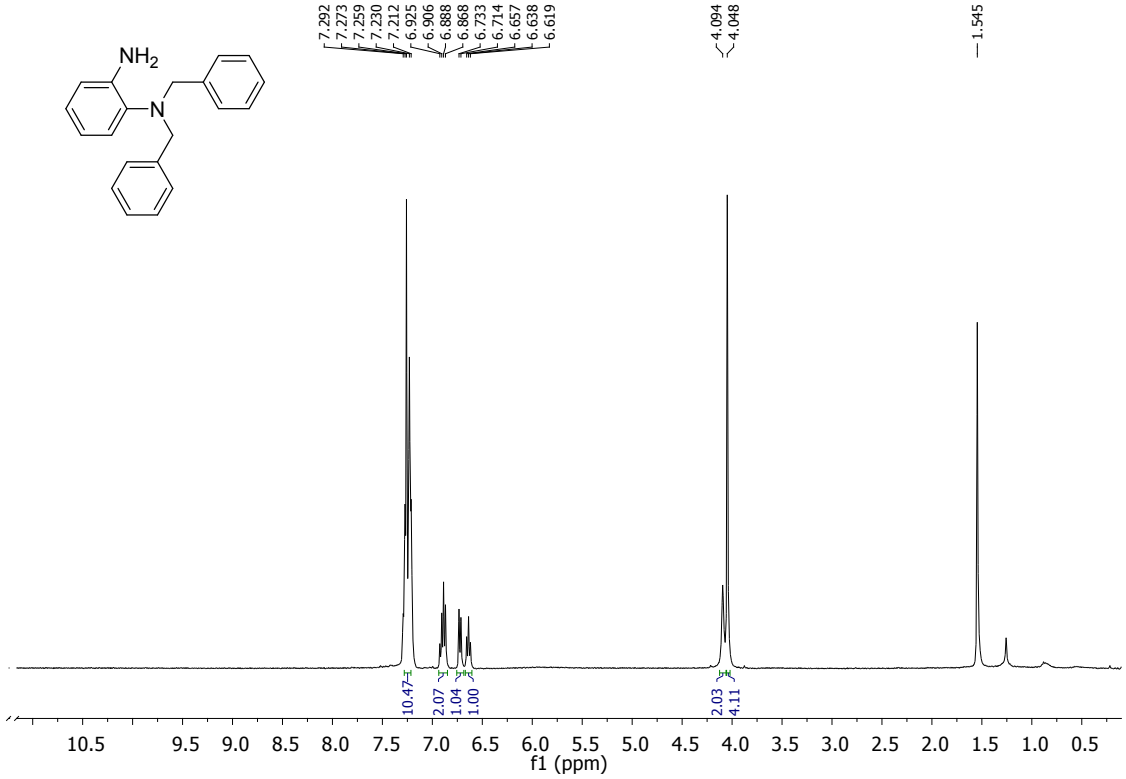


Fig. S3. ^{1}H NMR of N^{1},N^{1}-dibenzylbenzene-1,2-diamine (**1a**)

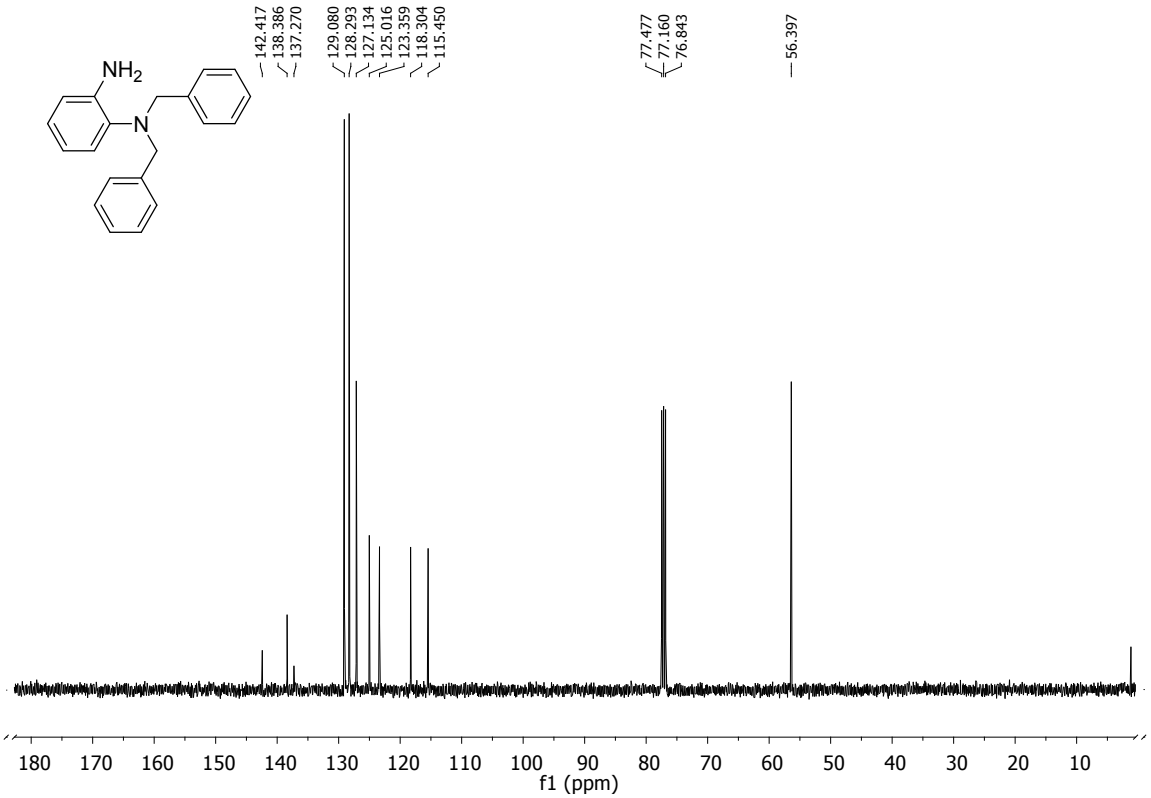


Fig. S4. ^{13}C NMR of N^1,N^1-dibenzylbenzene-1,2-diamine (**1a**)

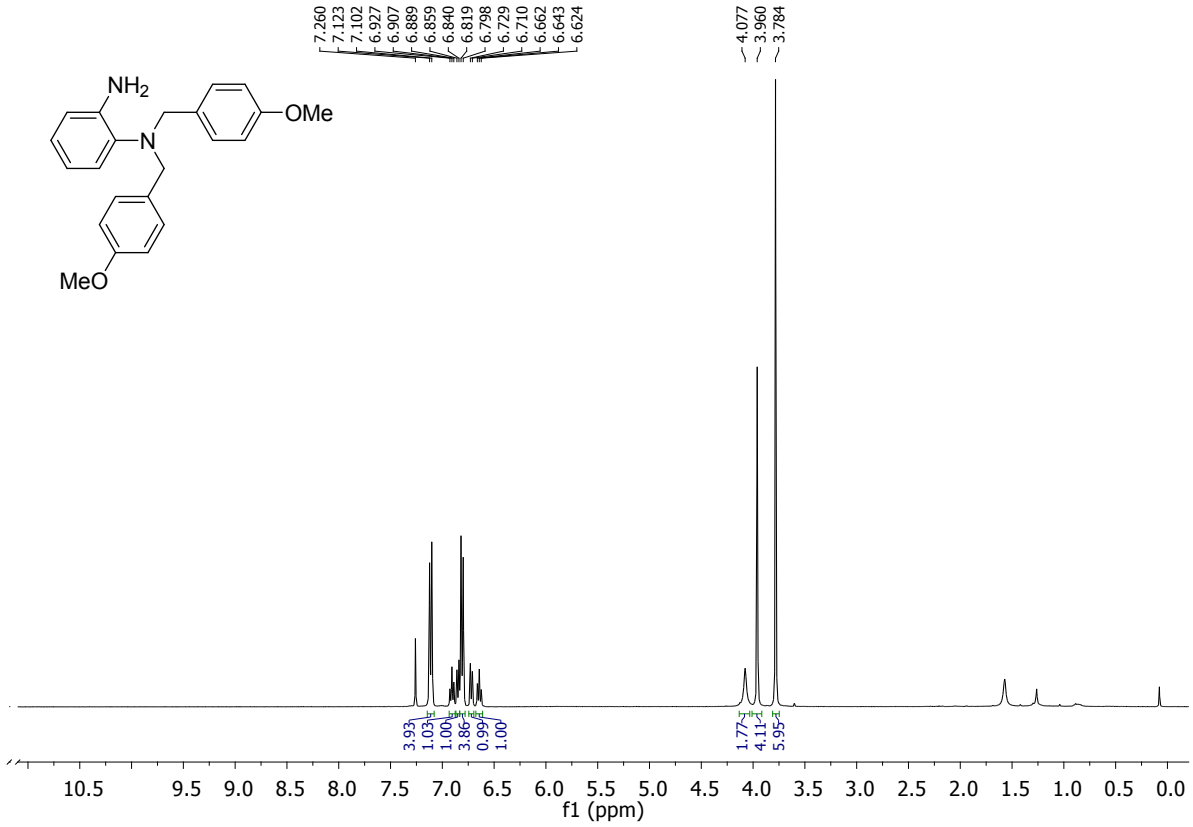


Fig. S5. ^{1}H NMR of N^1,N^1- bis(4-methoxybenzyl)benzene-1,2-diamine (**1b**)

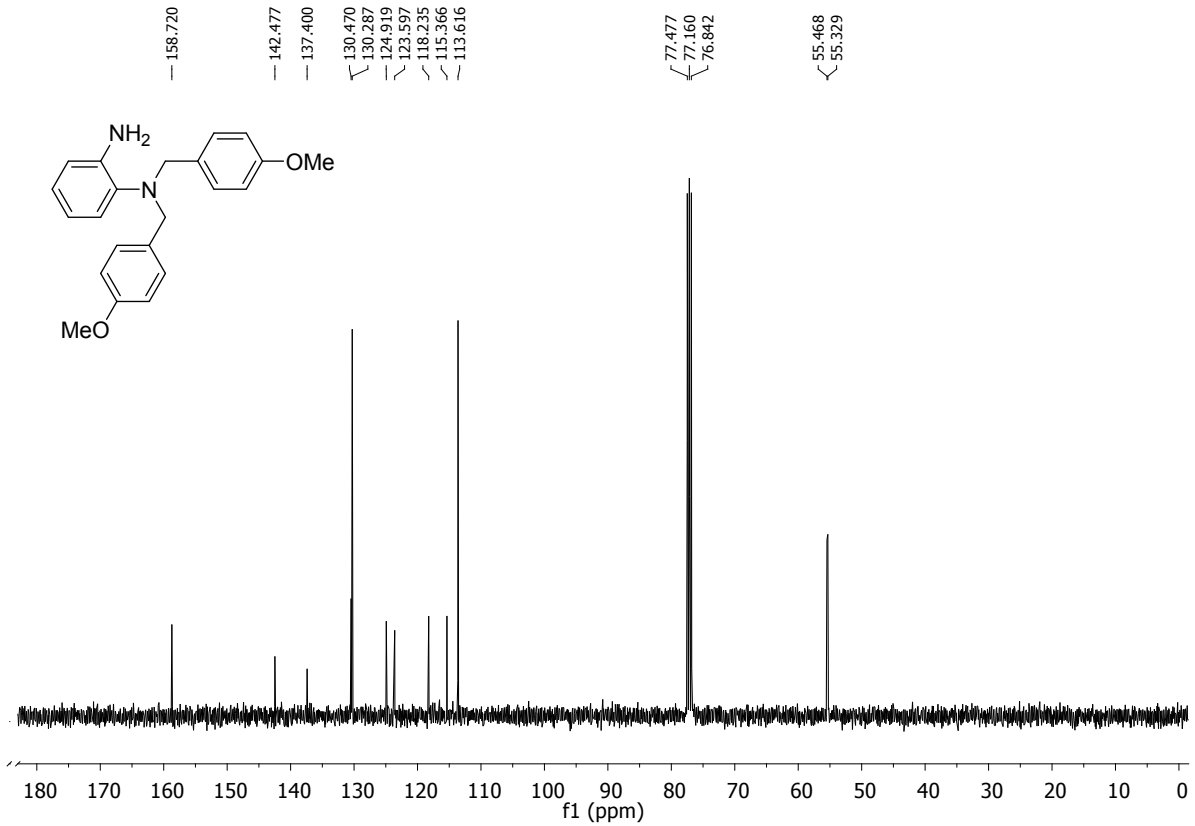


Fig. S6. ^{13}C NMR of N^1,N^1- bis(4-methoxybenzyl)benzene-1,2-diamine (**1b**)

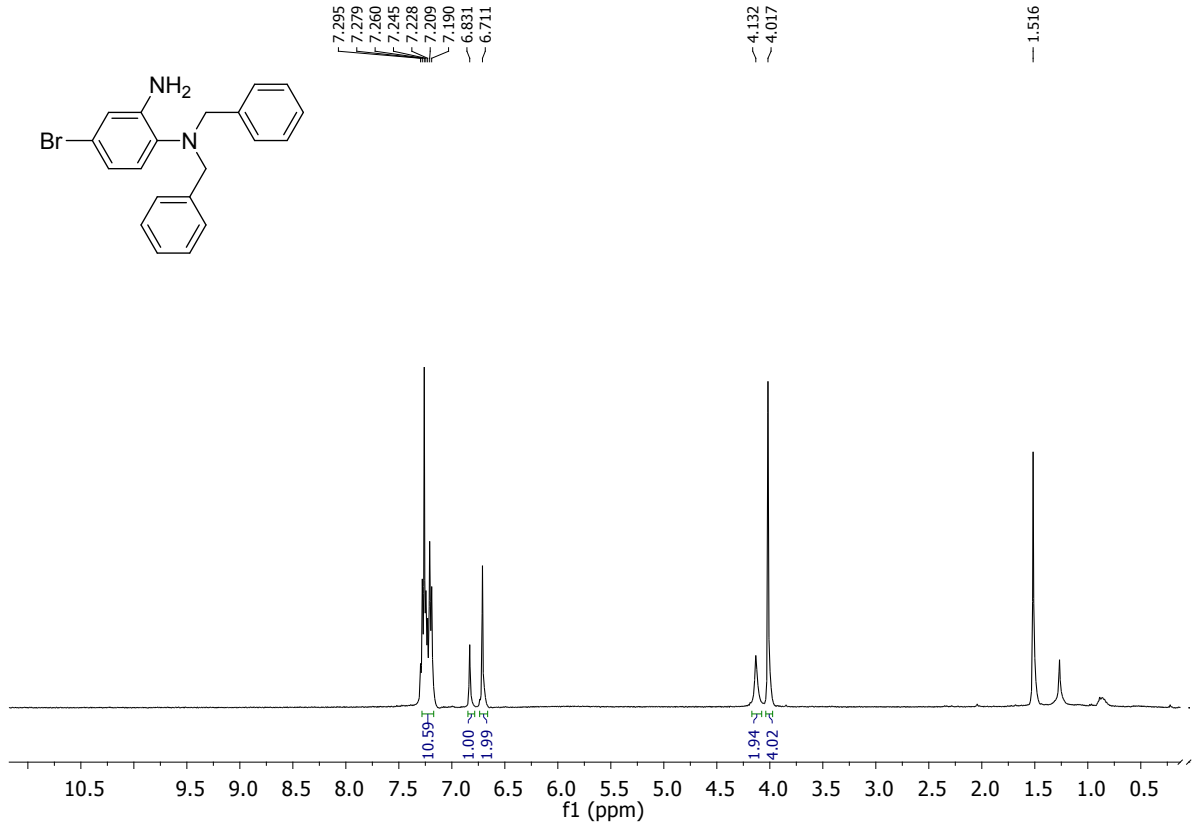


Fig. S7. ^{1}H NMR of N^1,N^1- dibenzyl-4-bromobenzene-1,2-diamine (**1c**)

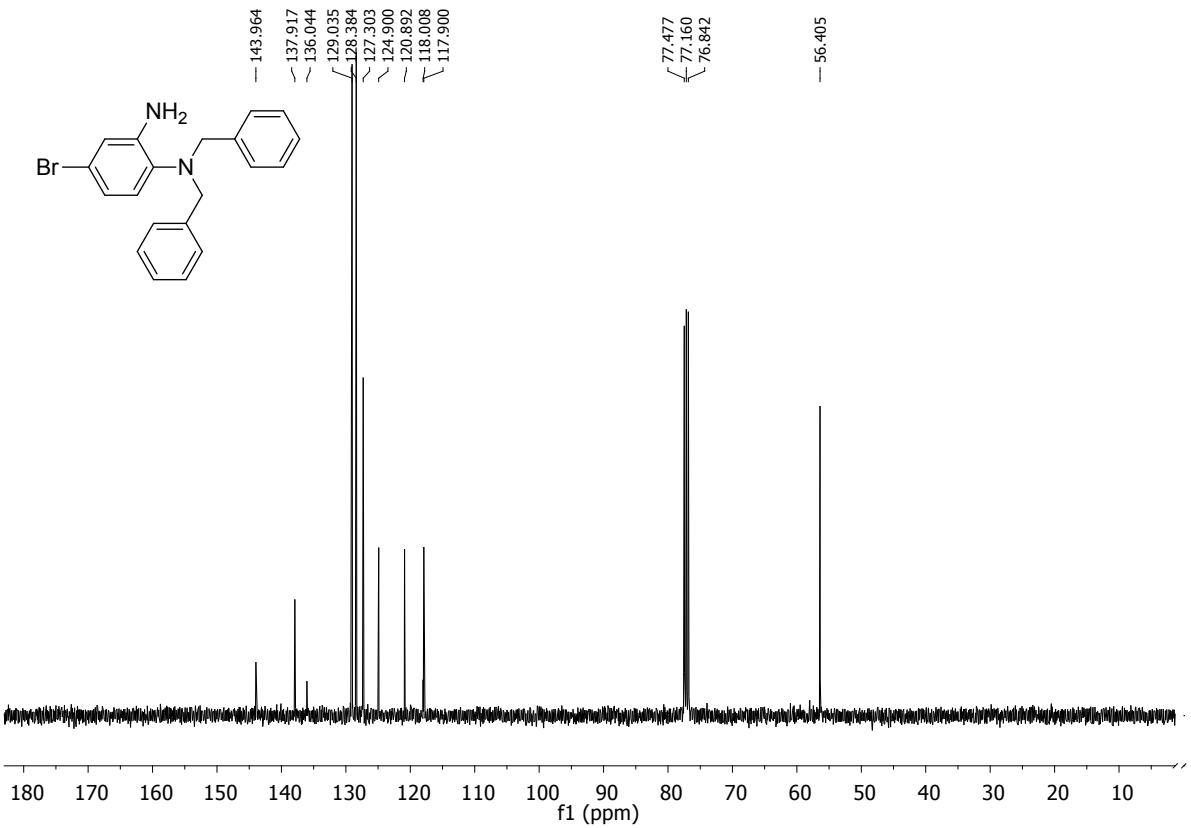


Fig. S8. ^{13}C NMR of N^1,N^1- dibenzyl-4-bromobenzene-1,2-diamine (**1c**)

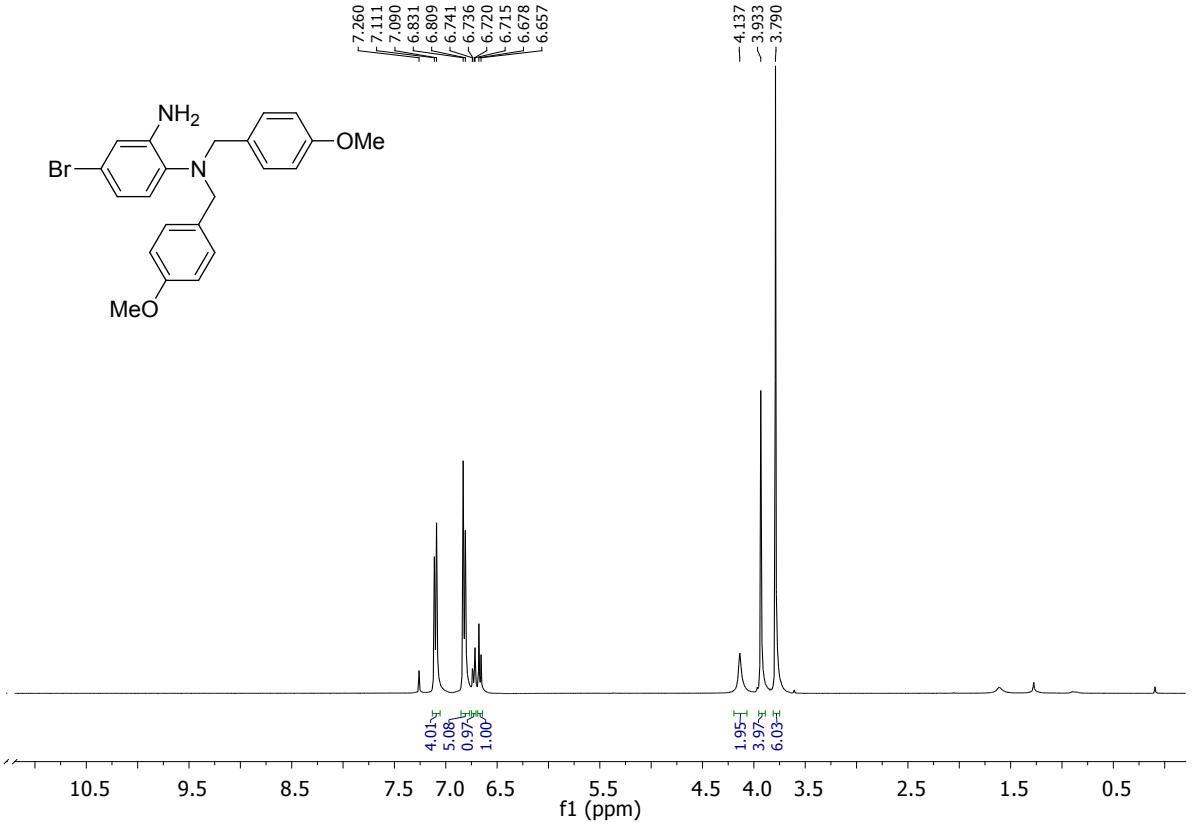


Fig. S9. ^{1}H NMR of 4-Bromo-N^1,N^1-bis(4-methoxybenzyl)benzene-1,2-diamine (**1d**)

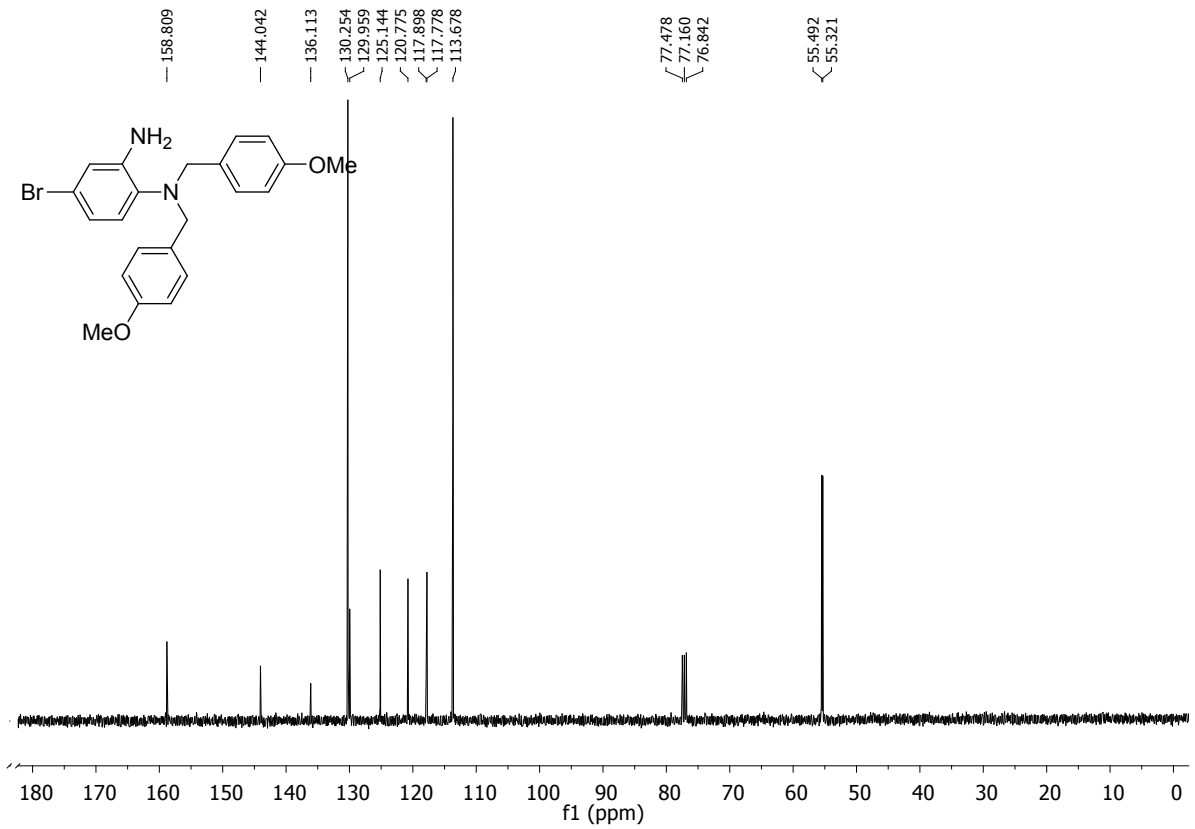


Fig. S10. ^{13}C NMR of 4-Bromo-N^1,N^1-bis(4-methoxybenzyl)benzene-1,2-diamine (**1d**)

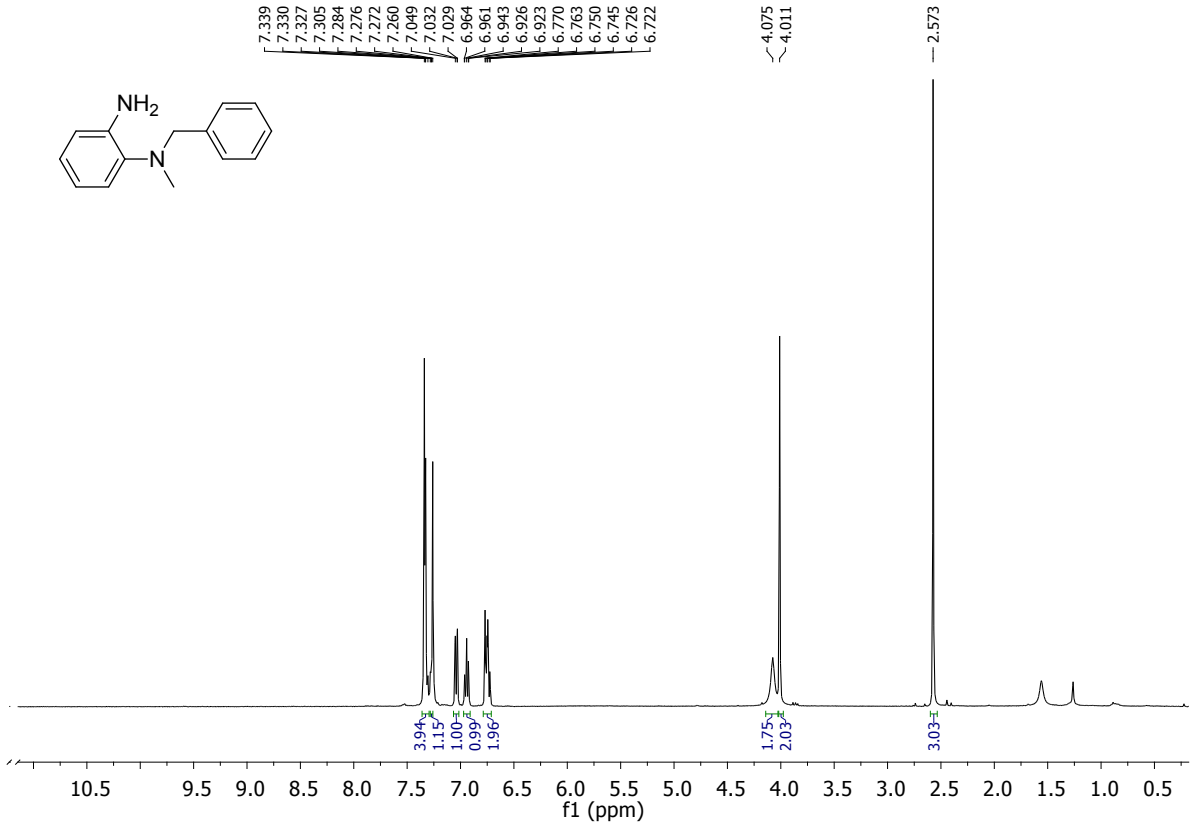


Fig. S11. ^{1}H NMR of N^1-benzyl-N^1-methylbenzene-1,2-diamine (**1e**)

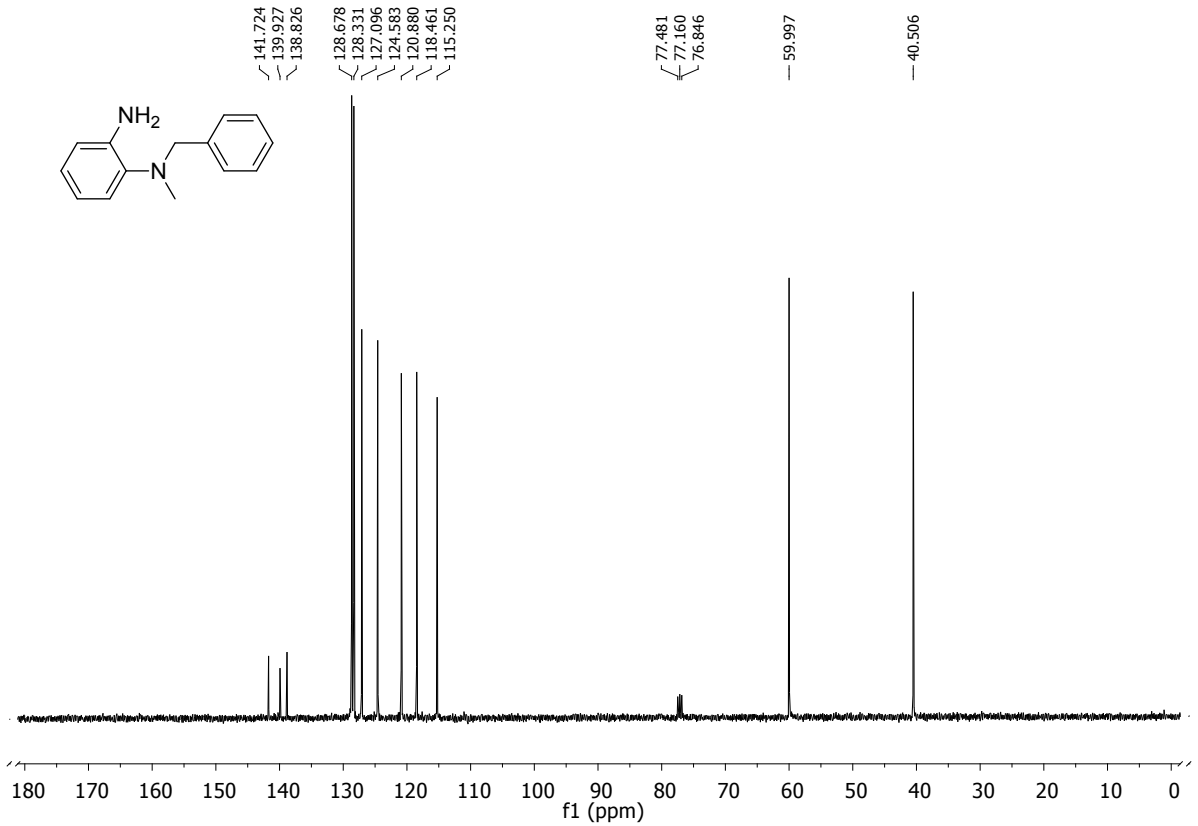


Fig. S12. ^{13}C NMR of N^1-benzyl-N^1-methylbenzene-1,2-diamine (**1e**)

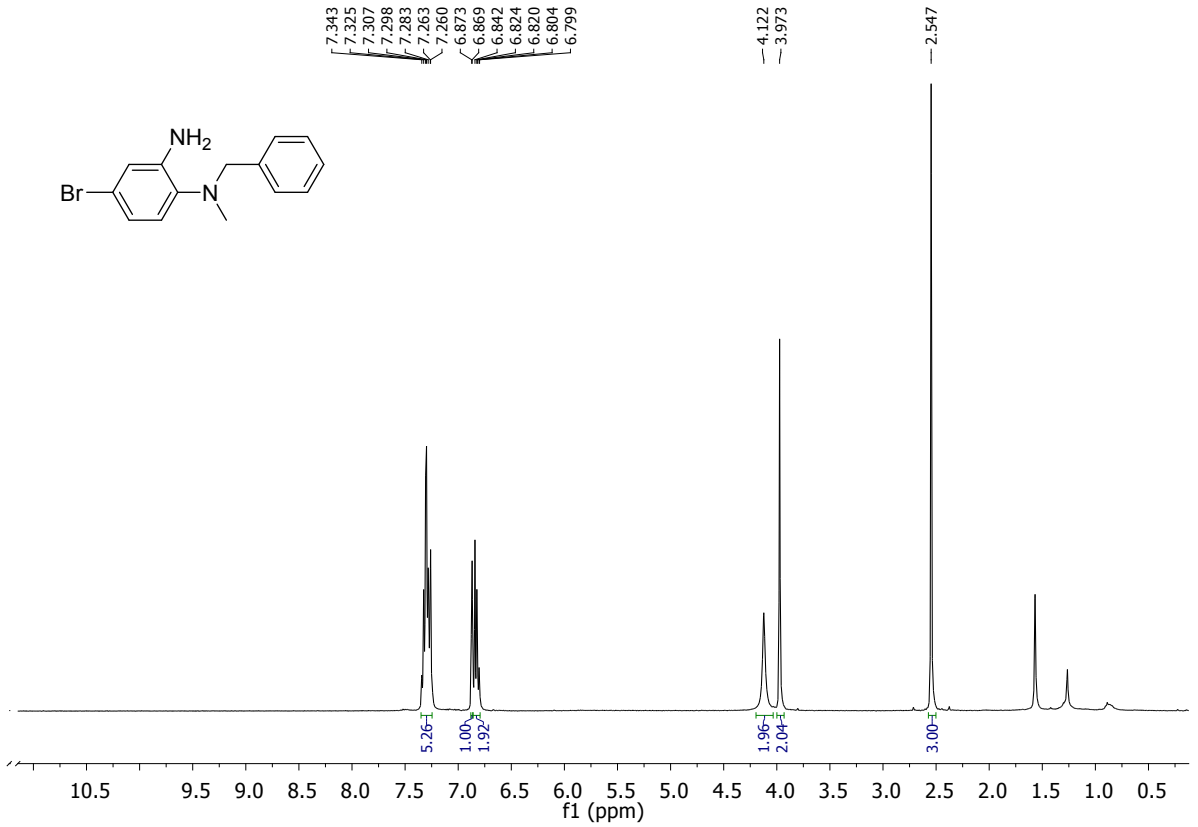


Fig. S13. ^{1}H NMR of N^1-Benzyl-4-bromo-N^1-methylbenzene-1,2-diamine (**1f**)

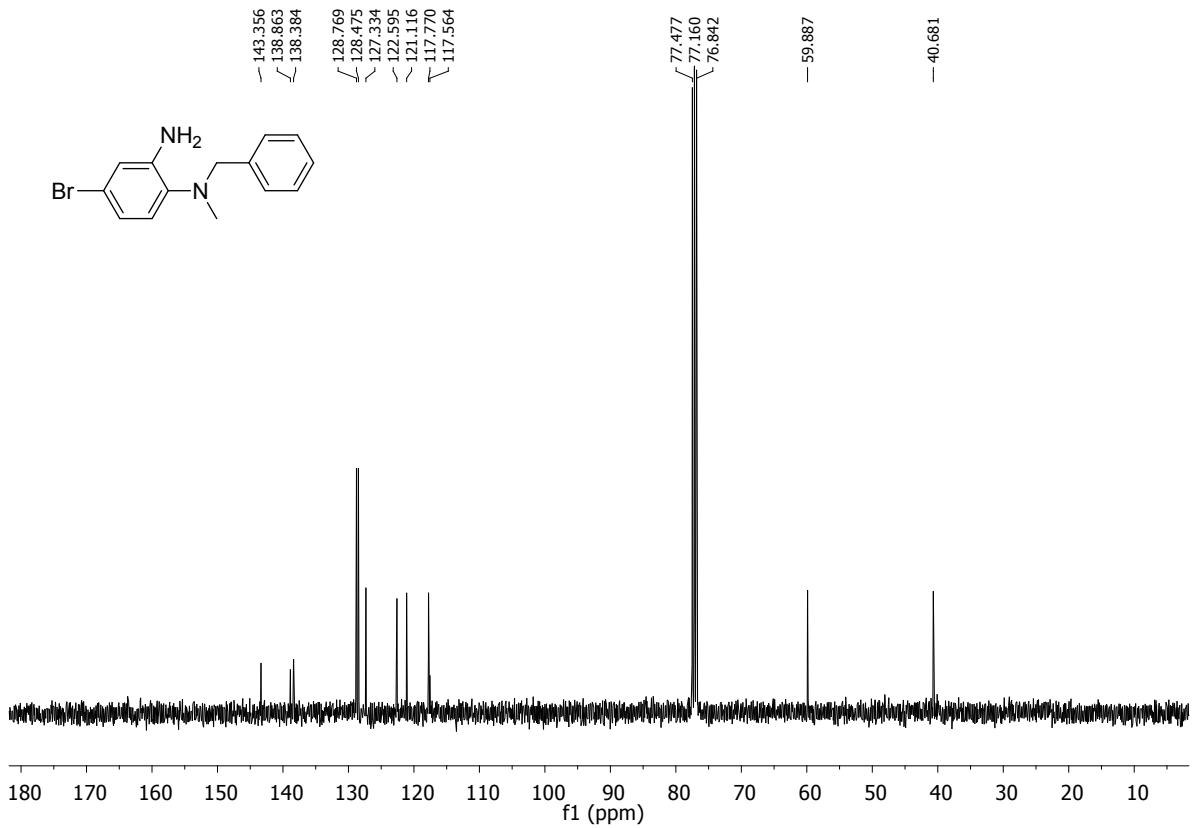


Fig. S14. ^{13}C NMR of N^1-Benzyl-4-bromo-N^1-methylbenzene-1,2-diamine (**1f**)

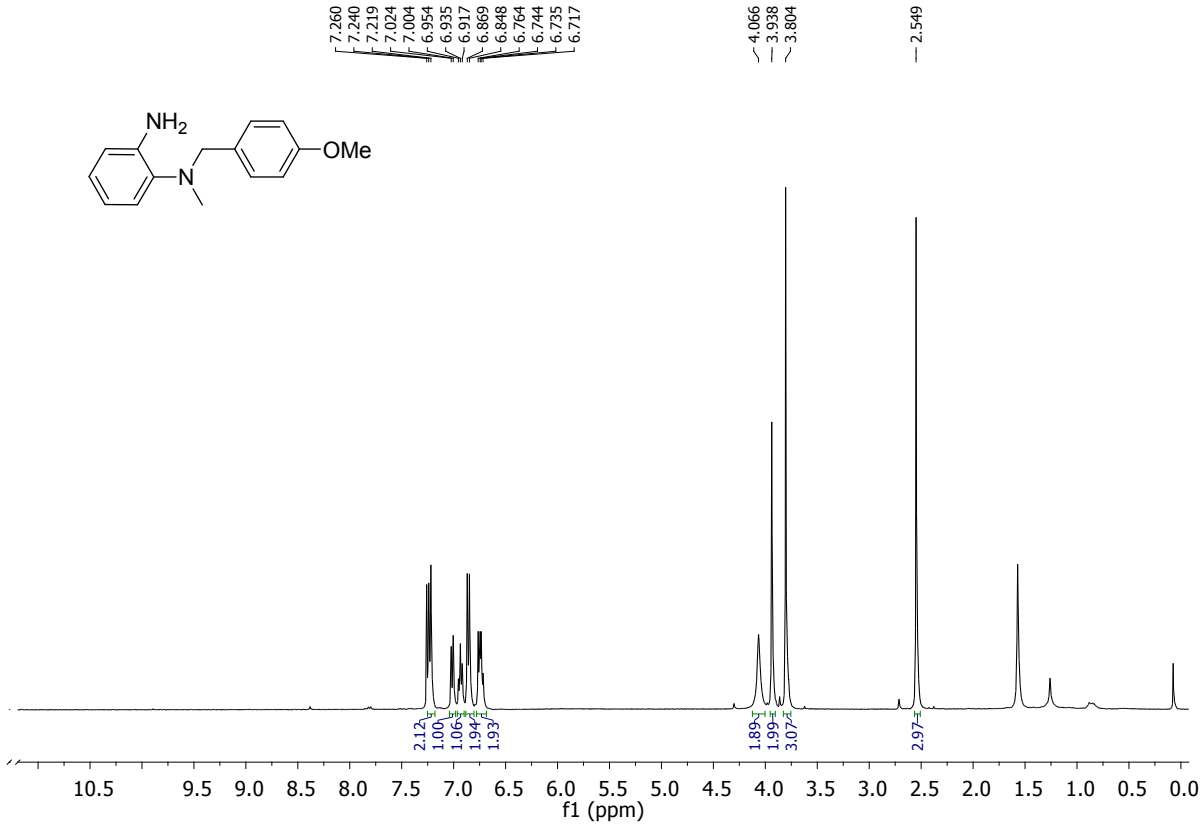


Fig. S15. ^{1}H NMR of N^1-(4-methoxybenzyl)-N^1-methylbenzene-1,2-diamine (**1g**)

