Supporting Information

Electrocatalytic Redox Neutral [3+2] Annulation of *N*-Cyclopropylanilines and Alkenes

Qi Wang,[1] Qile Wang,[2] Yuexiang Zhang,[3] Yasmine M. Mohamed,[1] Carlos Pacheco,[1] Nan Zheng,*[2] Richard N. Zare*[4] and Hao Chen*[1,3]

[1]Department of Chemistry & Environmental Science, New Jersey Institute of Technology, Newark, NJ, 07102, USA

[2]Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA

[3]Department of Chemistry and Biochemistry, Ohio University, Athens, OH 45701, USA

[4]Department of Chemistry, Stanford University, Stanford, California 94305-5080, USA

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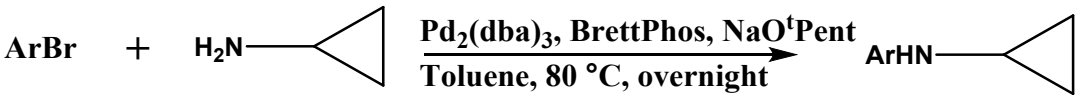
General Considerations:

All reactions were carried out under a nitrogen atmosphere. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance DPX-500 spectrometer. All ^{1}H-NMR experiments were reported in δ units, parts per million (ppm), and measured relative to the signal for residual chloroform (7.26 ppm) in the deuterated solvent. All ^{13}C NMR experiments were reported in ppm relative to deuterochloroform (77.23 ppm) and obtained with 1H decoupling. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectroscopy. The relative configuration of new compounds was established by NOSEY experiment. High-resolution mass spectra were recorded on a High-resolution Q Executive hybrid quadrupole-Orbitrap mass spectrometer (Thermo Fisher Scientific, San Jose, CA).

General Procedure 1 (GP1): Synthesis of N-cyclopropylanilines

All *N*-cyclopropylanilines were synthesized according to a modified procedure of Loeppky and co-workers as described below.[1]



To an oven-dried tube equipped with a stir bar were added 0.03 mmol of $Pd_2(dba)_3$, 0.09 mmol of BrettPhos, 4.5 mmol of NaO^{t}Pent, 3 mmol of aryl bromide, 3.3 mmol of cyclopropylamine and 6 mL of toluene. After degassing by using the freeze-pump-thaw method and heating at 80 °C for overnight, the reaction mixture was cooled to room temperature, diluted with diethyl ether, filtered through a short pad of silica gel, and concentrated under vacuum. Purification of the residual mass by column chromatography on silica gel afforded *N*-cyclopropylaniline.

3,5-Dimethyl-*N*-cyclopropylaniline. Following **GP1** with bromobenzene (416 μL, 3 mmol, 1 equiv.), the product (**1a**) was isolated after column chromatography on silica gel (3% EtOAc/hexane) as a colorless liquid (363 mg, 75%). ^{1}H NMR (500 MHz, Chloroform-d) δ 6.43 (s, 2H), 6.41 (s, 1H), 4.06 (s, 1H), 2.41 (m, 1H), 2.25 (s, 6H), 0.71 (m, 2H), 0.50 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 148.85, 138.89, 119.87, 111.20, 25.40, 21.63, 7.53. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{11}H_{16}N$ 162.128; found 162.128.

4-Chloro-*N*-cyclopropylaniline. Following **GP1** with 4-chlorobromobenzene (574 mg, 3 mmol, 1 equiv.), the product was isolated after column chromatography on silica gel (3% EtOAc/hexane) as a colorless oil (300 mg, 60%). Spectral data correspond to those described in the literature.[2]

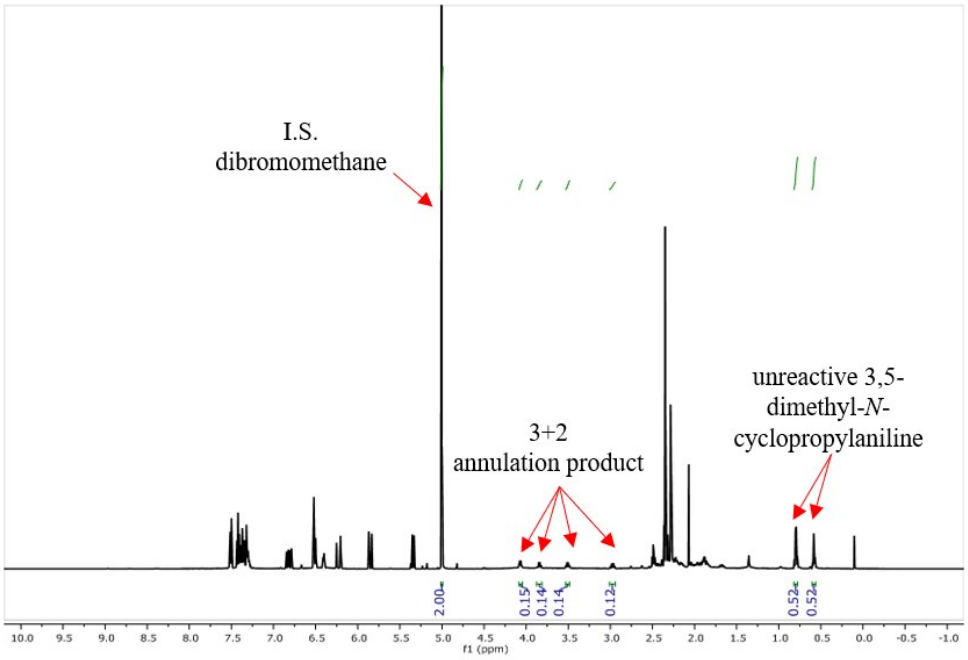
***N*-Cyclopropyl-2-biphenylamine.** Following **GP1** with 2-bromobiphenyl (701 mg, 3 mmol, 1 equiv.), the product was isolated after column chromatography on silica gel (2% EtOAc/hexane) as a colorless liquid (564 mg, 90%). Spectral data correspond to those described in the literature.[3]

***N*-Cyclopropyl-1-napthylamine.** Following **GP1** with 1-bromonaphthalene (623 mg, 3 mmol, 1 equiv.), the product was isolated after column chromatography on silica gel (3% EtOAc/hexane) as a white solid (467 mg, 85%). Spectral data correspond to those described in the literature.[1]

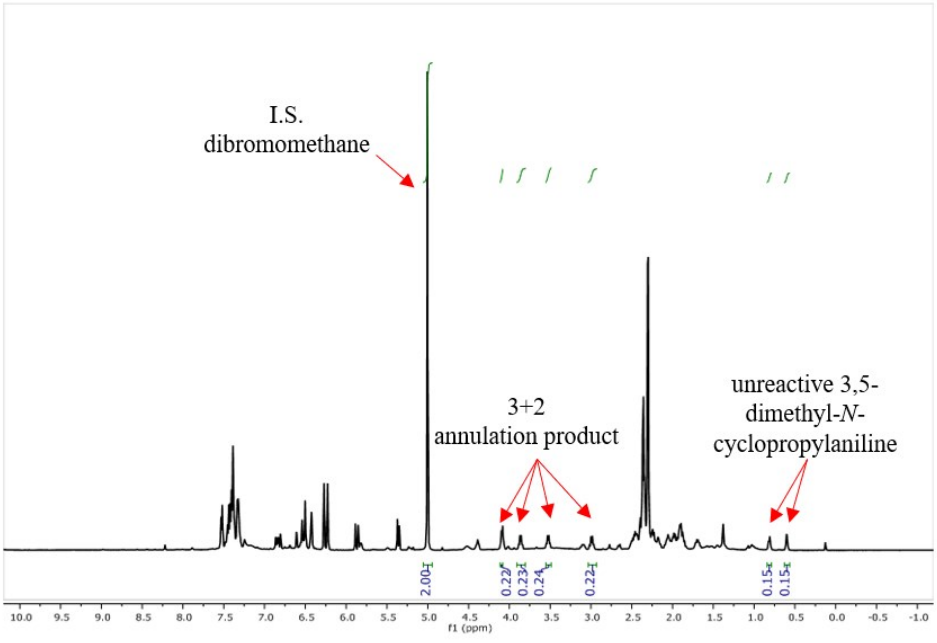
General Procedure 2 (GP2): Scale-up Bulk Electrochemistry-assisted [3+2] Annulation Reaction

A 20 mL clear screw glass vial equipped with one Pt plate (2 cm×1 cm×0.1 cm, length ×width ×thickness) and one piece of reticulated vitreous carbon electrode (2 cm×1.3 cm×1.3 cm, length×width×thickness) as cathode and anode respectively, was charged with *N*-cyclopropylaniline (1 mmol), styrene (10 mmol), and LiOTf (10 mmol) and 10 mL MeCN. The reaction mixture was degassed by the freeze-pump-thaw cycles. A TEKPOWER variable linear direct current (DC) power supply was used to control the current (1 mA) for electro-oxidation. After the reaction was complete as shown by TLC, the mixture was filtered through a short silica pad and eluted with Et_2O (10 mL). The solution was concentrated by vacuum, and the residue was purified by silica gel flash chromatography to afford the corresponding annulation reaction products. The diastereoisomers were assigned by NOSEY.

GP2 was used to conduct the optimization studies shown in Table 1. Additionally, we performed two studies to identify the optimal loading for LiOTf and styrene. For the first study, we reduced the amount of electrolyte, LiOTf by 50% and performed the reaction under the optimized conditions otherwise (1 mmol of 3,5-dimethyl-*N*-cyclopropylaniline, 10 mmol of styrene, 5 mmol of LiOTf, 10 mL of MeCN, I_{cell}=1 mA, 9 h) and obtained the product in an NMR yield of 29% with 26% of unreactive 3,5-dimethyl-*N*-cyclopropylaniline (shown below). The yield was significantly lower than the one under the optimized reaction condition (NMR yield 75%). For the second study, we performed the reaction using 5 mmol of styrene rather than 10 mmol of styrene under the optimized condition otherwise (1 mmol of 3,5-dimethyl-*N*-cyclopropylaniline, 5 mmol of styrene, 10 mmol of LiOTf, 10 mL of MeCN, I_{cell}=1 mA, 9 h) and obtained the product in an NMR yield of 45% with 7.5% remaining 3,5-dimethyl-*N*-cyclopropylaniline (shown below). The yield was also lower than the one (75%) under the optimized condition.



^{1}H NMR spectrum of scale-up bulk electrochemistry-assisted [3+2] annulation reaction (1 mmol of 3,5-dimethyl-N-cyclopropylaniline, 10 mmol of styrene, 5 mmol of LiOTf, 10 mL of MeCN, Icell=1 mA, 9 h)



^{1}H NMR spectrum of scale-up bulk electrochemistry-assisted [3+2] annulation reaction (1 mmol of 3,5-dimethyl-N-cyclopropylaniline, 5 mmol of styrene, 10 mmol of LiOTf, 10 mL of MeCN, Icell=1 mA, 9 h)

Procedure for Electrolysis in Divided Cell

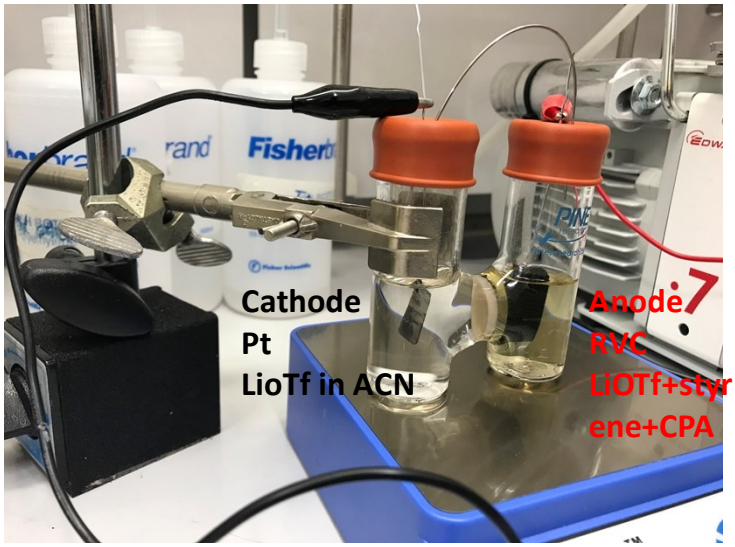


Figure S1. Divided electrolysis cell setup

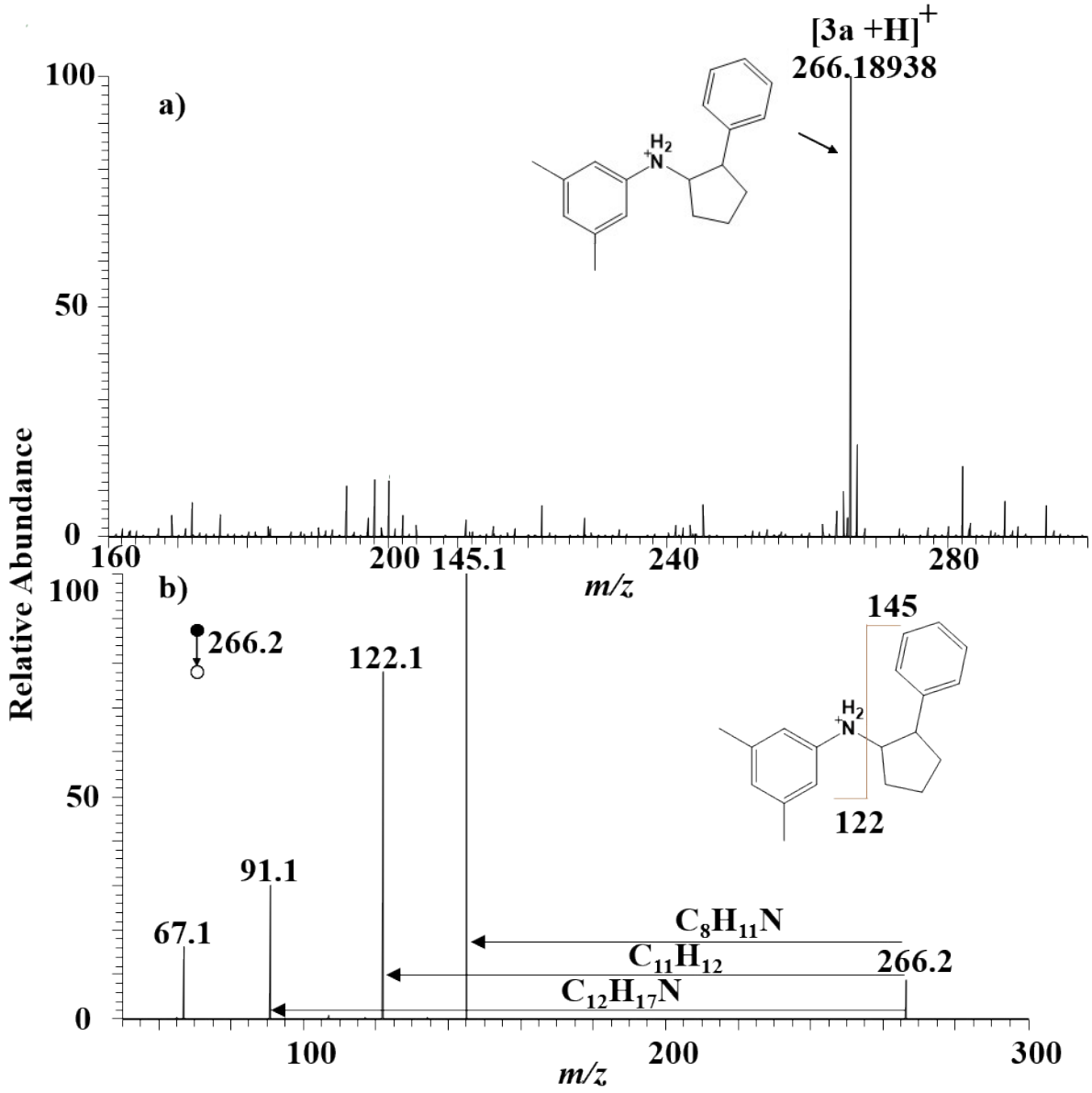
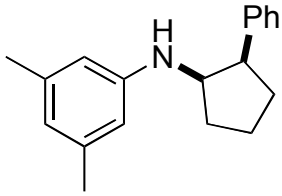


Figure S2. a) NanoESI-MS spectrum showing the formation of the product **3a** by divided cell electrolysis (the anode RVC side); b) MS/MS spectrum of [**3a**+H]$^+$.

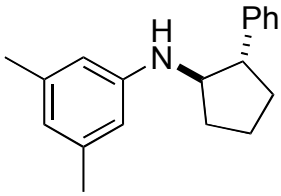
Compound characterization and NMR Spectra

Following GP2 with cyclopropylaniline (102 mg, 0.63 mmol), cycloadduct **3a** was obtained after silica gel column chromatography (15% EtOAc/hexane) as a separable mixture of two diastereoisomers.



Data for **3a-*cis***: colorless oil (78 mg,47%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.28 (m, 2H), 7.22 (dt, *J* = 7.2, 3.0 Hz, 3H), 6.31 (s, 1H), 6.12 (s, 2H), 3.99 (q, *J* = 5.8 Hz, 1H), 3.42 (q, *J* = 7.6 Hz, 1H), 2.20 (s, 6H), 2.16 – 2.05 (m, 3H), 1.96 (tq, *J* = 7.1, 3.4 Hz, 1H), 1.81 (dddd, *J* = 13.3, 8.9, 4.9, 2.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.87, 140.75, 138.69, 128.65, 128.31, 126.44, 118.92, 111.11, 57.40, 48.20, 31.98, 28.65, 22.04, 21.48.HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{19}H_{23}N$ 266.190; found 266.191. The cis configuration was established by NOSEY experiment based on the integration of correlation peak (1735).

Data for **3a-*trans***: colorless oil (43 mg,26%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 (q, *J* =

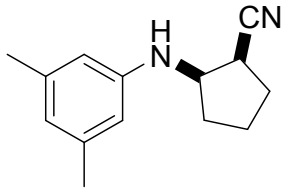


5.8, 3.8 Hz, 4H), 7.15 – 7.09 (m, 1H), 6.24 (s, 1H), 6.08 (s, 2H), 3.67 (t, *J* = 7.5 Hz, 1H), 2.81 (q, *J* = 8.6 Hz, 1H), 2.28 (dq, *J* = 14.6, 7.5 Hz, 1H), 2.10 (s, 6H), 1.87 – 1.63 (m, 4H), 1.57 – 1.46 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.10, 143.89, 138.78, 128.53, 127.40, 126.36, 119.07, 111.32, 61.55, 53.22, 33.63, 29.72, 23.38, 21.46. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{19}H_{23}N$ 266.190; found 266.191. The trans configuration was established by NOSEY experiment based on the integration of correlation peak (157).

The *cis/trans* configuration for the rest of the products was assigned by analogy to **3a**.

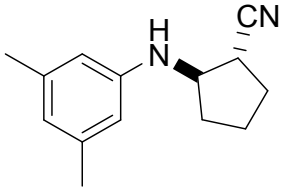
Following GP2 with cyclopropylaniline (89 mg, 0.55 mmol), cycloadduct **3b** was obtained after silica gel column chromatography (15% EtOAc/hexane) as a separable mixture of two diastereoisomers.

Data for **3b-*cis***: colorless oil (61 mg, 52%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.44 (tt, *J* = 1.6,



0.8 Hz, 1H), 6.32 – 6.29 (m, 2H), 3.97 (dt, *J* = 9.3, 6.7 Hz, 1H), 3.29 – 3.24 (m, 1H), 2.26 (s, *J* = 0.8 Hz, 6H), 2.20 – 2.10 (m, 2H), 2.10 – 2.02 (m, 1H), 2.02 – 1.93 (m, 1H), 1.78 – 1.67 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.60, 139.14, 120.53, 120.34, 111.68, 56.92, 34.34, 31.17, 28.77, 21.56, 21.20. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{14}H_{18}N_2$ 215.154; found 215.154.

Data for **3b-*trans***): colorless oil (33 mg, 28%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.48 – 6.45

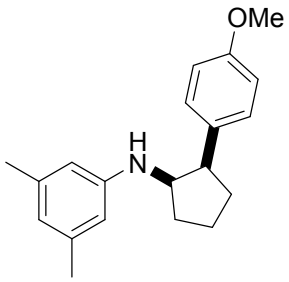


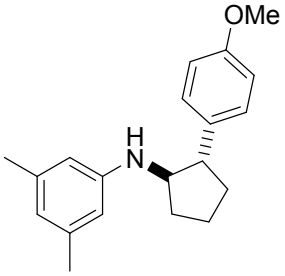
(m, 1H), 6.31 (d, *J* = 1.4 Hz, 2H), 4.13 (ddd, *J* = 7.0, 4.8, 3.7 Hz, 1H), 2.79 (ddd, *J* = 8.5, 4.9, 3.7 Hz, 1H), 2.26 (s, 6H), 2.13 – 1.98 (m, 3H), 1.93 – 1.86 (m, 2H), 1.58 (dtd, *J* = 12.4, 7.4, 4.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.80, 139.41, 122.28, 120.86, 111.74, 59.65, 35.30,

33.27, 29.56, 23.61, 21.55. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{14}H_{18}N_2$ 215.154; found 215.154.

Following GP2 with cyclopropylaniline (93 mg, 0.58 mmol), cycloadduct **3c** was obtained after silica gel column chromatography (3% EtOAc/hexane) as a separable mixture of two diastereoisomers.

Data for **3c-*cis***: colorless oil (62 mg, 36%) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 – 7.11 (m, 2H), 6.86 – 6.83 (m, 2H), 6.31 (dq, J = 1.8, 0.9 Hz, 1H), 6.12 (d, J = 1.5 Hz, 2H), 3.92 (q, J = 5.6 Hz, 1H), 3.80 (s, 3H), 3.36 (q, J = 7.7 Hz, 1H), 2.22 – 2.16 (m, 6H), 2.14 – 2.01 (m, 3H), 1.98 – 1.88 (m, 1H), 1.83 – 1.72 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.16, 138.75, 132.66, 129.62, 127.64, 118.93, 113.75, 111.14, 55.31, 47.41, 31.91, 28.84, 26.05, 22.07, 21.55. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{20}H_{25}NO$ 296.201; found 296.200.

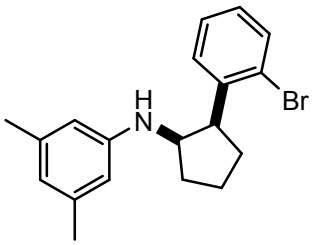




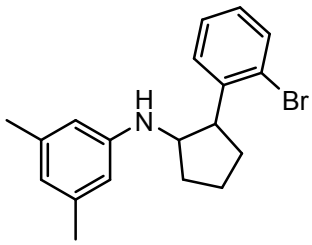
Data for **3c-*trans***: colorless oil (65 mg, 38%) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 – 7.21 (m, 2H), 6.95 – 6.86 (m, 2H), 6.38 (tt, J = 1.5, 0.7 Hz, 1H), 6.23 (d, J = 1.5 Hz, 2H), 3.85 (s, 3H), 3.77 – 3.72 (m, 1H), 2.90 (dt, J = 9.9, 8.0 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.25 (d, J = 0.7 Hz, 6H), 2.22 (td, J = 8.0, 4.1 Hz, 1H), 1.97 – 1.85 (m, 2H), 1.78 (ddt, J = 12.8, 10.0, 8.6 Hz, 1H), 1.63 (ddt, J = 12.9, 9.0, 6.4 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 158.19, 148.19, 138.83, 135.78, 128.34, 119.09, 113.98, 111.34, 61.58, 55.35, 52.38, 33.48, 29.78, 23.21, 21.54. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{20}H_{25}NO$ calc'd 296.201; found 296.200.

Following GP2 with cyclopropylaniline (135 mg, 0.84 mmol), cycloadduct **3d** was obtained after silica gel column chromatography (3% EtOAc/hexane) as a inseparable mixture of two diastereoisomers (only the ***cis*** isomer was isolated).

Data for **3d-*cis***: colorless oil. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.55 – 7.49 (m, 1H), 7.39 – 7.33 (m, 1H), 7.27 (d, J = 7.0 Hz, 1H), 7.06 (td, J = 7.7, 1.7 Hz, 1H), 6.25 (s, 1H), 6.04 (s, 2H), 4.16 (td, J = 6.2, 3.1 Hz, 1H), 3.67 (dt, J = 12.8, 6.7 Hz, 1H), 2.28 – 2.16 (m, 2H), 2.14 (s, 6H), 2.04 – 1.90 (m, 2H), 1.87 – 1.69 (m, 2H). 13C NMR (126 MHz, CDCl3) δ 147.58, 139.52, 138.59, 133.04, 129.08, 128.18, 127.25, 126.27, 119.04, 111.25, 55.17, 49.13, 33.49, 29.28, 22.66, 21.48. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{19}H_{22}NBr$ calc'd 344.101; found 344.101.



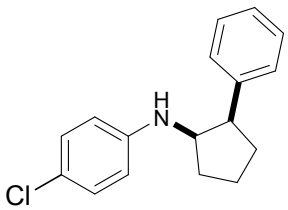
Data for **3d-mixture**: colorless oil (202 mg, 70%). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.52 (dd, J = 7.9, 1.3 Hz, 3H), 7.36 (dd, J = 7.8, 1.7 Hz, 2H), 7.33 – 7.22 (m, 5H), 7.05 (qd, J = 7.9, 1.8 Hz, 3H), 6.34 – 6.31 (m, 1H), 6.26 (tt, J = 1.5, 0.8 Hz, 2H), 6.18 (s, 1H), 6.07 – 6.03 (m, 4H), 4.17 (td, J = 6.1, 3.1 Hz, 2H), 3.83 (dt, J = 8.9, 7.3 Hz, 1H), 3.68 (dt, J = 11.4, 6.7 Hz, 2H), 3.45



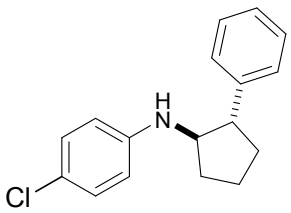
(dt, J = 10.0, 8.4 Hz, 1H), 2.47 – 2.37 (m, 1H), 2.22 – 2.13 (m, 20H), 2.01 – 1.72 (m, 12H), 1.67 – 1.56 (m, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 147.67, 142.74, 139.57, 139.06, 138.89, 138.59, 133.06, 132.91, 129.10, 128.20, 127.98, 127.90, 127.70, 127.27, 126.30, 125.54, 119.17, 119.01, 111.23, 111.19, 61.44, 55.17, 51.43, 49.17, 33.55, 33.42, 32.55, 29.33, 23.10, 22.70, 21.59, 21.53. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{19}H_{22}NBr$ calc'd 344.101; found 344.101.

