Cu-Catalyzed Electrophilic Amination of Internal Alkynes *via* Hydroalumination

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Supporting Information

General. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, with the solvent resonance as the internal standard ($CDCl_3$: δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.00 ppm). High-resolution mass spectra (HRMS) were obtained using an electrospray ionization (ESI) time-of-flight mass spectrometer. Melting points were determined using a melting point apparatus and are uncorrected. Unless otherwise noted, all reactions were carried out with distilled solvents under an atmosphere of dry N_2 in oven-dried (130 ^{o}C) glassware. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl immediately prior to use unless otherwise specified. All work-up and purification procedures were carried out with reagent grade solvents in air. A variety of *N,N*-dialkyl-*O*-benzoyl hydroxylamines[1] and internal alkynes[2] were prepared according to reported experimental procedures.

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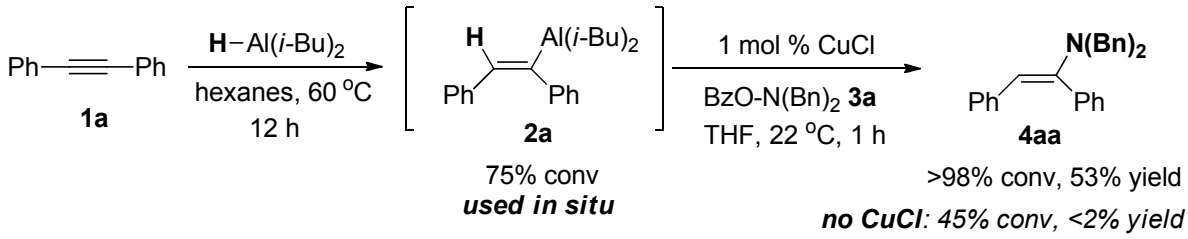
(1) (a) T. J. Barker, E. R. Jarvo, *J. Am. Chem. Soc.* **2009**, *131*, 15598. (b) A. M. Berman, J. S. Johnson, *J. Org. Chem.* **2006**, *71*, 219. (c) A. M. Berman, J. S. Johnson, *J. Org. Chem.* **2005**, *70*, 364. (d) A. M. Berman, A. M.; J. S. Johnson, *Synlett* **2005**, 1799. (e) A. M. Berman, J. S. Johnson, *J. Am. Chem. Soc.* **2004**, *126*, 5680.

■ **Experimental procedure for Cu-catalyzed electrophilic amination of vinylaluminum 2a *via* direct hydroalumination of diphenylacetylene (1a):**



To a solution of diphenylacetylene (**1a**) (178 mg, 1.00 mmol) in hexanes (1.25 mL) was added diisobutylaluminum hydride (178 μL, 1.00 mmol) slowly under N_2 gas. The solution was allowed to heat to 60 °C and stir for 12 h. After that time, the resulting vinylaluminum reagent **2a** (~0.7 M, >98% *E*-vinylAl) [3] was directly used for the amination without further filtration and purification.

O-Benzoyl-*N,N*-dibenzylhydroxylamine (**3a**) (47.6 mg, 0.150 mmol), CuCl (0.200 mg, 1.50×10^{-3} mmol) and THF (0.5 mL) were added to a 8 mL vial under N_2 gas and then vinylaluminum reagent **2a** (~0.7 M in hexanes, 0.320 mL, 0.225 mmol) was added slowly. The reaction mixture was allowed to stir at room temperature for 1 h. After that time, reaction was quenched with an aqueous solution of 1 M NaOH (1 mL) and a saturated aqueous solution of Rochelle`s salt (1 mL). The resulting solution was allowed to stir vigorously for 10 min and washed with EtOAc (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The stereoselectivity of *E*-enamine was determined by analysis of ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the previously reported data.[4] (*E*)-*N,N*-Dibenzyl-1,2-diphenylethenamine (**4aa**) was dominatly observed (>98:<2 *E*:*Z*-enamine).

The crude enamine product was dissolved in CH_2Cl_2 (1.5 mL) and then $NaB(OAc)_3H$ (127 mg, 0.60 mmol) and AcOH (34.3 μL, 0.60 mmol) were added. The reaction mixture was allowed to stir at 22 °C for 12 h. After that time, The resulting solution was quenched with an aqueous solution of 1 M NaOH (1

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(2) (a) T. Torigoe, T. Ohmura, M. Suginome, *Chem. Eur. J.* **2016**, *22*, 10415. (b) K. Park, G. Bae, J. Moon, J. Choe, K. H. Song, S. Lee, *J. Org. Chem.* **2010**, *75*, 6244.

(3) The vinylaluminum reagents reagent **2a** was quenched with H_2O and conversion and stereoselectivity were determined by analysis of ^{1}H NMR spectrum. The (*Z*)-1,2-diphenylethene was observed in >98:<2 *Z*:*E* selectivity. The spectra data of the obtained (*Z*)-1,2-diphenylethene match those reported previously. For spectra data of (*Z*)-1,2-diphenylethene, see: (a) Y. S. Wagh, N. Asao, *J. Org. Chem.* **2015**, *80*, 847. For spectra data of (*E*)-1,2-diphenylethene, see: (b) F. Zhao, J. Luo, Q. Tan, Y. Liao, S. Peng, G.-J. Deng, *Adv. Synth. Catal.* **2012**, *354*, 1914.

(4) J. S. Bandar, M. T. Pirnot, S. L. Buchwald, *J. Am. Chem. Soc.* **2015**, *137*, 14812.

mL) and washed with CH_2Cl_2 (3 x 1mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The desired product was quantified by analysis of ^1H NMR spectra using 1,3,5-trimethoxybenzene as an internal standard (53% NMR yield).

■ **Representative experimental procedures for Cu-catalyzed electrophilic amination of vinylaluminum 2 *via* Ni-catalyzed hydroalumination of internal aryl acetylene 1:**

General procedure A: 1,2-Bis(4-(trifluoromethyl)phenyl)ethyne (**1b**) (141 mg, 0.450 mmol), $Ni(PPh_3)_2Cl_2$ (2.90 mg, 0.00450 mmol) and THF (0.28 mL) were added to a 8 mL vial and then diisobutylaluminum hydride (80.0 μL, 0.450 mmol) was added slowly under N_2 gas. The solution was allowed to stir at 22 °C for 3 h. After that time, to a solution of *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**) (95.2 mg, 0.300 mmol) and CuCl (0.300 mg, 0.00300 mmol) in THF (1 mL) was added slowly the resulting vinylaluminum reagent **2b**. The reaction mixture was allowed to stir at room temperature for 0.5 h. And then the resulting solution was quenched with an aqueous solution of 1 M NaOH (1 mL) and a saturated aqueous solution of Rochelle`s salt (1 mL). The solution was allowed to stir vigorously for 10 min and washed with EtOAc (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was purified by neutral alumina (100% hexanes with 1% of Et_3N → EtOAc:hexanes=1:20) to afford the desired (*E*)-*N,N*-dibenzyl-1,2-bis(4-(trifluoromethyl) phenyl)ethenamine (**4ba**) (132 mg, 0.258 mmol, 86%) as a yellow sticky oil.

General procedure B: Diphenylacetylene (**1a**) (80.2 mg, 0.450 mmol), $Ni(PPh_3)_2Cl_2$ (2.90 mg, 0.00450 mmol) and THF (0.28 mL) were added to a 8 mL vial and then diisobutylaluminum hydride (80.0 μL, 0.450 mmol) was added slowly under N_2 gas. The solution was allowed to stir at 22 °C for 3 h. After that time, to a solution of *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**) (95.2 mg, 0.300 mmol) and CuCl (0.300 mg, 0.00300 mmol) in THF (1 mL) was added slowly the resulting vinylaluminum reagent **2b**. The reaction mixture was allowed to stir at room temperature for 0.5 h. And then the resulting solution was quenched with an aqueous solution of 1 M NaOH (1 mL) and a saturated aqueous solution of Rochelle`s salt (1 mL). The solution was allowed to stir vigorously for 10 min and washed with EtOAc (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude enamine product was dissolved in CH_2Cl_2 (3 mL). And then $NaB(OAc)_3H$ (254 mg, 1.20 mmol) and AcOH (68.7 μL, 1.20 mmol) were added to the mixture, which was allowed to stir at 22 °C for 12 h. After that time, the resulting solution was quenched with an aqueous solution of 1 M NaOH (2 mL) and washed with CH_2Cl_2 (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered and

concentrated. The crude product was purified by silica gel column chromatography (100% hexanes with 1% of Et_3N → EtOAc:hexanes=1:20) to afford the desired *N,N*-dibenzyl-1,2-diphenylethanamine (**4aa'**) (102 mg, 0.270 mmol, 90%) as a colorless oil.

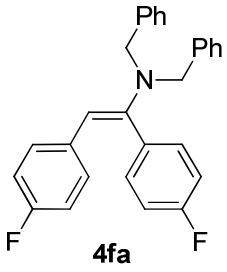
(*E*)-*N,N*-Dibenzyl-1,2-bis(4-(trifluoromethyl)phenyl)ethenamine (4ba). Compound **4ba** was synthesized according to general procedure A using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as a yellow solid in 86% yield (132 mg, 0.258 mmol). The compound exists as a 98:2 mixture of *E*:*Z* isomers after alumina purification. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.36 (dd, *J* = 7.2, 7.2 Hz, 4H), 7.30 (d, *J* = 6.8 Hz, 2H), 7.24 (d, *J* = 7 Hz, 6H), 6.74 (d, *J* = 8.1 Hz, 2H), 5.70 (s, 1H), 4.15 (s, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 149.8, 142.2, 140.6, 137.6, 131.0, 130.3 (q, *J* = 20 Hz), 129.9 (q, *J* = 20 Hz), 128.6, 128.0, 128.0, 127.4, 125.9 (q, *J* = 4.0 Hz), 124.7 (q, *J* = 4.0 Hz), 124.4 (q, *J* = 270 Hz), 124.0 (q, *J* = 271 Hz), 106.6, 52.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{24}F_6N$ 512.1813, Found 512.1807.

(*E*)-*N,N*-Dibenzyl-1,2-bis(3-(trifluoromethyl)phenyl)ethenamine (4ca). Compound **4ca** was synthesized according to general procedure A using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as slightly yellow sticky oil in 71% yield (108 mg, 0.220 mmol). The compound exists as a 96:4 mixture of *E*:*Z* isomers after alumina purification. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.71 (s, 1H), 7.65 (dd, *J* = 5.7, 5.7 Hz, 2H), 7.50 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.40-7.37 (m, 4H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.29-7.20 (m, 4H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.10 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.87 (s, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 5.73 (s, 1H), 4.19 (s, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 149.5, 139.1, 137.7, 134.0, 131.5 (q, *J* = 33 Hz), 130.1 (q, *J* = 32 Hz), 129.5, 128.9, 128.7, 128.6, 128.1, 128.0, 127.4 (q, *J* = 4.0 Hz), 127.4, 125.5 (q, *J* = 4.0 Hz), 124.7 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 272 Hz), 123.9 (q, *J* = 272 Hz), 120.7 (q, *J* = 4.0 Hz), 106.4, 52.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{24}F_6N$ 512.1813, Found 512.1810.

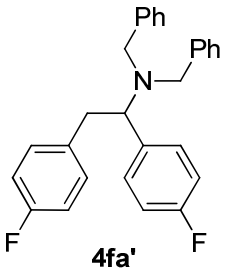
(*E*)-*N,N*-Dibenzyl-1,2-bis(3-methoxyphenyl)ethenamine (4da). Compound **4da** was synthesized according to general procedure A using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as slightly yellow sticky oil in 91% yield (119 mg, 0.273 mmol). The compound exists as a 93:7 mixture of *E*:*Z* isomers after alumina purification. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.36-7.31 (m, 5H), 7.30-7.26 (m, 6H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.06 (s, 1H), 6.99-6.89 (m, 2H), 6.49 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 1H), 6.28 (s, 1H), 5.62 (s, 1H), 4.17 (s, 4H), 3.76 (s, 3H), 3.53 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 160.1, 159.1, 149.5, 140.4, 138.9, 138.4, 129.8, 129.2, 128.5, 128.4, 128.1,

127.3, 127.0, 123.2, 121.0, 116.0, 114.2, 112.5, 110.4, 106.4, 55.2, 54.7, 52.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{30}NO_2$ 436.2277, Found 436.2265.

(*E*)-*N,N*-Dibenzyl-1,2-bis(4-chlorophenyl)ethenamine (4ea). Compound **4ea** was synthesized according to general procedure A using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as yellow-green sticky oil in 85% yield (114 mg, 0.256 mmol). The compound exists as a >98:<2 mixture of *E*:*Z* isomers after alumina purification. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.36-7.32 (m, 6H), 7.29-7.26 (m, 2H), 7.24-7.22 (m, 4H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 5.58 (s, 1H), 4.11 (s, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.8, 138.0 137.2, 135.5, 134.5, 132.0, 129.6, 129.4, 129.2, 129.1, 129.0, 128.6, 128.6, 128.5, 128.1, 127.9, 127.2, 106.6, 52.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{24}Cl_2N$ 444.1286, Found 444.1290.

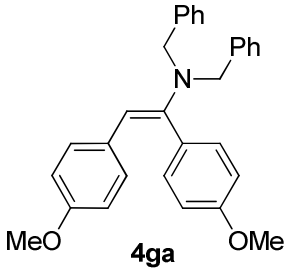


4fa

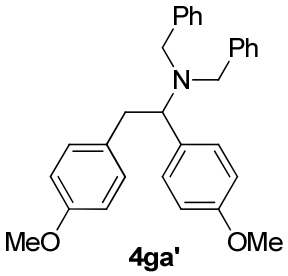


4fa'

***N,N*-Dibenzyl-1,2-bis(4-fluorophenyl)ethanamine (4fa').** Compound **4fa'** was synthesized according to general procedure B using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as a white solid in 95% yield (118 mg, 0.285 mmol). mp 107-108 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.30-7.27 (m, 5H), 7.25-7.20 (m, 7H), 7.08 (dd, *J* = 8.6, 8.6 Hz, 2H), 7.02 (dd, *J* = 8.6, 5.4 Hz, 2H), 6.94 (dd, *J* = 8.6, 8.6 Hz, 2H), 4.00 (t, *J* = 7.7 Hz, 1H), 3.87 (d, *J* = 13.9 Hz, 2H), 3.35 (dd, *J* = 13.9, 8.2 Hz, 1H), 3.18 (d, *J* = 13.9 Hz, 2H), 3.00 (dd, *J* = 13.9, 7.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 162.0 (d, *J* = 245 Hz), 161.5 (d, *J* = 243 Hz), 139.7, 135.3 (d, *J* = 3.0 Hz), 134.0 (d, *J* = 3.0 Hz), 130.8 (d, *J* = 8.0 Hz), 130.4 (d, *J* = 8.0 Hz), 128.6, 128.3, 126.9, 115.0 (d, *J* = 5.8 Hz), 114.7 (d, *J* = 5.8 Hz), 62.7, 53.5, 36.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{26}F_2N$ 414.2033, Found 414.2032.

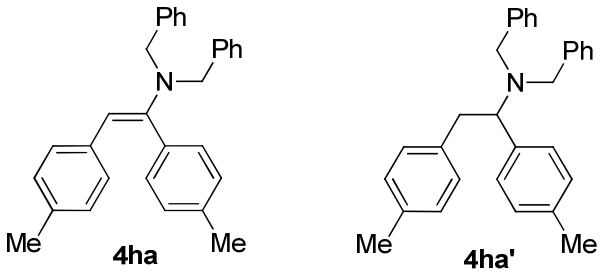


4ga



4ga'

***N,N*-Dibenzyl-1,2-bis(4-methoxyphenyl)ethanamine (4ga').** Compound **4ga'** was synthesized according to general procedure B using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as a white solid in 87% yield (114 mg, 0.261 mmol). mp 75-76 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.26-7.20 (m, 10H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 3.96 (t, *J* = 7.7 Hz, 1H), 3.86 (d, *J* = 14.4 Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.30 (dd, *J* = 13.9, 8.0 Hz, 1H), 3.19 (d, *J* = 14.1 Hz, 2H), 3.00 (dd, *J* = 14.0, 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 158.6, 157.9, 140.2, 132.9, 132.1, 130.4, 130.1, 128.6, 128.2, 126.7, 113.4, 113.2, 62.6, 55.2, 55.1, 53.4, 36.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{32}NO_2$ 438.2433, Found 438.2436.



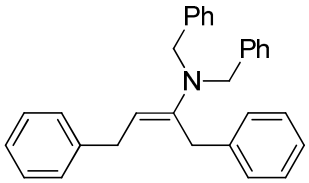
***N,N*-Dibenzyl-1,2-di-p-tolylethanamine (4ha').** Compound **4ha'** was synthesized according to general procedure B using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as colorless sticky oil in 93% yield (113 mg, 0.279 mmol). mp 66-67 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.26-7.18 (m, 10H), 7.16 (dd, *J* = 7.1, 7.1 Hz, 4H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 4.00 (t, *J* = 7.6 Hz, 1H), 3.86 (d, *J* = 13.9 Hz, 2H), 3.33 (dd, *J* = 13.9, 8.0 Hz, 1H), 3.19 (d, *J* = 13.9 Hz, 2H), 3.05 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.2, 136.9, 136.6, 135.4, 135.2, 129.4, 129.0, 128.7, 128.7, 128.2, 126.7, 62.8, 53.5, 37.1, 21.0, 21.0; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{32}N$ 406.2535, Found 406.2534.

(*E*)-*N,N*-Dibenzyl-1,2-bis(2-fluorophenyl)ethenamine (4ia). Compound **4ia** was synthesized according to general procedure A using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as pale yellow sticky oil in 62% yield (76.1 mg, 0.185 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.41-7.24 (m, 12H), 7.12-7.05 (m, 2H), 6.88 (dd, *J* = 6.0, 6.0 Hz, 2H), 6.66-6.62 (m, 1H), 6.46 (dd, *J* = 7.8, 7.8 Hz, 1H), 5.77 (s, 1H), 4.22 (s, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 160.9 (d, *J* = 248 Hz), 159.9 (d, *J* = 244 Hz), 144.5, 138.2, 132.6 (d, *J* = 4.0 Hz), 130.5 (d, *J* = 4.0 Hz), 128.8 (d, *J* = 3.0 Hz), 128.4, 128.0, 127.0, 126.7, 125.5 (d, *J* = 8.0 Hz), 124.9, 124.5 (d, *J* = 4.0 Hz), 123.1 (d, *J* = 4.0 Hz), 116.1 (d, *J* = 22.4 Hz), 114.7 (d, *J* = 22.4 Hz), 98.7, 52.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{24}F_2N$ 412.1877, Found 412.1880.

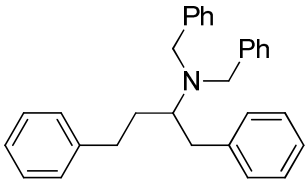
(*E*)-*N,N*-Dibenzyl-1,2-di-o-tolylethenamine (4ja). Compound **4ja** was synthesized according to

general procedure A using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as yellowish sticky oil in 30% yield (36.5 mg, 0.090 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.36-7.29 (m, 10H), 7.20 (dd, *J* = 6.7, 6.7 Hz, 2H), 7.12 (dd, *J* = 6.3, 6.3 Hz, 2H), 7.01 (d, 7.4 Hz, 1H), 6.82 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.66 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.36 (d, *J* = 7.9 Hz, 1H), 5.67 (s, 1H), 4.30 (d, *J* = 15.4 Hz, 2H), 4.14 (d, *J* = 15.3 Hz, 2H), 2.21 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.2, 139.6, 138.9, 137.8, 136.6, 135.2, 131.1, 130.3, 129.4, 129.1, 128.4, 128.0, 126.9, 126.6, 125.8, 125.0, 124.1, 103.5, 52.7, 20.3, 19.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{30}N$ 404.2378, Found 404.2376.

(*E*)-*N,N*-Dibenzyl-1,2-di(thiophen-2-yl)ethenamine (4ka). Compound **4ka** was synthesized according to general procedure A using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as yellow sticky oil in 76% yield (88.7 mg, 0.229 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.54 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.38-7.31 (m, 5H), 7.30-7.23 (m, 6H), 7.11 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.84 (dd, 5.3, 0.9 Hz, 1H), 6.78 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 5.94 (s, 1H), 4.20 (s, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.5, 140.5, 138.1, 137.7, 130.4, 128.5, 128.2, 127.9, 127.5, 127.1, 126.1, 124.0, 122.0, 102.6, 52.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{22}NS_2$ 388.1194, Found 388.1179.



4la



4la'

***N,N*-Dibenzyl-1,4-diphenylbutan-2-amine (4la'). Compound 4la'** was synthesized according to general procedure B using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as colorless oil in 72% yield (88.0 mg, 0.217 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.36-7.10 (m, 16H), 7.02 (dd, *J* = 5.6, 5.6 Hz, 4H), 3.83 (d, *J* = 13.6 Hz, 2H), 3.59 (d, *J* = 13.9 Hz, 2H), 3.13 (dd, *J* = 13.2, 4.6 Hz, 1H), 2.96-2.82 (m, 2H), 2.49 (dd, *J* = 13.2, 8.8 Hz, 1H), 2.35-2.26 (m, 1H), 1.94-1.82 (m, 1H), 1.66-1.56 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.7, 140.3, 139.7, 130.4, 130.0, 129.4, 128.9, 128.5, 128.4, 128.3, 126.9, 126.0, 57.9, 53.4, 35.2, 33.4, 32.3; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{32}N$ 406.2535, Found 406.2535.

***N,N*-Dibenzyl-1,2-diphenylethanamine (4aa')**. Compound **4aa'** was synthesized according to general procedure B using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as a white solid in 90% yield (102 mg, 0.270 mmol). This compound has been previously reported and spectra data

match described.[5] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.44-7.40 (m, 2H), 7.36-7.23 (m, 16H), 7.14-7.12 (m, 2H), 4.10 (dd, *J* = 7.4, 7.4 Hz, 1H), 3.93 (d, *J* = 14.2 Hz, 2H), 3.43 (dd, *J* = 14.0, 8.5 Hz, 1H), 3.24 (d, *J* = 13.9 Hz, 2H), 3.12 (dd, *J* = 13.9, 7.1 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.0, 139.9, 138.5, 129.6, 129.1, 128.7, 128.2, 128.1, 128.0, 127.2, 126.7, 126.0, 63.1, 53.5, 37.6.

***N*-(1,2-Diphenylethyl)-*N*-isopropylpropan-2-amine (4ab)**. Compound **4ab** was synthesized according to general procedure B using *O*-benzoyl-*N,N*-diisopropylhydroxylamine (**3b**, 0.300 mmol). The resulting reaction product was purified by acid/base workup. The crude product was diluted with Et_2O (1 mL) and acidified with 1 N HCl (3 x 1 mL). The aqueous layers were combined, basified with 1 N NaOH (3 mL) and washed with Et_2O (3 x 3 mL). Then the organic layers were combined, dried over $MgSO_4$ and concentrated to afford as a colorless oil in 66% yield (56.1 mg, 0.199 mmol). This compound has been previously reported and spectra data match described.[6] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.33 (d, *J* = 7.3 Hz, 2H), 7.24-7.13 (m, 5H), 7.13-7.07 (m, 3H), 4.22 (dd, *J* = 8.8, 5.9 Hz, 1H), 3.30 (sept, *J* = 6.7 Hz, 2H), 3.21-3.10 (m, 2H), 1.06 (d, *J* = 6.6 Hz, 6H), 0.91 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 144.1, 140.6, 129.3, 128.8, 128.0, 127.8, 126.2, 125.6, 60.5, 45.6, 41.0, 23.0, 22.4.

***N*-Allyl-*N*-(1,2-Diphenylethyl)prop-2-en-1-amine (4ac)**. Compound **4ac** was synthesized according to general procedure B using *N,N*-diallyl-*O*-benzoylhydroxylamine (**3c**, 0.300 mmol) to obtain as colorless oil in 61% yield (51.1 mg, 0.184 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.30-7.27 (m, 2H), 7.24-7.17 (m, 5H), 7.13 (d, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 7.1 Hz, 2H), 5.82-5.72 (m, 2H), 5.16-5.09 (m, 4H), 4.03 (t, *J* = 7.5 Hz, 1H), 3.36-3.27 (m, 3H), 2.97 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.86 (dd, *J* = 14.4, 7.3 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.1, 139.9, 136.9, 129.4, 128.9, 127.9, 127.9, 127.0, 125.8, 116.8, 65.1, 52.7, 38.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{24}N$ 278.1909, Found 278.1897.

***N*-Benzyl-*N*-methyl-1,2-diphenylethanamine (4ad)**. Compound **4ad** was synthesized according to general procedure B using *O*-benzoyl-*N*-benzyl-*N*-methylhydroxylamine (**3d**, 0.300 mmol) to obtain as colorless oil in 75% yield (68.0 mg, 0.226 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.44-7.26 (m, 13H), 7.16 (d, *J* = 7.3 Hz, 2H), 3.95 (t, *J* = 7.5 Hz, 1H), 3.76 (d, *J* = 13.2 Hz, 1H), 3.49 (dd, *J* = 13.7, 6.6 Hz, 1H), 3.43 (d, *J* = 13.4 Hz, 1H), 3.14 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.0, 140.0, 139.5, 129.5, 128.9, 128.7, 128.2, 128.0, 127.9, 127.0, 126.8, 125.8, 69.5, 58.8, 38.8, 38.0; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{24}N$ 302.1909, Found 302.1910.

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(5) S. Zhu, N. Niljianskul, S. L. Buchwald, *J. Am. Chem. Soc.* **2013**, *135*, 15746

(6) H. Takahashi, T. Tsubuki, K. Higashiyama, *Synthesis* **1988**, *3*, 238.

1-(1,2-Diphenylethyl)piperidine (4ae). Compound **4ae** was synthesized according to general procedure B using piperidin-1-yl benzoate (**3e**, 0.300 mmol) to obtain as colorless oil in 80% yield (63.5 mg, 0.239 mmol). This compound has been previously reported and spectra data match described.[7] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.33-7.25 (m, 3H), 7.22-7.14 (m, 5H), 7.08 (d, *J* = 7.0 Hz, 2H), 3.67 (dd, *J* = 9.2, 5.1 Hz, 1H), 3.39 (dd, *J* = 13.3, 5.0 Hz, 1H), 3.07 (dd, *J* = 13.0, 9.6 Hz, 1H), 2.56-2.51 (m, 4H), 1.71-1.58 (m, 4H), 1.45 (q, *J* = 5.6 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.0, 139.5, 129.4, 129.0, 127.9, 127.7, 126.7, 125.7, 72.3, 51.3, 39.1, 26.3, 24.6.

4-(1,2-Diphenylethyl)thiomorpholine (4af). Compound **4af** was synthesized according to general procedure B using thiomorpholino benzoate (**3f**, 0.300 mmol) to obtain as a white solid in 85% yield (72.6 mg, 0.256 mmol). This compound has been previously reported and spectra data match described.[7] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.30-7.21 (m, 3H), 7.20-7.09 (m, 5H), 7.06 (d, *J* = 7.1 Hz, 2H), 3.73 (t, *J* = 7.3 Hz, 1H), 3.27 (dd, *J* = 13.7, 6.3 Hz, 1H), 3.02 (dd, *J* = 13.7, 8.5 Hz, 1H), 2.87-2.82 (m, 2H), 2.74-2.67 (m, 2H), 2.65-2.59 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.8, 139.0, 129.3, 128.7, 128.1, 128.0, 127.2, 125.9, 72.0, 52.2, 29.6, 28.2.

4-(1,2-Diphenylethyl)morpholine (4ag). Compound **4ag** was synthesized according to general procedure B using morpholino benzoate (**3g**, 0.300 mmol) to obtain as colorless oil in 79% yield (63.3 mg, 0.237 mmol). This compound has been previously reported and spectra data match described.[7] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.25-7.19 (m, 3H), 7.17-7.08 (m, 5H), 6.94 (d, *J* = 6.9 Hz, 2H), 3.71 (t, *J* = 4.7 Hz, 4H), 3.49 (dd, *J* = 9.4, 5.3 Hz, 1H), 3.34 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.89 (dd, *J* = 12.9, 9.5 Hz, 1H), 2.56-2.45 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.8, 139.3, 129.4, 128.8, 127.9, 127.1, 125.8, 72.5, 67.2, 51.2, 39.2.