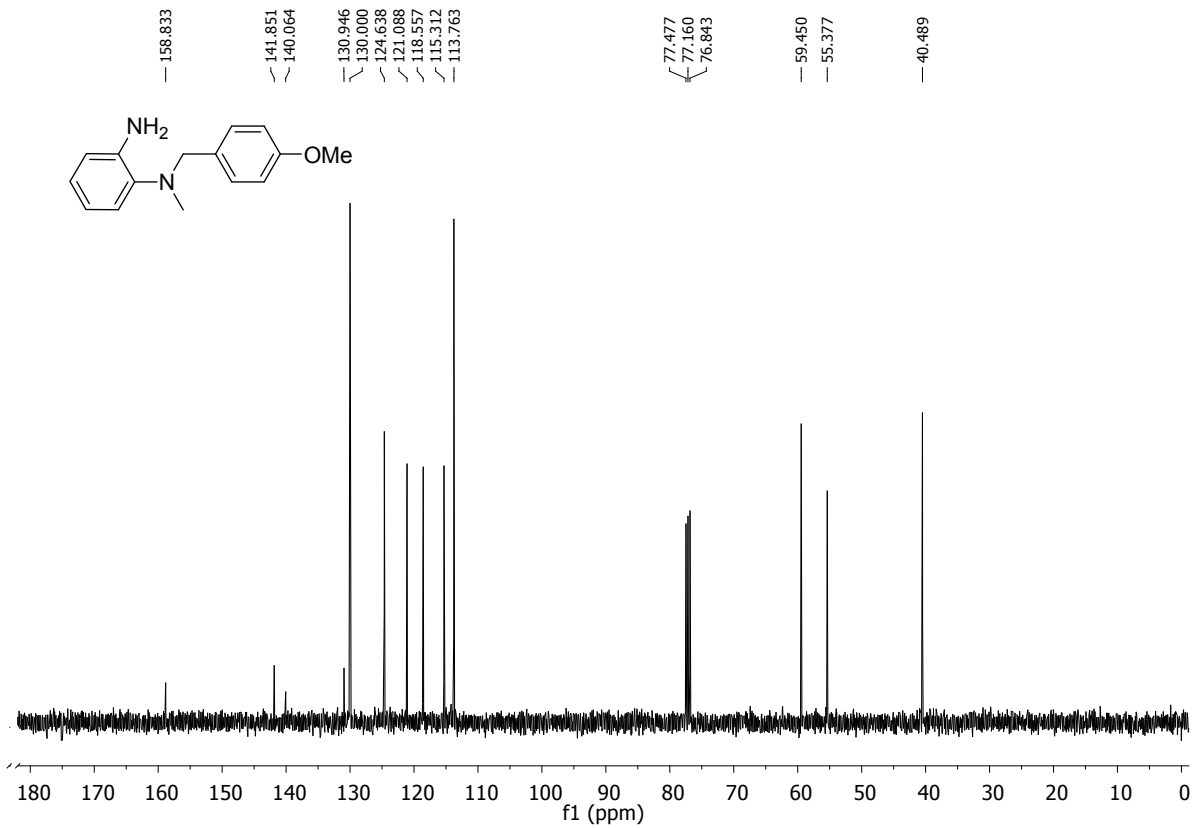


Fig. S16. ^{13}C NMR of N^1-(4-methoxybenzyl)-N^1-methylbenzene-1,2-diamine (**1g**)

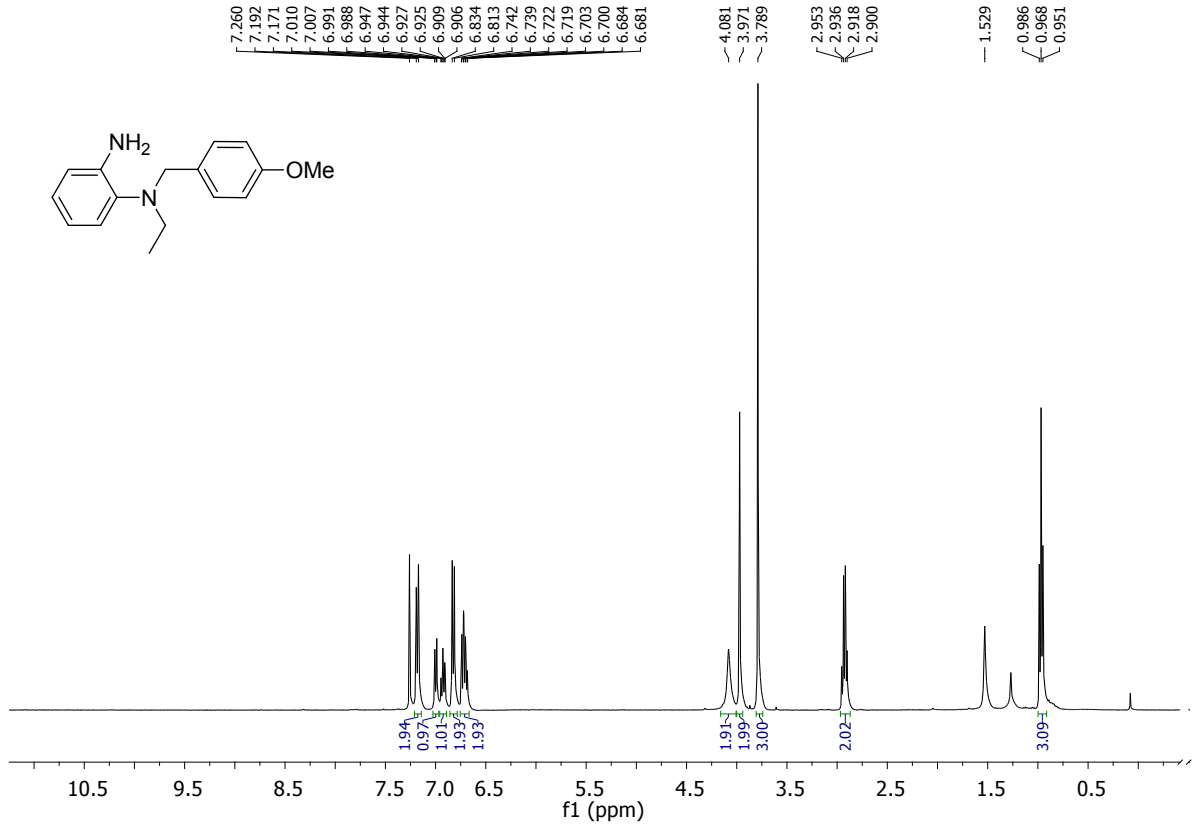


Fig. S17. ^{1}H NMR of N^1-ethyl-N^1-(4-methoxybenzyl)benzene-1,2-diamine (**1h**)

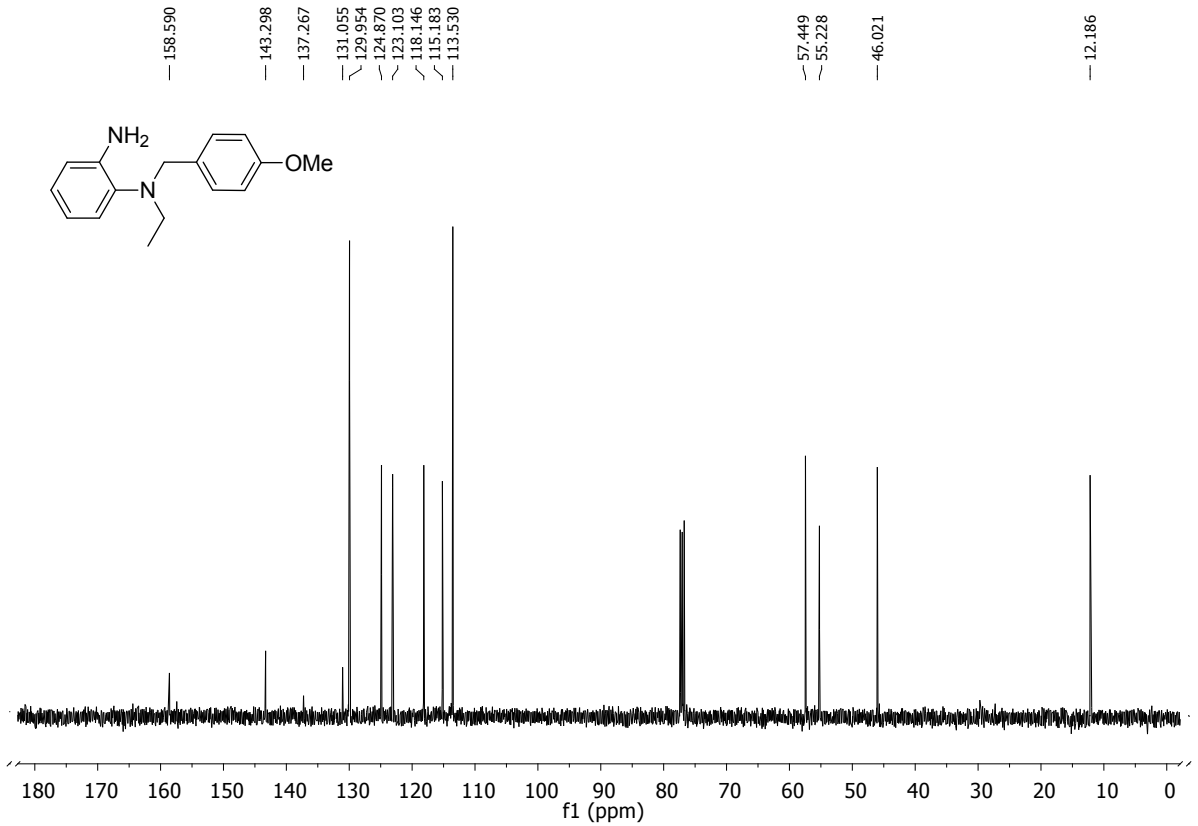


Fig. S18. ^{13}C NMR of N^1-ethyl-N^1-(4-methoxybenzyl)benzene-1,2-diamine (**1h**)

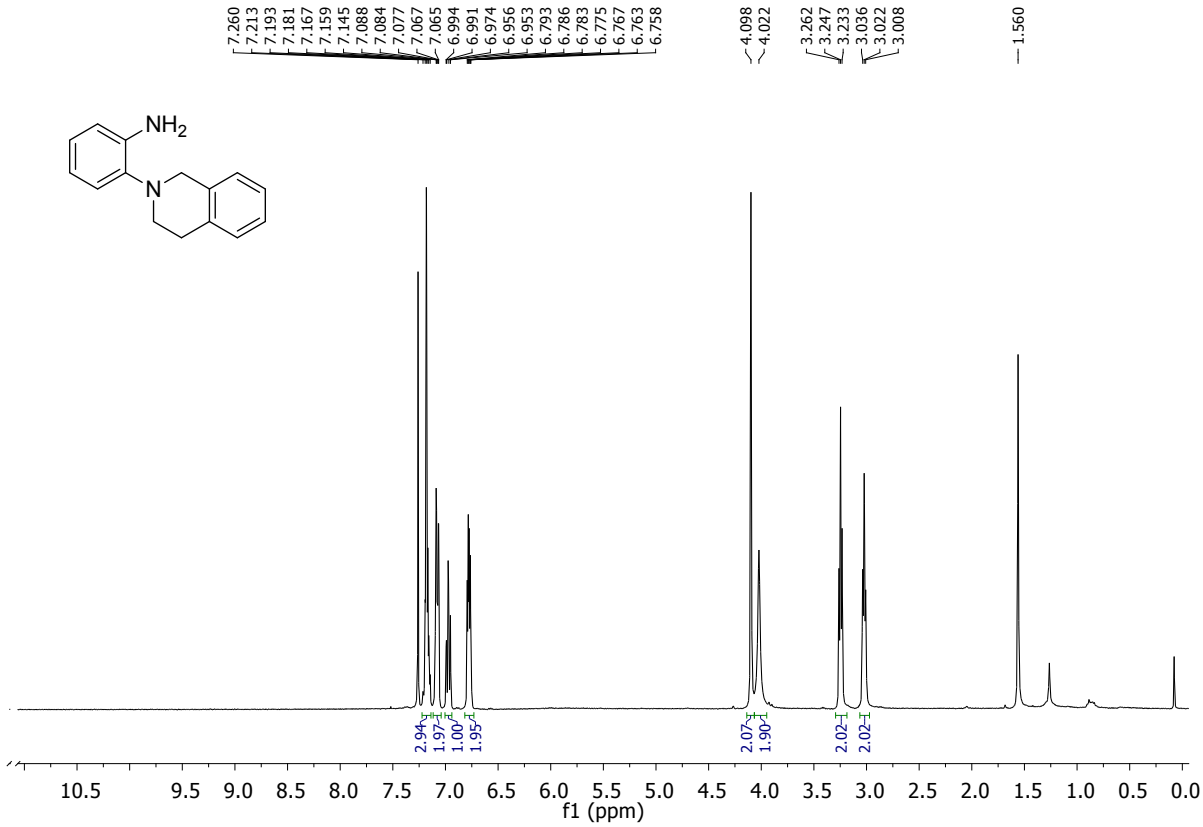


Fig. S19. ^{1}H NMR of 2-(3,4-Dihydroisoquinolin-2-yl)aniline (**1i**)

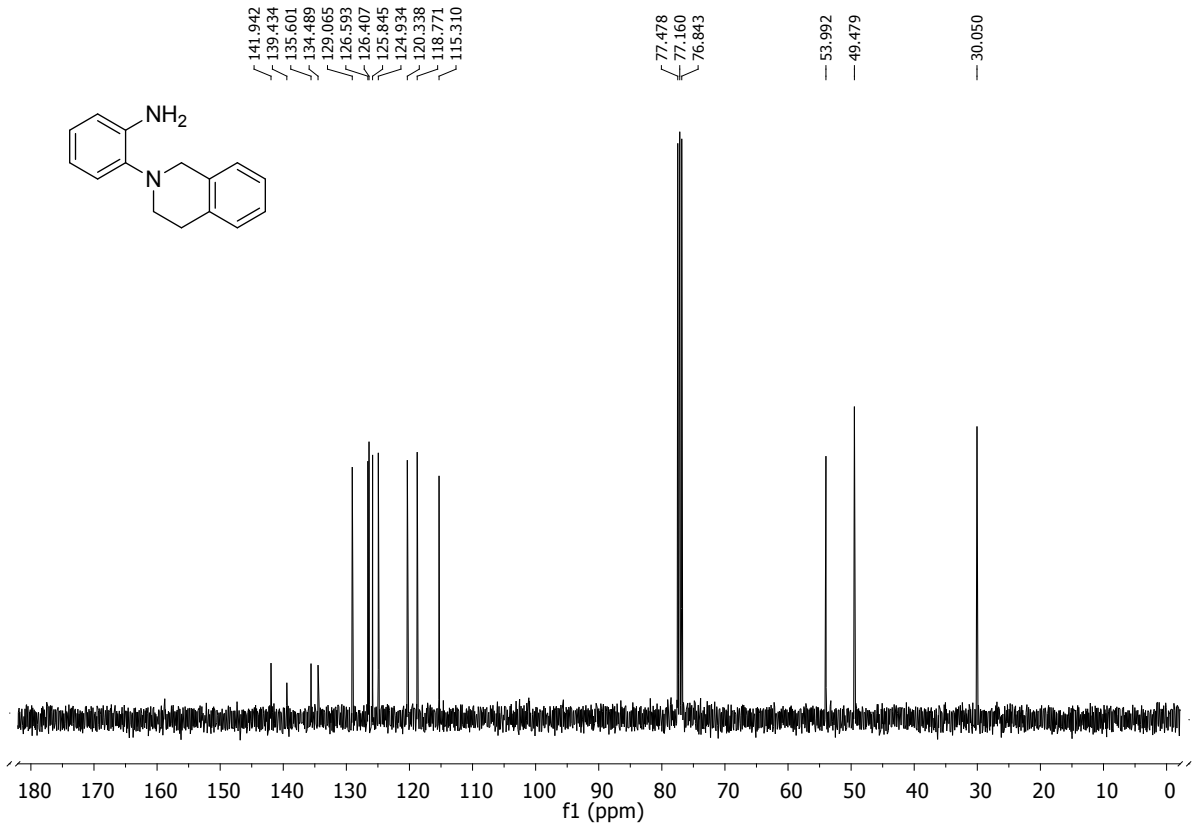


Fig. S20. ^{13}C NMR of 2-(3,4-Dihydroisoquinolin-2-yl)aniline (**1i**)

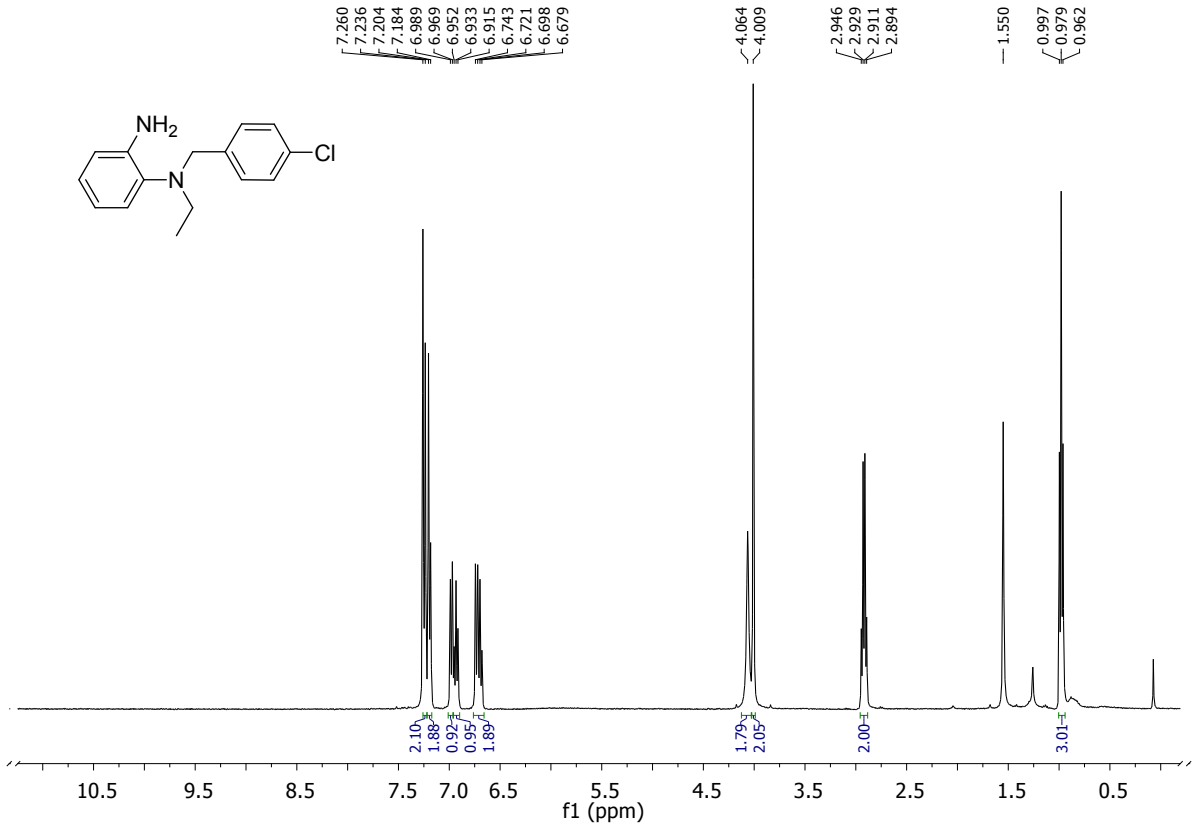


Fig. S21. ^{1}H NMR of *N*^{1}-(4-chlorobenzyl)-*N*^{1}-ethylbenzene-1,2-diamine (**1j**)

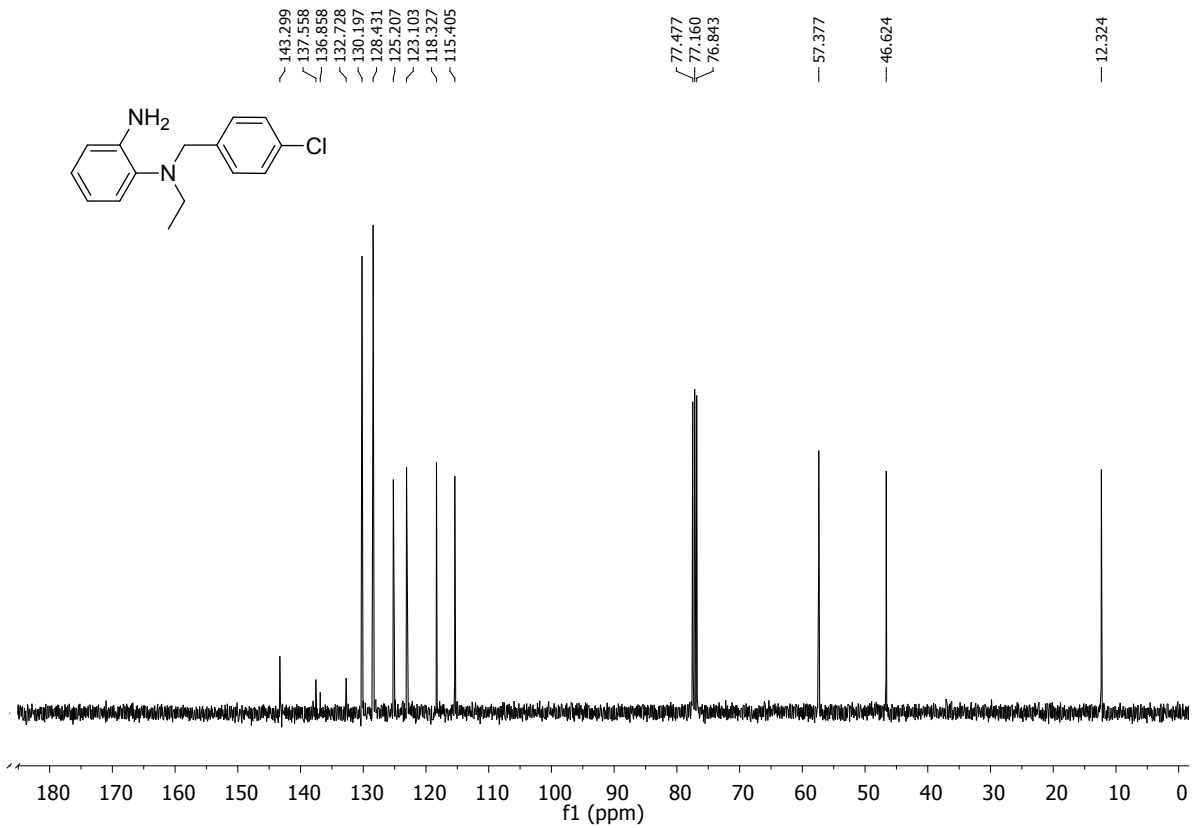


Fig. S22. ^{13}C NMR of *N*^{1}-(4-chlorobenzyl)-*N*^{1}-ethylbenzene-1,2-diamine (**1j**)

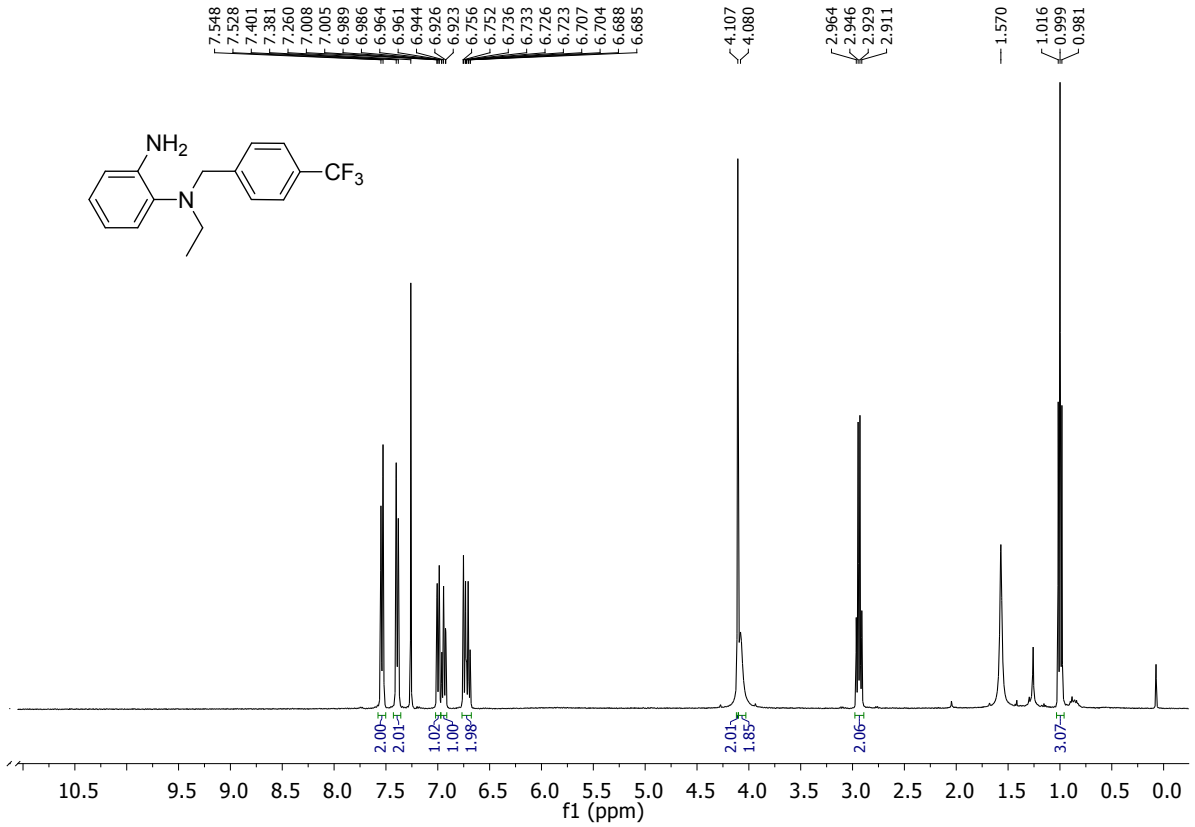


Fig. S23. ^{1}H NMR of *N*^{1}-ethyl-*N*^{1}-(4-(trifluoromethyl)benzyl)benzene-1,2-diamine (**1k**)

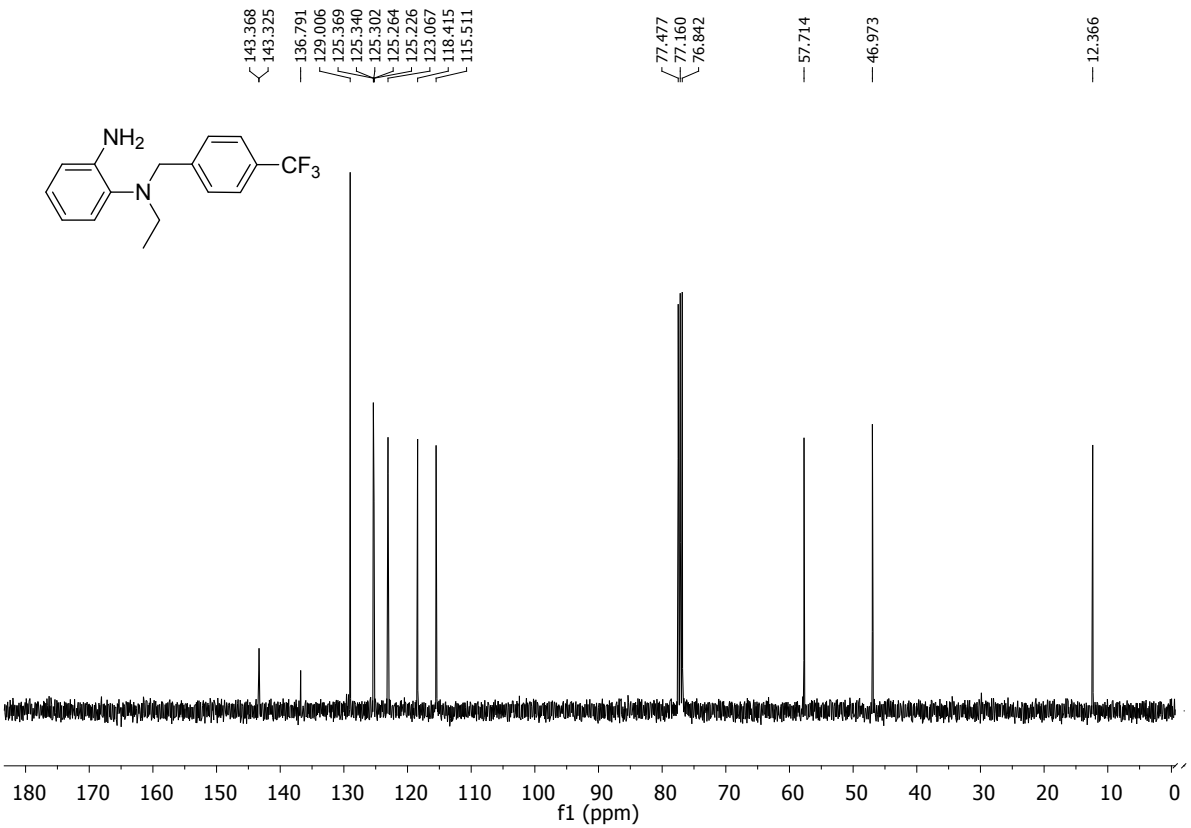


Fig. S24. ^{13}C NMR of N^1-ethyl-N^1-(4-(trifluoromethyl)benzyl)benzene-1,2-diamine (**1k**)

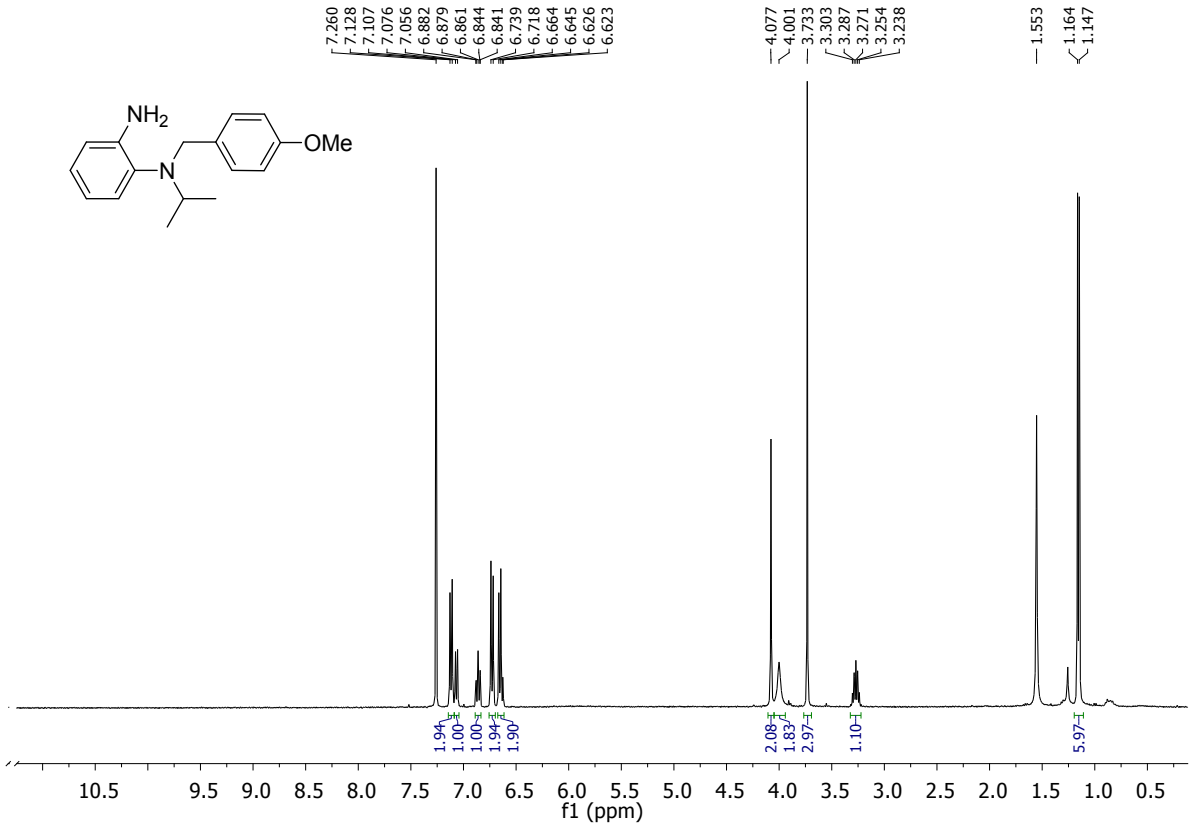


Fig. S25. ^{1}H NMR of N^1-isopropyl-N^1-(4-methoxybenzyl)benzene-1,2-diamine (**1l**)

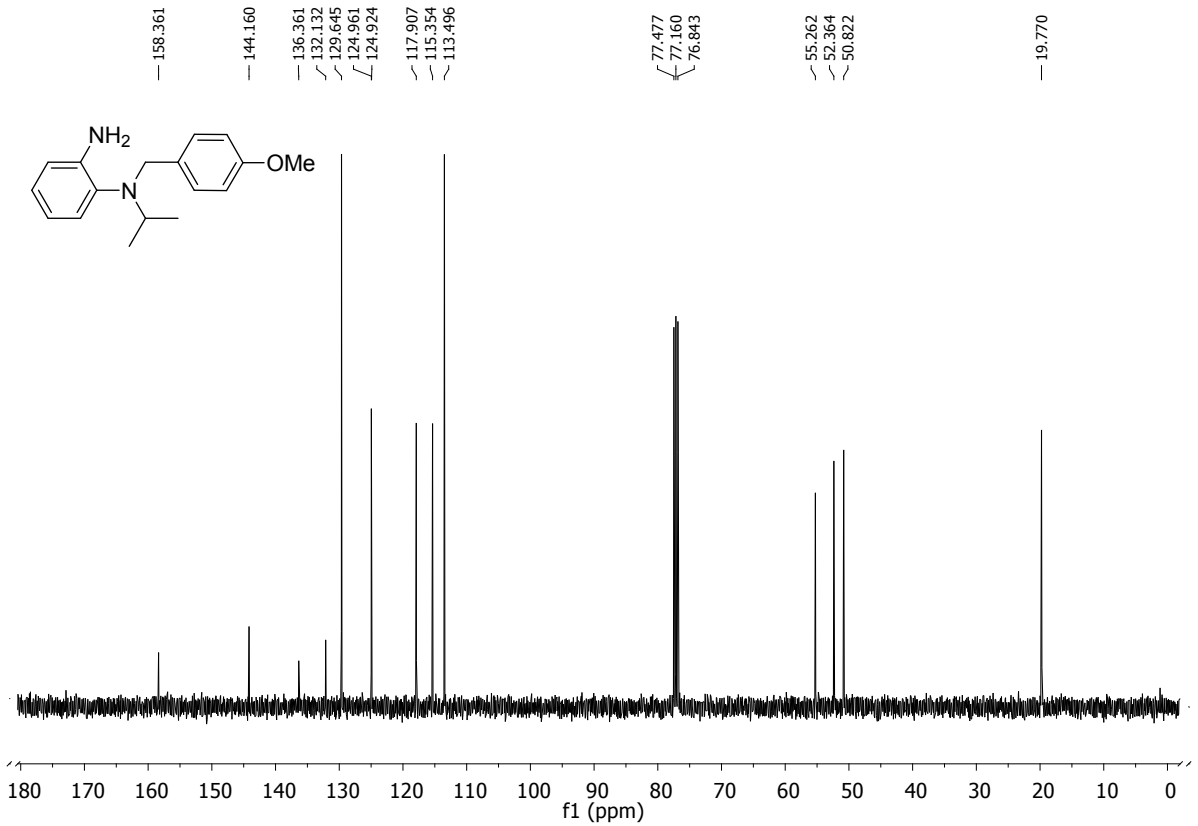


Fig. S26. ^{13}C NMR of N^1-isopropyl-N^1-(4-methoxybenzyl)benzene-1,2-diamine (**1l**)

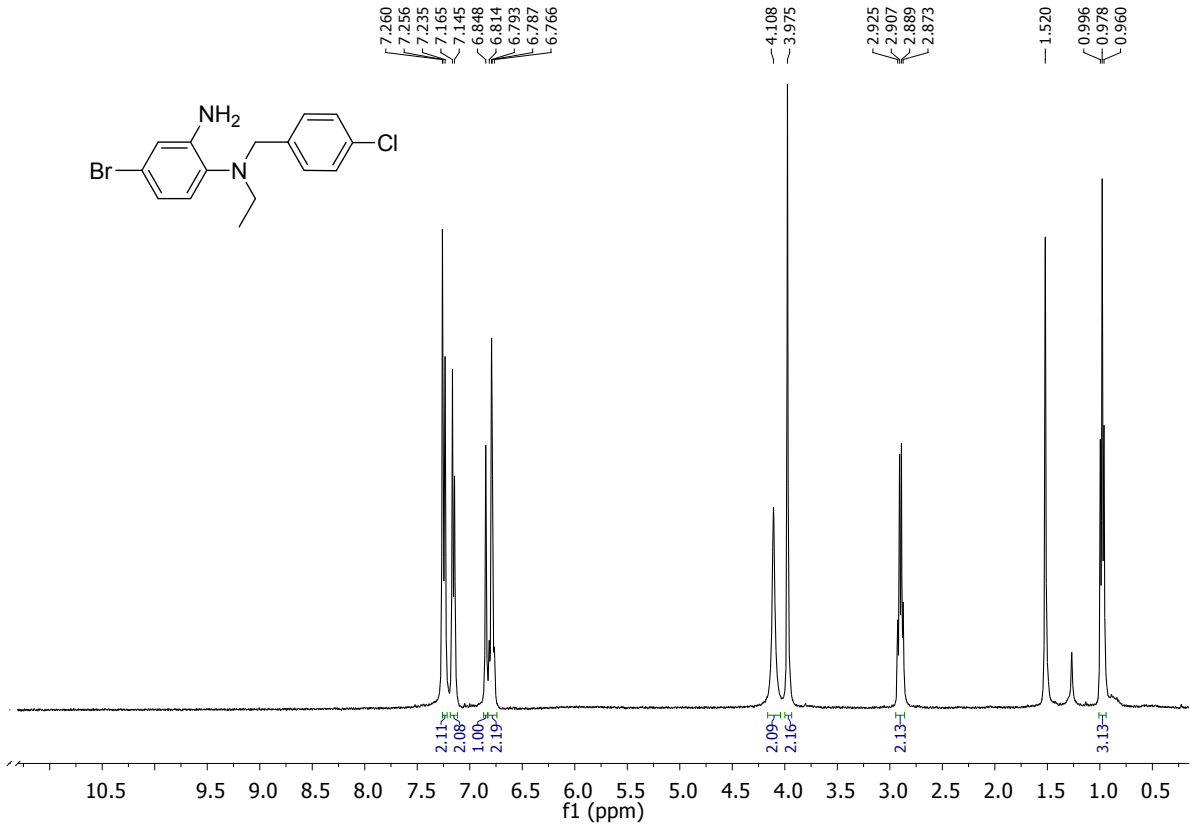


Fig. S27. ^{1}H NMR of 4-Bromo-N^1-(4-chlorobenzyl)-N^1-ethylbenzene-1,2-diamine (**1m**)