Following GP2 with cyclopropylaniline (97 mg, 0.58 mmol), cycloadduct **4a** was obtained after silica gel column chromatography (5% EtOAc/hexane) as a separable mixture of two diastereoisomers.

Data for **4a-*cis***: colorless oil (85 mg, 54%) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 (q, *J* = 8.9, 8.2 Hz, 2H), 7.23 (d, *J* = 7.1 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.07 – 7.00 (m, 2H), 6.38 (d, *J* = 8.5 Hz, 2H), 3.95 (q, *J* = 6.0 Hz, 1H), 3.44 (q, *J* = 7.4 Hz, 1H), 2.22 – 2.04 (m, 3H), 1.97 (ddt, *J* = 13.2, 8.9, 4.6 Hz, 1H), 1.86 – 1.70 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.24, 140.56, 128.82, 128.59, 128.32, 126.54, 121.67, 114.38, 57.84, 48.03, 31.94, 29.03, 22.09. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{17}H_{18}NCl$ calc'd 272.120; found 272.120.

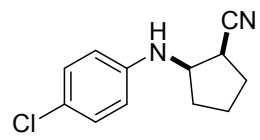


Data for **4a-*trans***: colorless oil (43 mg, 27%) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.15 (m, 3H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.41 (d, *J* = 8.4 Hz, 2H), 3.71 (q, *J* = 7.3 Hz, 1H), 2.87 (q, *J* = 8.5 Hz, 1H), 2.31 (dq, *J* = 14.5, 7.5 Hz, 1H), 2.18 (dtd, *J* = 12.3, 7.9, 7.5, 3.9 Hz, 1H), 1.84 (dp, *J* = 13.4, 6.9, 6.2 Hz, 2H), 1.74 (dq, *J* = 12.8, 9.2 Hz, 1H), 1.56 (ddd, *J* = 15.4, 12.9, 6.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.41, 143.56, 128.96, 127.43, 126.58, 121.83, 114.76, 114.41, 61.97, 53.27, 33.41, 23.35, 14.25. HRMS (ESI) *m/z* $[M+H]^+$, $C_{17}H_{18}NCl$ calc'd 272.120; found 272.120.

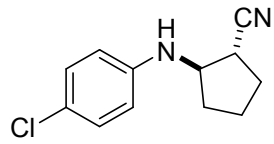


Following GP2 with cyclopropylaniline (67 mg, 0.40 mmol), cycloadduct **4b** was obtained after silica gel column chromatography (15% EtOAc/hexane) as a separable mixture of two diastereoisomers.

Data for **4b-*cis***: colorless oil (35 mg, 40%). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.18 – 7.07 (m, 2H), 6.60 – 6.52 (m, 2H), 4.05 – 3.88 (m, 2H), 3.23 (td, J = 8.75, 4.2 Hz, 1H), 2.23 – 2.04 (m, 3H), 2.02 – 1.92 (m, 1H), 1.80 – 1.62 (m, 2H). 13C NMR (126 MHz, CDCl3) δ 145.22, 129.27, 122.99, 120.06, 114.67, 56.79, 34.12, 31.30, 28.85, 21.37. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{12}H_{13}ClN_2$ 221.084; found 221. 084.



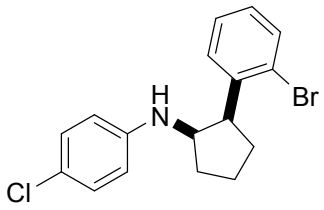
Data for **4b-*trans***:colorless oil (26 mg, 30%). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.25 – 7.19 (m, 2H), 6.66 – 6.60 (m, 2H), 4.20 – 4.11 (m, 1H), 2.78 (ddd, J = 8.1, 5.4, 4.1 Hz, 1H), 2.40 (dq, J = 14.1, 7.2 Hz, 1H), 2.21 – 2.07 (m, 2H), 1.62 (dtd, J = 12.9, 7.5, 5.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 144.72,



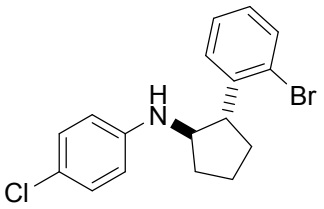
129.44, 123.22, 122.10, 114.52, 59.54, 35.42, 33.41, 29.63, 23.60. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{12}H_{13}ClN_2$ 221.084; found 221.084.

Following GP2 with cyclopropylaniline (86 mg, 0.52 mmol), cycloadduct **4c** was obtained after silica gel column chromatography (10% EtOAc/hexane) as a separable mixture of two diastereoisomers.

Data for **4c-*cis***: colorless oil (69 mg, 38%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (dd, J = 8.0, 1.3 Hz, 1H), 7.33 (dd, J = 7.8, 1.7 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.05 (ddd, J = 8.0, 7.3, 1.7 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.32 – 6.27 (m, 2H), 4.15 (td, J = 6.4, 3.4 Hz, 1H), 3.68 (dt, J = 11.2, 6.7 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.16 – 2.07 (m, 1H), 2.01 (ddd, J = 12.8, 7.4, 2.6 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.81 – 1.71 (m, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 146.15, 139.32, 133.08, 129.07, 128.68, 128.27, 127.26, 126.16, 121.40, 114.18, 55.30, 48.99, 33.46, 29.43, 22.70. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{17}H_{17}NClBr$; 350.031; found 350.030.

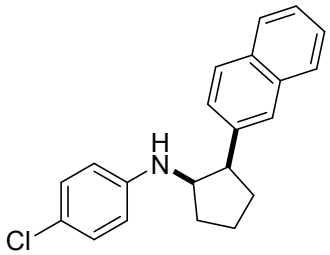


Data for **4c-*trans***: colorless oil (67 mg, 37%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (dt, J = 7.6, 0.7 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.18 – 7.07 (m, 3H), 6.52 – 6.46 (m, 2H), 3.86 (dt, J = 8.6, 7.2 Hz, 1H), 3.51 (dt, J = 9.9, 8.3 Hz, 1H), 2.49 – 2.40 (m, 1H), 2.40 – 2.31 (m, 1H), 1.96 (ddt, J = 12.5, 8.8, 5.6 Hz, 2H), 1.74 – 1.62 (m, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 146.54, 142.42, 139.58, 132.98, 128.95, 128.01, 127.49, 125.44, 121.59, 114.20, 61.62, 51.43, 33.16, 32.46, 23.00. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{17}H_{17}NClBr$ 350.031; found 350.030.

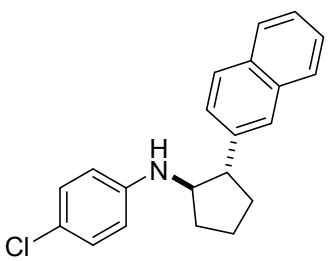


Following GP2 with cyclopropylaniline (72 mg, 0.43 mmol), cycloadduct **4d** was obtained after silica gel column chromatography (5% EtOAc/hexane) as a separable mixture of two diastereoisomers.

Data for **4d-*cis***: colorless oil (50 mg, 36%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 – 7.72 (m, 3H), 7.66 (d, *J* = 2.3 Hz, 1H), 7.57 – 7.41 (m, 2H), 7.32 (dd, *J* = 10.5, 2.3 Hz, 1H), 7.10 – 7.00 (m, 2H), 6.45 – 6.32 (m, 2H), 4.07 (q, *J* = 7.4 Hz, 1H), 3.62 (q, *J* = 9.4 Hz, 1H), 2.27 (dt, *J* = 11.8, 8.3 Hz, 2H), 2.19 – 1.99 (m, 2H), 1.95 – 1.78 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.30, 138.14, 133.37, 132.31, 128.86, 127.91, 127.70, 127.39, 126.74, 126.11, 125.63, 121.49, 114.27, 57.64, 48.08, 31.86, 28.83, 22.12. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{21}H_{20}ClN$ 322.136; found 322.135.



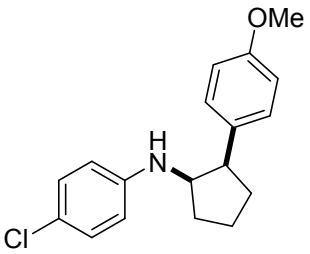
Data for **4d-*trans***: colorless oil (58 mg, 42%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 – 7.77 (m, 3H), 7.72 (s, 1H), 7.55 – 7.37 (m, 3H), 7.15 – 7.02 (m, 2H), 6.54 – 6.37 (m, 2H), 3.90 (q, *J* = 9.1 Hz,



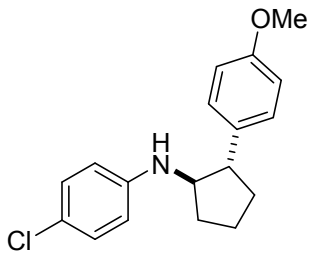
1H), 3.09 (q, *J* = 10.4 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.37 – 2.25 (m, 1H), 2.05 – 1.85 (m, 3H), 1.73 – 1.60 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.60, 141.04, 133.59, 132.44, 129.43, 128.96, 128.43, 127.67, 126.15, 125.52, 121.71, 119.17, 114.50, 61.62, 53.41, 33.55, 33.50, 23.45. HRMS (ESI) *m/z* $[M+H]^+$,calc'd for $C_{21}H_{20}ClN$ 322.136; found 322.135.

Following GP2 with cyclopropylaniline (70 mg, 0.42 mmol), cycloadduct **4e** was obtained after silica gel column chromatography (3% EtOAc/hexane) as a separable mixture of two diastereoisomers.

Data for **4e-*cis***: colorless oil (57 mg, 45%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.14 – 7.06 (m, 2H), 7.07 – 6.99 (m, 2H), 6.88 – 6.77 (m, 2H), 6.42 – 6.33 (m, 2H), 3.89 (p, *J* = 6.9 Hz, 1H), 3.79 (s, 3H), 3.38 (q, *J* = 9.4 Hz, 1H), 2.19 – 2.01 (m, 3H), 1.94 (dtd, *J* = 16.3, 8.8, 4.1 Hz, 1H), 1.86 – 1.65 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.25, 146.43, 132.46, 129.53, 128.85, 121.39, 114.26, 113.77, 57.60, 55.26, 47.12, 31.75, 29.08, 22.05. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{18}H_{20}ClNO$ 302.131; found 302.130.

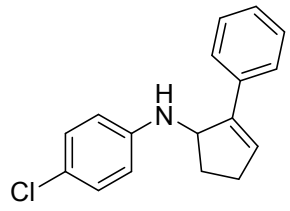


Data for **4e-*trans***: colorless oil (44 mg, 35%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 – 7.15 (m, 2H), 7.10 – 7.02 (m, 2H), 6.89 – 6.82 (m, 2H), 6.48 – 6.40 (m, 2H), 3.79 (s, 3H), 3.68 (q, *J* = 9.3 Hz, 1H), 2.84 (dt, *J* = 12.1, 10.0 Hz, 1H), 2.39 – 2.28 (m, 1H), 2.18 (dp, *J* = 15.1, 4.6 Hz, 1H), 1.93 – 1.80 (m, 2H), 1.78 – 1.67 (m, 1H), 1.56 (ddt, *J* = 16.3, 11.1, 8.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.27, 146.68, 135.46, 128.91, 128.22, 121.58, 114.41, 114.05, 61.72, 55.30, 52.41, 33.48, 33.23, 23.13. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{18}H_{20}ClNO$ 302.131; found 302.130.

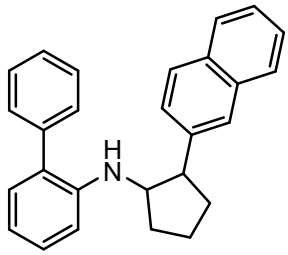


Following GP2 with cyclopropylaniline (79 mg, 0.47 mmol), cycloadduct **4f** was obtained after silica gel column chromatography (3% EtOAc/hexane).

Data for **4f**: colorless oil (74 mg, 58%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.45 (m, 2H), 7.34 (dd, *J* = 10.4, 8.3 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.21 – 7.12 (m, 2H), 6.62 – 6.54 (m, 2H), 6.44 (d, *J* = 2.9 Hz, 1H), 4.87 (d, *J* = 9.1 Hz, 1H), 3.80 (s, 1H), 2.75 – 2.62 (m, 1H), 2.55 (ddt, *J* = 22.0, 11.3, 3.9 Hz, 1H), 2.38 (ddt, *J* = 17.4, 11.3, 8.9 Hz, 1H), 2.02 (ddt, *J* = 17.0, 10.4, 3.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.20, 142.55, 134.48, 130.27, 129.14, 128.63, 127.50, 126.16, 121.64, 114.09, 59.25, 31.47, 31.01. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{17}H_{16}ClN$ 270.104; found 270.104.



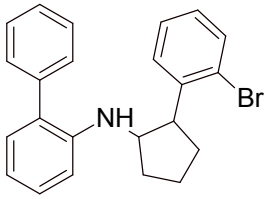
Following GP2 with cyclopropylaniline (125 mg, 0.60 mmol), cycloadduct **5a** was obtained after silica gel column chromatography (3% EtOAc/hexane) as an inseparable mixture of two diastereoisomers (*cis*/*trans*=1:1).



Data for **5a-mixture**: yellowish oil (129 mg, 59%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.85 (m, 4H), 7.80 – 7.74 (m, 2H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.61 – 7.52 (m, 5H), 7.46 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.40 (dd, *J* = 4.9, 2.0 Hz, 3H), 7.36 – 7.24 (m, 5H), 7.12 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.06 – 6.97 (m, 2H), 6.88 – 6.72 (m, 8H), 4.20 (d, *J* = 5.9 Hz, 1H), 3.91 (q, *J* = 7.5 Hz, 1H), 3.66 (dt, *J* = 9.5, 7.2 Hz, 1H), 3.03 (q, *J* = 8.5 Hz, 1H), 2.59 – 2.45 (m, 1H), 2.32 – 2.15 (m, 4H), 2.11 – 1.82 (m, 6H), 1.77 – 1.59 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.05, 144.52, 140.89, 139.46, 138.98, 138.09, 133.60, 133.56, 132.52, 132.41, 130.23, 130.17, 129.39, 128.89, 128.71, 128.51, 128.38, 128.31, 128.03, 127.79, 127.71, 127.69, 127.61, 127.41, 127.17, 126.62, 126.51, 126.21, 126.10, 125.95, 125.60, 125.51, 116.86, 116.31, 111.50, 110.45, 62.54, 57.61, 53.37, 48.78, 33.64, 32.60, 31.72, 28.76, 23.34, 22.71. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{27}H_{25}N$ 364.206; found 364.206.

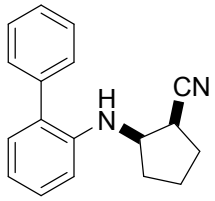
Following GP2 with cyclopropylaniline (104 mg, 0.50 mmol), cycloadduct **5b** was obtained after silica gel column chromatography (2% EtOAc/hexane) as an inseparable mixture of two diastereoisomers (*cis*/*trans*=1:1).

Data for **5b-mixture**: yellowish oil (137 mg, 70%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (td,



J = 8.0, 1.6 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.27 (m, 8H), 7.20 – 7.14 (m, 2H), 7.10 – 6.91 (m, 8H), 6.76 – 6.58 (m, 4H), 4.20 (d, *J* = 2.7 Hz, 1H), 3.80 (dt, *J* = 8.8, 7.3 Hz, 1H), 3.65 (dt, *J* = 11.3, 6.9 Hz, 1H), 3.37 (q, *J* = 8.9 Hz, 1H), 2.17 (d, *J* = 8.2 Hz, 2H), 2.01 – 1.80 (m, 6H), 1.79 – 1.59 (m, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 207.06, 144.93, 144.17, 142.58, 139.31, 139.02, 132.91, 132.67, 130.17, 129.92, 129.32, 129.20, 129.00, 128.89, 128.65, 128.57, 128.52, 128.41, 127.91, 127.79, 127.68, 127.54, 127.22, 127.05, 126.74, 125.86, 125.36, 116.53, 116.20, 110.92, 110.40, 62.50, 54.71, 51.08, 48.88, 33.08, 32.40, 30.96, 28.99, 23.11, 22.67. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{23}H_{22}BrN$ 392.101; found 392.101.

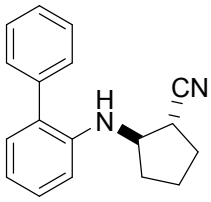
Following GP2 with cyclopropylaniline (92 mg, 0.44 mmol), cycloadduct **5c** was obtained after silica gel column chromatography (1% EtOAc/hexane) as a separable mixture of two diastereoisomers (*cis*/*trans*=4:1).



Data for **5c-*cis***: colorless oil (60 mg, 52%). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.53 (t, J = 7.5 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.39 – 7.34 (m, 3H), 7.30 (ddd, J = 8.1, 7.4, 1.6 Hz, 1H), 7.11 (dd, J = 7.5, 1.7 Hz, 1H), 6.88 – 6.78 (m, 1H), 4.15 (dt, J = 7.1, 4.5 Hz, 1H), 2.72 (td, J = 6.6, 3.8 Hz, 1H), 2.32 – 2.21

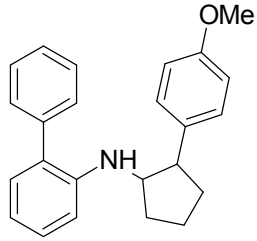
(m, 1H), 2.00 (q, J = 7.2 Hz, 2H), 1.89 – 1.70 (m, 2H), 1.46 – 1.38 (m, 1H). ^{13}C NMR (126 MHz, CDCl3) δ 143.03, 139.07, 130.60, 129.28, 129.09, 128.41, 128.19, 127.51, 122.27, 118.17, 111.46, 59.47, 35.38, 33.27, 29.45, 23.52. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{18}H_{18}N_2$ 263.154; found 263.153.

Data for **5c-*trans***:colorless oil (15 mg, 13%). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.59 – 7.51 (m, 4H), 7.47 – 7.41 (m, 1H), 7.35 – 7.28 (m, 1H), 7.20 (dd, J = 7.5, 1.6 Hz, 1H), 6.90 (td, J = 7.4, 1.1 Hz, 1H), 6.75 (dd, J = 8.3, 1.1 Hz, 1H), 4.04 (dt, J = 9.4, 6.7 Hz, 1H), 3.38 (td, J = 6.9, 4.2 Hz, 1H), 2.20 – 2.07 (m, 3H), 2.01 – 1.92 (m, 1H), 1.76 (dqd, J = 13.3, 8.4, 6.0 Hz, 1H), 1.64 (dtd, J = 12.9, 9.5, 8.2 Hz, 1H).^{13}C NMR (126 MHz, CDCl3) δ 143.40, 138.99, 130.72, 129.43, 129.11, 128.73, 128.39, 127.52, 120.24, 117.93, 110.80, 56.69, 34.12, 31.34, 28.95, 21.28. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{18}H_{18}N_2$ 263.154; found 263.153.



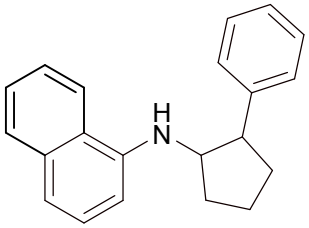
Following GP2 with cyclopropylaniline (121 mg, 0.58 mmol), cycloadduct **5d** was obtained after silica gel column chromatography (3% EtOAc/hexane) as an inseparable mixture of two diastereoisomers (*cis*/*trans*=1:1).

Data for **5d-mixture**: colorless oil (123 mg, 62%). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.47 (td, J = 7.3, 2.5 Hz, 2H), 7.44 – 7.38 (m, 1H), 7.36 – 7.22 (m, 7H), 7.16 (dd, J = 8.7, 3.1 Hz, 2H), 7.11 (dt, J = 7.4, 2.1 Hz, 1H), 7.09 – 7.04 (m, 3H), 7.01 (dd, J = 8.7, 2.4 Hz, 2H), 6.90 (dd, J = 8.7, 2.9 Hz, 2H), 6.83 – 6.63 (m, 6H), 3.99 (dd, J = 10.2, 4.8 Hz, 1H), 3.87 (t, J = 2.4 Hz, 6H), 3.82 (d, J = 12.1 Hz, 1H), 3.71 (dp, J = 10.7, 6.6, 4.5 Hz, 1H), 3.46 – 3.38 (m, 1H), 2.79 (q, J = 8.5 Hz, 1H), 2.42 (d, J = 12.3 Hz, 1H), 2.15 (tdd, J = 13.6, 10.9, 7.9 Hz, 3H), 2.03 – 1.89 (m, 3H), 1.89 – 1.75 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.31, 158.14, 145.18, 144.66, 139.57, 139.38, 135.48, 132.51, 130.23, 130.19, 129.45, 129.36, 129.17, 128.94, 128.72, 128.68, 128.58, 128.39, 127.78, 127.69, 127.18, 126.75, 116.73, 116.30, 114.00, 113.86, 111.42, 110.55, 62.57, 57.65, 55.40, 55.33, 52.35, 47.69, 33.42, 32.68, 32.27, 29.13, 23.11, 22.52. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{24}H_{25}NO$ 344.201; found 344.200.



Following GP2 with cyclopropylaniline (95 mg, 0.52 mmol), cycloadduct **6a** was obtained after silica gel column chromatography (10% EtOAc/hexane) as an inseparable mixture of two diastereoisomers (*cis*/*trans*=1:1).

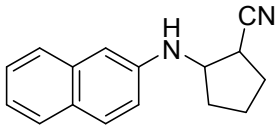
Data for **6a-mixture**: colorless oil (69 mg, 46%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 (ddt, *J* = 23.7, 16.2, 8.2 Hz, 4H), 7.40 – 7.30 (m, 5H), 7.22 (ddd, *J* = 10.5, 6.7, 3.5 Hz, 7H), 7.17 – 7.07 (m, 6H), 6.53 (dd, *J* = 24.2, 7.5 Hz, 2H), 4.05 (q, *J* = 5.9 Hz, 1H), 3.88 (q, *J* = 7.2 Hz, 1H), 3.50 (p, *J* = 7.4 Hz, 1H), 3.04 (q, *J* = 8.4 Hz, 1H), 2.57 (d, *J* = 6.7 Hz, 1H), 2.42 (dq, *J* = 14.8, 7.6 Hz, 1H), 2.29 – 2.09 (m, 4H), 1.92 – 1.73 (m, 6H). ^{13}C NMR

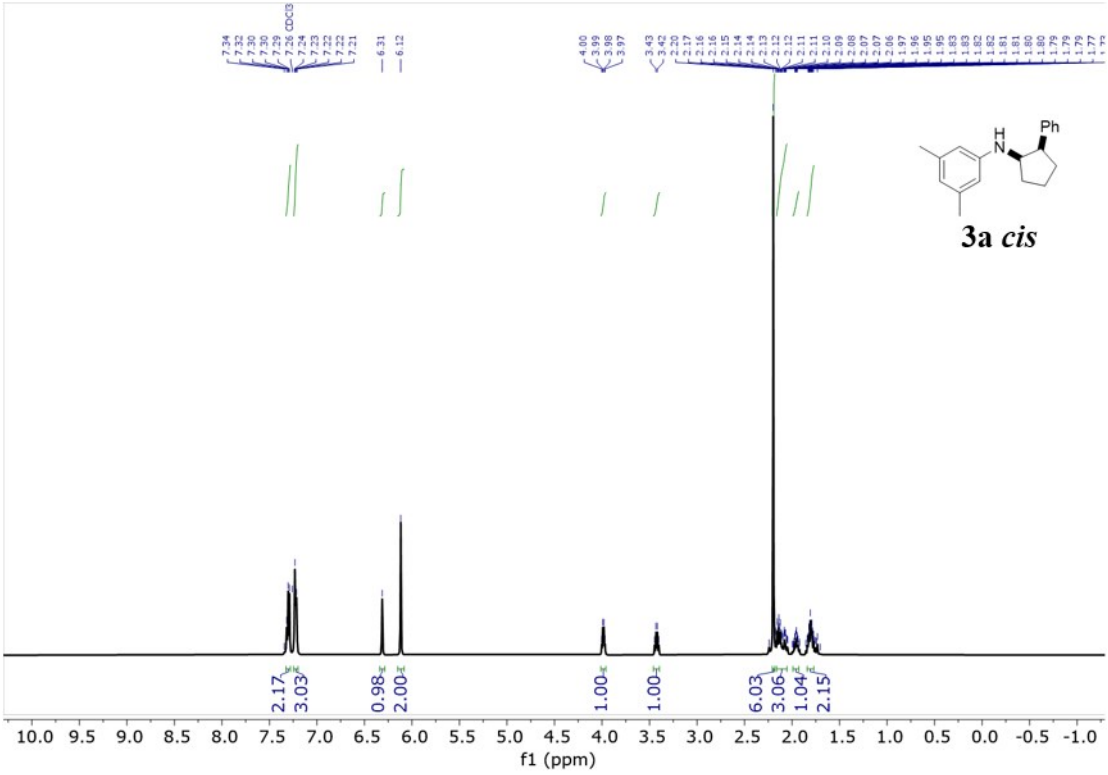


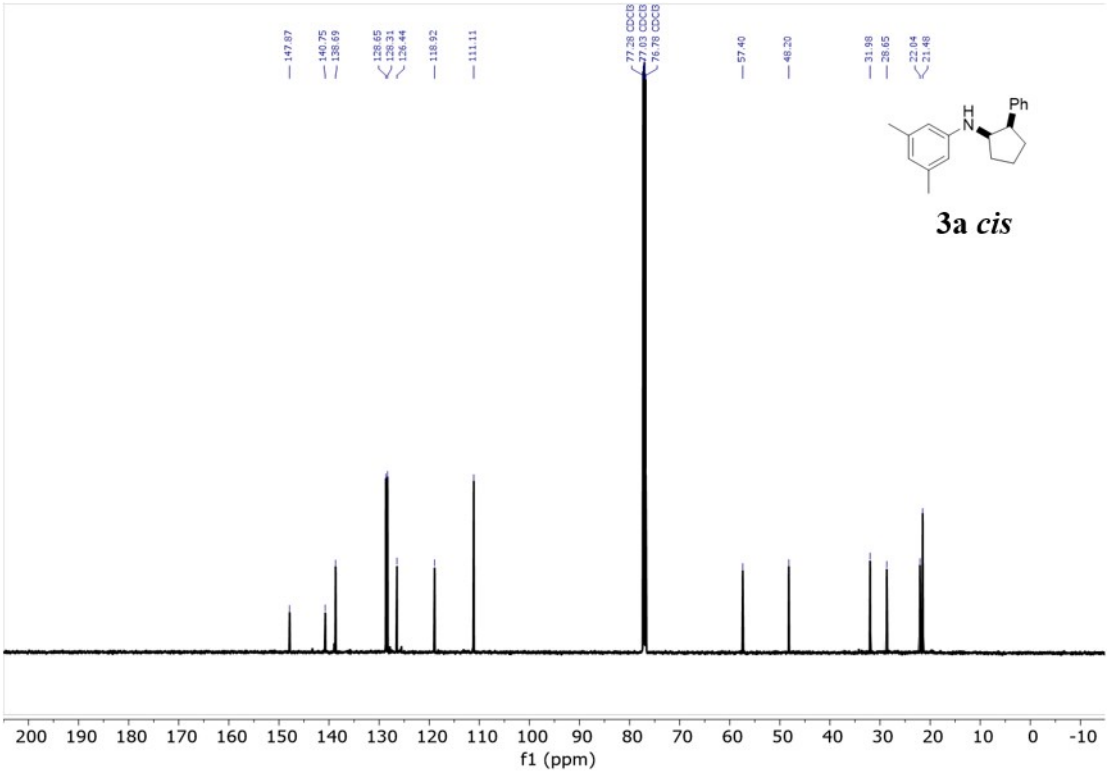
(126 MHz, $CDCl_3$) δ 143.76, 142.91, 140.53, 134.38, 128.74, 128.68, 128.59, 128.52, 128.36, 127.43, 126.87, 126.69, 126.63, 126.60, 125.73, 125.61, 124.73, 124.55, 123.82, 123.63, 120.00, 119.85, 119.78, 117.85, 117.34, 116.97, 105.90, 104.93, 61.69, 57.40, 53.33, 48.79, 33.60, 33.40, 32.05, 28.96, 23.70, 22.79. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{21}H_{21}N$ 288.175; found 288.174.