***tert*-Butyl 4-(1,2-diphenylethyl)piperazine-1-carboxylate (4ah).** Compound **4ah** was synthesized according to general procedure B using *tert*-butyl 4-(benzoyloxy)piperazine-1-carboxylate (**3h**, 0.300 mmol) to obtain as colorless oil in 83% yield (91.3 mg, 0.249 mmol). This compound has been previously reported and spectra data match described.[7] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.25-7.20 (m, 3H), 7.17-7.10 (m, 5H), 6.98 (d, *J* = 6.8 Hz, 2H), 3.59 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.40 (brs, 4H), 3.32 (dd, *J* = 13.3, 5.7 Hz, 1H), 2.96 (dd *J* = 13.3, 9.2 Hz, 1H), 2.44 (brs, 4H), 1.43 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 154.7, 139.4, 139.4, 129.4, 128.7, 128.0, 127.2, 125.8, 79.4, 71.8, 50.1, 44.2, 39.1, 28.3.

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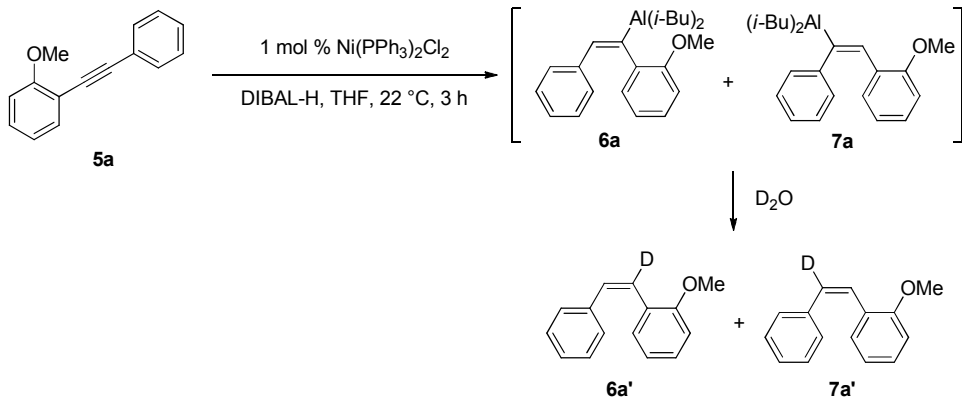
(7) K. D. Hesp, M. Stradiotto, M. *J. Am. Chem. Soc*. **2010**, *132*, 18026.

***tert*-Butyl 4-(1,2-diphenylethyl)-1,4-diazepane-1-carboxylate (4ai).** Compound **4ai** was synthesized according to general procedure B using *tert*-butyl 4-(benzoyloxy)-1,4-diazepane-1-carboxylate (**3i**, 0.300 mmol) to obtain as colorless sticky oil in 69% yield (78.4 mg, 0.206 mmol). The compound exists as a 1:1 mixture of ratamers. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.26-7.09 (m, 8H), 7.05 (dd, *J* = 7.5, 7.5 Hz, 2H), 3.90 (dd, *J* = 12.7, 5.9 Hz, 1H), 3.52-3.30 (m, 4H), 3.30-3.20 (m, 1H), 3.04-2.92 (m, 1H), 2.86-2.70 (m, 2H), 2.70-2.62 (m, 1H), 2.62-2.52 (m, 1H), 1.79-1.72 (m, 1H), 1.72-1.65 (m, 1H), 1.44 (d, *J* = 3.9 Hz, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 155.6, 140.6, 139.9, 129.3, 128.4, 128.0, 127.9, 127.0, 125.8, 79.1, 70.4, 52.9, 51.9, 47.6, 45.9, 39.2, 28.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{33}N_2O_2$ 381.2542, Found 381.2549.

***N*-(1,2-Diphenylethyl)-2-methylpropan-2-amine (4aj)**. Compound **4aj** was synthesized according to general procedure B using *O*-benzoyl-*N*-(*tert*-butyl)hydroxylamine (**3j**, 0.300 mmol). The resulting reaction product was purified by acid/base workup. The crude product was diluted with Et_2O (1 mL) and acidified with 1 N HCl (3 x 1 mL). The aqueous layers were combined, basified with 1 N NaOH (3 mL) and washed with Et_2O (3 x 3 mL). Then the organic layers were combined, dried over $MgSO_4$ and concentrated to afford as colorless oil in 36% yield (27.0 mg, 0.107 mmol). This compound has been previously reported and spectra data match described.[8] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.26 (dd, *J* = 13.7, 7.1 Hz, 3H), 7.18 (dd, *J* = 7.1, 7.1 Hz, 3H), 7.13 (d, *J* = 7.6 Hz, 2H), 3.98 (dd, *J* = 8.8, 5.7 Hz, 1H), 2.91 (dd, *J* = 13.5, 5.4 Hz, 1H), 2.70 (dd, *J* = 13.5, 9.1 Hz, 1H), 0.82 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.6, 139.3, 129.4, 128.3, 128.1, 127.2, 126.5, 126.4, 59.2, 51.1, 47.1, 29.8.

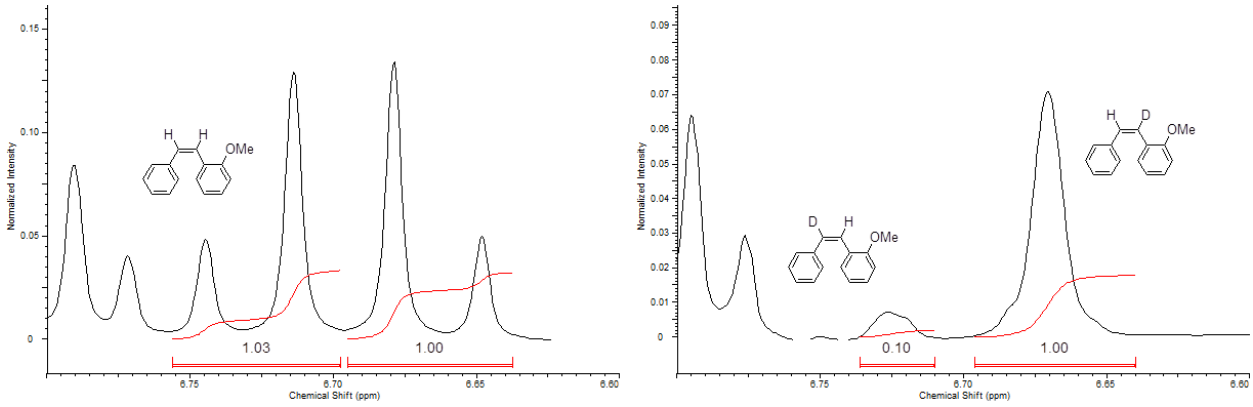
■ **Ni-catalyzed hydroalumination of internal aryl acetylene 5a:**



(8) M. Esteruelas, A. M. López, A. C. Mateo, E. Oñate, *Organometallics* **2005**, *24*, 5084.

1-Methoxy-2-(phenylethynyl)benzene (**5a**) (41.7 mg, 0.200 mmol), $Ni(PPh_3)_2Cl_2$ (1.30 mg, 0.00200 mmol) and THF (0.2 mL) were added to a 8 mL vial and then diisobutylaluminum hydride (35.6 μL, 0.200 mmol) was added slowly under N_2 gas. The solution was allowed to stir at 22 °C for 3 h. After that time, the solution was quenched with D_2O (or H_2O) and the stereo- and site selectivity were determined by analysis of ^{1}H NMR spectra. The (*Z*)-1-methoxy-2-styrylbenzene was observed in >98:<2 *Z*:*E* selectivity. The (*Z*)-1-methoxy-2-styrylbenzene has been previously reported and spectra data match described.[9] **(*Z*)-1-methoxy-2-styrylbenzene: ^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.27-7.16 (m, 6H), 6.90 (d, *J* = 8.3 Hz , 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 12.2 Hz, 1H), 6.64 (d, *J* = 12.2 Hz, 1H), 3.86 (s, 3H); **(*Z*)-1-(1-deutrio-2-phenylvinyl)-2-methoxybenzene (6a'): ^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.27-7.16 (m, 6H), 6.90 (d, *J* = 8.3 Hz , 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.64 (s, 1H), 3.86 (s, 3H).

Site selectivity (91:9) was determined by analysis of ^{1}H NMR spectra of the unpurified reaction mixtures through comparison of the protonated sample (below left) with deuterated sample (below right).



(*E*)-*N*,*N*-Dibenzyl-1-(2-methoxyphenyl)-2-phenylethenamine (8aa). Compound **8aa** was synthesized according to general procedure A using *O*-benzoyl-*N*,*N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as slightly yellow oil in 89% yield (108 mg, 0.267 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.38-7.32 (m, 10H), 7.29-7.22 (m, 2H), 6.99-6.94 (m, 4H), 6.85 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 2H), 5.64 (s, 1H), 4.32 (d, *J* = 15.9 Hz, 2H), 4.23 (d, *J* = 15.9 Hz, 2H), 3.78 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 158.1, 145.7, 139.5, 138.9, 132.0, 129.9, 128.3, 127.8, 127.6, 127.1, 128.7, 126.3, 123.3, 121.3, 111.3, 103.6, 55.4, 52.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{28}NO$ 406.2171, Found 406.2148.

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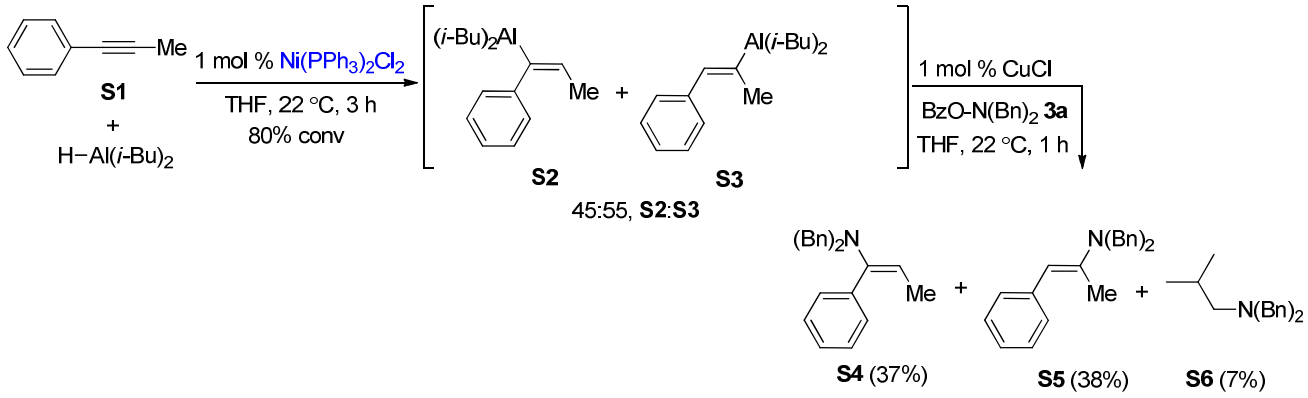
(9) J. Li, R. Hua, T. Liu, *J. Org. Chem.* **2010**, *75*, 2966.

(*E*)-*N,N*-Dibenzyl-2-(3-chlorophenyl)-1-(2-methoxyphenyl)ethenamine (8ba). Compound **8ba** was synthesized according to general procedure A using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as slightly yellow sticky oil in 84% yield (111 mg, 0.252 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.40-7.24 (m, 12H), 6.98 (dd, *J* = 7.3, 7.3 Hz, 2H), 6.85 (dd, 7.7, 7.7 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.58 (s, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.53 (s, 1H), 4.35 (d, *J* = 15.8 Hz, 2H), 4.25 (d, *J* = 15.8 Hz, 2H), 3.80 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 157.9, 147.0, 141.6, 138.6, 133.4, 131.7, 130.3, 128.6, 128.4, 127.6, 126.8, 126.8, 125.7, 124.9, 122.9, 121.5, 111.3, 101.3, 55.4, 52.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{27}ClNO$ 440.1781, Found 440.1787.

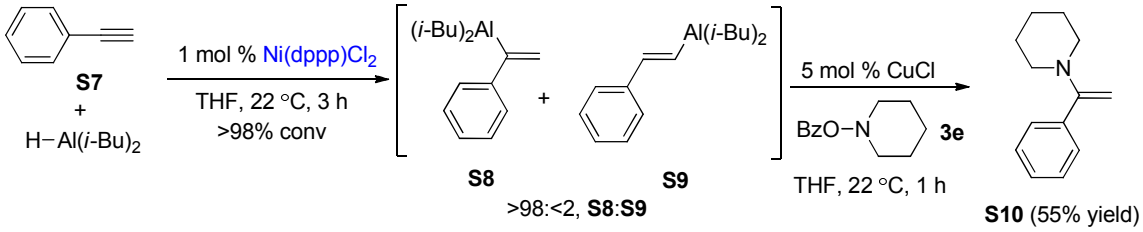
(*E*)-*N,N*-Dibenzyl-1-(2-methoxyphenyl)-2-(3-(trifluoromethyl)phenyl)ethenamine (8ca). Compound **8ca** was synthesized according to general procedure A using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as yellow sticky oil in 80% yield (114 mg, 0.241 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.39-7.24 (m, 12H), 7.03-7.01 (m, 2H), 6.96 (dd, *J* =7.3, 4.4 Hz, 2H), 6.80 (s, 1H), 6.75 (d, *J* = 6.8 Hz, 1H), 5.58 (s, 1H), 4.34 (d, *J* = 15.8 Hz, 2H), 4.24 (d, *J* = 15.8 Hz, 2H), 3.76 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 157.9, 147.4, 140.4, 138.5, 131.7, 130.4, 129.8 (q, *J* = 32 Hz), 128.4, 128.4 (q, *J* = 17 Hz), 127.6, 127.7 (q, *J* = 16 Hz), 126.9, 125.5, 124.4 (q, *J* = 272 Hz), 123.5 (q, *J* = 4 Hz), 121.5, 111.2, 101.2, 55.5, 52.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{27}F_3NO$ 474.2045, Found 474.2048.

(*E*)-*N,N*-Dibenzyl-2-(4-fluorophenyl)-1-(2-methoxyphenyl)ethenamine (8da). Compound **8da** was synthesized according to general procedure A using *O*-benzoyl-*N,N*-dibenzylhydroxylamine (**3a**, 0.300 mmol) to obtain as colorless sticky oil in 87% yield (111 mg, 0.262 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.58-7.50 (m, 1H), 7.38-7.23 (m, 10H), 6.98-6.93 (m, 3H), 6.66 (dd, *J* = 12.2, 8.8 Hz, 2H), 6.59 (dt, *J* = 6.0, 2.7 Hz, 2H), 5.58 (s, 1H), 4.28 (d, *J* = 15.6 Hz, 2H), 4.21 (d, *J* = 15.6 Hz, 2H), 3.77 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 159.7 (d, *J* = 242 Hz), 158.0, 145.5, 138.9, 135.6 (d, *J* = 3.0 Hz), 133.6 (d, *J* = 3.0 Hz), 132.1, 130.0, 129.9, 128.3 (d, *J* = 6.0 Hz), 127.8, 126.8, 126.1, 121.2, 120.6, 114.2 (d, *J* = 12 Hz), 111.2, 102.5, 55.3, 52.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{29}H_{27}FNO$ 424.2077, Found 424.2063.

■ **Cu-catalyzed electrophilic amination of 1-phenyl-1-propyne:**[10]



■ **Cu-catalyzed electrophilic amination of phenylacetylene:**[11]



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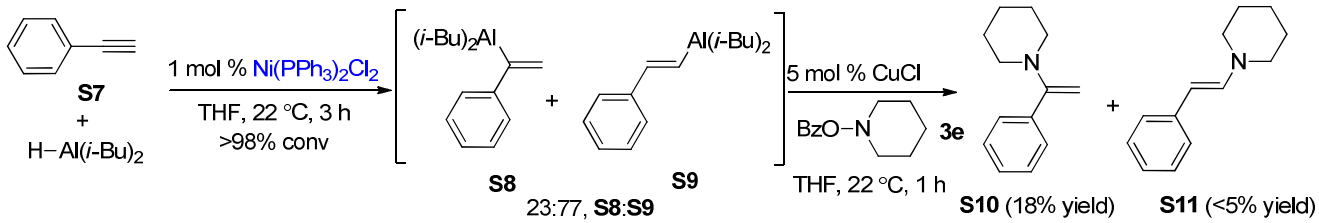
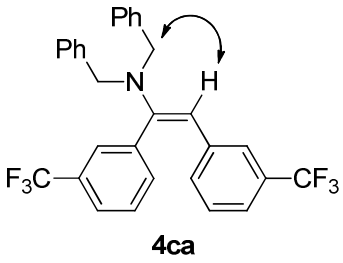
(10) (a) Reaction was performed according to general procedure A. Yields were determined by ^{1}H NMR spectrum analysis using 1,3,5-trimethoxybenzene as an internal standard. (b) The hydroalumination of 1-phenyl-1-propyne (**S1**) in the presence of 1 mol % of Ni(dppp)Cl_2 was also not regioselective, delivering a 55:45 mixture of **S2** and **S3** vinylaluminums.

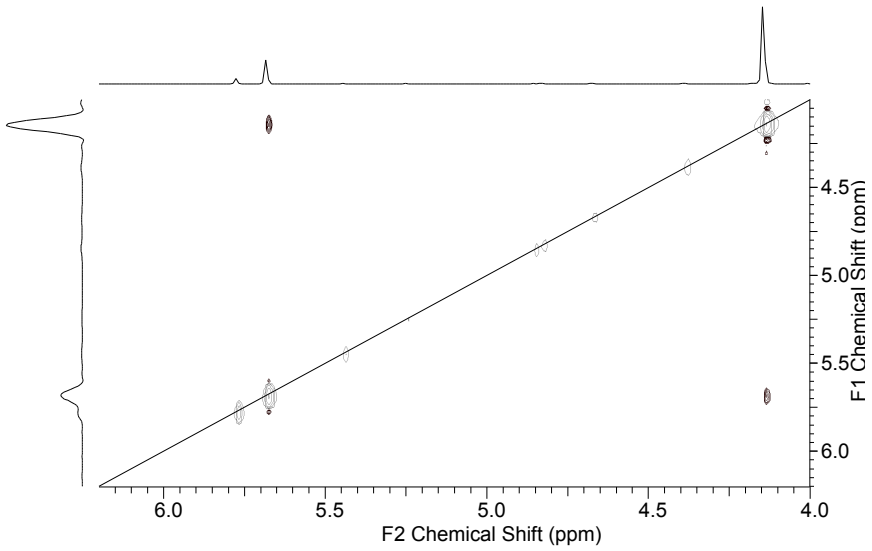
(11) Reactions were performed according to general procedure A. Yields were determined by ^{1}H NMR spectrum analysis using 1,3,5-trimethoxybenzene as an internal standard. Hydroalumination of phenylacetylene (**S7**) with 1 mol % Ni(dppp)Cl_2 provided the internal vinylaluminum **S8** in >98% yield. Cu-catalyzed electrophilic amination of **S8** with **3e** was less efficient than that of 1,2-diaryl-substituted vinylaluminums, affording the desired enamine product **S10** in 55% yield with unidentified byproducts. In the presence of 1 mol % Ni(PPh_3)$_2Cl_2$, hydroalumination of **S7** resulted in a 23:77 mixture of **S8** and **S9** vinylaluminums (a 12:88 mixture of **S8** and **S9** under the conditions developed by the Hoveyda group (F. Gao, A. H. Hoveyda, *J. Am. Chem. Soc.* **2010**, *132*, 10961.)). When the following amination with a mixture of regioisomers was carried out, vinylaluminum **S8** was aminated in 18% yield of the desired enamine **S10**. However, amination of terminal vinylaluminum **S9** did not proceed efficiently to give the enamine product **S11** (<5% yield) under the optimized conditions for internal aryl acetylenes.

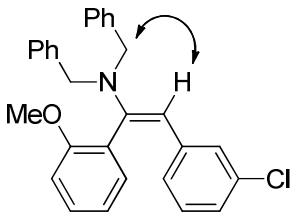


■ 2D-NOSEY proton NMR specta of enamines 4ca and 8ba and ^{1}H NOESY correlations

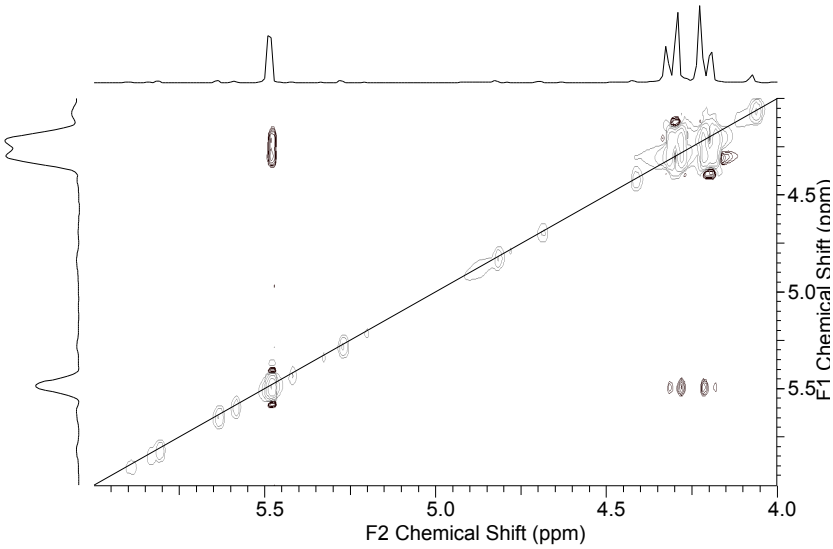


4ca





8ba



■ **^{1}H NMR and ^{13}C NMR spectra for all products:**

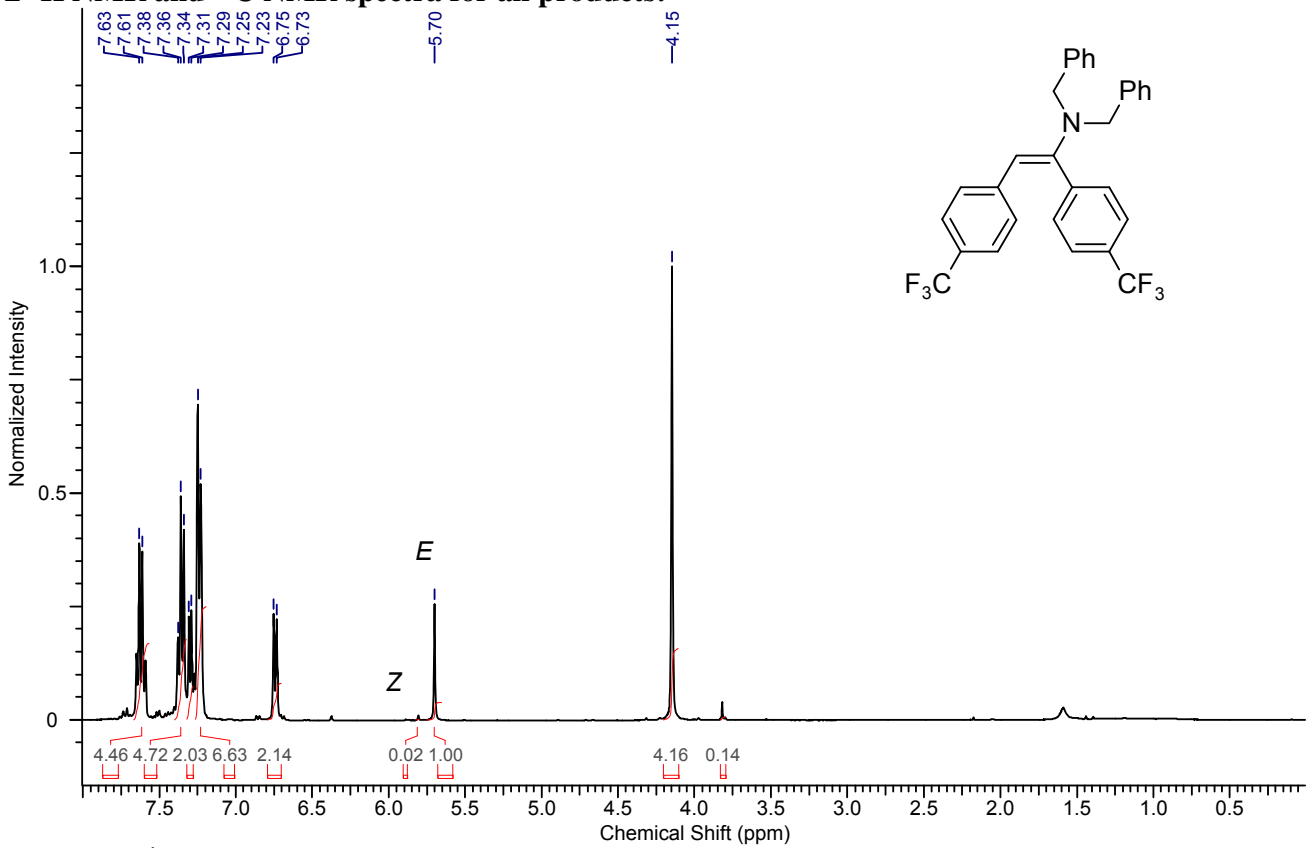


Figure S1. ^{1}H NMR spectrum of the compound **4ba** (98:2 mixture of *E*:*Z* isomers)

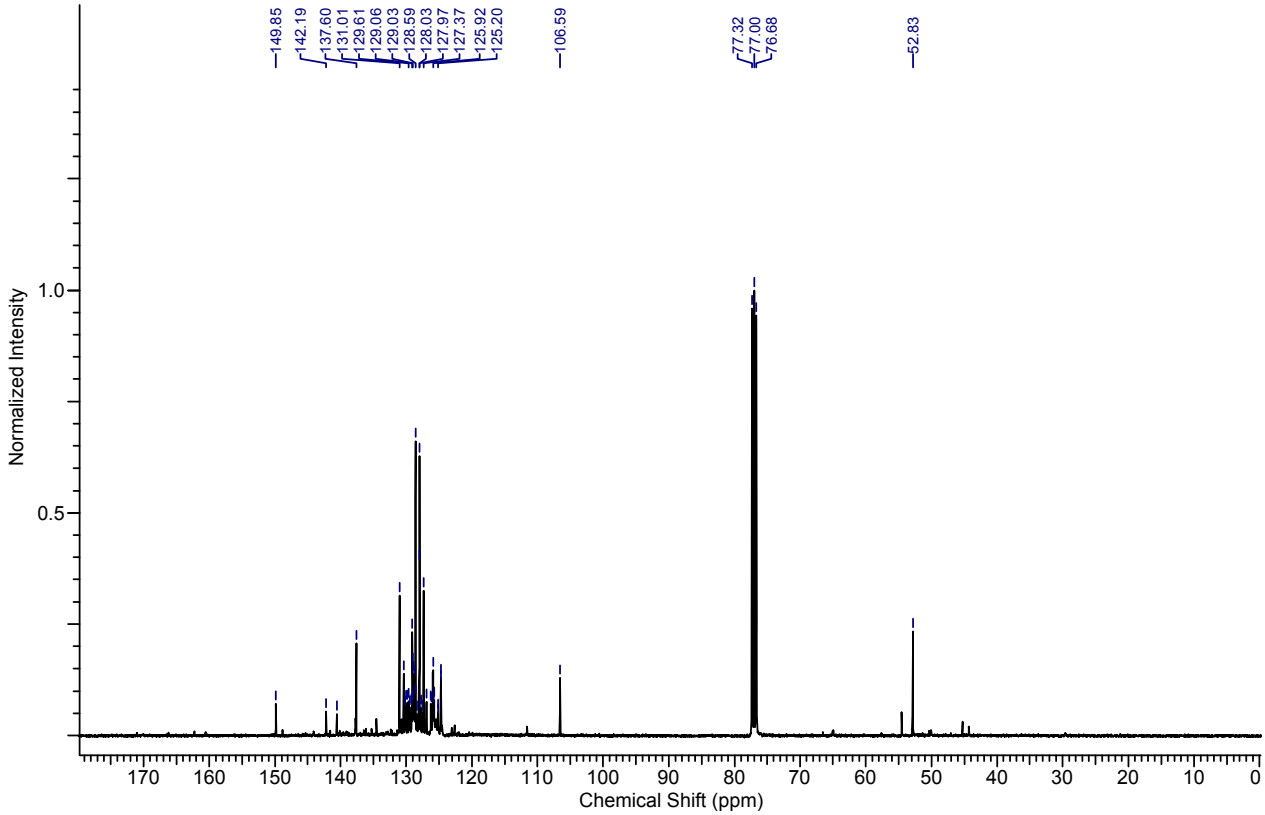


Figure S2. ^{13}C NMR spectrum of the compound **4ba**

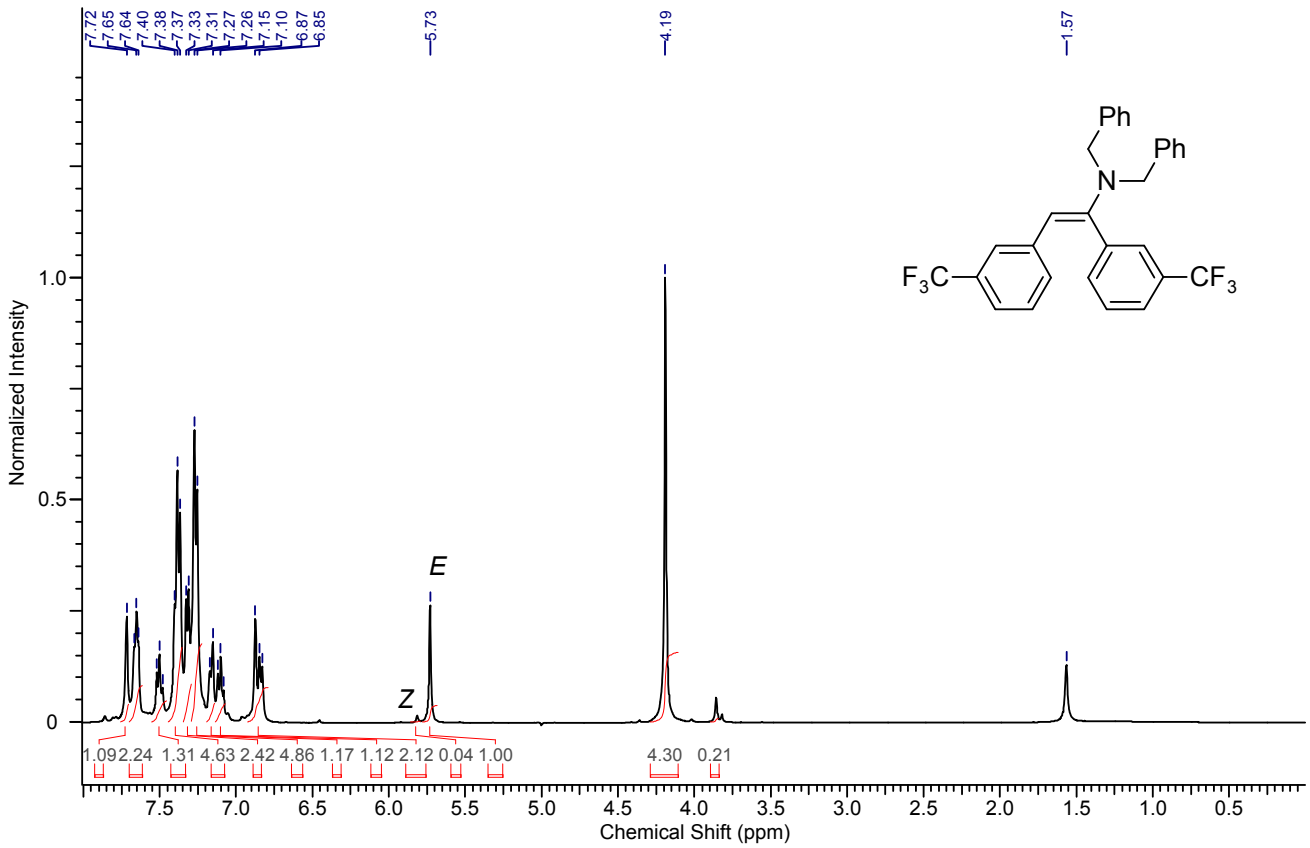


Figure S3. ^{1}H NMR spectrum of the compound **4ca** (96:4 mixture of *E*:*Z* isomers)

