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Supporting Information

Trifluoromethylated thermally activated delayed fluorescence molecule as a versatile photocatalyst for electron-transfer- and energy-transfer-driven reactions

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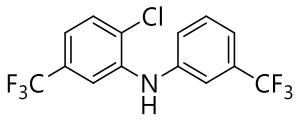
1. General

$Pd_2(dba)_3$•$CHCl_3$, ±BINAP, toluene, 3-amino-4-chlorobenzotrifluoride, NaO^{t}Bu, 3-bromobenzotrifluoride, ^{t}BuOMe, K_2CO_3, *N*,*N*-dimethylacetamide, $Pd(OAc)_2$, tri-*tert*-butylphosphonium tetrafluoroborate, THF, NaH, tetrafluoroisophthalonitrile, cyclohexanecarboxylic acid, diethyl 2-ethlylidenemalonate, K_2HPO_4, dimethylformamide, benzyl methacrylate, benzalmalononitrile, *trans*-4-octene, *cis*-cyclooctene, and cyclododecene were commercially available. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Cyclohexylsilicate **3**,[1] *N*-*tert*-butoxycarbonyl-*N*-methylaniline,[2] lepidinium triflate,[3] 4-isopropylquinolinium triflate,[3] 4-methoxyquinolinium triflate,[3] and 2-methylquinolinium triflate[3] were synthesized according to the literature. Flash chromatography was carried out on a silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40-100 μm). Preparative gel permeation chromatography (GPC) was carried out on Japan Analytical Industry LC-918 equipped with JAIGEL-1H and 2H using $CHCl_3$ as an eluent. Photoreactions were carried out in a Schlenk tube (30 mL) with photoirradiation using blue LED (Kessil, A 160WE TUNA Blue) and a cooling fan was used to avoid heating the reaction mixture. All NMR spectra were measured on Resonance ECZ 400S (JEOL, 400 MHz for ^{1}H, 100 MHz for ^{13}C) or AVANCE III HD Nano Bay (Bruker Co., 400 MHz for ^{1}H, 100 MHz for ^{13}C) at 22 °C using $CDCl_3$ as a solvent unless otherwise noted. Tetramethylsilane (TMS) ($\delta = 0$), $CHCl_3$ ($\delta = 7.26$), or acetone ($\delta = 2.05$) served as an internal standard for ^{1}H NMR spectra, and $CDCl_3$ ($\delta = 77.16$) was used as an internal standard for ^{13}C NMR spectra. Hexafluorobenzene ($\delta = -164.9$) was used as an external standard for ^{19}F NMR. All HRMS were measured on Micro-TOF (Bruker, TOF, ESI). Ultraviolet–visible (UV-vis) absorption and photoluminescence (PL) spectra of 4[$Cz(CF_3)_2$IPN] were recorded on a Perkin-Elmer Lambda 950 PKA spectrophotometer and JASCO FP-8600 Photoluminescence spectrometer, respectively.

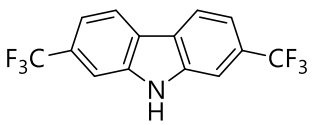
[1] G. Ikarashi, T. Morofuji, N. Kano, *Chem. Commun.*, 2020, **56**, 10006–10009.
[2] R. Bisht, M. E. Hoque, B. Chattopadhyay, *Angew. Chem. Int. Ed.,* 2018, **57**, 15762–15766.
[3] T. Morofuji, S. Nagai, Y. Chitose, M. Abe, N. Kano, *Org. Lett.*, 2021, **23**, 6257–6261.

2. Synthesis of 4[Cz(CF$_3$)$_2$IPN]

2-Chloro-5-(trifluoromethyl)-N-[3-(trifluoromethyl)phenyl]aniline (**S1**) was synthesized according to the literature.[4] A 100 mL flask equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the flask to 23 °C, it was purged with argon gas. $Pd_2(dba)_3$•$CHCl_3$ (0.23 g, 0.22 mmol), ±BINAP (0.42 g, 0.67 mmol), toluene (22 mL), 3-amino-4-chlorobenzotrifluoride (5.0 g, 22 mmol), NaO^{t}Bu (3.1 g, 32 mmol), and 3-bromobenzotrifluoride (5.2 g, 26 mmol) were added to the flask. The resulting mixture was stirred at 95 °C for 18 hours. After the reaction, the crude mixture was diluted with ^{t}BuOMe (100 mL) and was passed through a celite plug. The filtrate was dried under vacuum to produce a crude material. The crude material was purified by flash chromatography (hexane/EtOAc = 100/0 to 95/5) to obtain the desired product 2-chloro-5-(trifluoromethyl)-*N*-[3-(trifluoromethyl)phenyl]aniline (**S1**) as colorless oil (5.9 g, 79%)**.**

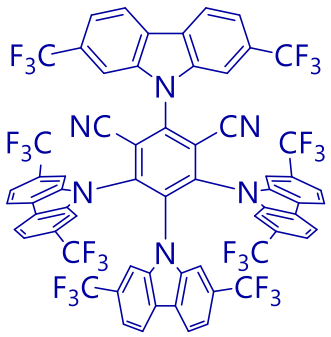
	**2-chloro-5-(trifluoromethyl)-*N*-[3-(trifluoromethyl)phenyl]aniline (S1)[4]** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (t, *J* = 7.8 Hz, 3H), 7.42-7.35 (m, 3H), 7.11 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 140.2, 132.5 (q, *J* = 32.3 Hz), 130.6, 130.45, 130.38 (q, *J* = 32.6 Hz), 125.2, 124.0 (q, *J* = 270.8 Hz), 123.8 (q, *J* = 270.8 Hz), 123.2, 120.2 (q, *J* = 3.8 Hz), 117.7 (q, *J* = 3.8 Hz), 117.2 (q, *J* = 4.9 Hz), 112.1 (q, *J* = 3.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.85 (s, 3F), –62.90 (s, 3F).

2,7-Bis(trifluoromethyl)-9*H*-carbazole (**S2**) was synthesized by modified procedure of the literature.[4] *N*,*N*-dimethylacetamide was used instead of toluene as solvent. A 40 mL pressure tube equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. K_2CO_3 (2.4 g, 18 mmol), *N*,*N*-dimethylacetamide (20 mL), $Pd(OAc)_2$ (66 mg, 0.30 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.17 g, 0.59 mmol), and 2-chloro-5-(trifluoromethyl)-*N*-[3-(trifluoromethyl)phenyl]aniline (1.8 g, 5.2 mmol) were added to the tube, which was then sealed with a Teflon cap. The tube was heated to 145 °C under magnetic stirring for 48 h. The reaction mixture was cooled to room temperature, and the tube was opened to air. The reaction was quenched by HCl aq. (2.0 M, 20 mL). The organic phase was extracted with EtOAc (30 mL × 3) and dried over Na_2SO_4. The resulting organic solution was dried under vacuum to produce a crude material. The crude material was purified by flash chromatography (hexane/EtOAc = 100/0 to 95/10) to obtain the desired product 2,7-bis(trifluoromethyl)-9*H*-carbazole (**S2**) as white solid (1.6 g, 100%)**.**

	**2,7-bis(trifluoromethyl)-9*H*-carbazole (S2)[4]** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 2H), 7.75 (s, 2H), 7.54 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 129.1 (q, *J* = 27.8 Hz), 125.0, 124.7 (q, *J* = 270.6 Hz), 121.5, 117.0 (q, *J* = 3.8 Hz), 108.5 (q, *J* = 4.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –61.14 (s, 6F).

[4] M. Gantenbein, M. Hellstern, L. Le Pleux, M. Neuburger, M. Mayor, *Chem. Mat.*, 2015, **27**, 1772-1779.

A 50 mL two-necked flask equipped with a magnetic stirring bar and two septum was dried under vacuum with heating. After cooling the flask to 23 °C, it was purged with argon gas. 2,7-bis(trifluoromethyl)-9*H*-carbazole (1.0 g, 3.3 mmol), THF (35 mL), and NaH (50% in oil, 2.0 g, 4.1 mmol) were added to the flask. The resulting mixture was stirred at 23 °C for 1 hour. Tetrafluoroisophthalonitrile (0.13 g, 0.65 mmol) was added to the flask. The resulting mixture was stirred at 23 °C for 18 hours. The reaction was quenched by water (200 mL). After precipitation, the precipitate was collected with filtration and washed with water (30 mL × 3) and Et_2O (30 mL × 3). The obtained solid was dried under vacuum to produce **4[Cz(CF$_3$)$_2$]IPN** as yellow solid (0.56 g, 77%).



4[Cz(CF$_3$)$_2$]IPN[5]

^{1}H NMR (400 MHz, acetone-d_6): δ 8.79 (d, J = 7.6 Hz, 2H), 8.32 (d, J = 8.0 Hz, 4H), 8.04 (s, 2H), 7.99-7.85 (m, 10H), 7.60 (d, J = 8.4 Hz, 4H), 7.32 (d, J = 8.0 Hz, 2H); ^{19}F NMR (376 MHz, acetone-d_6): δ –61.6 (s, 6F), –62.0 (s, 6F), –62.0 (s, 12F).

3. DPV analysis of 4[Cz(CF$_3$)$_2$IPN]

The reduction potential of **4[Cz(CF$_3$)$_2$IPN]** was determined by differential pulse voltammetry (DPV) analysis (Figure S1). Substrate concentration was 1 mM, and 50 mM solution of Bu_4NBF_4 in CH_2Cl_2 was used for solvent. A glassy carbon working electrode, a platinum counter electrode, an $Ag/AgNO_3$ reference electrode were used. The redox potential was measured with respect to the $[FeCp_2]/[FeCp_2]^+$ couple, which was converted to saturated calomel electrode (SCE) by adding 0.630 V.[6]

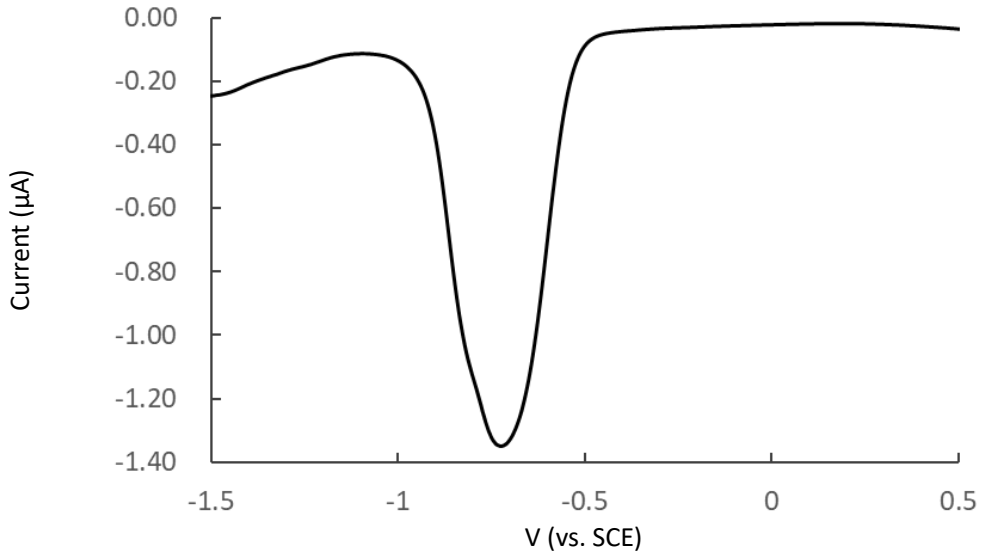


Figure S1. DPV analysis of **4[Cz(CF$_3$)$_2$IPN]**

[5] M. Yokoyama, K. Inada, Y. Tsuchiya, H. Nakanotani, C. Adachi, *Chem. Commun.*, 2018, **54**, 8261–8264.
[6] D. Bao, B. Millare, W. Xia, B. G. Steyer, A. A. Gerasimenko, A. Ferreira, A. Contreras, V. I. Vullev, *J. Phys. Chem. A*, 2009, **113**, 1259–1267.

4. Phosphorescence spectrum of 4[Cz(CF$_3$)$_2$IPN]

Ultraviolet–visible (UV-vis) absorption and photoluminescence (PL) spectra of 4[Cz(CF$_3$)$_2$IPN] were recorded on a Perkin-Elmer Lambda 950 PKA spectrophotometer and JASCO FP-8600 Photoluminescence spectrometer, respectively. For PL measurement, a solution of 4[Cz(CF$_3$)$_2$IPN] (8.8 μM) was irradiated at 390 nm. Phosphorescence spectrum was recorded at 77K after a 200 ms delay.

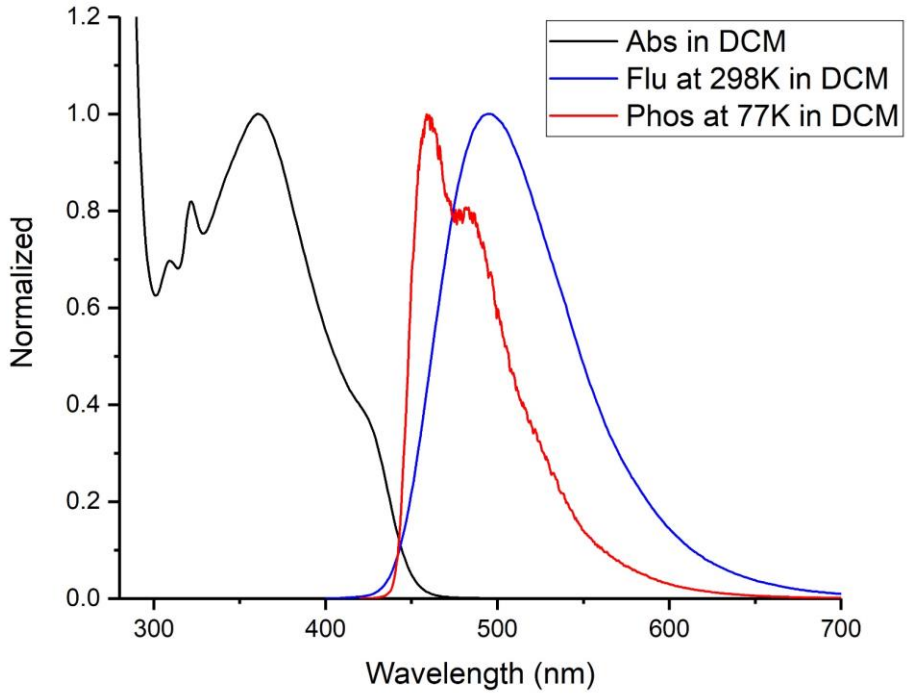
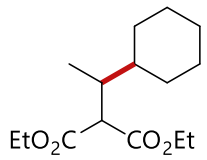


Figure S2. UV-vis absorption (298 K), fluorescence (298 K), and phosphorescence (77 K) spectra of 4[Cz(CF$_3$)$_2$IPN] in dichloromethane.