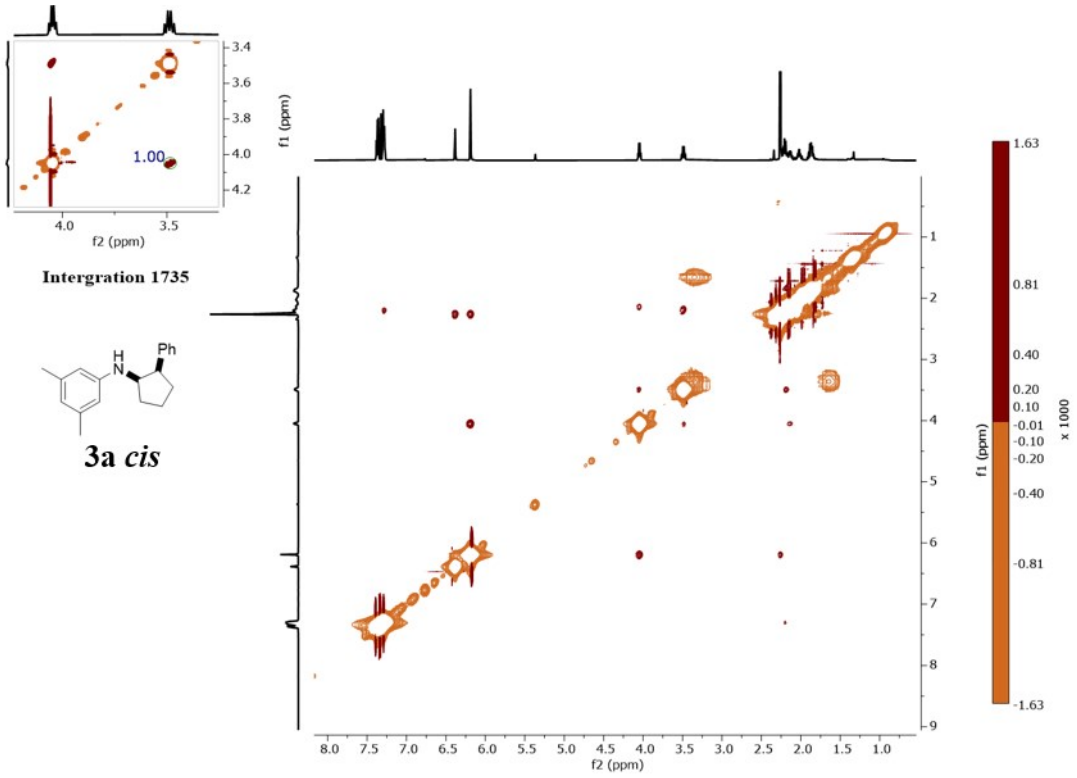
Following GP2 with cyclopropylaniline (62 mg, 0.34 mmol), cycloadduct **6c** was obtained after silica gel column chromatography (3% EtOAc/hexane) as an inseparable mixture of two diastereoisomers (*cis*/*trans*=1:1).

Data for **6b-mixture**: colorless oil (40 mg, 50%). ^{1}H 1H NMR (500 MHz, Chloroform-d) δ 7.84 (dddd, J = 40.0, 28.1, 8.3, 2.9 Hz, 3H), 7.55 – 7.27 (m, 6H), 6.64 (dd, J = 9.0, 1.6 Hz, 1H), 4.70 (d, J = 9.9 Hz, 1H), 4.34 (d, J = 6.4 Hz, 1H), 4.17 (p, J = 9.1 Hz, 1H), 3.41 (td, J = 8.9, 5.1 Hz, 1H), 2.47 (dq, J = 17.5, 8.8 Hz, 1H), 2.33 (ddt, J = 14.1, 10.4, 5.4 Hz, 1H), 2.28 – 1.95 (m, 5H), 1.95 – 1.71 (m, 3H). ^{13}C 13C NMR (126 MHz, CDCl3) δ 141.88, 141.27, 134.44, 128.87, 128.67, 128.56, 126.57, 126.22, 126.02, 126.00, 125.18, 125.09, 123.71, 123.55, 122.31, 120.26, 120.02, 119.62, 118.70, 118.58, 106.00, 105.59, 59.35, 56.62, 35.32, 34.33, 33.63, 31.46, 29.84, 29.04, 23.94, 21.59. HRMS (ESI) *m/z* $[M+H]^+$, calc'd for $C_{16}H_{16}N_2$ 237.139; found 237.138.

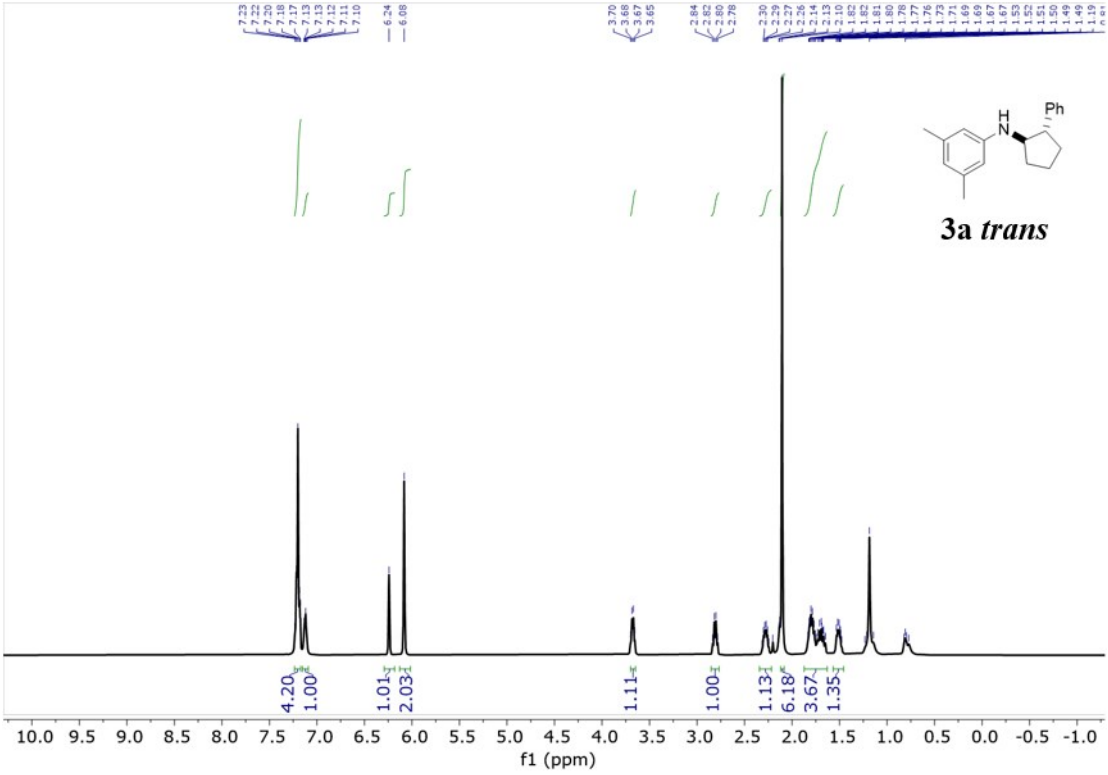


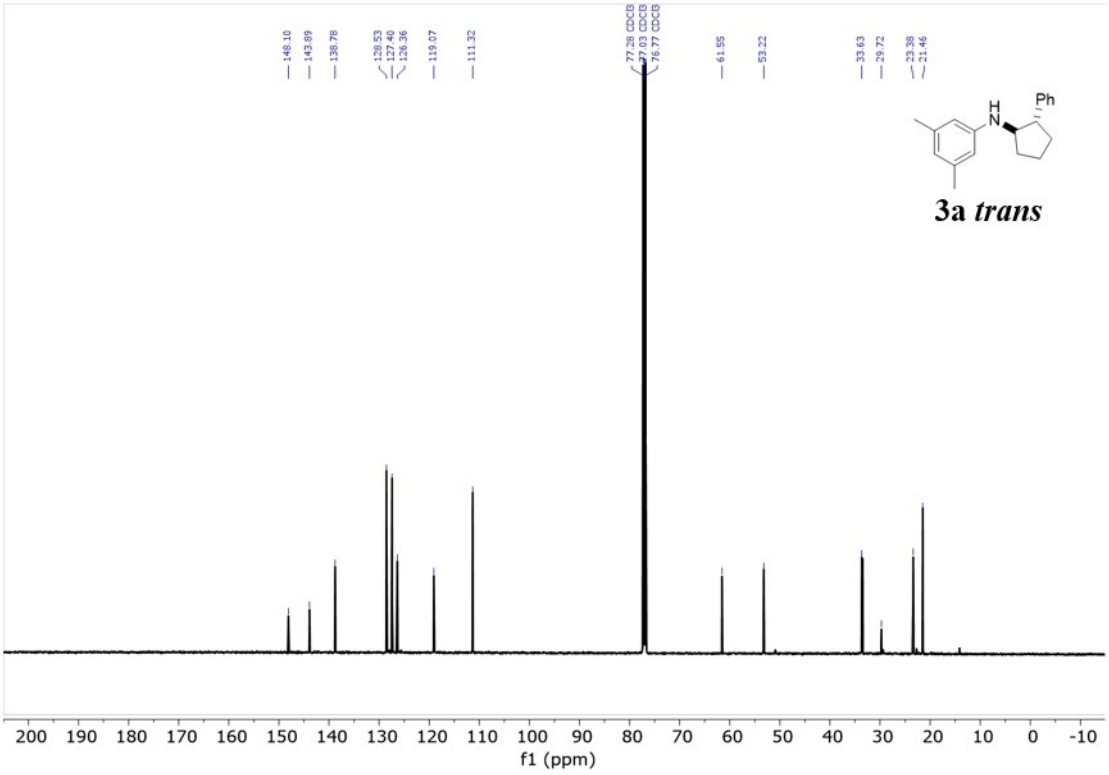

Ph
H
N
3a *cis*
2.17
3.03
0.98
2.00
1.00
1.00
6.03
3.06
1.04
2.15
f1 (ppm)

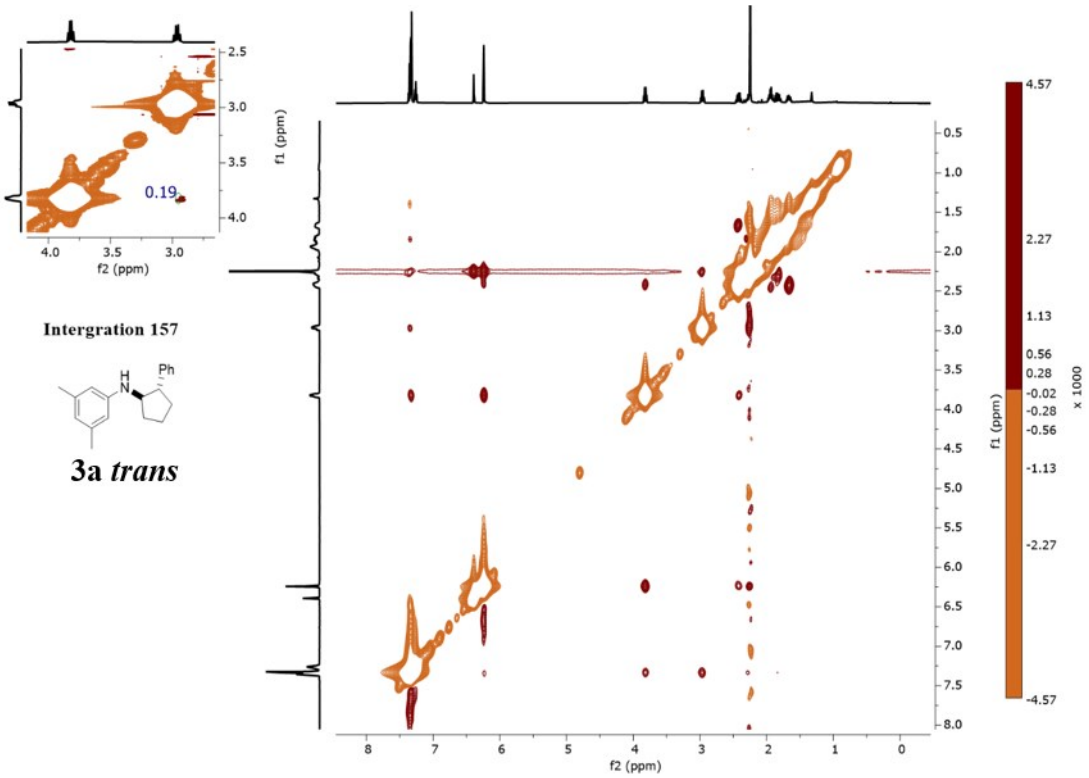

Ph
H
N
3a *cis*
f1 (ppm)



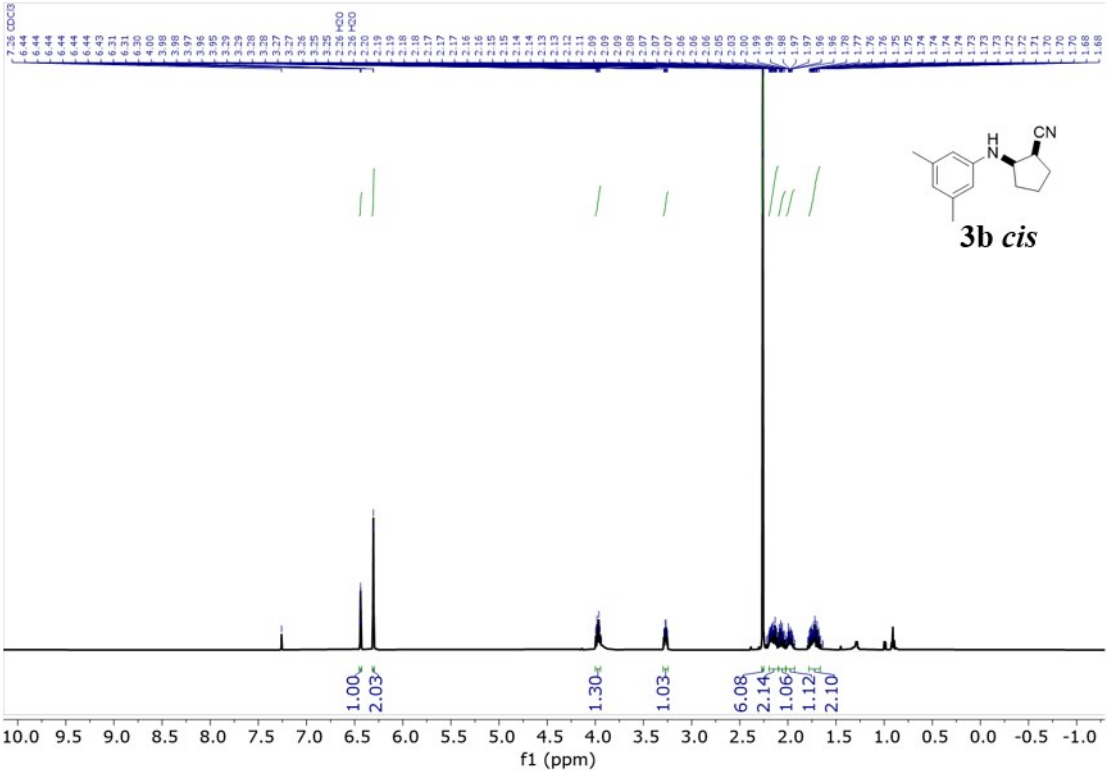
Correlation peak integration is 1735

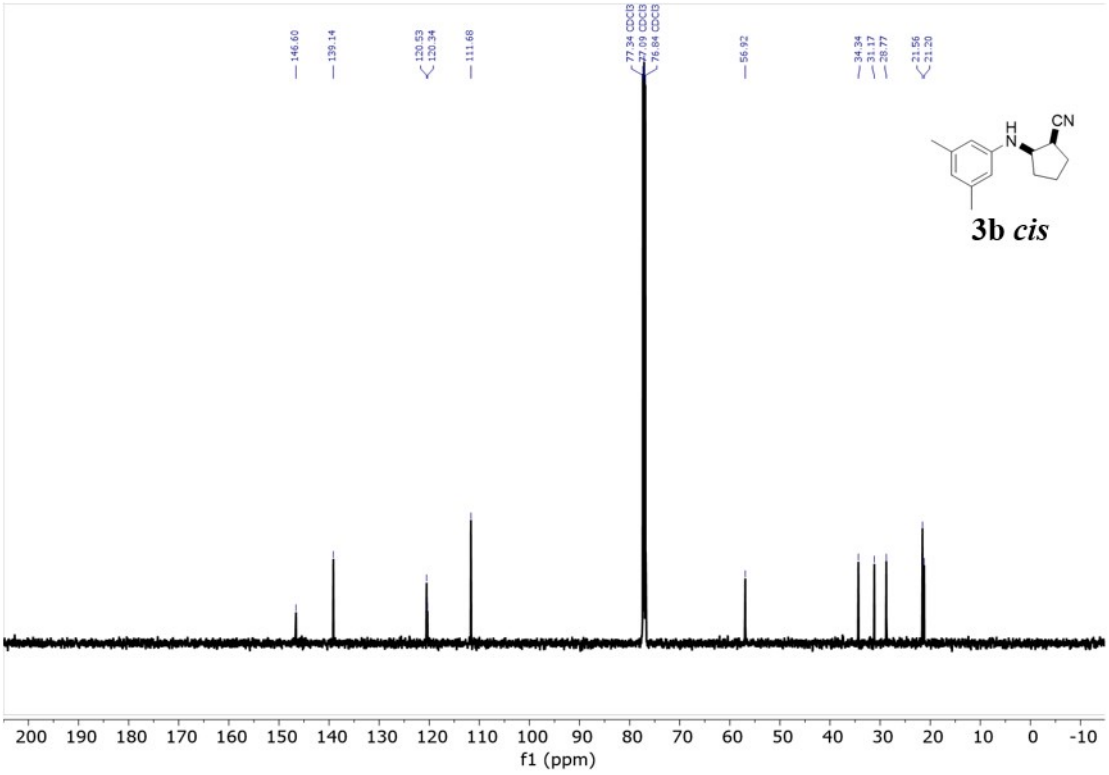

3a *trans*
4.20
1.00
1.01
2.03
1.11
1.00
1.13
6.18
3.67
1.35
f1 (ppm)

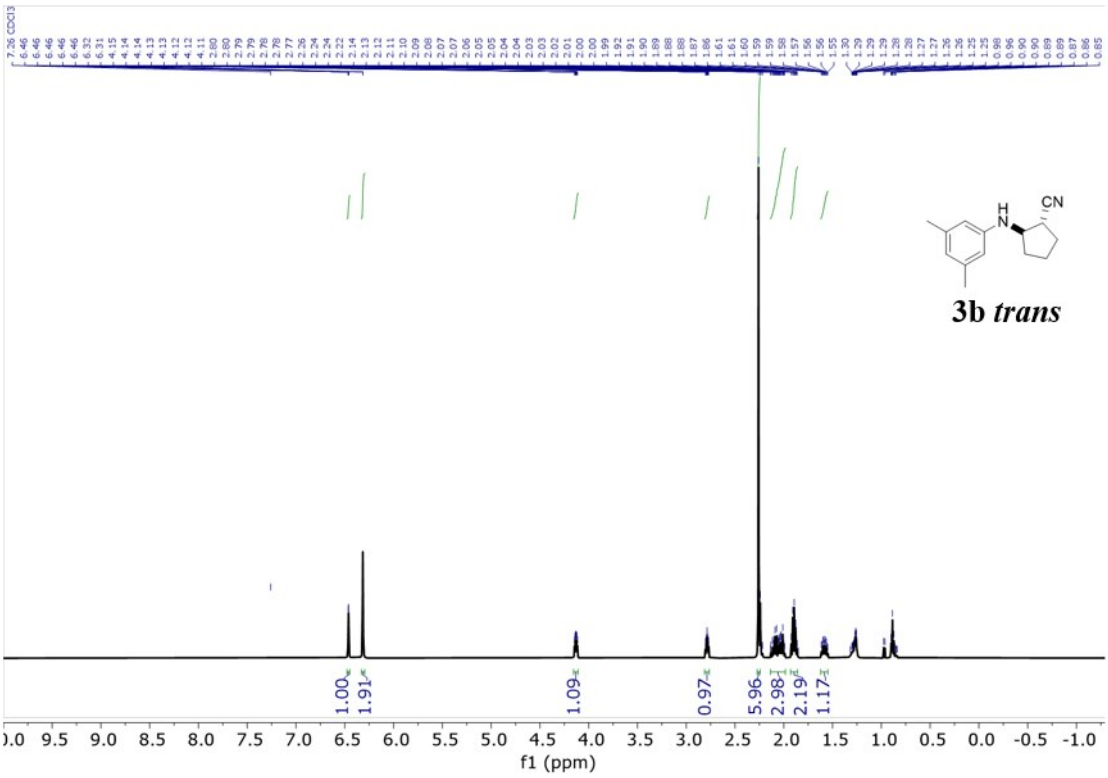

3a *trans*
f1 (ppm)