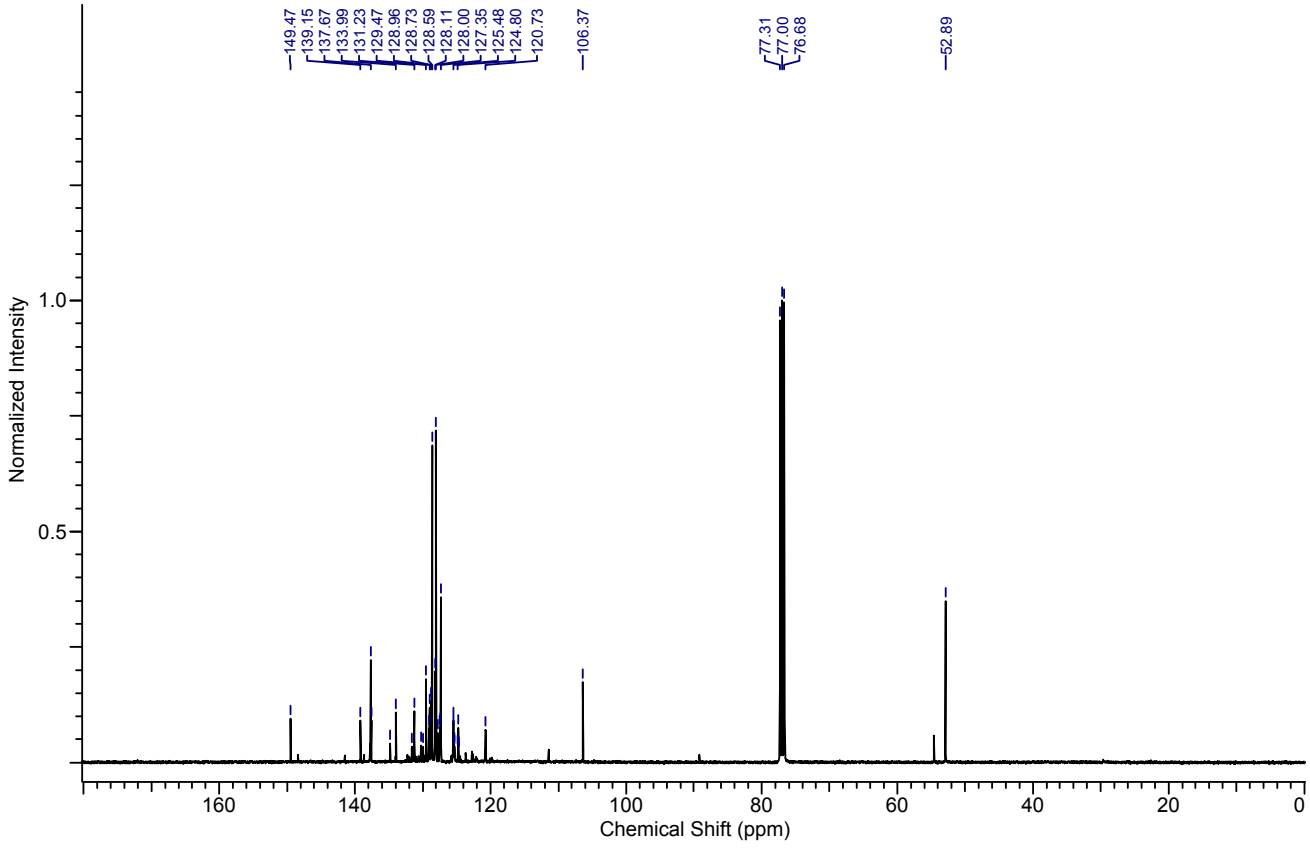


Figure S4. ^{13}C NMR spectrum of the compound **4ca**

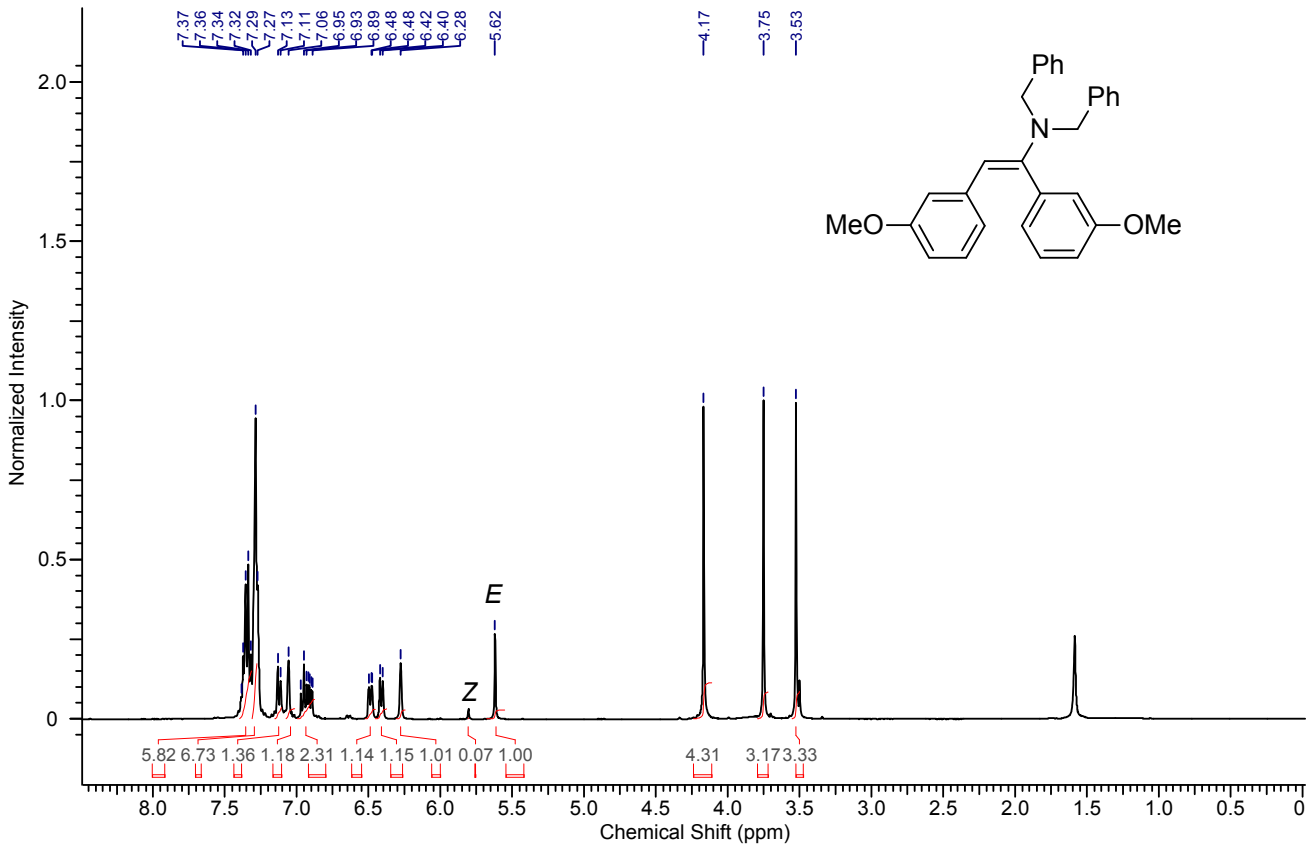


Figure S5. ^{1}H NMR spectrum of the compound **4da** (93:7 mixture of *E*:*Z* isomers)

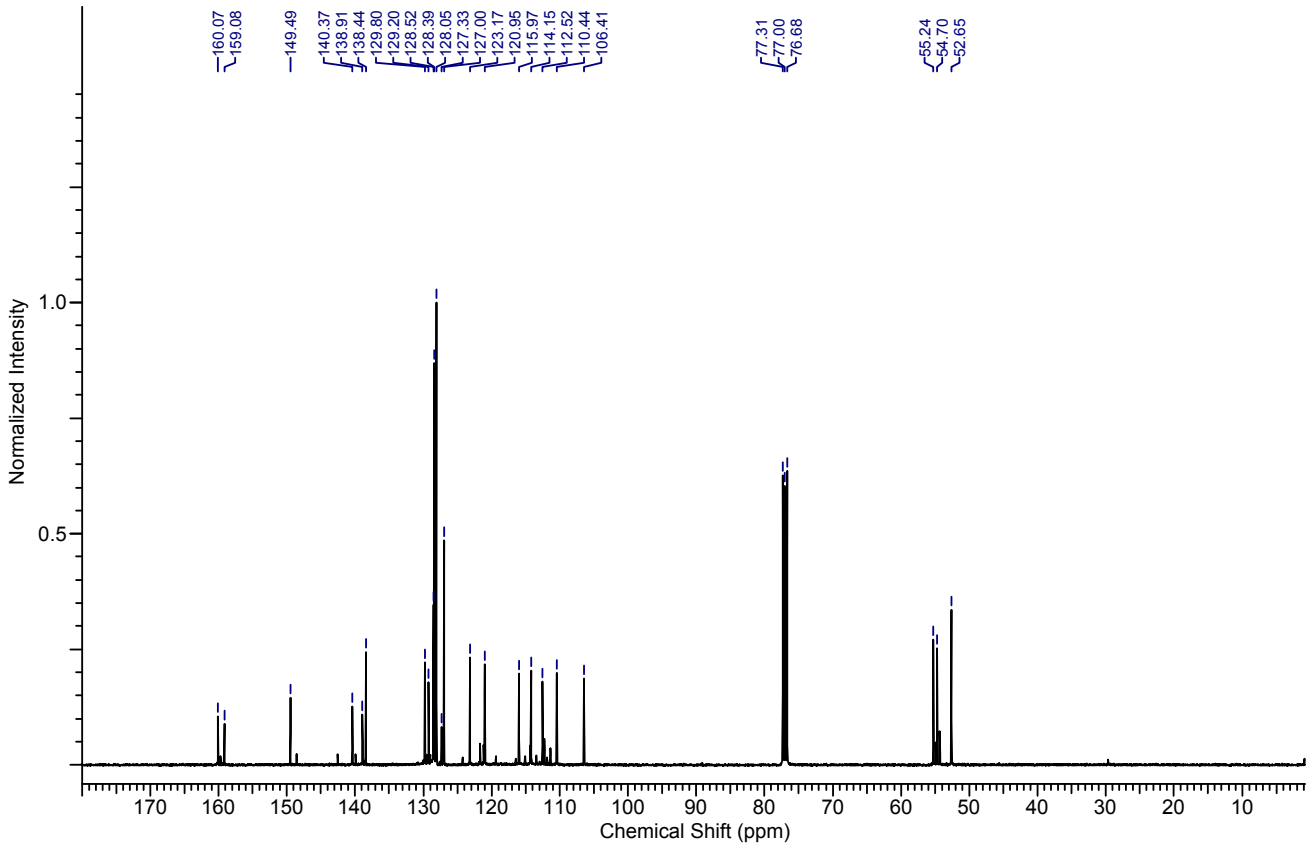


Figure S6. ^{13}C NMR spectrum of the compound **4da**

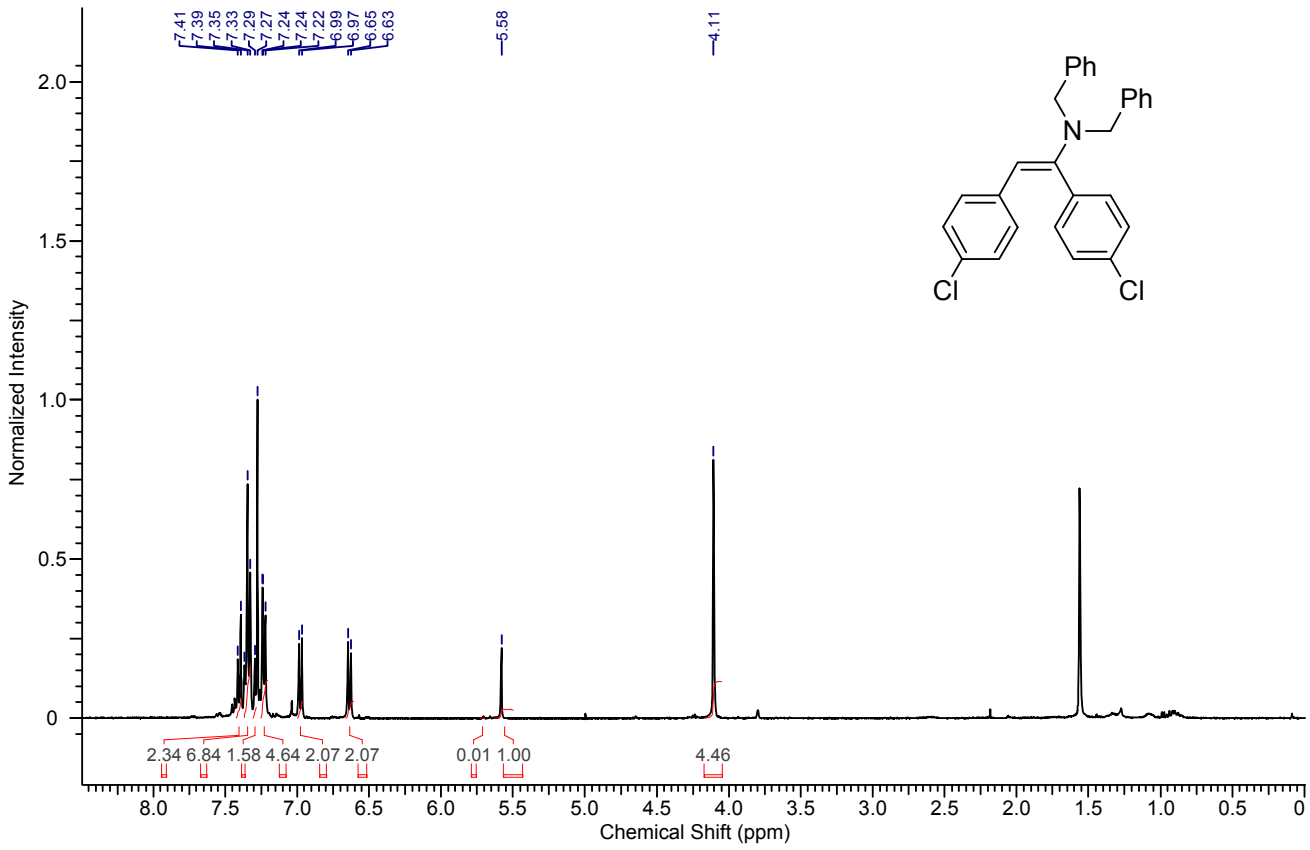


Figure S7. ^{1}H NMR spectrum of the compound **4ea** (>98:<2 mixture of *E*:*Z* isomers)