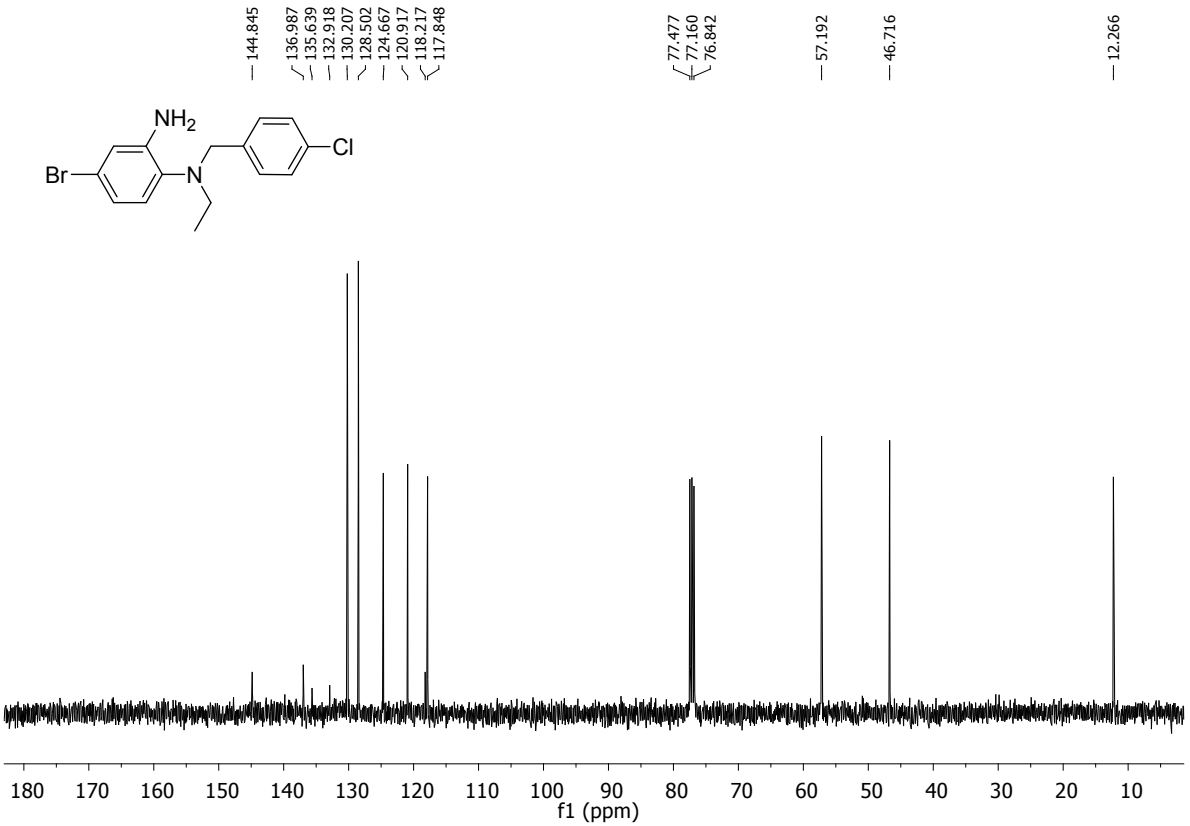


Fig. S28. ^{13}C NMR of 4-Bromo-*N*^{1}-(4-chlorobenzyl)-*N*^{1}-ethylbenzene-1,2-diamine (**1m**)

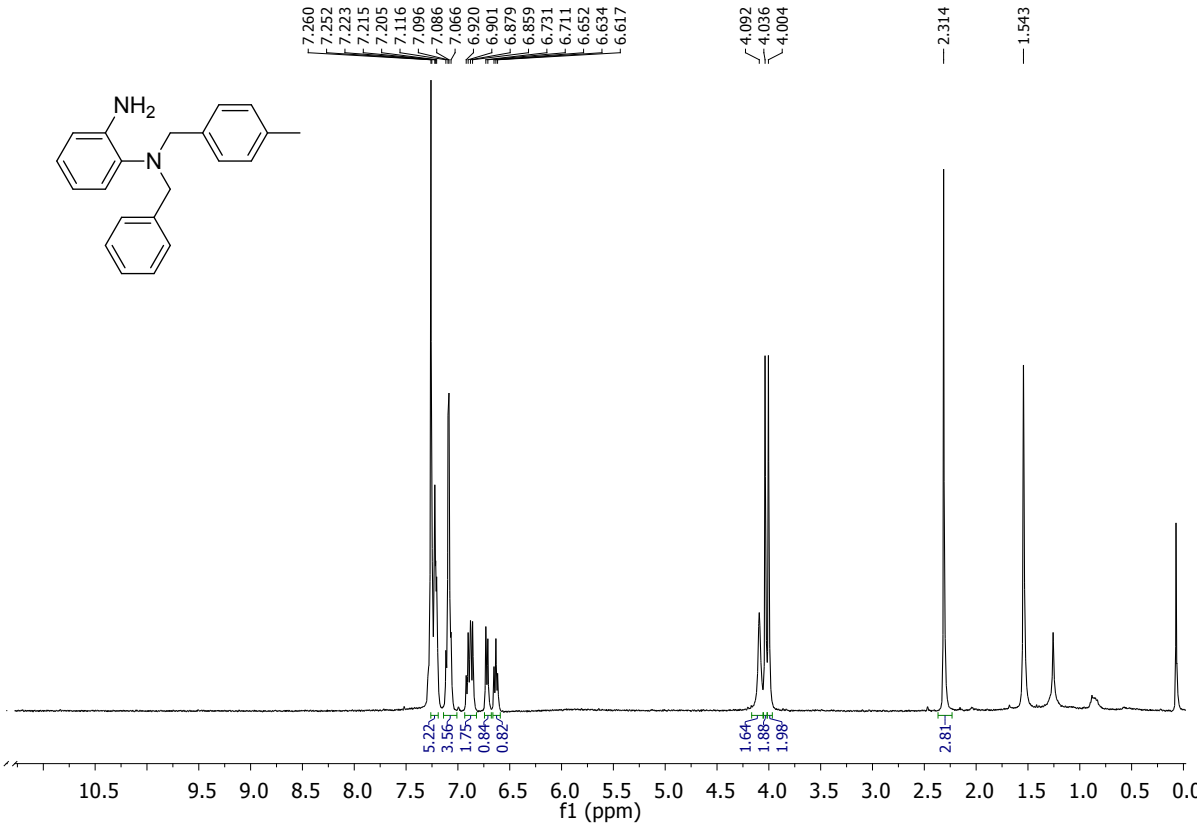


Fig. S29. ^{1}H NMR of *N*^{1}-benzyl-*N*^{1}-(4-methylbenzyl)benzene-1,2-diamine (**1n**)

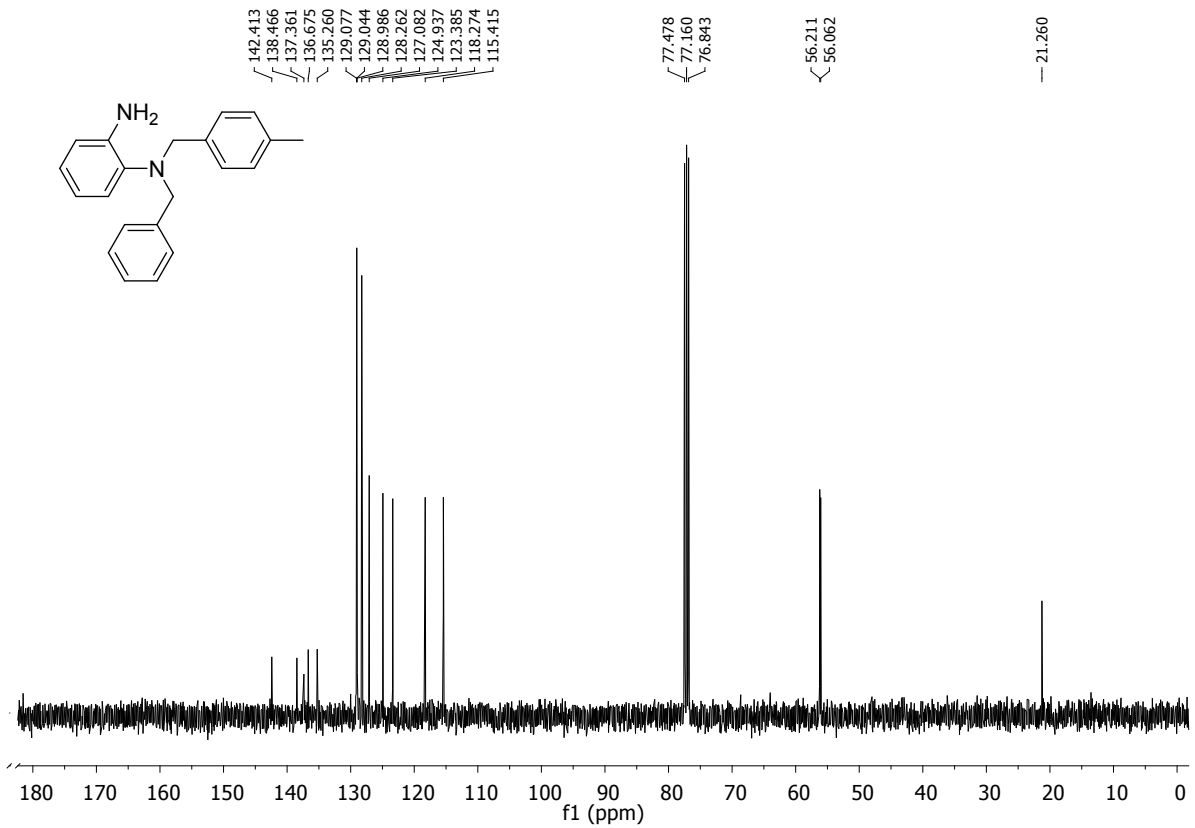


Fig. S30. ^{13}C NMR of N^1-benzyl-N^1-(4-methylbenzyl)benzene-1,2-diamine (**1n**)

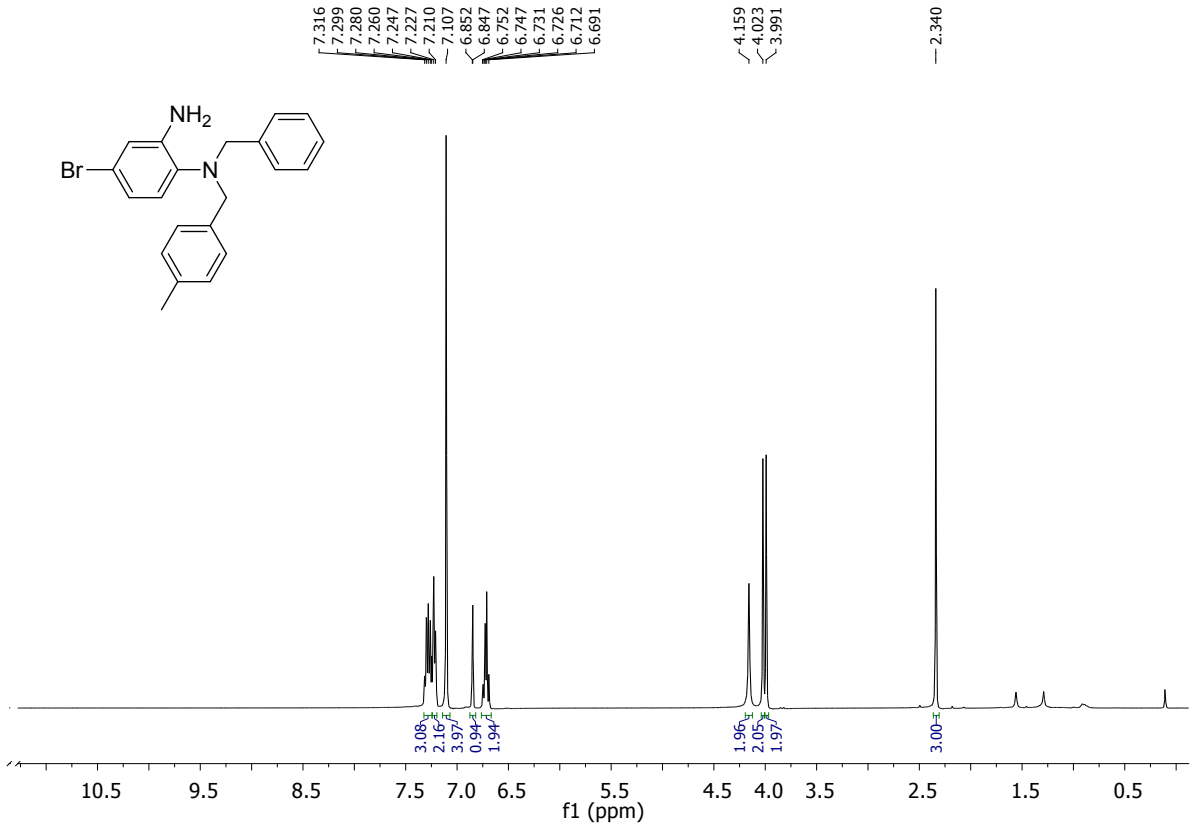


Fig. S31. ^{1}H NMR of N^1-benzyl-4-bromo-N^1-(4-methylbenzyl)benzene-1,2-diamine (**1o**)

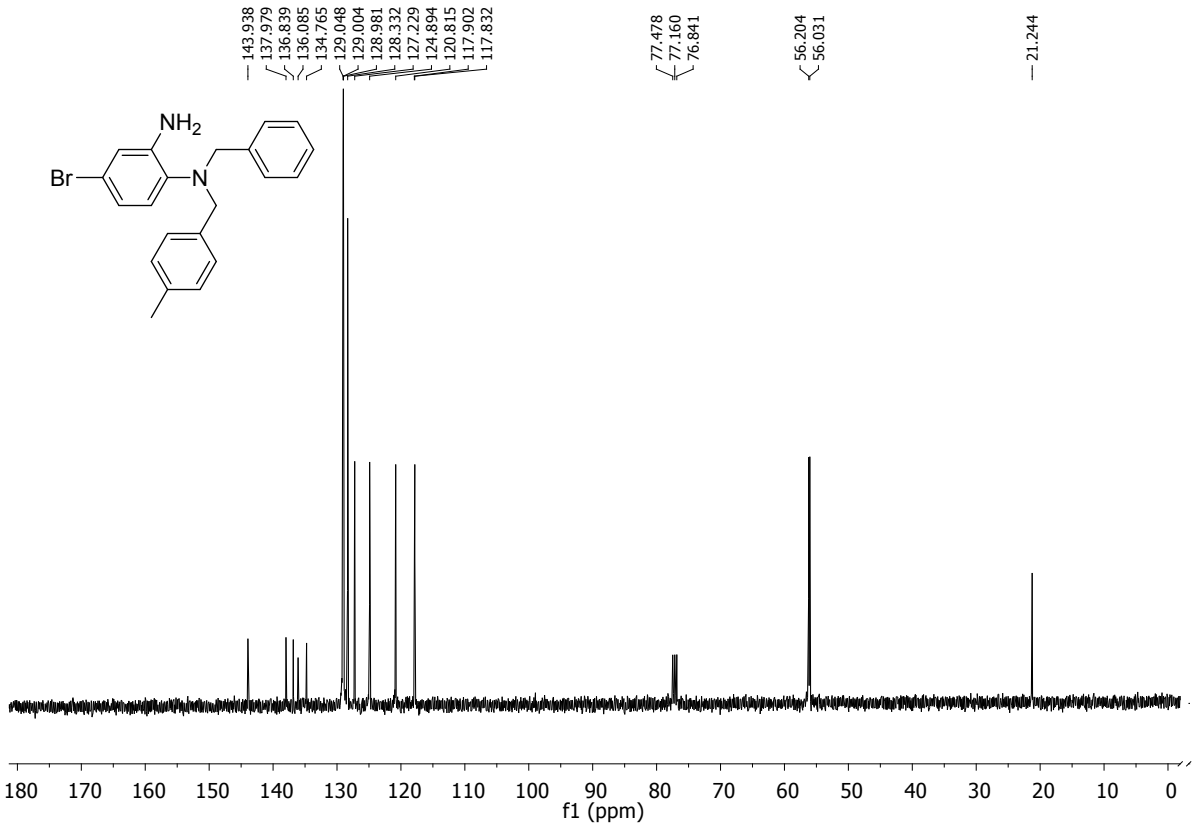


Fig. S32. ^{13}C NMR of N^1-benzyl-4-bromo-N^1-(4-methylbenzyl)benzene-1,2-diamine (**1o**)

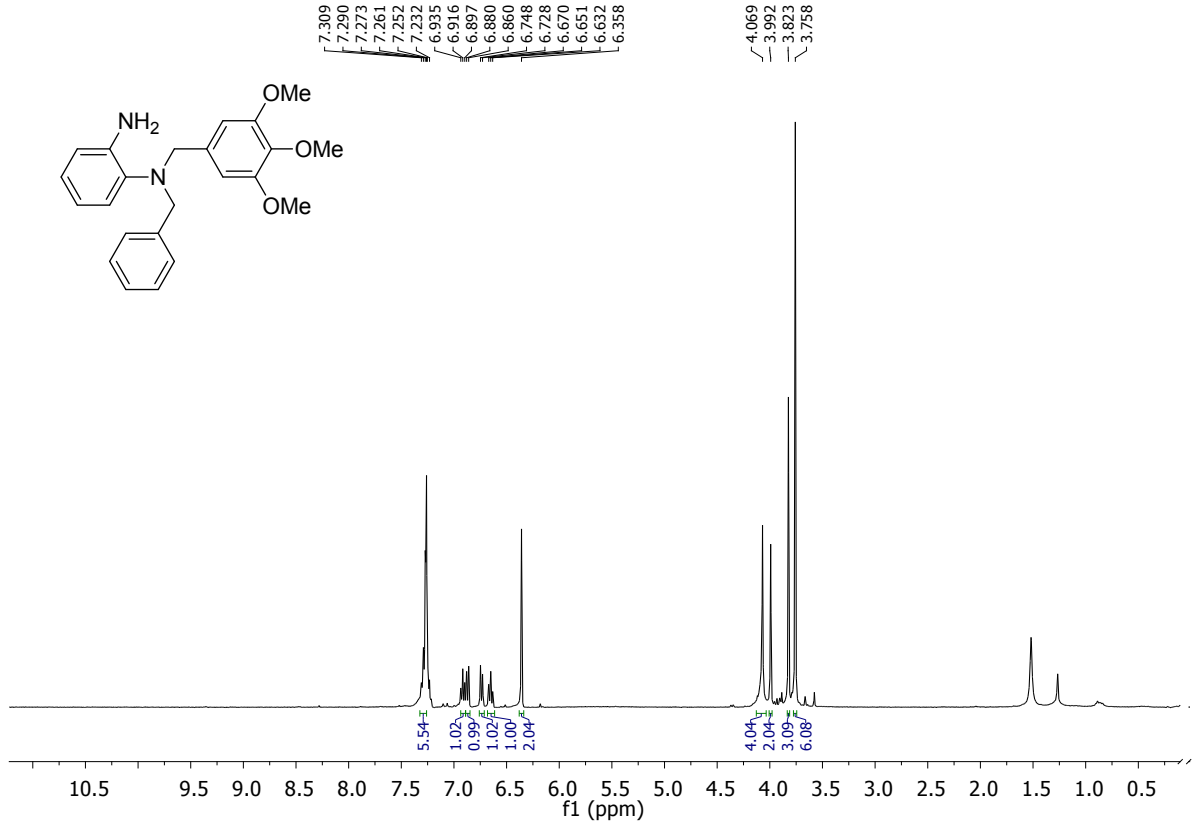


Fig. S33. ^{1}H NMR of N^1-benzyl-N^1-(3,4,5-trimethoxybenzyl)benzene-1,2-diamine (**1p**)

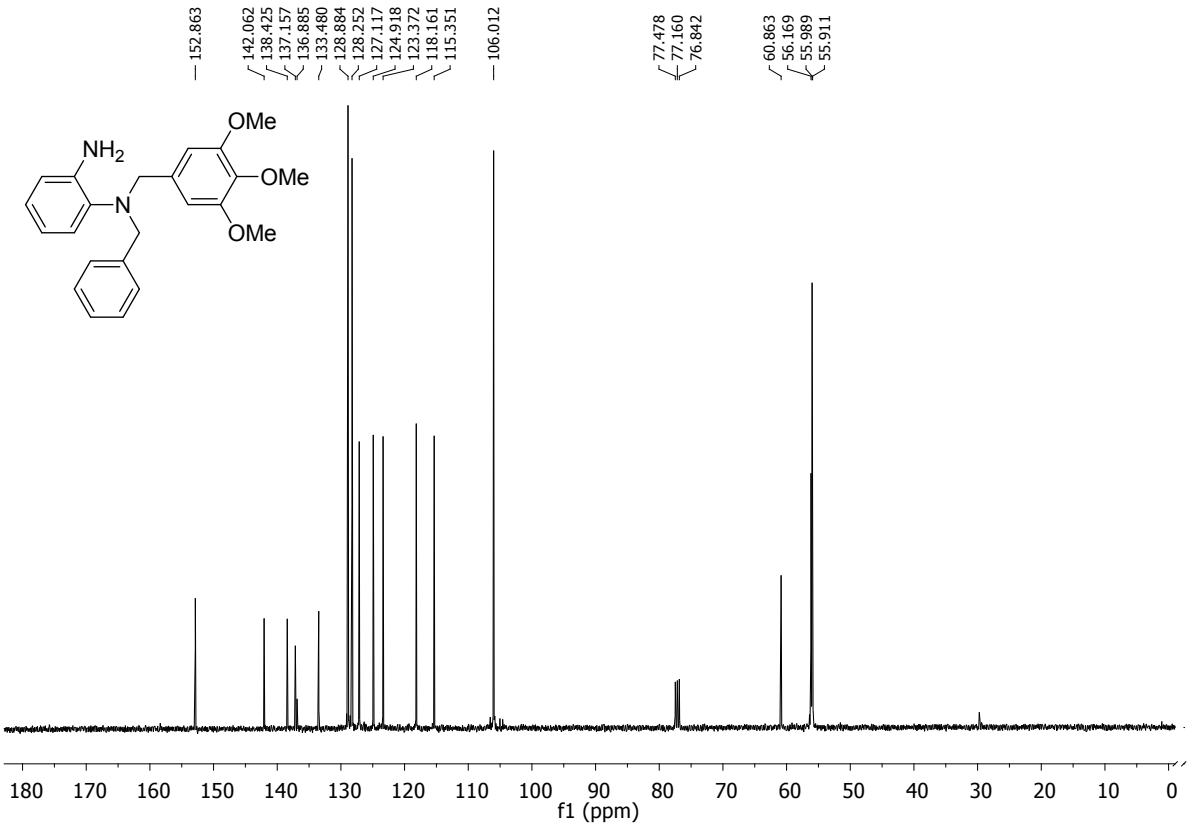


Fig. S34. ^{13}C NMR of N^1-benzyl-N^1-(3,4,5-trimethoxybenzyl)benzene-1,2-diamine (**1p**)

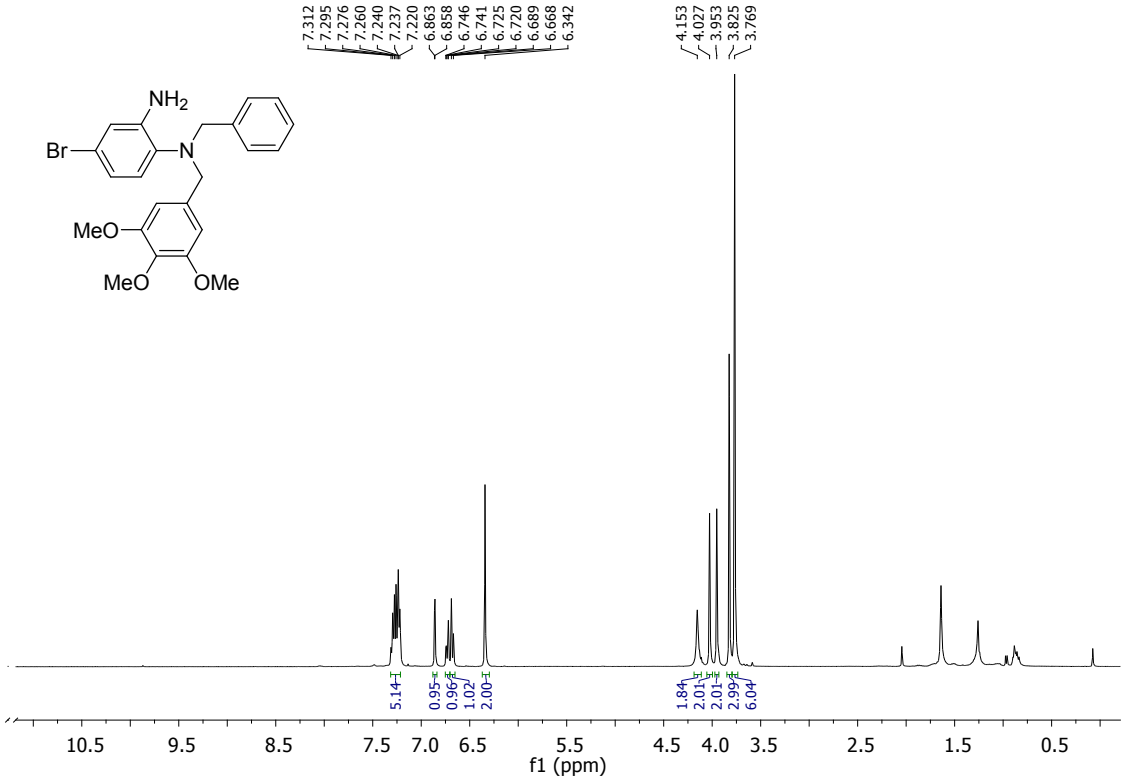


Fig. S35. ^{1}H NMR of N^1-benzyl-4-bromo-N^1-(3,4,5-trimethoxybenzyl)benzene-1,2-diamine (**1q**)

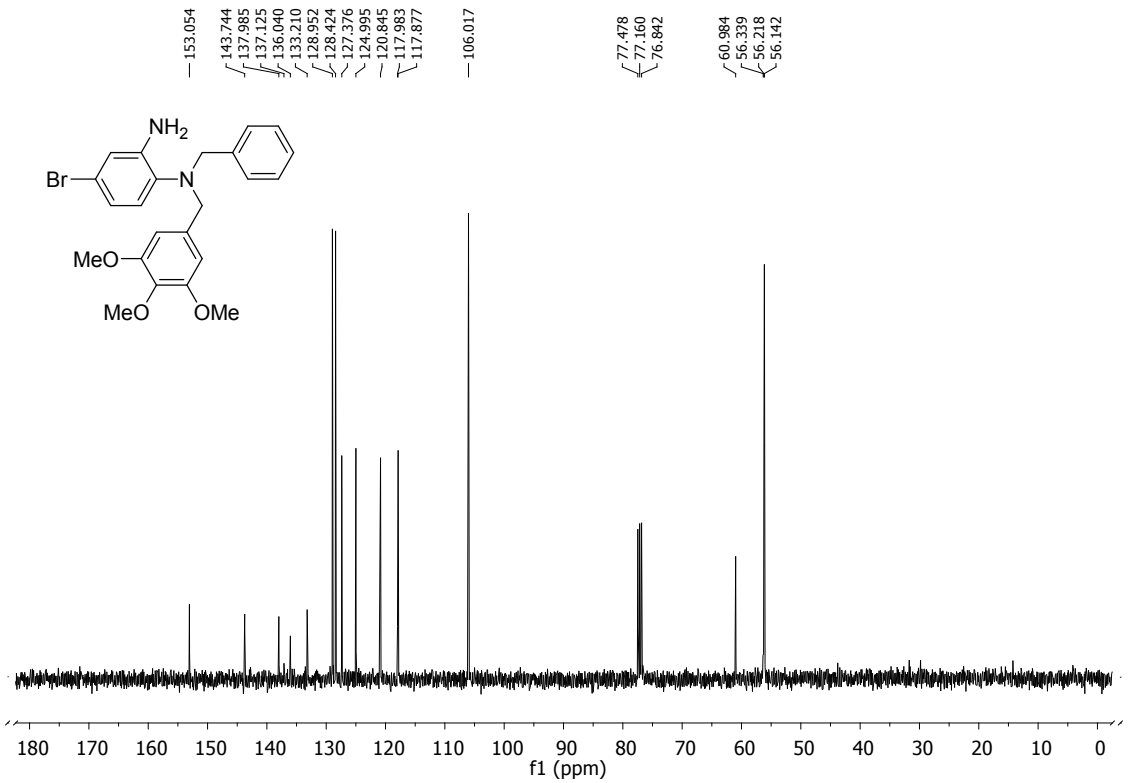


Fig. S36. ^{13}C NMR of N^1-benzyl-4-bromo-N^1-(3,4,5-trimethoxybenzyl)benzene-1,2-diamine (**1q**)

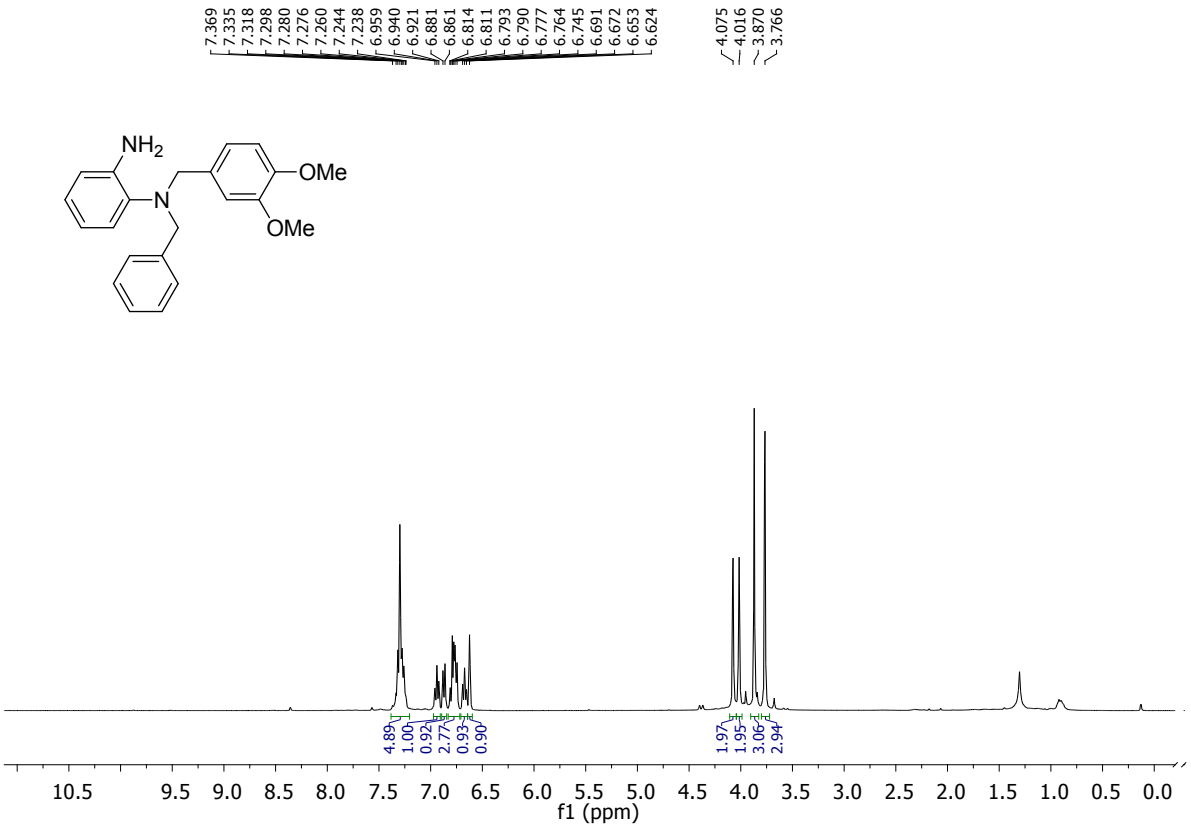


Fig. S37. ^{1}H NMR of N^1-benzyl-N^1-(3,4-dimethoxybenzyl)benzene-1,2-diamine (**1r**)

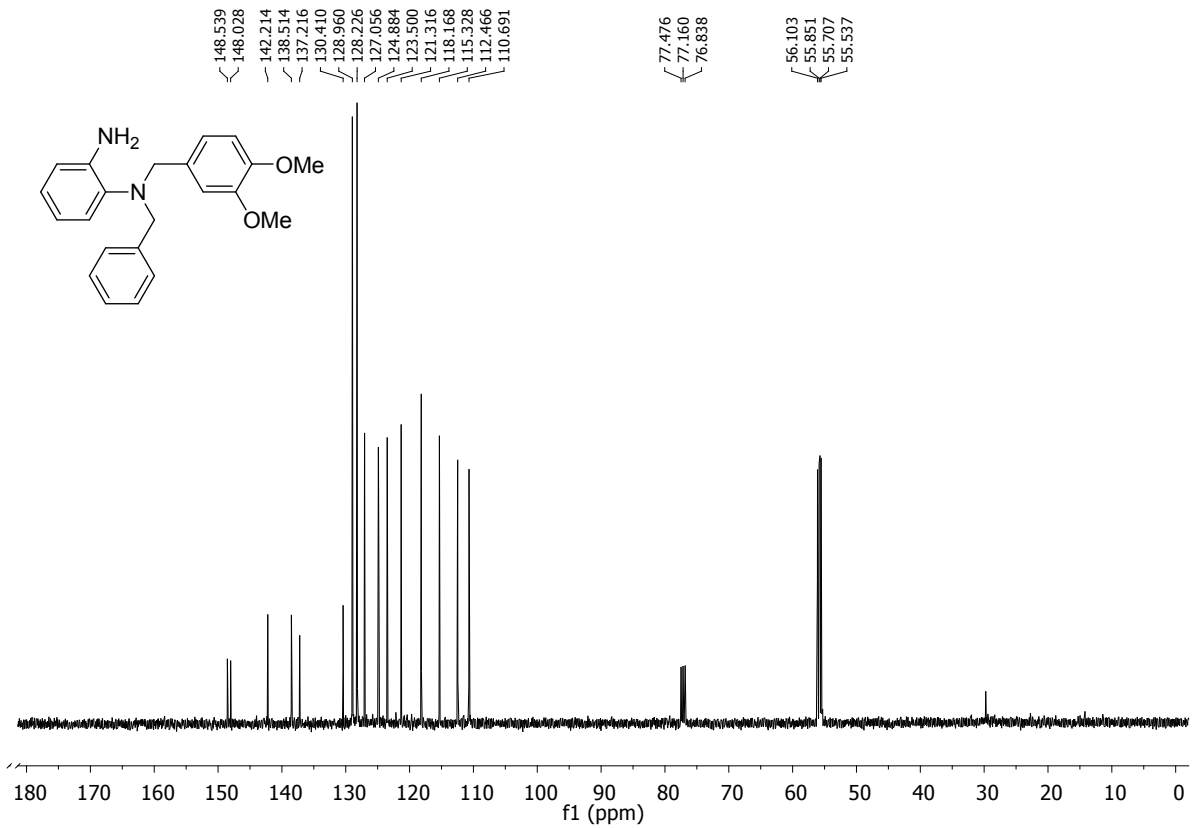


Fig. S38. ^{13}C NMR of *N*^{1}-benzyl-*N*^{1}-(3,4-dimethoxybenzyl)benzene-1,2-diamine (**1r**)

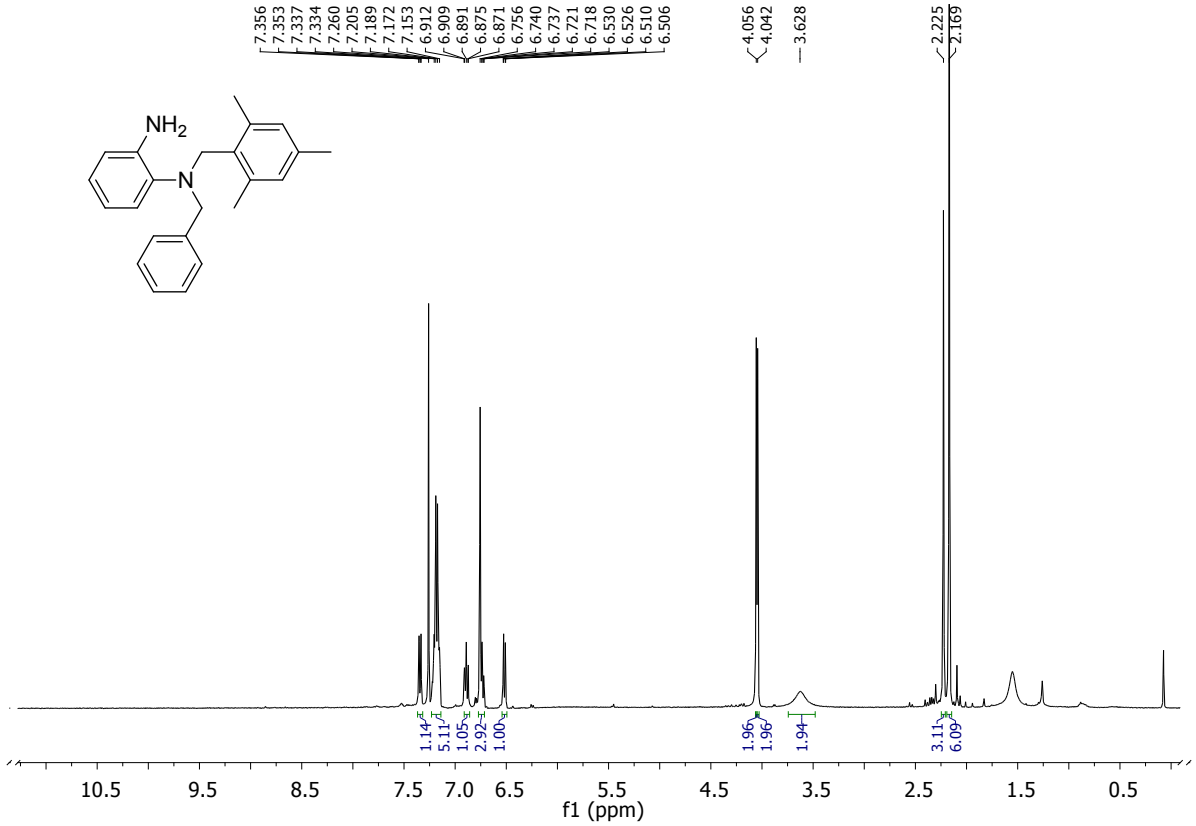


Fig. S39. ^{1}H NMR of *N*^{1}-benzyl-*N*^{1}-(2,4,6-trimethylbenzyl)benzene-1,2-diamine (**1s**)

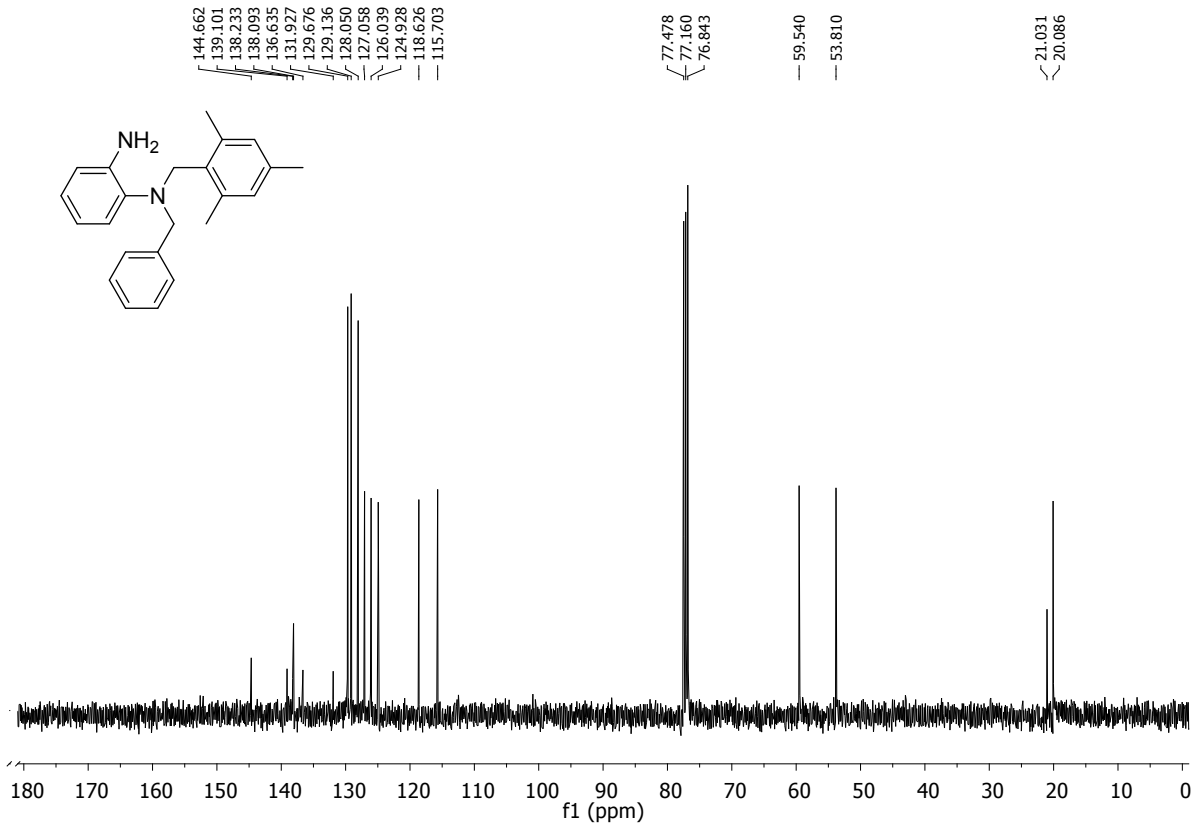


Fig. S40. ^{13}C NMR of N^1-benzyl-N^1-(2,4,6-trimethylbenzyl)benzene-1,2-diamine (**1s**)