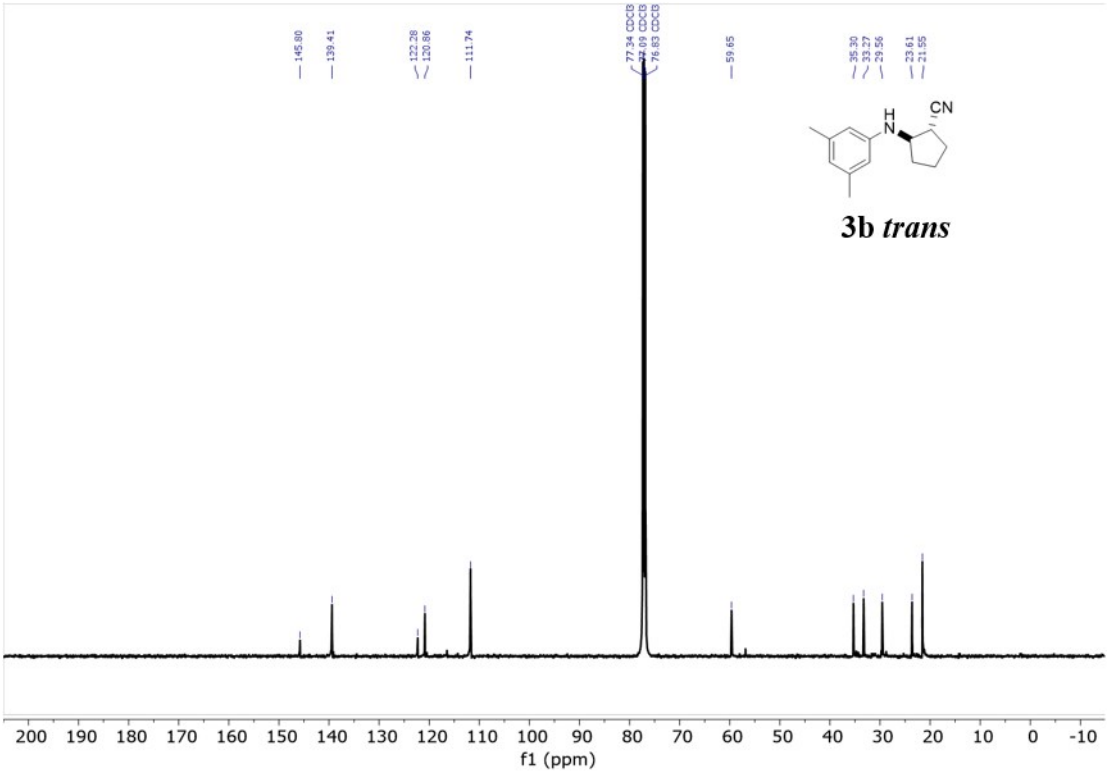


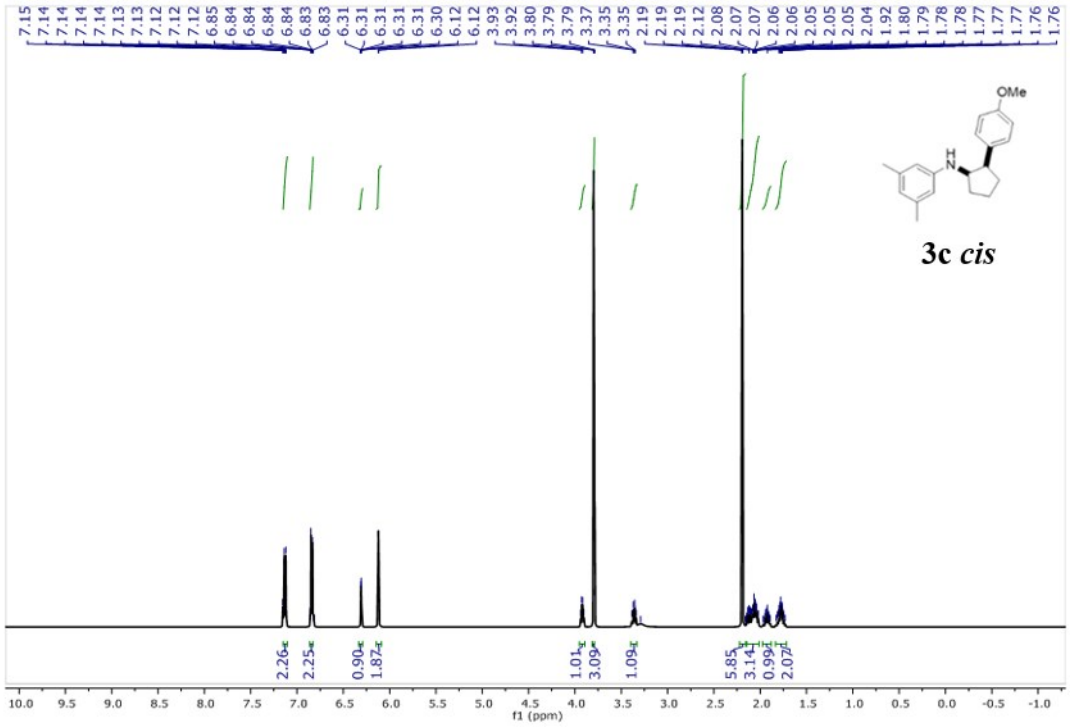
Correlation peak integration is 157

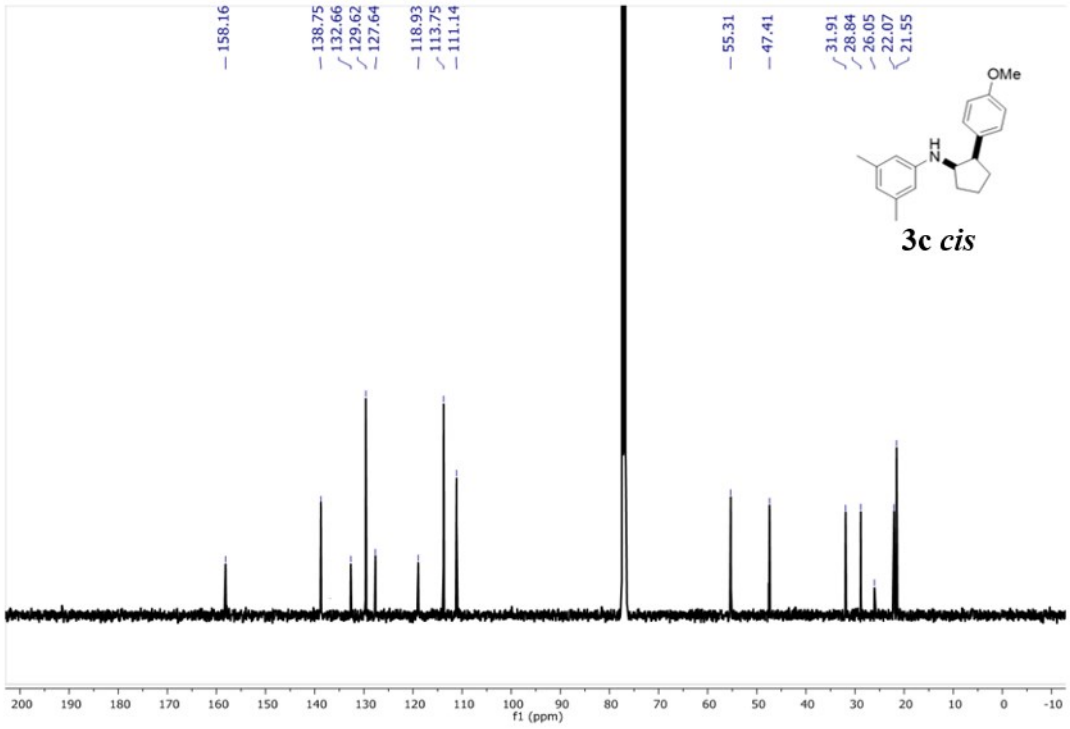

3b *cis*
1.00
2.03
1.30
1.03
6.08
2.14
1.06
1.12
2.10
f1 (ppm)

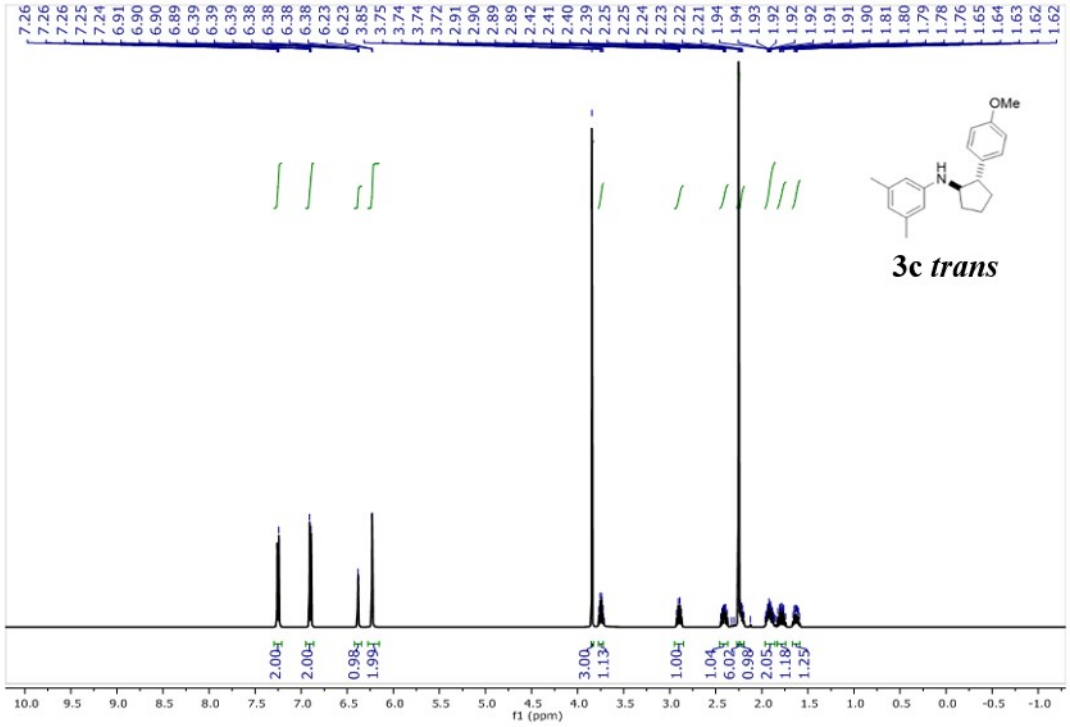

3b *cis*
f1 (ppm)

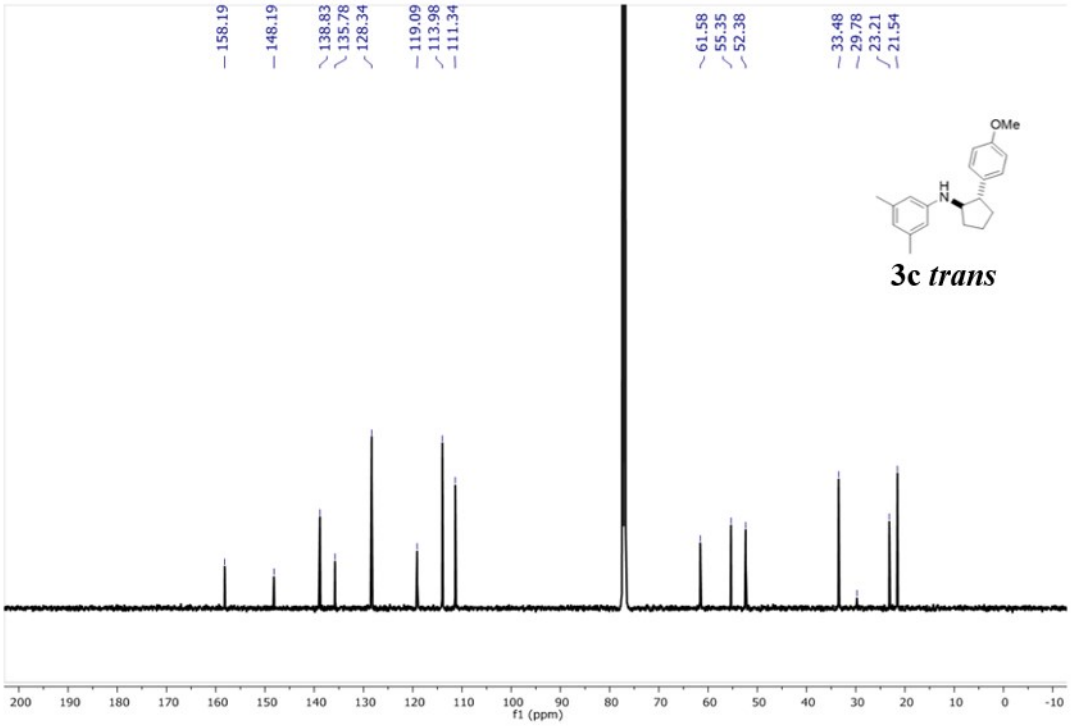

CN
3b *trans*
1.00
1.91
1.09
0.97
5.96
2.98
2.19
1.17
f1 (ppm)

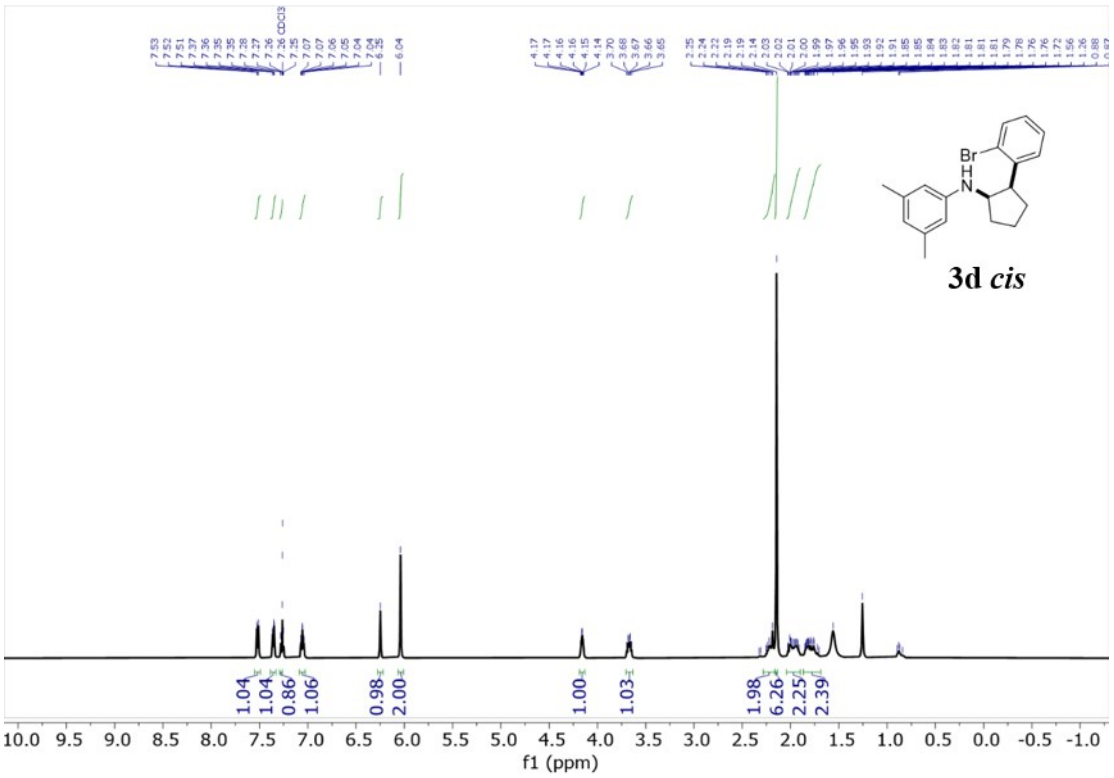

145.80
139.41
122.28
120.86
111.74
77.34 CDCl3
77.09 CDCl3
76.83 CDCl3
59.65
35.30
33.27
29.56
23.61
21.55
CN
3b *trans*
f1 (ppm)

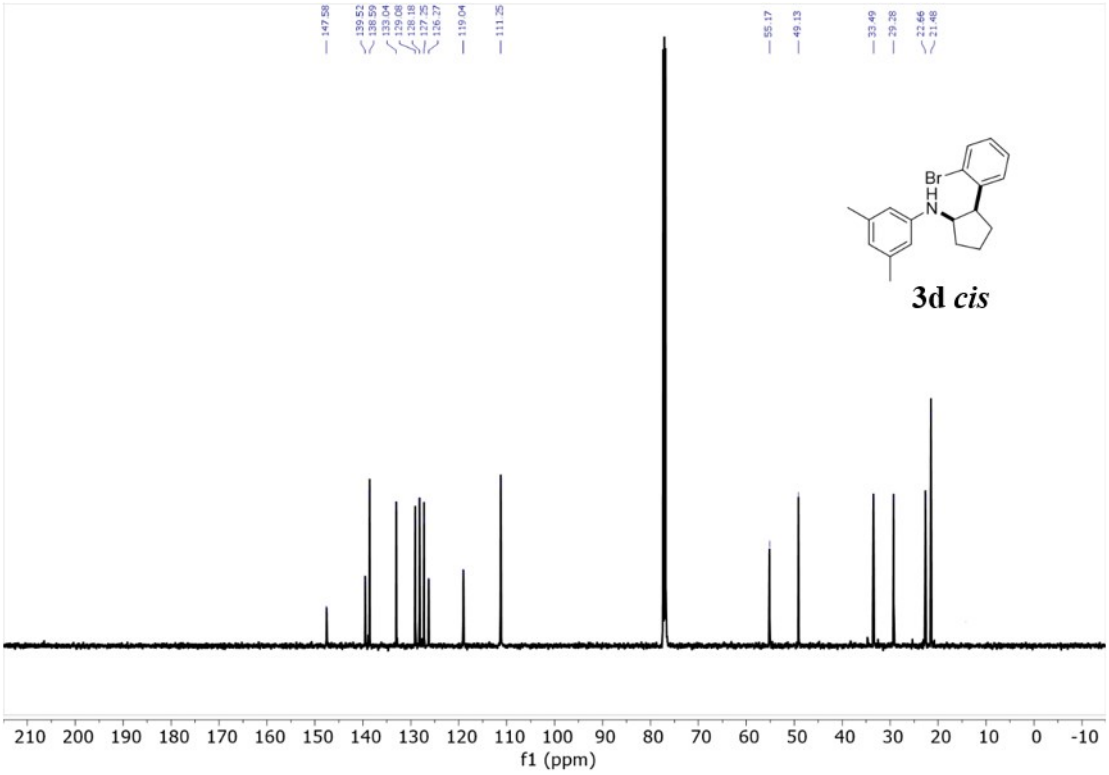

7.15 7.14 7.14 7.14 7.14 7.13 7.13 7.12 7.12 7.12 6.85 6.84 6.84 6.84 6.84 6.83 6.83 6.31 6.31 6.31 6.31 6.31 6.30 6.12 6.12 3.93 3.92 3.80 3.79 3.79 3.37 3.35 3.35 2.19 2.19 2.19 2.12 2.08 2.07 2.07 2.06 2.06 2.05 2.05 2.05 2.04 1.92 1.80 1.79 1.78 1.78 1.77 1.77 1.77 1.76 1.76
OMe
H
N
3c *cis*
2.26 2.25 0.90 1.87 1.01 3.09 1.09 5.85 3.14 0.99 2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

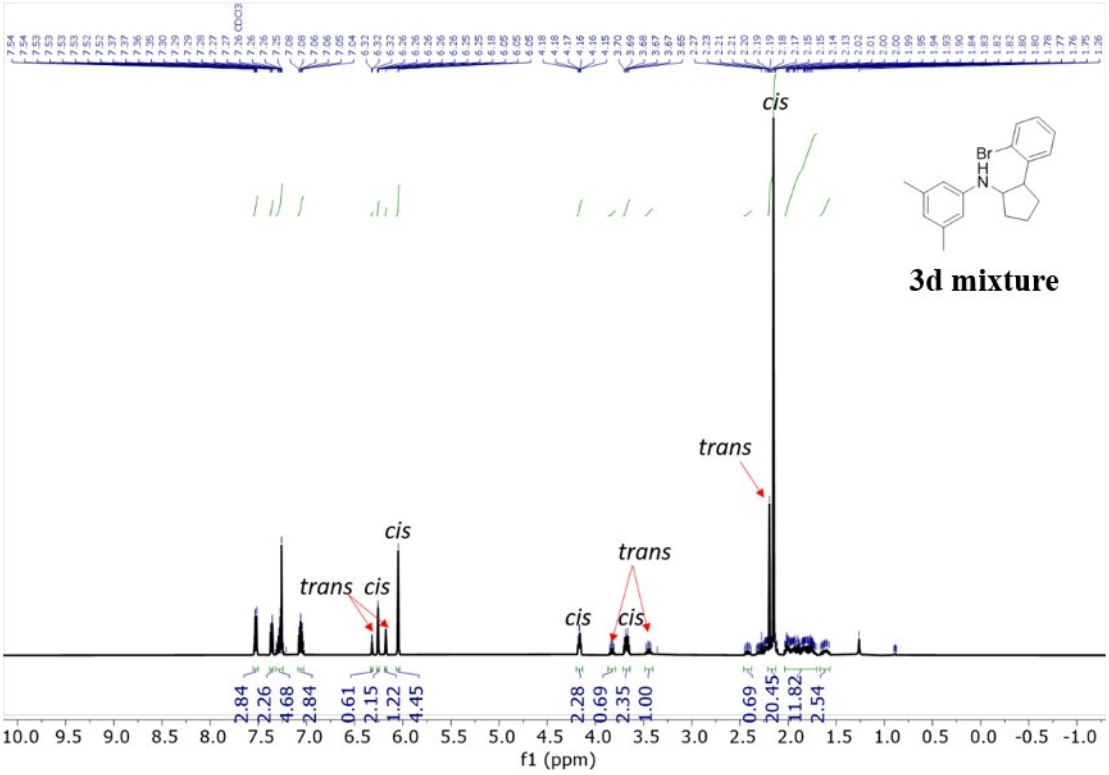

158.16
138.75 132.66 129.62 127.64 118.93 113.75 111.14
55.31 47.41 31.91 28.84 26.05 22.07 21.55
OMe
H
N
3c *cis*
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

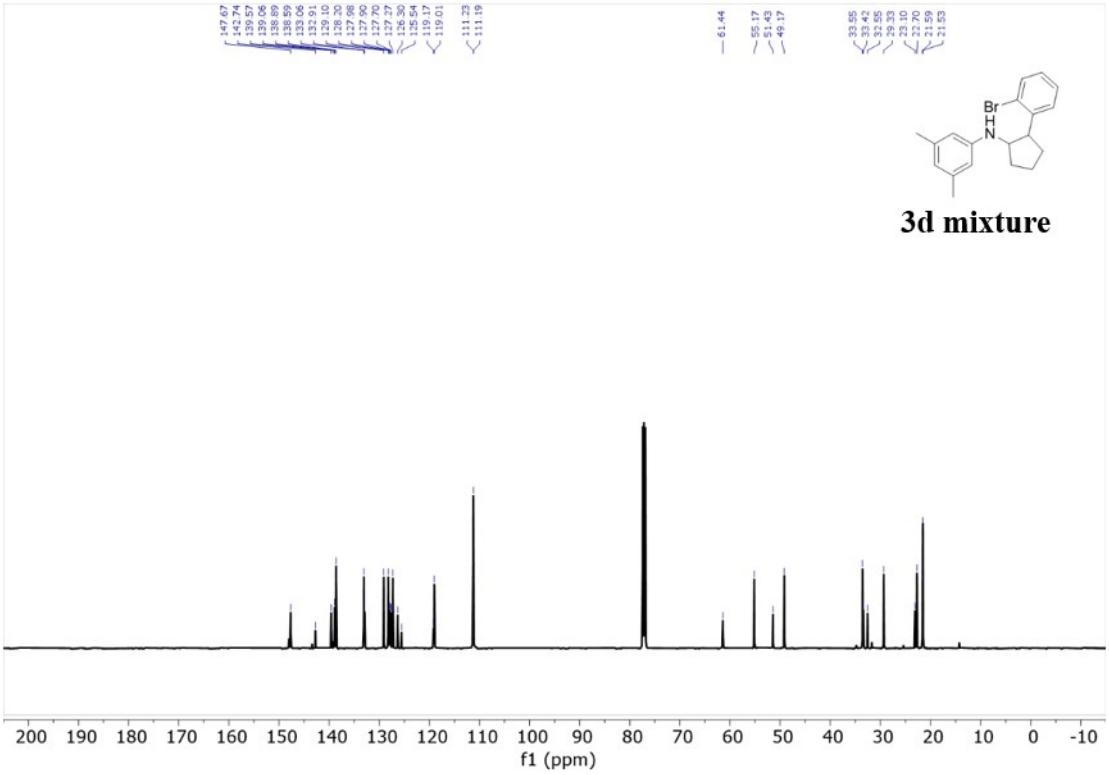

OMe
3c *trans*
f1 (ppm)

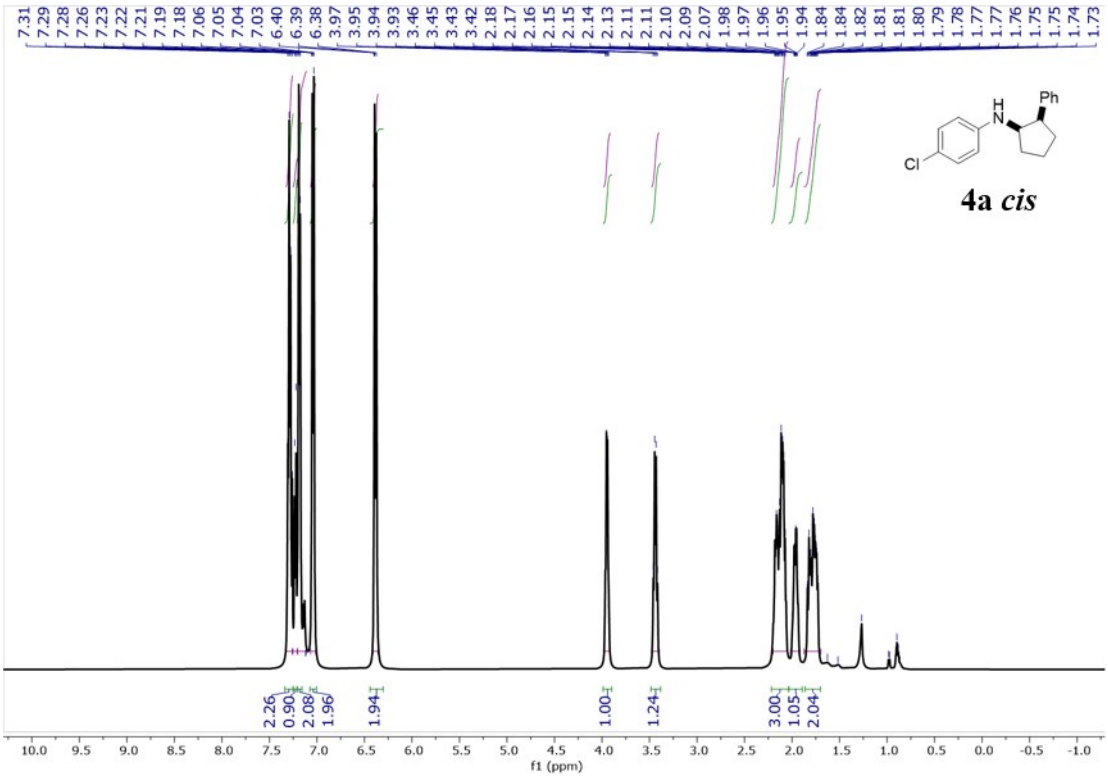

OMe
3c *trans*
f1 (ppm)