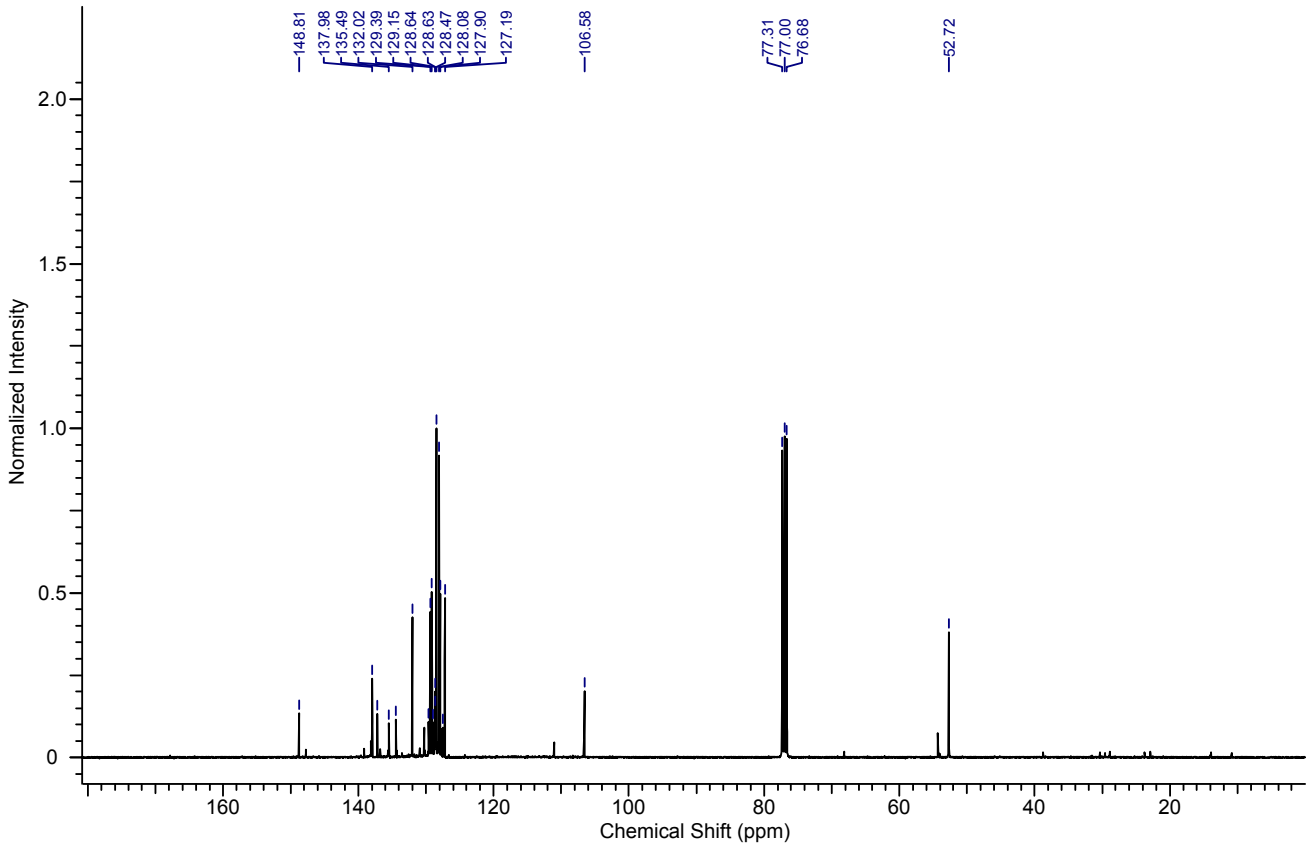


Figure S8. ^{13}C NMR spectrum of the compound **4ea**

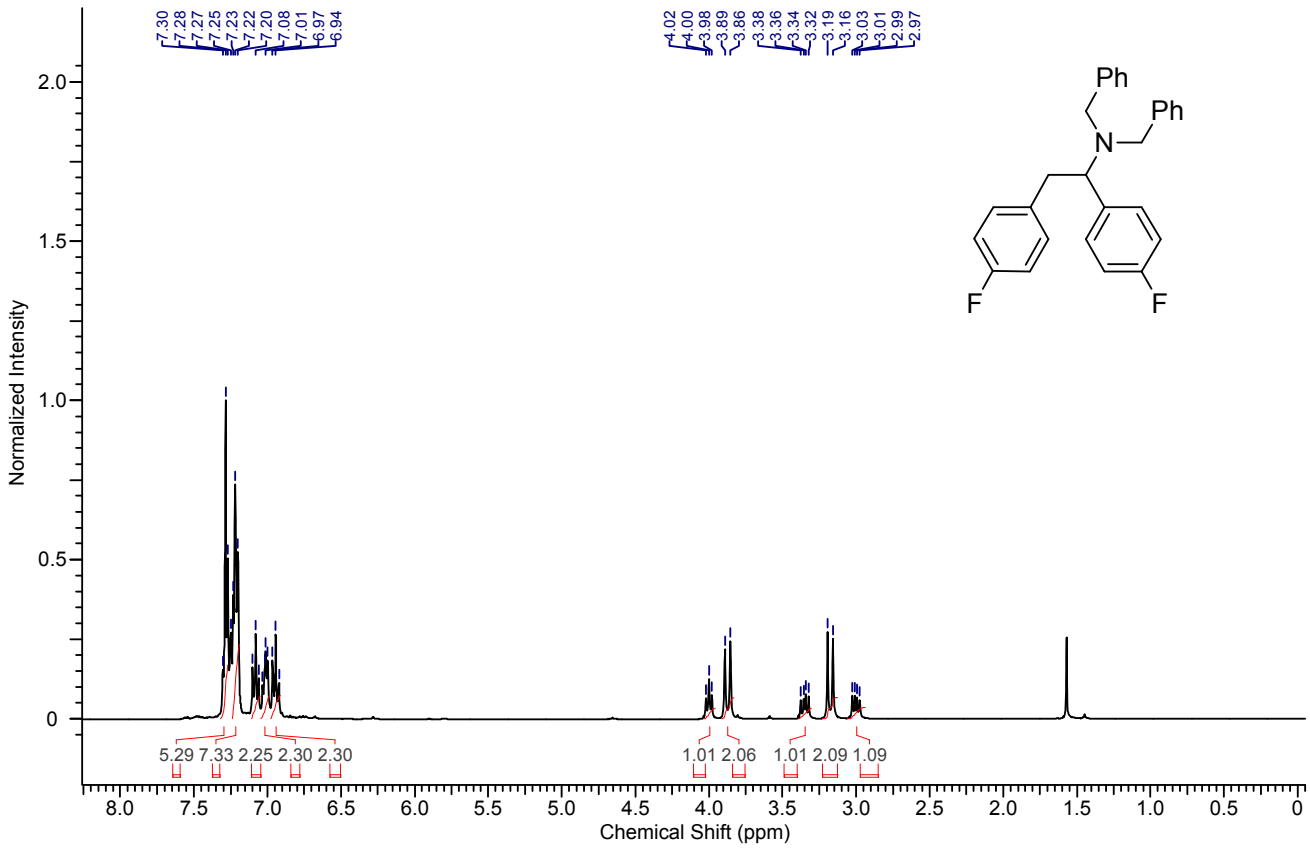


Figure S9. ^{1}H NMR spectrum of the compound **4fa'**

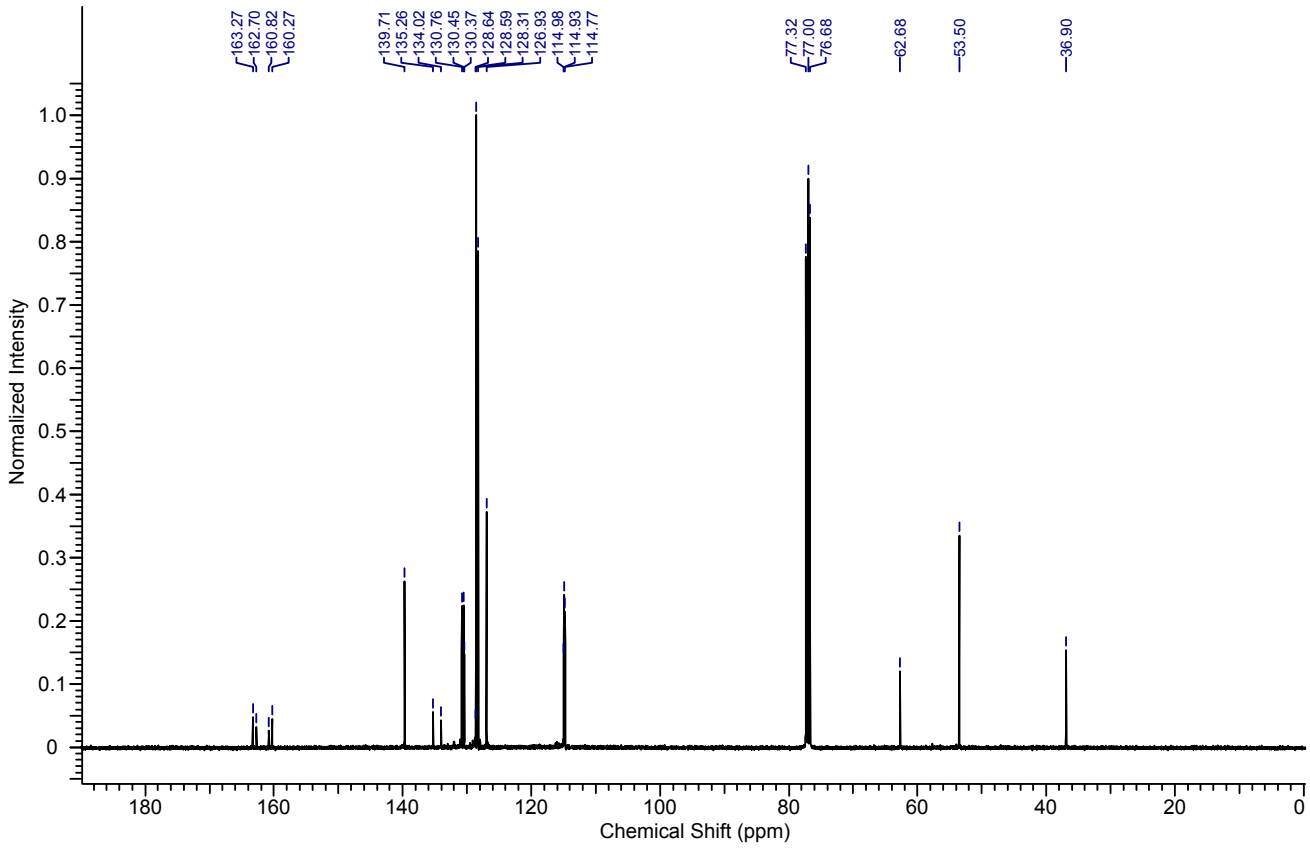


Figure S10. ^{13}C NMR spectrum of the compound **4fa'**

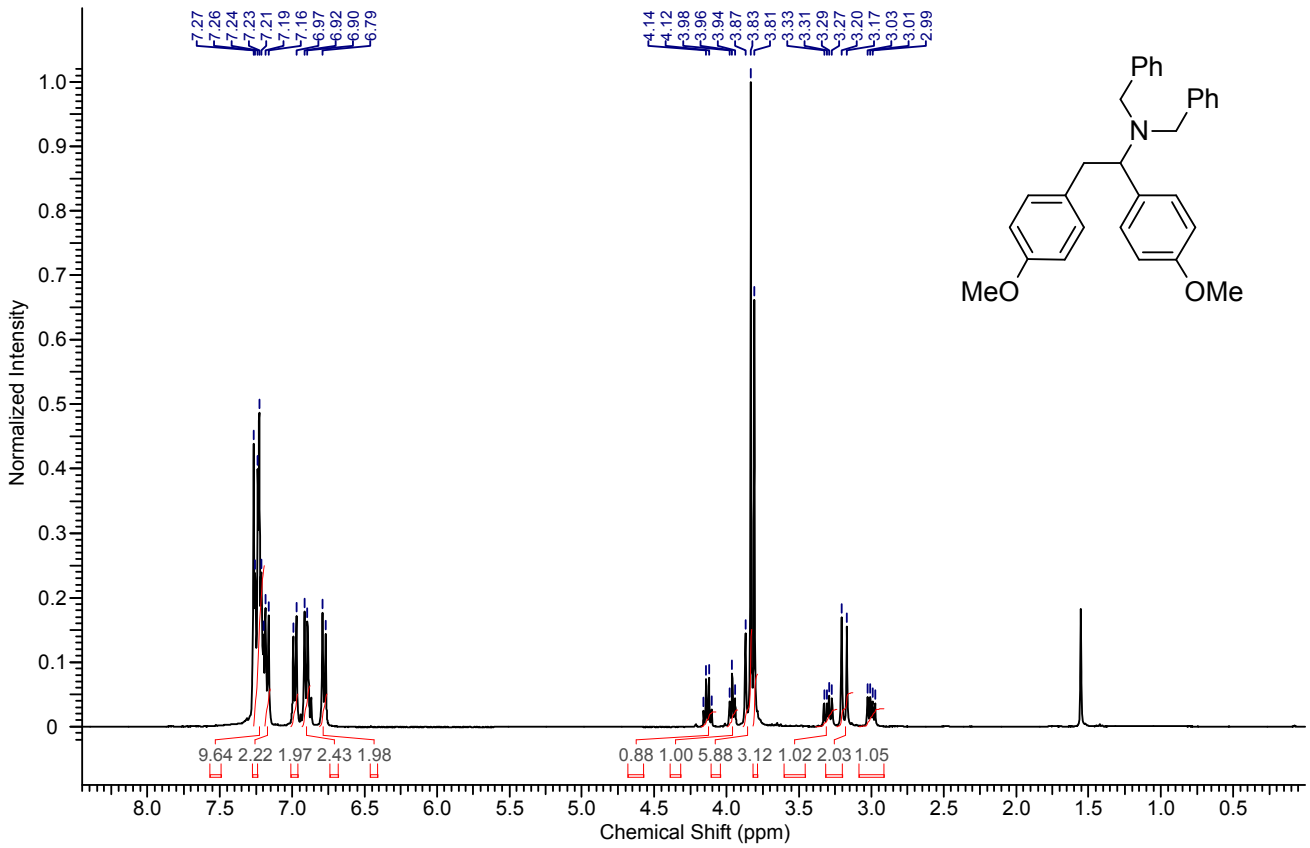


Figure S11. [1]H NMR spectrum of the compound **4ga'**

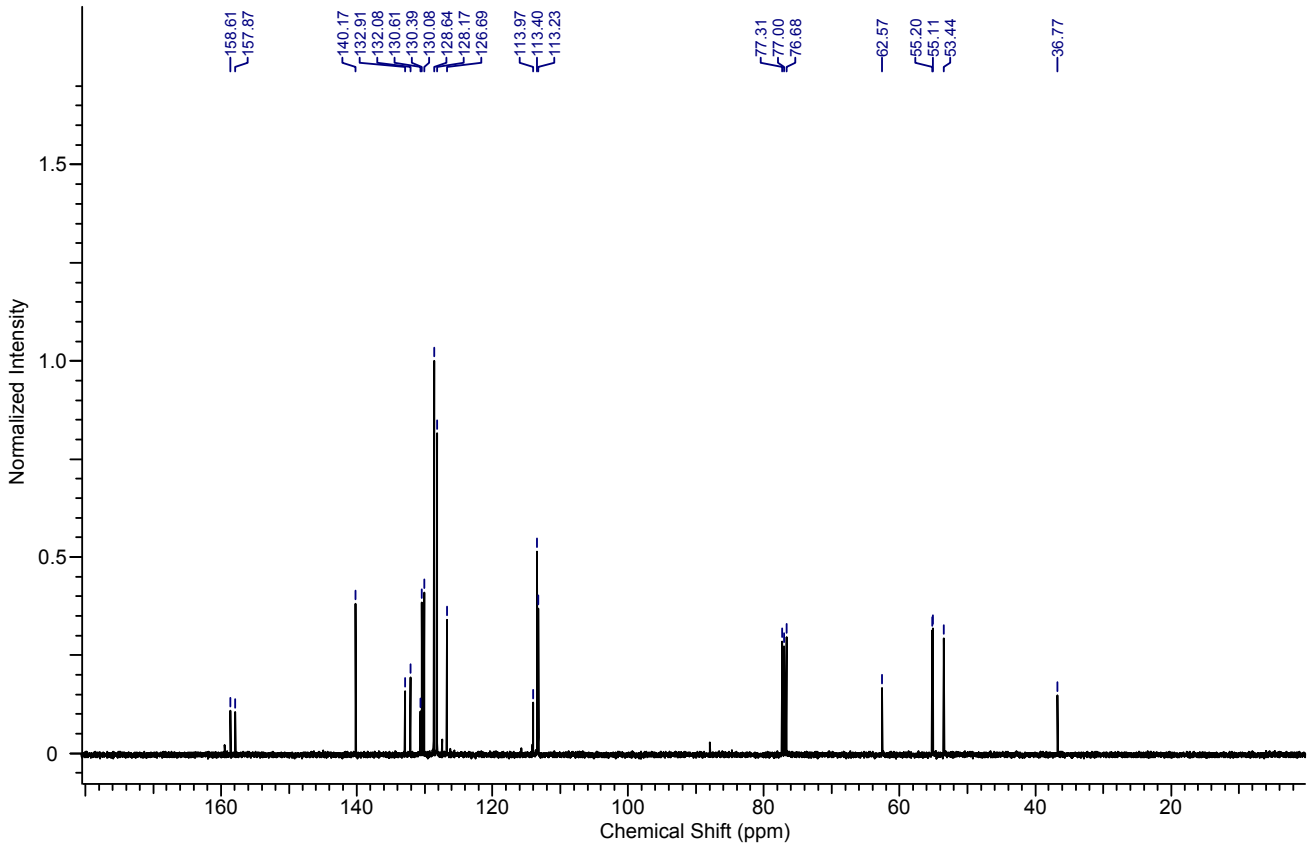


Figure S12. [13]C NMR spectrum of the compound **4ga'**

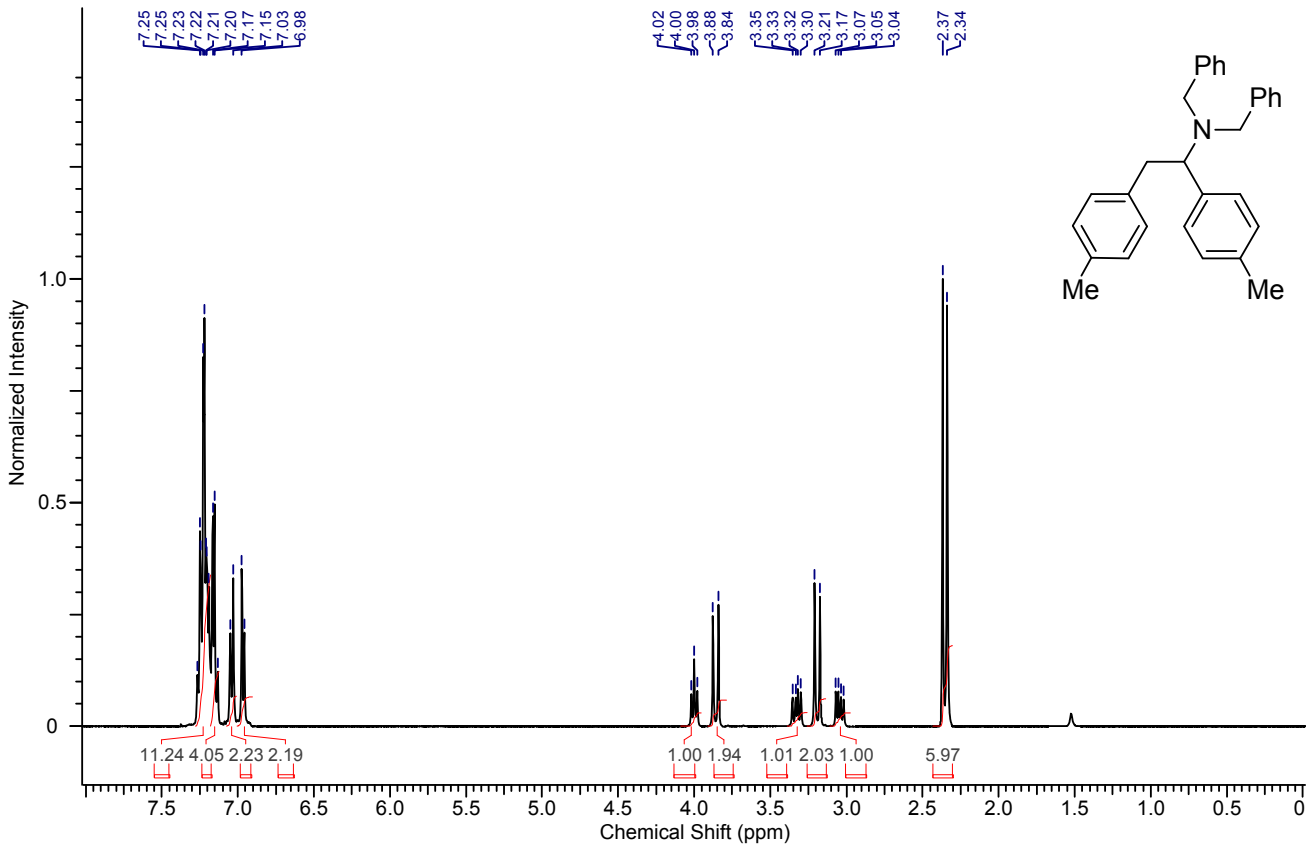


Figure S13. ^{1}H NMR spectrum of the compound **4ha'**

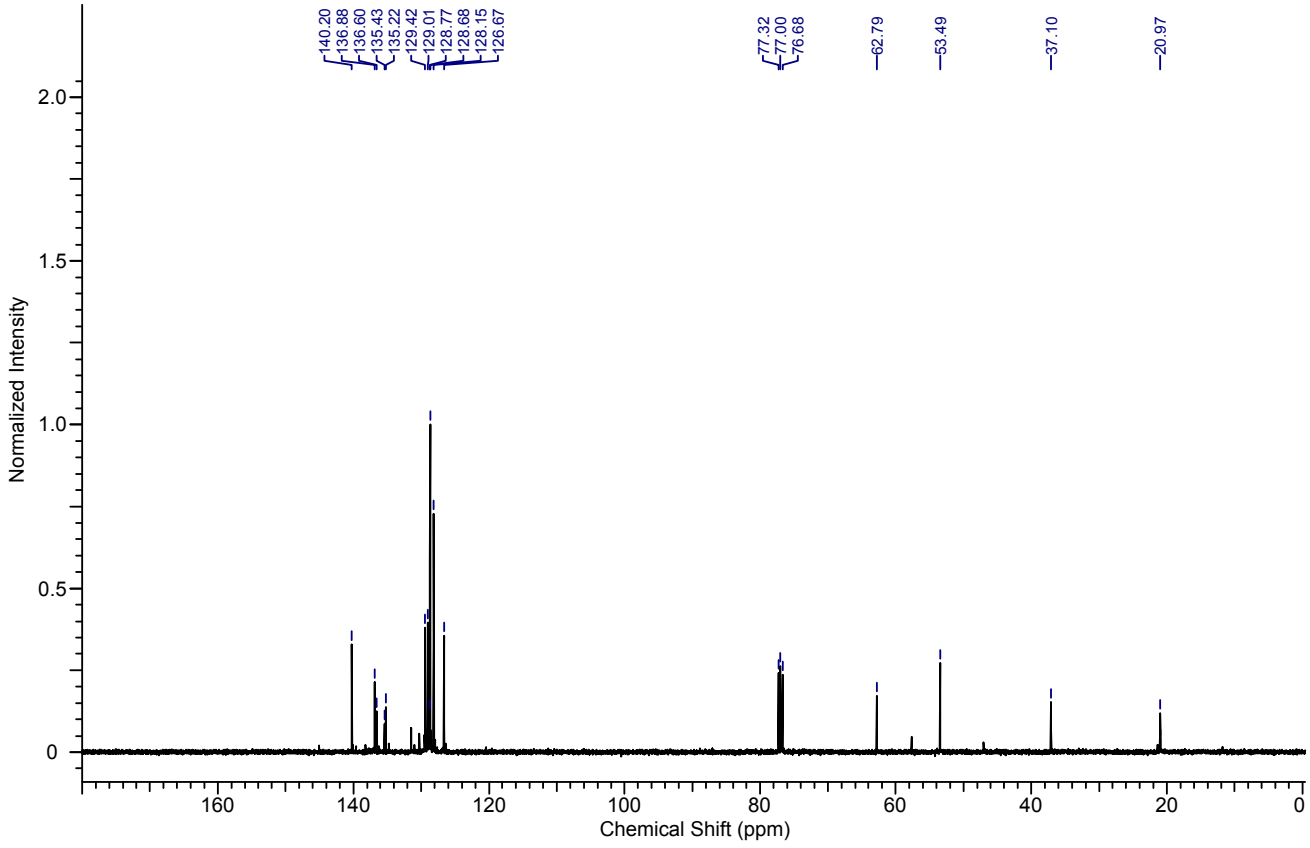


Figure S14. ^{13}C NMR spectrum of the compound **4ha'**

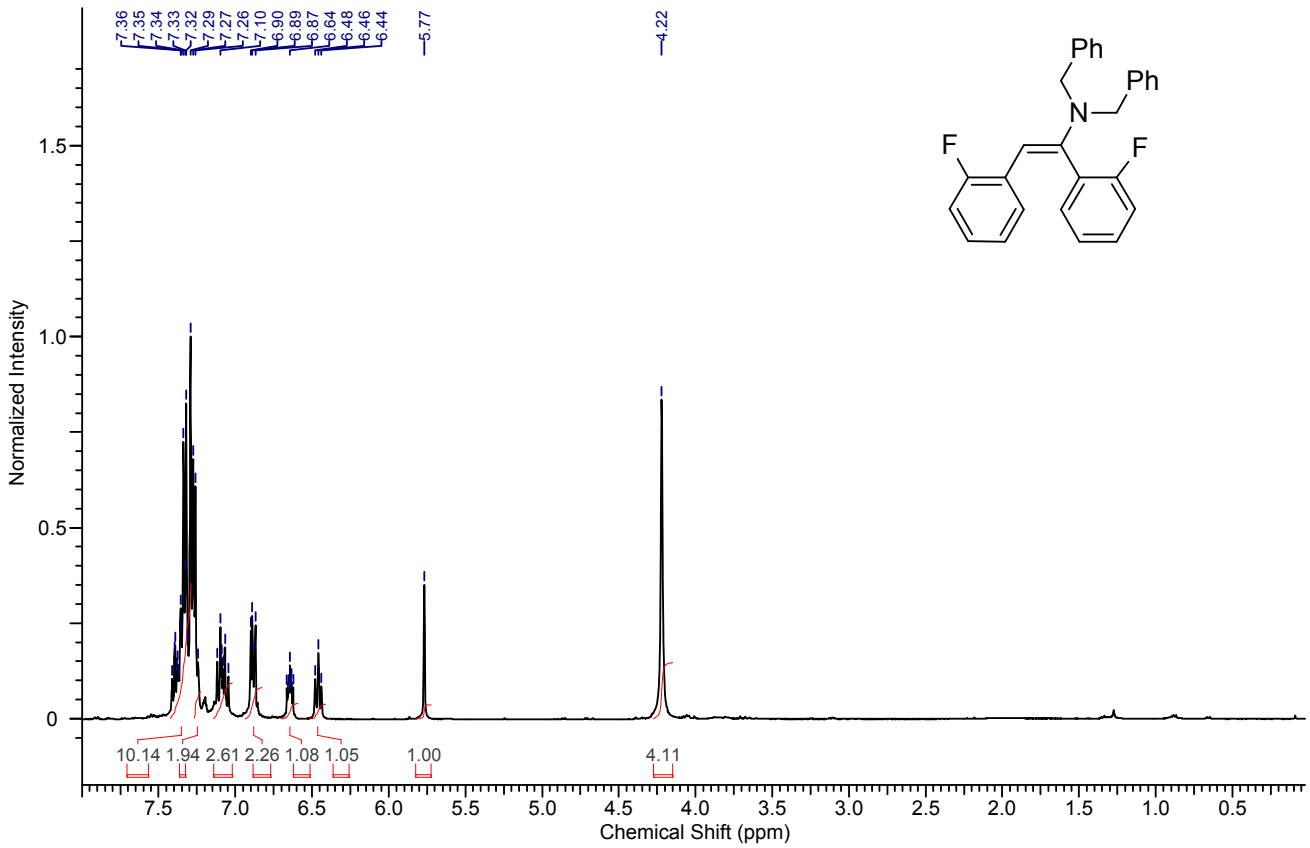


Figure S15. ^{1}H NMR spectrum of the compound **4ia**

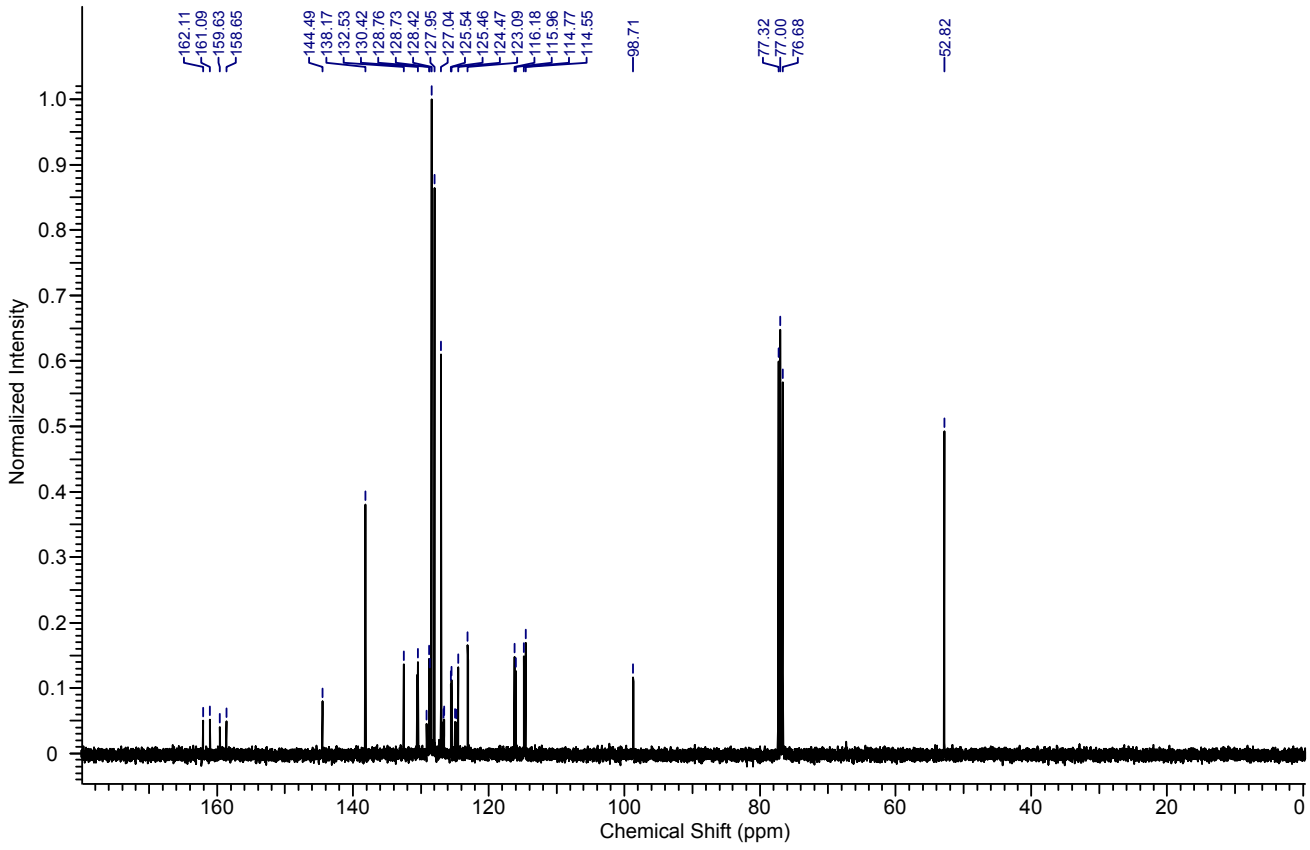