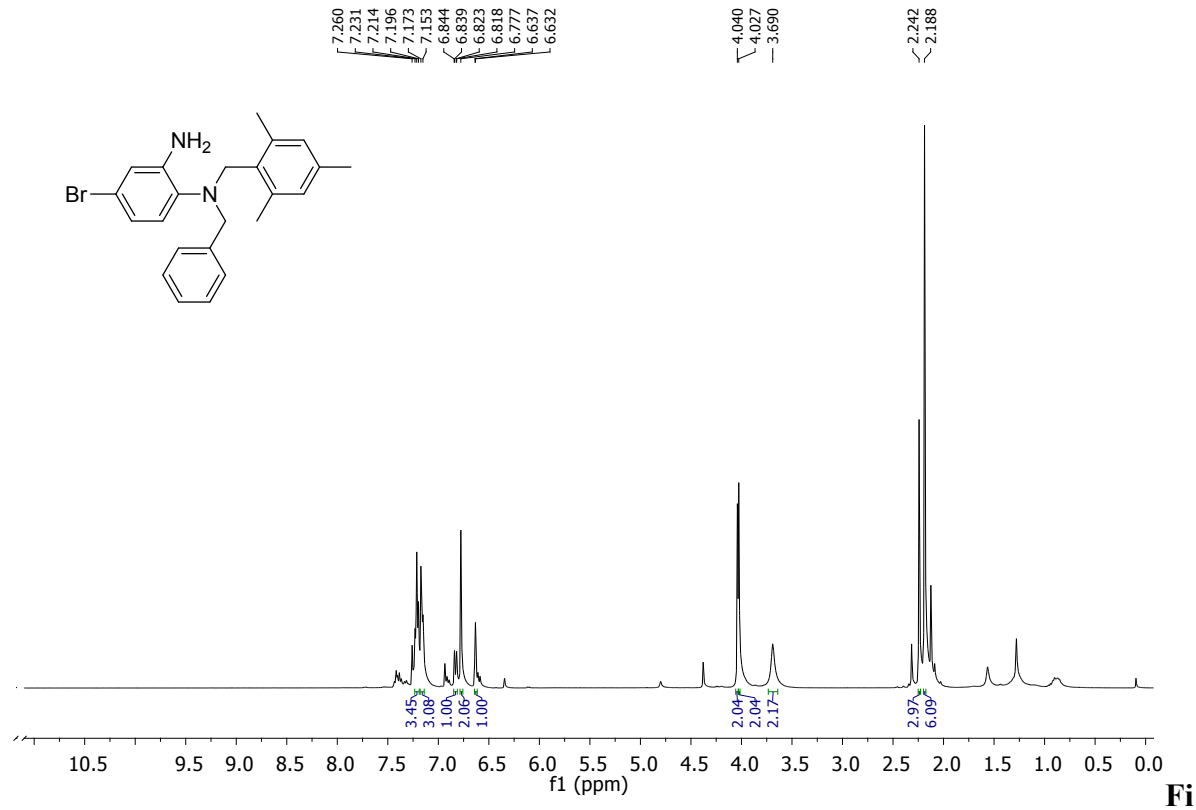


Fig. S41. ^{1}H NMR of N^1-benzyl-4-bromo-N^1-(2,4,6-trimethylbenzyl)benzene-1,2-diamine (**1t**)

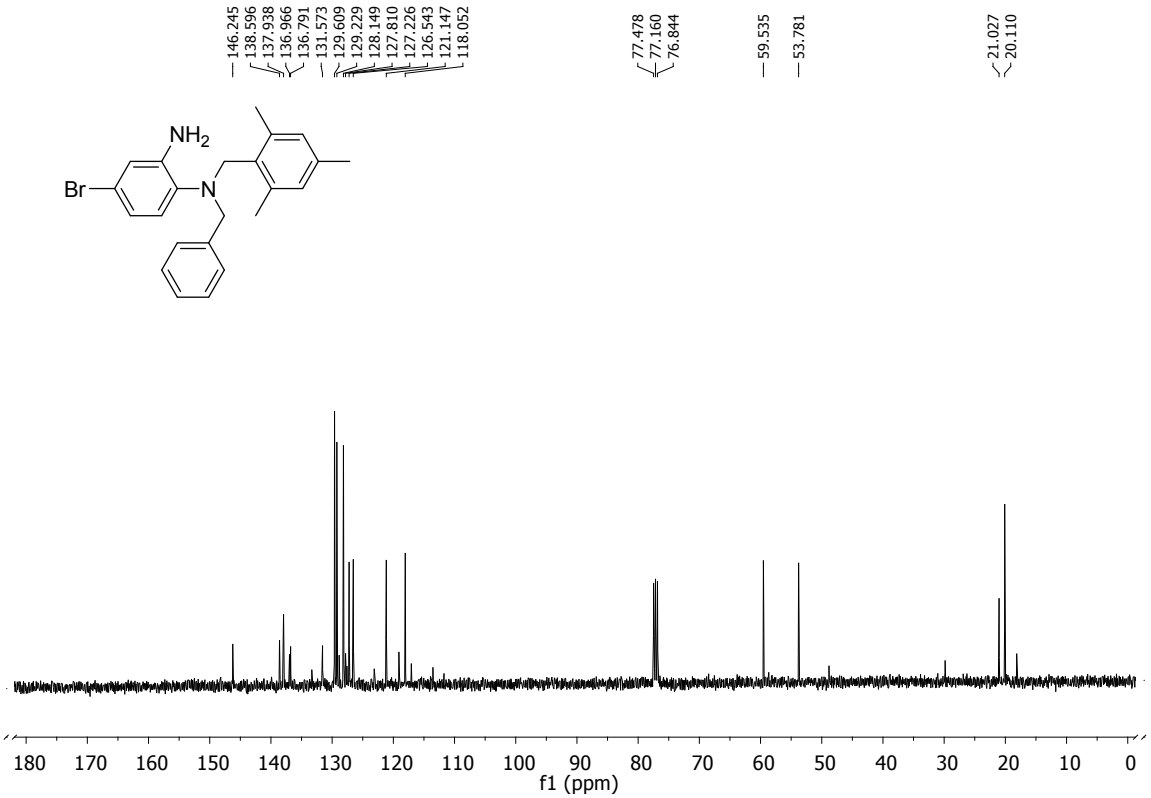


Fig. S42. ^{13}C NMR of N^1-benzyl-4-bromo-N^1-(2,4,6-trimethylbenzyl)benzene-1,2-diamine (**1t**)

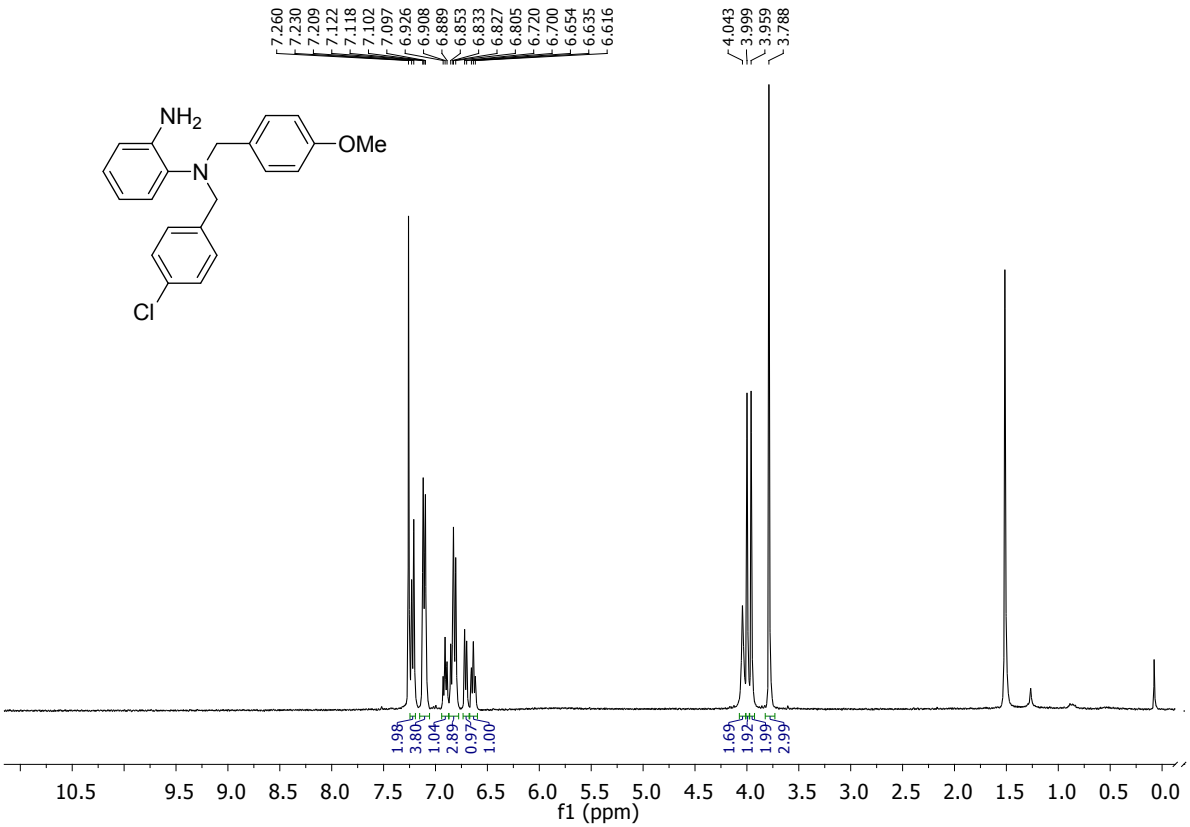


Fig. S43. ^{1}H NMR of N^1-(4-chlorobenzyl)-N^1-(4-methoxybenzyl)benzene-1,2-diamine (**1u**)

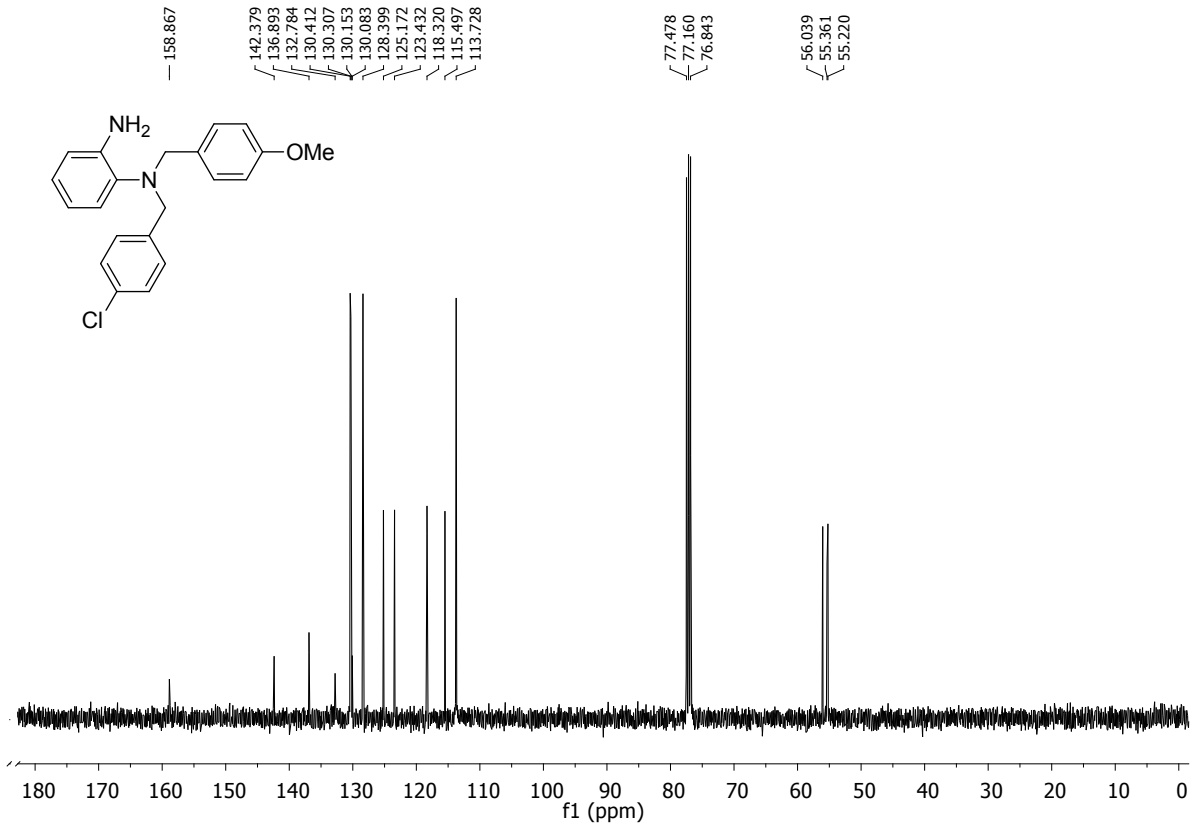


Fig. S44. ^{13}C NMR of N^1-(4-chlorobenzyl)-N^1-(4-methoxybenzyl)benzene-1,2-diamine (**1u**)

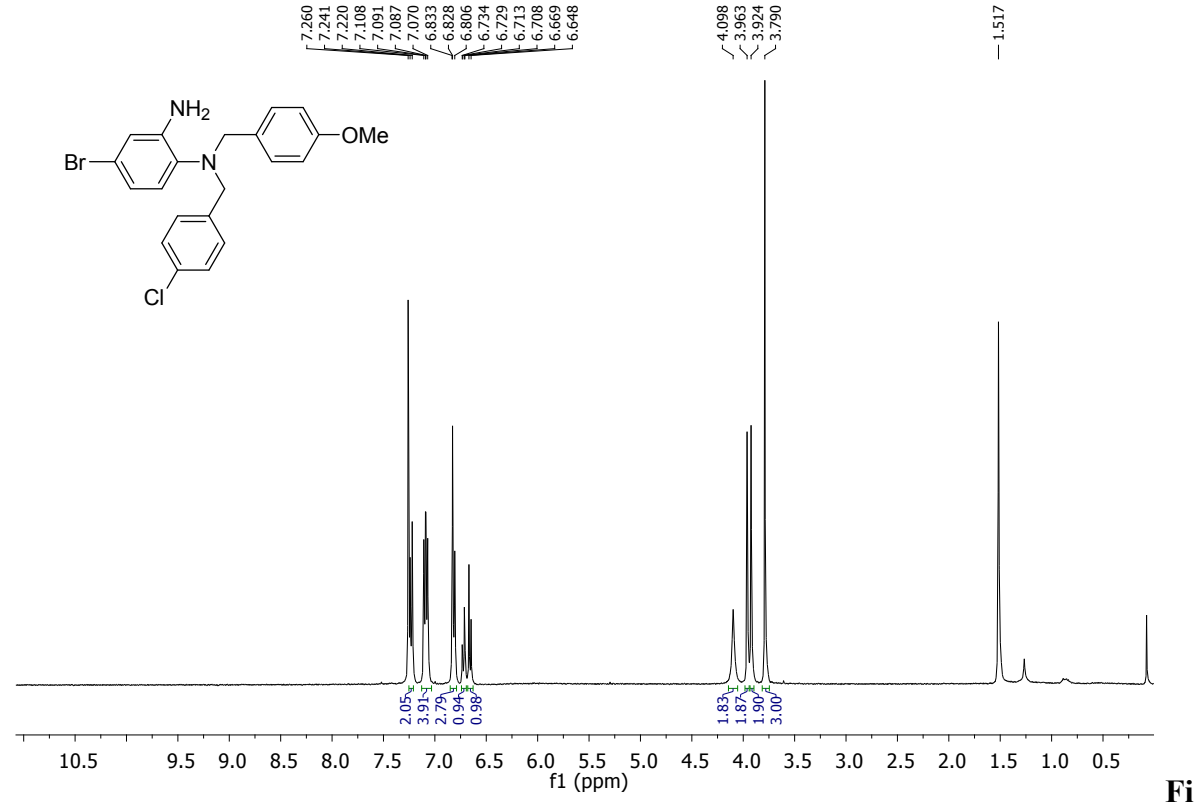


Fig. S45. ^{1}H NMR of 4-Bromo-N^1-(4-chlorobenzyl)-N^1-(4-methoxybenzyl)benzene-1,2-diamine (**1v**)

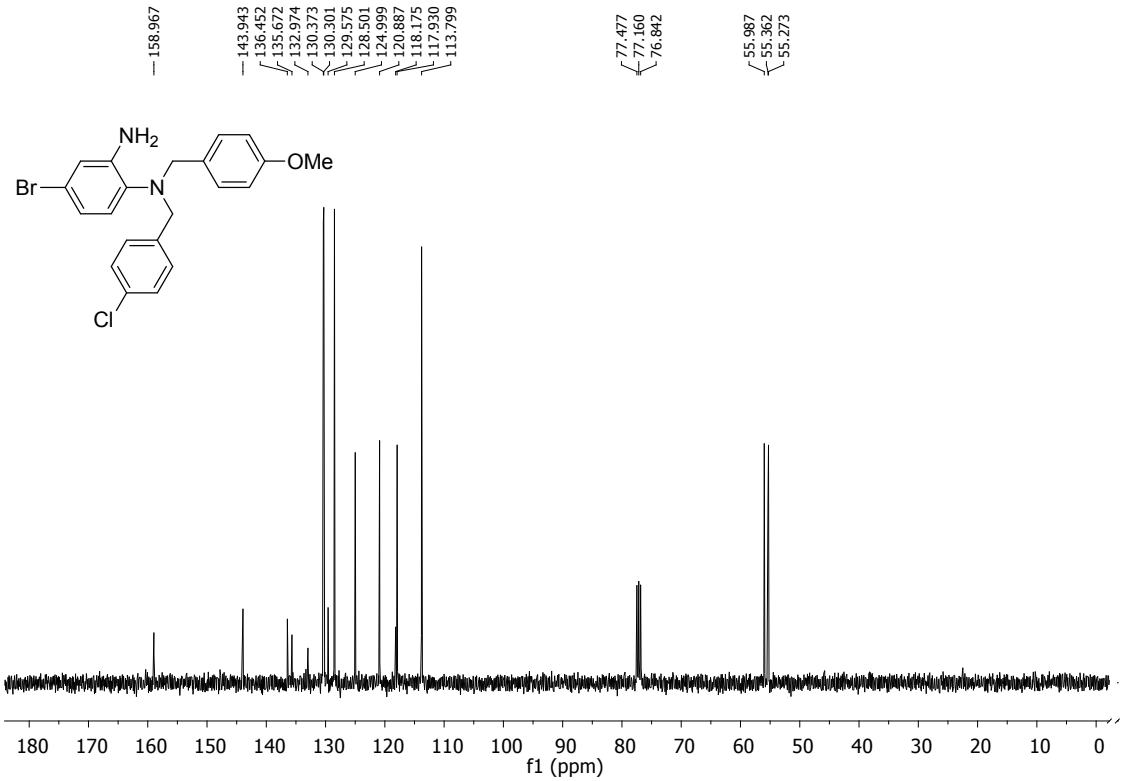


Fig. S46. ^{13}C NMR of 4-Bromo-*N*^{1}-(4-chlorobenzyl)-*N*^{1}-(4-methoxybenzyl)benzene-1,2-diamine (**1v**)

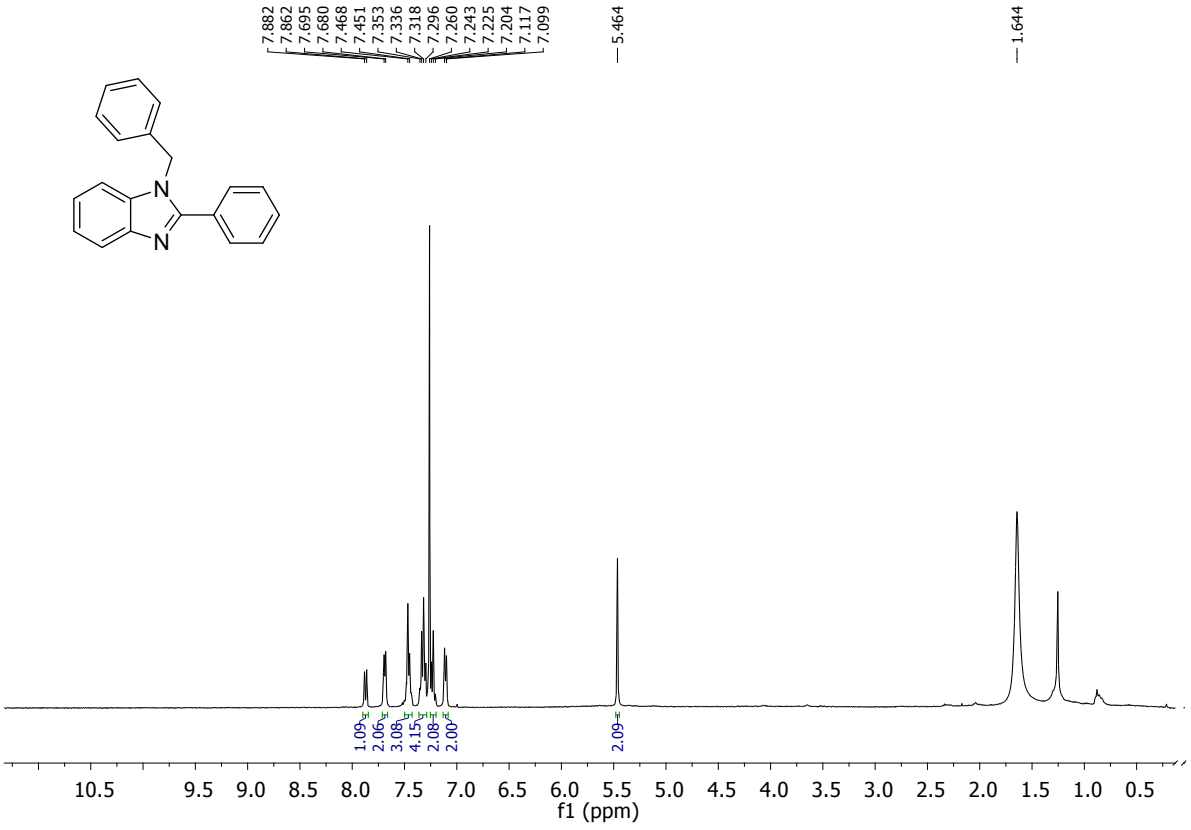


Fig. S47. ^{1}H NMR of 1-Benzyl-2-phenyl-benzo[d]imidazole (**2a**)

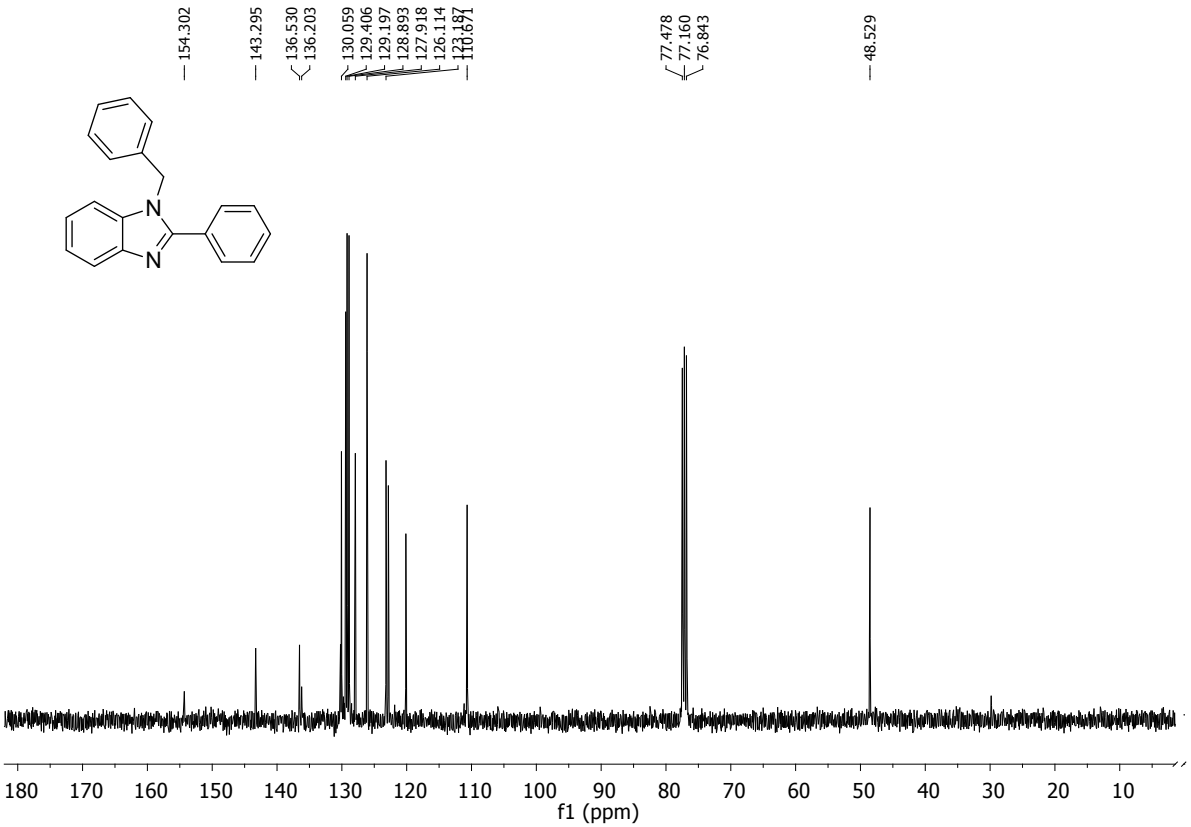


Fig. S48. ^{13}C NMR of 1-Benzyl-2-phenyl-benzo[d]imidazole (**2a**)

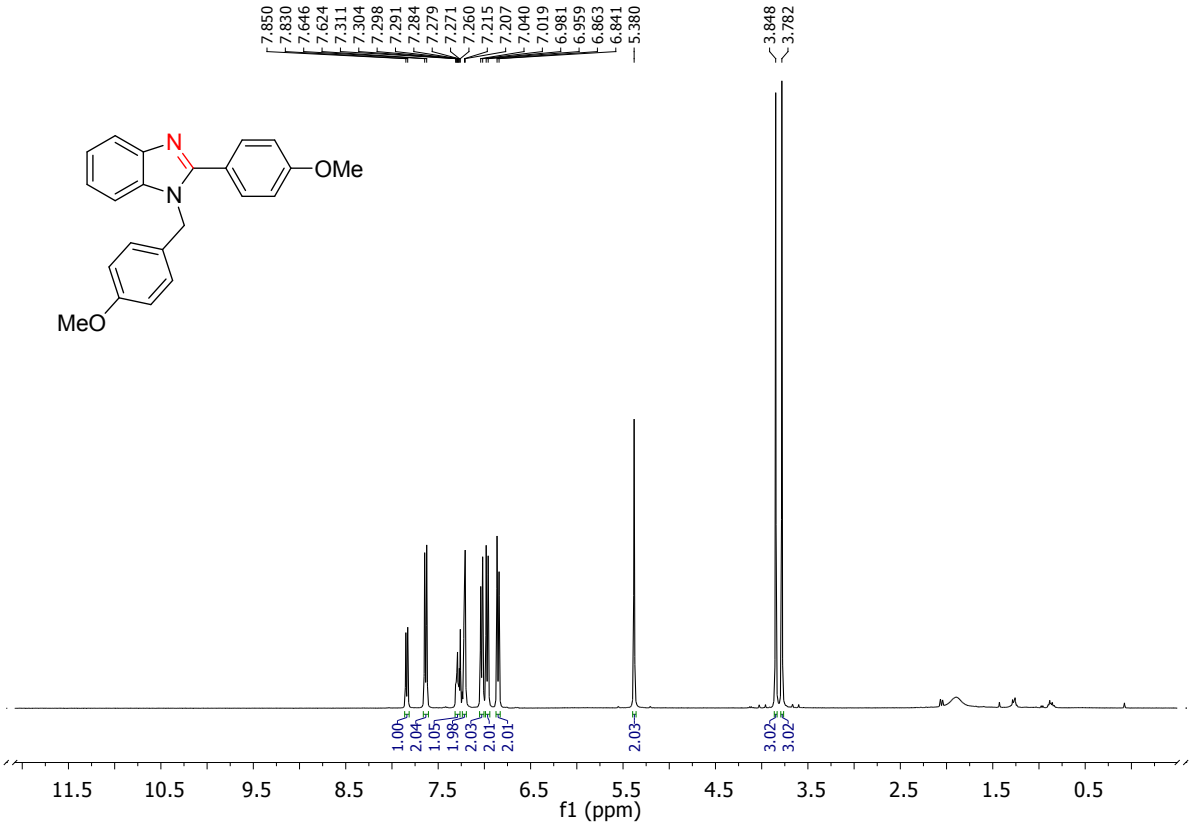


Fig. S49. ^{1}H NMR of 1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (**2b**)

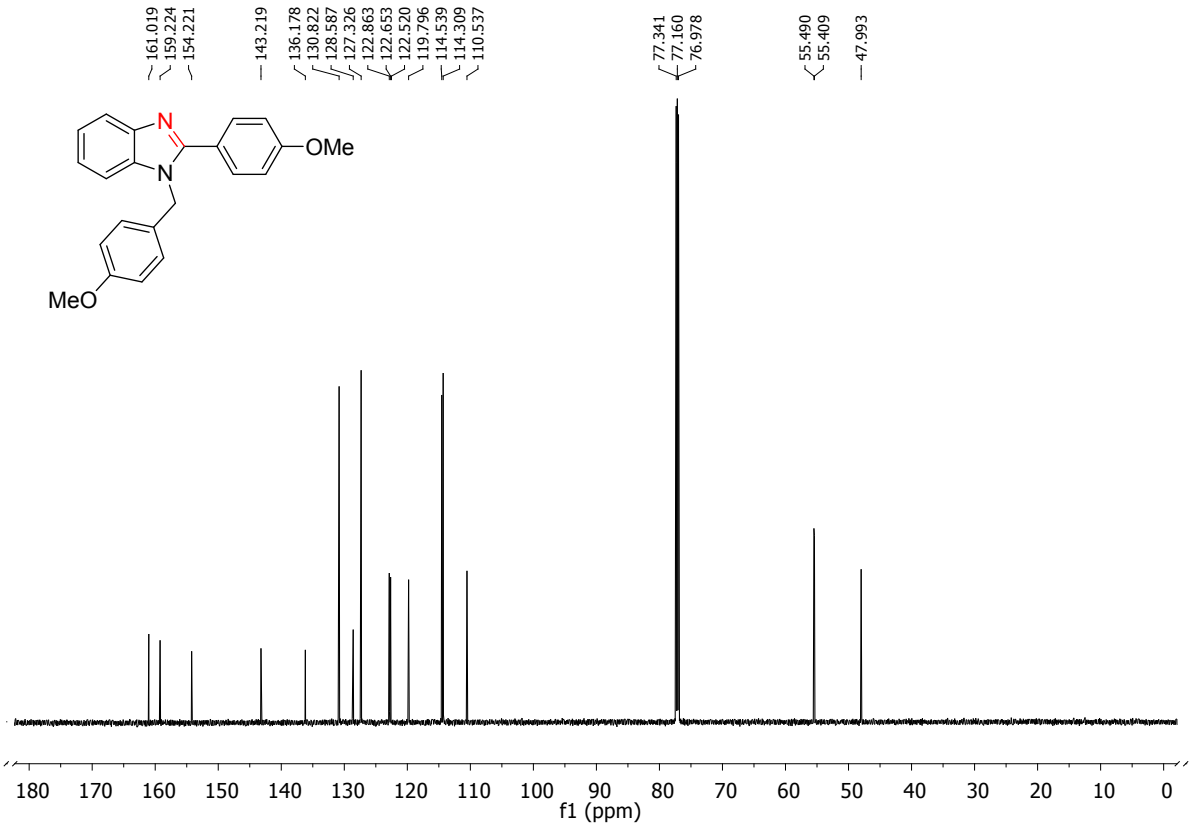


Fig. S50. ^{13}C NMR of 1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (**2b**)

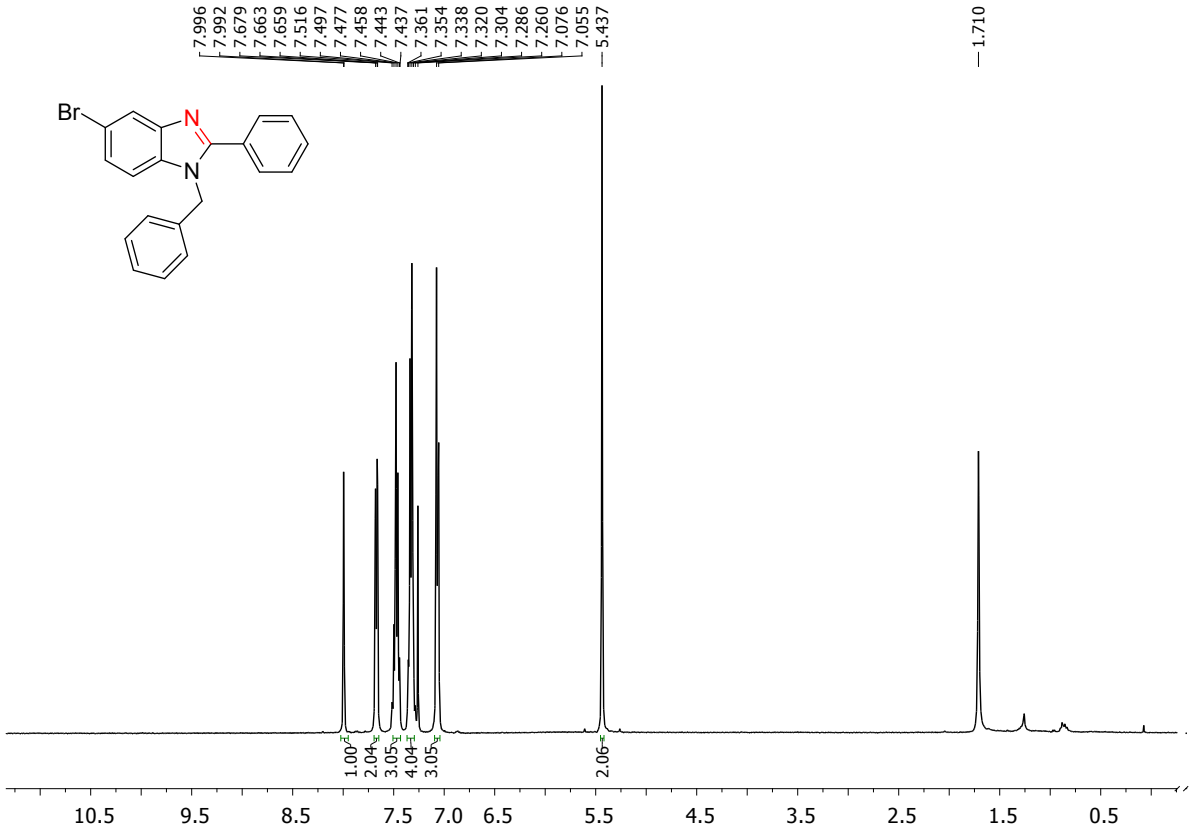


Fig. S51. ^{1}H NMR of 1-Benzyl-5-bromo-2-phenyl-benzo[d]imidazole (**2c**)

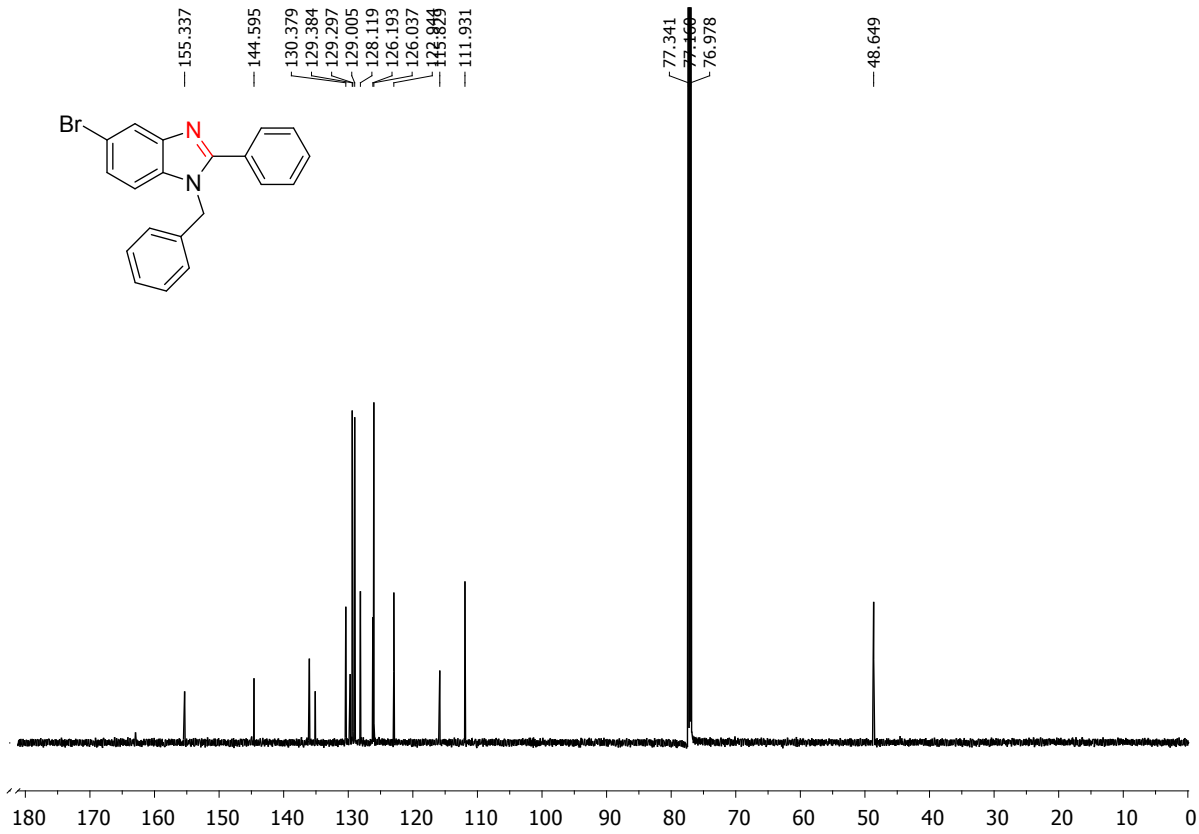


Fig. S52. ^{13}C NMR of 1-Benzyl-5-bromo-2-phenyl-benzo[d]imidazole (**2c**)

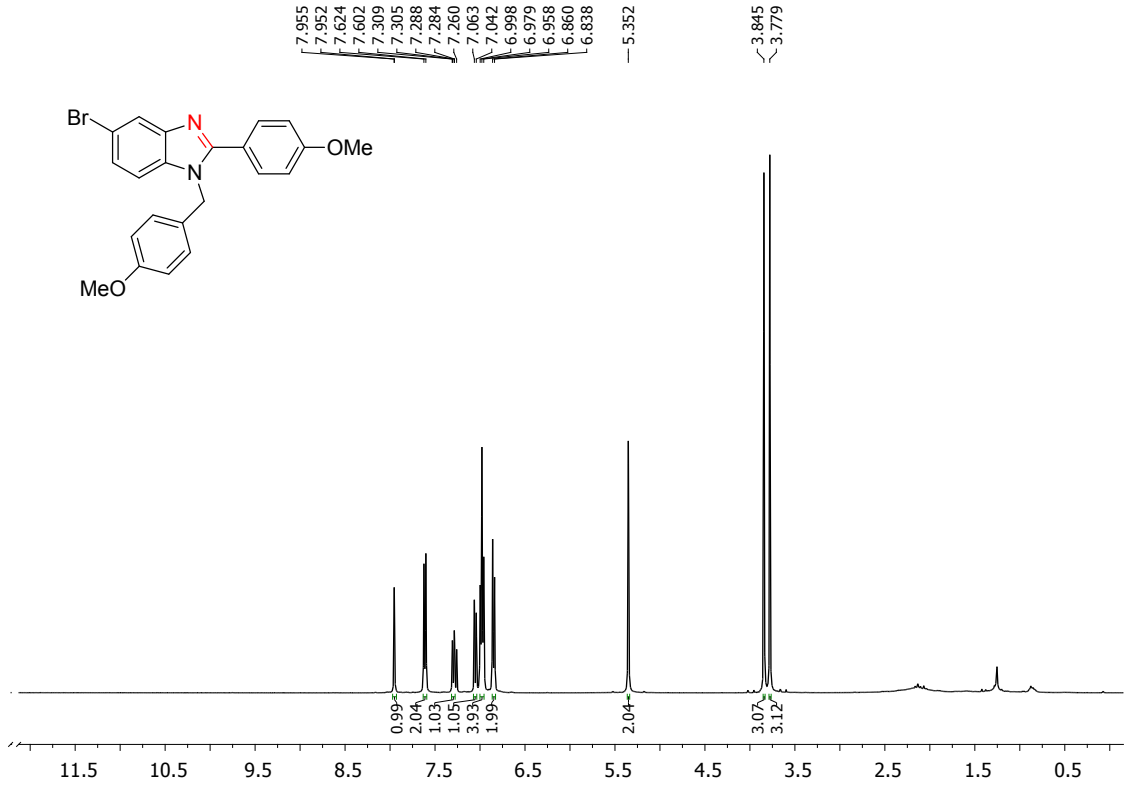


Fig. S53. ^{1}H NMR of 5-Bromo-1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (**2d**)