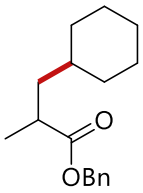
5. Procedure of the decarboxylative alkylation

A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. Cyclohexanecarboxylic acid (27 mg, 0.21 mmol), diethyl 2-ethylidenemalonate (37 mg, 0.20 mmol), **4[Cz(CF_3)$_2$IPN]** (11 mg, 0.010 mmol), K_2HPO_4 (42 mg, 0.24 mmol), and dimethylformamide (1 mL) were added to the tube. The reaction mixture was stirred under argon bubbling for 15 min. Photoirradiation using blue LED was carried out at 23 °C with stirring for 24 hours. After the photoirradiation, $NaHCO_3$ *aq. sat.* (10 mL) was added. The organic phase was extracted with Et_2O (30 mL × 3), washed with water (30 mL × 2), and dried over Na_2SO_4. The solvent was evaporated to give a crude material. The crude material was purified by flash chromatography (hexane/EtOAc = 100/0 to 70/30) to obtain diethyl 2-(1-cyclohexylethyl)malonate **(2)** as colorless oil (38 mg, 70%).

 **2**	**diethyl 2-(1-cyclohexylethyl)malonate (2)**[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.26-4.13 (m, 4H), 3.39 (d, *J* = 8.8 Hz, 1H), 2.22-2.13 (m, 1H), 1.78-1.71 (m, 2H), 1.68-1.57 (m, 3H), 1.30-1.04 (m, 11H), 0.98-0.88 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 169.2, 61.3, 61.2, 55.9, 40.4, 38.7, 31.6, 27.5, 26.8, 26.7, 26.6, 14.2, 13.0 (One peak is missing due to overlapping.).

6. Procedure of the Giese-type reaction using silicate 3

A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. Cyclohexylsilicate **3** (0.18 g, 0.24 mmol), benzyl methacrylate (35 mg, 0.20 mmol), **4[Cz(CF_3)$_2$IPN]** (11 mg, 0.010 mmol), and acetone/MeOH (1.5 mL/1.5 mL) were added to the tube, and the reaction mixture was stirred under argon bubbling for 15 min. Photoirradiation using blue LED was carried out at 23 °C with stirring for 24 hours. The solvents were evaporated to give a crude material, which was purified by flash chromatography (hexane/EtOAc = 50/50) and GPC to obtain benzyl 3-cyclohexyl-2-methylpropanoate **(4)** (44 mg, 84%) as colorless oil.

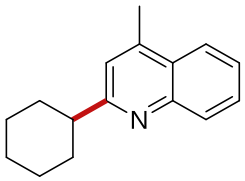
 **4**	**benzyl 3-cyclohexyl-2-methylpropanoate (4)**[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.28 (m, 5H), 5.14 (d, *J* = 12.4 Hz, 1H), 5.10 (d, *J* = 12.4 Hz, 1H), 2.67-2.55 (m, 1H), 1.78-1.57 (m, 6H), 1.29-1.08 (m, 8H), 0.91-0.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 136.4, 128.6, 128.2, 66.1, 41.7, 37.0, 35.5, 33.34, 33.31, 26.7, 26.3, 17.7 (Two peaks are missing due to overlapping.).

7. Procedure of the Minisci-type reaction using silicate 3

A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. Cyclohexylsilicate **3** (0.17 g, 0.24 mmol), lepidinium triflate (59 mg, 0.20 mmol), **4[Cz(CF_3)$_2$IPN]** (11 mg, 0.010 mmol), and dichloromethane (4 mL) were added to the tube. Photoirradiation using blue LED was carried out at 23 °C with stirring for 24 hours. The reaction was quenched

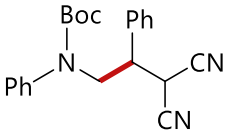
[7] L. Chu, C. Ohta, Z. Zuo, D. W. C. Macmillan, *J. Am. Chem. Soc.*, 2014, **136**, 10886-10889.
[8] T. Morofuji, Y. Matsui, M. Ohno, G. Ikarashi, N. Kano, *Chem. Eur. J.*, 2021, **27**, 6713-6718.

by Et_3N (31 mg, 0.30 mmol). The solvents were evaporated to give a crude material, which was purified by flash chromatography (hexane/EtOAc = 100/0 to 70/30) and GPC to obtain 2-cyclohexyl-4-methylquinoline **(5)** (34 mg, 75%) as colorless oil.

 **5**	**2-cyclohexyl-4-methylquinoline (5)**[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.67 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.49 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.17 (s, 1H), 2.88 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.69 (s, 3H), 2.04-1.97 (m, 2H), 1.93-1.86 (m, 2H), 1.84-1.75 (m, 1H), 1.68-1.55 (m, 2H), 1.54-1.40 (m, 2H), 1.40-1.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 147.6, 144.5, 129.5, 129.1, 127.2, 125.5, 123.7, 120.4, 47.7, 33.0, 26.7, 26.3, 19.0.

8. Procedure of the generation and alkylation of α-carbamyl radical

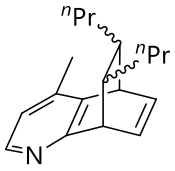
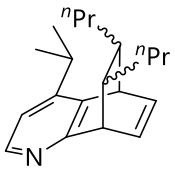
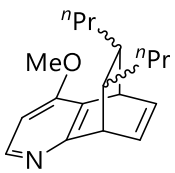
A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. *N*-*tert*-Butoxycarbonyl-*N*-methylaniline **6** (63 mg, 0.30 mmol), benzalmalononitrile (15 mg, 0.10 mmol), **4[Cz(CF$_3$)$_2$IPN]** (6 mg, 0.010 mmol), and CH_2Cl_2 (1 mL) were added to the tube, and the reaction mixture was stirred under argon bubbling for 15 min. Photoirradiation using blue LED was carried out at 23 °C with stirring for 6 hours. The solvent was evaporated to give a crude material. The crude material was purified by flash chromatography (hexane/EtOAc = 100/0 to 80/20) to obtain *N*-*tert*-butoxycarbonyl-*N*-(3,3-dicyano-2-phenylpropyl)aniline (**7**) (32 mg, 88%) as a colorless oil.

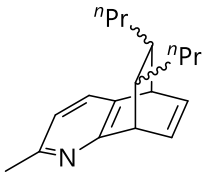
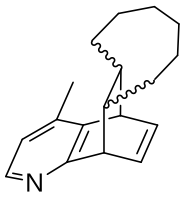
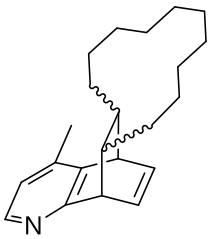
 **7**	***N*-*tert*-butoxycarbonyl-*N*-(3,3-dicyano-2-phenylpropyl)aniline (7)**[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.36 (m, 3H), 7.35-7.20 (m, 5H), 7.02 (d, *J* = 7.6 Hz), 4.41 (dd, *J* = 14.2 Hz, 8.2 Hz, 1H), 4.15 (d, *J* = 5.6 Hz, 1H), 4.08 (dd, *J* = 14.8 Hz, 6.8 Hz, 1H), 3.52 (q, *J* = 6.9 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 141.4, 134.8, 129.4, 129.33, 129.26, 128.4, 127.0, 112.0, 111.5, 81.7, 51.6, 45.4, 28.3, 27.6 (One peak is missing due to overlapping).

9. Procedure of the dearomative photocycloaddition

A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. Qunolinium triflate **8** (0.20 mmol), alkene (0.50 mmol), **4[Cz(CF$_3$)$_2$IPN]** (0.01 mmol), and CH_2Cl_2 (4 mL) were added to the tube, and the reaction mixture was stirred under argon bubbling for 15 min. Photoirradiation using blue LED was carried out at 23 °C with stirring for 24 hours. After the photoirradiation, Et_3N (0.3 mmol) was added. The solvent was evaporated to give a crude material. The crude material was purified by flash chromatography (hexane/EtOAc = 80/20 to 60/40) to obtain the desired product **9** as a mixture of two diastereomers. Diastereomer ratios were determined by ^{1}H NMR analysis.

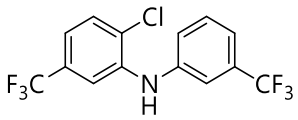
[9] J. B. McManus, N. P. R. Onuska, D. A. Nicewicz, *J. Am. Chem. Soc.*, 2018, **140**, 9056-9060.

 **9a**	**compound 9a**[3] Reaction of lepidinium triflate (**8a**) (59 mg, 0.20 mmol) and *trans*-4-octene (57 mg, 0.50 mmol) gave compound **9a** as a mixture of two diastereomers (47 mg, 92%, dr = 1.5/1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of two diastereomers): δ 8.07 (d, *J* = 5.6 Hz, 1H), 6.82 (d, *J* = 5.2 Hz, 1H), 6.62 (dt, *J* = 6.9, 1.4 Hz, 1H, minor), 6.54 (dt, *J* = 7.0, 1.6 Hz, 1H, major), 6.42 (t, *J* = 6.6 Hz, 1H, major), 6.33 (t, *J* = 6.8 Hz, 1H, minor), 3.98 (d, *J* = 6.0 Hz, 1H, minor), 3.95 (d, *J* = 6.4 Hz, 1H, major), 3.91 (d, *J* = 6.4 Hz, 1H, major), 3.84 (d, *J* = 6.4 Hz, 1H, minor), 2.32 (s, 3H, minor), 2.30 (s, 3H, major), 1.53-1.12 (m, 8H), 1.05-0.72 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of two diastereomers): δ 164.5, 162.4, 144.0, 143.7, 141.7, 139.2, 136.8, 135.8, 135.5, 134.4, 132.6, 132.3, 122.2, 122.0, 47.4, 47.2, 46.3, 45.9, 45.6, 45.3, 40.3, 39.6, 38.9, 38.7, 38.2, 37.9, 21.4, 21.3, 21.13, 21.05, 17.9, 17.8, 14.43, 14.40, 14.34, 14.30.
 **9b**	**compound 9b**[3] Reaction of 4-isopropylquinolinium triflate (64 mg, 0.20 mmol) and *trans*-4-octene (56 mg, 0.50 mmol) gave compound **9b** as a mixture of two diastereomers (52 mg, 91%, dr = 2.9/1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of two diastereomers): δ 8.18-8.12 (m, 1H), 6.98 (d, *J* = 5.6 Hz, 1H), 6.63 (dt, *J* = 6.2, 1.2 Hz, 1H, minor), 6.56 (dt, *J* = 7.0, 1.2 Hz, 1H, major), 6.43 (t, *J* = 6.6 Hz, 1H, major), 6.35 (t, *J* = 6.6 Hz, 1H, minor), 4.10-3.97 (m, 2H), 3.22 (sept, *J* = 6.9 Hz, 1H), 1.55-1.14 (m, 13H. A peak of water is overlappling.), 1.04-0.72 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of two diastereomers): δ 164.2, 161.9, 153.0, 150.4, 143.3, 143.0, 136.4, 135.9, 135.8, 133.4, 132.7, 132.4, 117.3, 117.2, 46.8, 46.7, 45.6, 45.38, 45.36, 39.7, 39.1, 38.9, 38.6, 38.2, 38.0, 29.0, 28.6, 24.0, 22.8, 22.4, 22.3, 21.4, 21.3, 21.1, 21.0, 14.40, 14.36, 14.30, 14.26 (One peak is missing due to overlapping.).
 **9c**	**compound 9c**[3] Reaction of 4-methoxyquinolinium triflate (62 mg, 0.20 mmol) and *trans*-4-octene (57 mg, 0.50 mmol) gave compound **9c** as a mixture of two diastereomers (49 mg, 90%, dr = 1.9/1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of two diastereomers): δ 8.12 (d, *J* = 6.0 Hz, 1H), 6.62-6.56 (m, 1H + 1H (major)), 6.52 (dt, *J* = 6.8, 1.2 Hz, 1H, minor), 6.40 (t, *J* = 6.8 Hz, 1H, minor), 6.33 (t, *J* = 6.6 Hz, 1H, major), 4.19-4.12 (m, 1H), 3.92-3.80 (m, 4H), 1.52-1.18 (m, 7H), 1.17-0.66 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of two diastereomers): δ 166.9, 165.0, 160.9, 158.5, 146.9, 146.6, 135.8, 135.6, 132.7, 125.5, 123.1, 104.0, 103.8, 55.3, 55.2, 47.6, 47.5, 46.5, 46.1, 45.7, 45.6, 39.2, 38.8, 38.4, 38.0, 37.1, 36.5, 21.4, 21.2, 21.1, 21.0, 14.5, 14.41, 14.36 (Two peaks are missing due to

	overlapping).
 **9d**	**compound 9d[3]** Reaction of 2-methylquinolinium triflate (59 mg, 0.20 mmol) and *trans*-4-octene (57 mg, 0.50 mmol) gave compound **9d** as a mixture of two diastereomers (45 mg, 88%, dr = 1.3/1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of two diastereomers): δ 7.26-7.20 (m, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.62-6.53 (m, 1H), 6.40 (t, *J* = 6.8 Hz, 1H, major), 6.35 (t, *J* = 6.6 Hz, 1H, minor), 3.88 (d, *J* = 6.0 Hz, 1H, major), 3.80 (d, *J* = 6.0 Hz, 1H, minor), 3.71 (d, *J* = 6.0 Hz, 1H, minor), 3.64 (d, *J* = 6.0 Hz, 1H, major), 2.50 (s, 3H, major), 2.49 (s, 3H, minor), 1.51-1.05 (m, 8H), 1.00-0.70 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of two diastereomers): δ 164.7, 162.8, 153.3, 153.0, 135.9, 135.5, 133.0, 132.5, 132.0, 129.8, 119.6, 119.3, 47.6, 47.3, 47.0, 46.0, 45.5, 45.4, 43.7, 43.4, 39.1, 38.8, 38.3, 38.0, 24.0, 21.3, 21.2, 21.1, 21.0, 14.5, 14.43, 14.35, 14.33 (Three peaks are missing due to overlapping.).
 **9e**	**compound 9e** Reaction of lepidinium triflate (**8a**) (59 mg, 0.20 mmol) and *cis*-cyclooctene (56 mg, 0.50 mmol) gave compound **9e** as a mixture of two diastereomers (48 mg, 94%, dr = 1.3/1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of two diastereomers): δ 8.06 (d, *J* = 5.2 Hz, 1H), 6.84 (s, 1H), 6.64 (t, *J* = 6.8 Hz, 1H, minor), 6.55 (t, *J* = 6.8 Hz, 1H, major), 6.39 (t, *J* = 6.6 Hz, 1H, major), 6.31 (t, *J* = 6.6 Hz, 1H, minor), 3.88-3.78 (m, 1H + 1H (major)), 3.75 (d, *J* = 6.0 Hz, 1H, minor), 2.34 (s, 3H, minor), 2.30 (s, 3H, major), 1.84-1.25 (m, 12H), 1.22-1.08 (m, 1H), 0.52-0.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of two diastereomers): δ 164.1, 161.5, 143.2, 143.0, 142.5, 139.5, 137.6, 136.2, 135.9, 134.4, 131.94, 131.87, 122.4, 122.1, 50.2, 50.0, 43.7, 43.5, 43.1, 43.0, 42.5, 37.0, 36.3, 35.9, 35.7, 27.2, 27.07, 27.05, 26.95, 24.0, 23.9, 23.8, 23.7, 18.0 (Two peaks are missing due to overlappling.) ; HRMS (ESI, positive) *m/z* calcd for $C_{18}H_{24}N$ $[M+H]^+$: 254.1903, found: 254.1904.
 **9f**	**compound 9f[3]** Reaction of lepidinium triflate (**8a**) (59 mg, 0.20 mmol) and cyclododecene (83 mg, 0.50 mmol) gave compound **9f** as a mixture of two diastereomers (60 mg, 97%, dr = 3.3/1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of two diastereomers): δ 8.06 (d, *J* = 5.2 Hz, 1H), 6.88-6.79 (m, 1H), 6.62 (t, *J* = 6.4 Hz, 1H, minor), 6.54 (t, *J* = 6.8 Hz, 1H, major), 6.43 (t, *J* = 6.6 Hz, 1H, major), 6.35 (t, *J* = 6.6 Hz, 1H, minor), 3.89 (d, *J* = 5.6 Hz, 1H), 3.83 (d, *J* = 6.0 Hz, 1H, major), 3.77 (d, *J* = 6.0 Hz, 1H, minor), 2.33 (s, 3H, minor), 2.30 (s, 3H, major), 1.58-1.08 (m, 21H), 0.93-0.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$,