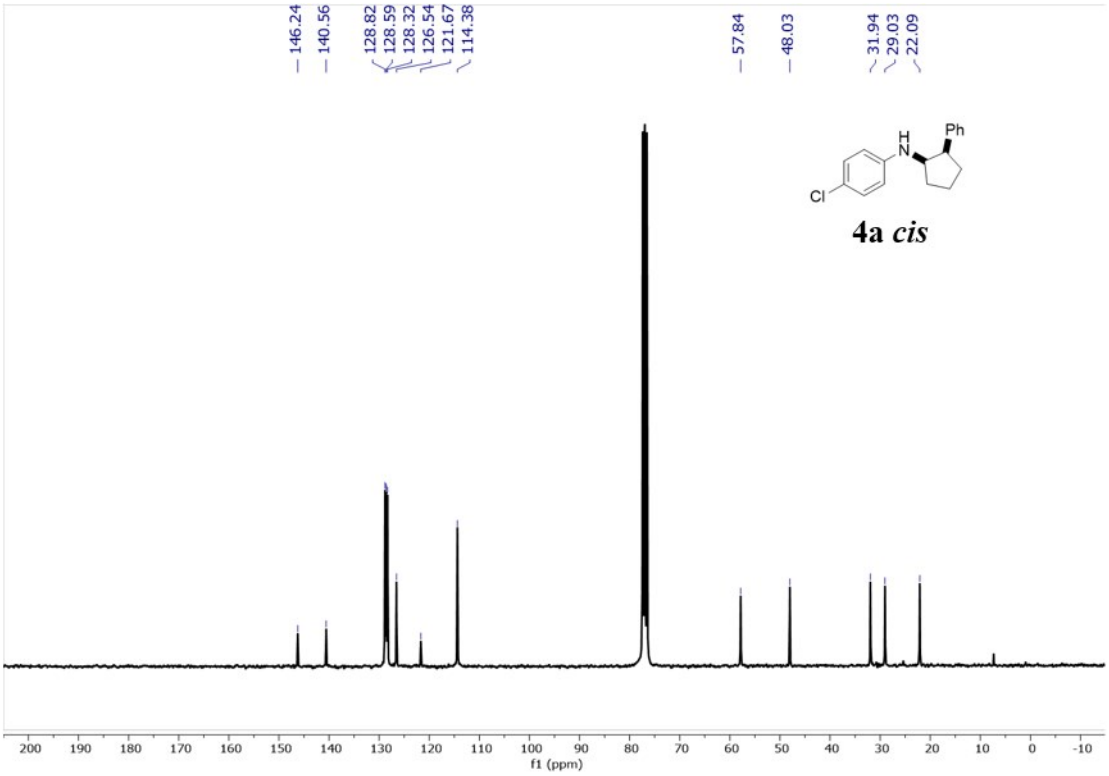

Br
H
N
3d *cis*
1.04
1.04
0.86
1.06
0.98
2.00
1.00
1.03
1.98
6.26
2.25
2.39
f1 (ppm)

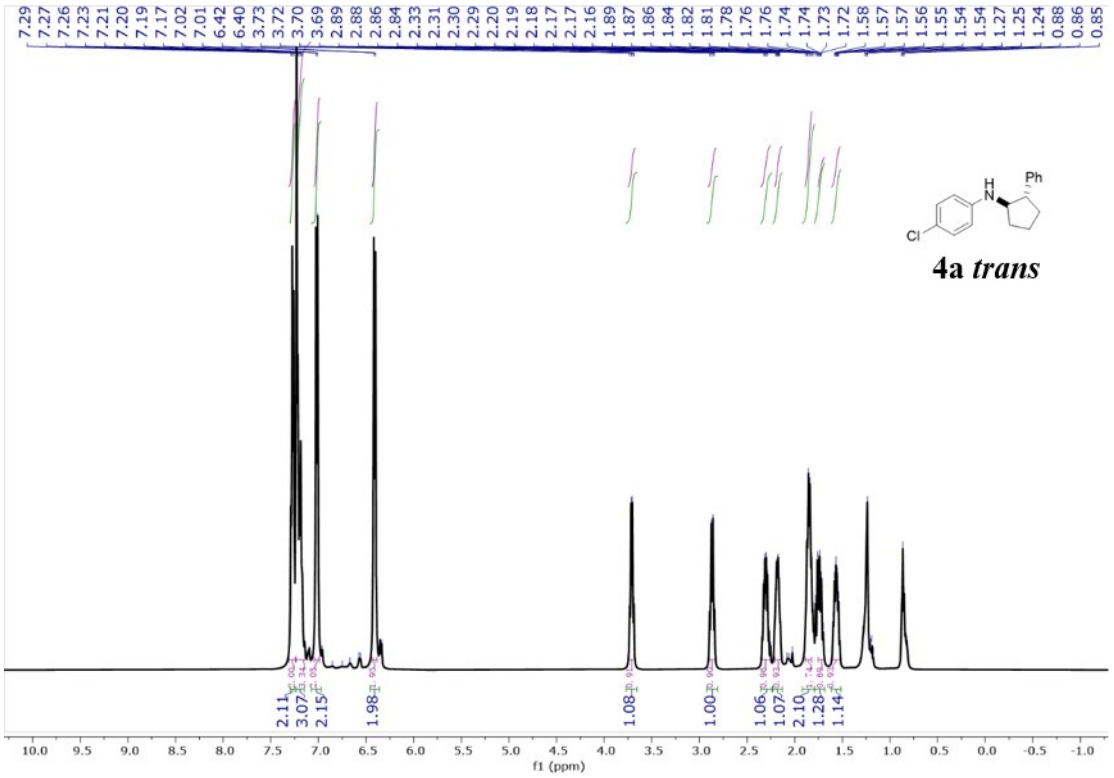

Br
H
N
3d *cis*
f1 (ppm)

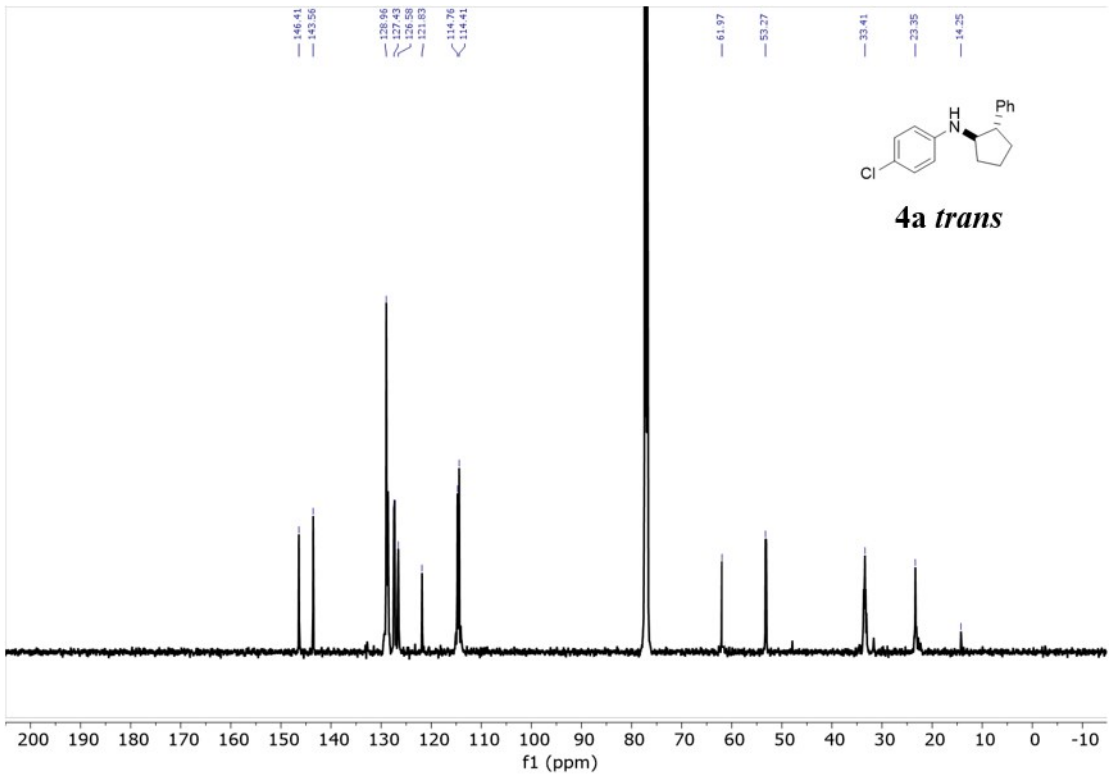

cis
Br
H
N
3d mixture
trans
cis
trans
cis
trans
cis
cis
2.84
2.26
4.68
2.84
0.61
2.15
1.22
4.45
2.28
0.69
2.35
1.00
0.69
20.45
11.82
2.54
f1 (ppm)

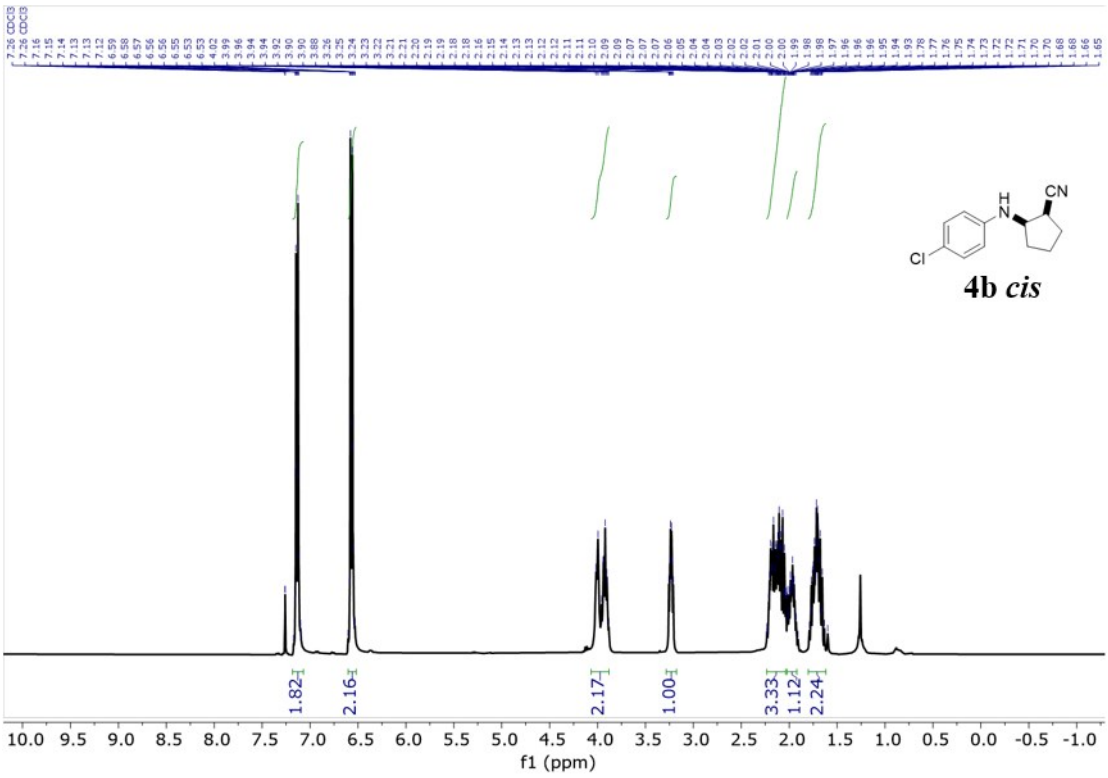

Br
H
N
3d mixture
f1 (ppm)

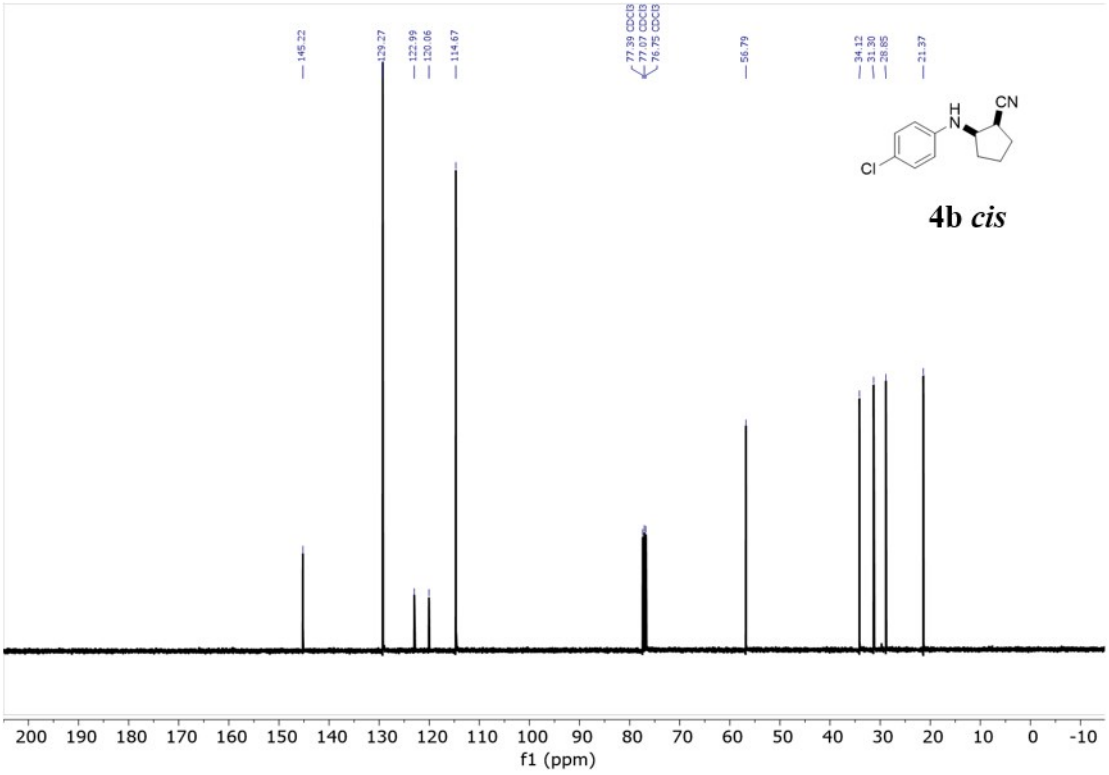

7.31 7.29 7.28 7.26 7.23 7.22 7.21 7.19 7.18 7.06 7.05 7.04 7.03 6.40 6.39 6.38 3.97 3.95 3.94 3.93 3.46 3.45 3.43 3.42 2.18 2.17 2.16 2.15 2.15 2.14 2.13 2.11 2.11 2.10 2.09 2.07 1.98 1.97 1.96 1.95 1.94 1.84 1.84 1.82 1.81 1.81 1.80 1.79 1.78 1.77 1.77 1.76 1.75 1.75 1.74 1.73
2.26 0.90 2.08 1.96 1.94 1.00 1.24 3.00 1.05 2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
Ph
H
N
Cl
4a *cis*

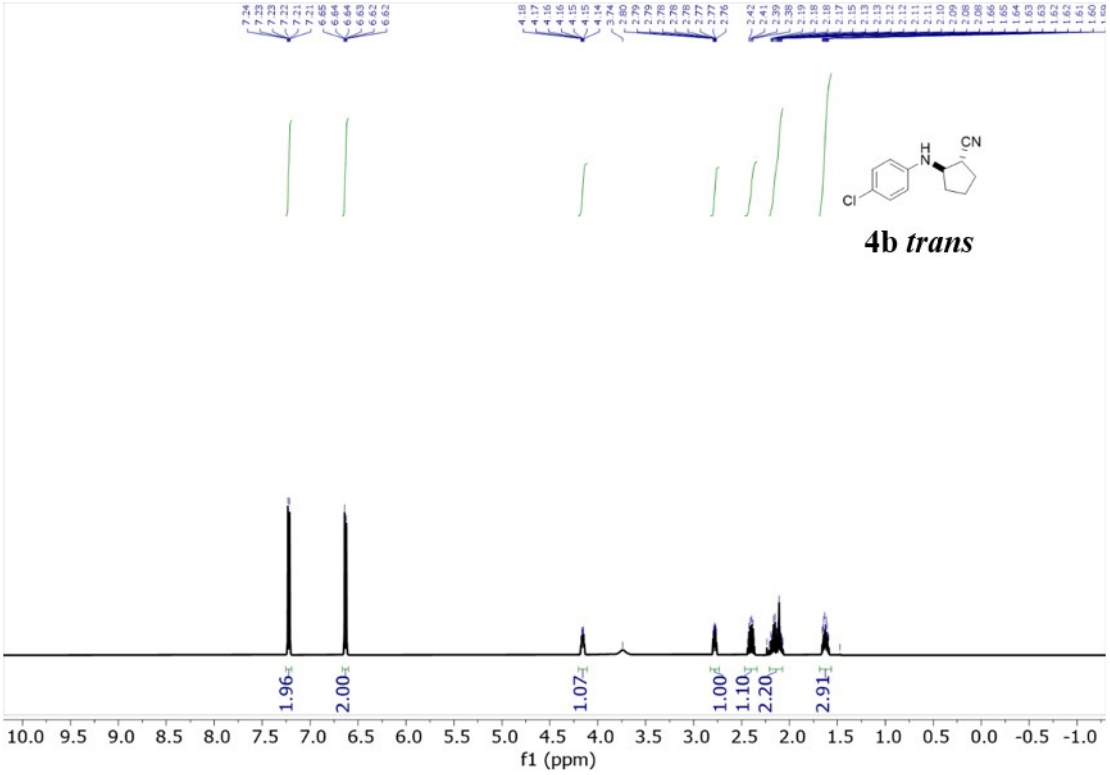

146.24 140.56 128.82 128.59 128.32 126.54 121.67 114.38 57.84 48.03 31.94 29.03 22.09
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Ph
H
N
Cl
4a *cis*

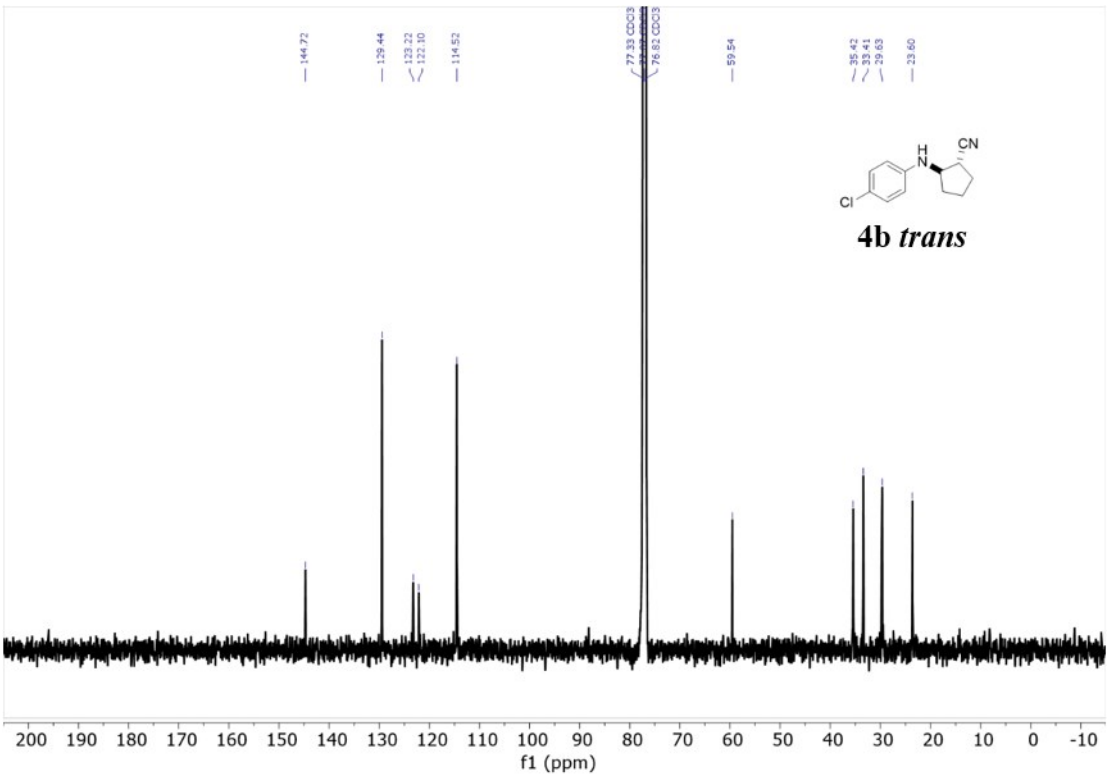

7.29 7.27 7.26 7.23 7.21 7.20 7.19 7.17 7.02 7.01 6.42 6.40 3.73 3.72 3.70 3.69 2.89 2.88 2.86 2.84 2.33 2.31 2.30 2.29 2.20 2.19 2.18 2.17 2.17 2.16 1.89 1.87 1.86 1.84 1.82 1.81 1.78 1.76 1.76 1.74 1.74 1.73 1.72 1.58 1.57 1.57 1.56 1.55 1.54 1.54 1.27 1.25 1.24 0.88 0.86 0.85
2.11 3.07 2.15 1.98 1.08 1.00 1.06 1.07 2.10 1.28 1.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
Ph
H
N
Cl
4a *trans*

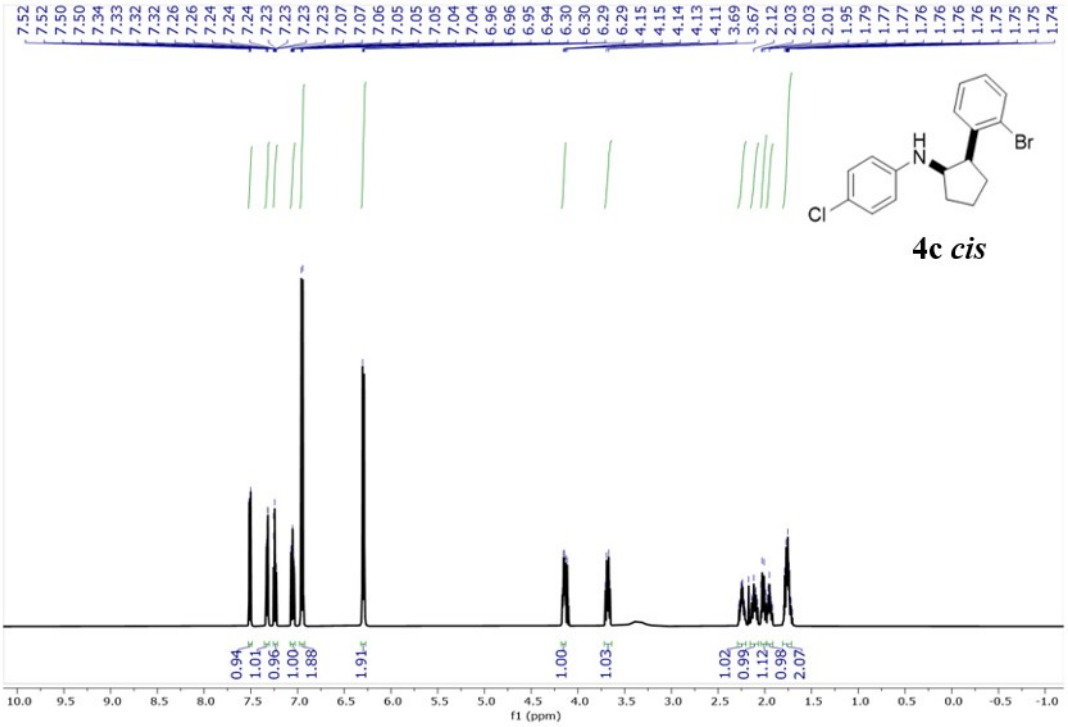

146.41 143.56 128.96 127.43 126.58 121.83 114.76 114.41 61.97 53.27 33.41 23.35 14.25
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Ph
H
N
Cl
4a *trans*