Figure S16. ^{13}C NMR spectrum of the compound **4ia**

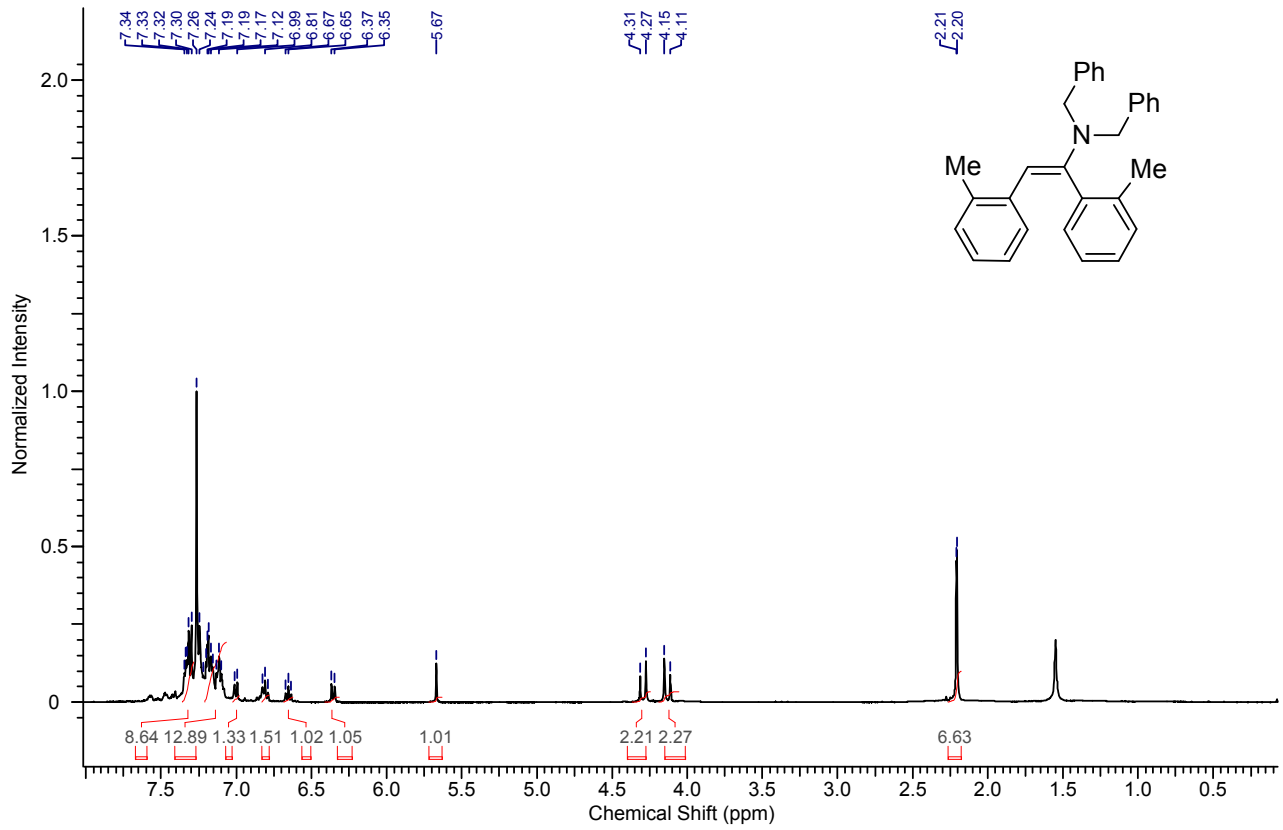


Figure S17. ^{1}H NMR spectrum of the compound **4ja**

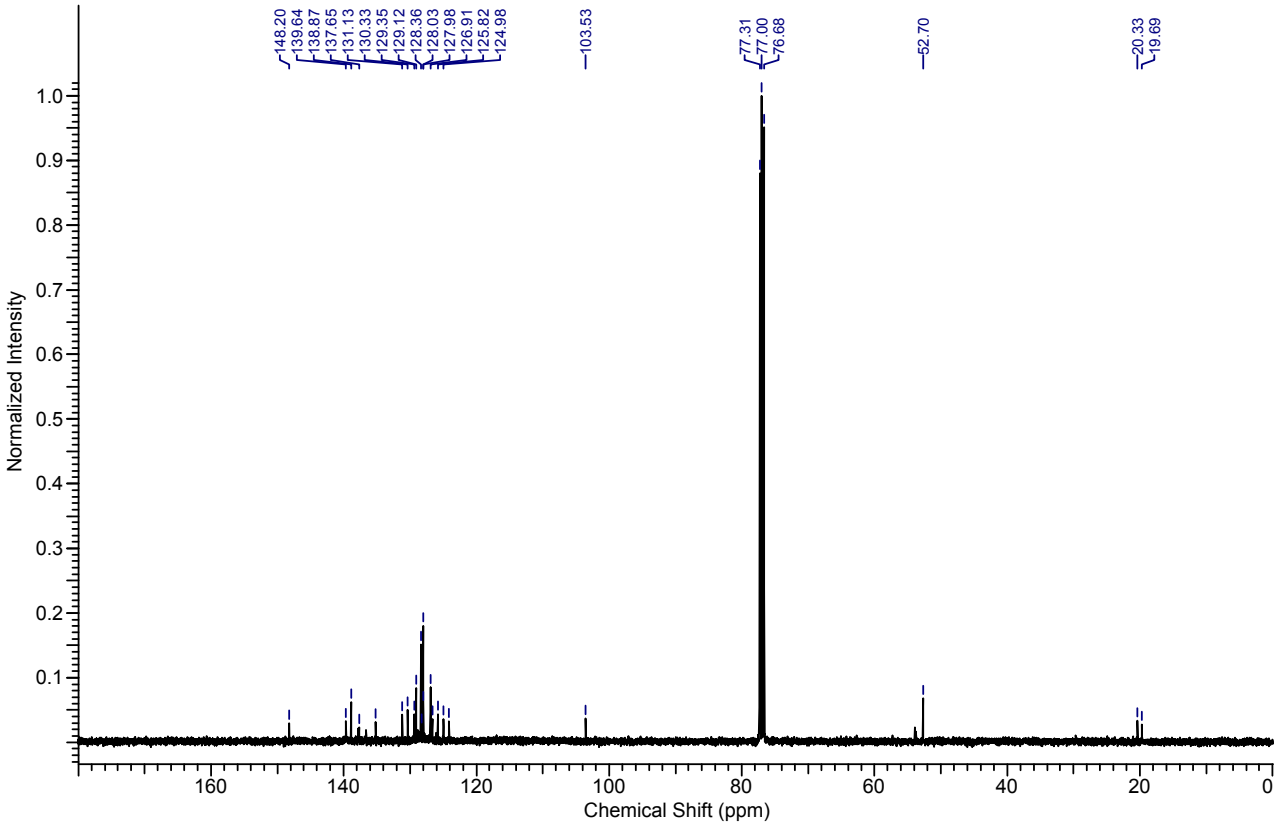


Figure S18. ^{13}C NMR spectrum of the compound **4ja**

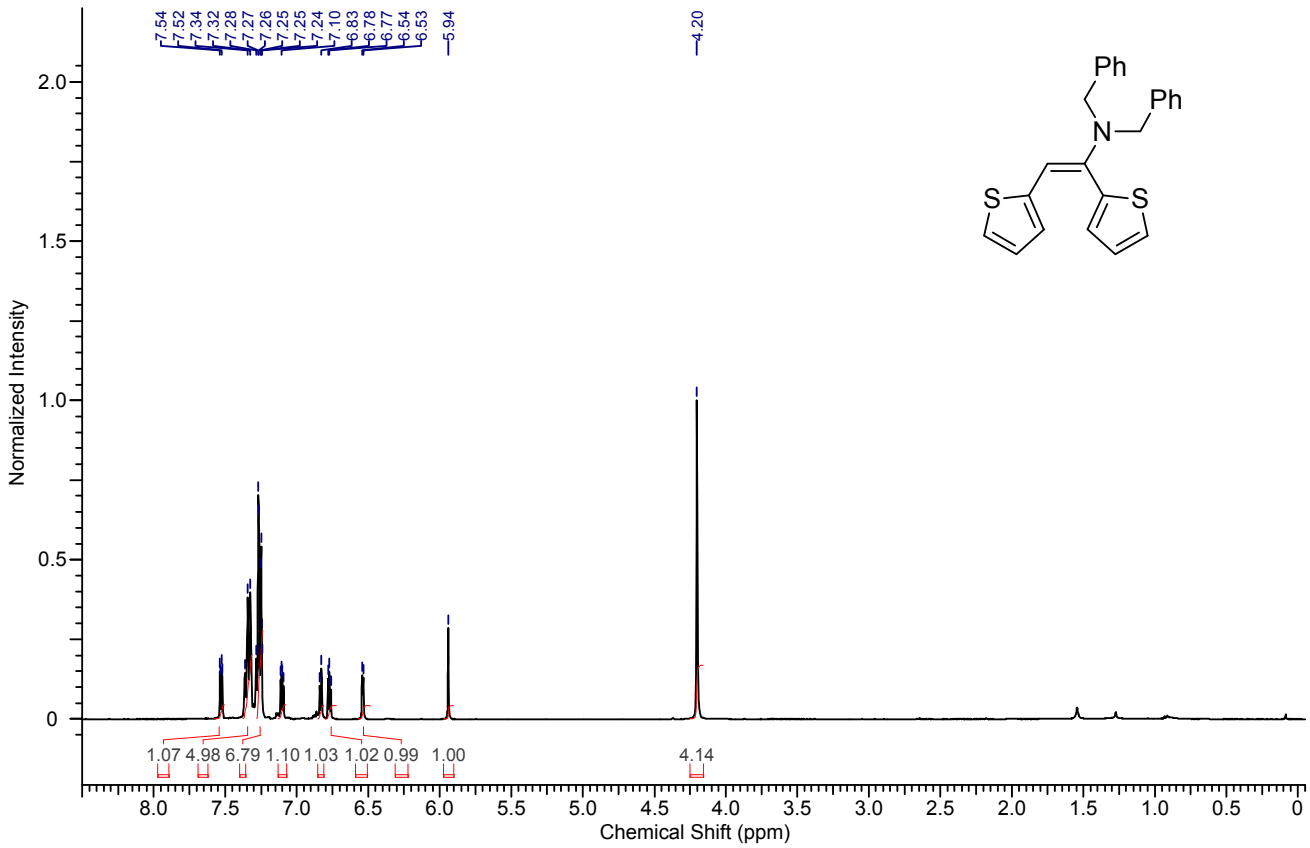


Figure S19. ^{1}H NMR spectrum of the compound **4ka**

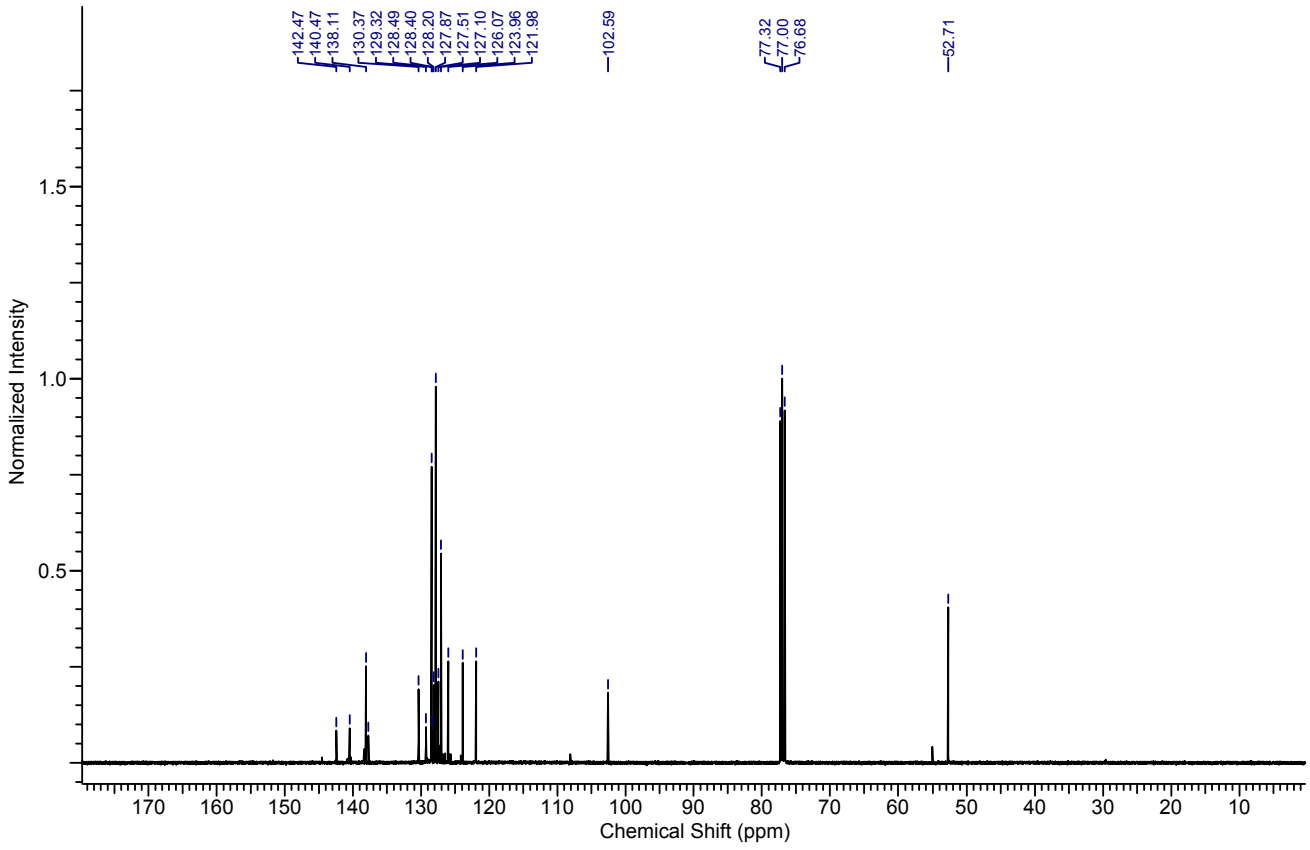


Figure S20. ^{13}C NMR spectrum of the compound **4ka**

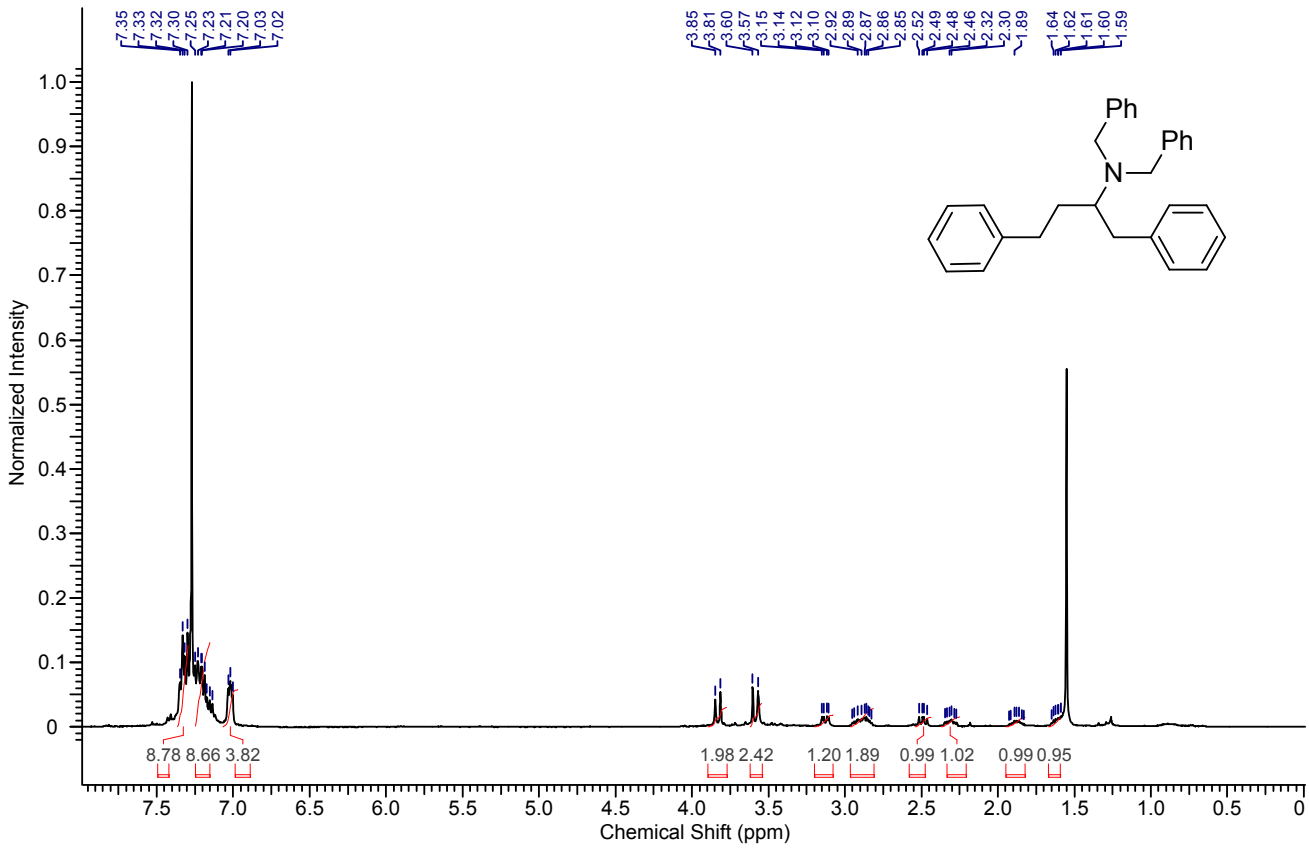


Figure S21. ^{1}H NMR spectrum of the compound **4la'**

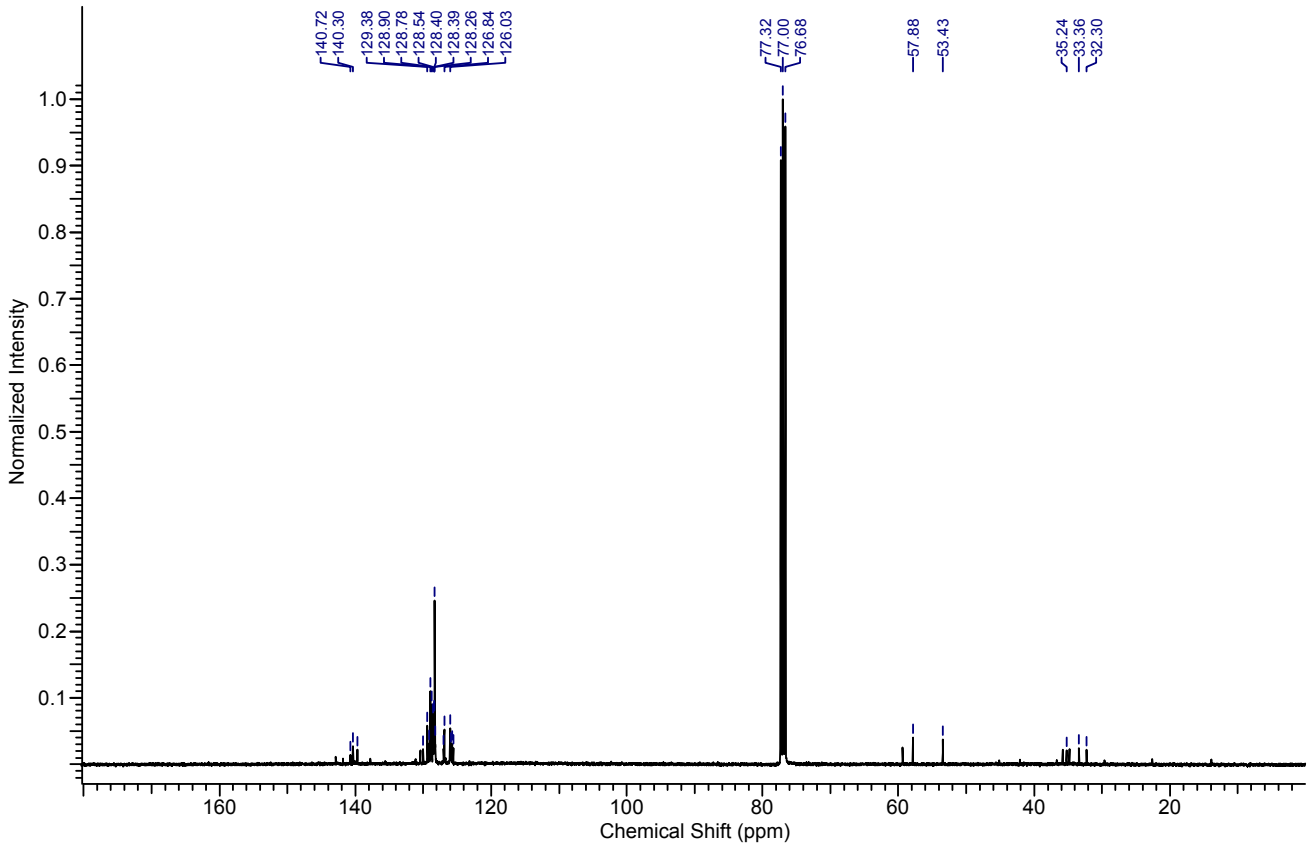


Figure S22. ^{13}C NMR spectrum of the compound **4la'**

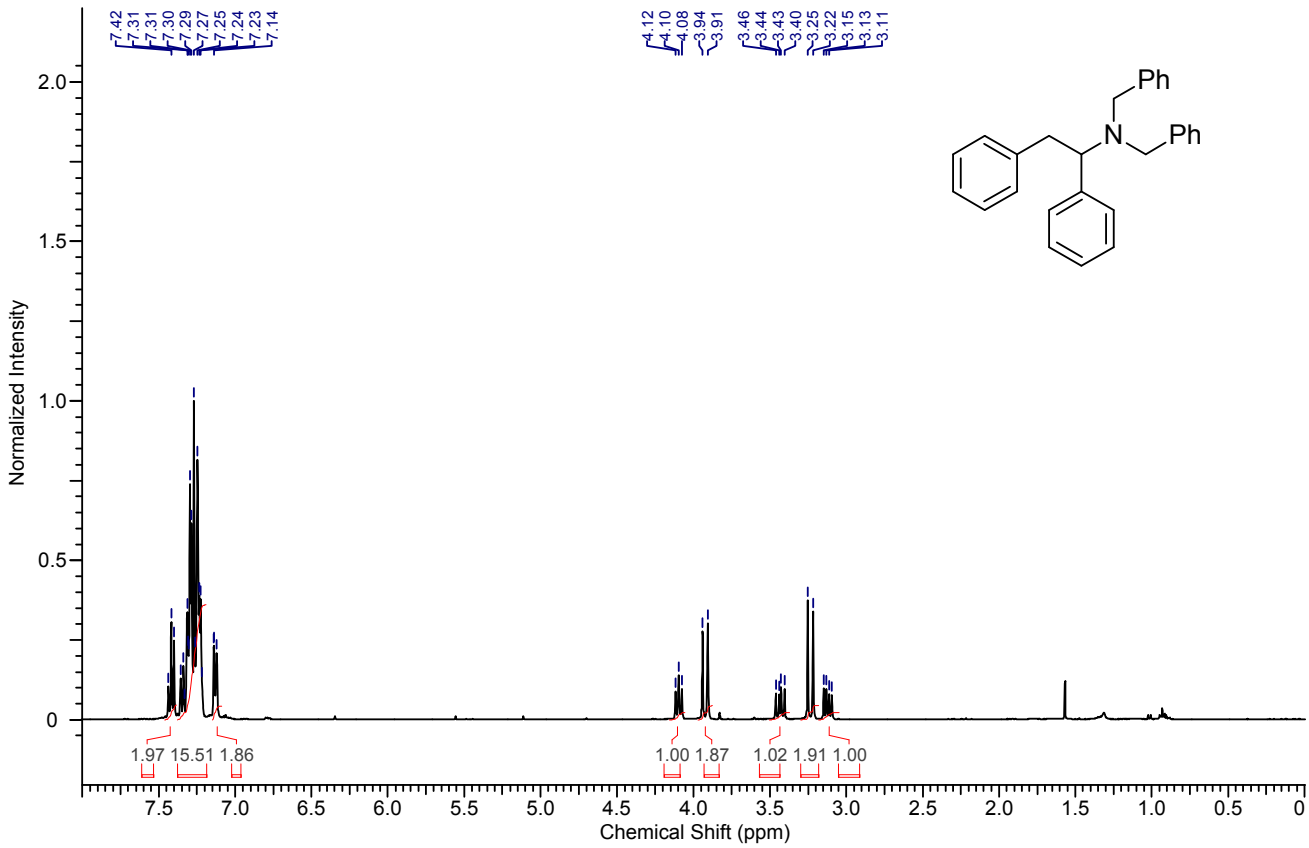


Figure S23. ^{1}H NMR spectrum of the compound **4aa'**

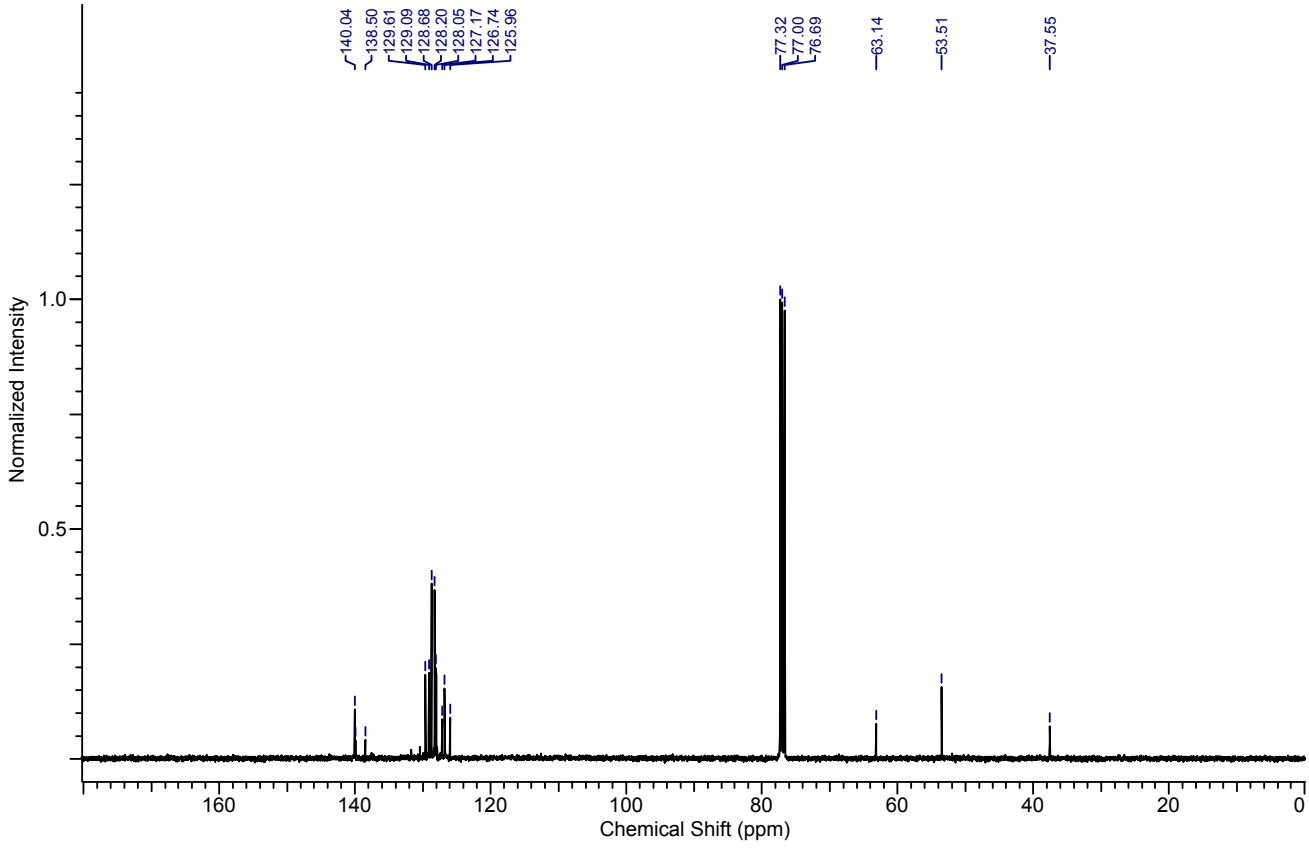


Figure S24. ^{13}C NMR spectrum of the compound **4aa'**