	mixture of two diastereomers): δ 164.8, 162.9, 144.5, 144.2, 141.3, 138.7, 136.9, 136.0, 135.5, 134.5, 133.2, 132.9, 122.2, 121.9, 49.3, 49.2, 45.0, 44.5, 44.3, 43.7, 41.8, 41.4, 35.2, 34.7, 34.2, 34.0, 26.0, 25.9, 25.8, 25.7, 25.6, 25.4, 24.9, 24.7, 17.94, 17.88.

9. NMR spectra



S1

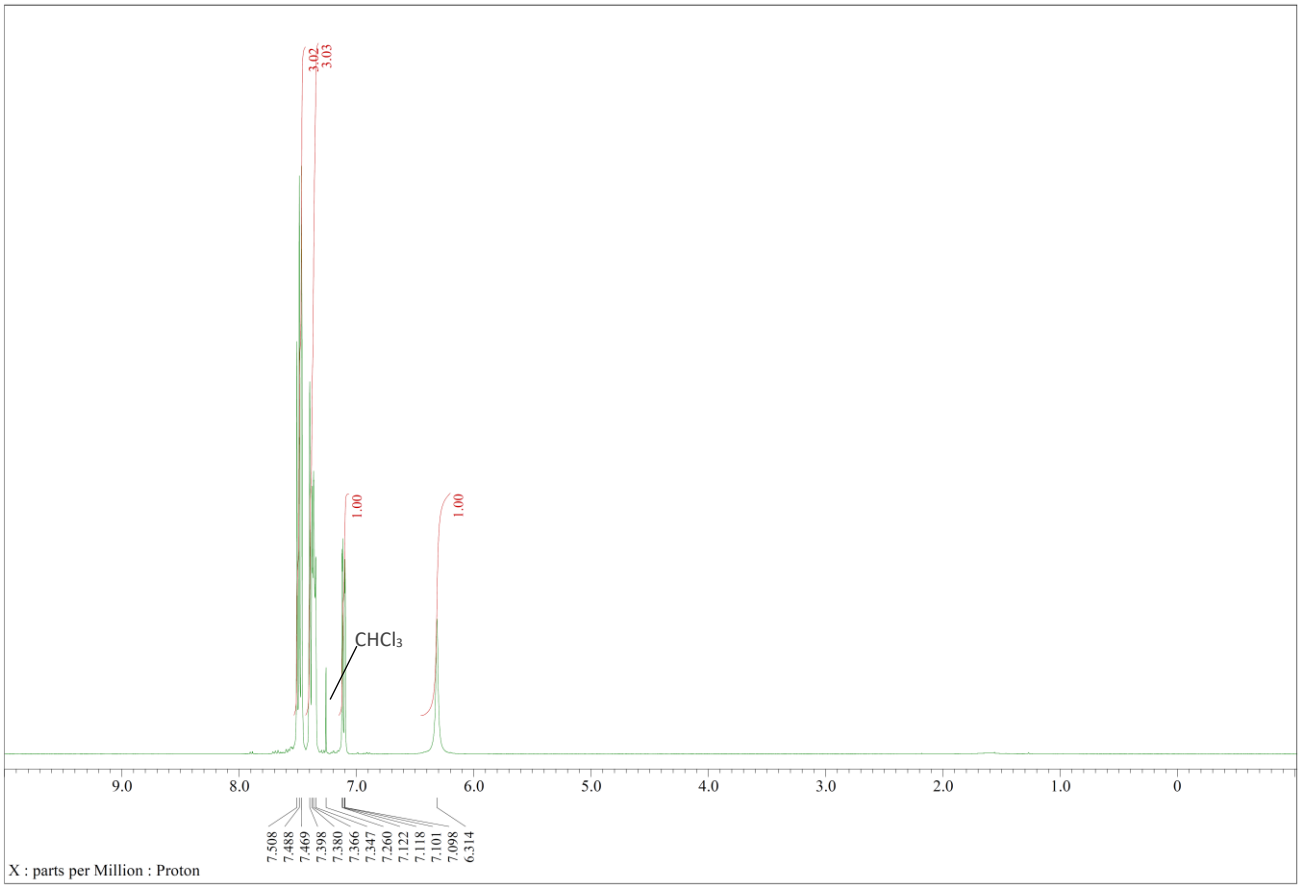
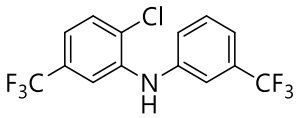


Figure S3. ^{1}H NMR (400 MHz) spectrum of **S1** in $CDCl_3$.



S1

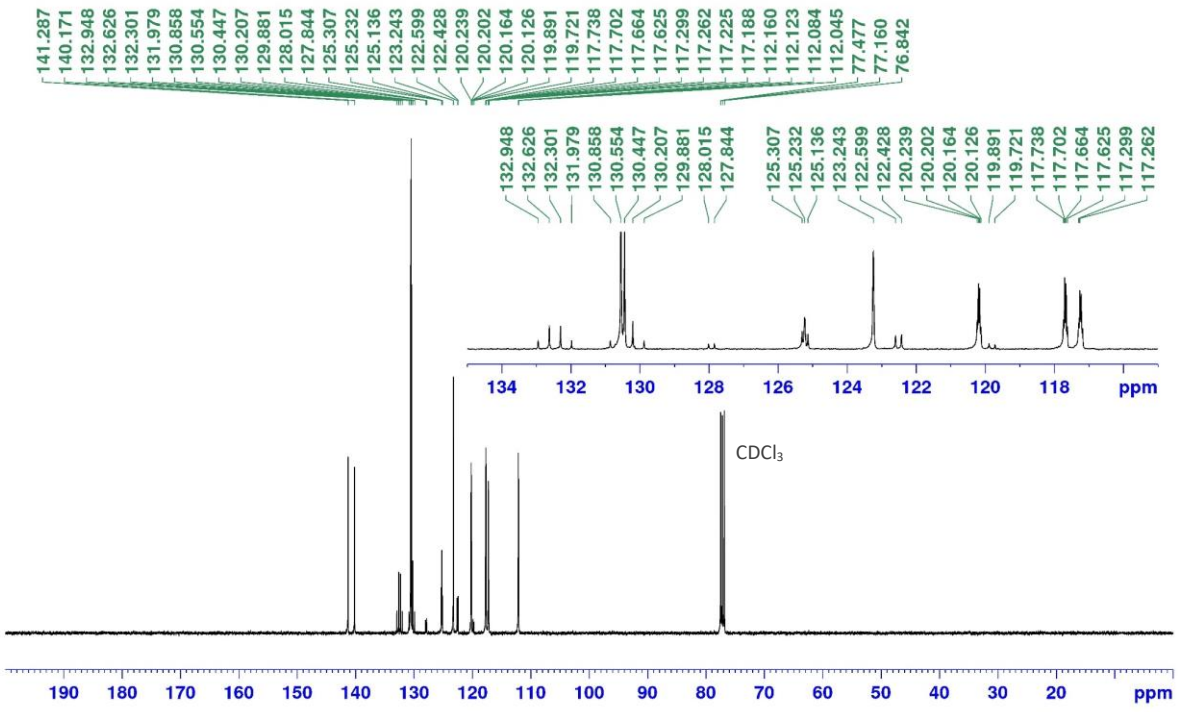
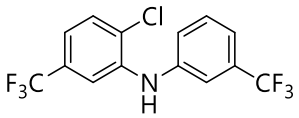


Figure S4. ^{13}C NMR (100 MHz) spectrum of **S1** in $CDCl_3$.



S1

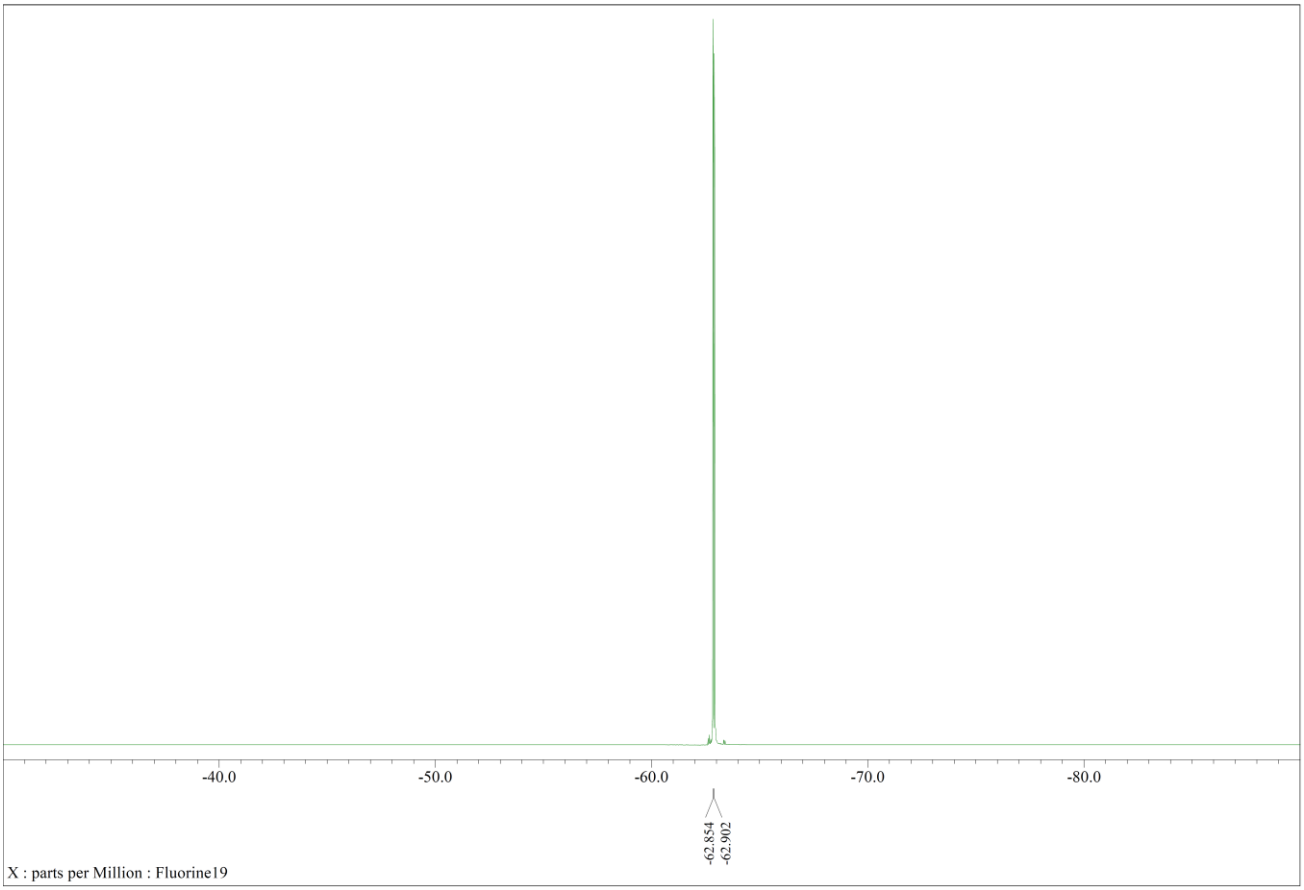
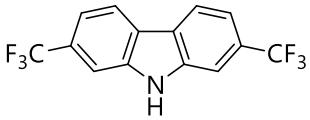


Figure S5. ^{19}F NMR (376 MHz) spectrum of **S1** in $CDCl_3$.