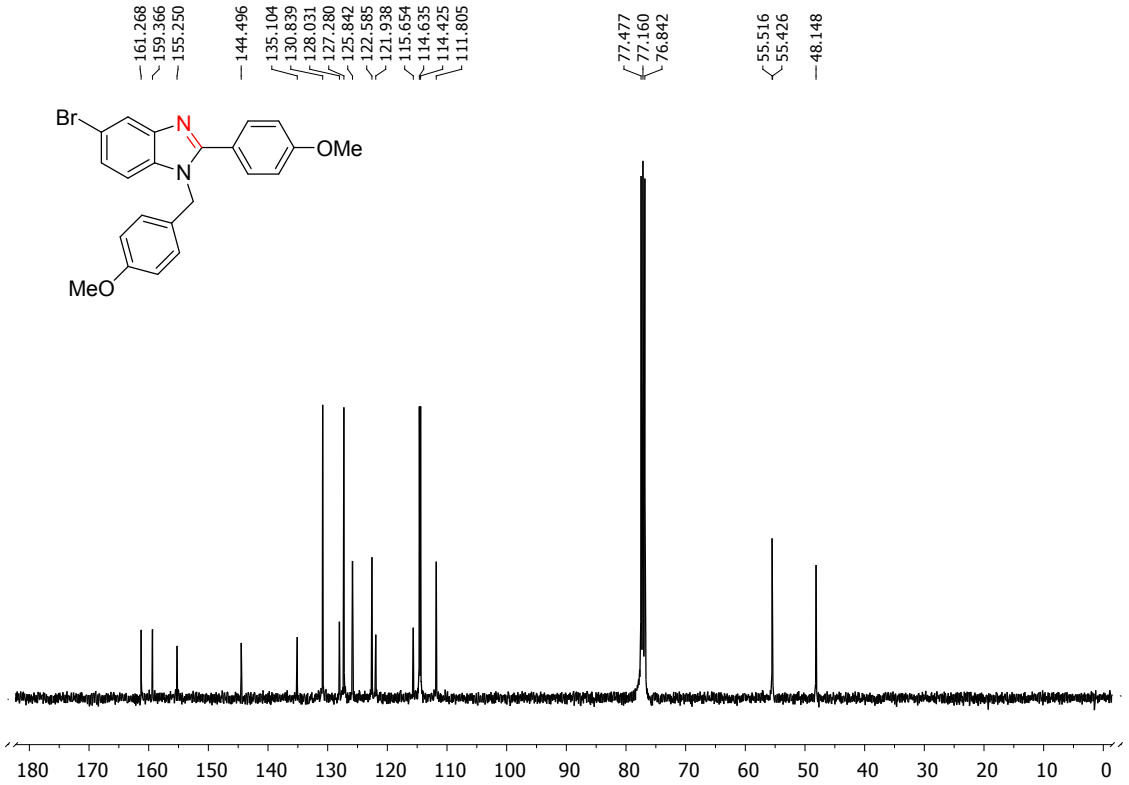


Fig. S54. ^{13}C NMR of 5-Bromo-1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (**2d**)

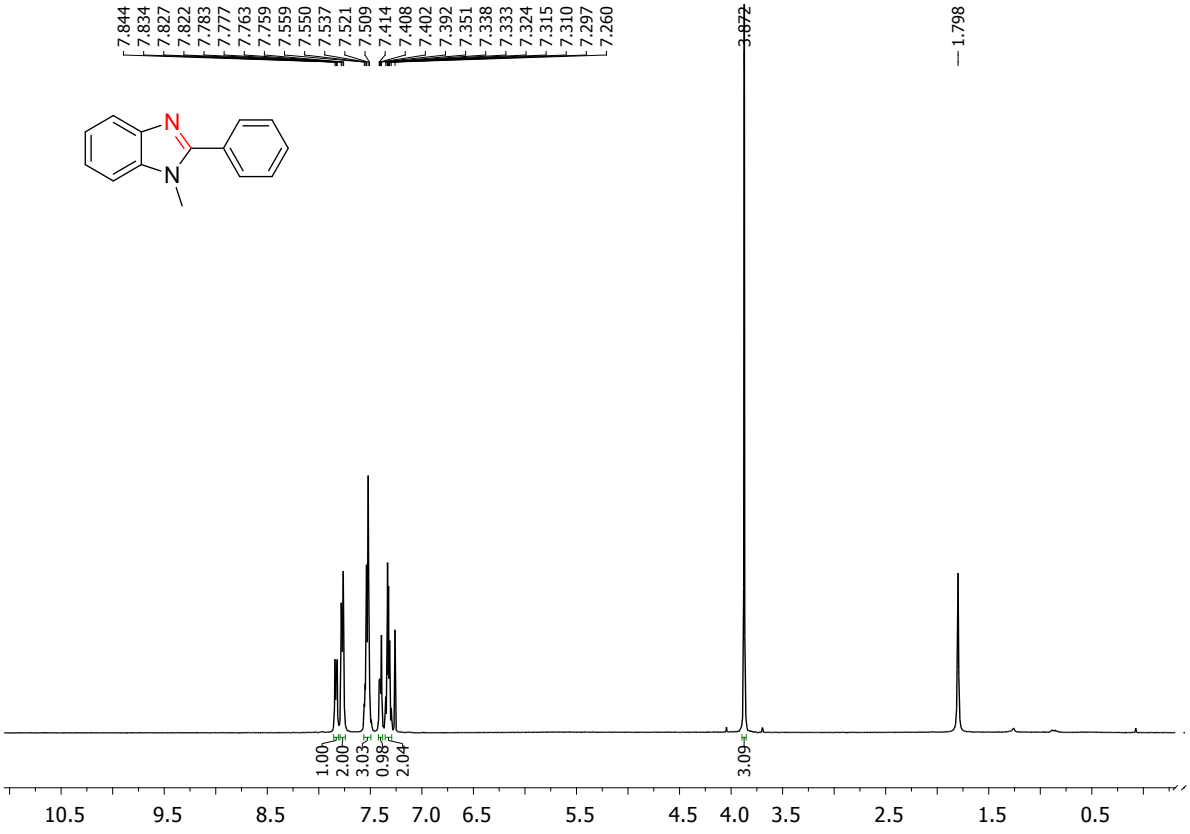


Fig. S55. ^{1}H NMR of 1-Methyl-2-phenyl-benzo[d]imidazole (**2e**)

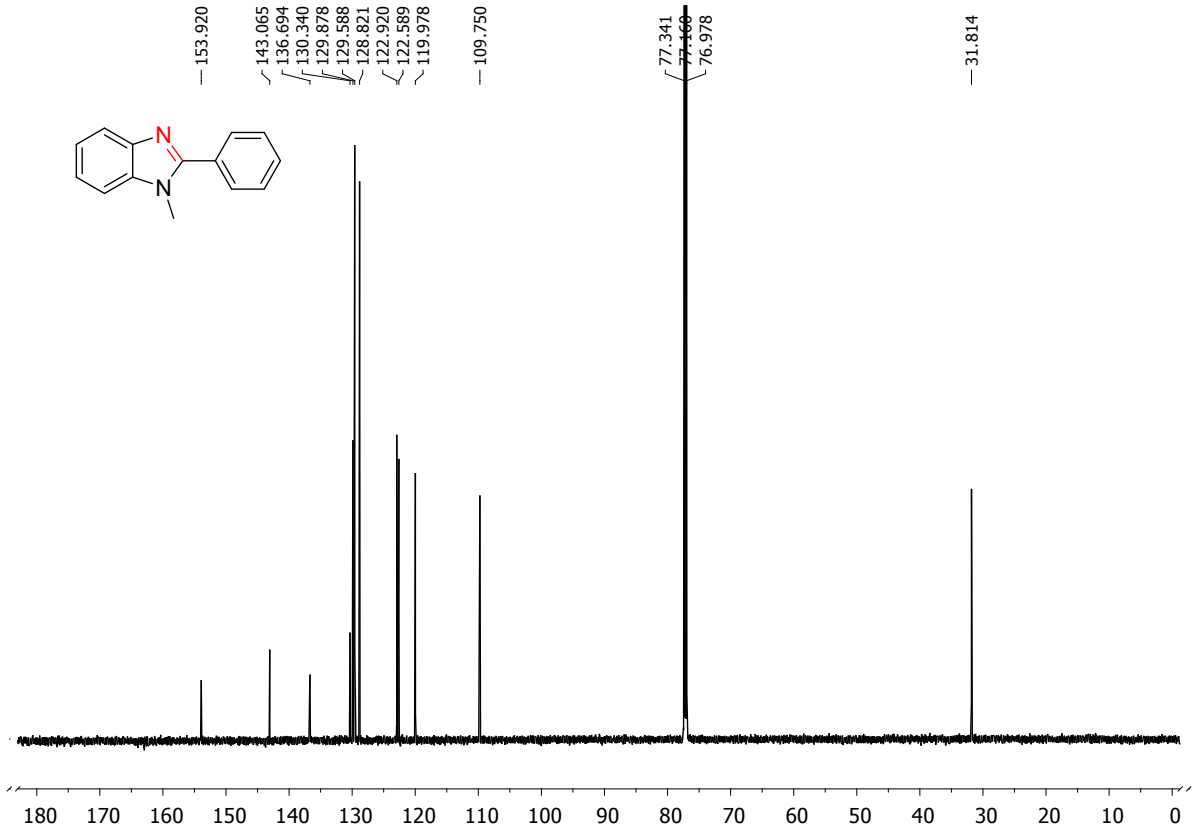


Fig. S56. ^{13}C NMR of 1-Methyl-2-phenyl-benzo[d]imidazole (**2e**)

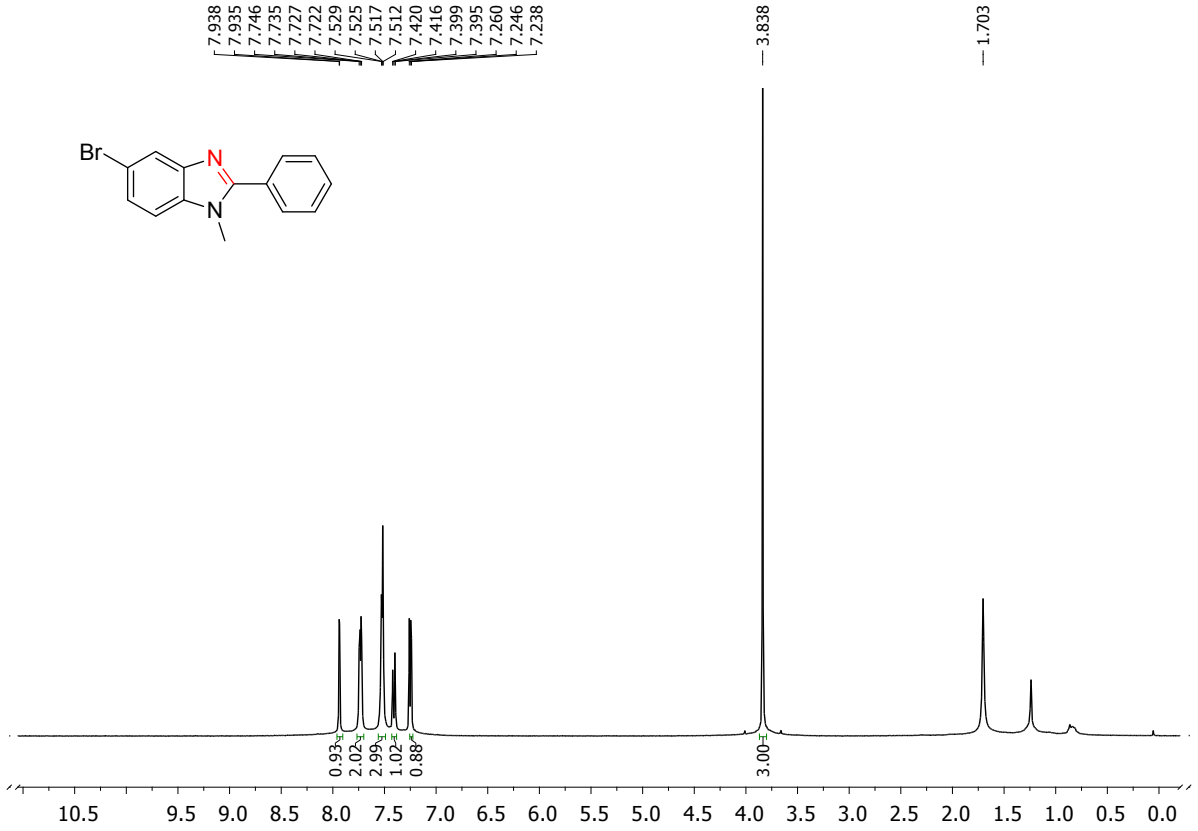


Fig. S57. ^{1}H NMR of 5-Bromo-1-methyl-2-phenyl-benzo[d]imidazole (**2f**)

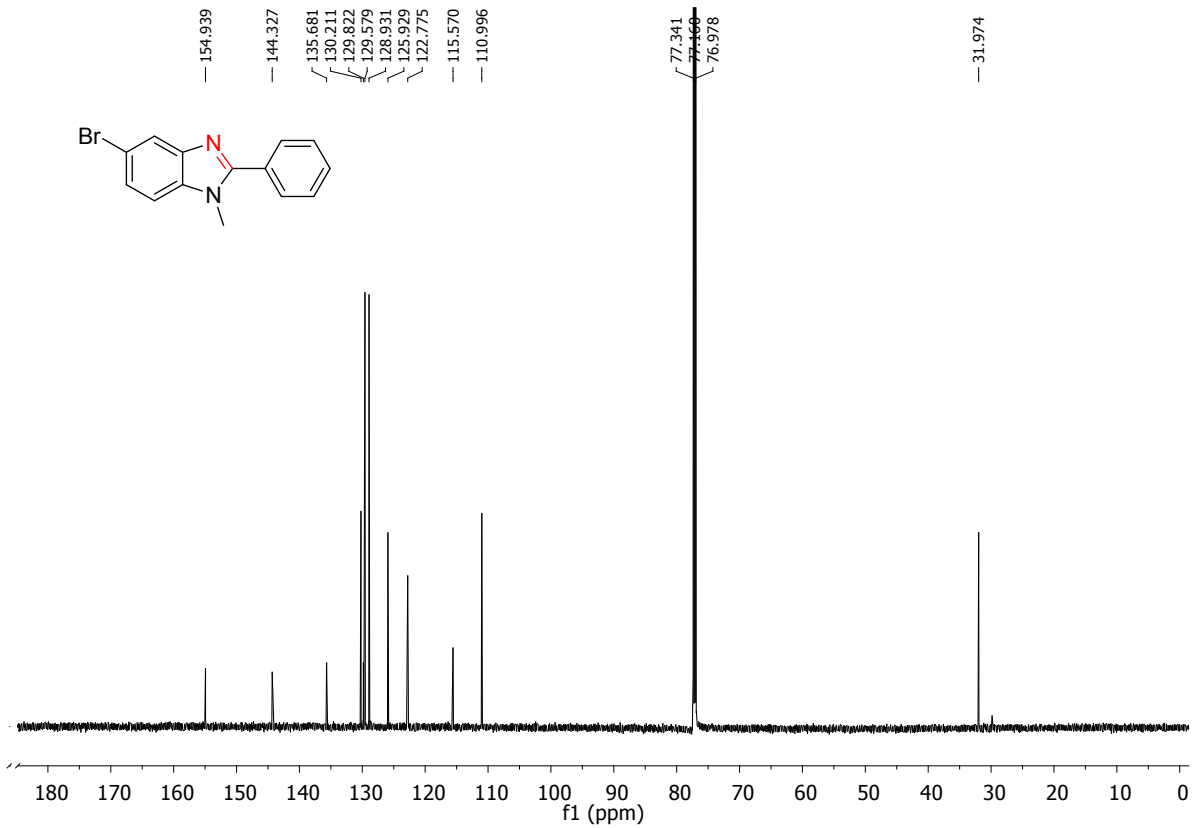


Fig. S58. ^{13}C NMR of 5-Bromo-1-methyl-2-phenyl-benzo[d]imidazole (**2f**)

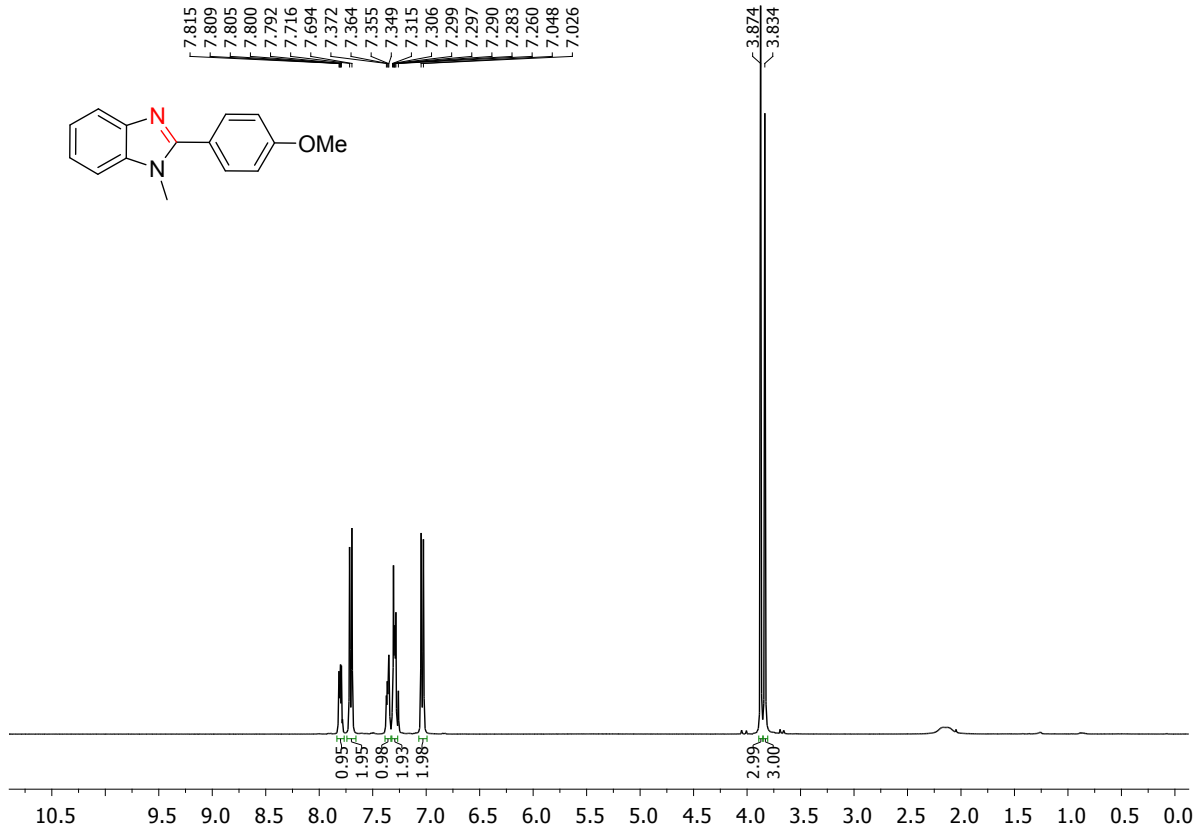


Fig. S59. ^{1}H NMR of 2-(4-Methoxyphenyl)-1-methyl-benzo[d]imidazole (**2g**)

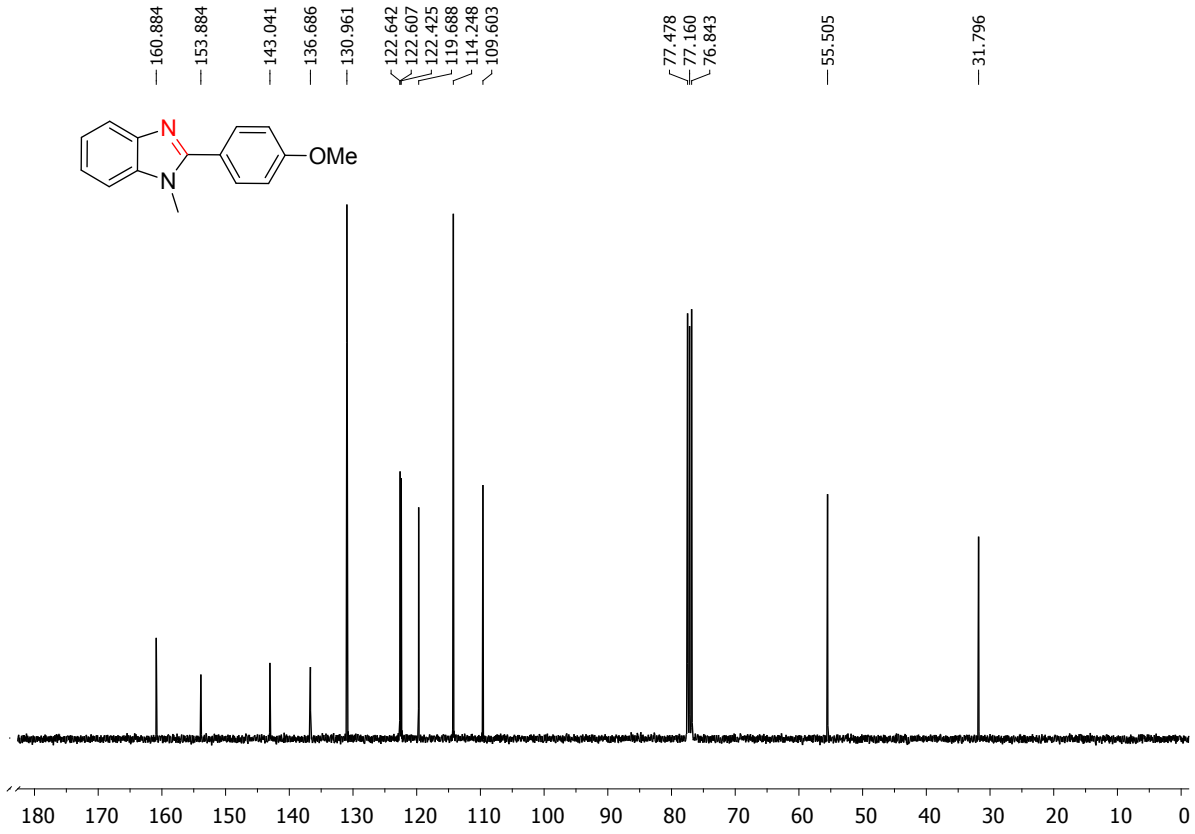


Fig. S60. ^{13}C NMR of 2-(4-Methoxyphenyl)-1-methyl-benzo[d]imidazole (**2g**)

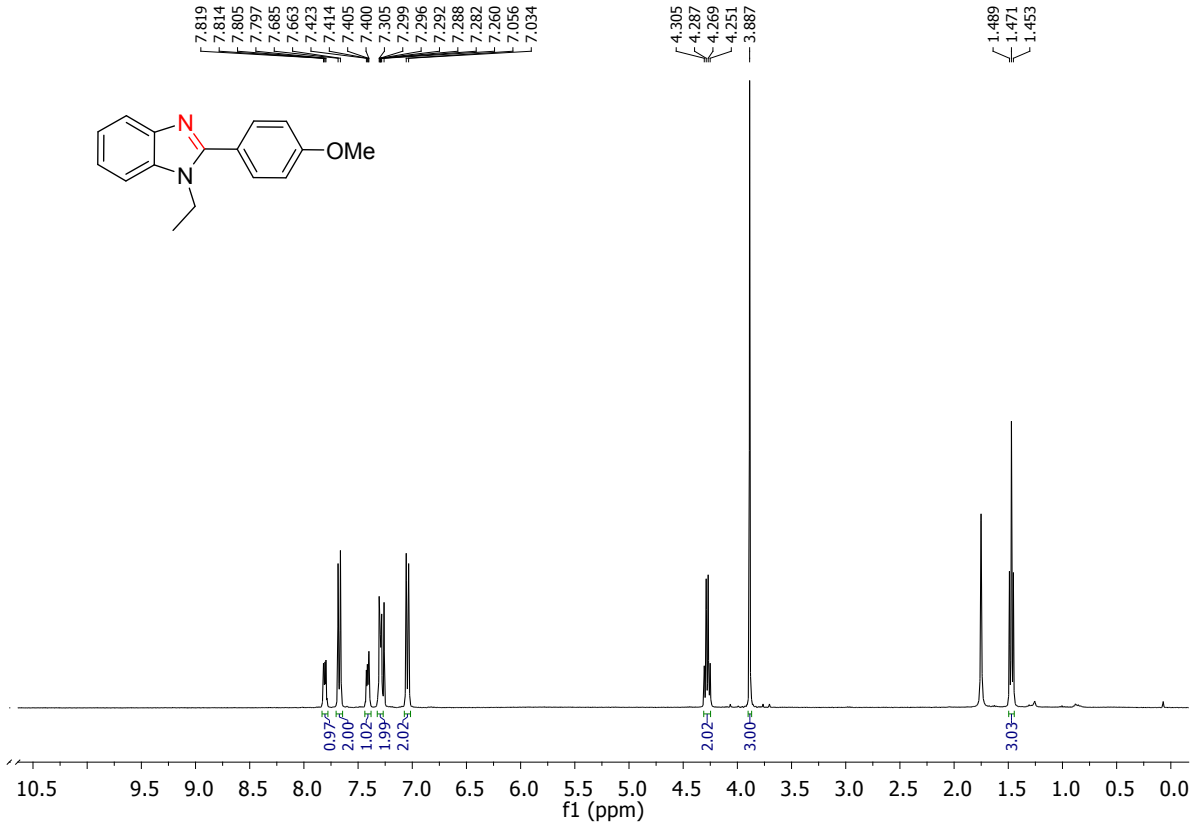


Fig. S61. ^{1}H NMR of 1-Ethyl-2-(4-methoxyphenyl)-benzo[d]imidazole (**2h**)

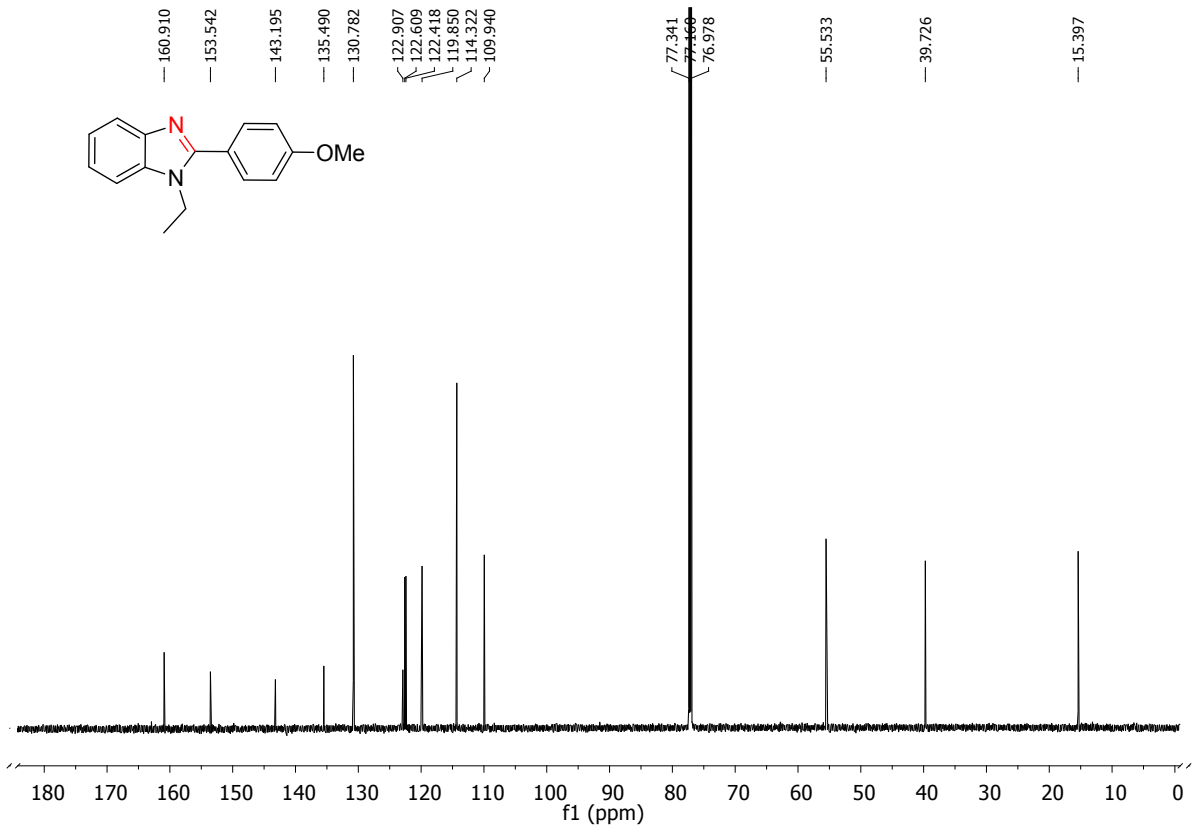


Fig. S62. ^{13}C NMR of 1-Ethyl-2-(4-methoxyphenyl)-benzo[d]imidazole (**2h**)

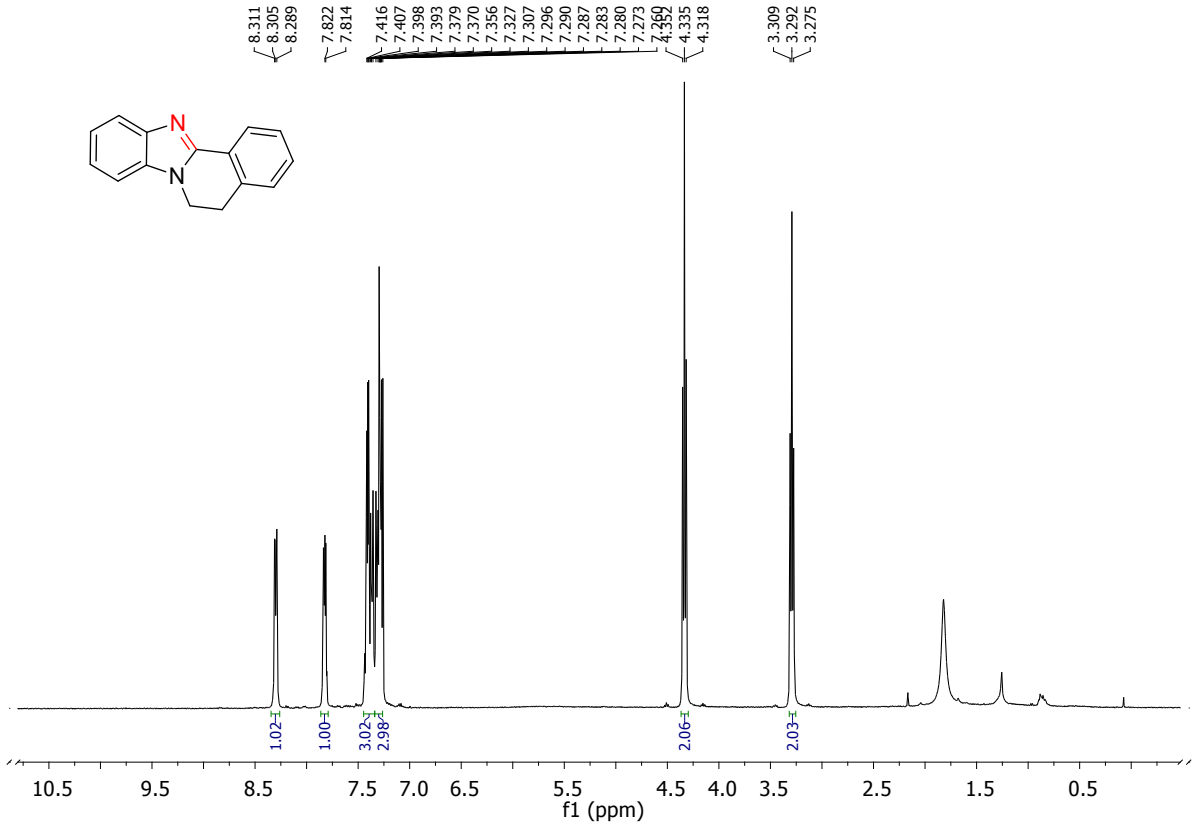


Fig. S63. ^{1}H NMR of 5,6-Dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (**2i**)

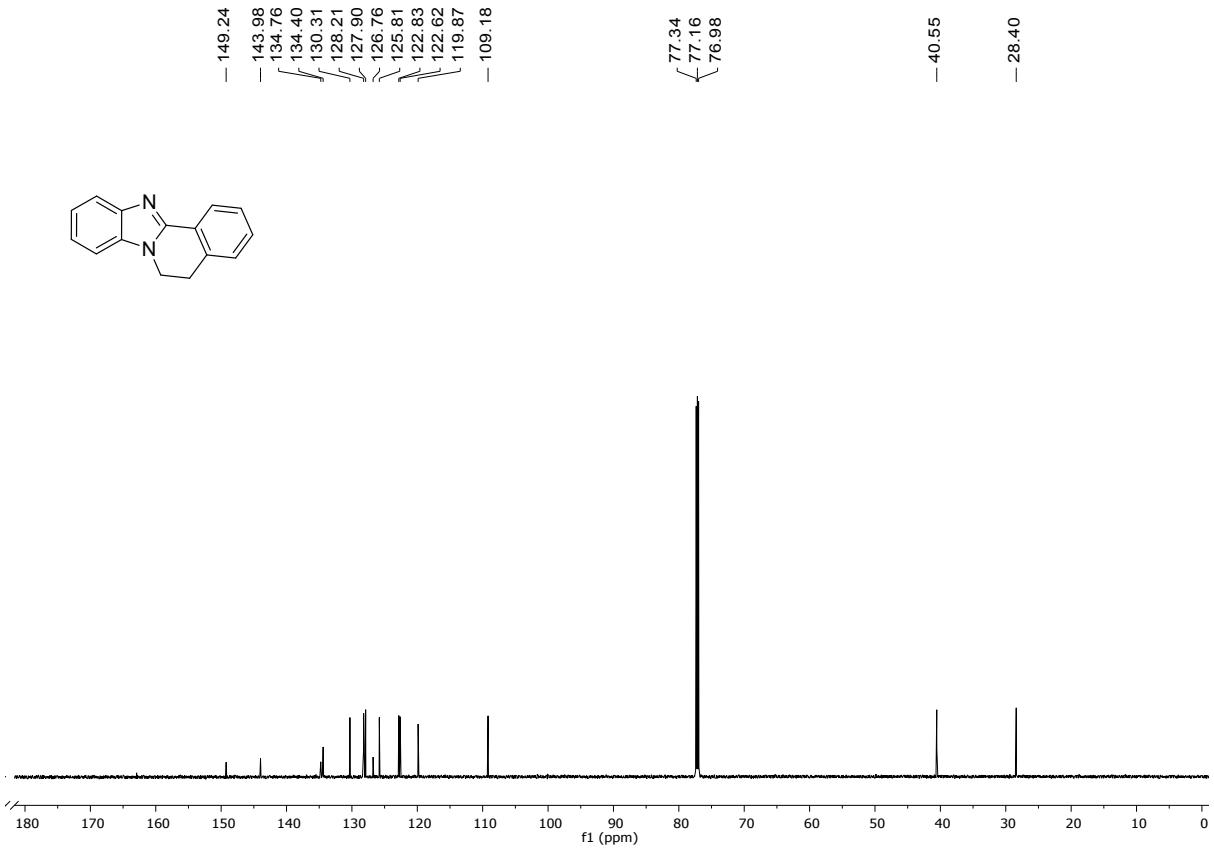


Fig. S64. ^{13}C NMR of 5,6-Dihydrobenzo[4,5]imidazo[2,1-a]isoquinoline (**2i**)

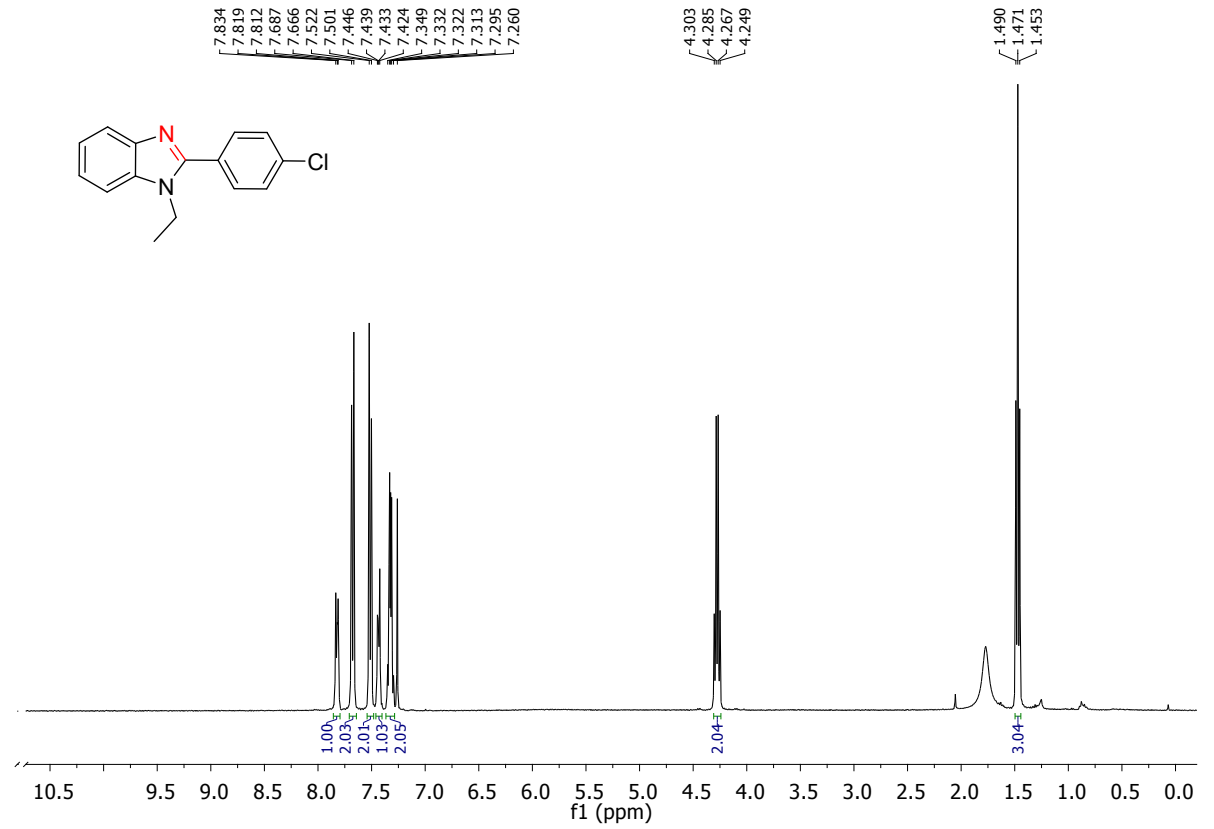


Fig. S65. ^{1}H NMR of 2-(4-Chlorophenyl)-1-ethyl-benzo[d]imidazole (**2j**)