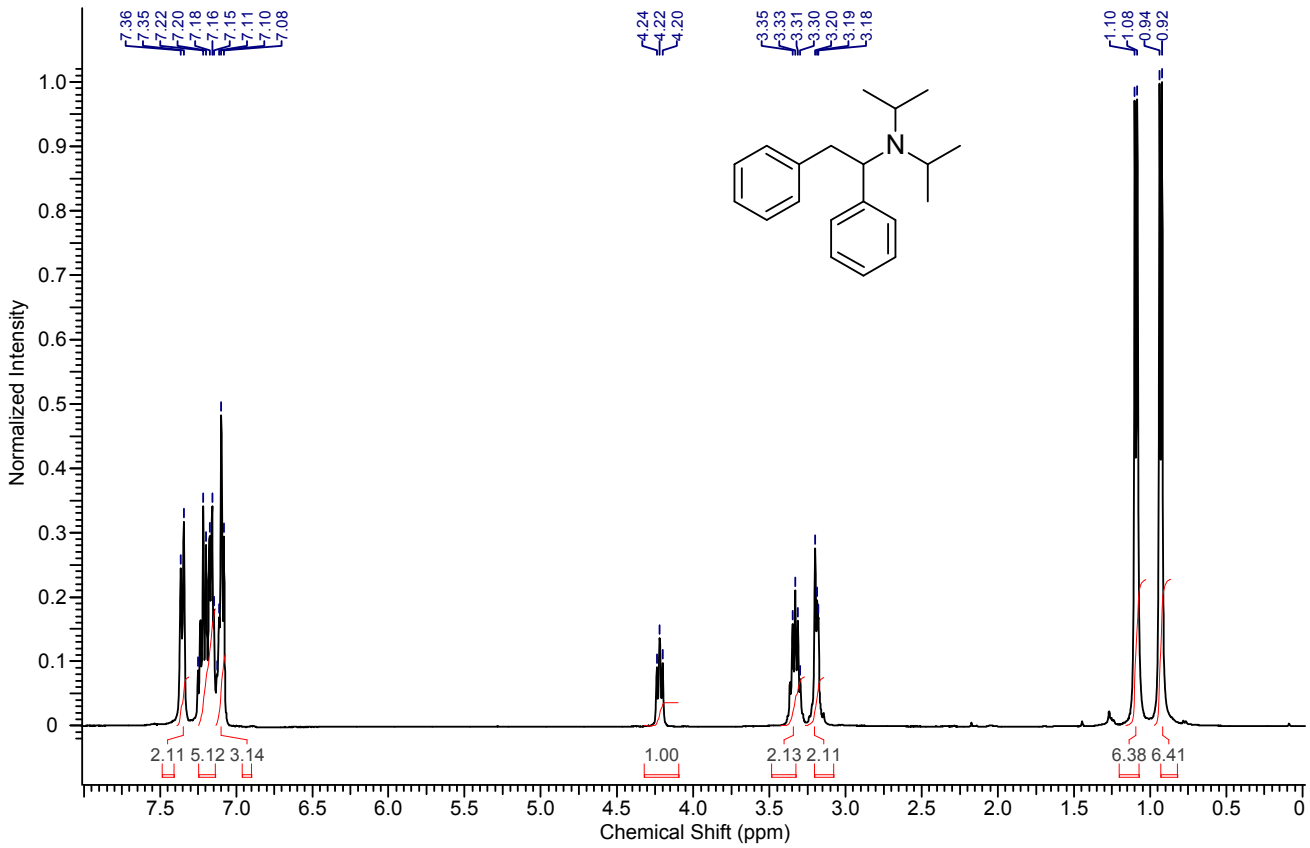


Figure S25. ^{1}H NMR spectrum of the compound **4ab**

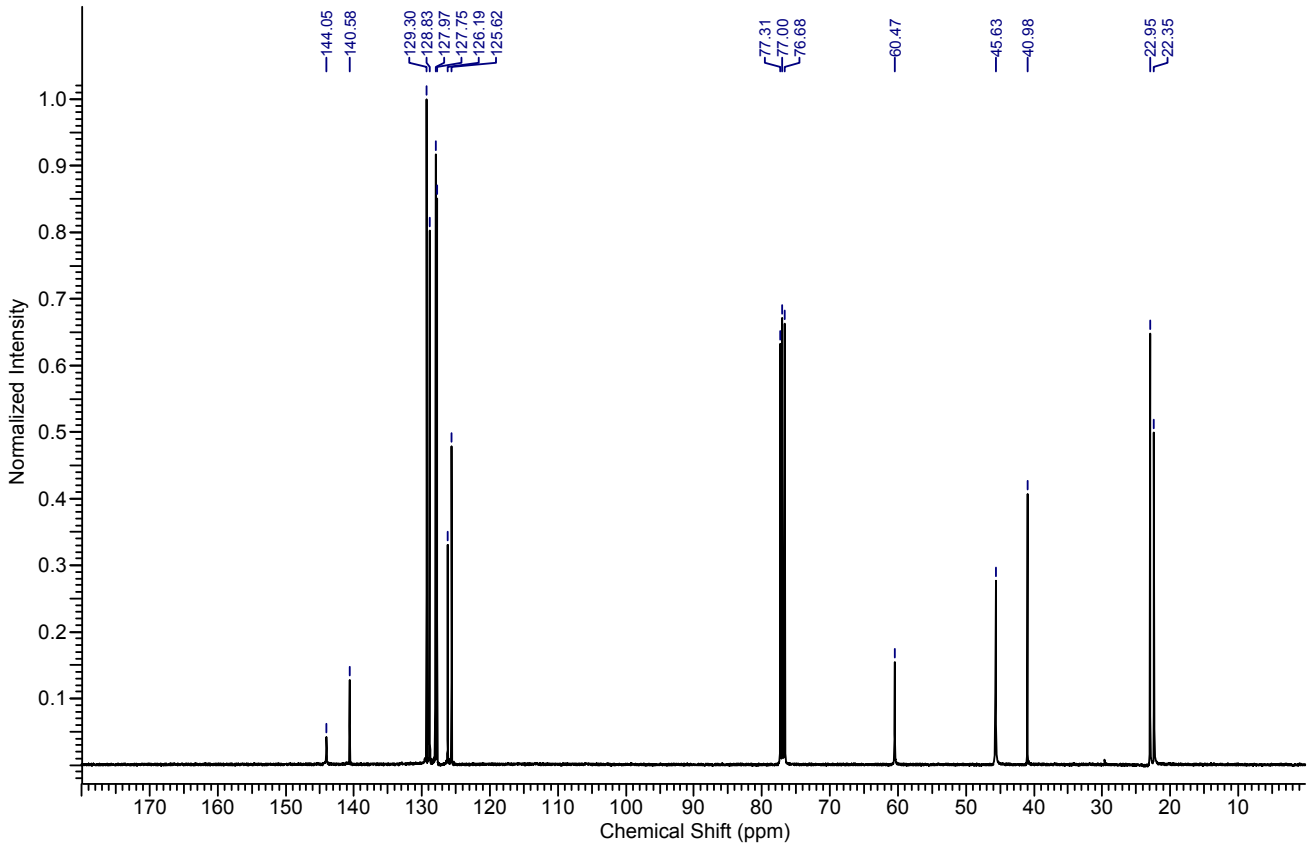


Figure S26. ^{13}C NMR spectrum of the compound **4ab**

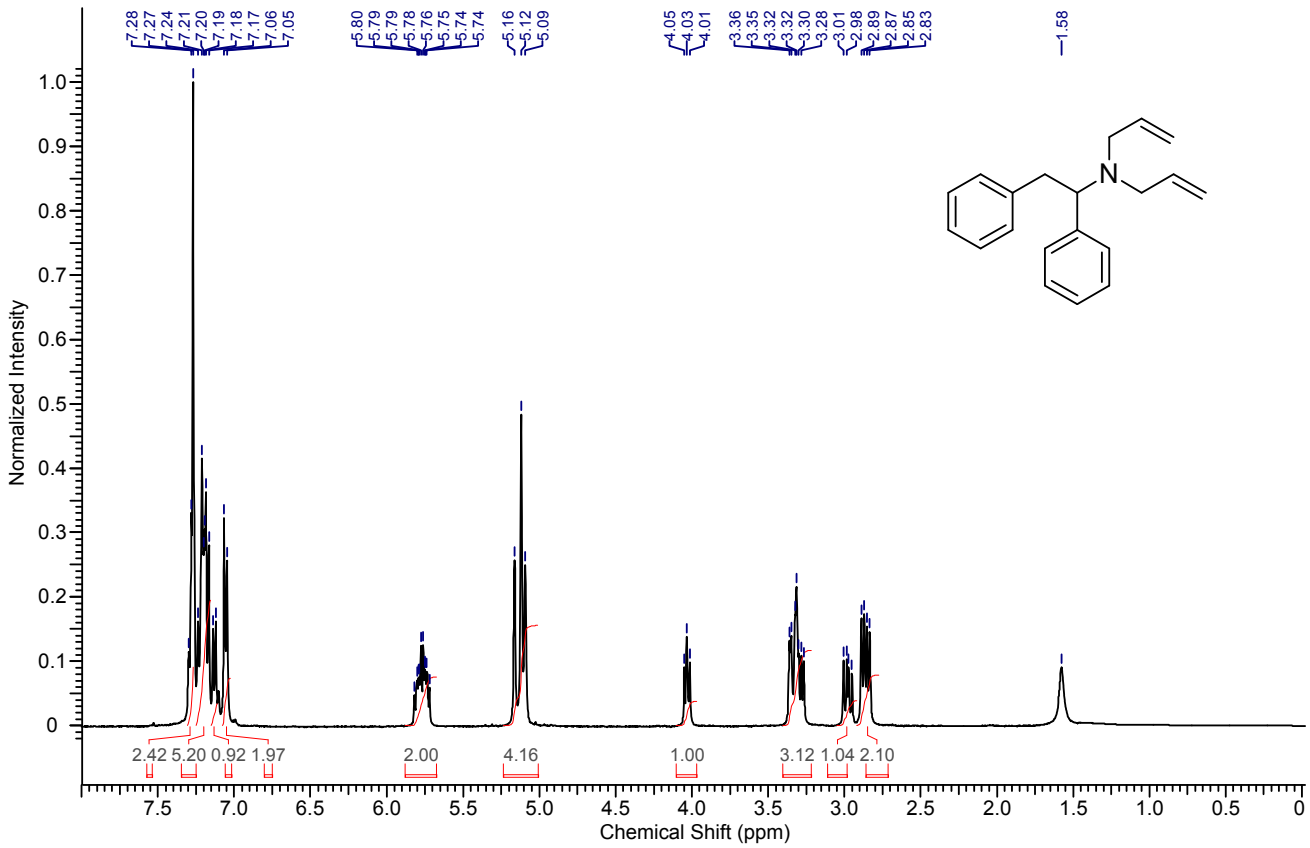


Figure S27. ^{1}H NMR spectrum of the compound **4ac**

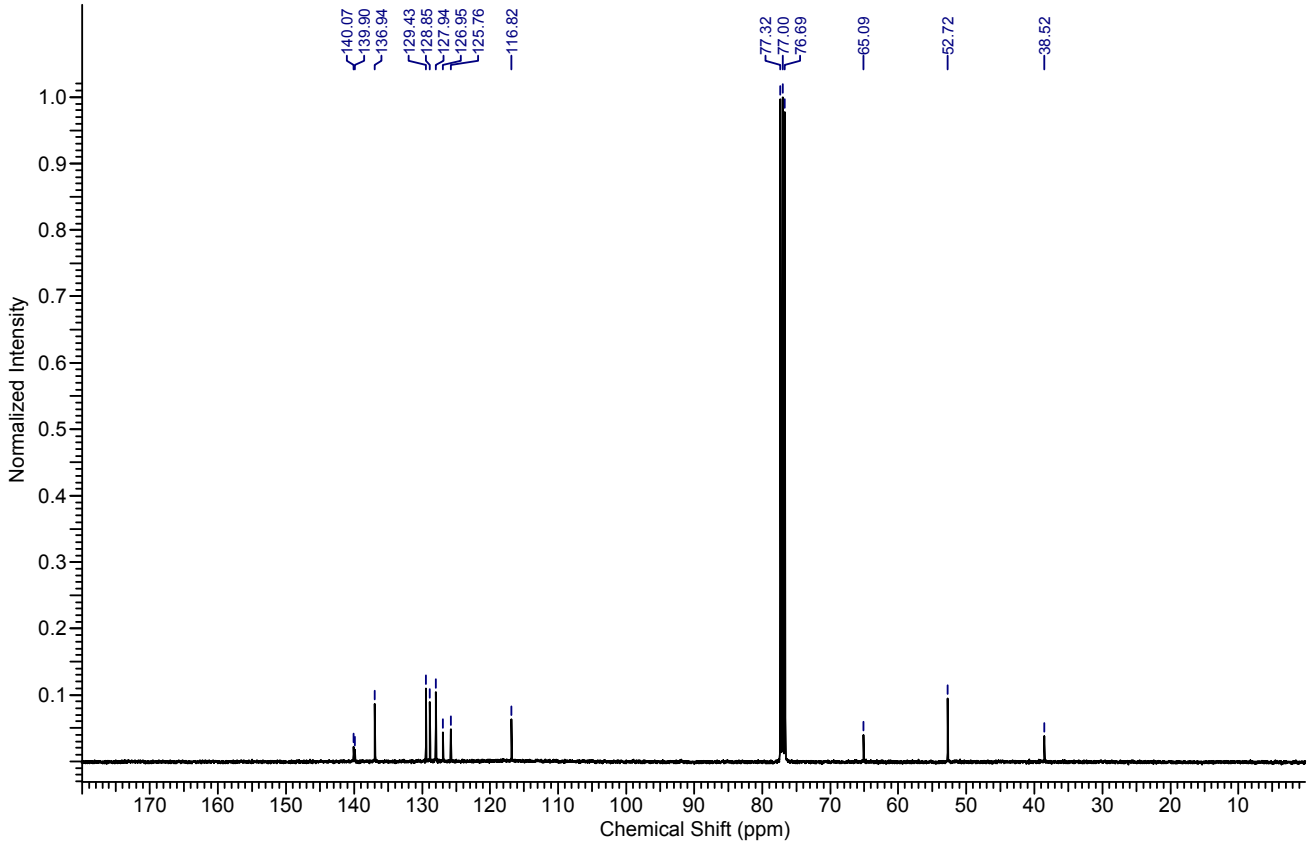


Figure S28. ^{13}C NMR spectrum of the compound **4ac**

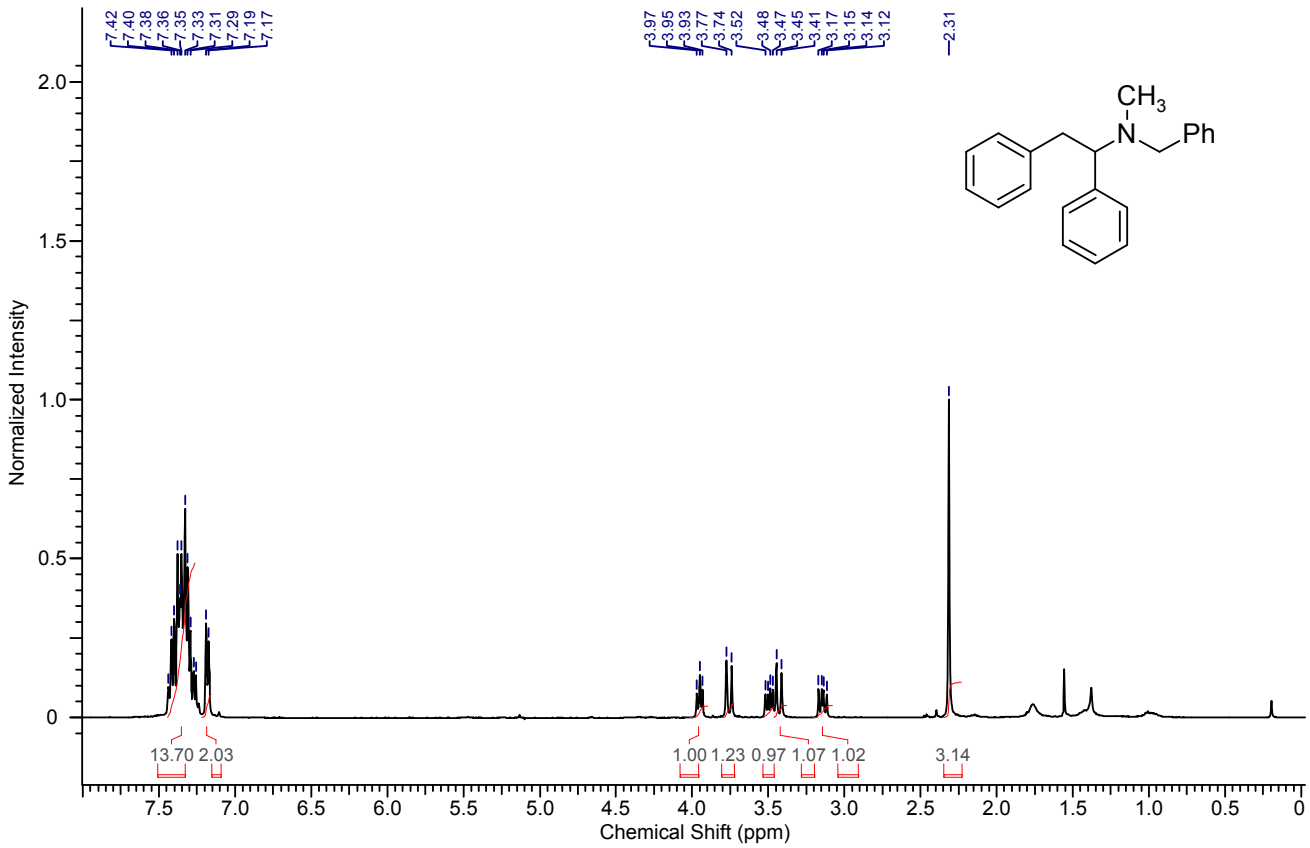


Figure S29. ^{1}H NMR spectrum of the compound **4ad**

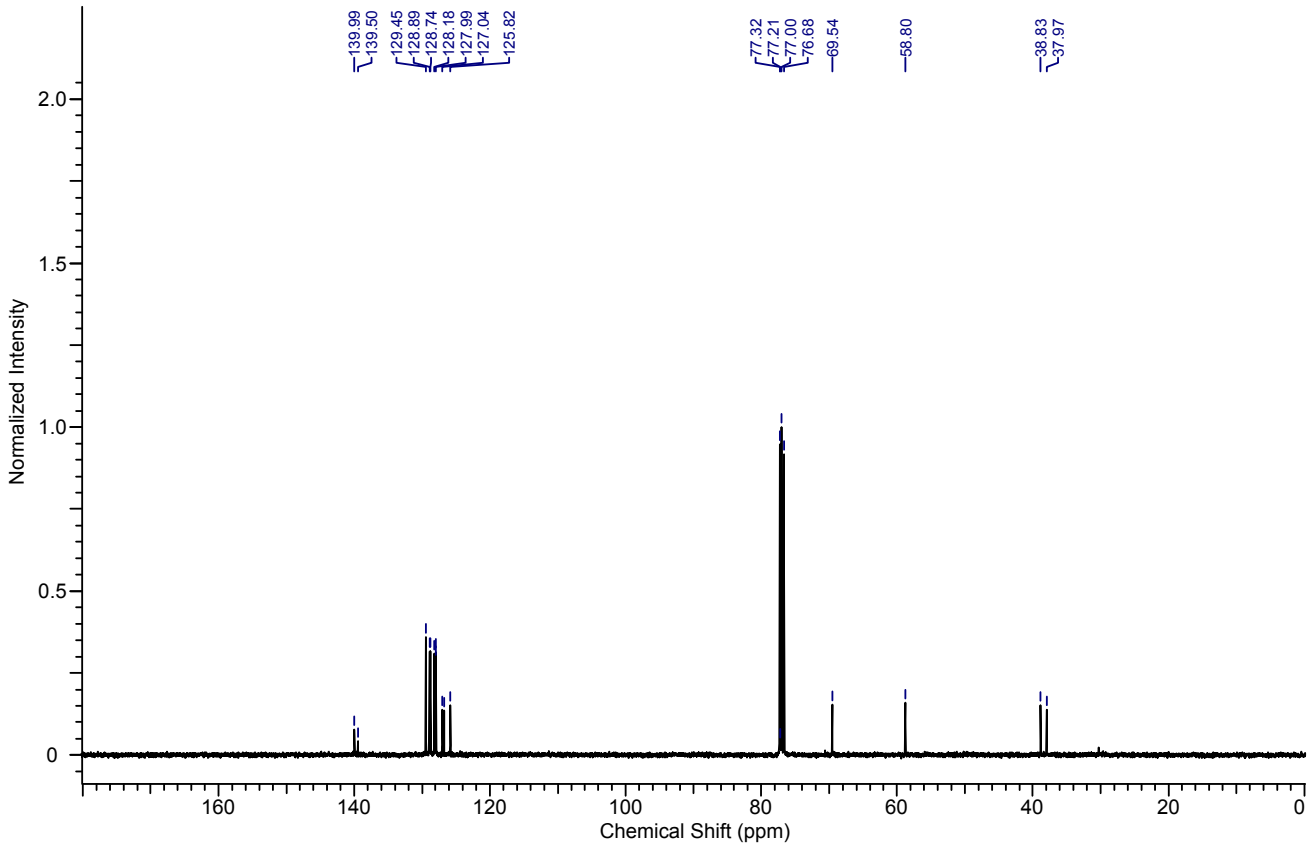


Figure S30. ^{13}C NMR spectrum of the compound **4ad**

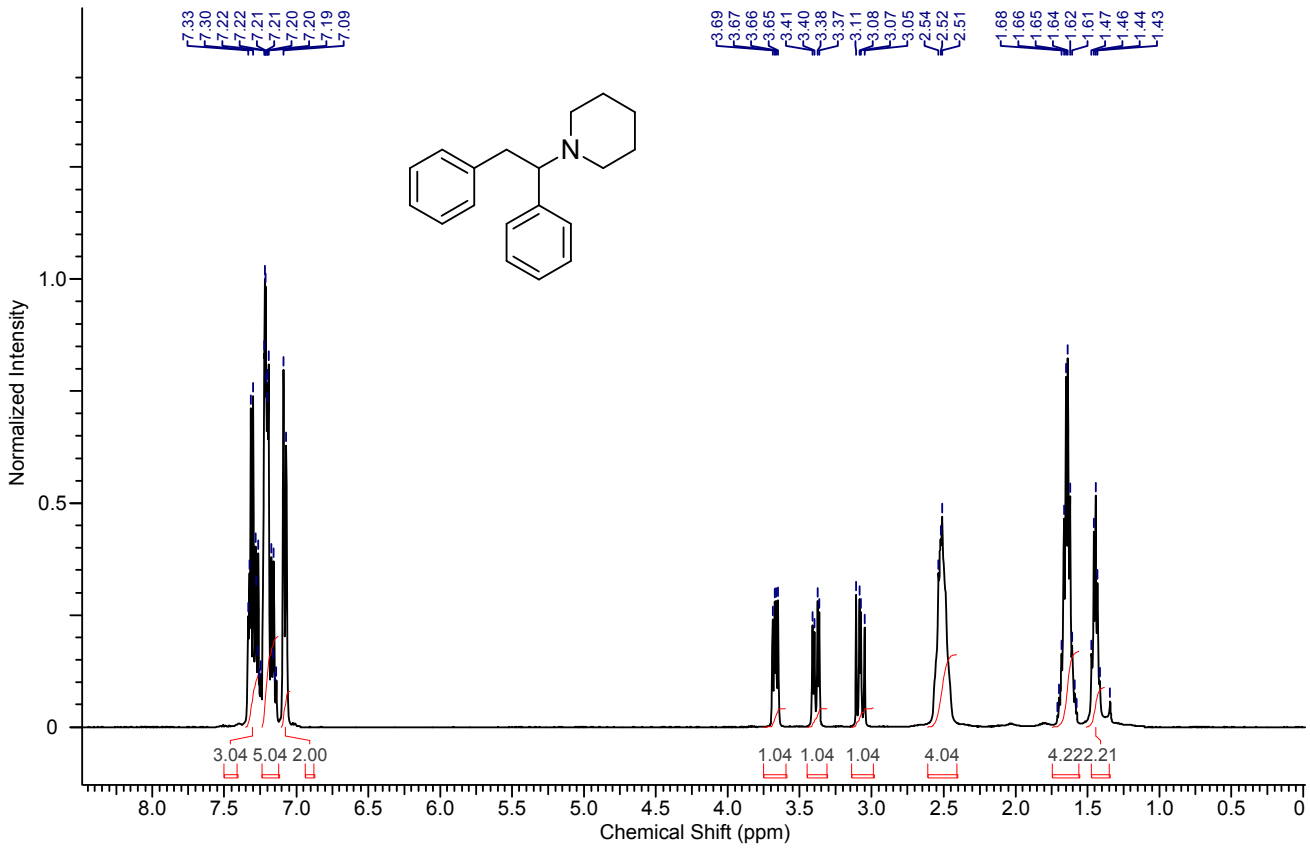


Figure S31. ^{1}H NMR spectrum of the compound **4ae**

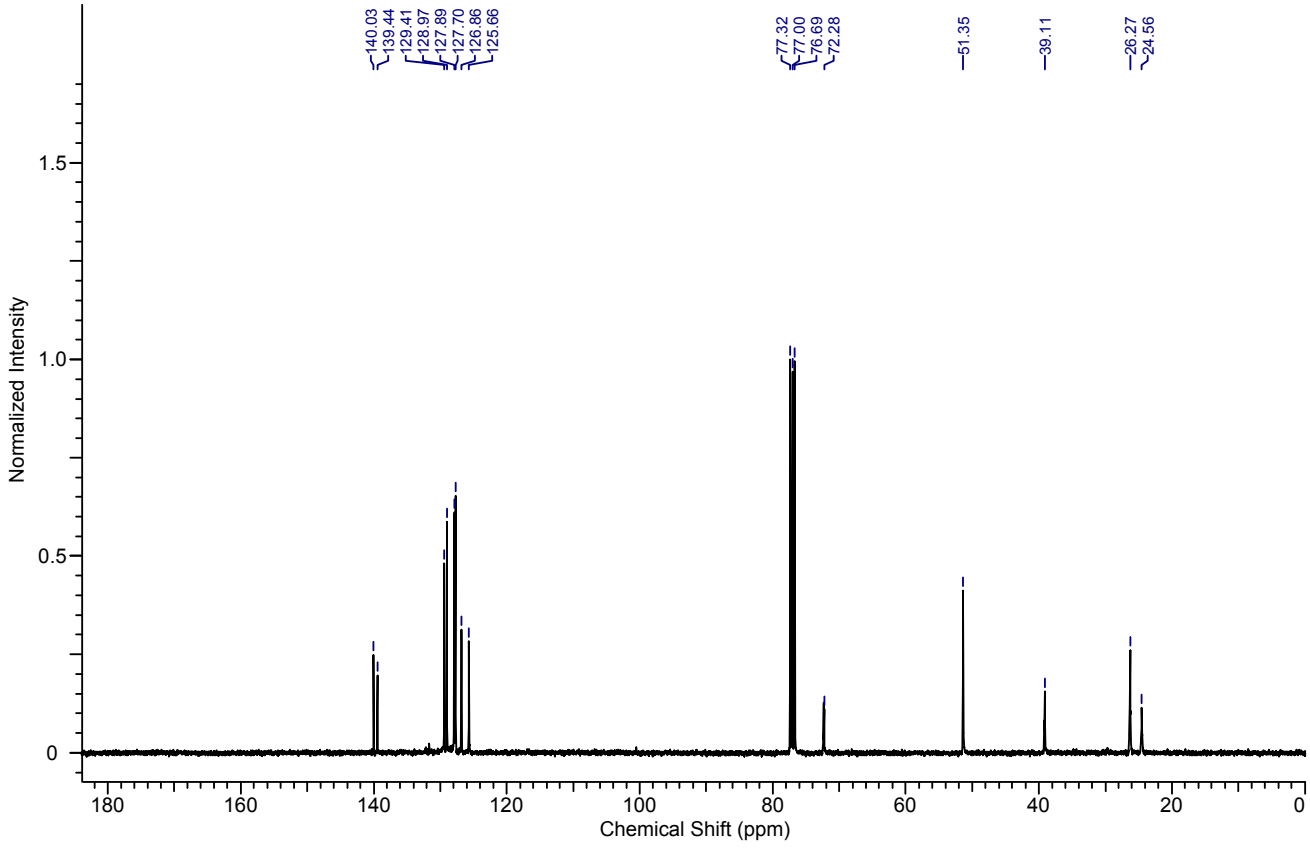


Figure S32. ^{13}C NMR spectrum of the compound **4ae**

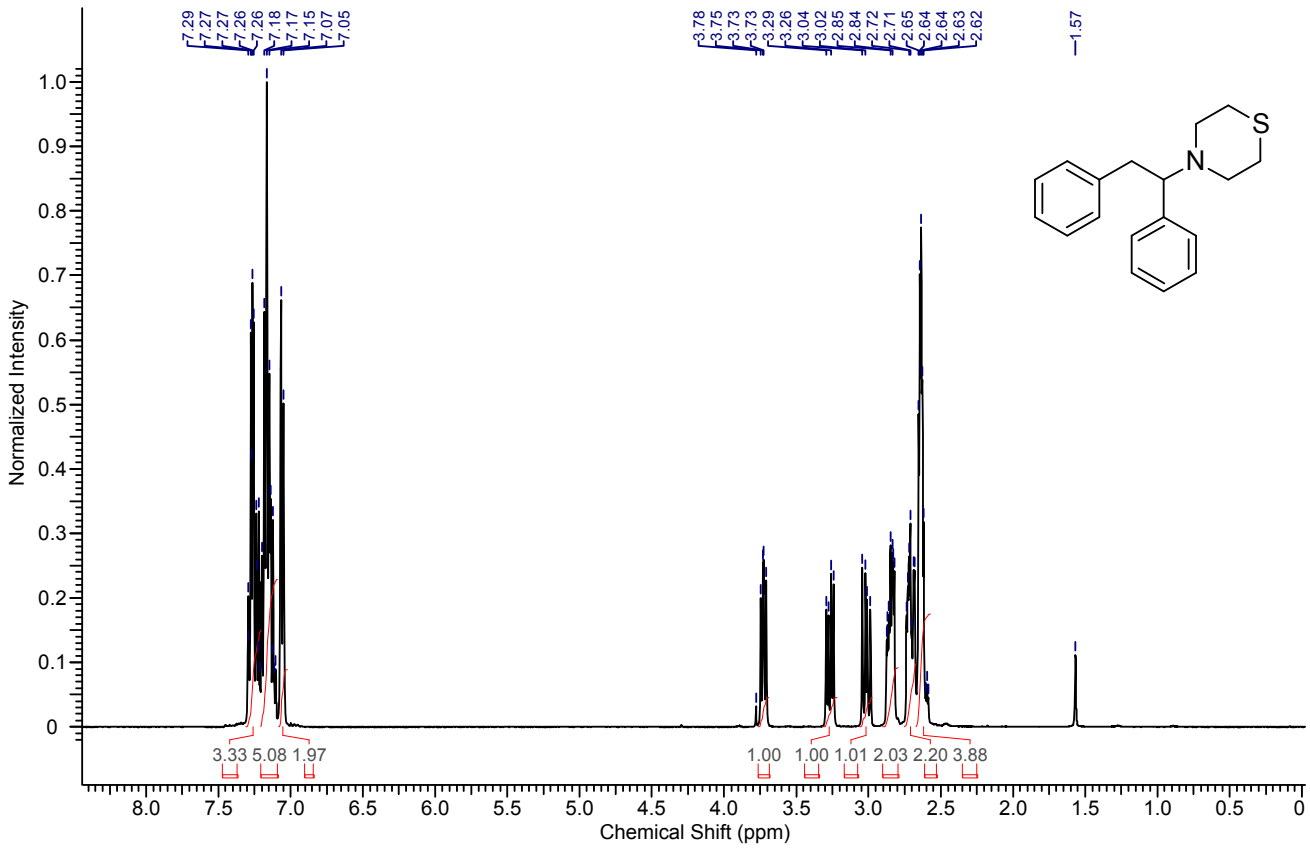


Figure S33. ^{1}H NMR spectrum of the compound **4af**