S2

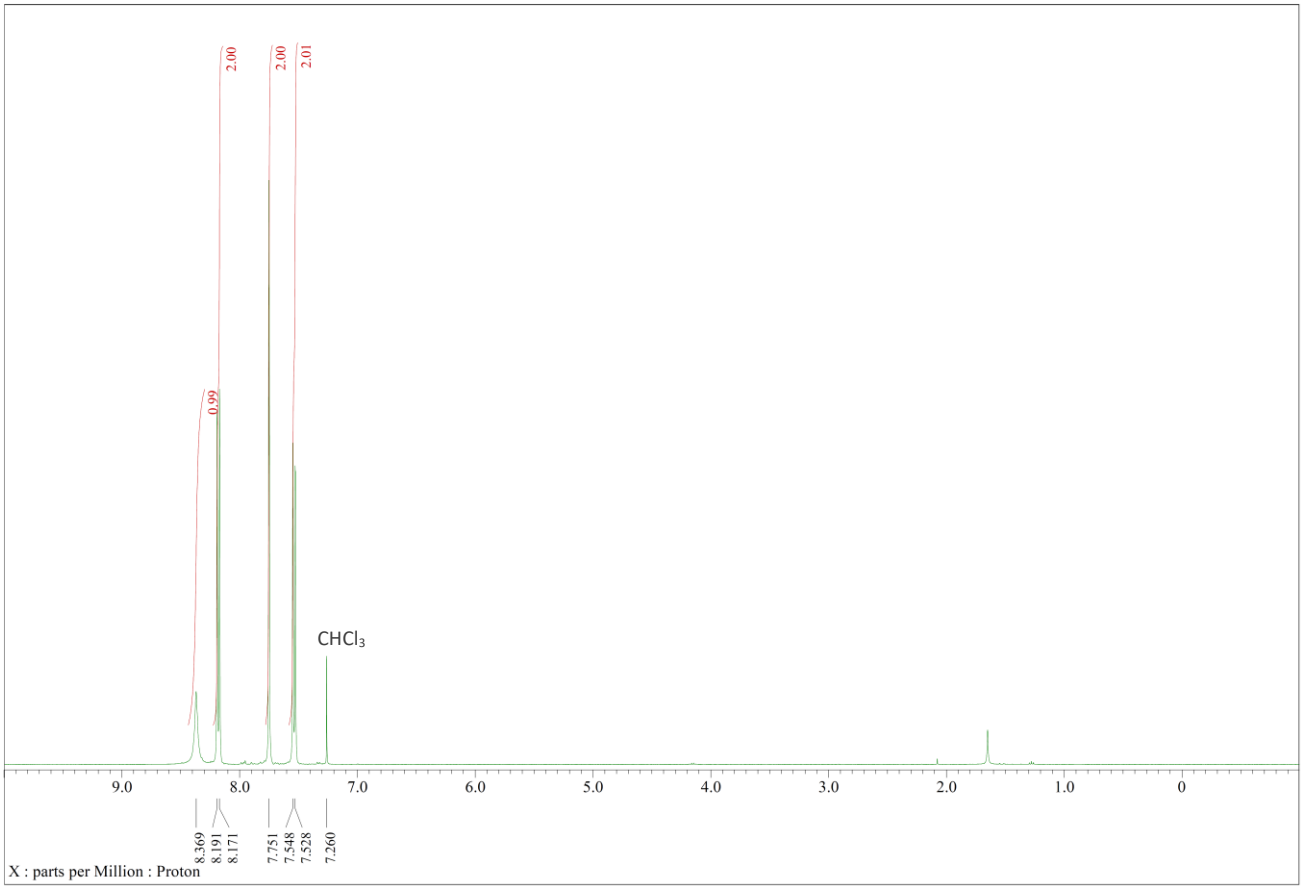
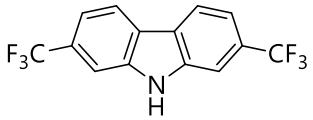


Figure S6. ^{1}H NMR (400 MHz) spectrum of **S2** in $CDCl_3$.



S2

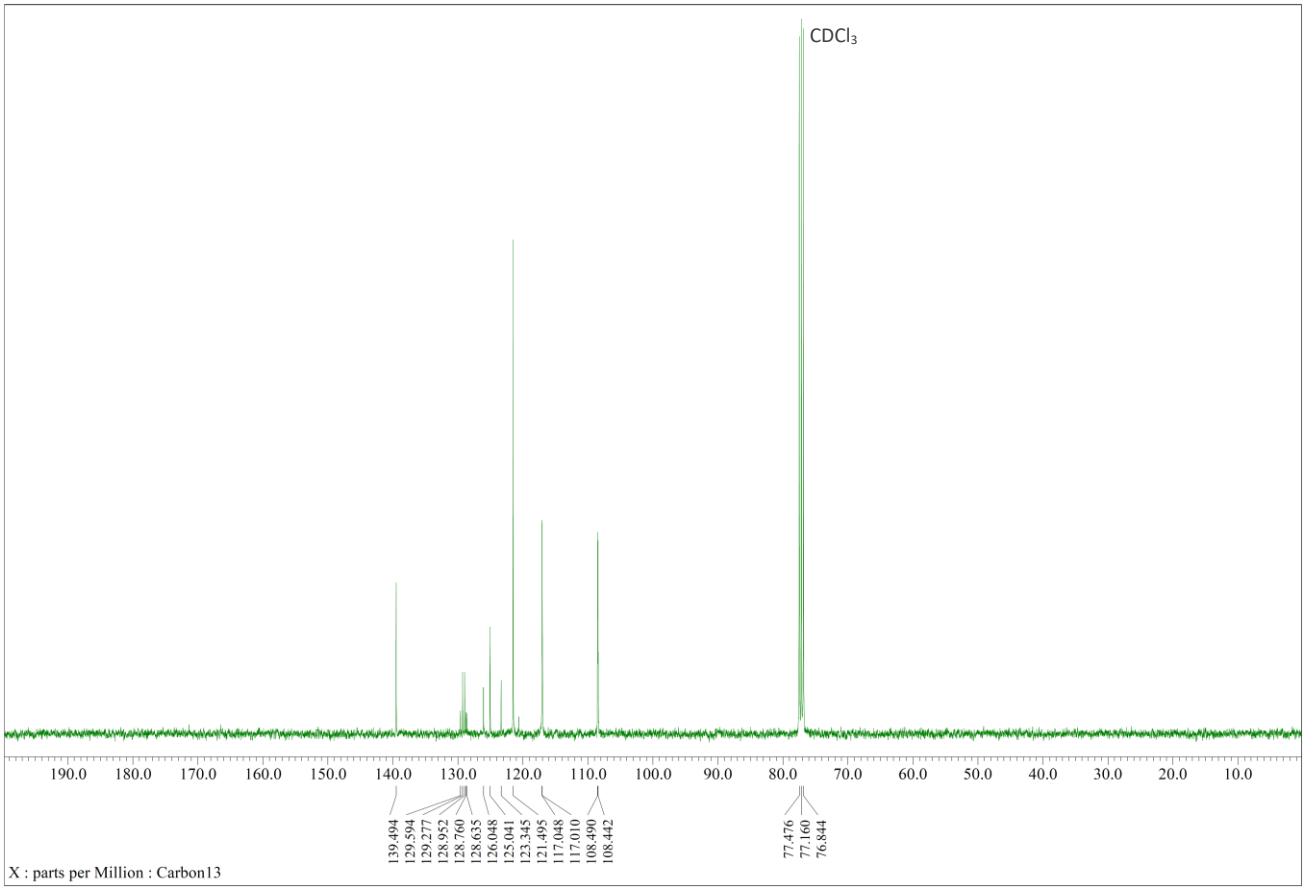
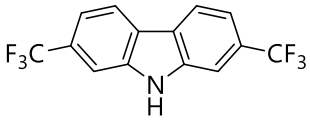


Figure S7. ^{13}C NMR (100 MHz) spectrum of **S2** in $CDCl_3$.



S2

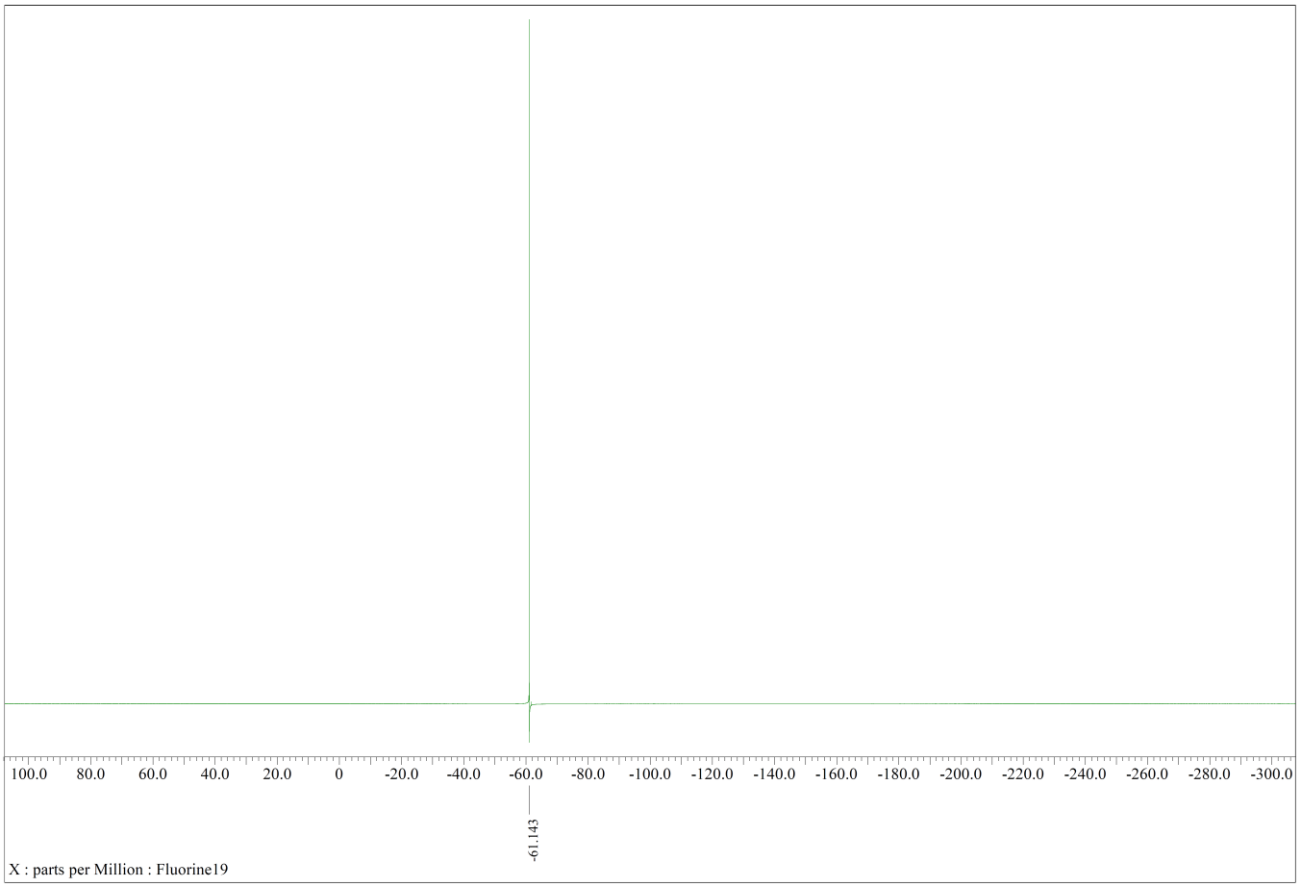
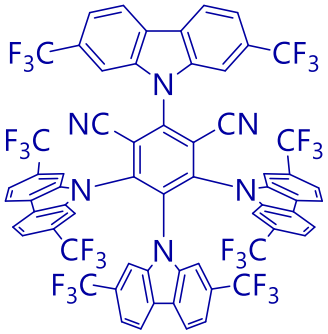


Figure S8. ^{19}F NMR (376 MHz) spectrum of **S2** in $CDCl_3$.



4[Cz(CF$_3$)$_2$]IPN

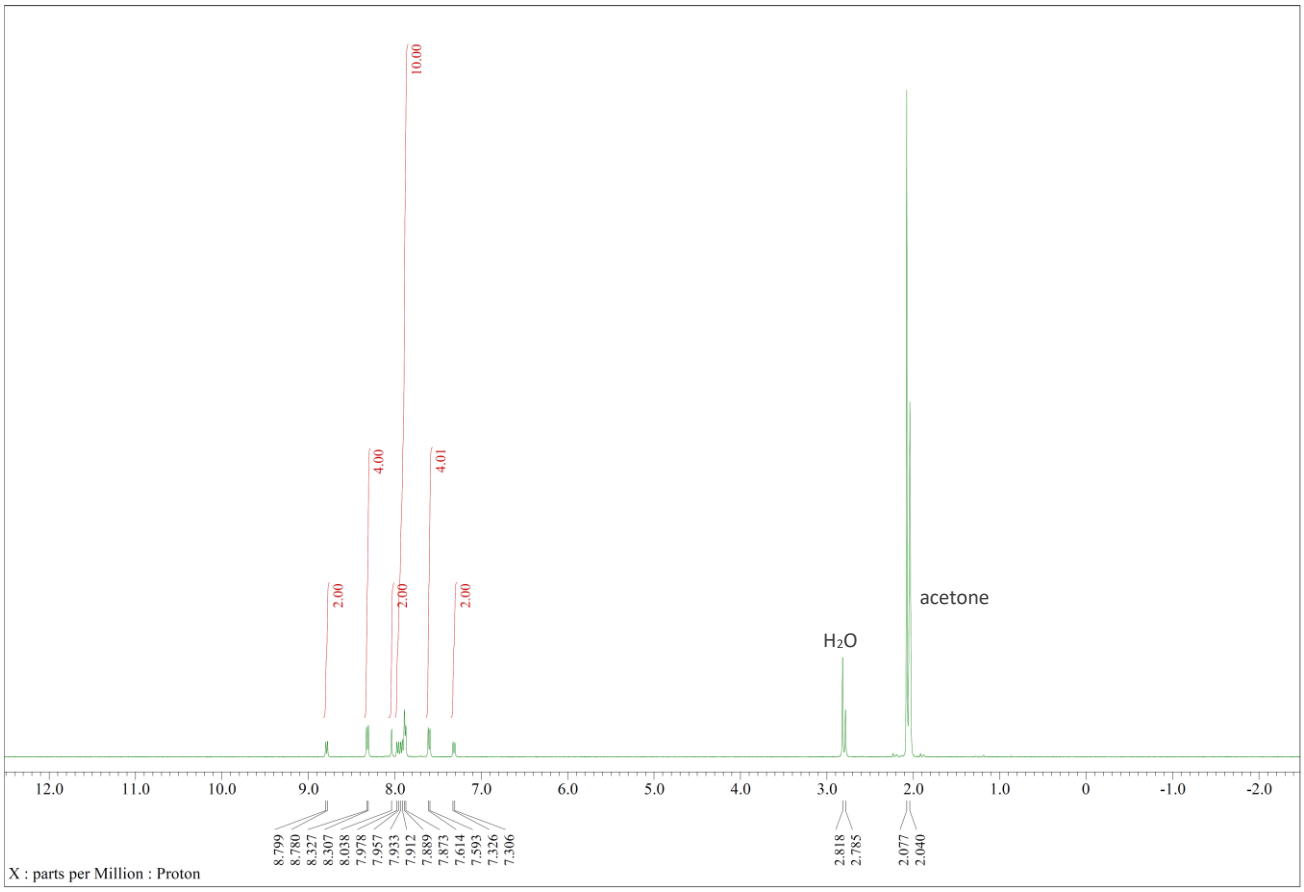
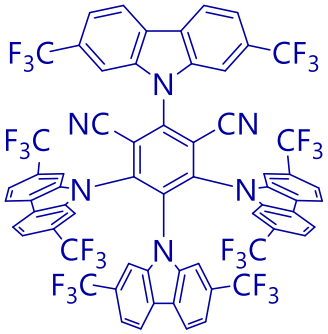


Figure S9. ^{1}H NMR (400 MHz) spectrum of **4[Cz(CF$_3$)$_2$]IPN** in acetone-d_6.