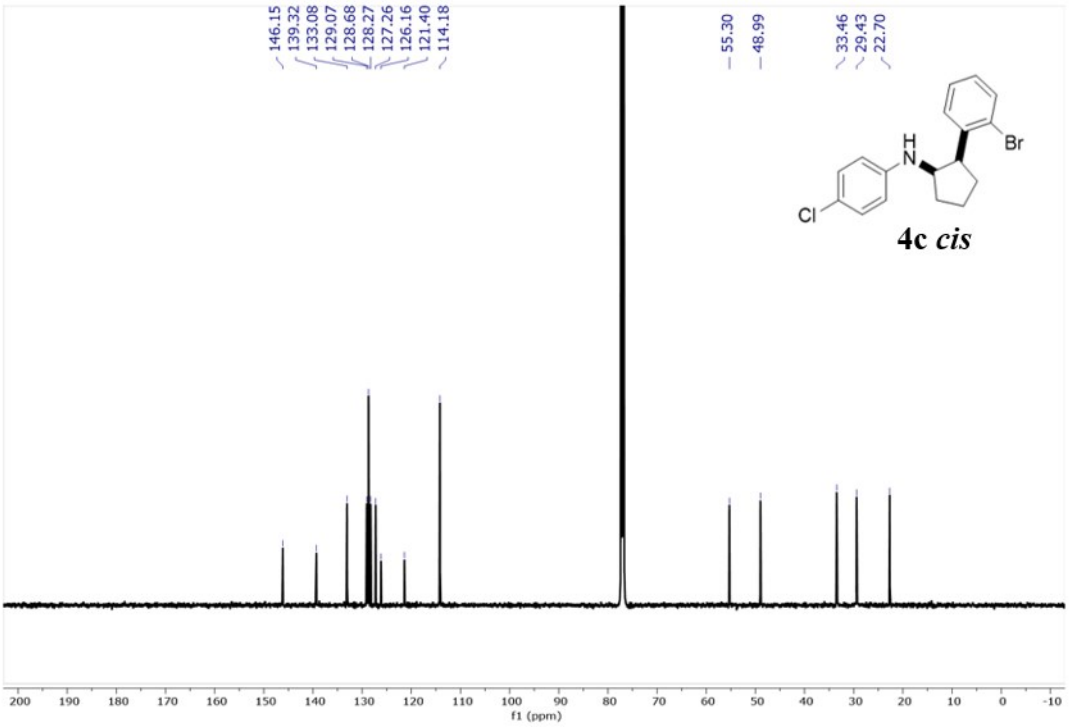

1.82
2.16
2.17
1.00
3.33
1.12
2.24
f1 (ppm)
4b *cis*

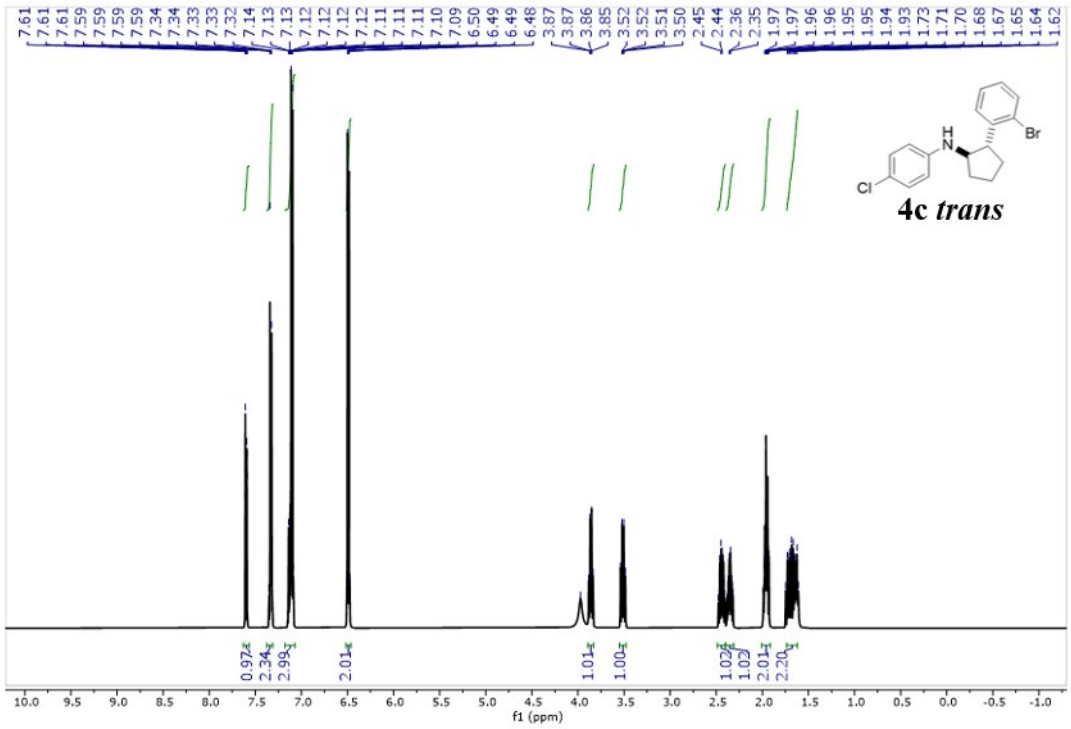

145.22
129.27
122.99
120.06
114.67
77.39 CDCl3
77.07 CDCl3
76.75 CDCl3
56.79
34.12
31.30
28.85
21.37
f1 (ppm)
4b *cis*

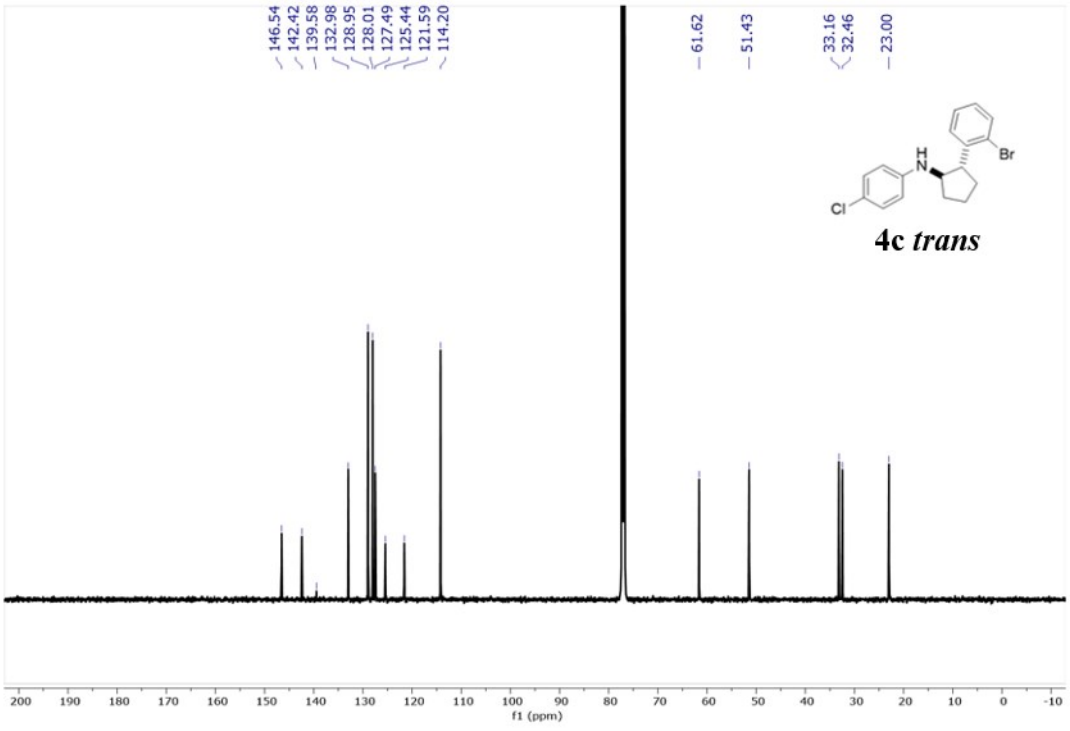

4b *trans*
1.96
2.00
1.07
1.00
1.10
2.20
2.91
f1 (ppm)

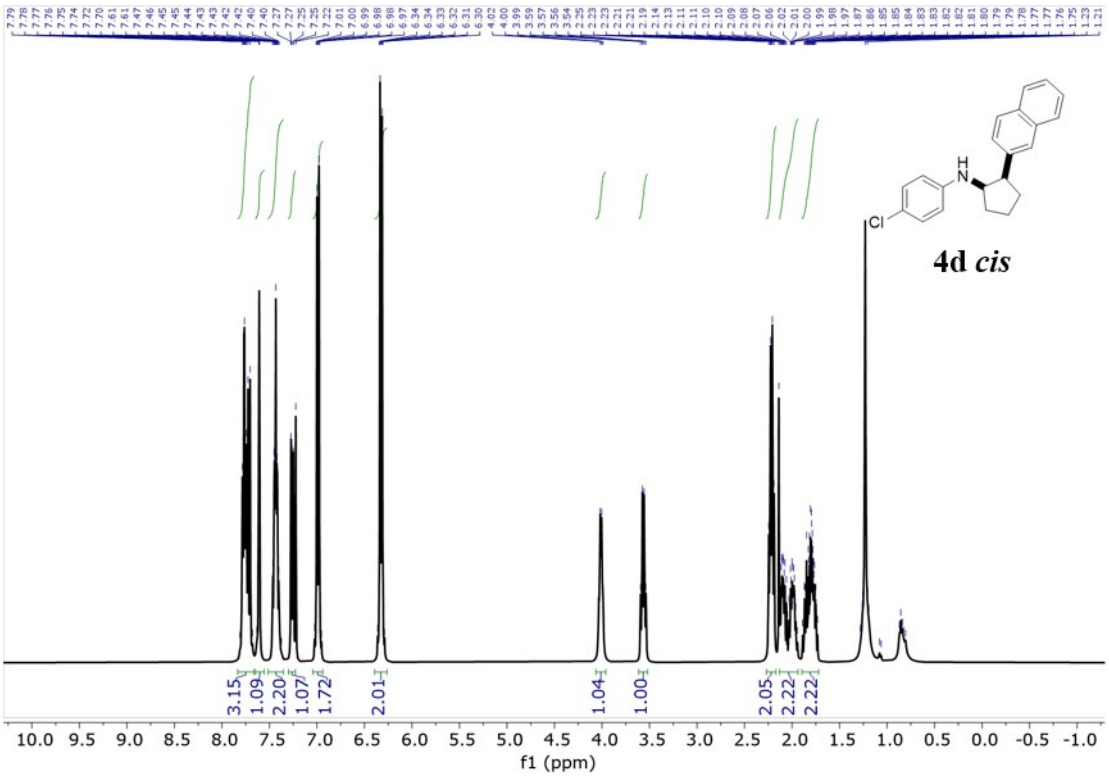

4b *trans*
f1 (ppm)

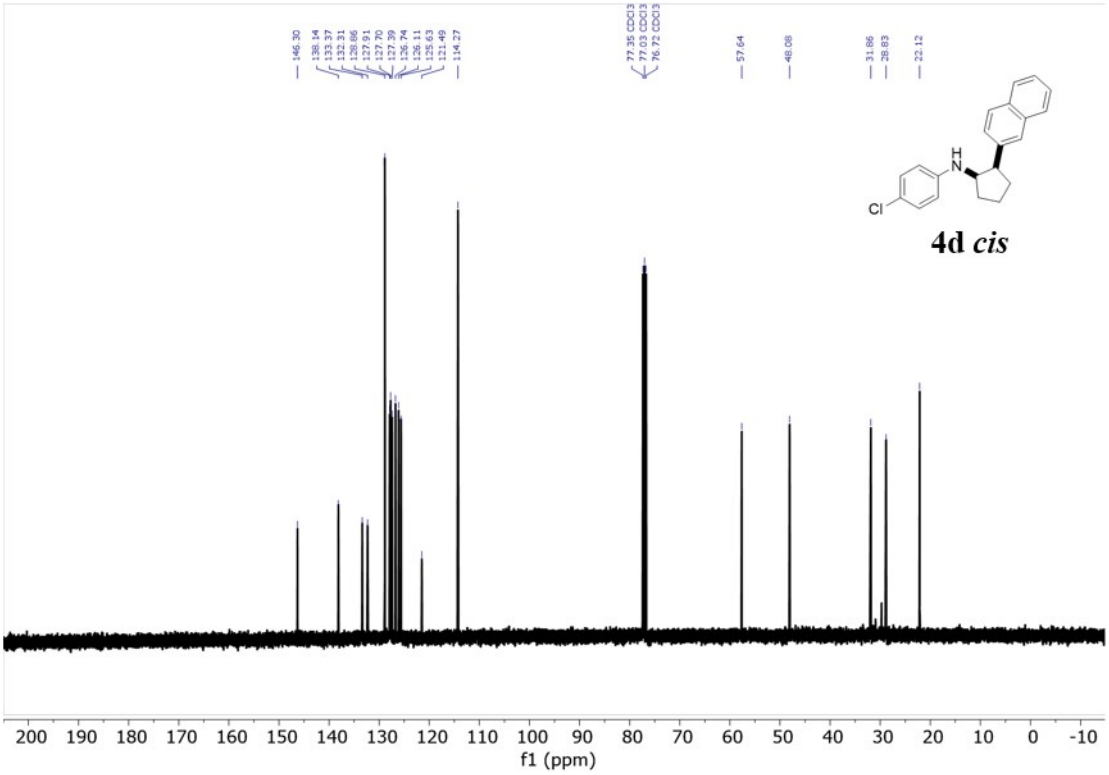

7.52 7.52 7.50 7.50 7.34 7.33 7.32 7.32 7.26 7.24 7.24 7.24 7.23 7.23 7.23 7.23 7.07 7.07 7.06 7.05 7.05 7.05 7.04 7.04 6.96 6.96 6.95 6.94 6.30 6.30 6.29 6.29 4.15 4.15 4.14 4.13 4.11 3.69 3.67 2.12 2.03 2.03 2.01 1.95 1.79 1.77 1.77 1.76 1.76 1.76 1.76 1.75 1.75 1.75 1.74
H
N
Br
Cl
4c *cis*
0.94 1.01 0.96 1.00 1.88 1.91 1.00 1.03 1.02 0.99 1.12 0.98 2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

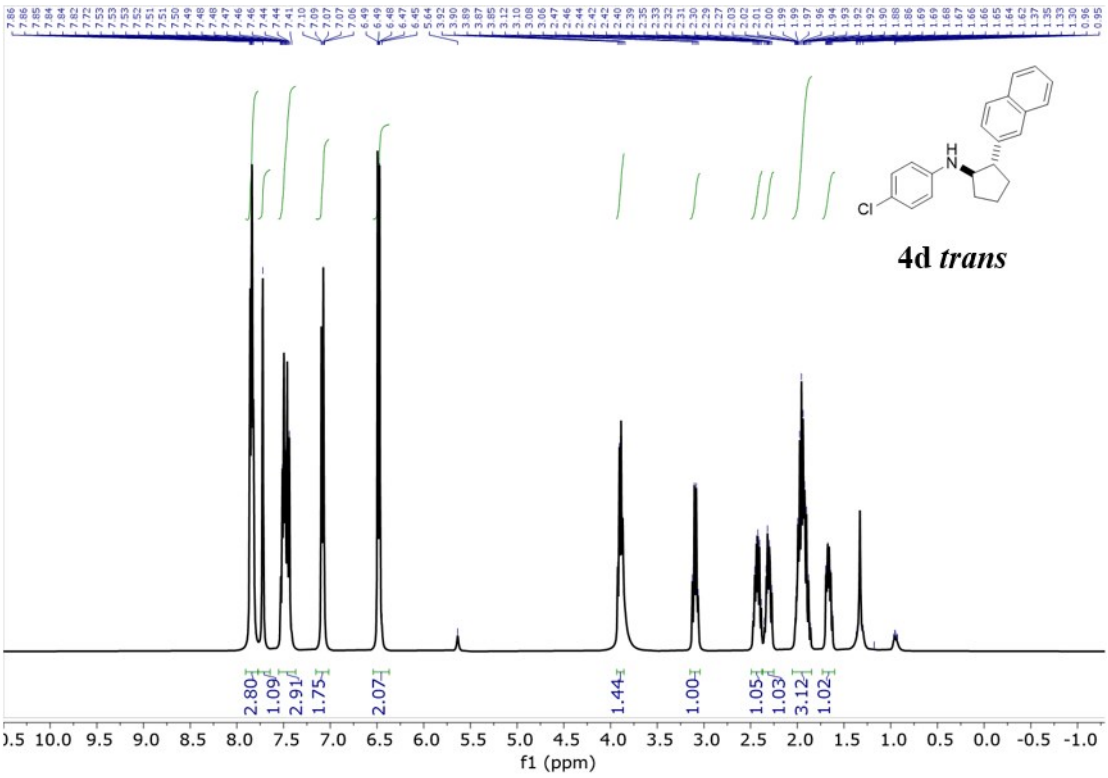

146.15 139.32 133.08 129.07 128.68 128.27 127.26 126.16 121.40 114.18
55.30 48.99 33.46 29.43 22.70
H
N
Br
Cl
4c *cis*
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

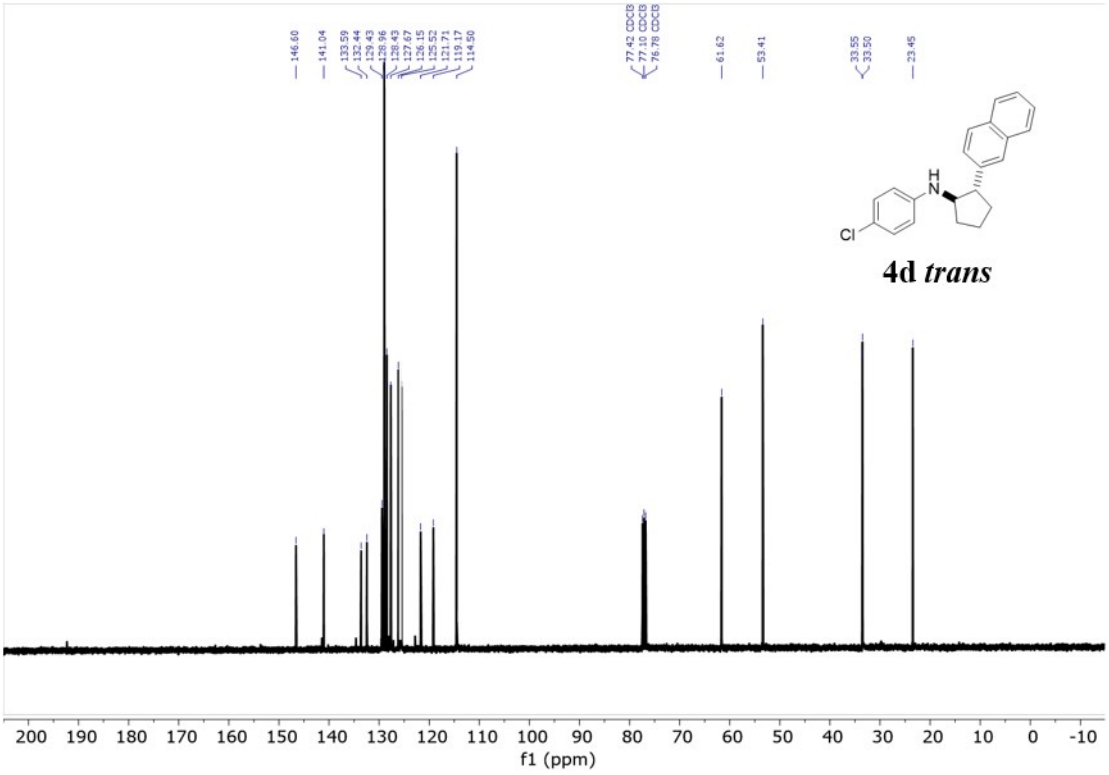

7.61 7.61 7.61 7.59 7.59 7.59 7.59 7.34 7.34 7.33 7.33 7.32 7.14 7.13 7.13 7.12 7.12 7.12 7.12 7.11 7.11 7.11 7.10 7.09 6.50 6.49 6.48 3.87 3.87 3.86 3.85 3.52 3.52 3.51 3.50 2.45 2.44 2.36 2.35 1.97 1.96 1.96 1.95 1.95 1.94 1.93 1.73 1.71 1.70 1.68 1.67 1.65 1.64 1.62
0.97 2.34 2.99 2.01 1.01 1.00 1.02 1.03 2.01 2.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
Br
H
N
Cl
4c *trans*

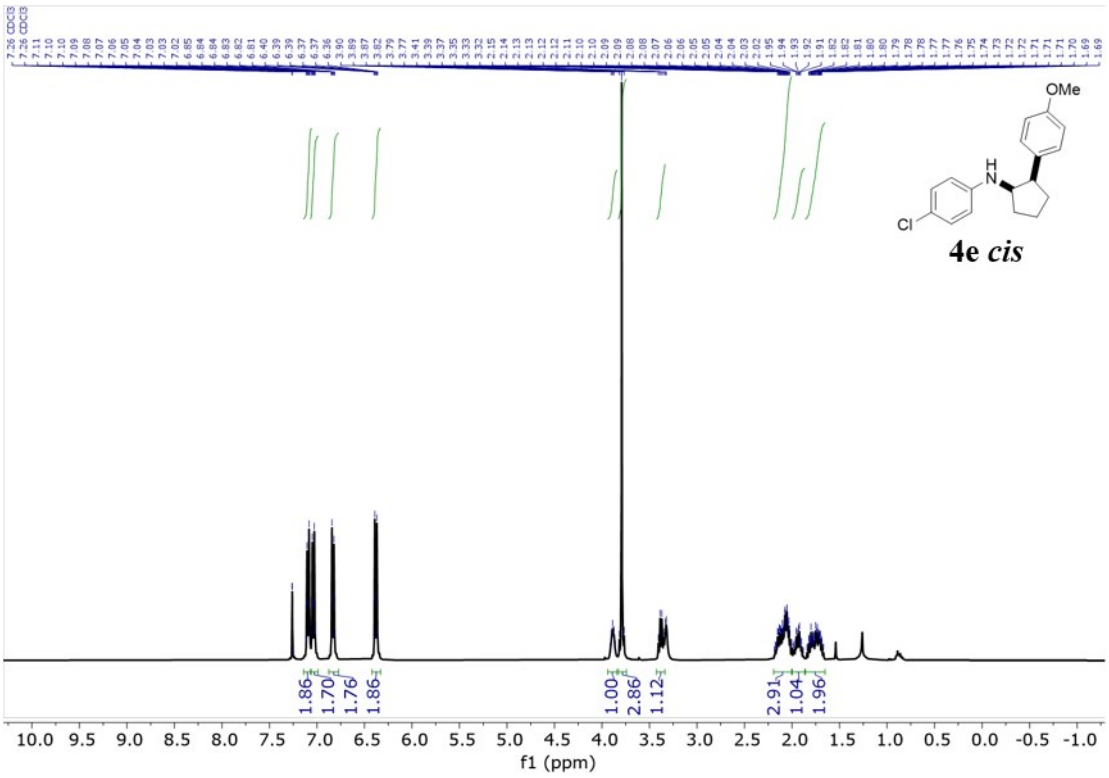

146.54 142.42 139.58 132.98 128.95 128.01 127.49 125.44 121.59 114.20
61.62 51.43 33.16 32.46 23.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Br
H
N
Cl
4c *trans*

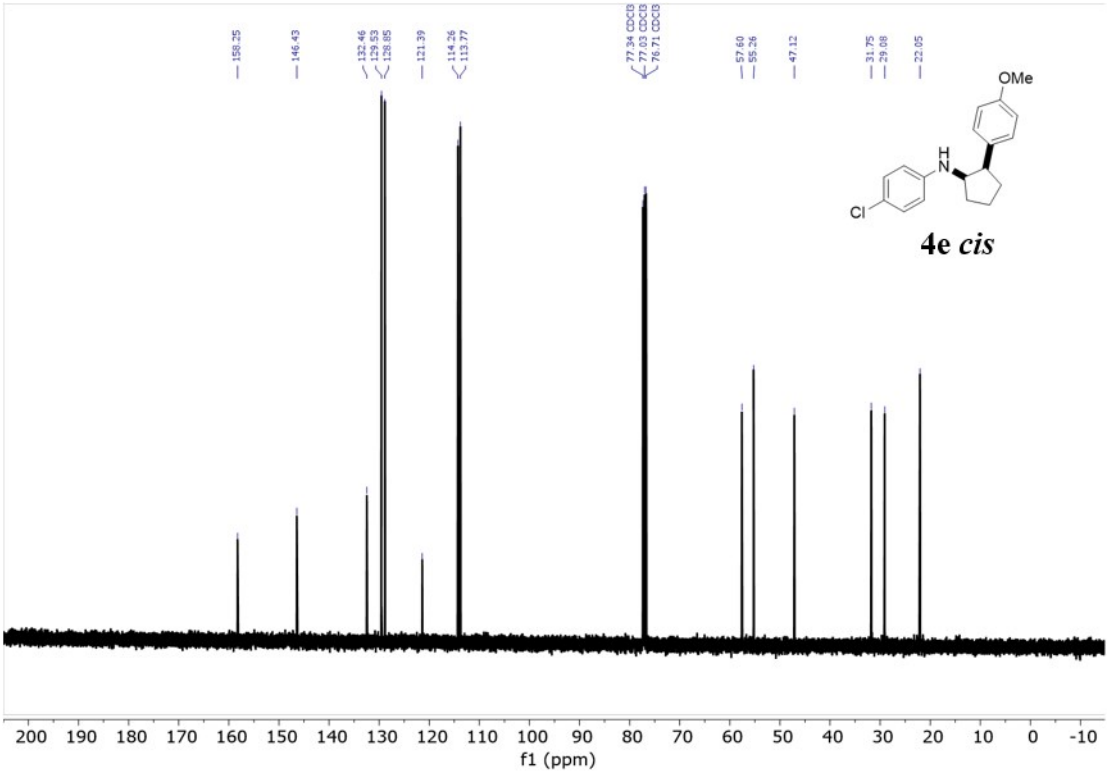

4d *cis*
3.15
1.09
2.20
1.07
1.72
2.01
1.04
1.00
2.05
2.22
2.22
f1 (ppm)

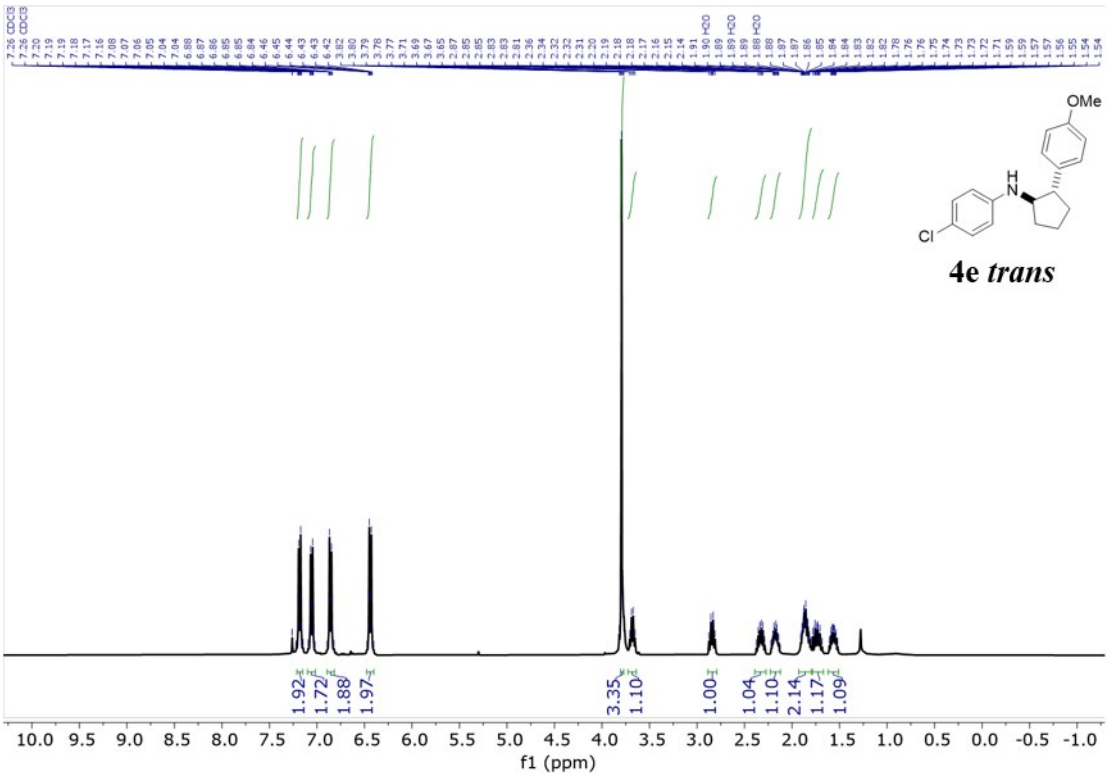

4d *cis*
f1 (ppm)