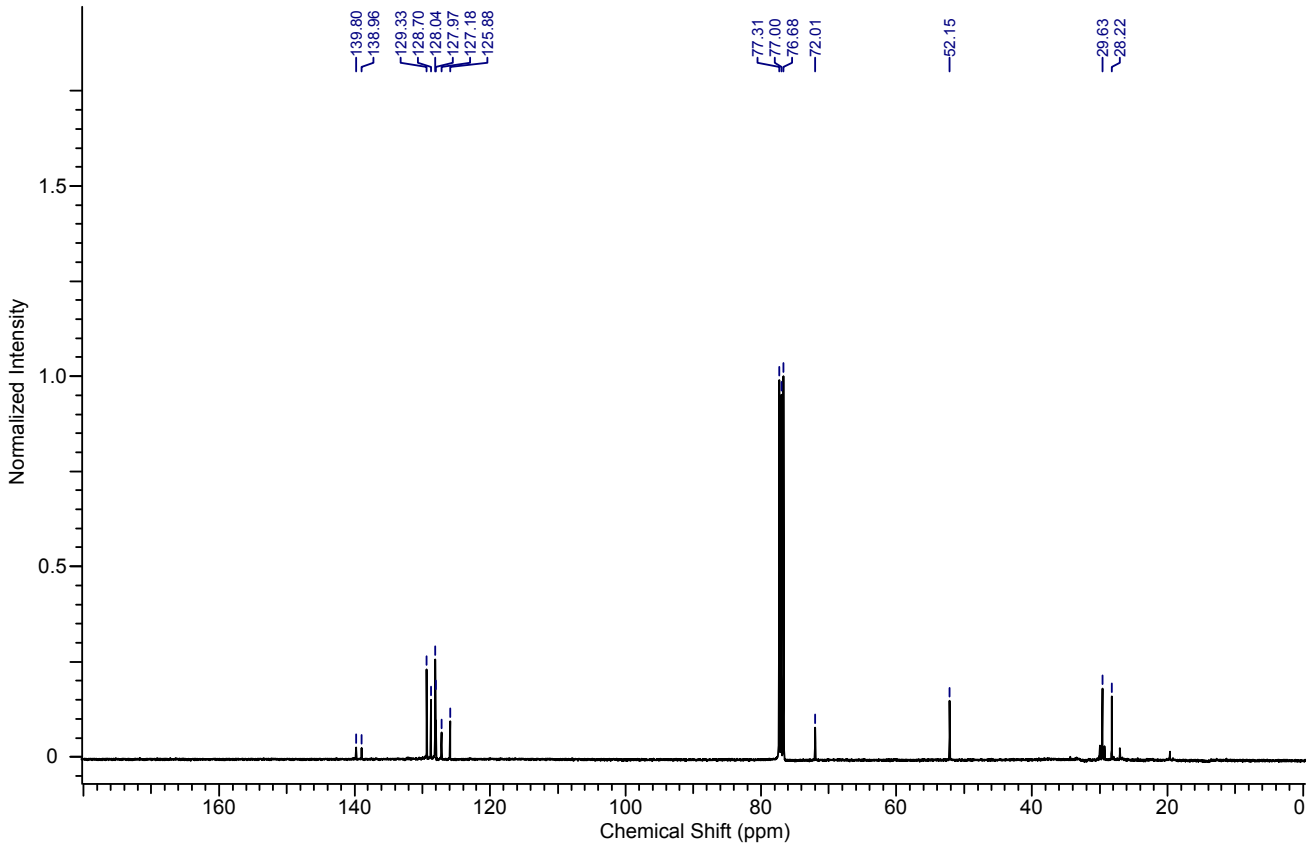


Figure S34. ^{13}C NMR spectrum of the compound **4af**

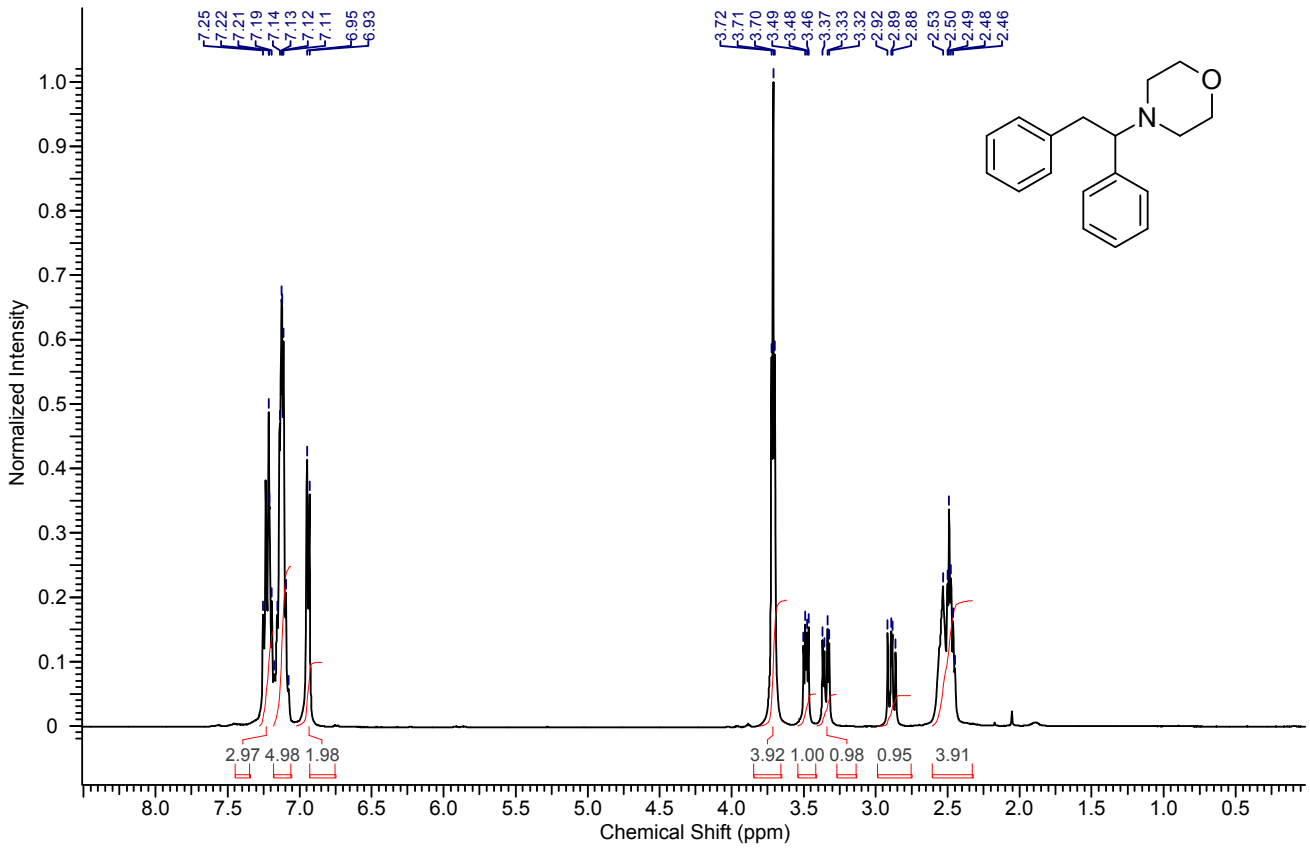


Figure S35. ^{1}H NMR spectrum of the compound **4ag**

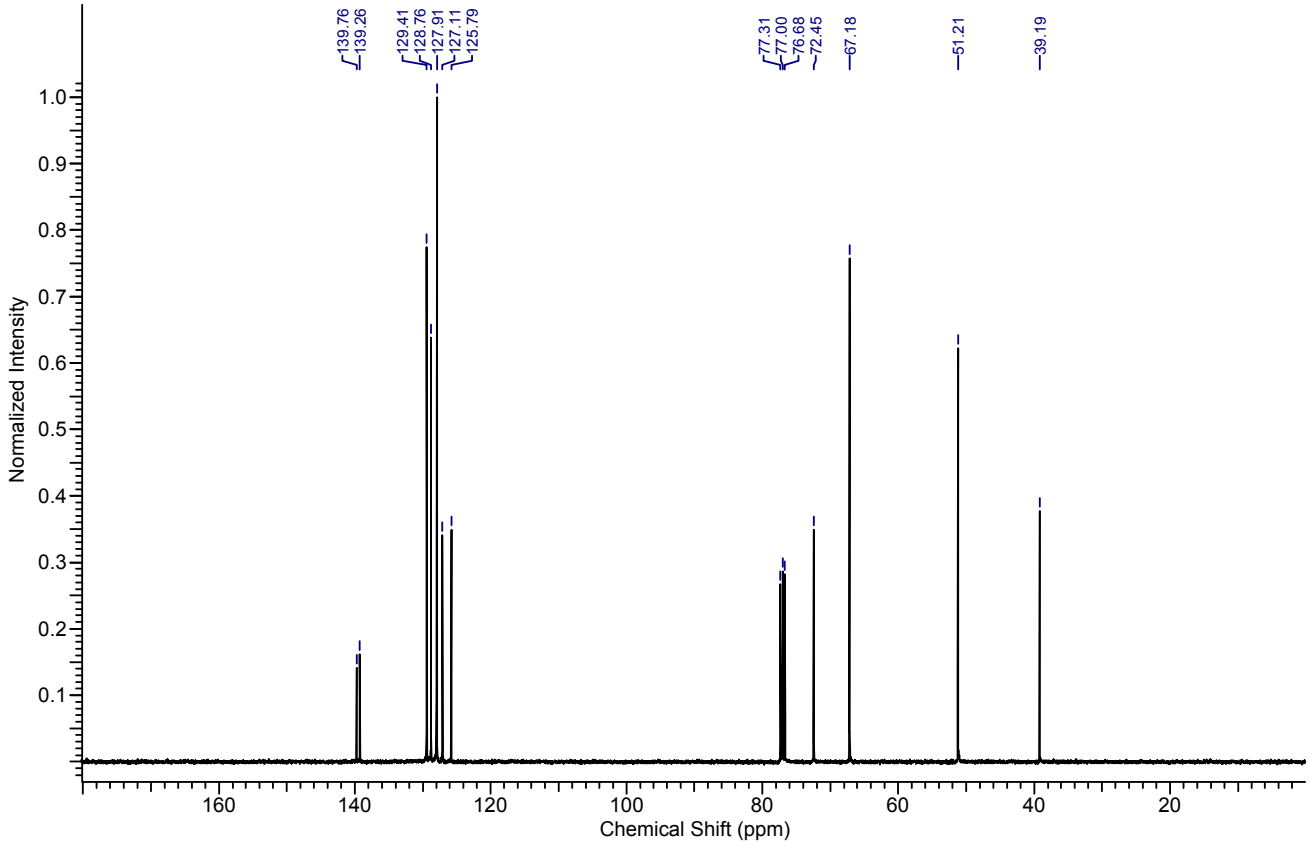


Figure S36. ^{13}C NMR spectrum of the compound **4ag**

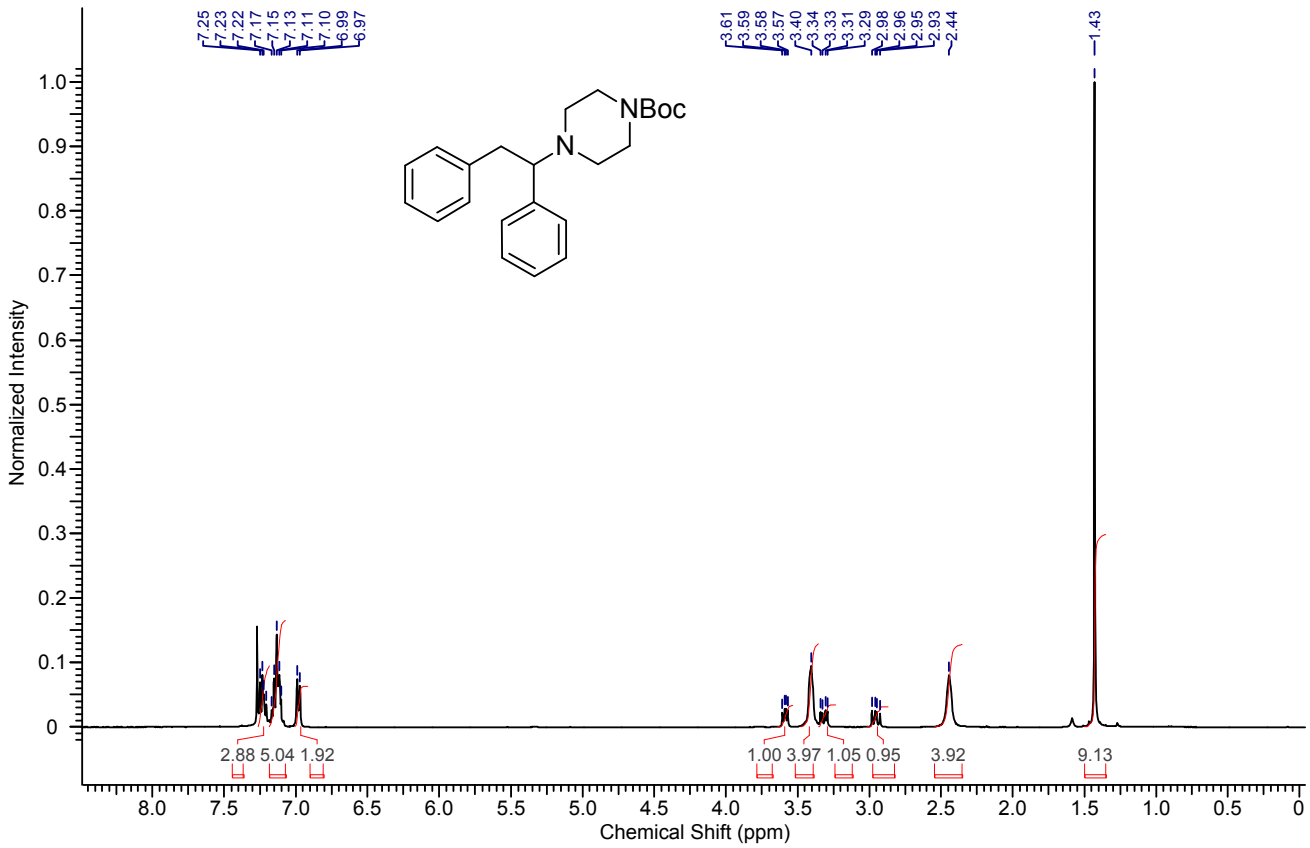


Figure S37. ^{1}H NMR spectrum of the compound **4ah**

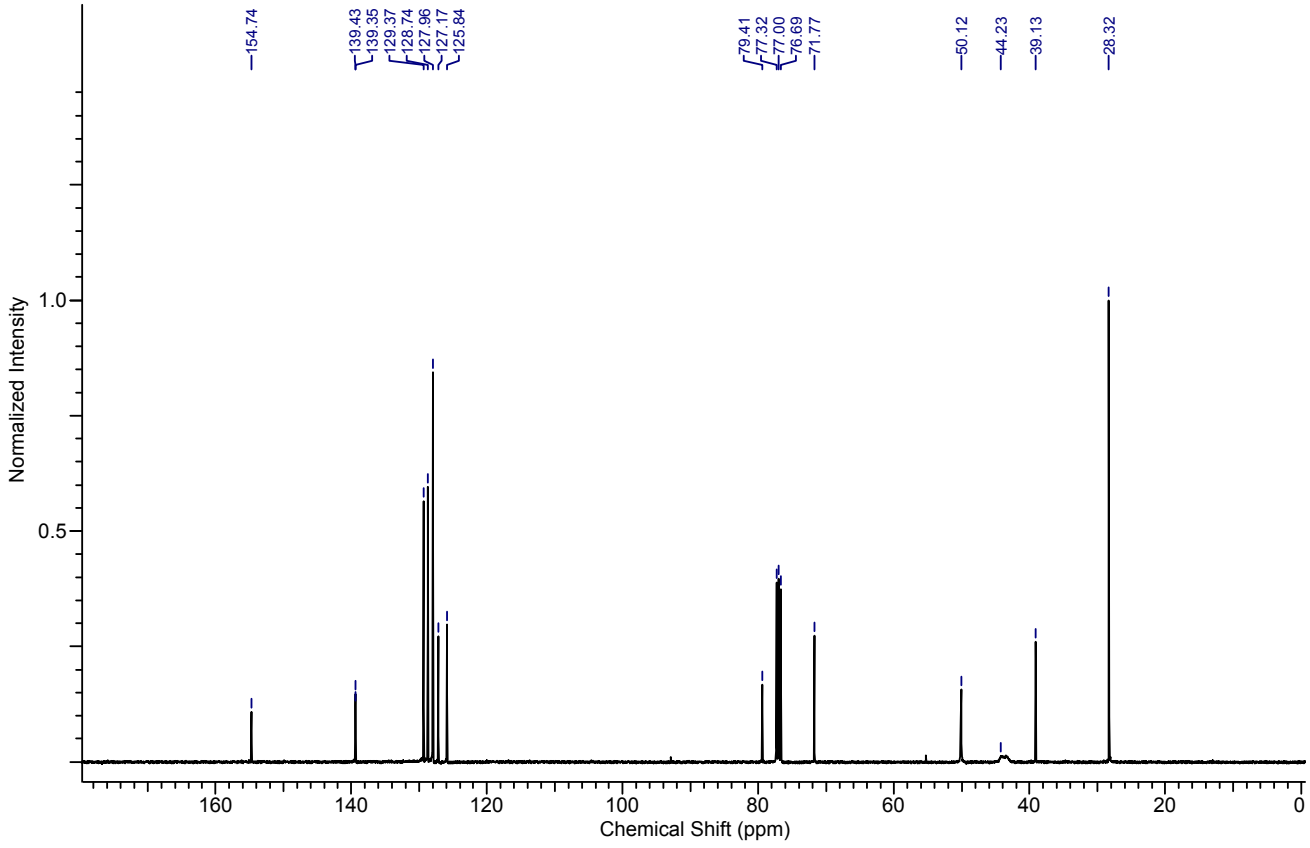


Figure S38. ^{13}C NMR spectrum of the compound **4ah**

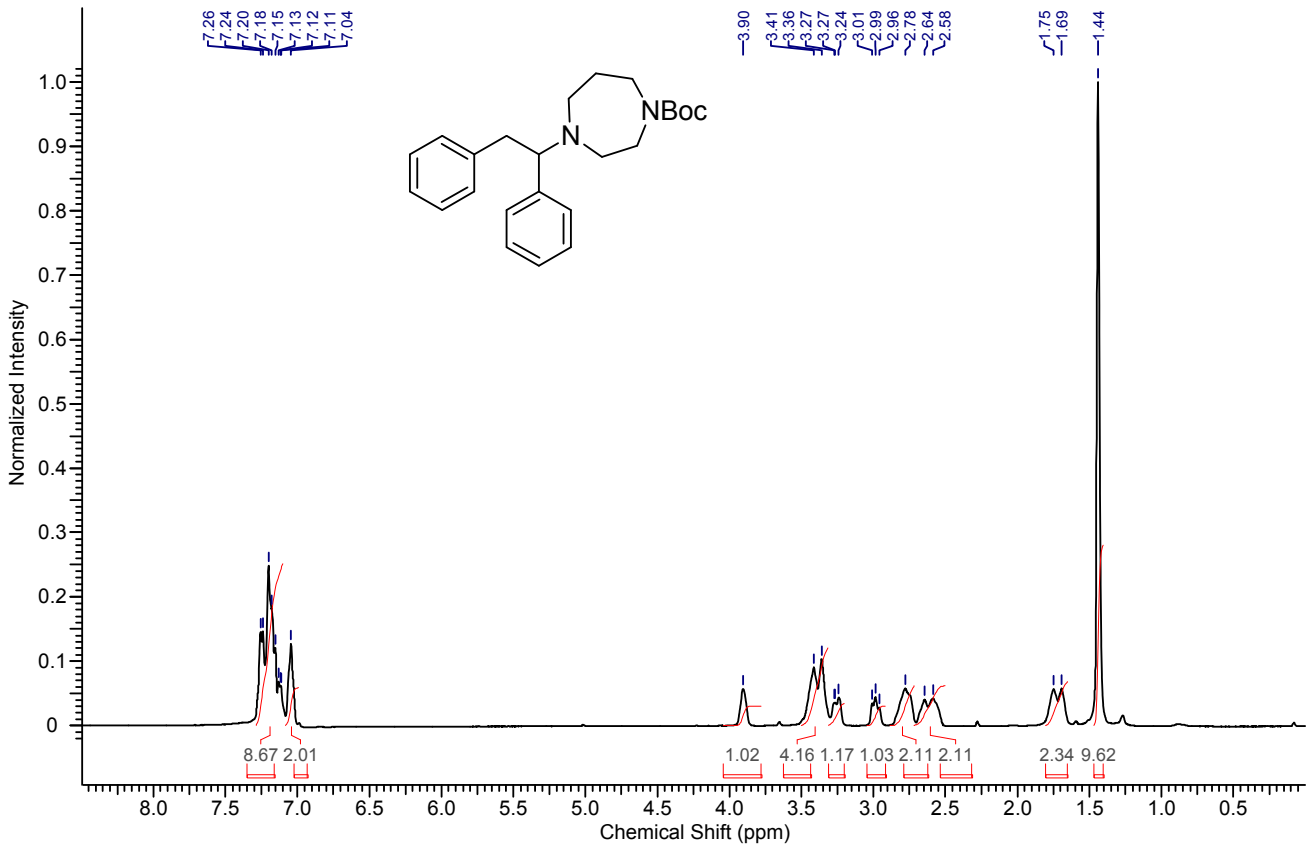


Figure S39. ^{1}H NMR spectrum of the compound **4ai**

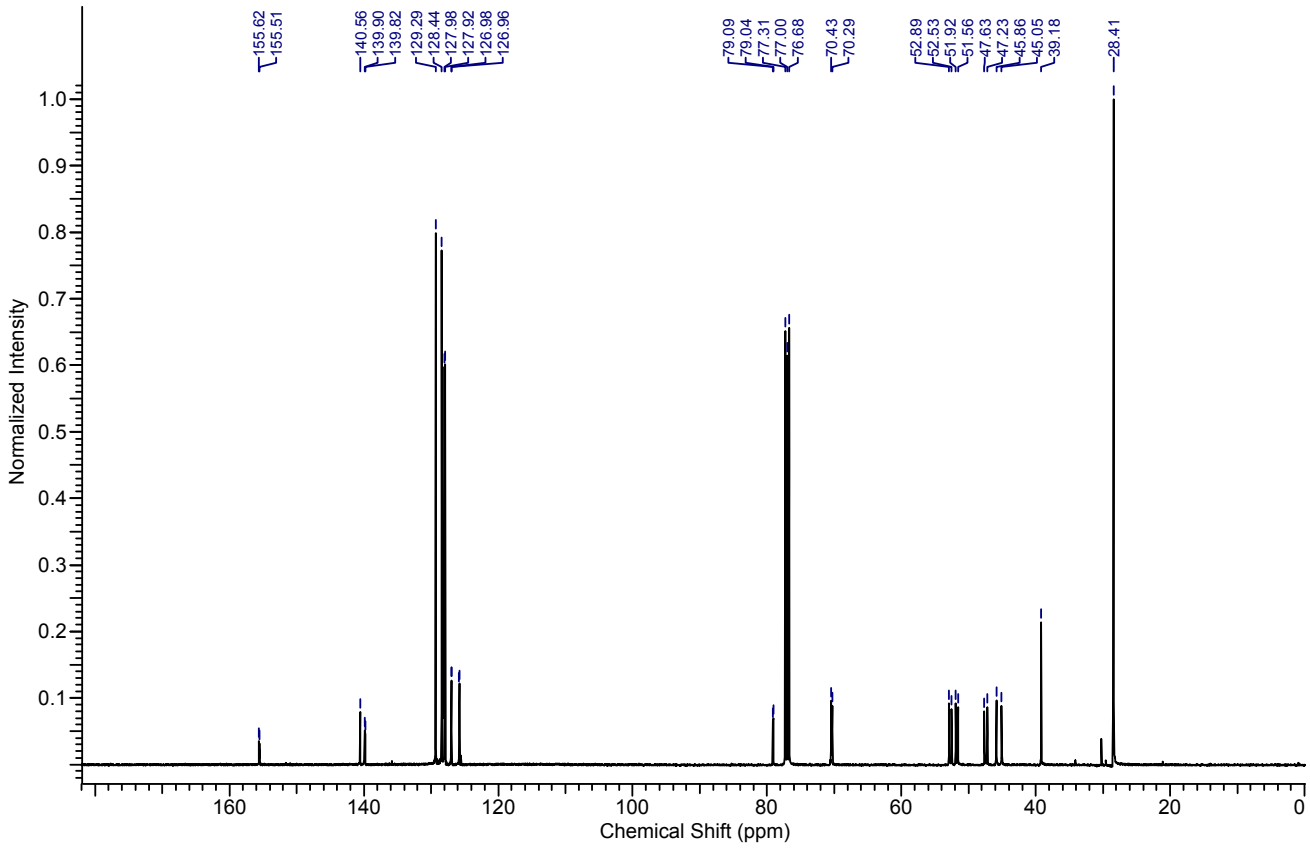


Figure S40. ^{13}C NMR spectrum of the compound **4ai**

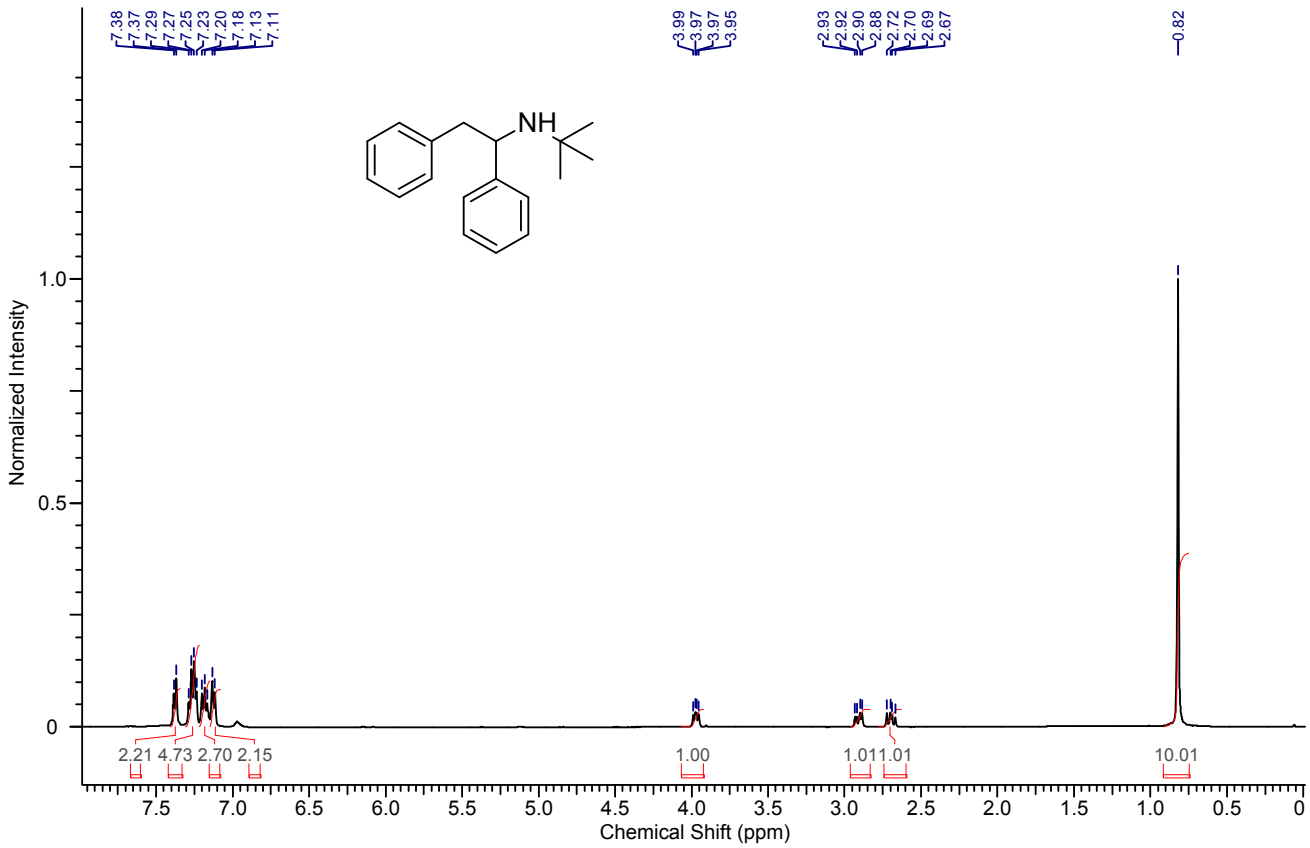


Figure S41. ^{1}H NMR spectrum of the compound **4ai**

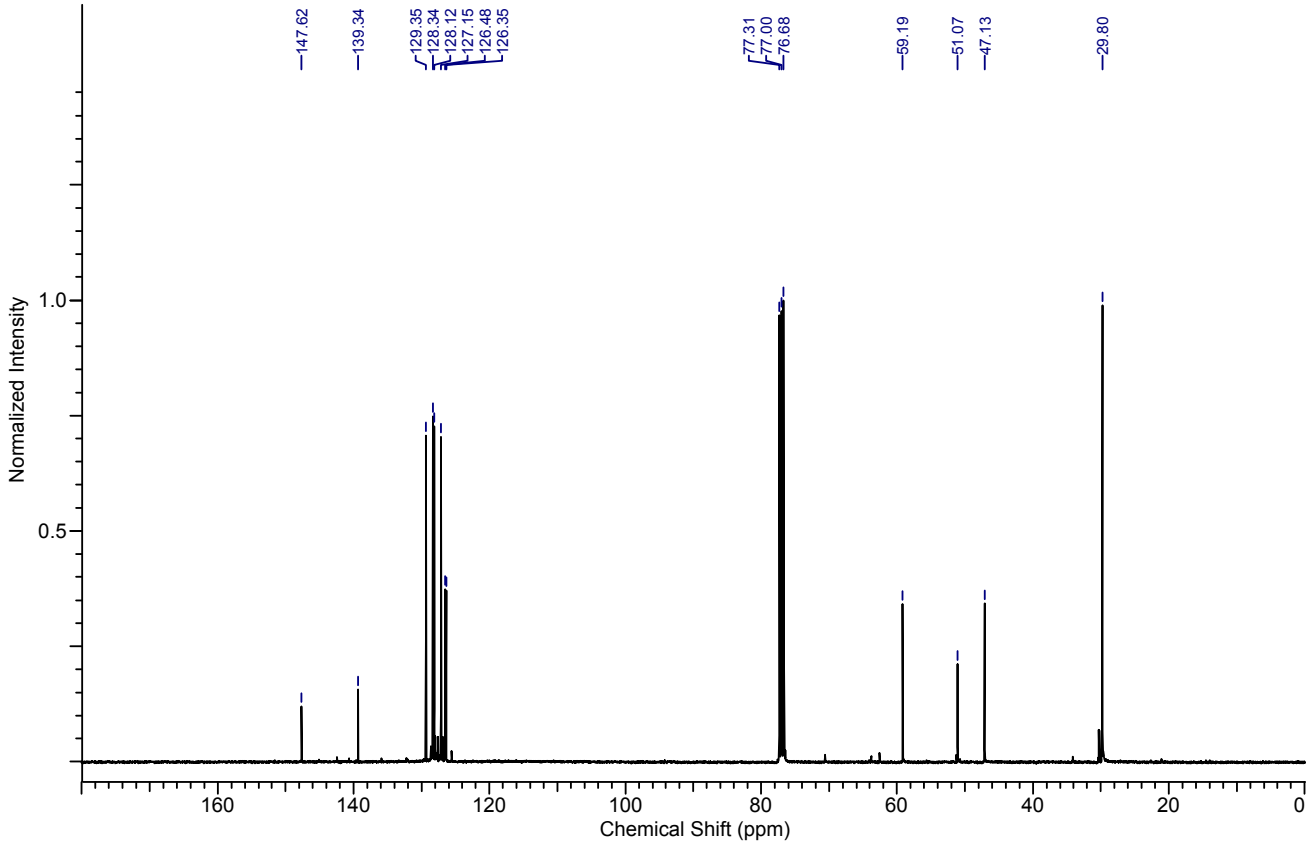