4[Cz(CF$_3$)$_2$]IPN

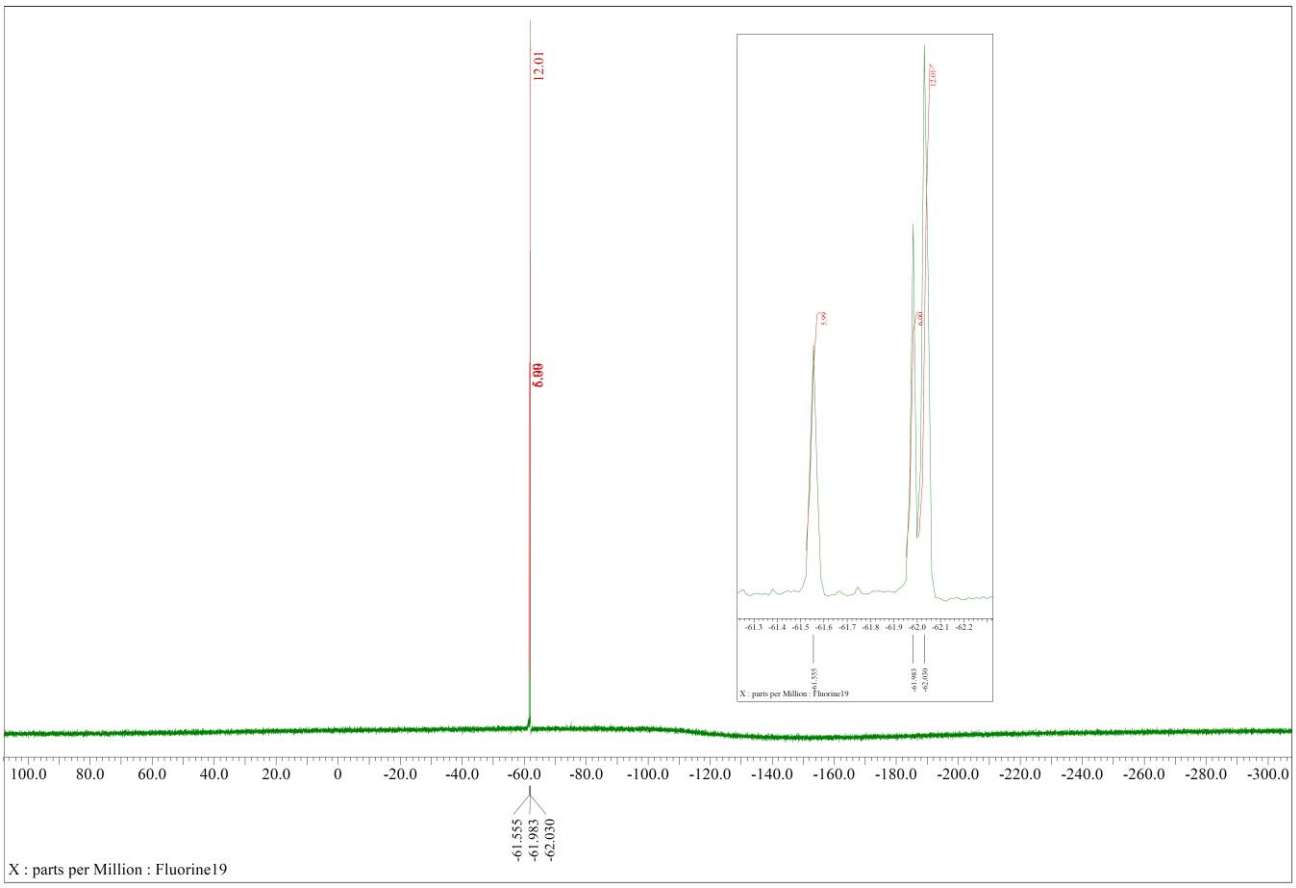
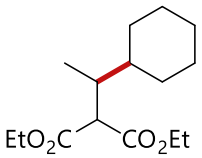


Figure S10. ^{19}F NMR (376 MHz) spectrum of **4[Cz(CF$_3$)$_2$]IPN** in acetone-d_6.



2

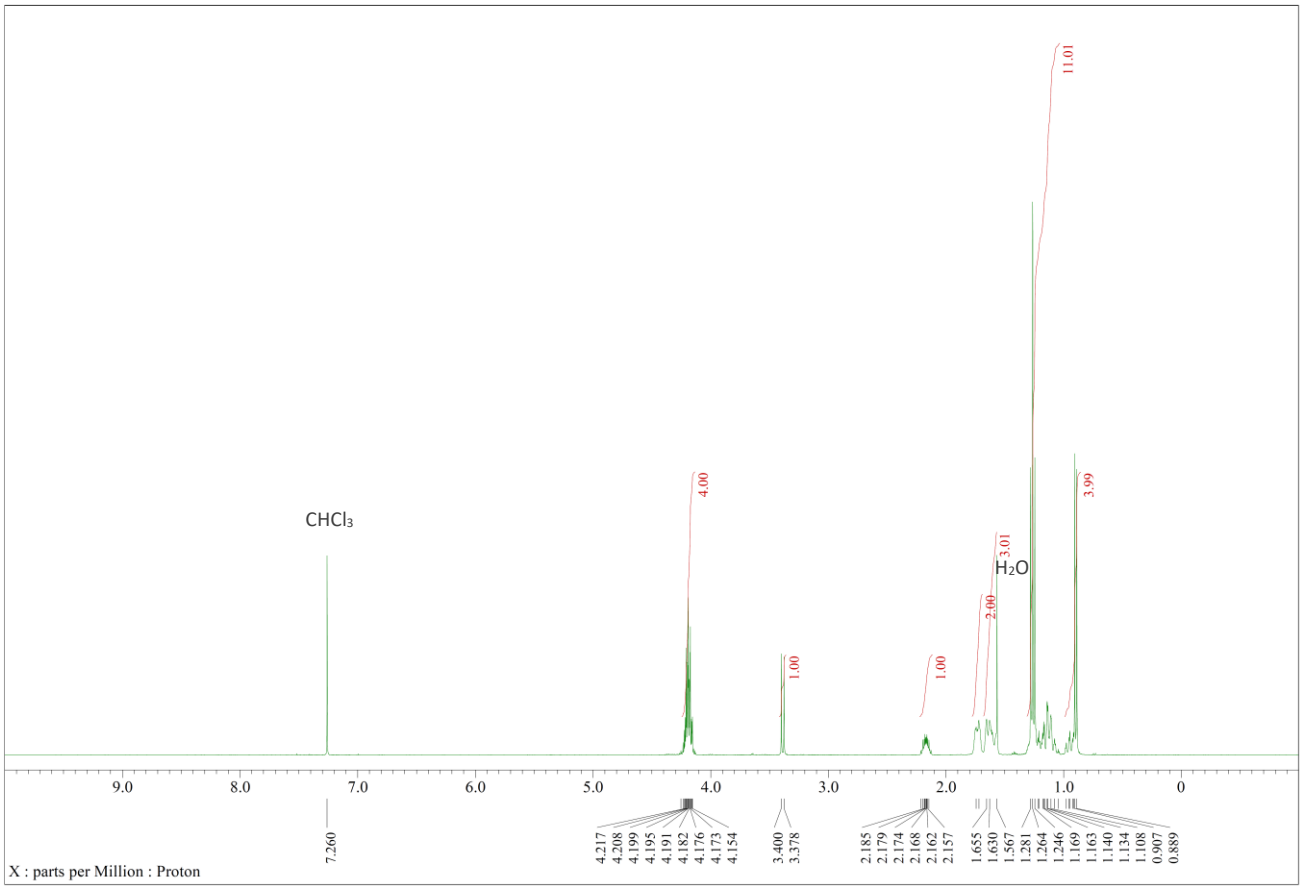
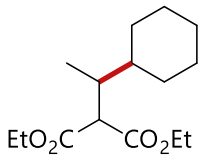


Figure S11. ^{1}H NMR (400 MHz) spectrum of **2** in $CDCl_3$.



2

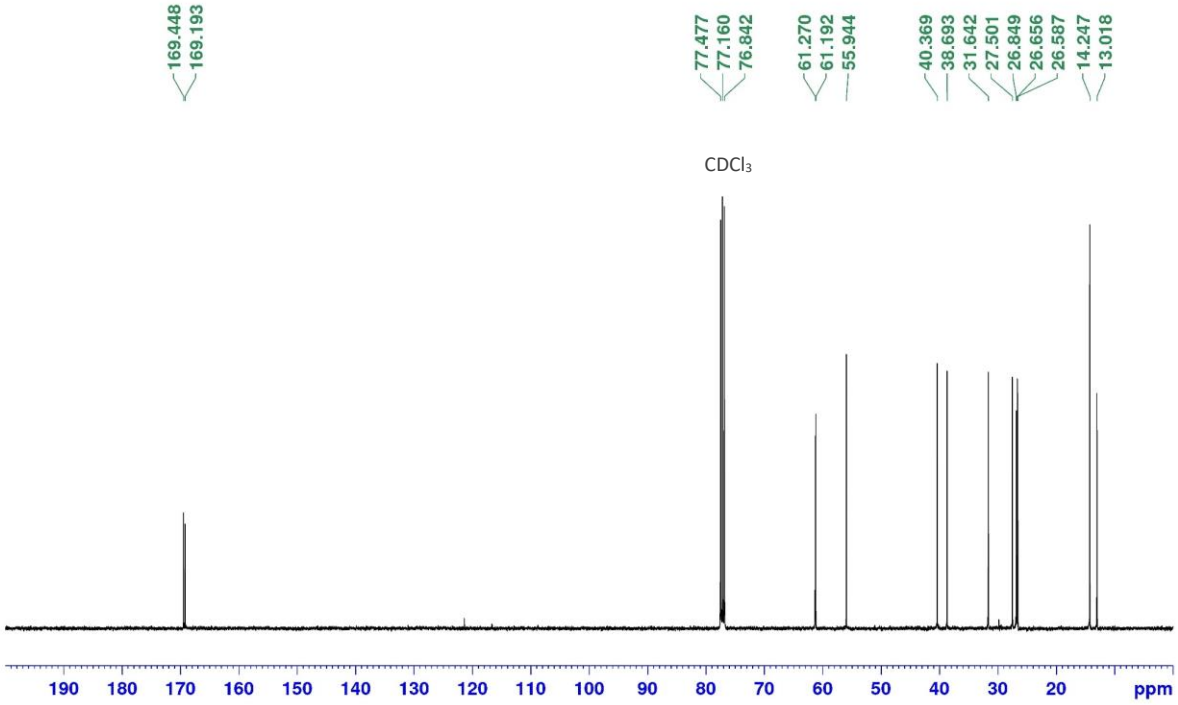
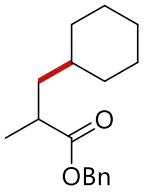


Figure S12. ^{13}C NMR (100 MHz) spectrum of **2** in $CDCl_3$.



4

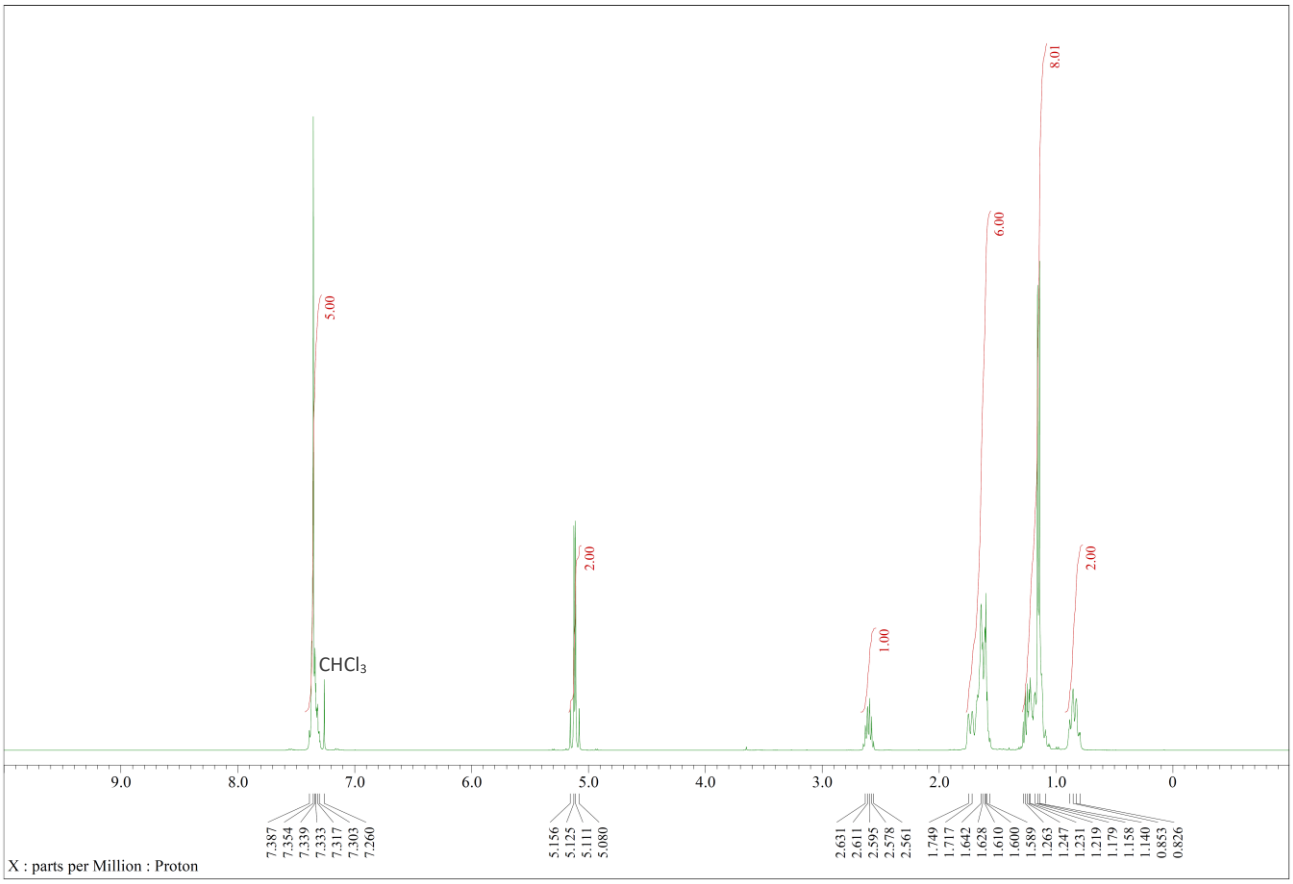


Figure S13. ^{1}H NMR (400 MHz) spectrum of **4** in $CDCl_3$.