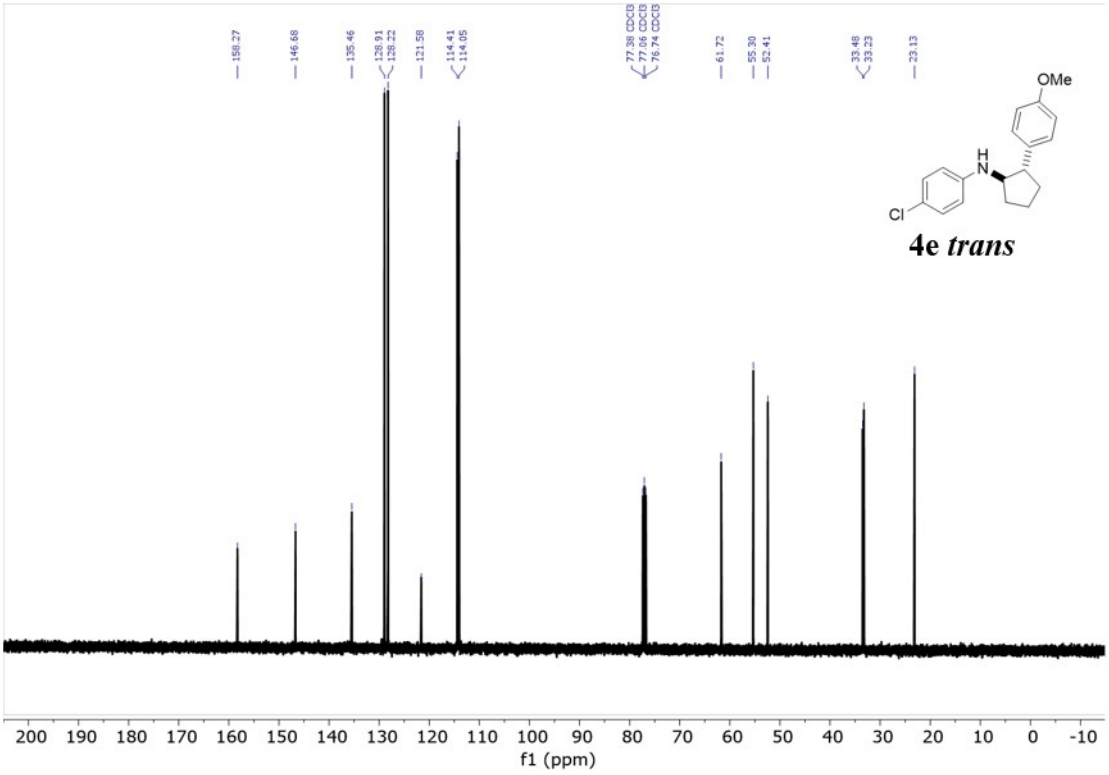

4d *trans*
2.80
1.09
2.91
1.75
2.07
1.44
1.00
1.05
1.03
3.12
1.02
f1 (ppm)

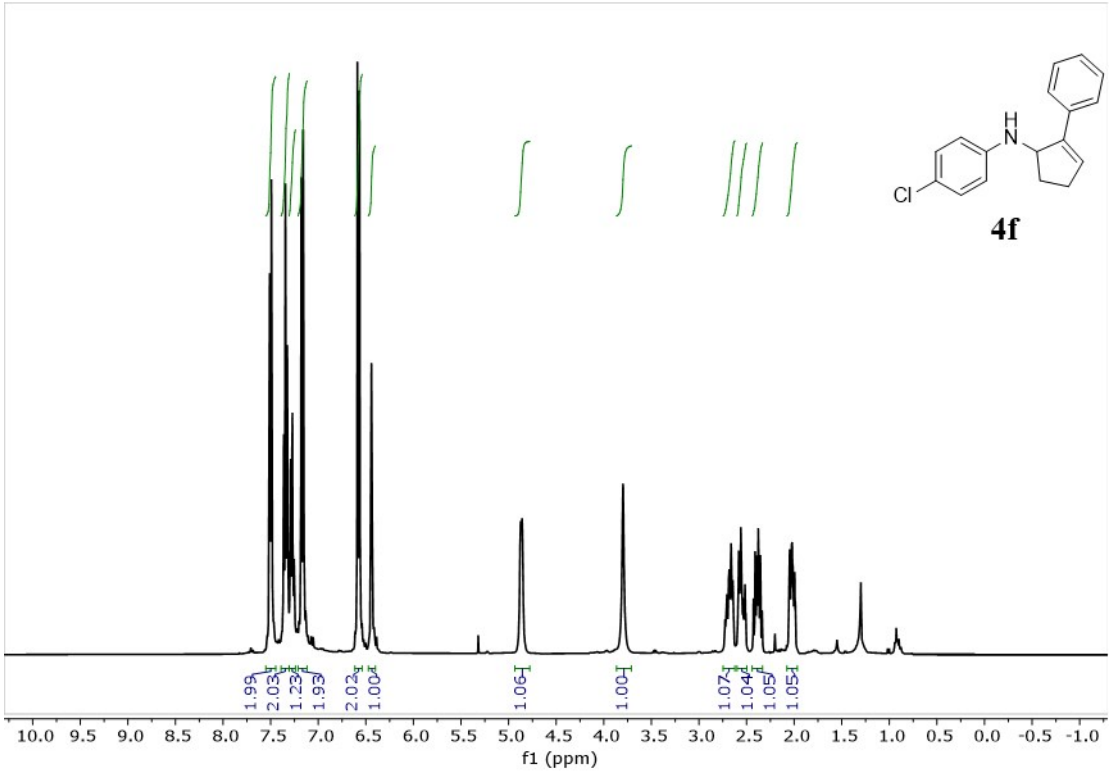

4d *trans*
f1 (ppm)

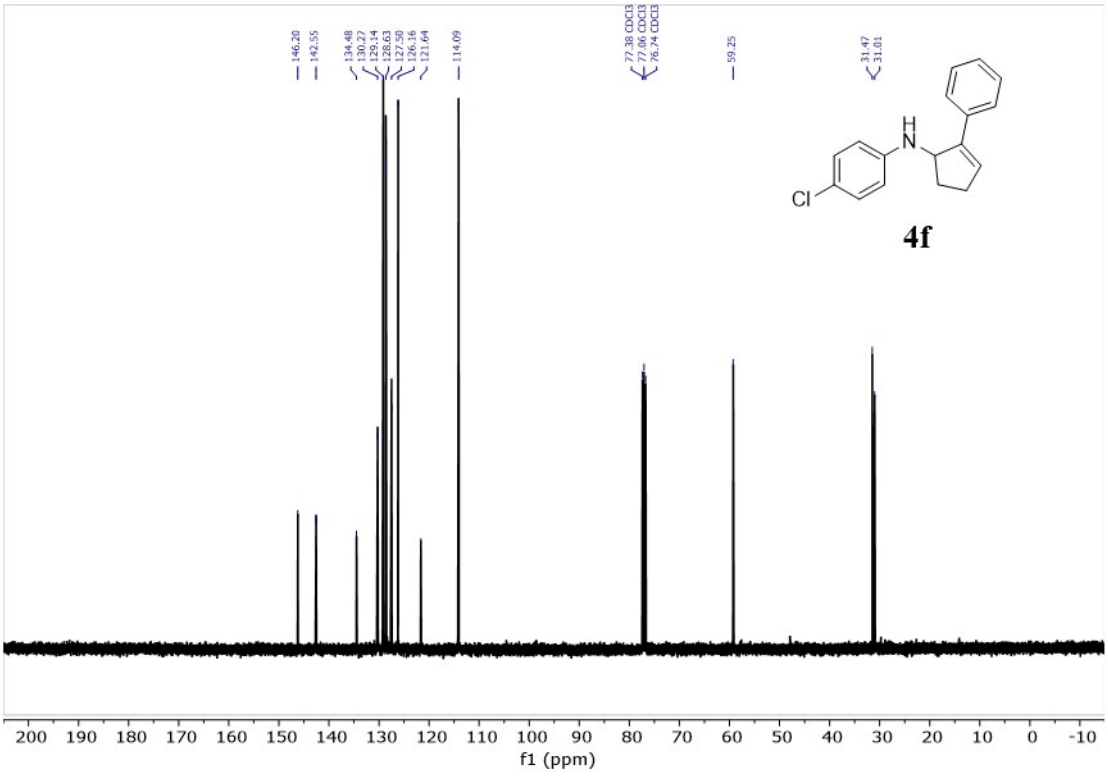

OMe
H
N
Cl
4e *cis*
1.86
1.70
1.76
1.86
1.00
2.86
1.12
2.91
1.04
1.96
f1 (ppm)

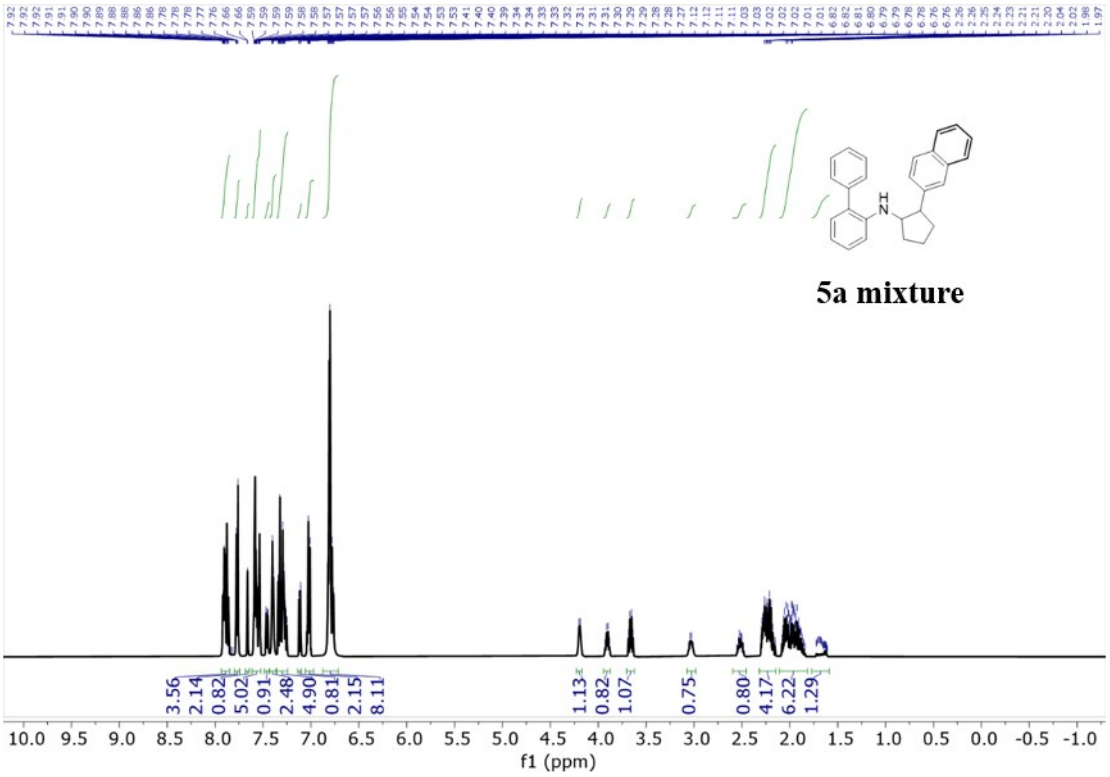

158.25
146.43
132.46
129.53
128.85
121.39
114.26
113.77
77.34 CDCl3
77.03 CDCl3
76.71 CDCl3
57.60
55.26
47.12
31.75
29.08
22.05
OMe
H
N
Cl
4e *cis*
f1 (ppm)

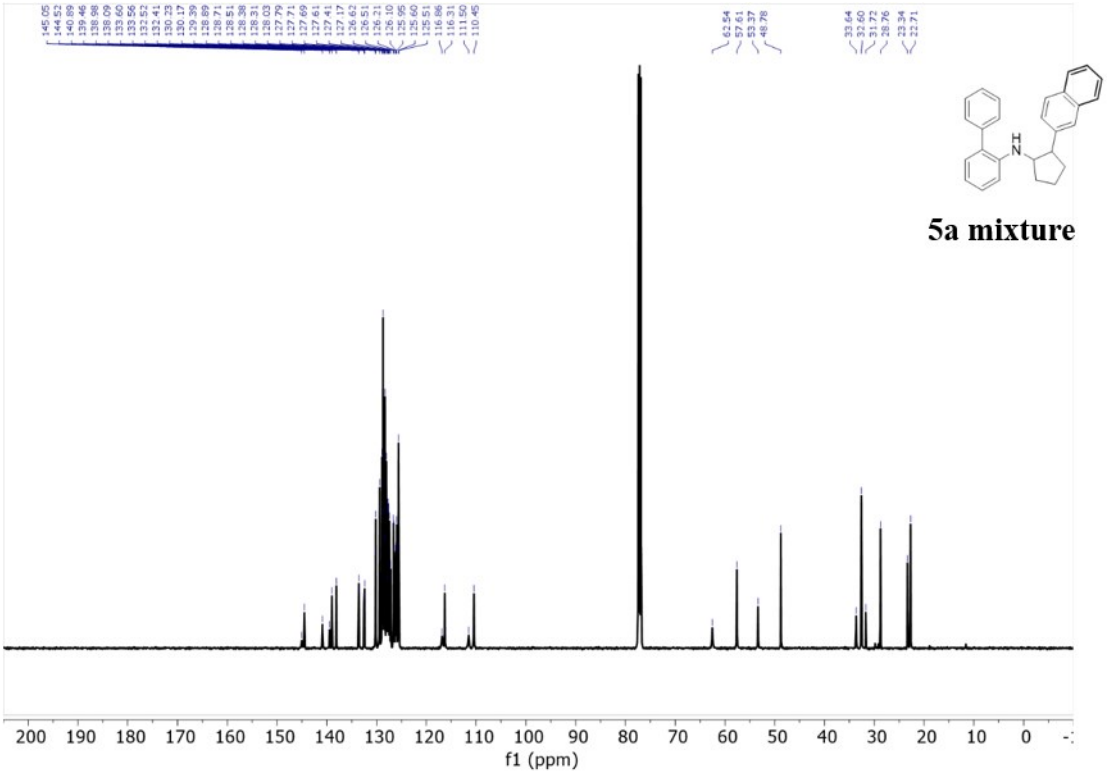

OMe
H
N
Cl
4e *trans*
1.92
1.72
1.88
1.97
3.35
1.10
1.00
1.04
1.10
2.14
1.17
1.09
f1 (ppm)

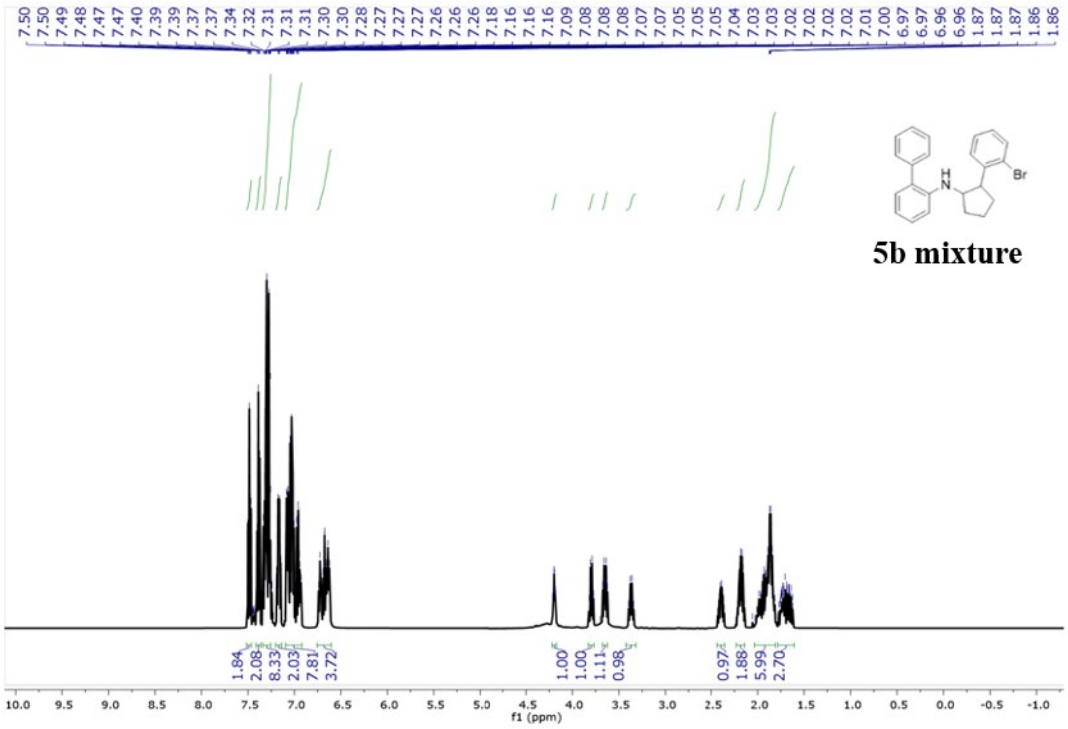

158.27
146.68
135.46
128.91
128.22
121.58
114.41
114.05
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
61.72
55.30
52.41
33.48
33.23
23.13
OMe
H
N
Cl
4e *trans*
f1 (ppm)

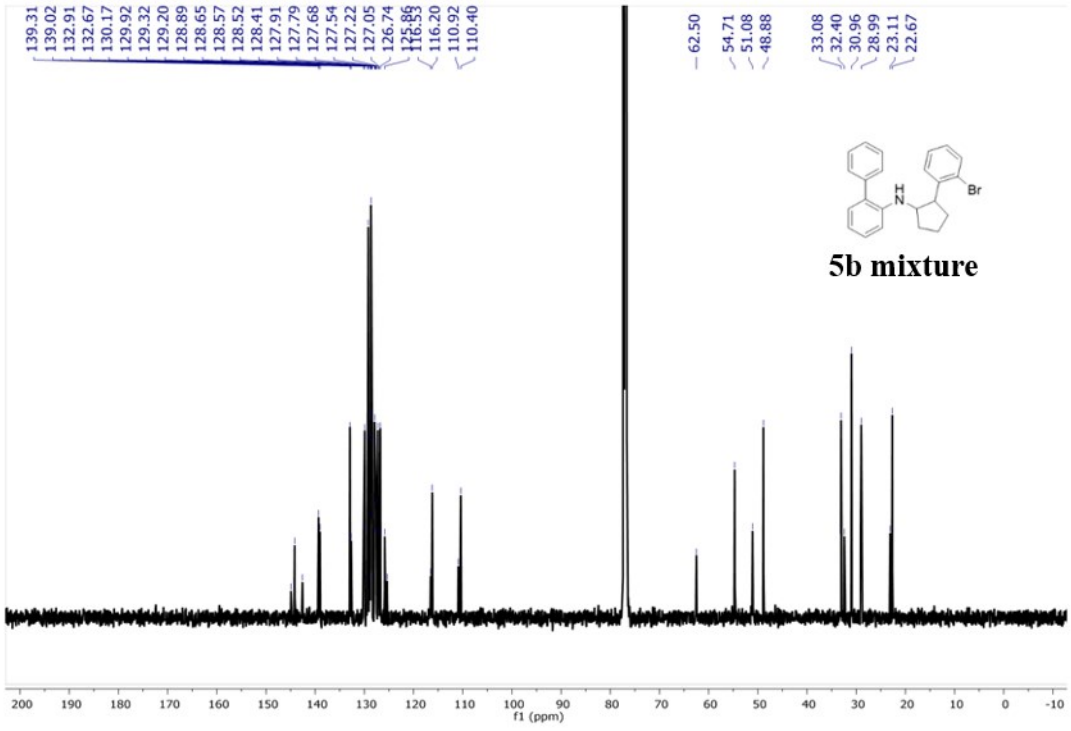

1.99
2.03
1.29
1.93
2.02
1.00
1.06
1.00
1.07
1.04
1.05
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
H
N
Cl
4f

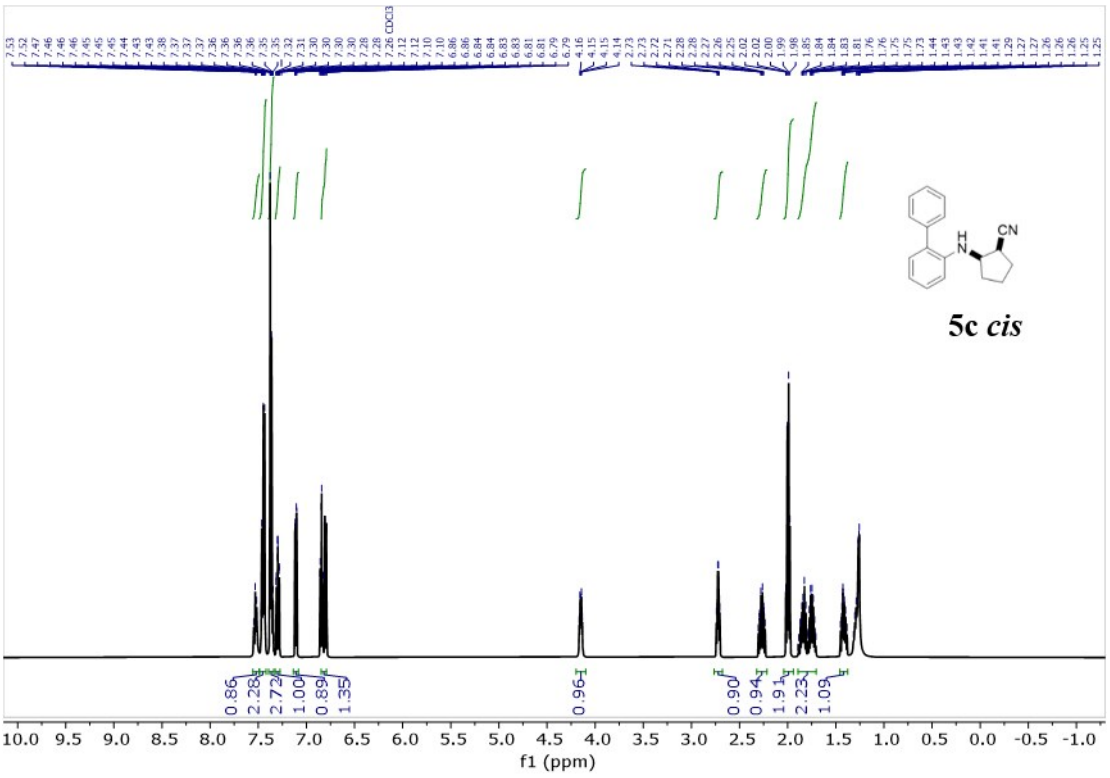

146.20
142.55
134.48
130.27
129.14
128.63
127.50
126.16
121.64
114.09
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
59.25
31.47
31.01
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
H
N
Cl
4f

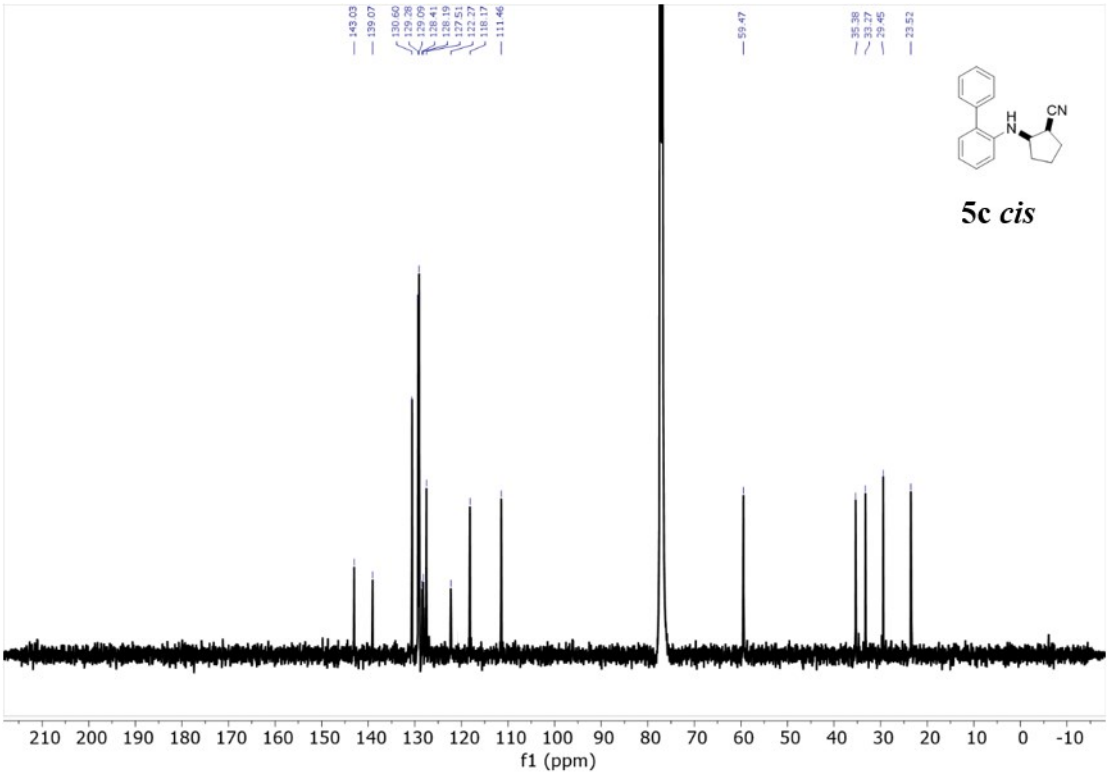

5a mixture
3.56
2.14
0.82
5.02
0.91
2.48
4.90
0.81
2.15
8.11
1.13
0.82
1.07
0.75
0.80
4.17
6.22
1.29
f1 (ppm)