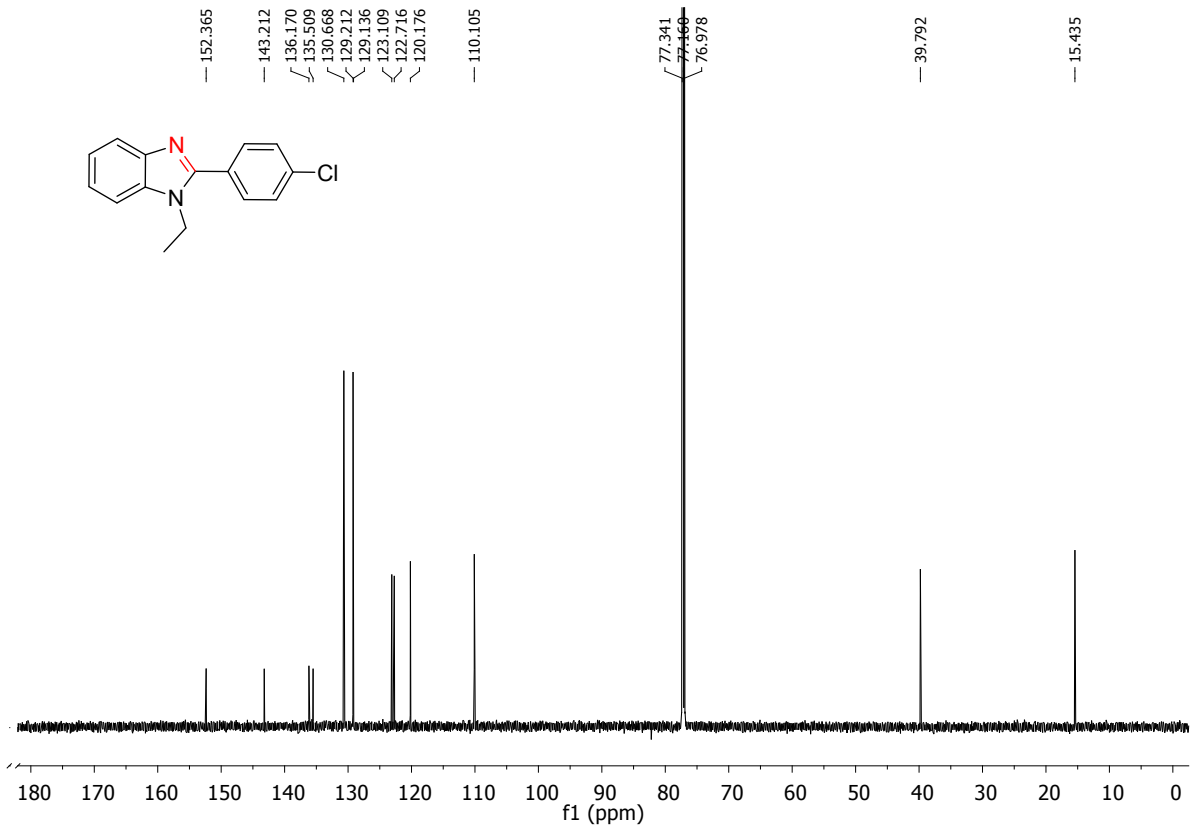


Fig. S66. ^{13}C NMR of 2-(4-Chlorophenyl)-1-ethyl-benzo[d]imidazole (**2j**)

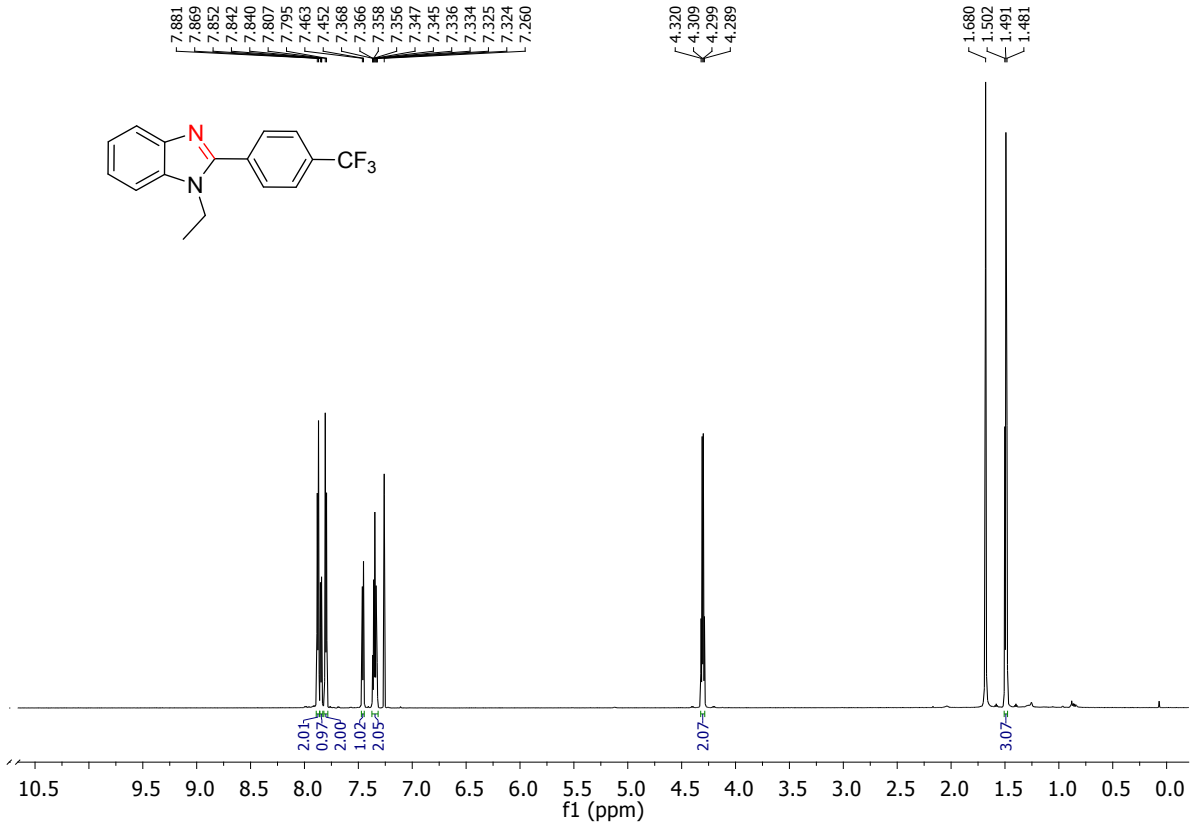


Fig. S67. ^{1}H NMR of 1-Ethyl-2-(4-(trifluoromethyl)phenyl)-benzo[d]imidazole (**2k**)

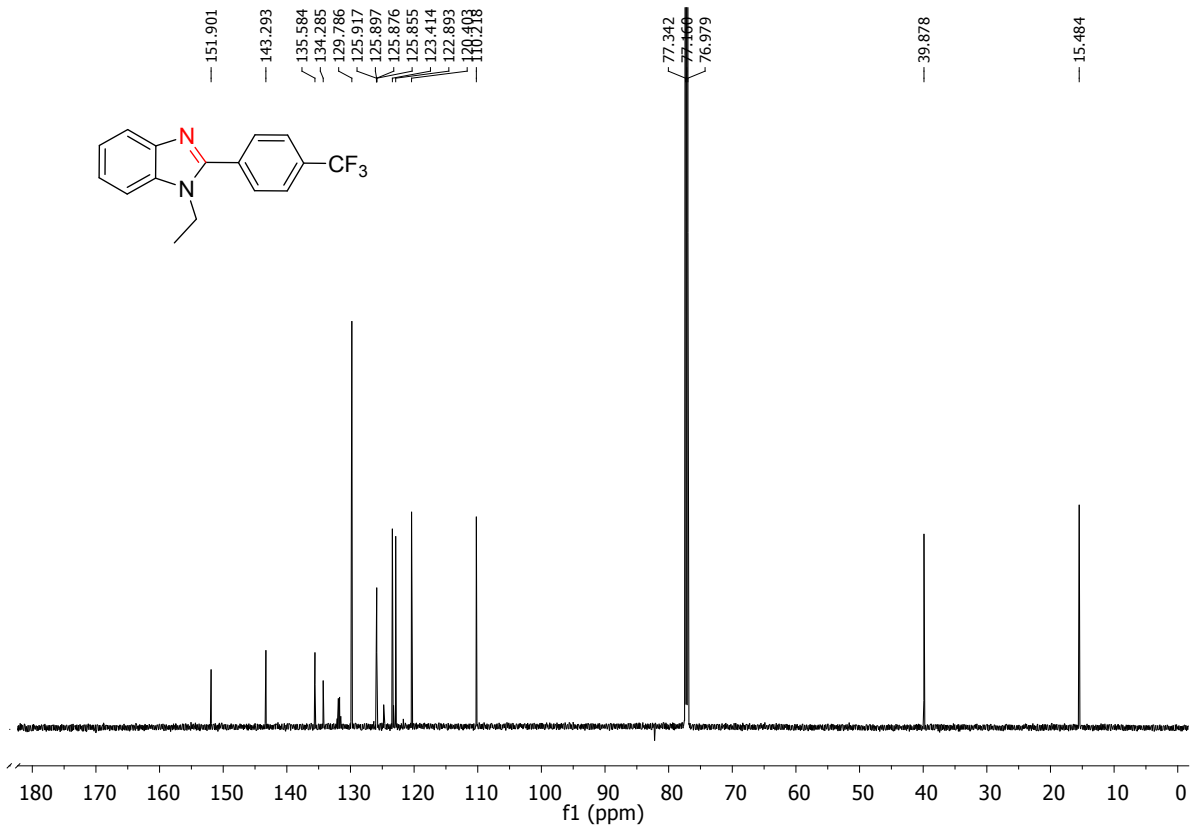


Fig. S68. ^{13}C NMR of 1-Ethyl-2-(4-(trifluoromethyl)phenyl)-benzo[d]imidazole (**2k**)

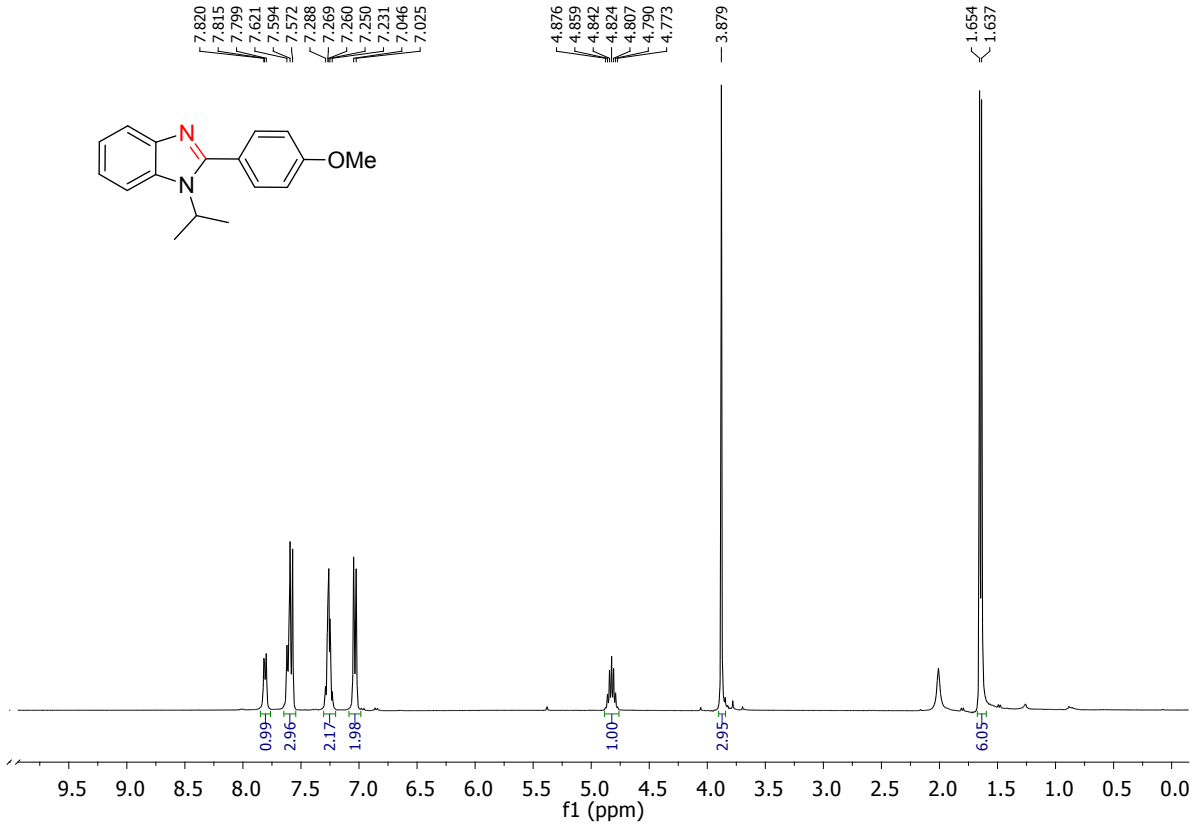


Fig. S69. ^{1}H NMR of 1-Isopropyl-2-(4-methoxyphenyl)-benzo[d]imidazole (**2l**)

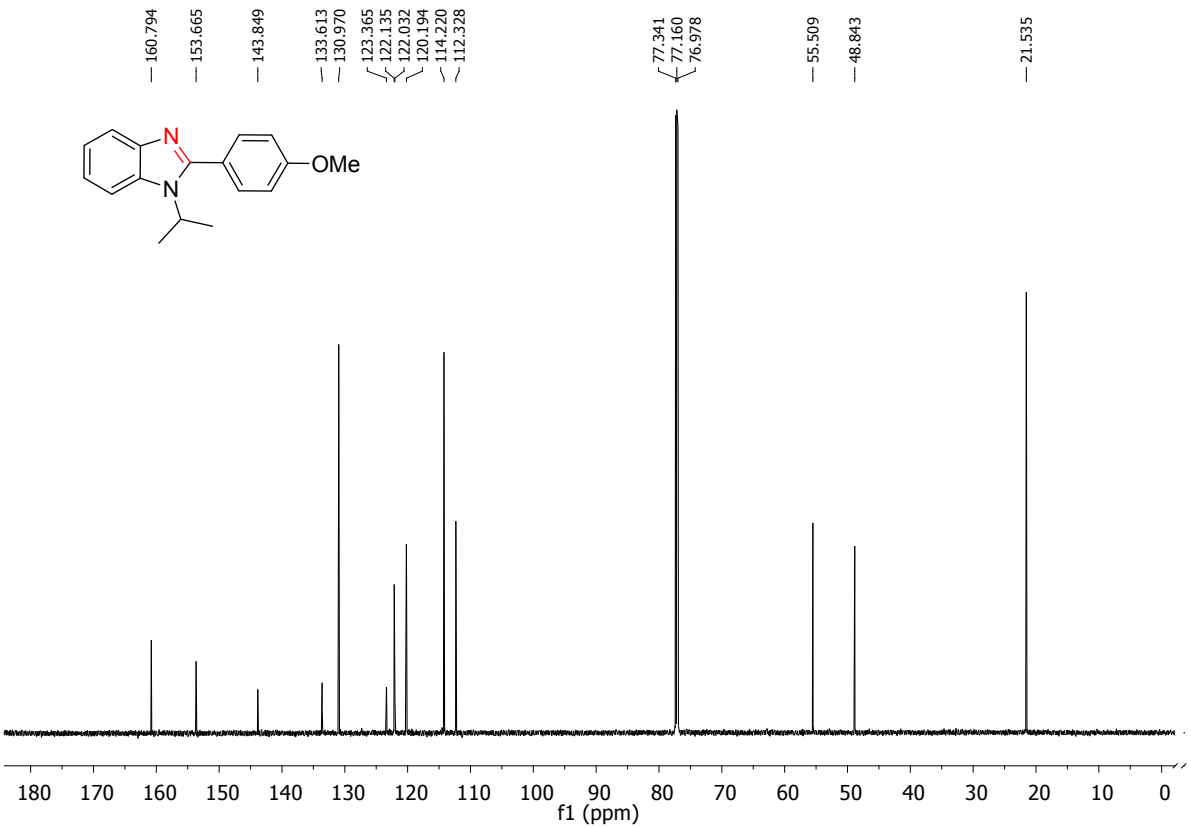


Fig. S70. ^{13}C NMR of 1-Isopropyl-2-(4-methoxyphenyl)-benzo[d]imidazole (**2l**)

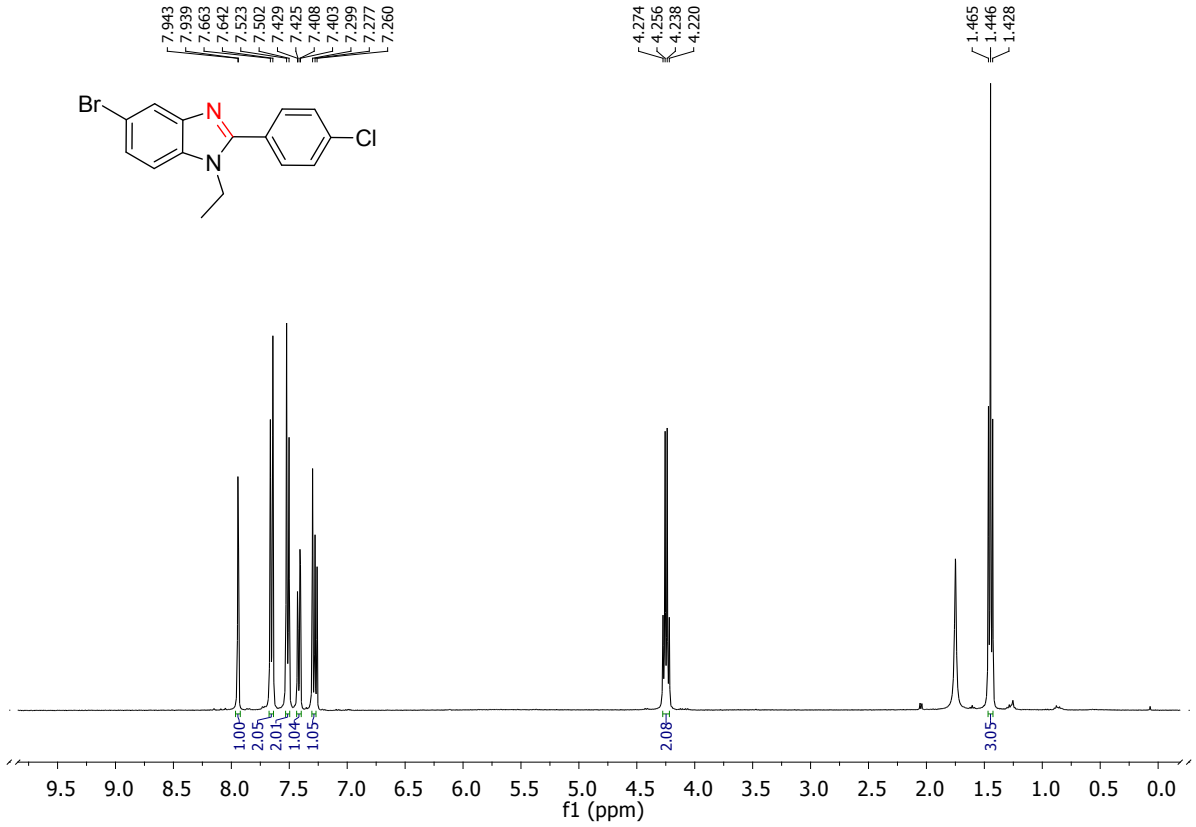


Fig. S71. ^{1}H NMR of 5-Bromo-2-(4-chlorophenyl)-1-ethyl-benzo[d]imidazole (**2m**)

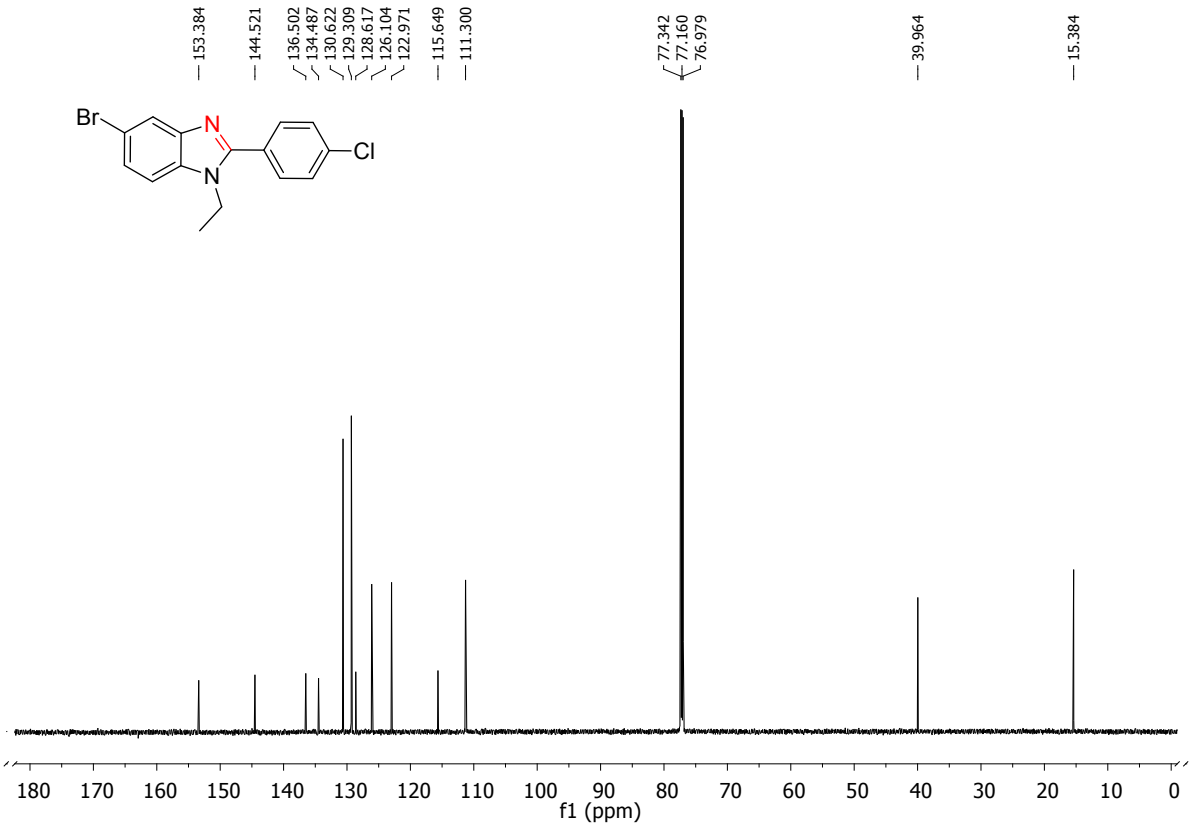
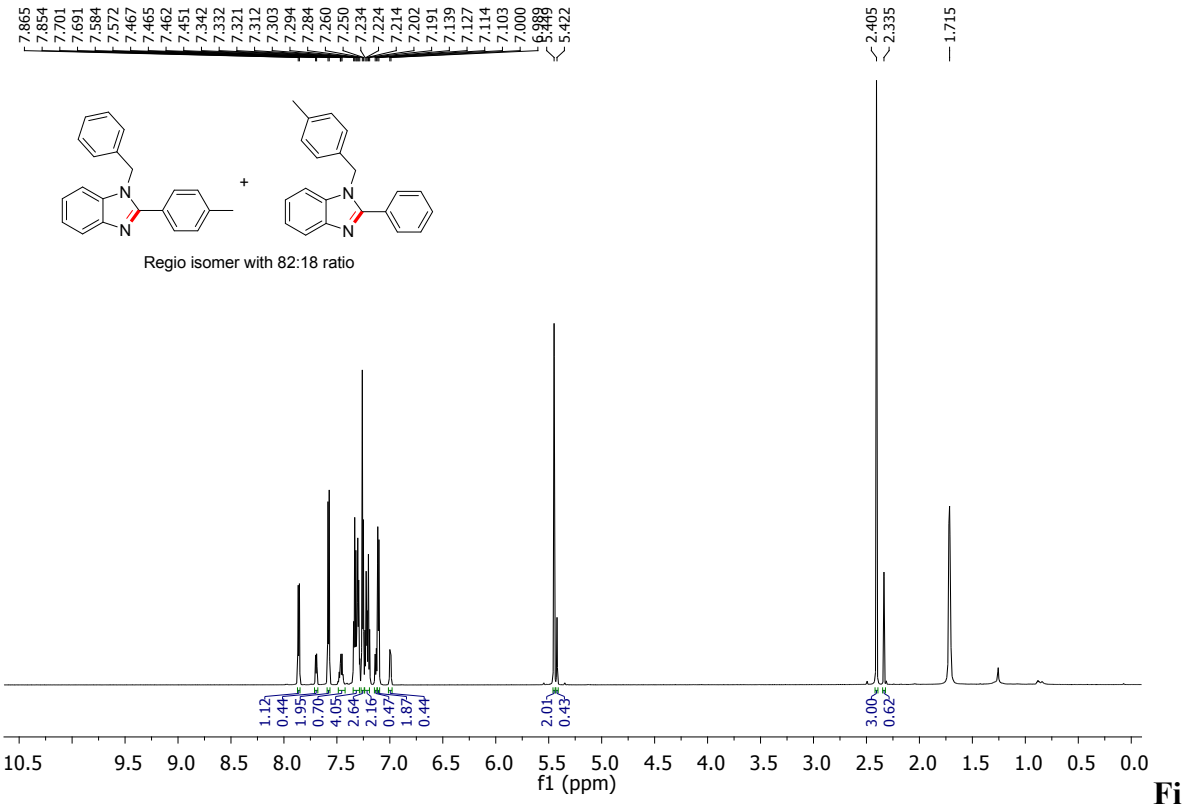


Fig. S72. ^{13}C NMR of 5-Bromo-2-(4-chlorophenyl)-1-ethyl-benzo[d]imidazole (**2m**)



Fi

g. S73. ^{1}H NMR of 1-Benzyl-2-(p-tolyl)-benzo[d]imidazole and 1-(4-Methylbenzyl)-2-phenyl-benzo[d]imidazole **(2n)**

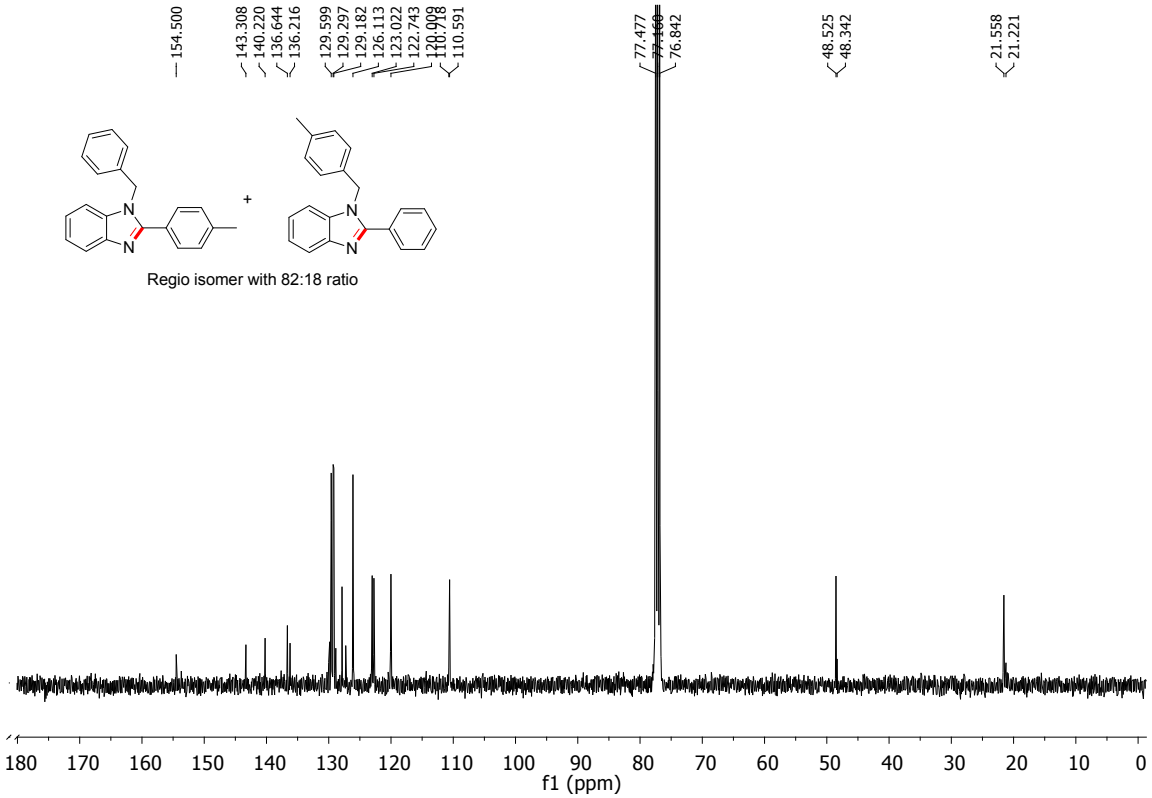
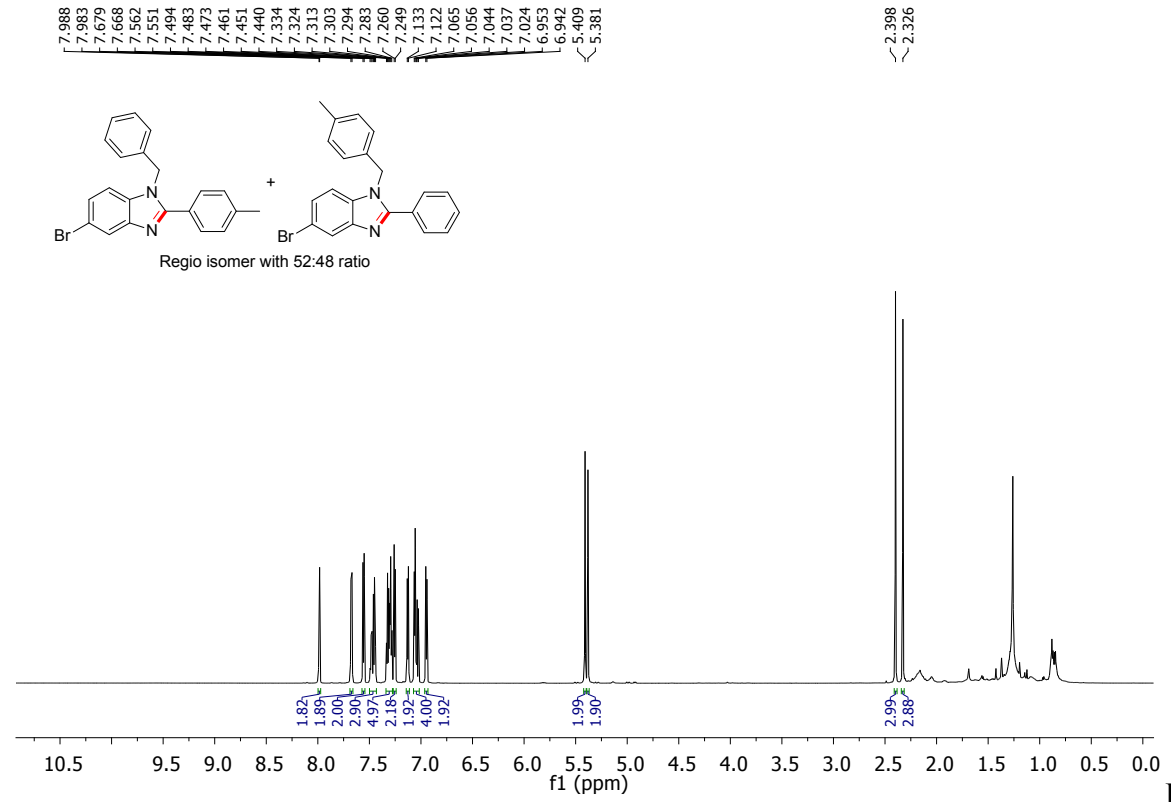


Fig. S74. ^{13}C NMR of 1-Benzyl-2-(p-tolyl)-benzo[d]imidazole and 1-(4-Methylbenzyl)-2-phenyl-benzo[d]imidazole **(2n)**



Fi

g. S75. ^{1}H NMR of 1-Benzyl-5-bromo-2-(p-tolyl)-benzo[d]imidazole and 5-Bromo-1-(4-methylbenzyl)-2-phenyl-benzo[d]imidazole **(2o)**

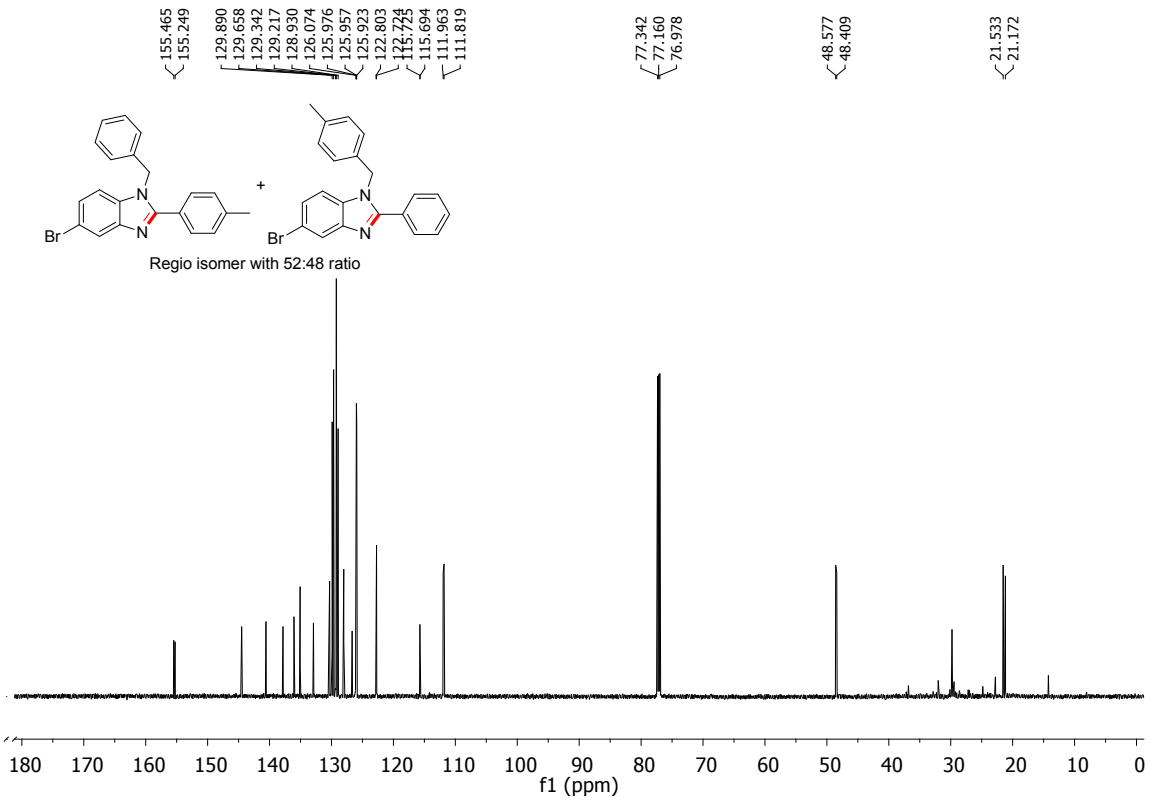


Fig. S76. [13]C NMR of 1-Benzyl-5-bromo-2-(p-tolyl)-benzo[d]imidazole and 5-Bromo-1-(4-methylbenzyl)-2-phenyl-benzo[d]imidazole **(2o)**

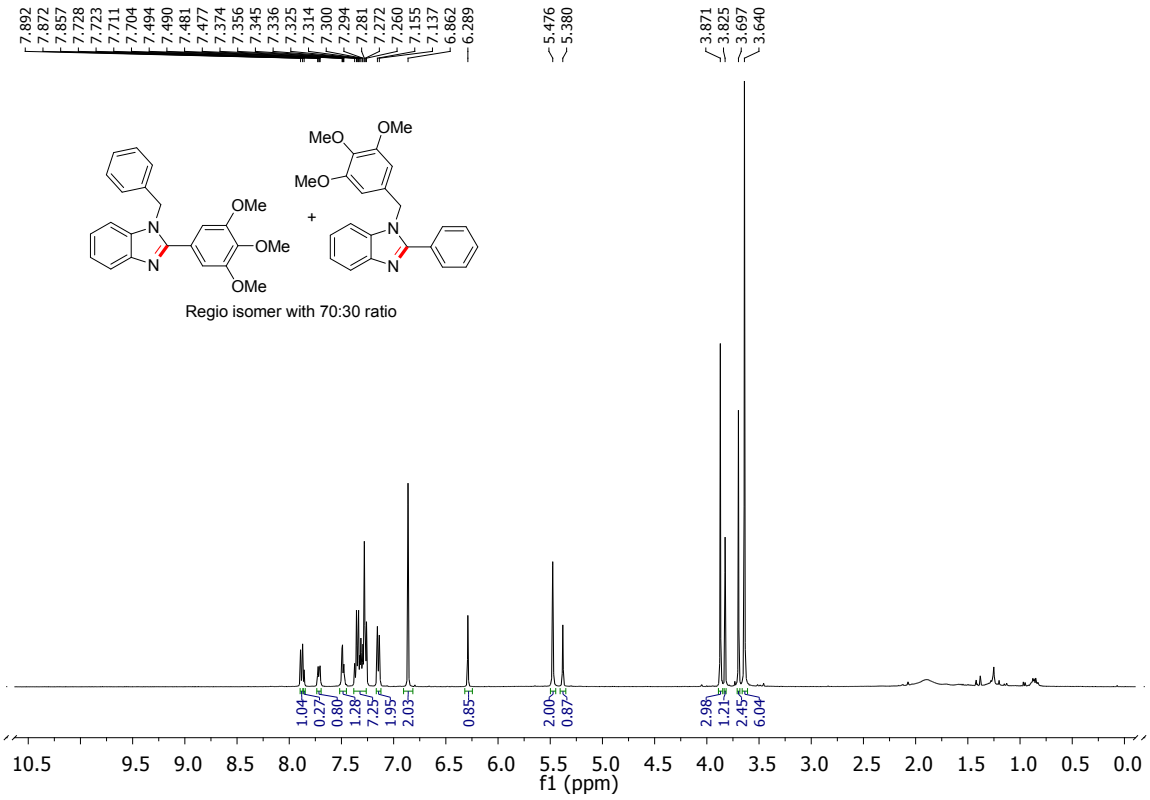
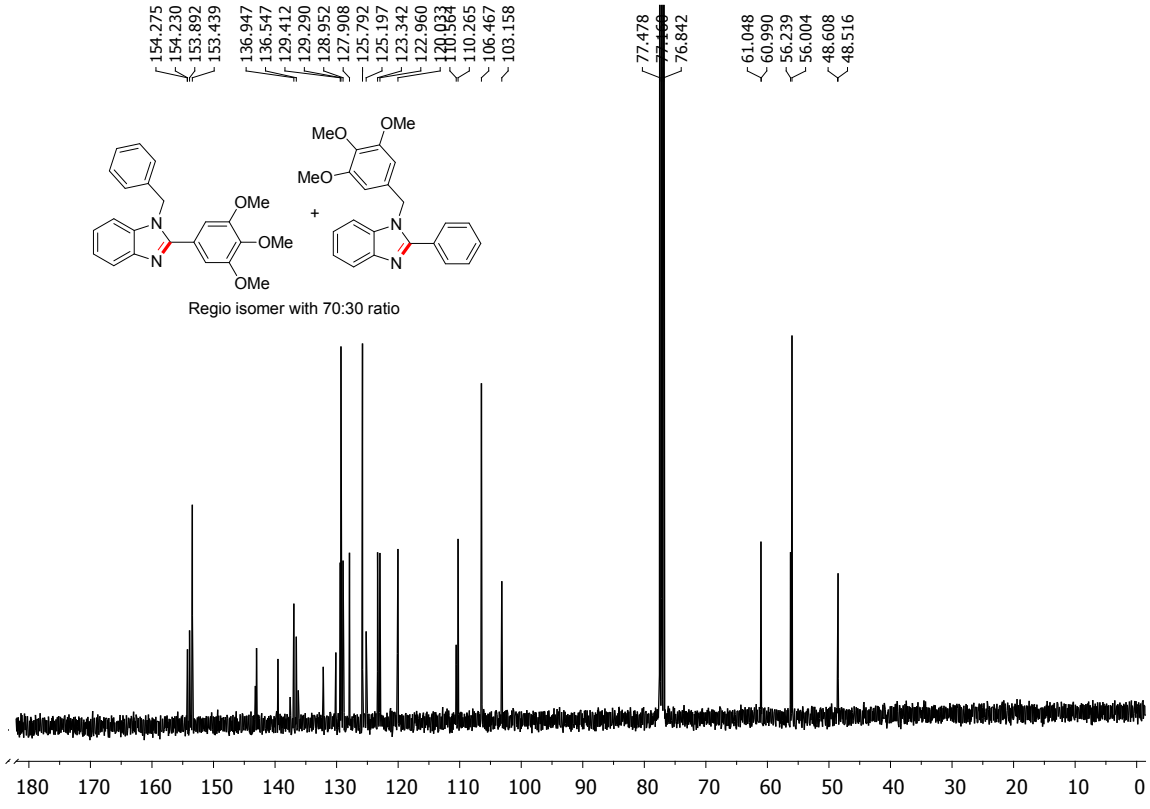
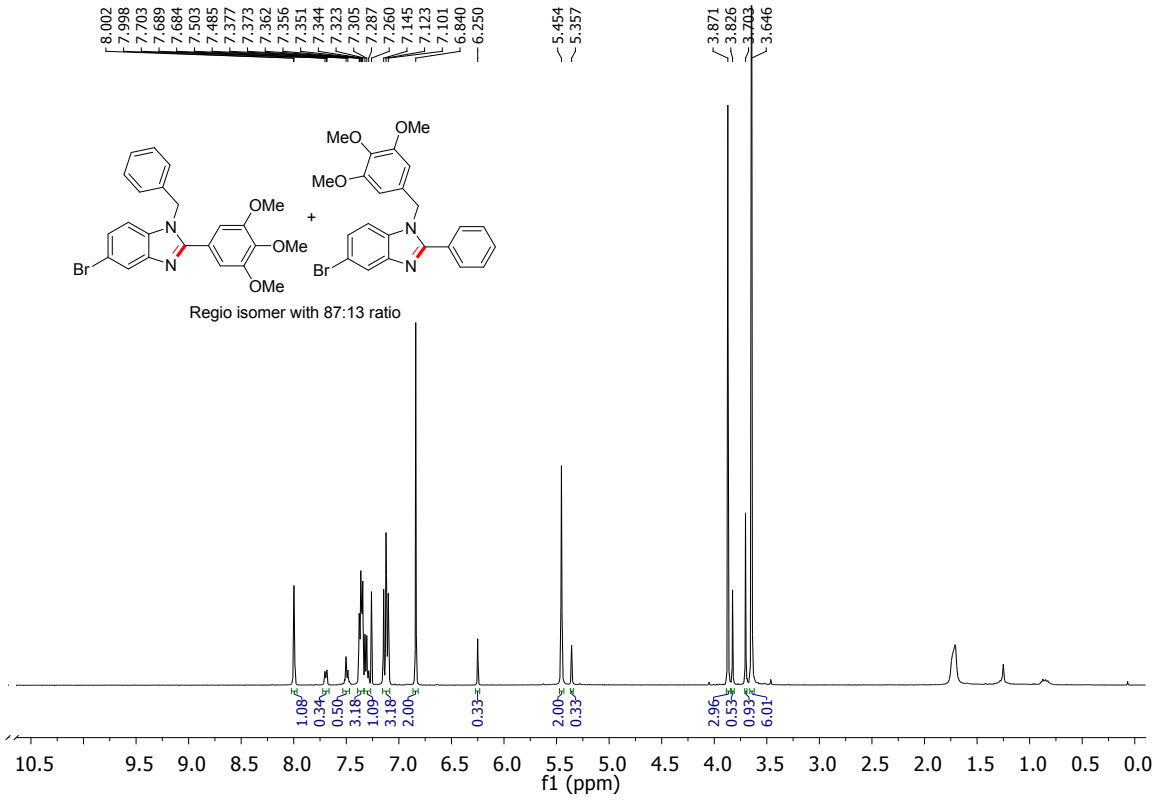