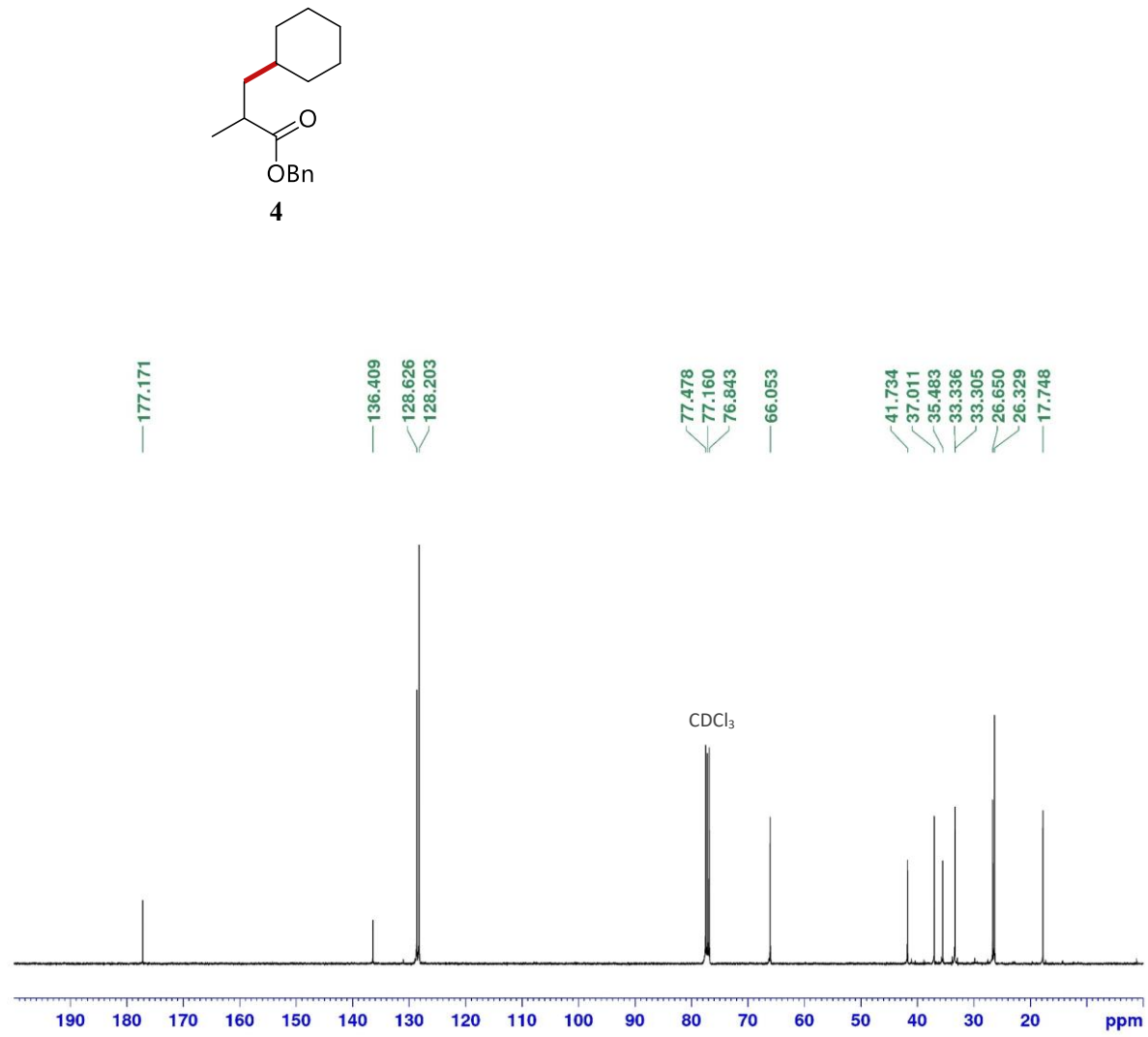
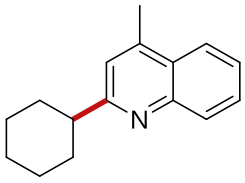


Figure S14. ^{13}C NMR (100 MHz) spectrum of **4** in $CDCl_3$.



5

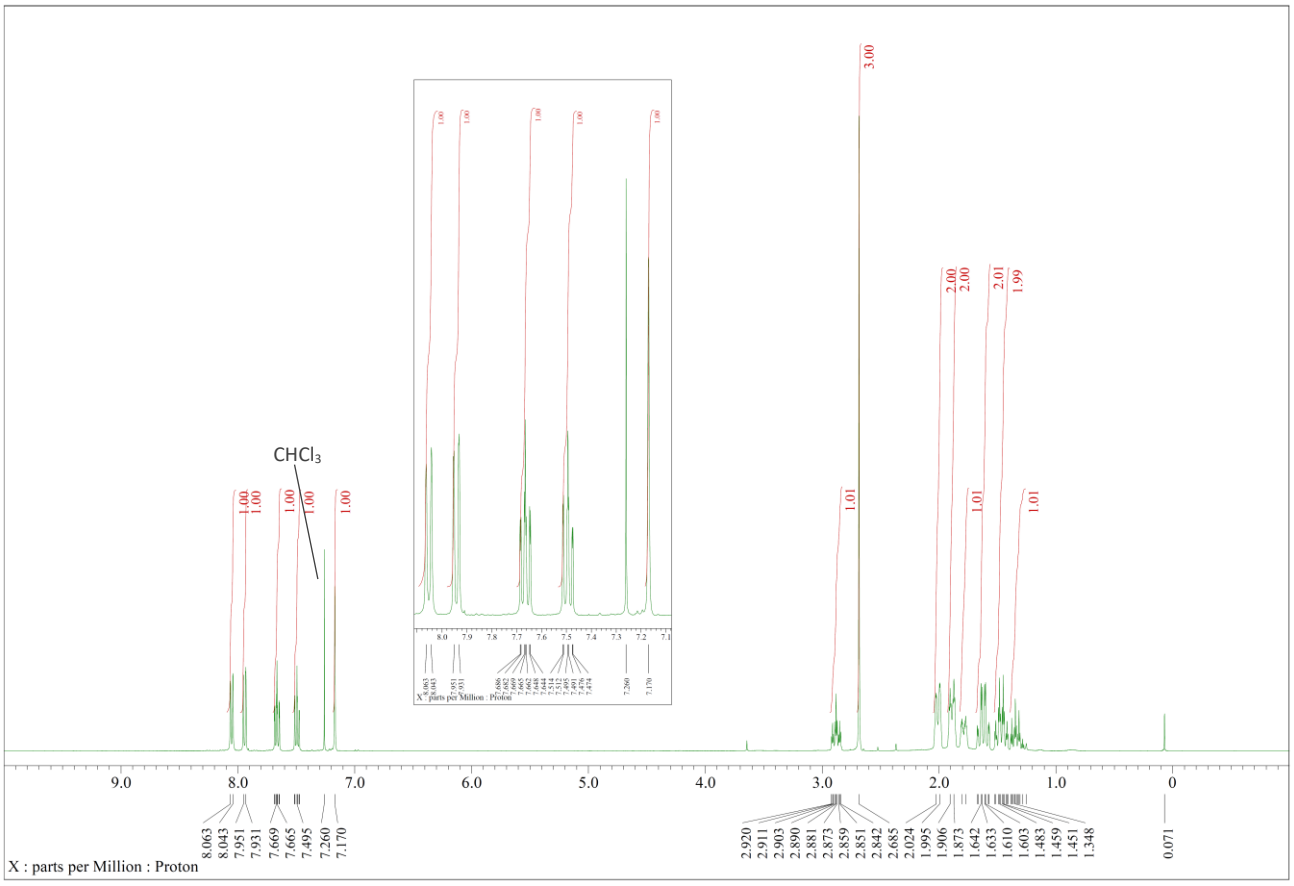
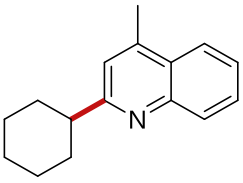


Figure S15. ^{1}H NMR (400 MHz) spectrum of **5** in $CDCl_3$.



5

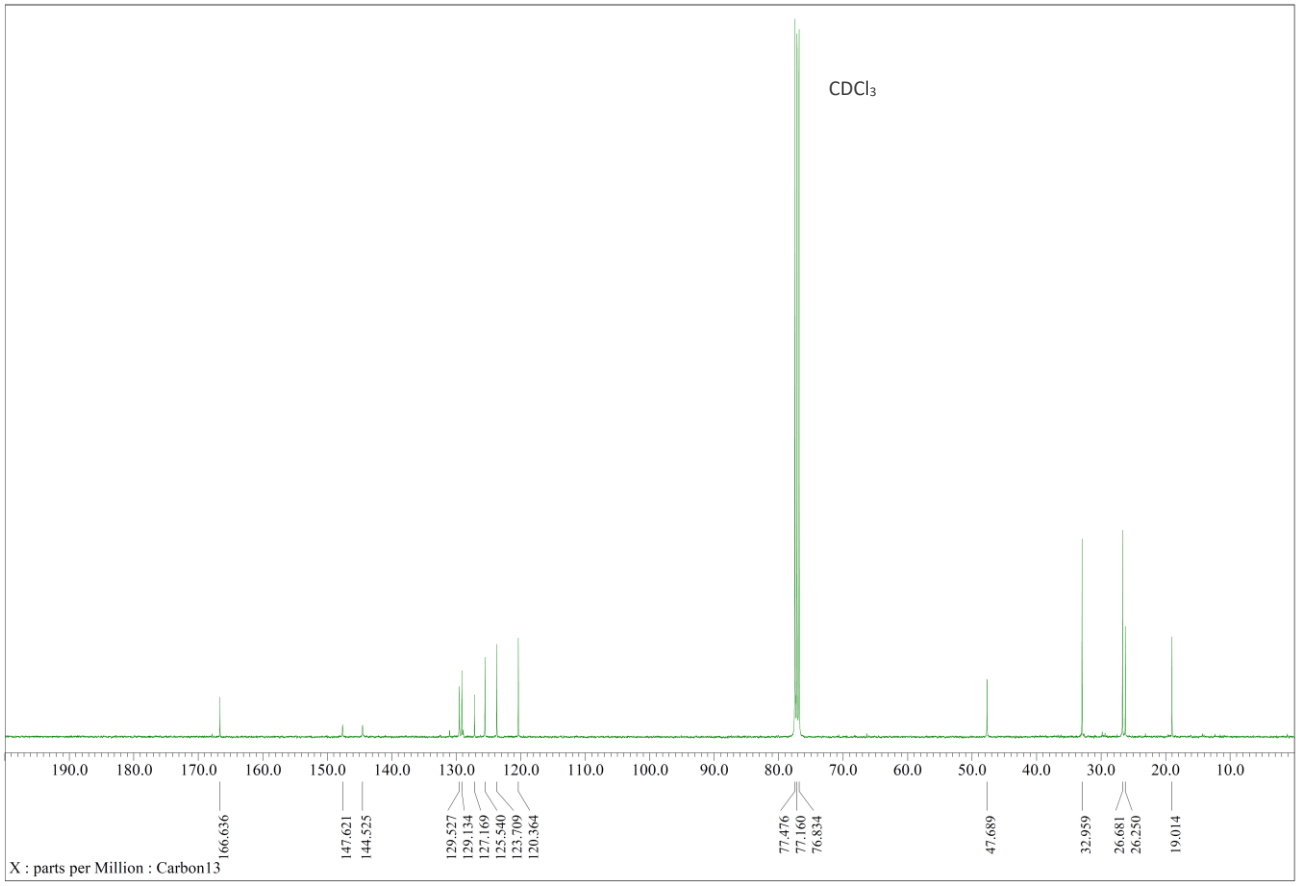
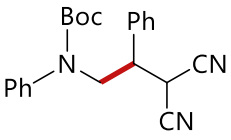


Figure S16. ^{13}C NMR (100 MHz) spectrum of **5** in $CDCl_3$.



7

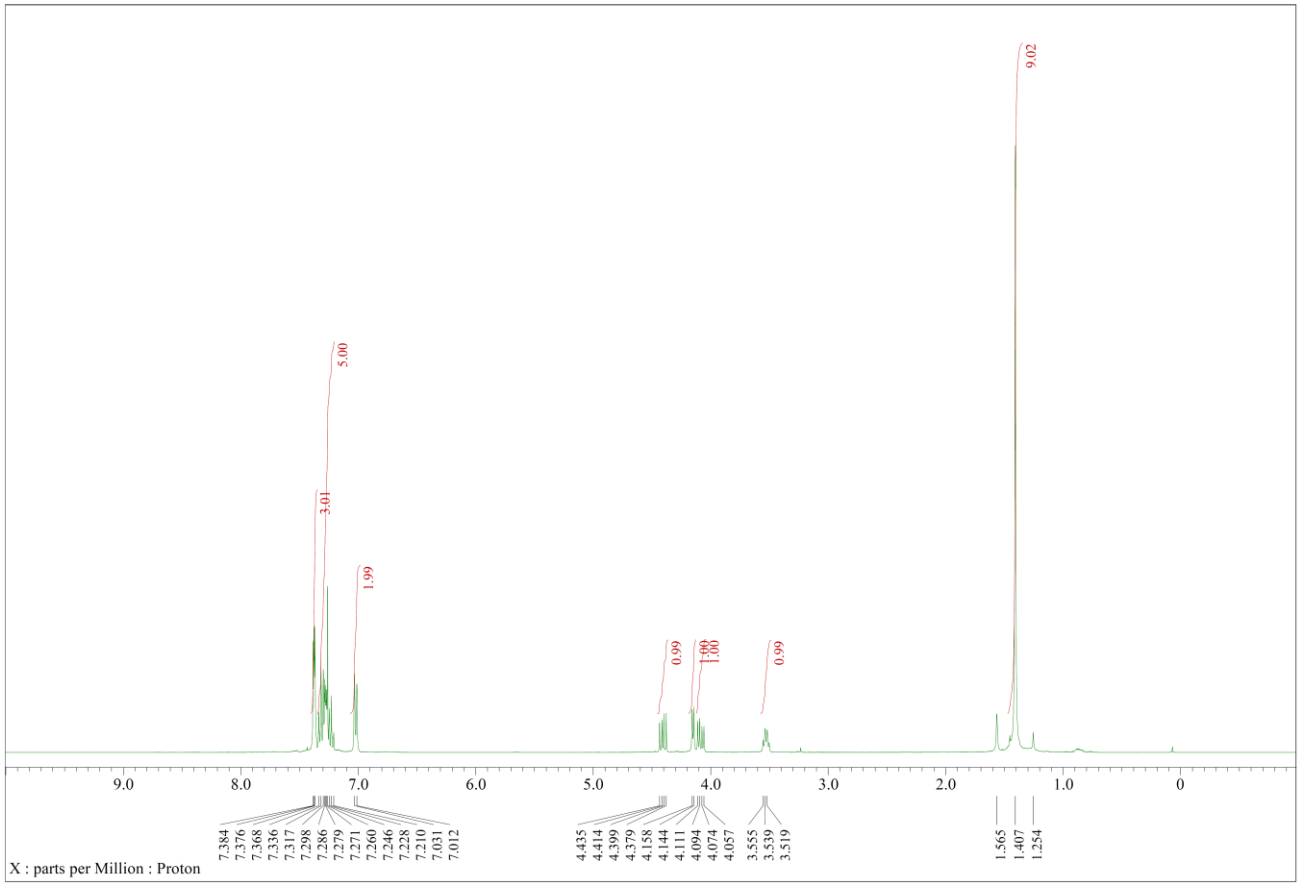
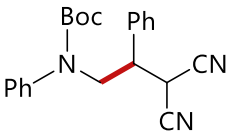


Figure S17. ^{1}H NMR (400 MHz) spectrum of **7** in $CDCl_3$.