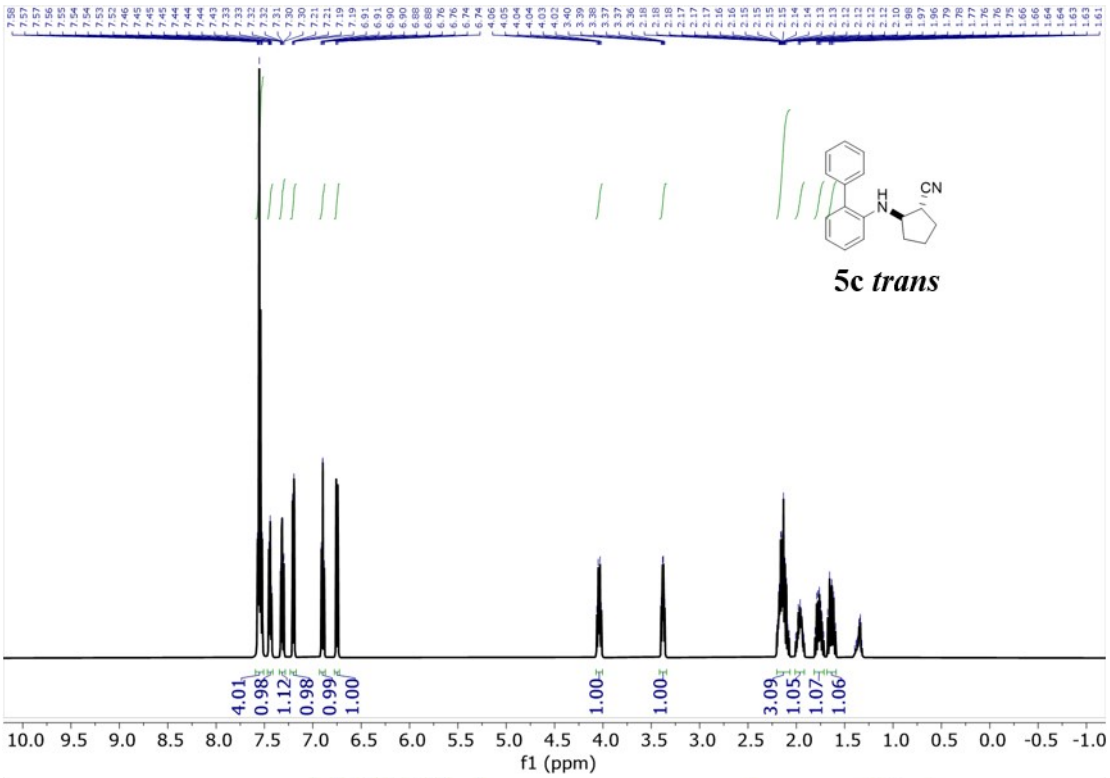

5a mixture
f1 (ppm)

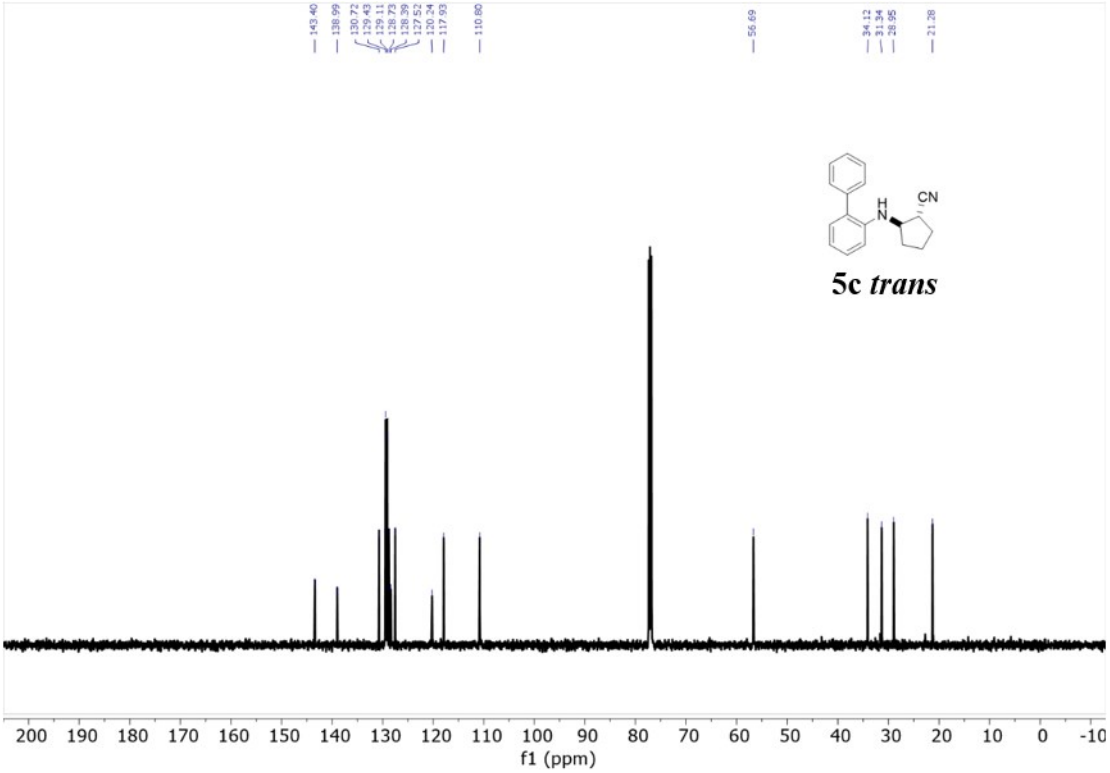

7.50 7.50 7.49 7.48 7.47 7.47 7.40 7.39 7.39 7.37 7.37 7.34 7.32 7.31 7.31 7.31 7.30 7.30 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.18 7.16 7.16 7.16 7.09 7.08 7.08 7.08 7.07 7.07 7.05 7.05 7.05 7.04 7.03 7.03 7.02 7.02 7.02 7.02 7.01 7.00 6.97 6.97 6.96 6.96 1.87 1.87 1.87 1.86 1.86
Br
H
N
5b mixture
1.84 2.08 8.33 2.03 7.81 3.72 1.00 1.00 1.11 0.98 0.97 1.88 5.99 2.70
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

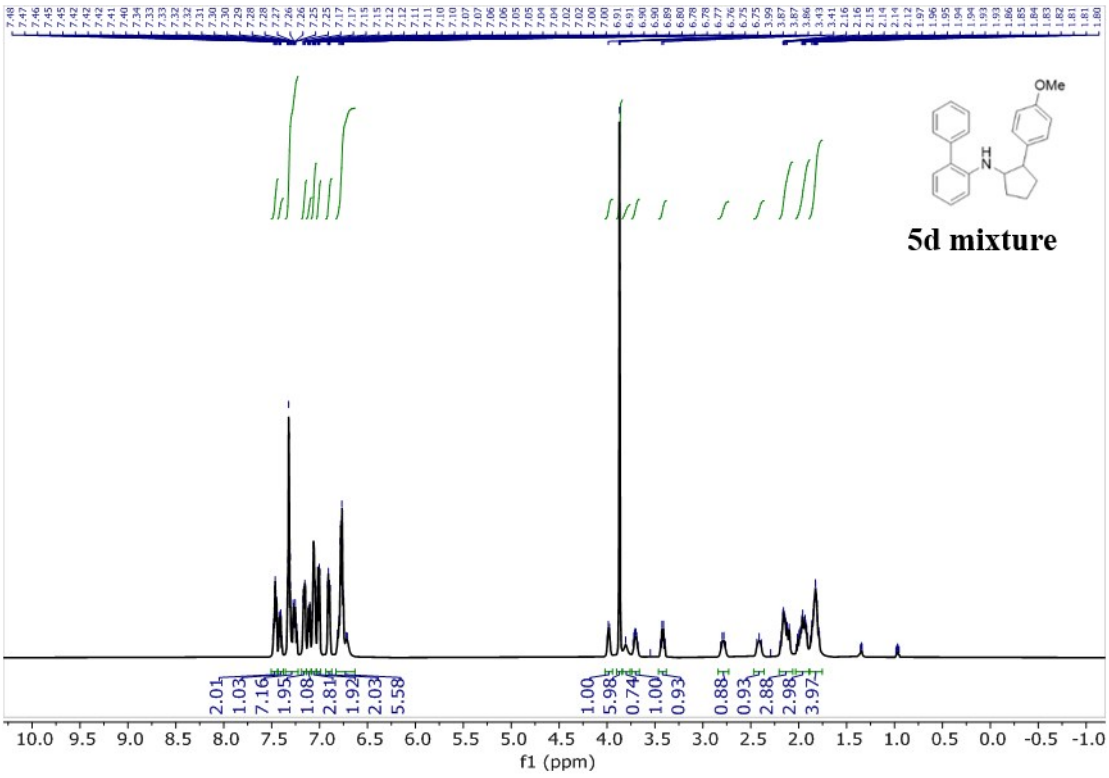

139.31 139.02 132.91 132.67 130.17 129.92 129.32 129.20 128.89 128.65 128.57 128.52 128.41 127.91 127.79 127.68 127.54 127.22 127.05 126.74 116.20 110.92 110.40
62.50 54.71 51.08 48.88 33.08 32.40 30.96 28.99 23.11 22.67
Br
H
N
5b mixture
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

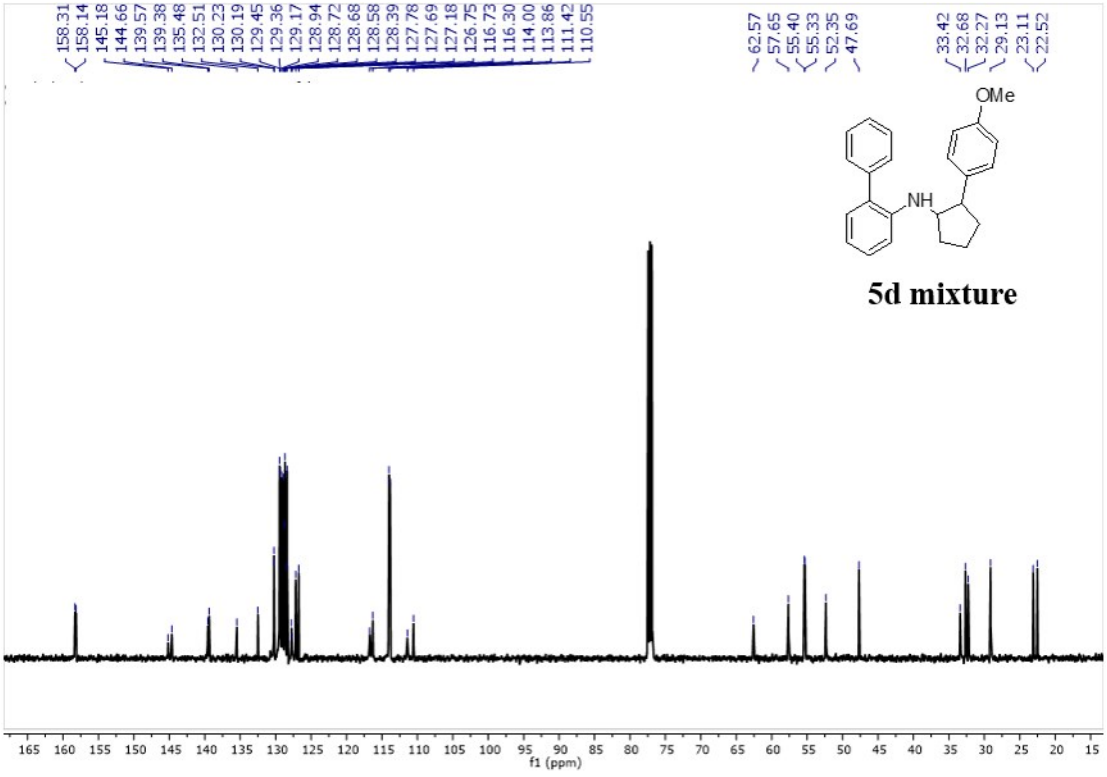

CDCl3
0.86
2.28
2.72
1.00
0.89
1.35
0.96
0.90
0.94
1.91
2.23
1.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
CN
H
N
5c *cis*

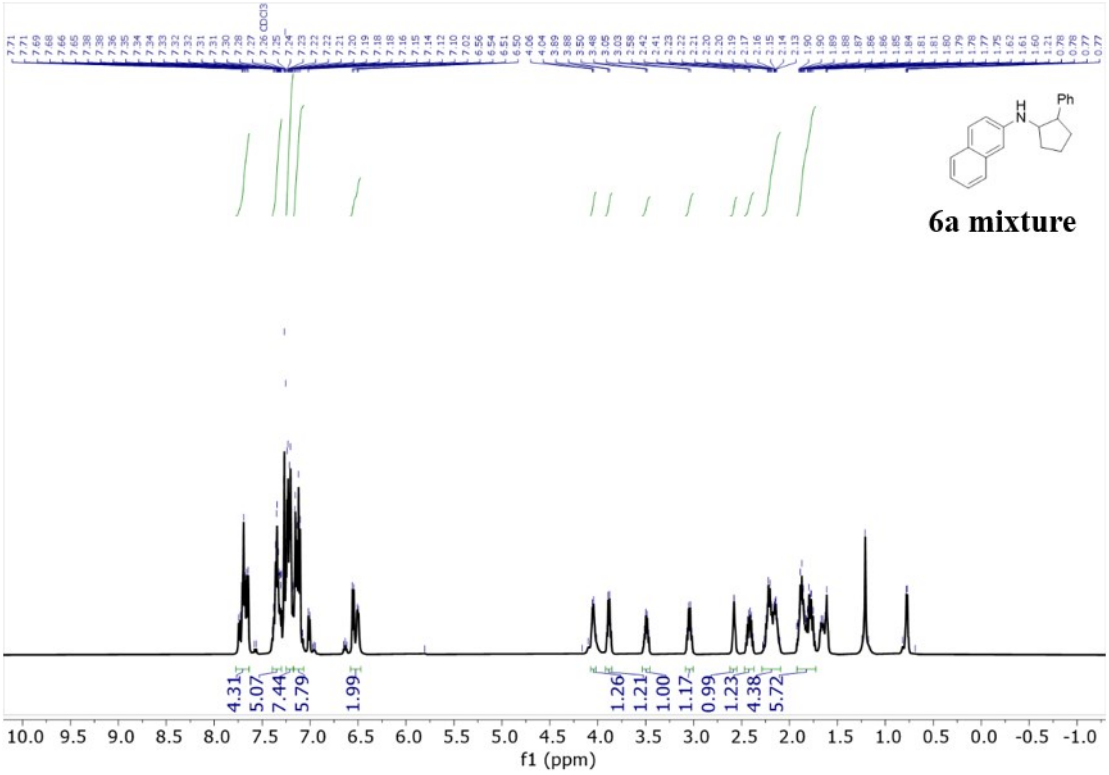

143.03
139.07
130.60
129.28
129.09
128.41
128.19
127.51
122.27
118.17
111.46
59.47
35.38
33.27
29.45
23.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
CN
H
N
5c *cis*

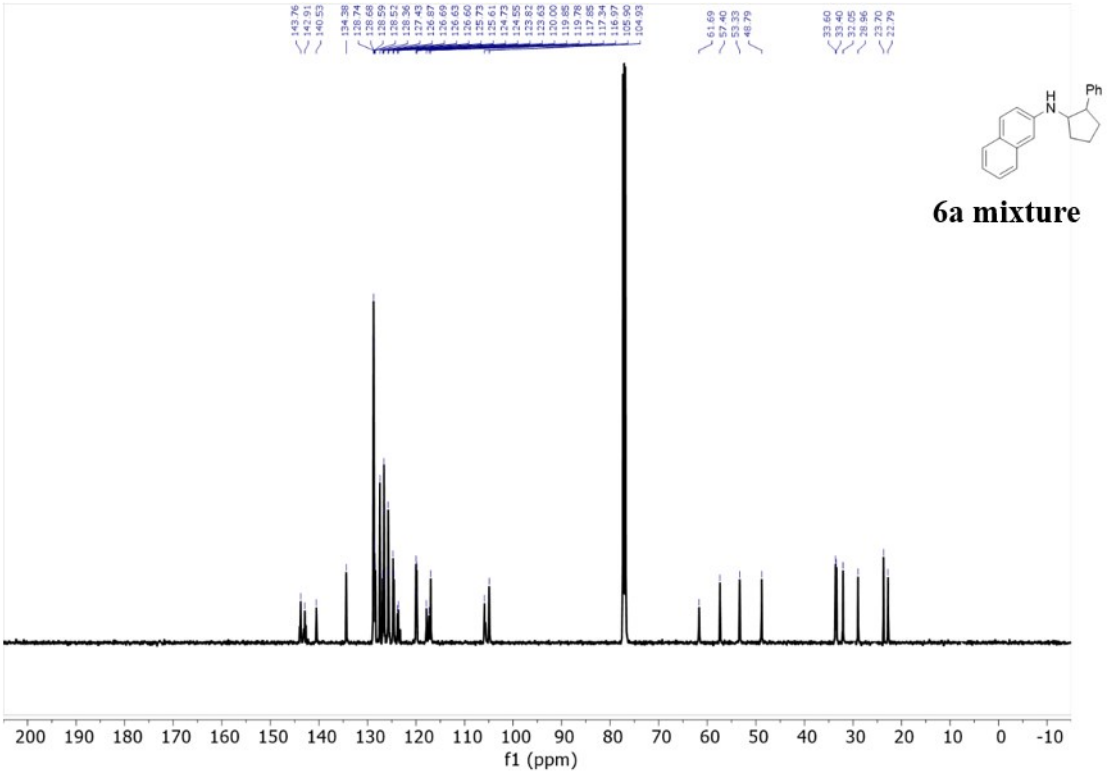

CN
H
N
5c *trans*
4.01
0.98
1.12
0.98
0.99
1.00
1.00
1.00
3.09
1.05
1.07
1.06
f1 (ppm)

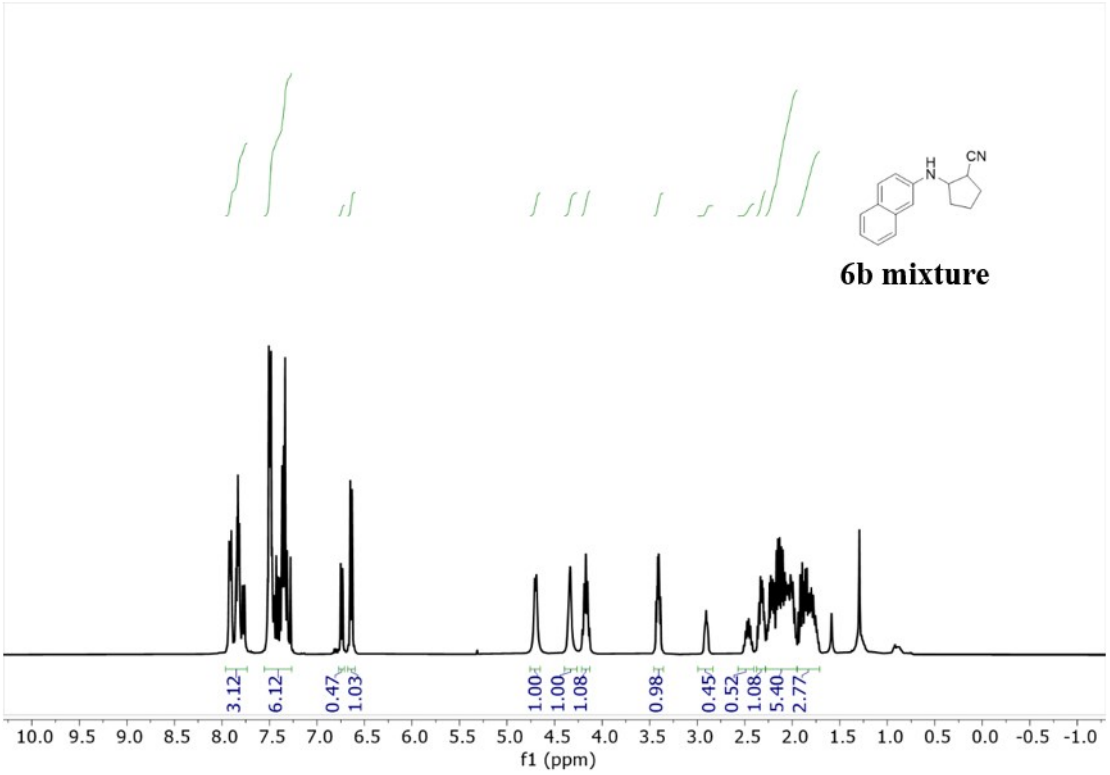

CN
H
N
5c *trans*
f1 (ppm)

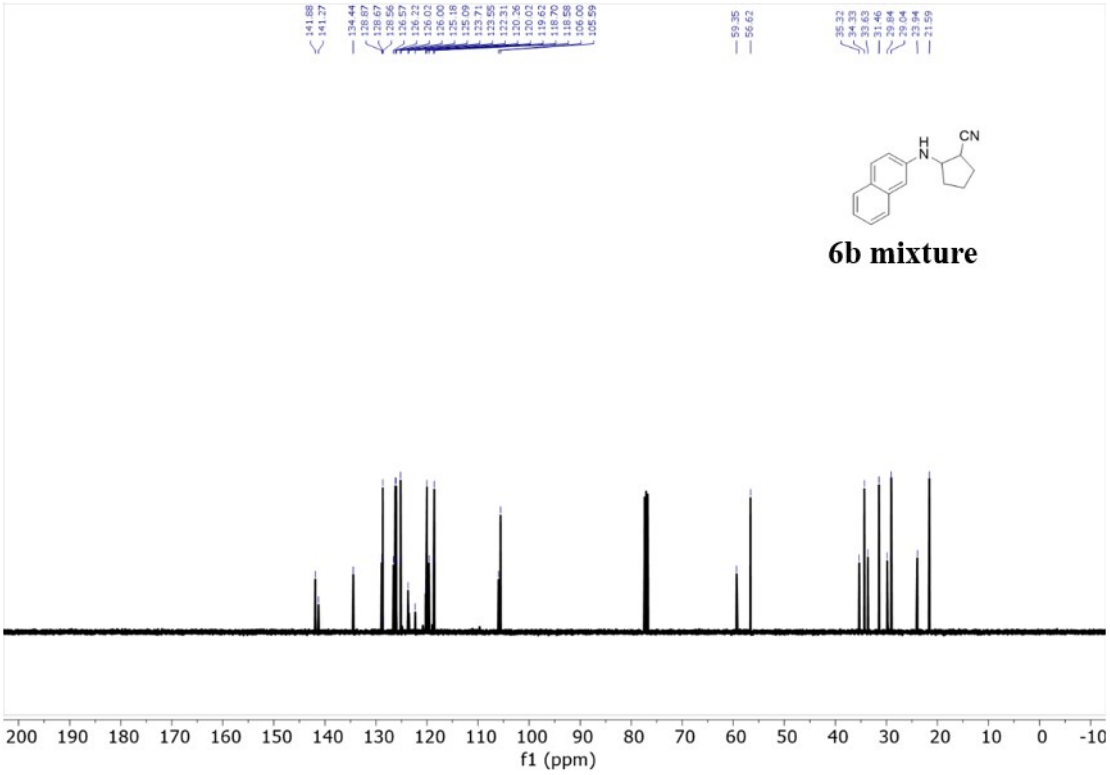

OMe
NH
5d mixture
2.01
1.03
7.16
1.95
1.08
2.81
1.92
2.03
5.58
1.00
5.98
0.74
1.00
0.93
0.88
0.93
2.88
2.98
3.97
f1 (ppm)


158.31
158.14
145.18
144.66
139.57
139.38
135.48
132.51
130.23
130.19
129.45
129.36
129.17
128.94
128.72
128.68
128.58
128.39
127.78
127.69
127.18
126.75
116.73
116.30
114.00
113.86
111.42
110.55
62.57
57.65
55.40
55.33
52.35
47.69
33.42
32.68
32.27
29.13
23.11
22.52
OMe
NH
5d mixture
f1 (ppm)


6a mixture
4.31
5.07
7.44
5.79
1.99
1.26
1.21
1.00
1.17
0.99
1.23
4.38
5.72
f1 (ppm)


6a mixture
f1 (ppm)


CN
H
N
6b mixture
3.12
6.12
0.47
1.03
1.00
1.00
1.08
0.98
0.45
0.52
1.08
5.40
2.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


141.88
141.27
134.44
128.87
128.67
128.56
126.57
126.22
126.02
126.00
125.18
125.09
123.71
123.55
122.31
120.26
120.02
119.62
118.70
118.58
106.00
105.59
59.35
56.62
35.32
34.33
33.63
31.46
29.84
29.04
23.94
21.59
CN
H
N
6b mixture
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

References

1. Cui, W.; Loeppky, R. N., The synthesis of N-arylcyclopropylamines via palladium-catalyzed C–N bond formation. *Tetrahedron* **2001,** *57*, 2953-2956.
2. Loeppky, R. N.; Elomari, S., N-Alkyl-N-Cyclopropylanilines as Mechanistic Probes in the Nitrosation of N,N-Dialkyl Aromatic Amines. *J. Org. Chem.* **2000,** *65*, 96-103.
3. Maity, S.; Zhu, M.; Shinabery, R. S.; Zheng, N., Intermolecular [3+2] Cycloaddition of Cyclopropylamines with Olefins by Visible-Light Photocatalysis. Angew. Chem. Int. Ed. Engl. **2012,** *51*, 222-226.