Fig. S77. [1]H NMR of 1-Benzyl-2-(3,4,5-trimethoxyphenyl)-benzo[d]imidazole and 2-Phenyl-1-(3,4,5-trimethoxybenzyl)-benzo[d]imidazole **(2p)**



Fi

g. S78. [1]H NMR of 1-Benzyl-2-(3,4,5-trimethoxyphenyl)-benzo[d]imidazole and 2-Phenyl-1-(3,4,5-trimethoxybenzyl)-benzo[d]imidazole **(2p)**



Fi

g. S79. [1]H NMR of 1-Benzyl-5-bromo-2-(3,4,5-trimethoxyphenyl)-benzo[d]imidazole and 5-Bromo-2-phenyl-1-(3,4,5-trimethoxybenzyl)-benzo[d]imidazole **(2q)**

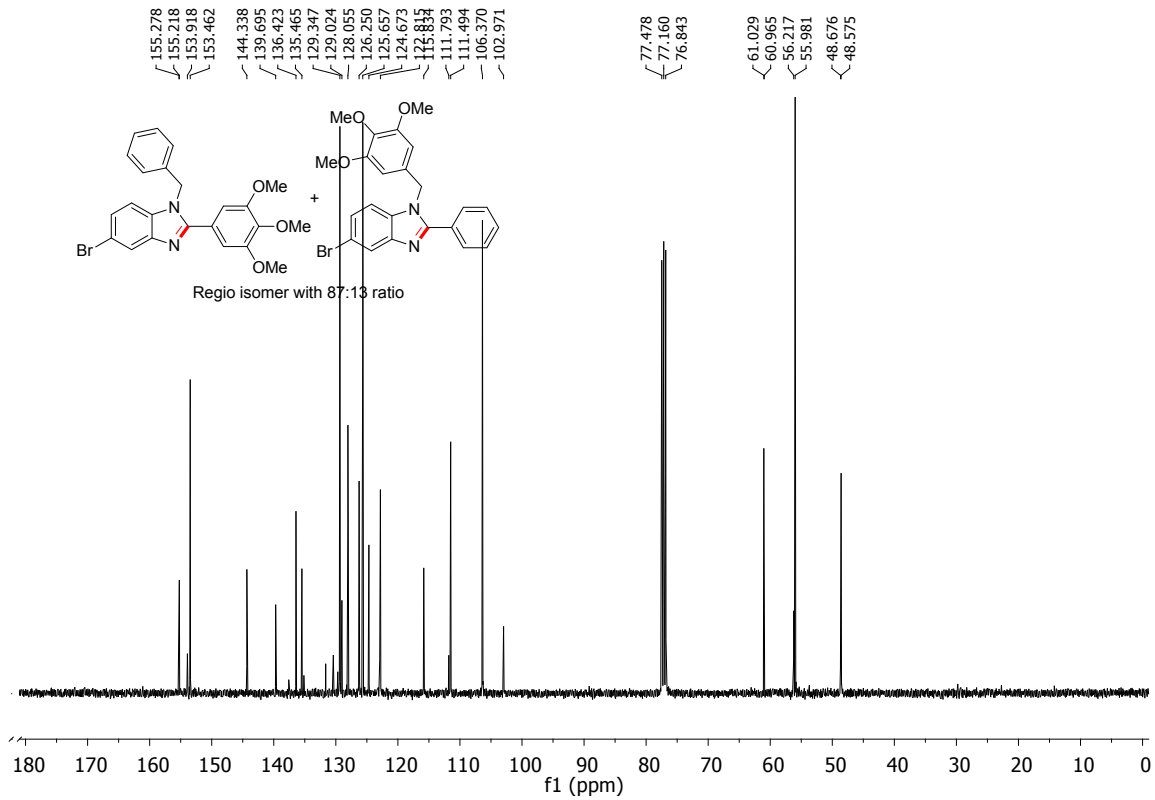


Fig. S80. ^{13}C NMR of 1-Benzyl-5-bromo-2-(3,4,5-trimethoxyphenyl)-benzo[d]imidazole and 5-Bromo-2-phenyl-1-(3,4,5-trimethoxybenzyl)-benzo[d]imidazole **(2q)**

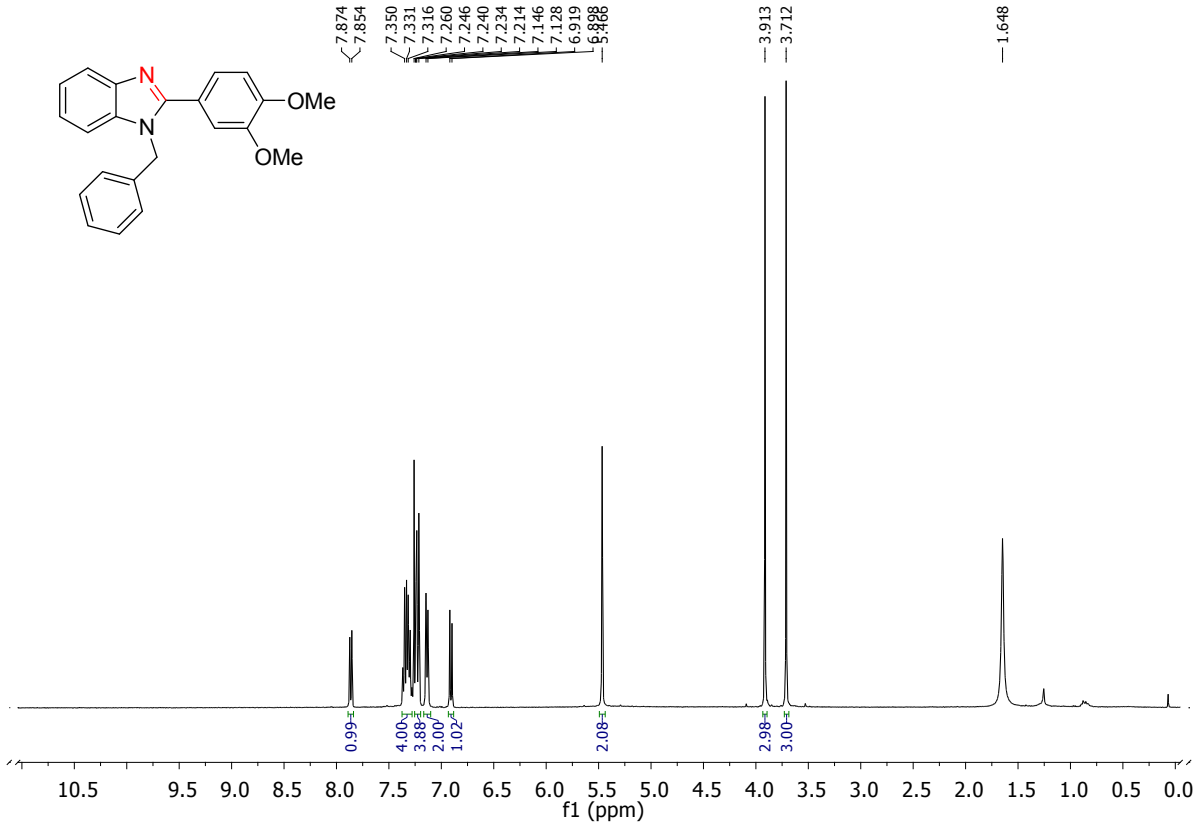


Fig. S81. ^{1}H NMR of 1-Benzyl-2-(3,4-dimethoxyphenyl)-benzo[d]imidazole (**2r**)

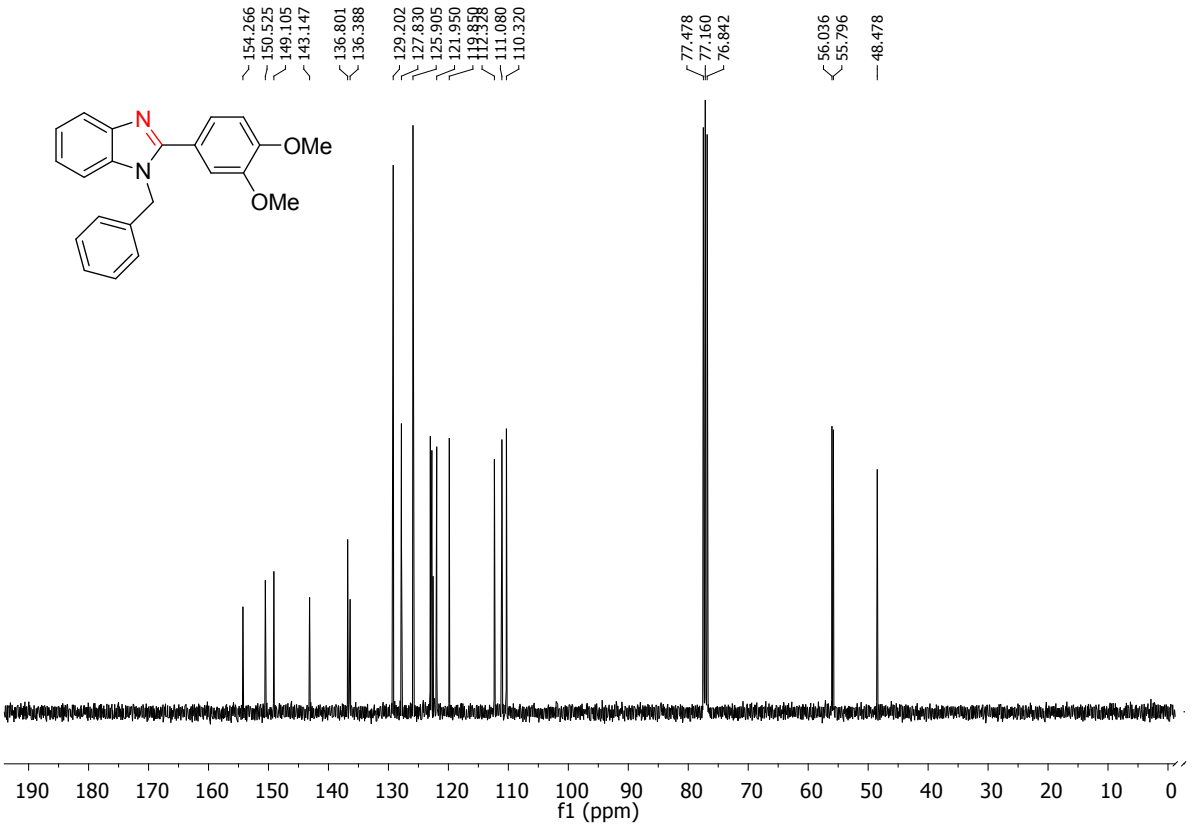


Fig. S82. ^{13}C NMR of 1-Benzyl-2-(3,4-dimethoxyphenyl)-benzo[d]imidazole (**2r**)

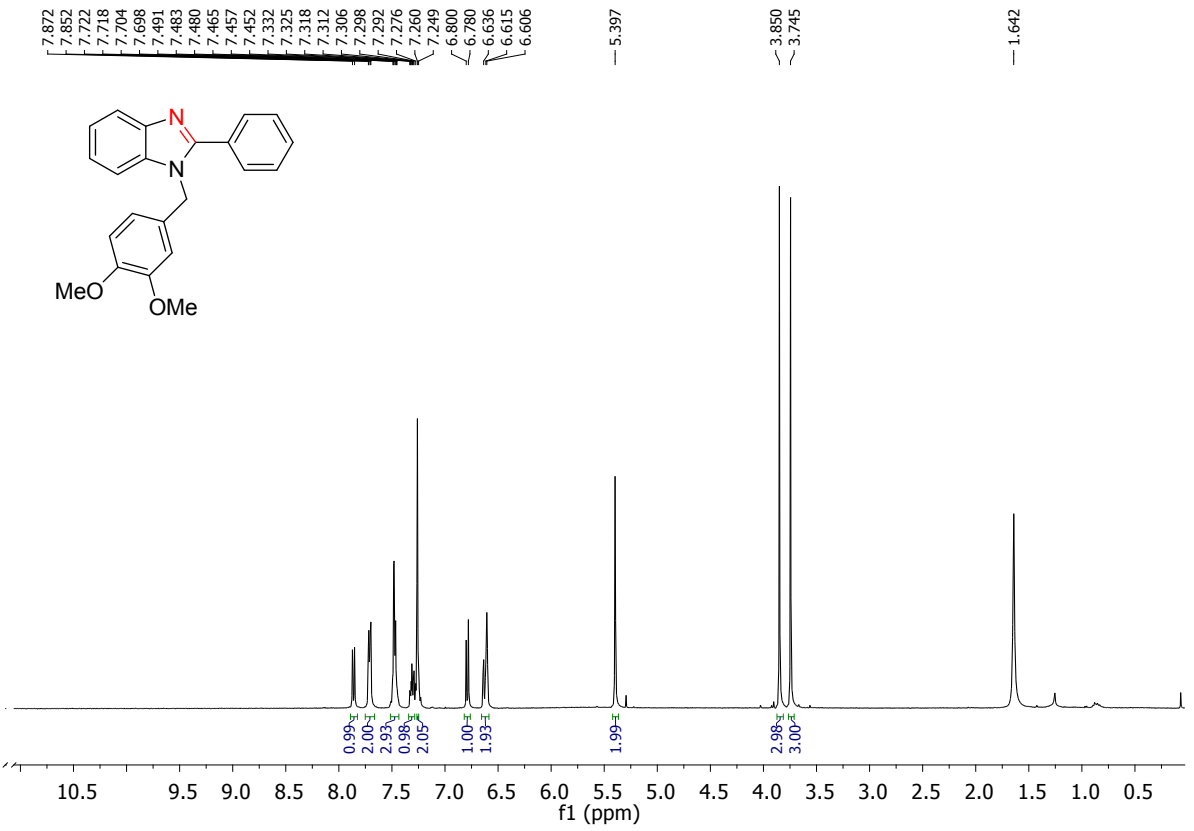


Fig. S83. ^{1}H NMR of 1-(3,4-Dimethoxybenzyl)-2-phenyl-benzo[d]imidazole (**2r'**)

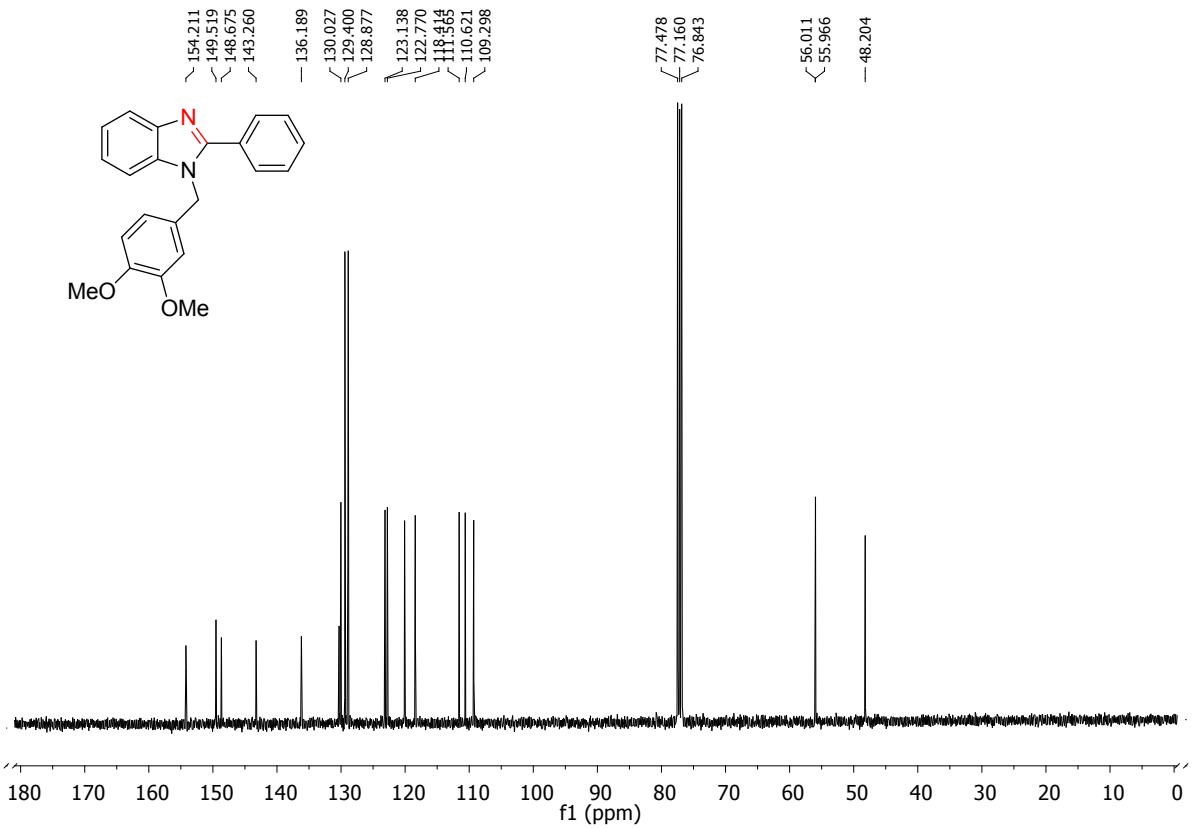


Fig. S84. ^{13}C NMR of 1-(3,4-Dimethoxybenzyl)-2-phenyl-benzo[d]imidazole (**2r'**)

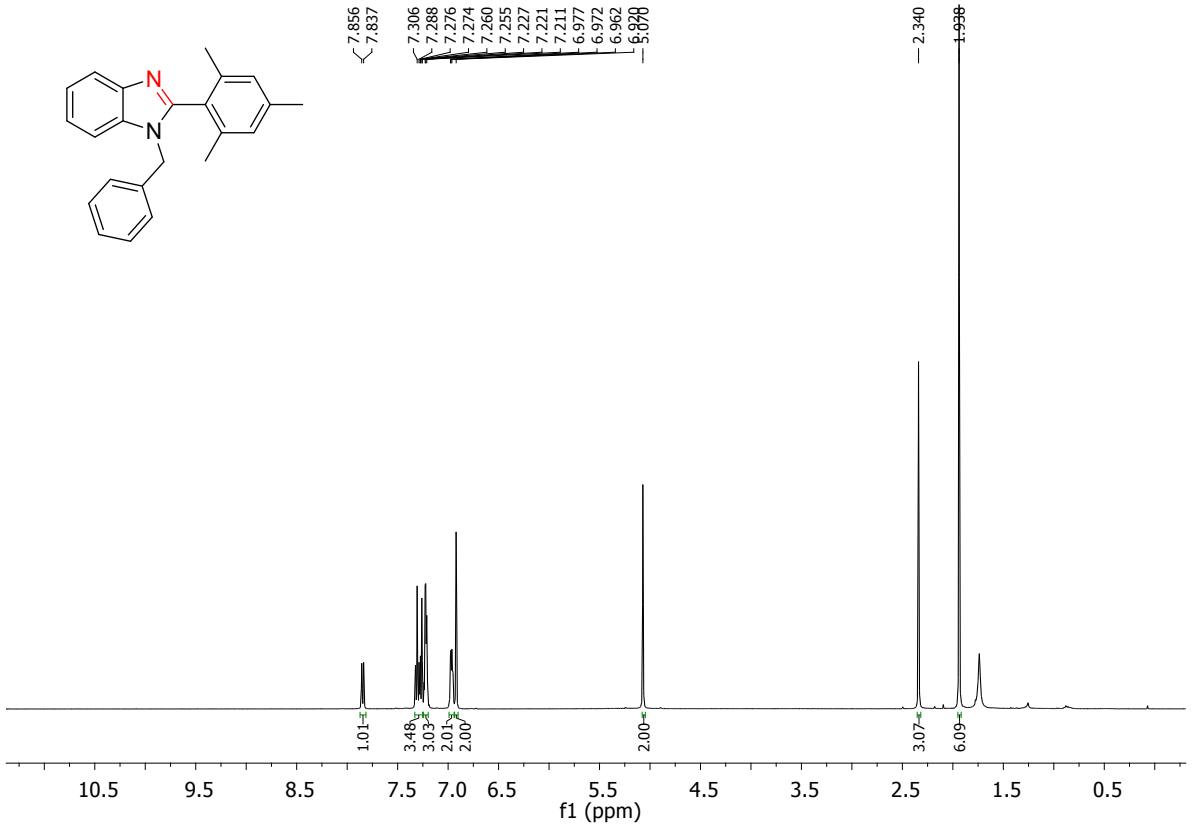


Fig. S85. ^{1}H NMR of 1-Benzyl-2-mesityl-benzo[d]imidazole (**2s**)

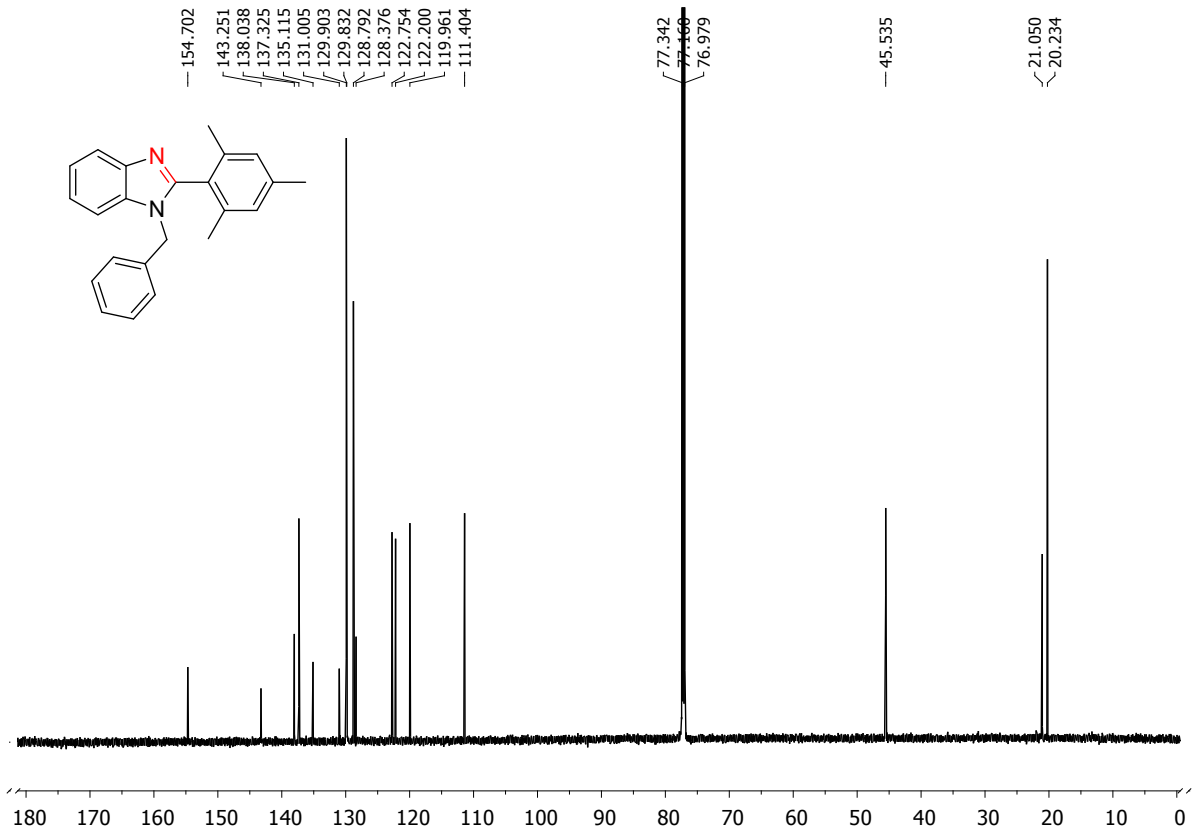


Fig. S86. ^{13}C NMR of 1-Benzyl-2-mesityl-benzo[d]imidazole (**2s**)

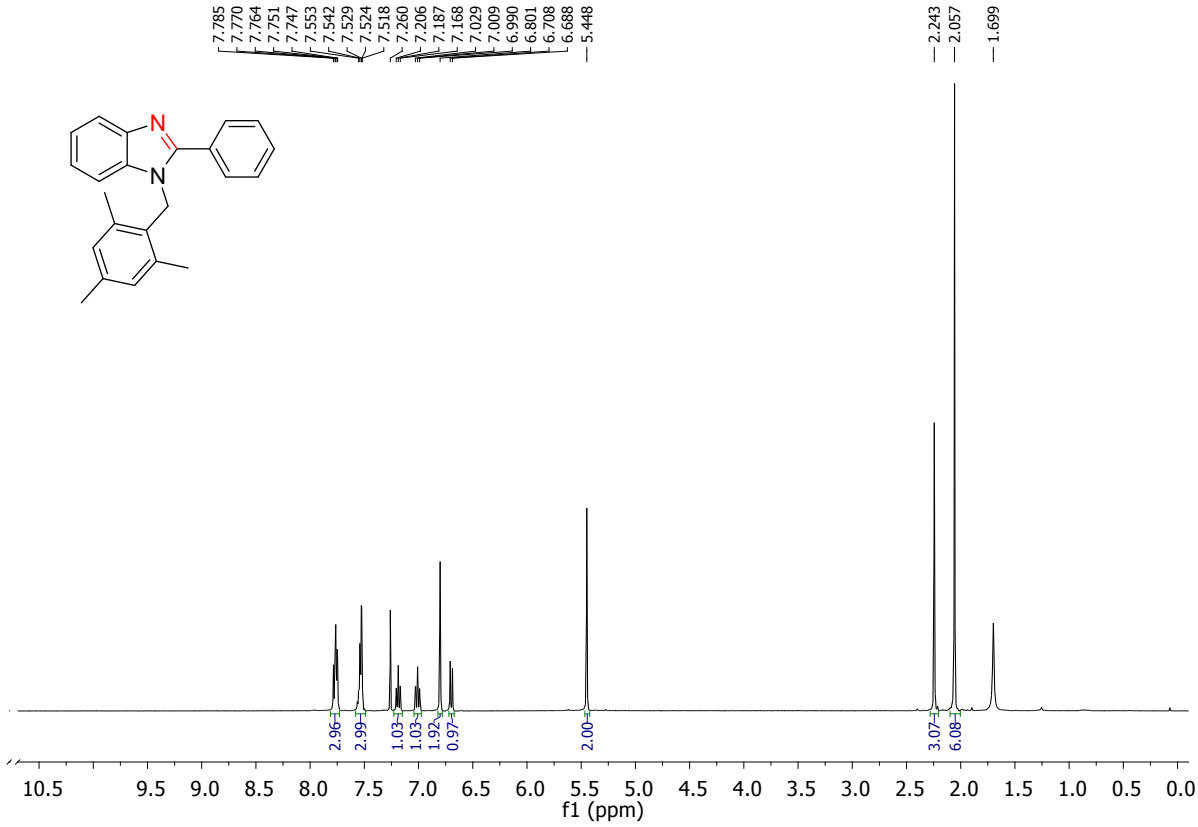


Fig. S87. ^{1}H NMR of 2-Phenyl-1-(2,4,6-trimethylbenzyl)-benzo[d]imidazole (**2s'**)

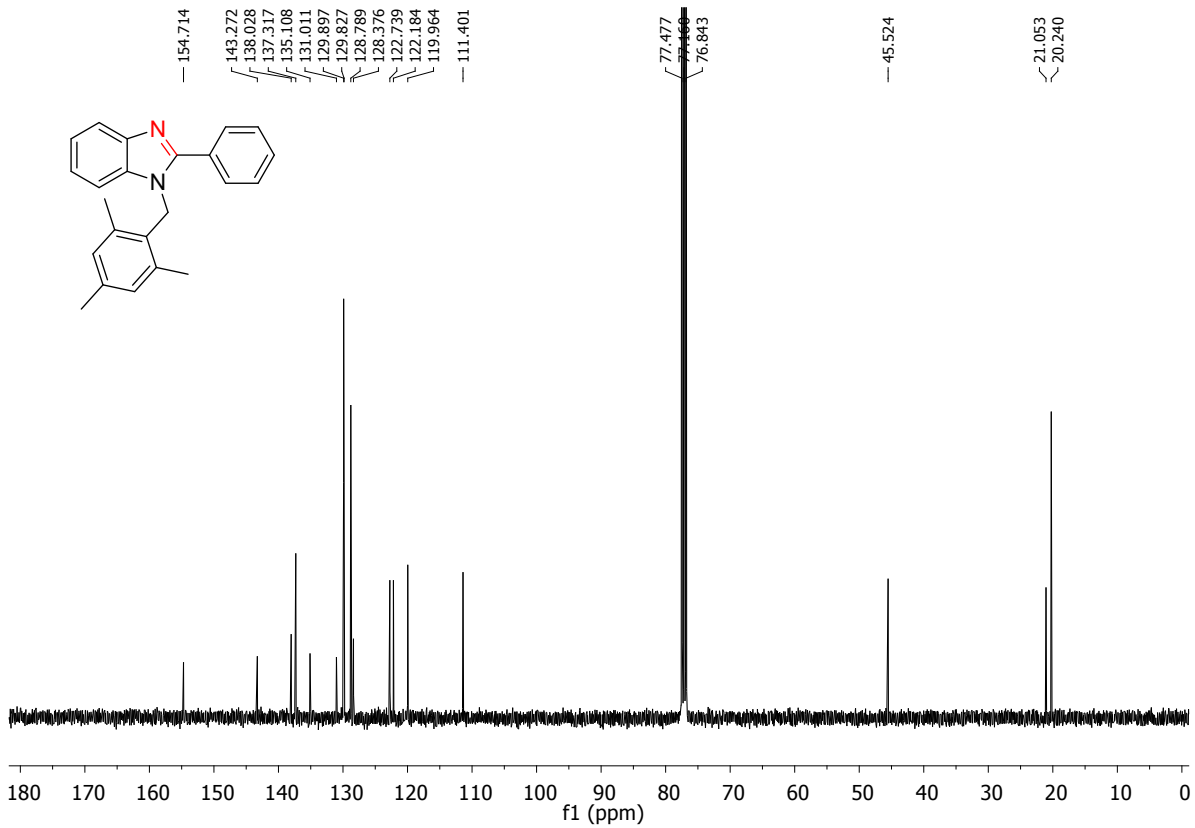


Fig. S88. ^{13}C NMR of 2-Phenyl-1-(2,4,6-trimethylbenzyl)-benzo[d]imidazole (**2s'**)

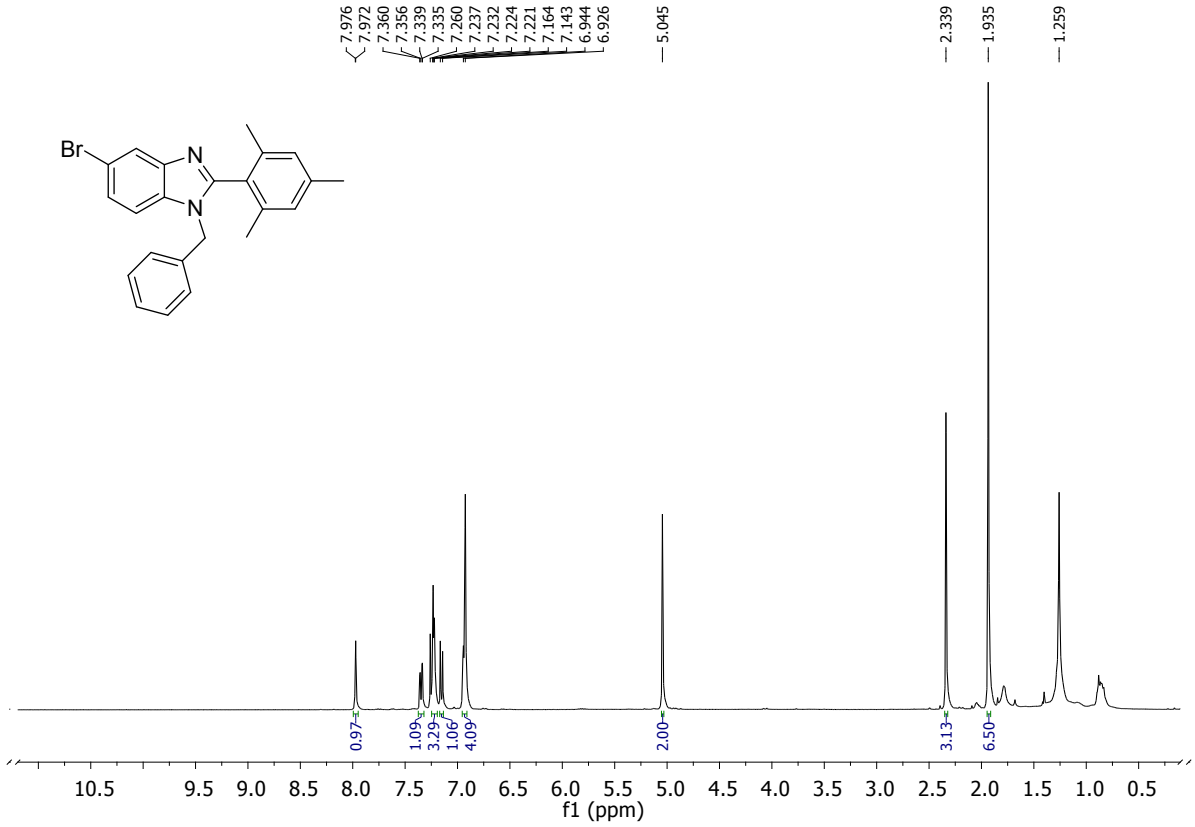


Fig. S89. ^{1}H NMR of 1-Benzyl-5-bromo-2-mesityl-benzo[d]imidazole (**2t**)

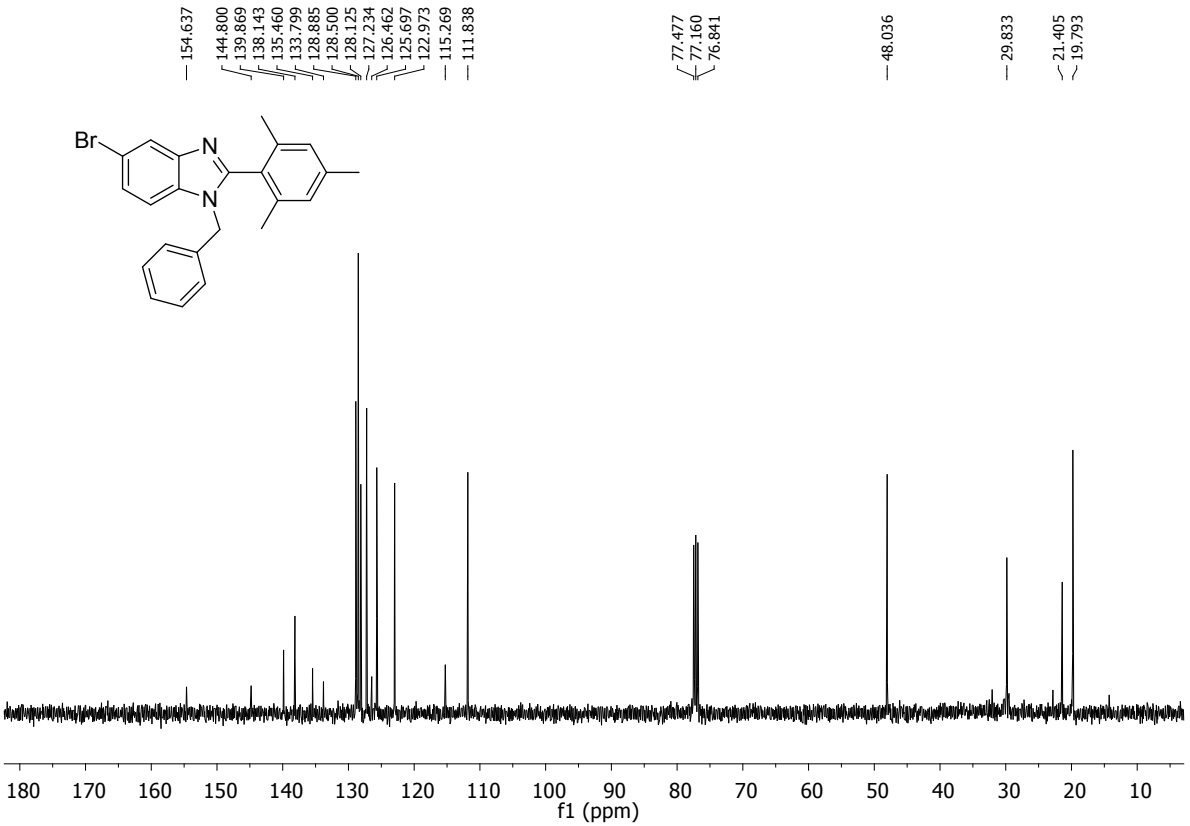


Fig. S90. ^{13}C NMR of 1-Benzyl-5-bromo-2-mesityl-benzo[d]imidazole (**2t**)