7

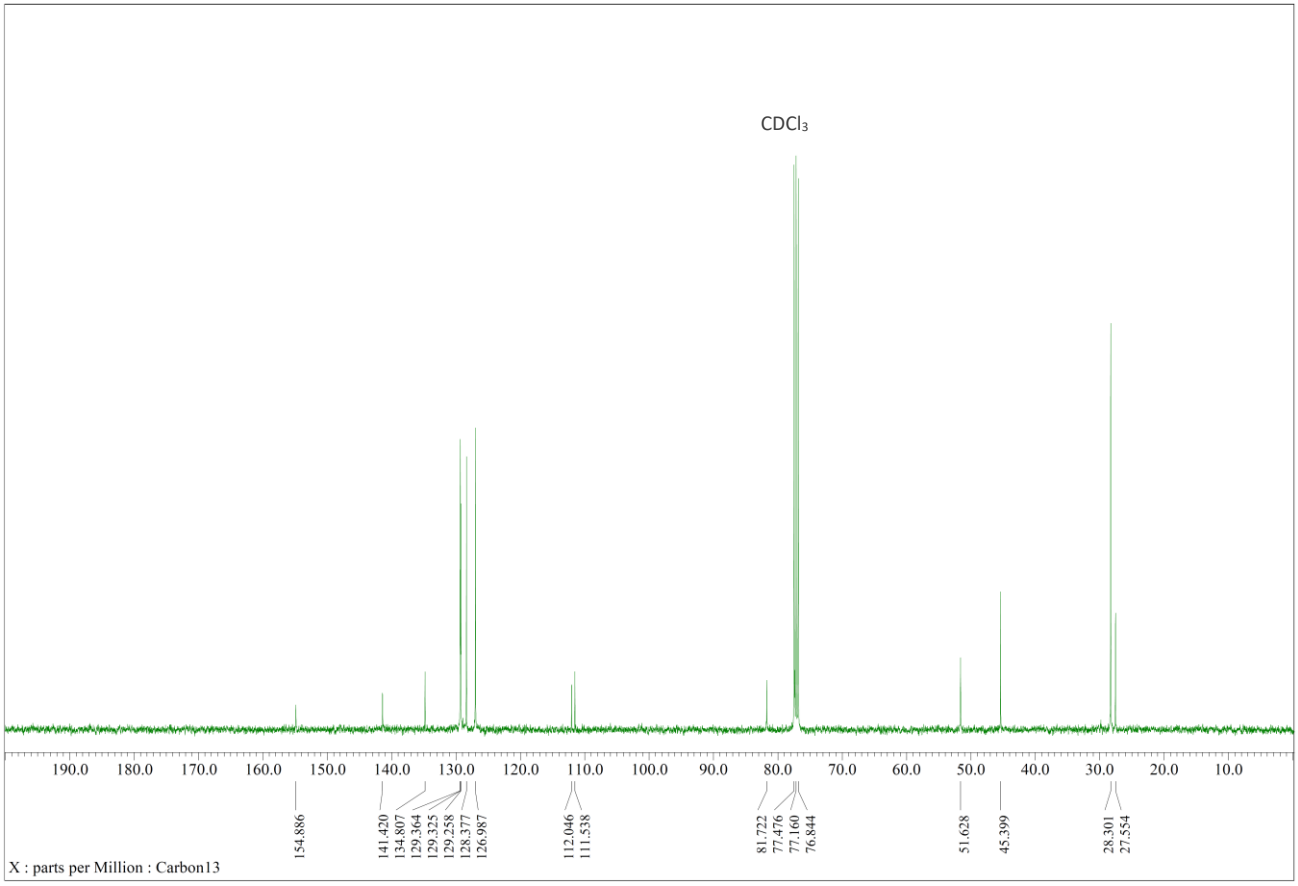
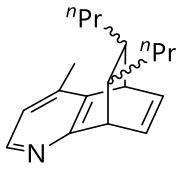


Figure S18. ^{13}C NMR (100 MHz) spectrum of **7** in $CDCl_3$.



9a

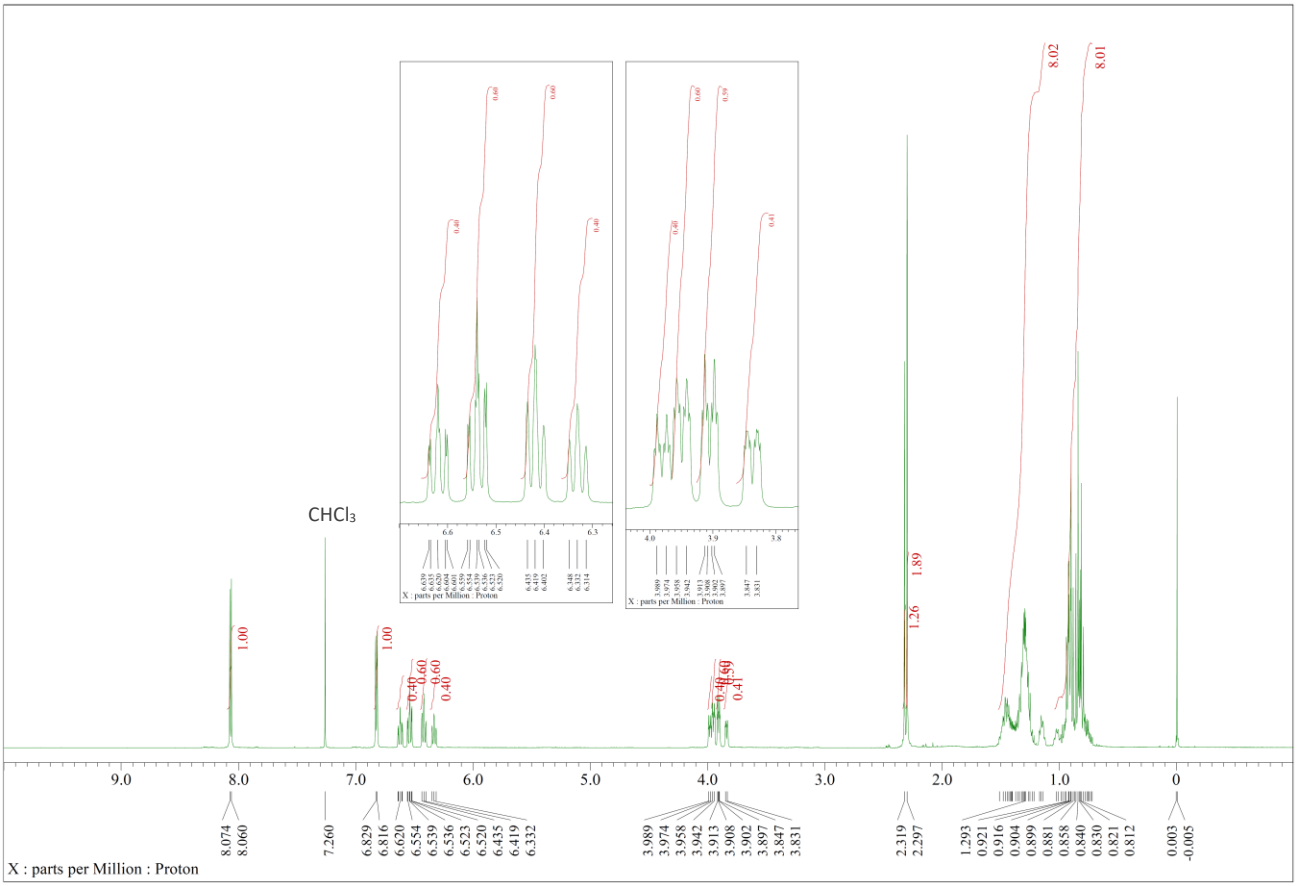
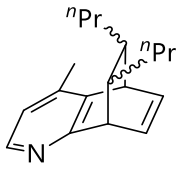


Figure S19. ^{1}H NMR (400 MHz) spectrum of **9a** in $CDCl_3$.



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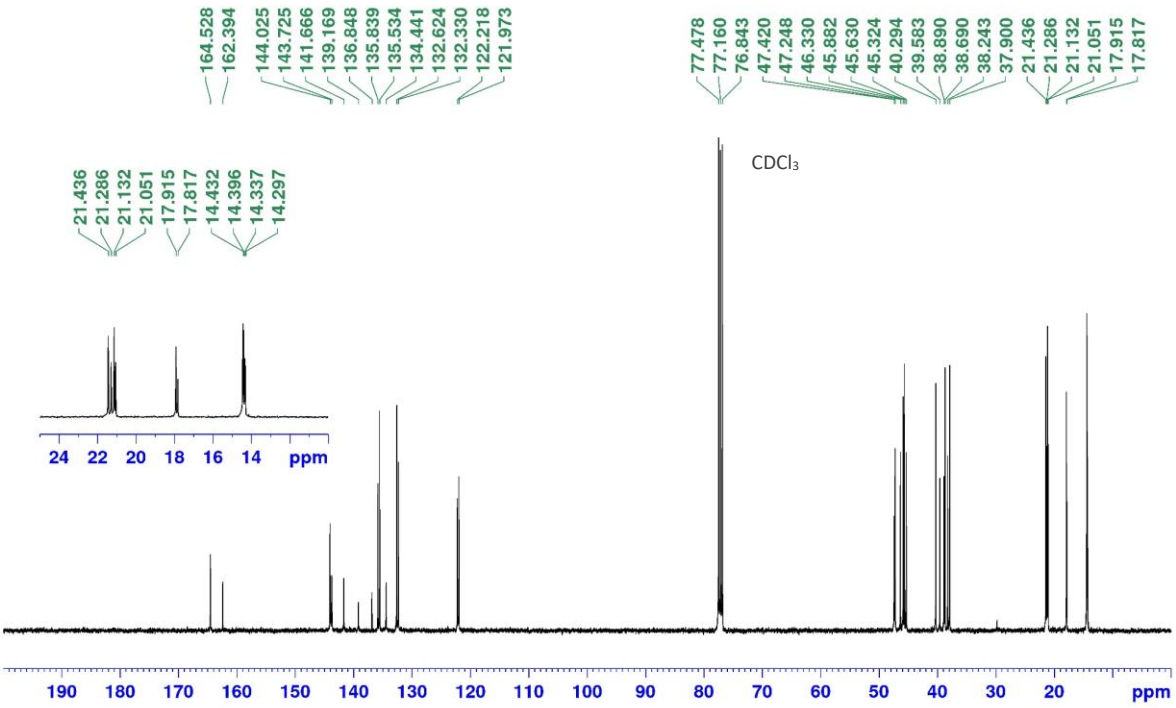
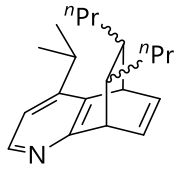


Figure S20. ^{13}C NMR (100 MHz) spectrum of **9a** in $CDCl_3$.



9b

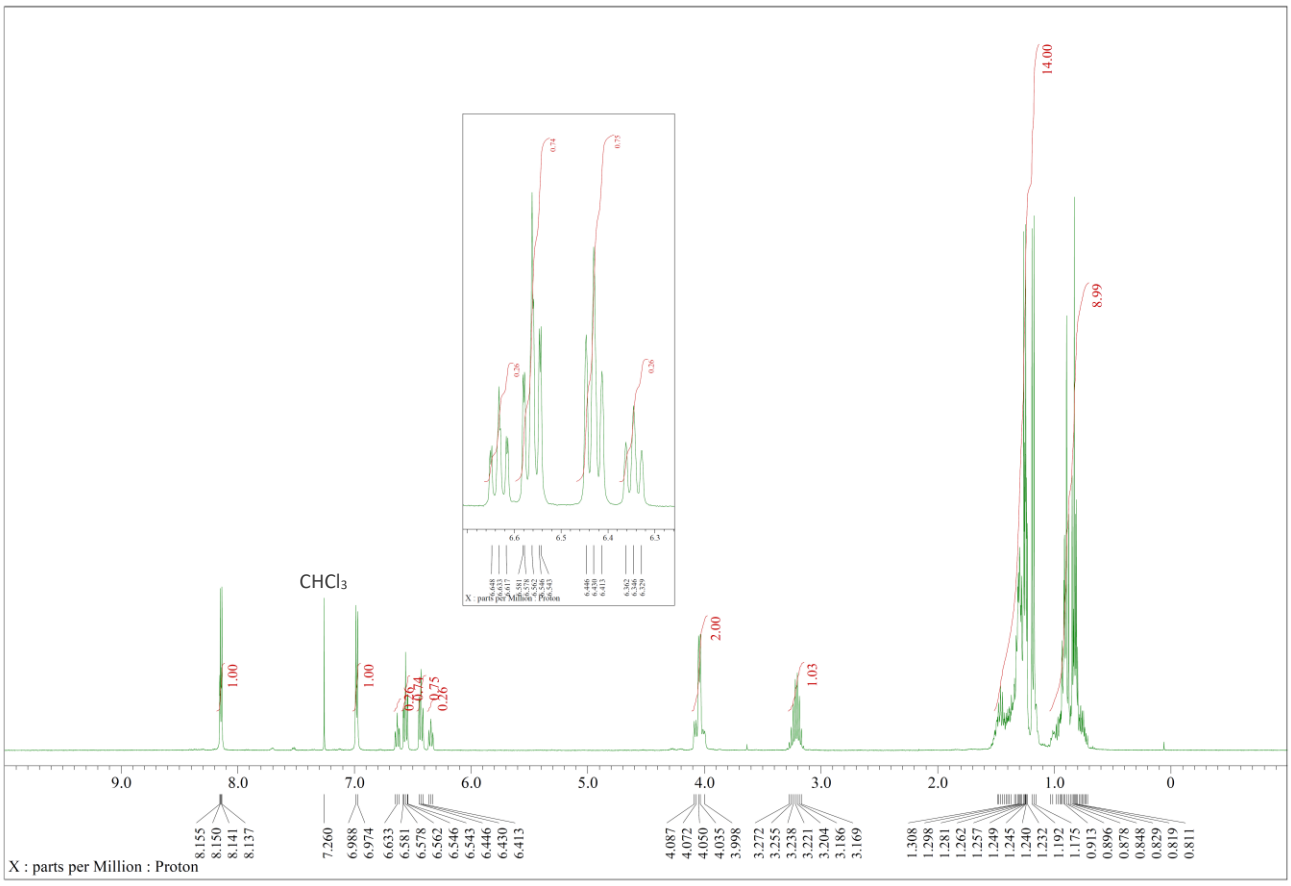
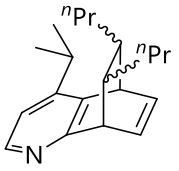


Figure S21. ^{1}H NMR (400 MHz) spectrum of **9b** in $CDCl_3$.