Figure S42. ^{13}C NMR spectrum of the compound **4ai**

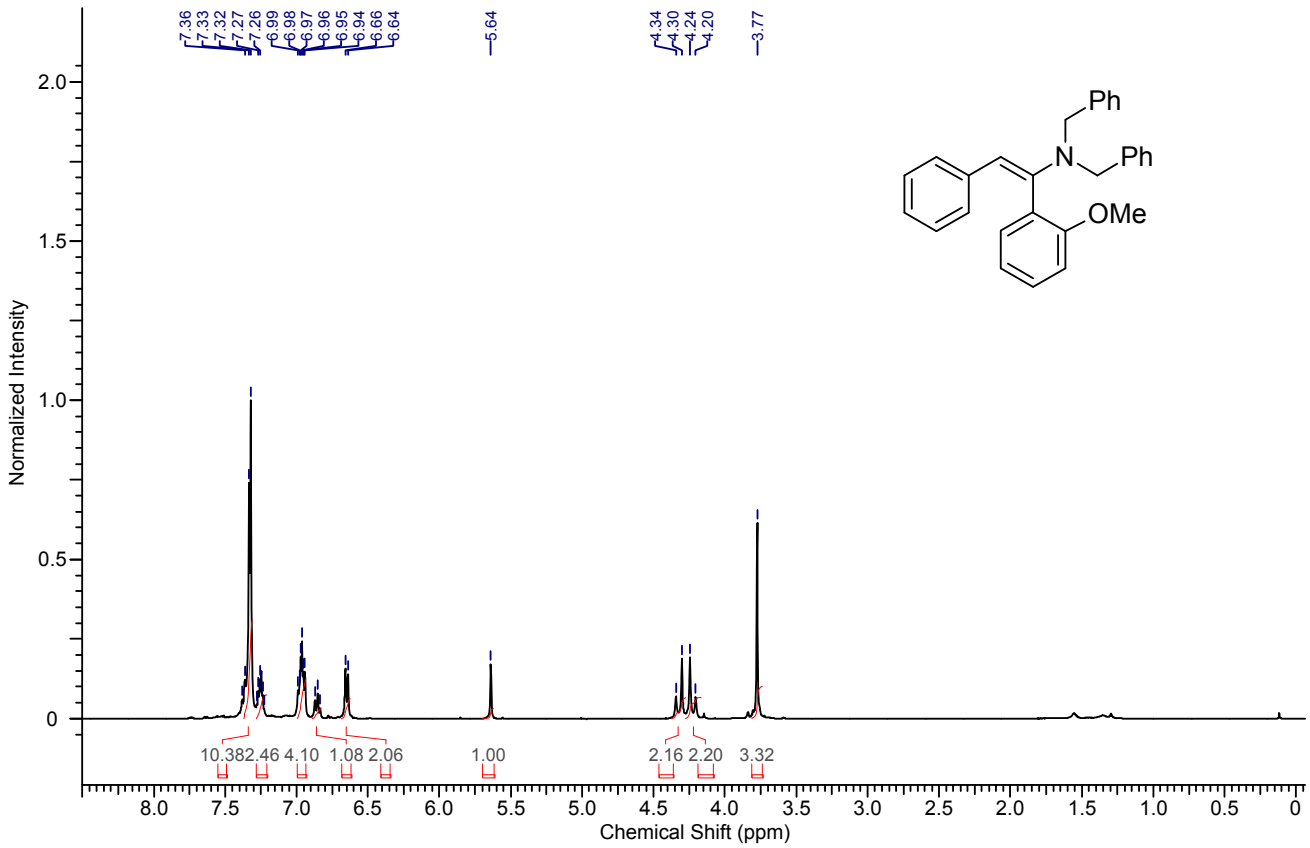


Figure S43. ^{1}H NMR spectrum of the compound **8aa**

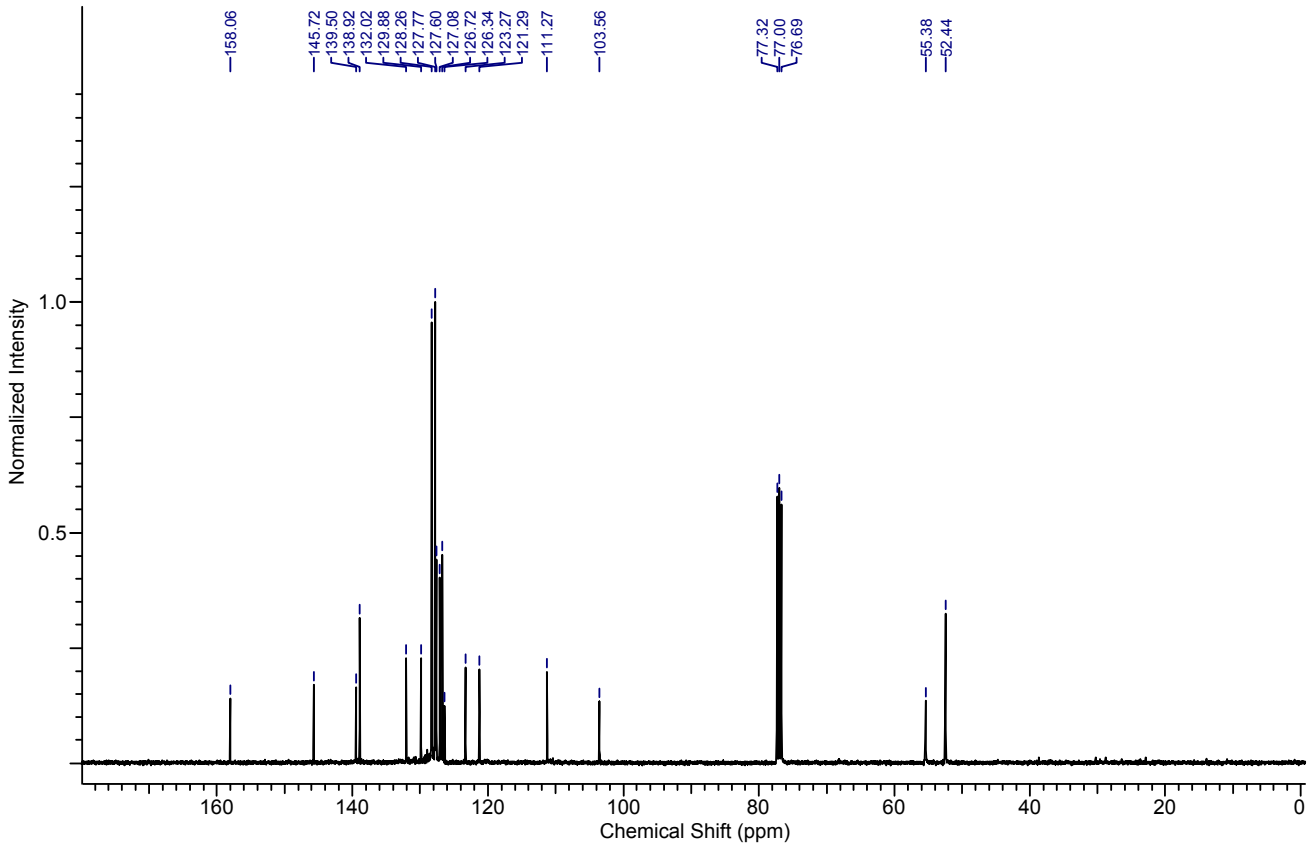


Figure S44. ^{13}C NMR spectrum of the compound **8aa**

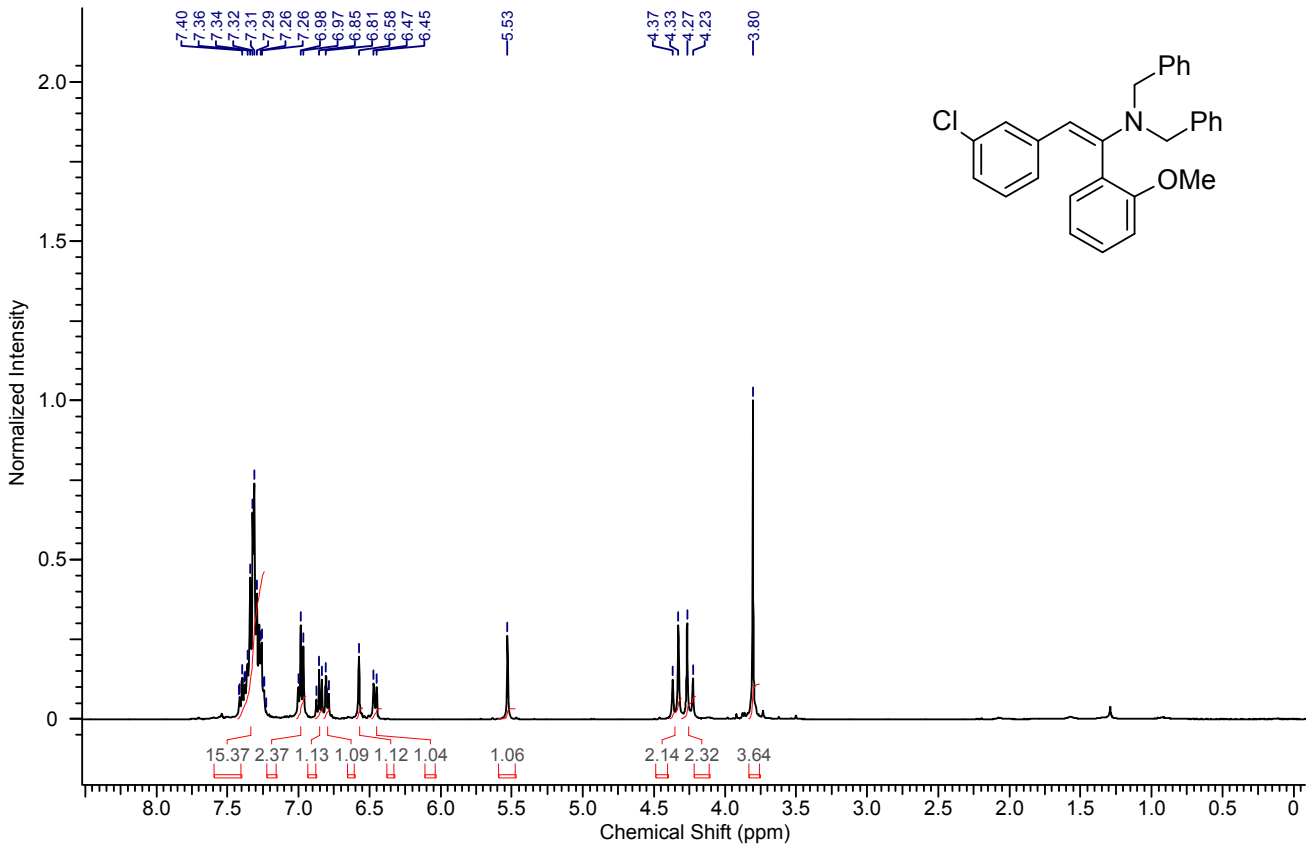


Figure S45. ^{1}H NMR spectrum of the compound **8ba**

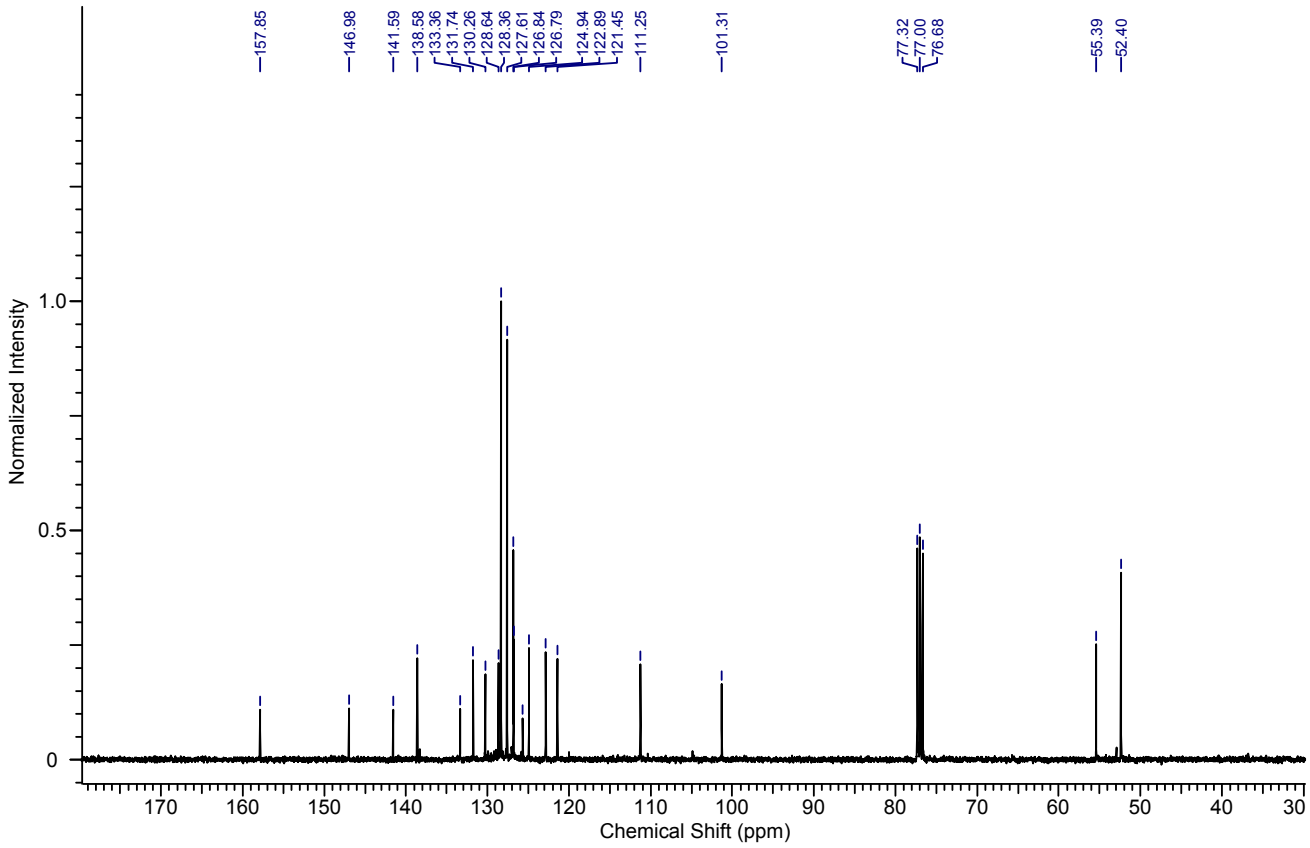


Figure S46. ^{13}C NMR spectrum of the compound **8ba**

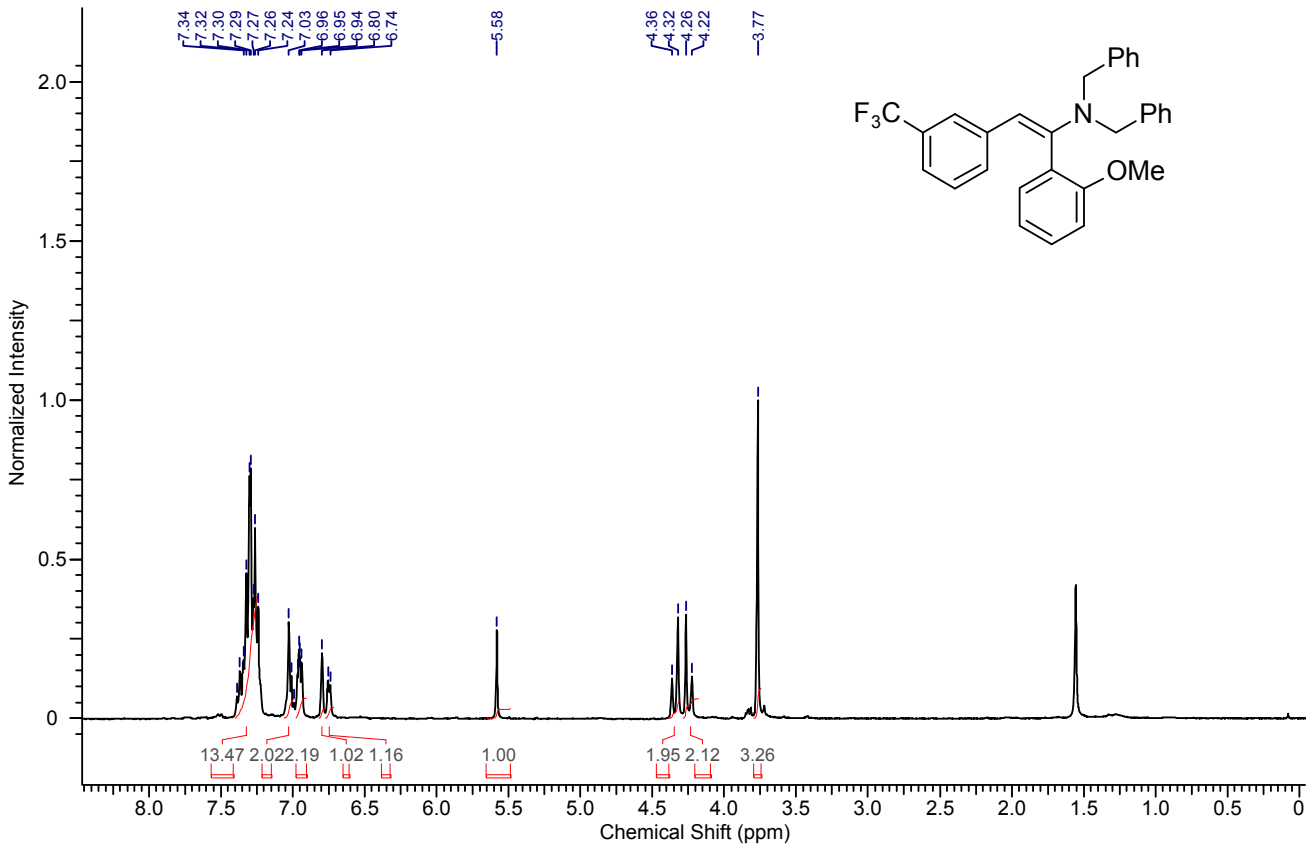


Figure S47. ^{1}H NMR spectrum of the compound **8ca**

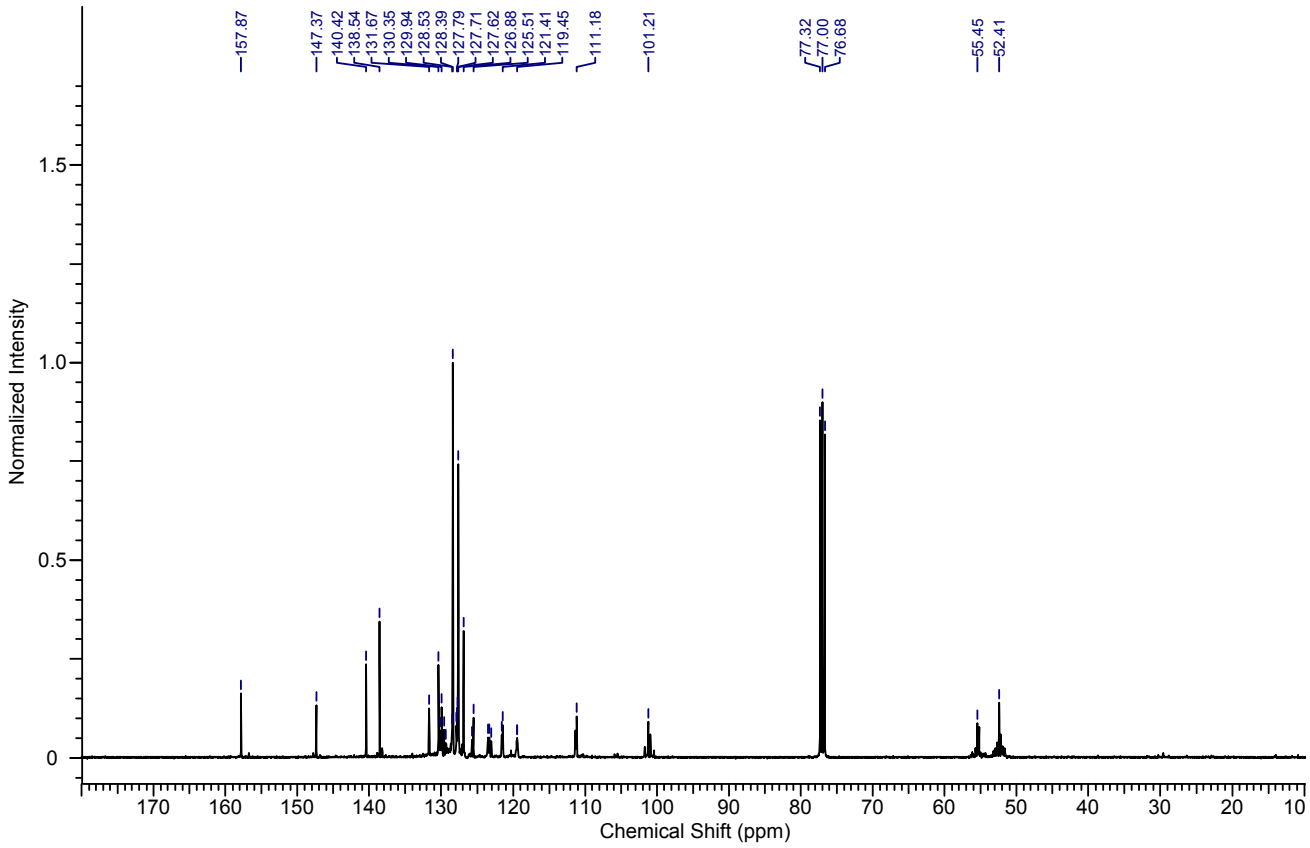


Figure S48. ^{13}C NMR spectrum of the compound **8ca**

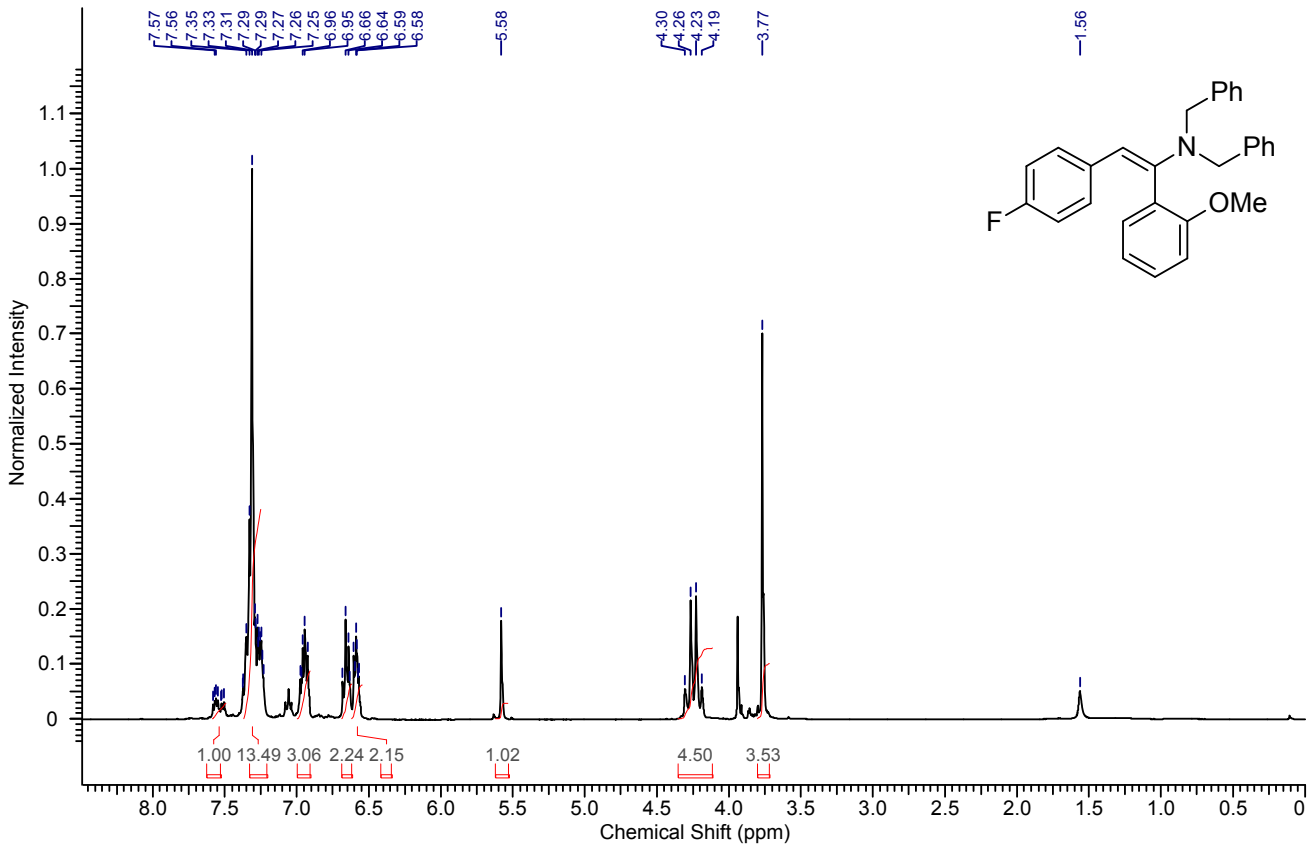


Figure S49. ^{1}H NMR spectrum of the compound **8da**

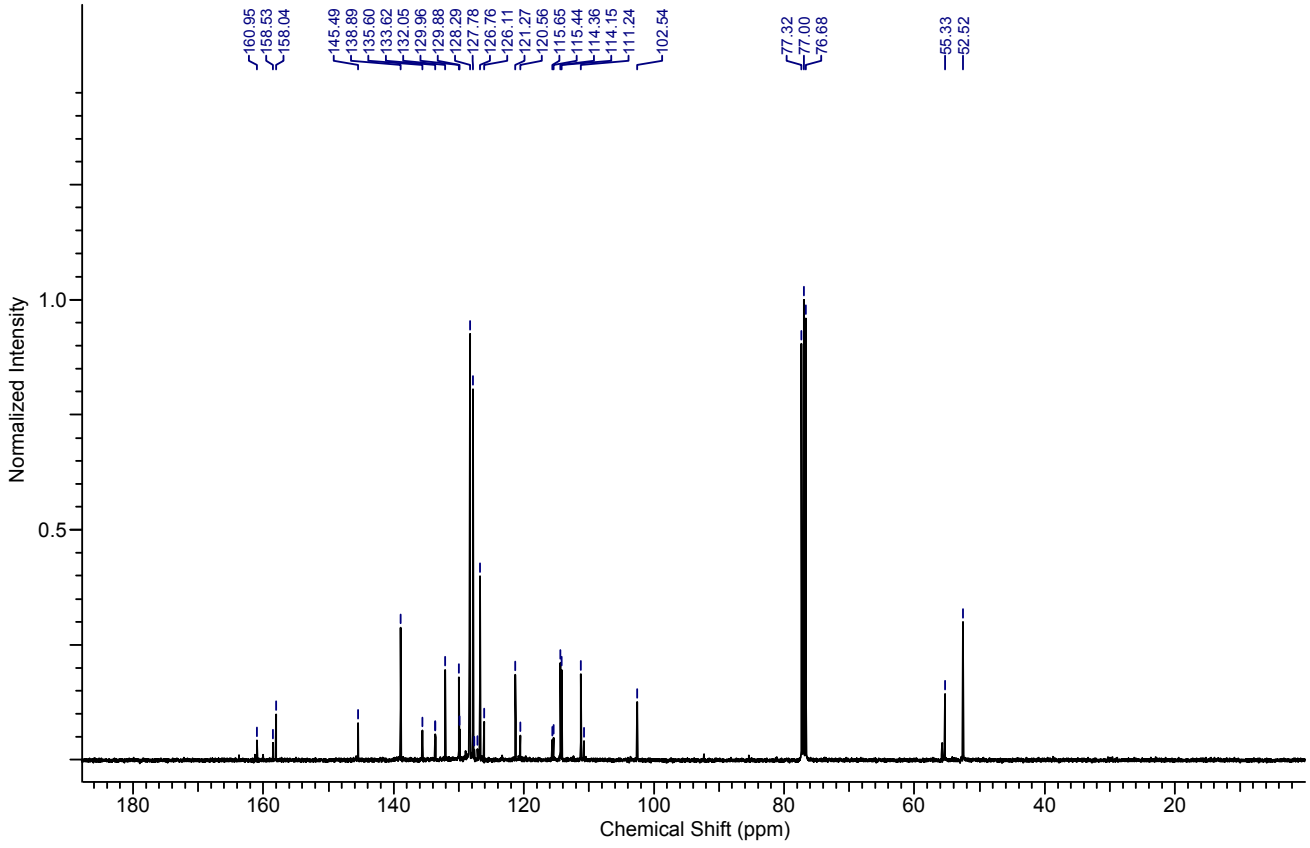


Figure S50. ^{13}C NMR spectrum of the compound **8da**