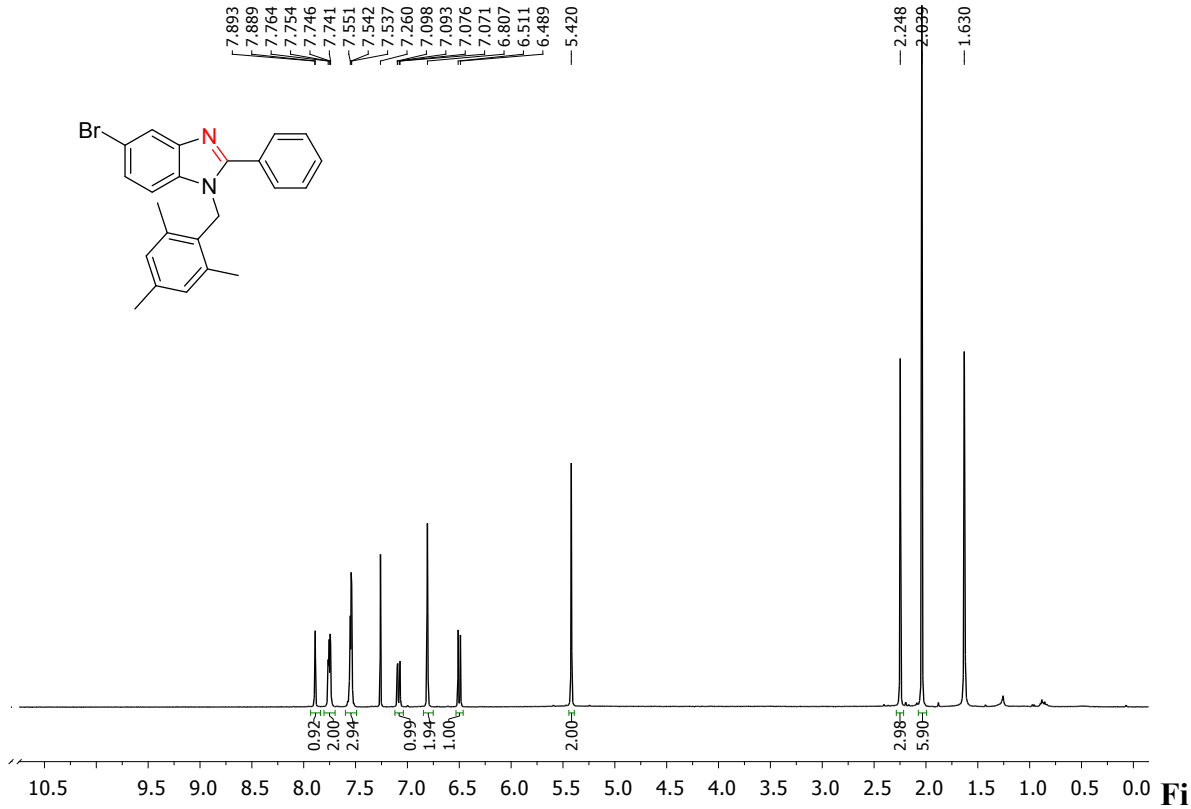


Fig. S91. ^{1}H NMR of 5-Bromo-2-phenyl-1-(2,4,6-trimethylbenzyl)-benzo[d]imidazole (**2t'**)

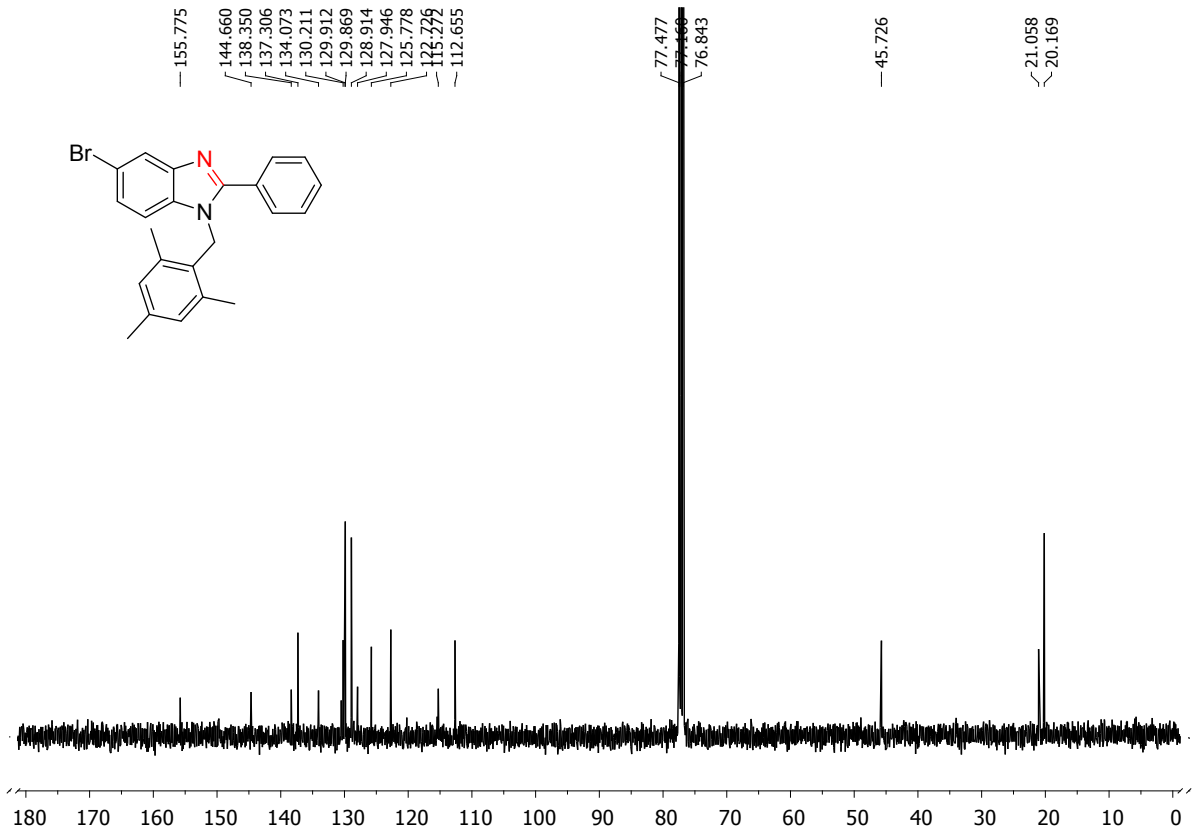


Fig. S92. ^{13}C NMR of 5-Bromo-2-phenyl-1-(2,4,6-trimethylbenzyl)-benzo[d]imidazole (**2t'**)

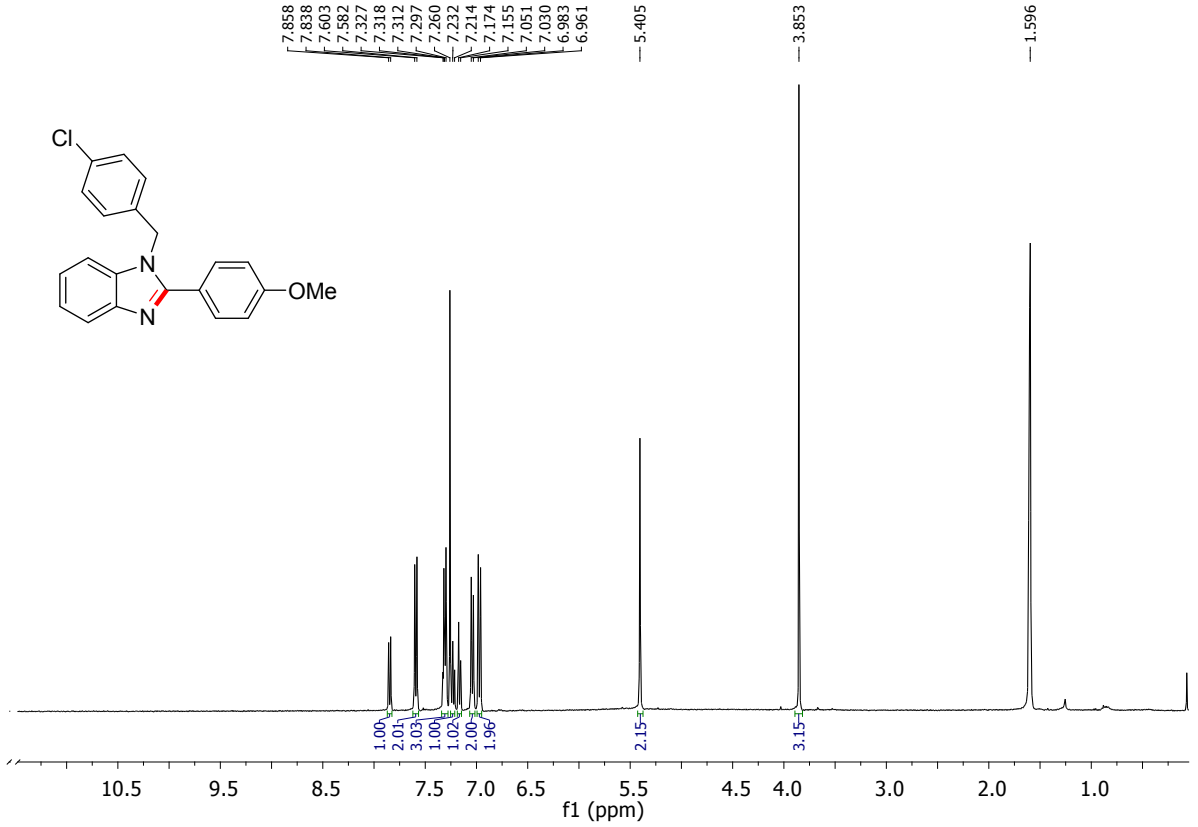


Fig. S93. ^{1}H NMR of 1-(4-chlorobenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (**2u**)

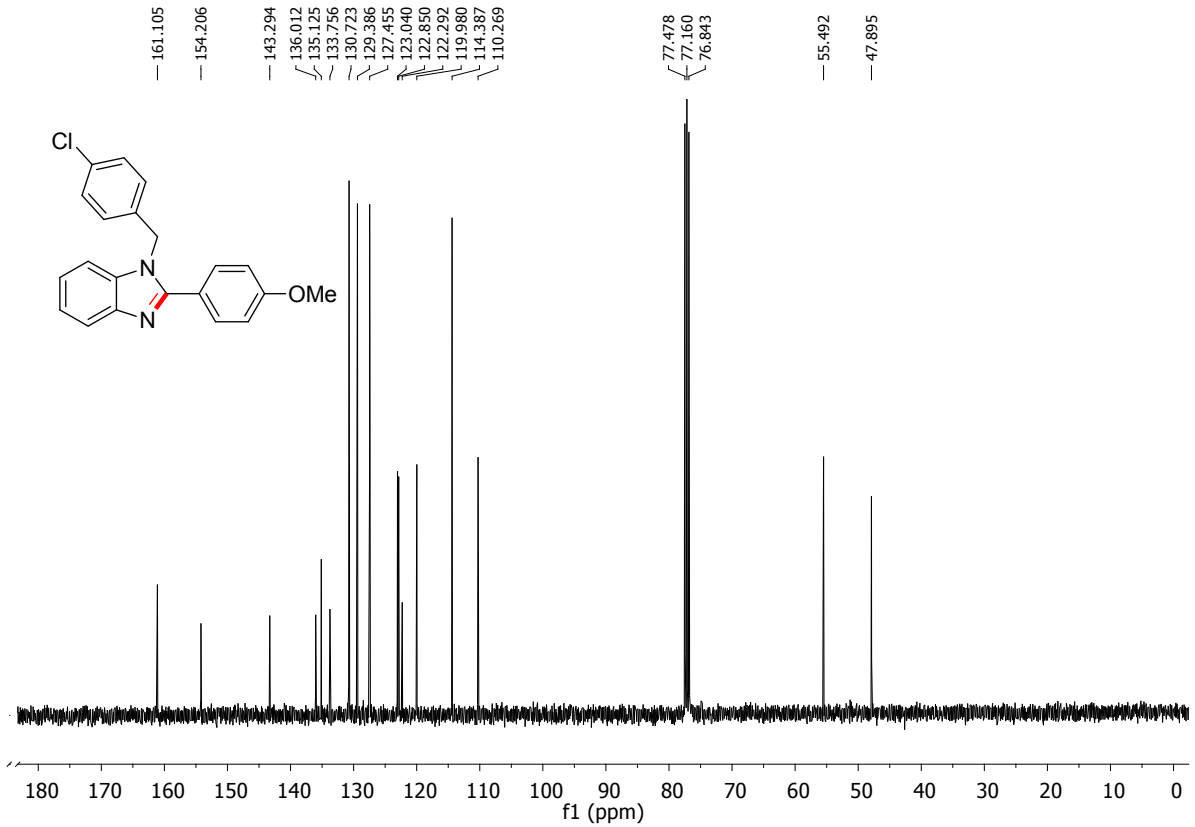


Fig. S94. ^{13}C NMR of 1-(4-chlorobenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (**2u**)

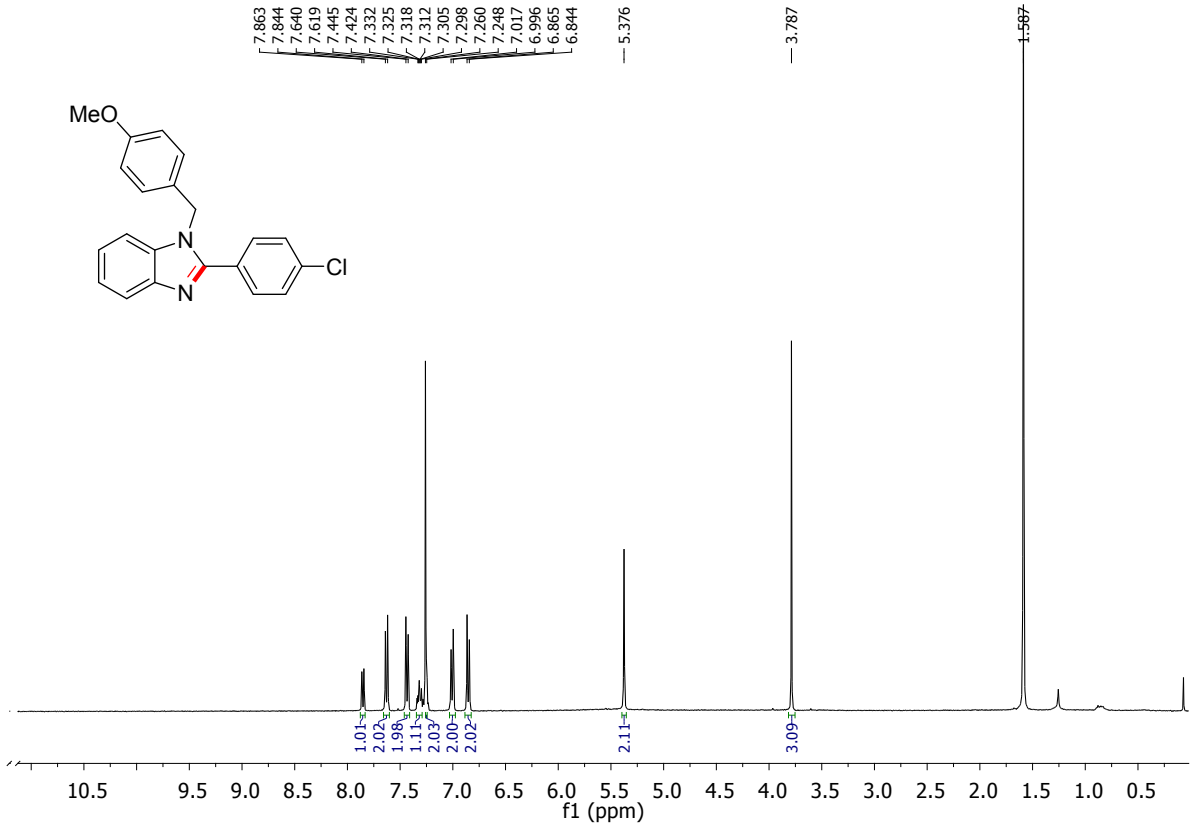


Fig. S95. ^{1}H NMR of 2-(4-chlorophenyl)-1-(4-methoxybenzyl)-benzo[d]imidazole (**2u'**)

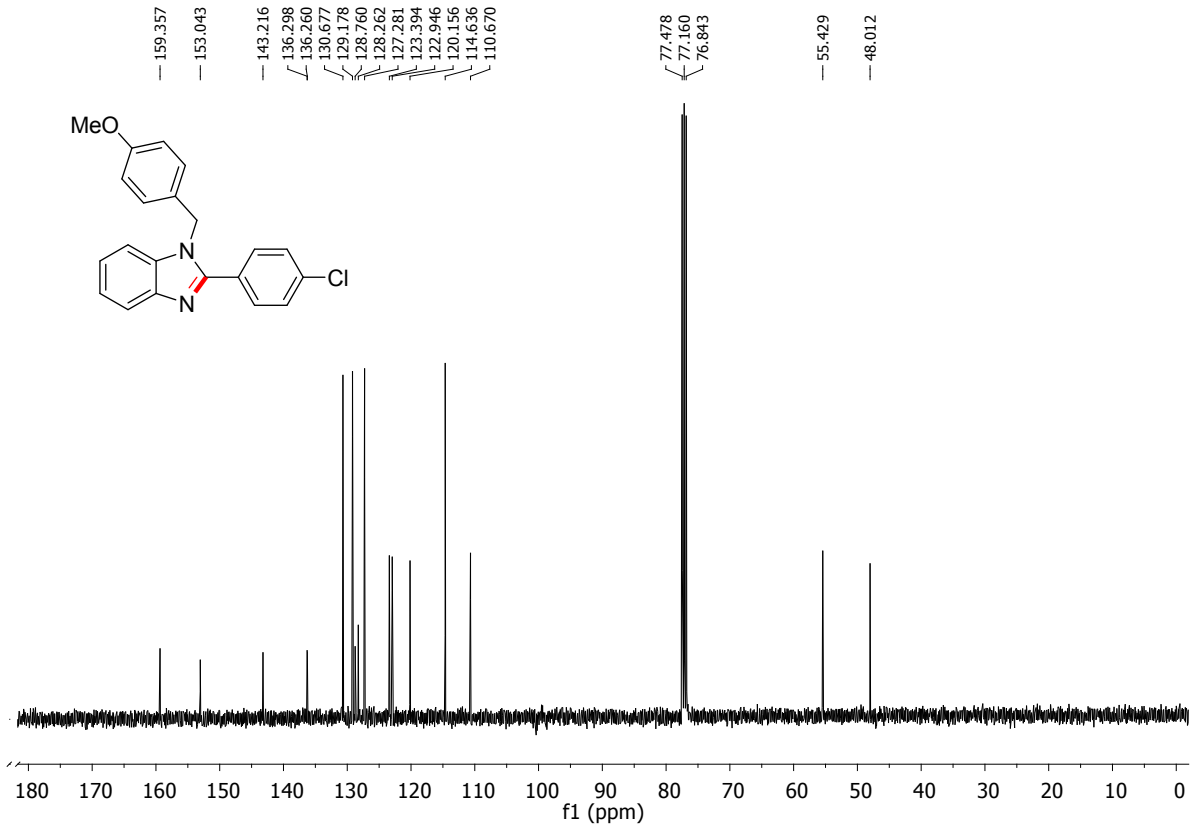


Fig. S96. ^{13}C NMR of 2-(4-chlorophenyl)-1-(4-methoxybenzyl)-benzo[d]imidazole (**2u'**)

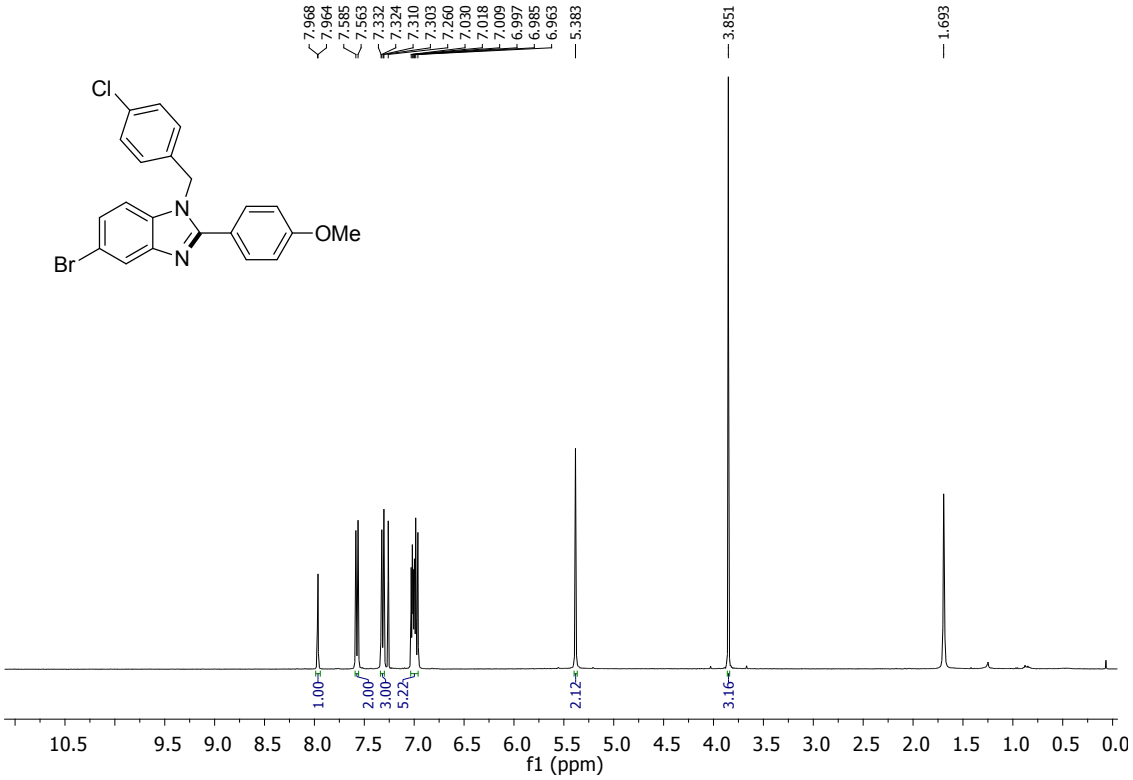


Fig. S97. ^{1}H NMR of 5-Bromo-1-(4-chlorobenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (**2v**)

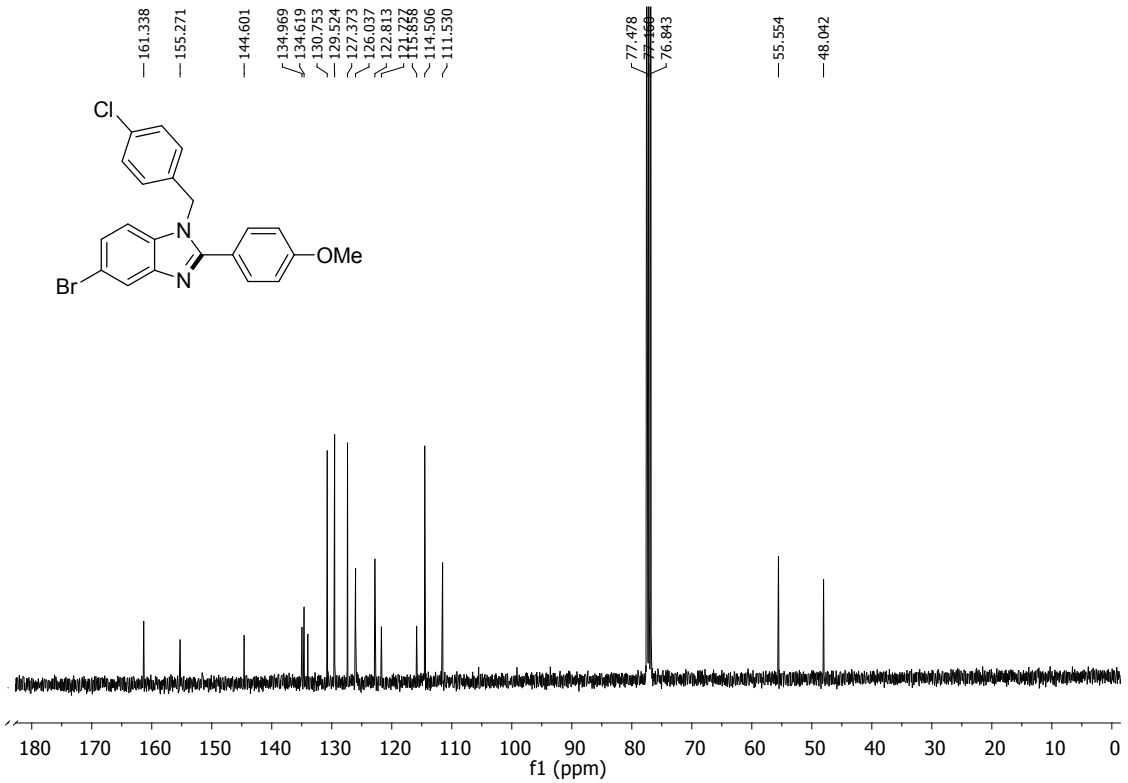


Fig. S98. ^{13}C NMR of 5-Bromo-1-(4-chlorobenzyl)-2-(4-methoxyphenyl)-benzo[d]imidazole (**2v**)

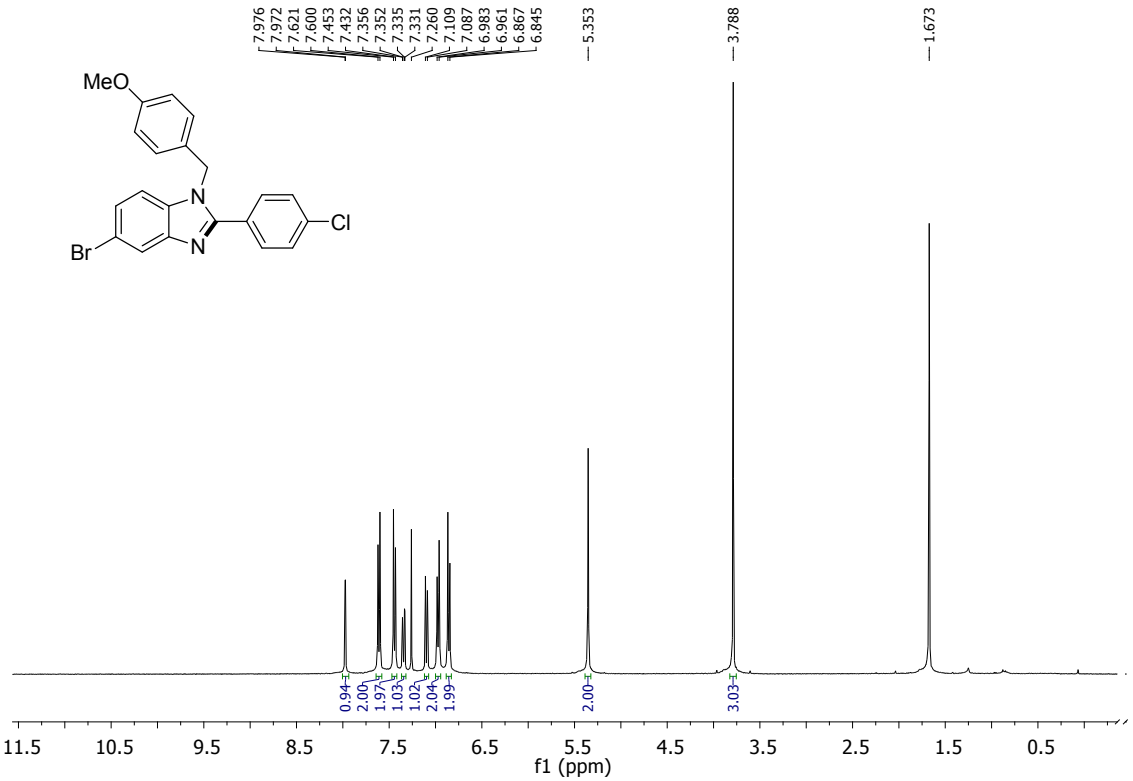


Fig. S99. ^{1}H NMR of 5-Bromo-2-(4-chlorophenyl)-1-(4-methoxybenzyl)-benzo[d]imidazole (**2v'**)

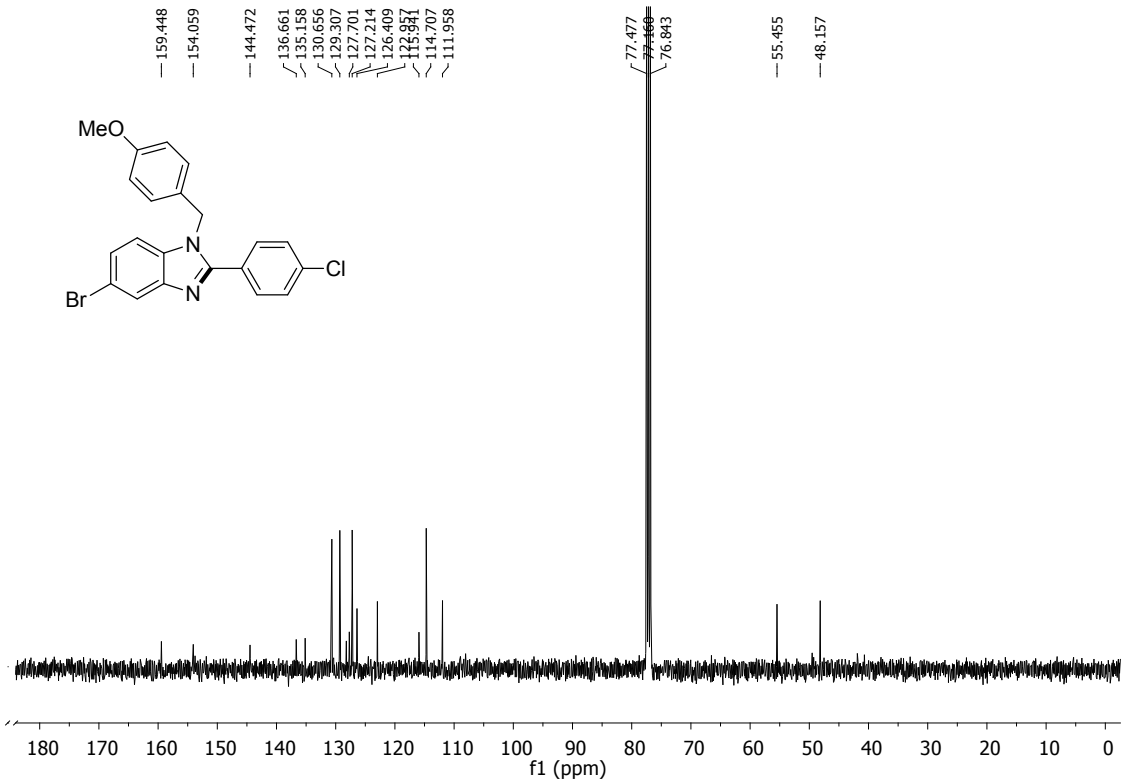


Fig. S100. ^{13}C NMR of 5-Bromo-2-(4-chlorophenyl)-1-(4-methoxybenzyl)-benzo[d]imidazole (**2v'**)

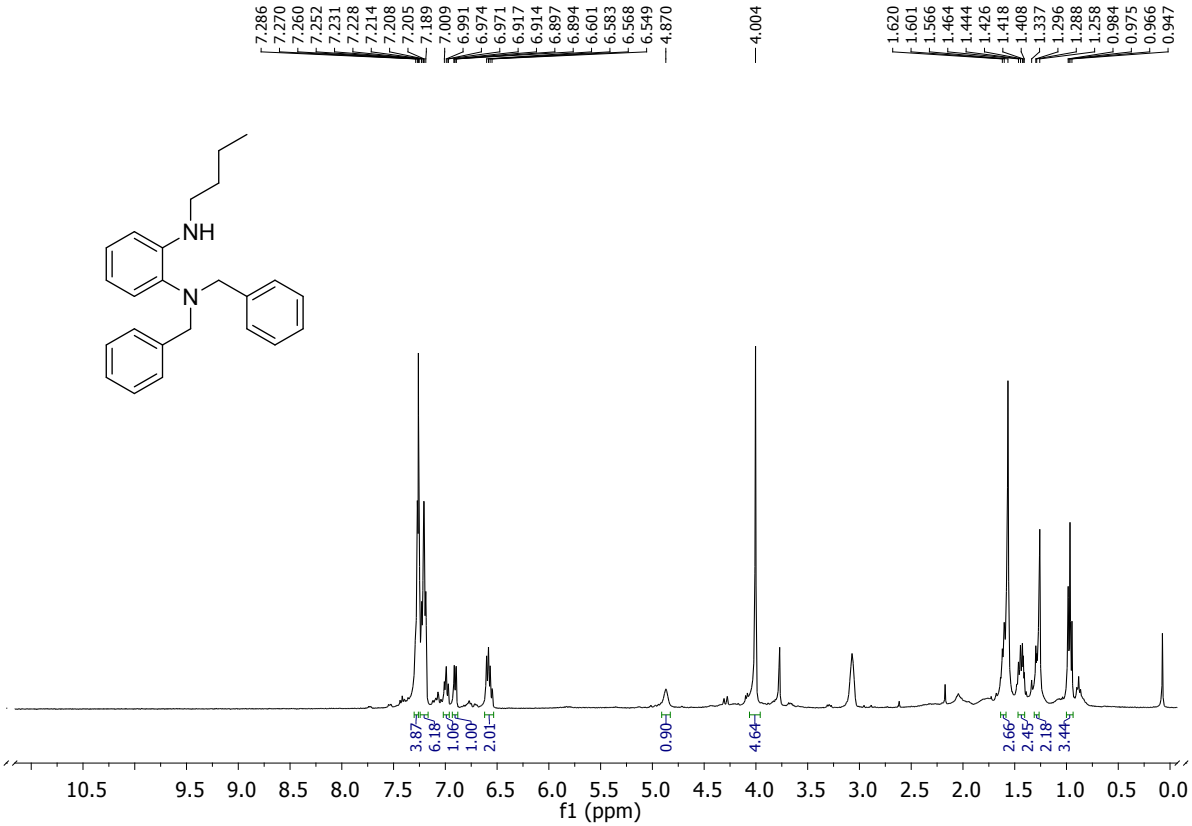


Fig. S101. ^{1}H NMR of N^{1},N^{1}-dibenzyl-N^{2}-butylbenzene-1,2-diamine (**3**)

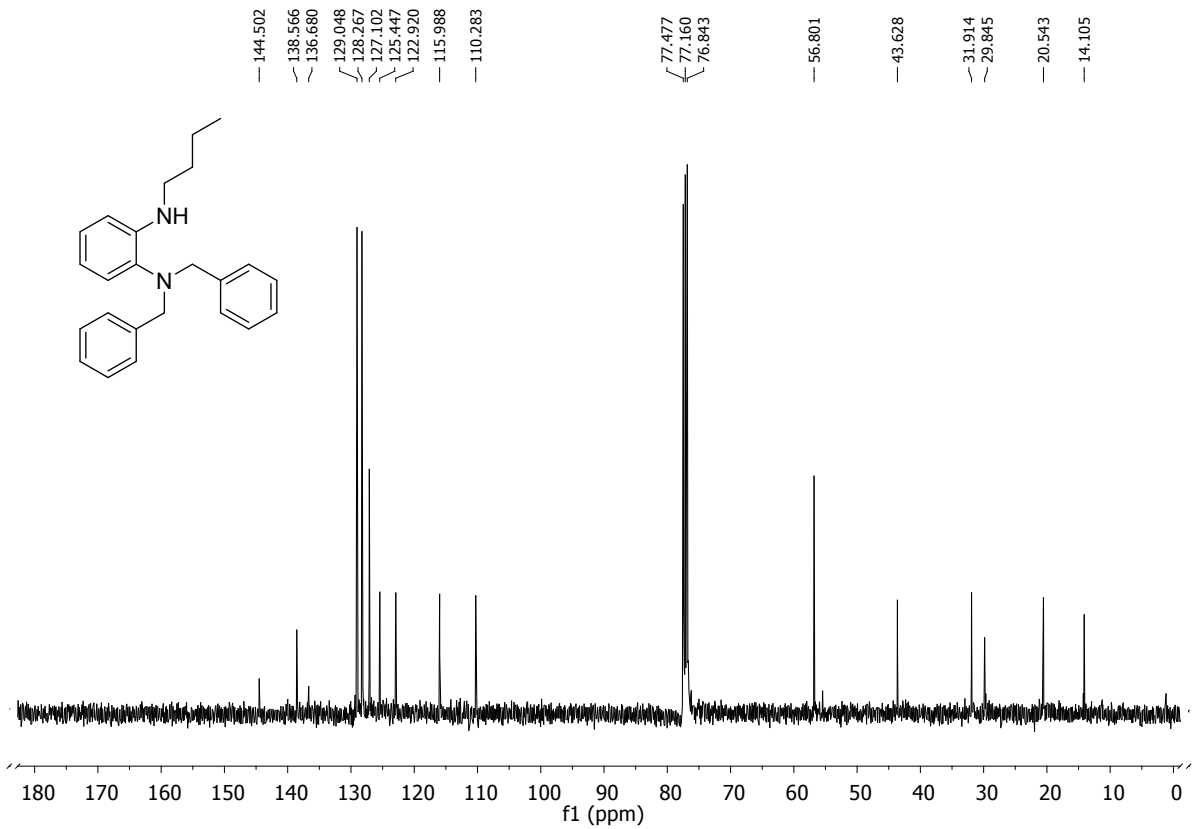


Fig. S102. ^{13}C NMR of N^1,N^1-dibenzyl-N^2-butylbenzene-1,2-diamine (**3**)

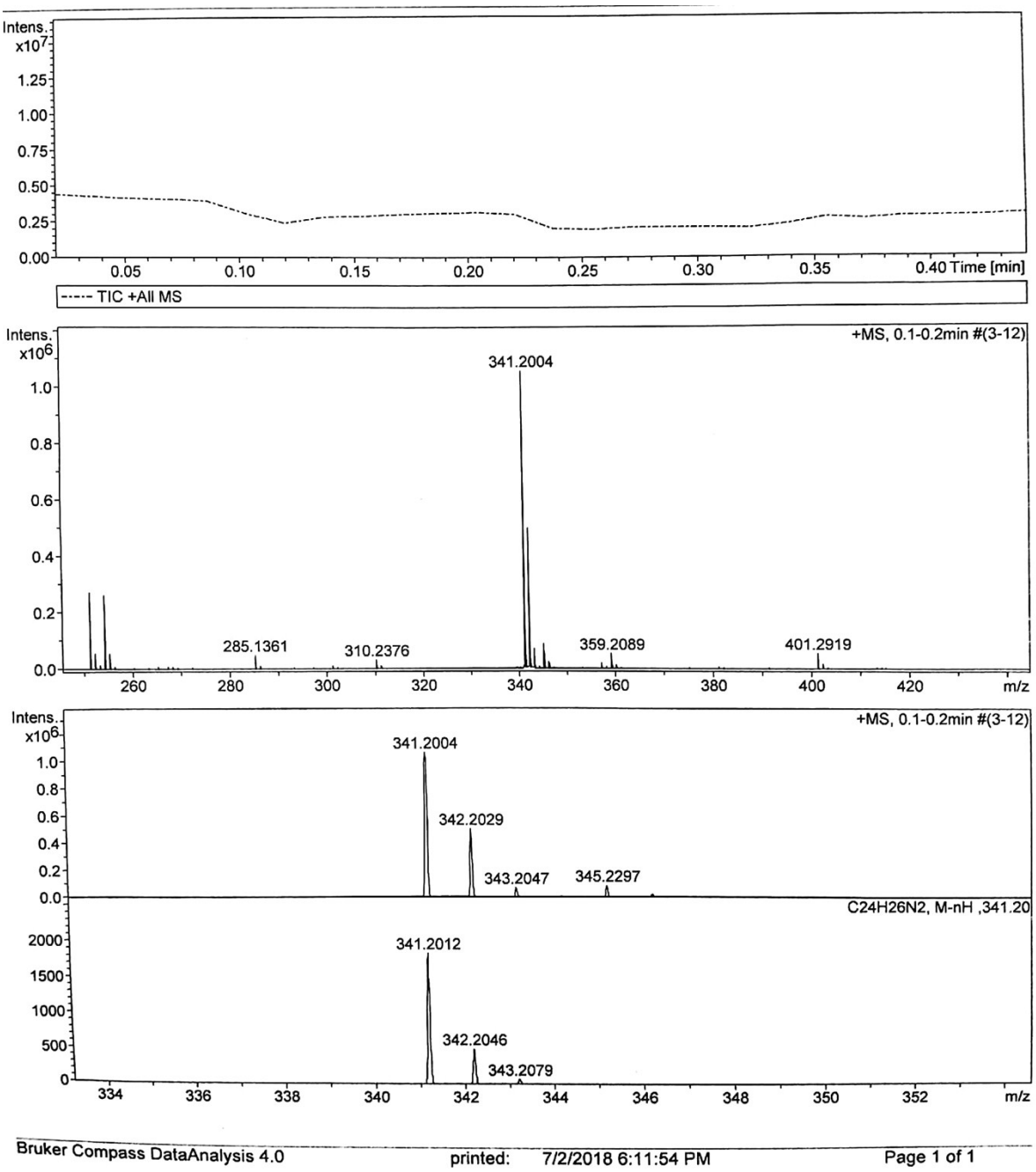


Fig. S103. HRMS of 1-Benzyl-3-butyl-2-phenyl-2,3-dihydro-benzo[d]imidazole (**4**)