9b

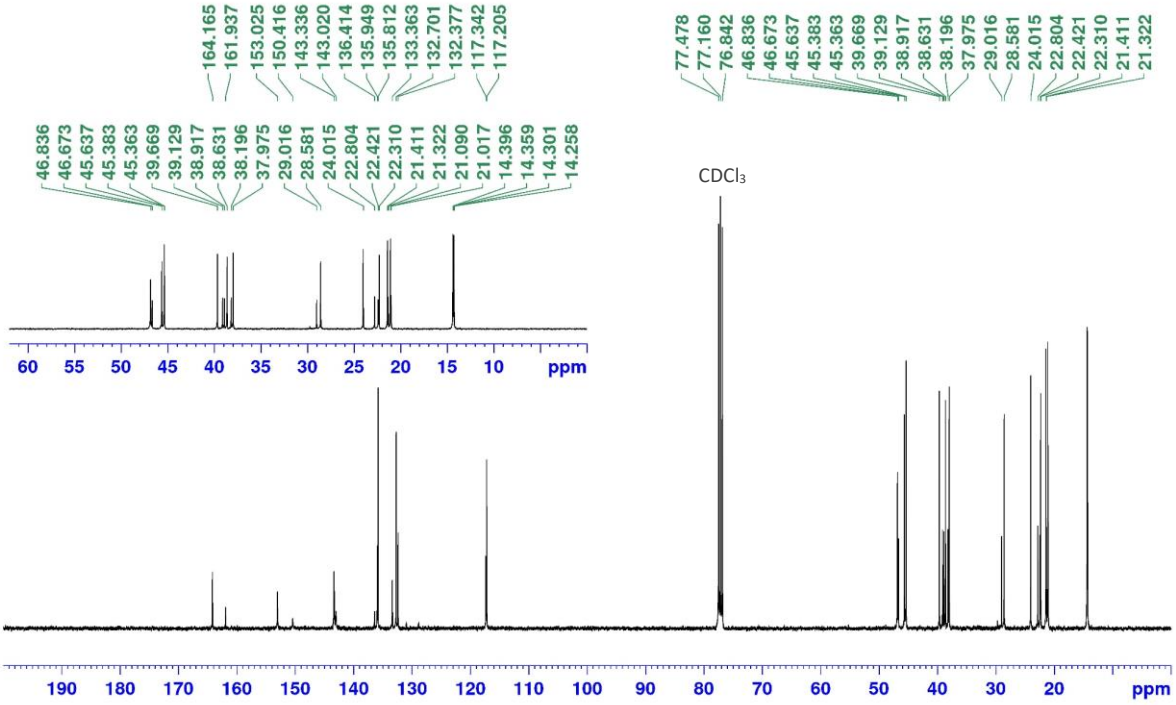
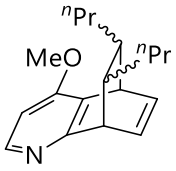


Figure S22. ^{13}C NMR (100 MHz) spectrum of **9b** in $CDCl_3$.



9c

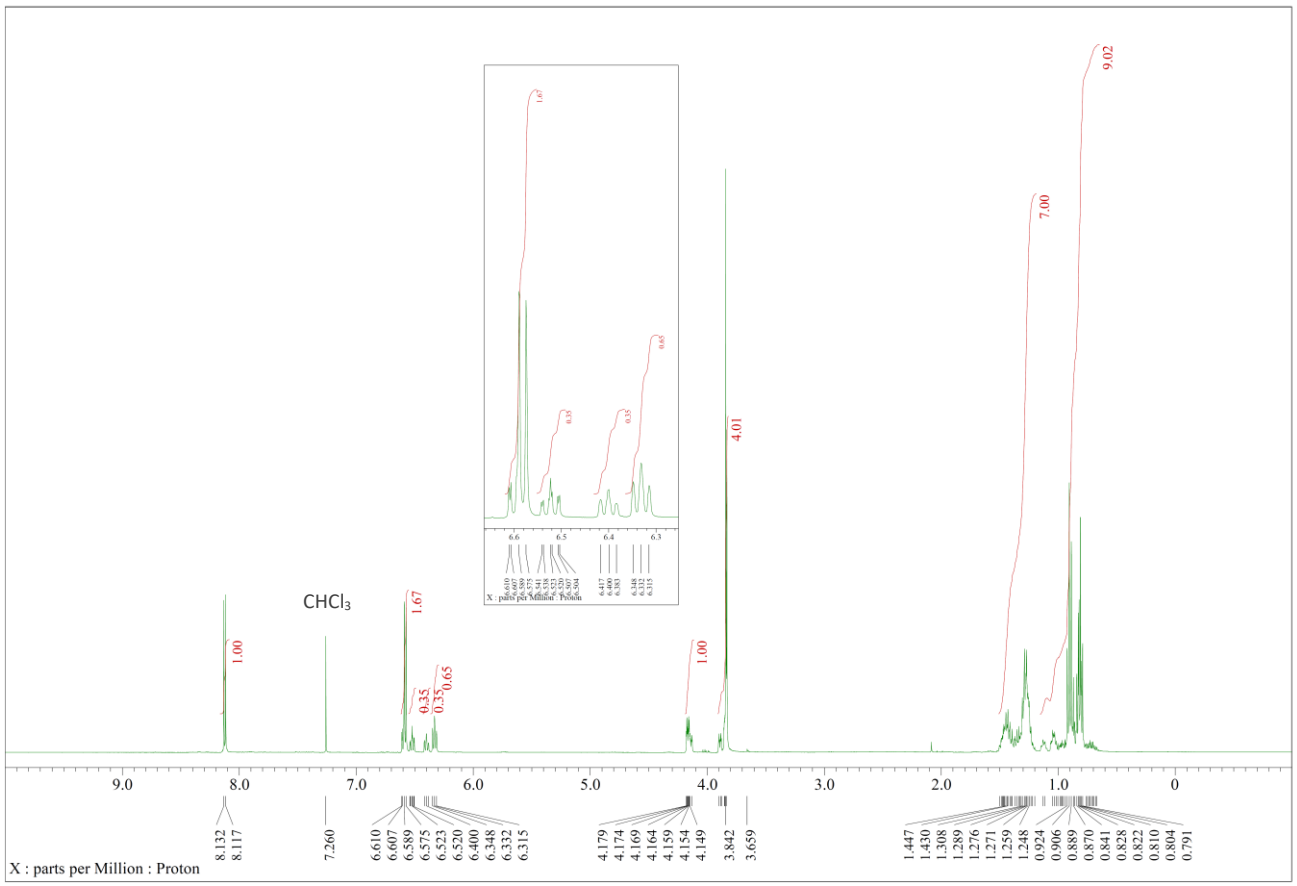
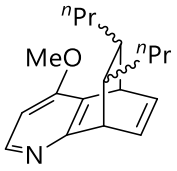


Figure S23. ^{1}H NMR (400 MHz) spectrum of **9c** in $CDCl_3$.



9c

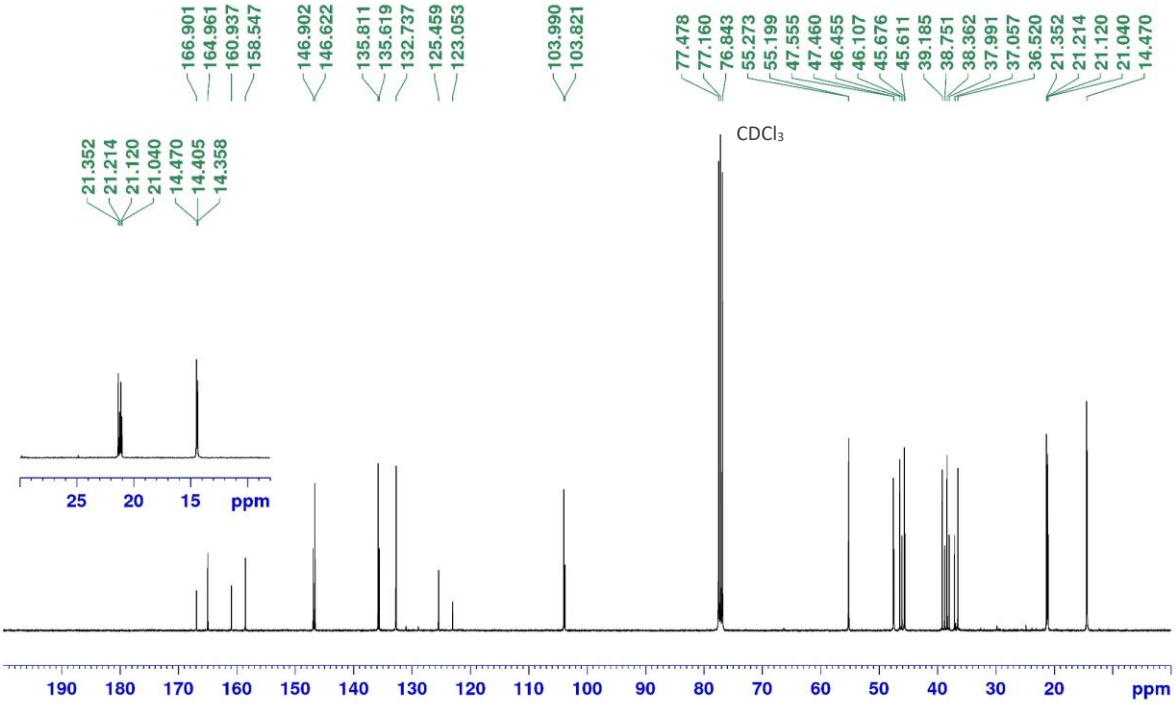
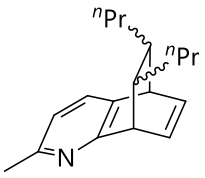


Figure S24. ^{13}C NMR (100 MHz) spectrum of **9c** in $CDCl_3$.



9d

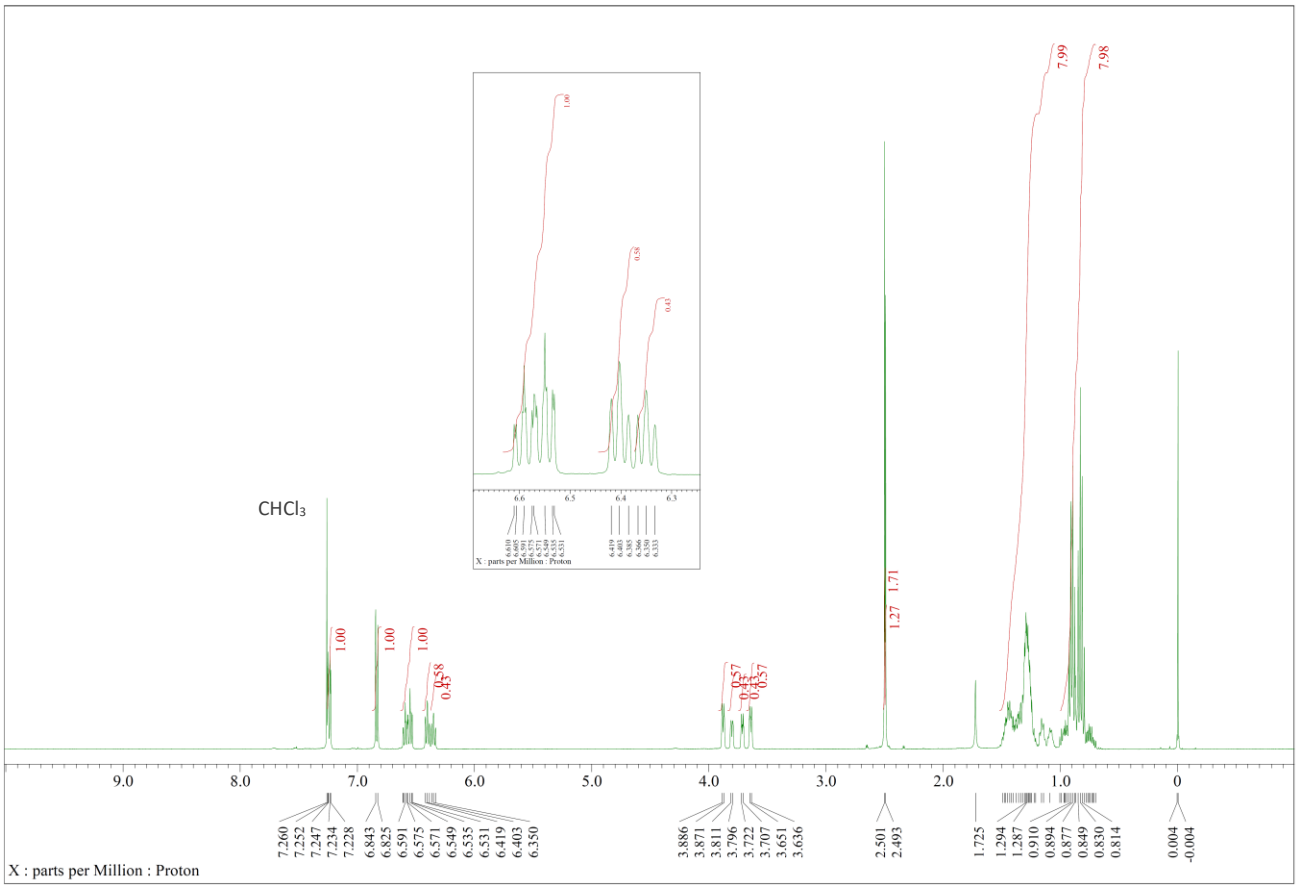
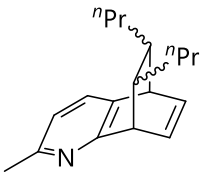


Figure S25. ^{1}H NMR (400 MHz) spectrum of **9d** in $CDCl_3$.



9d

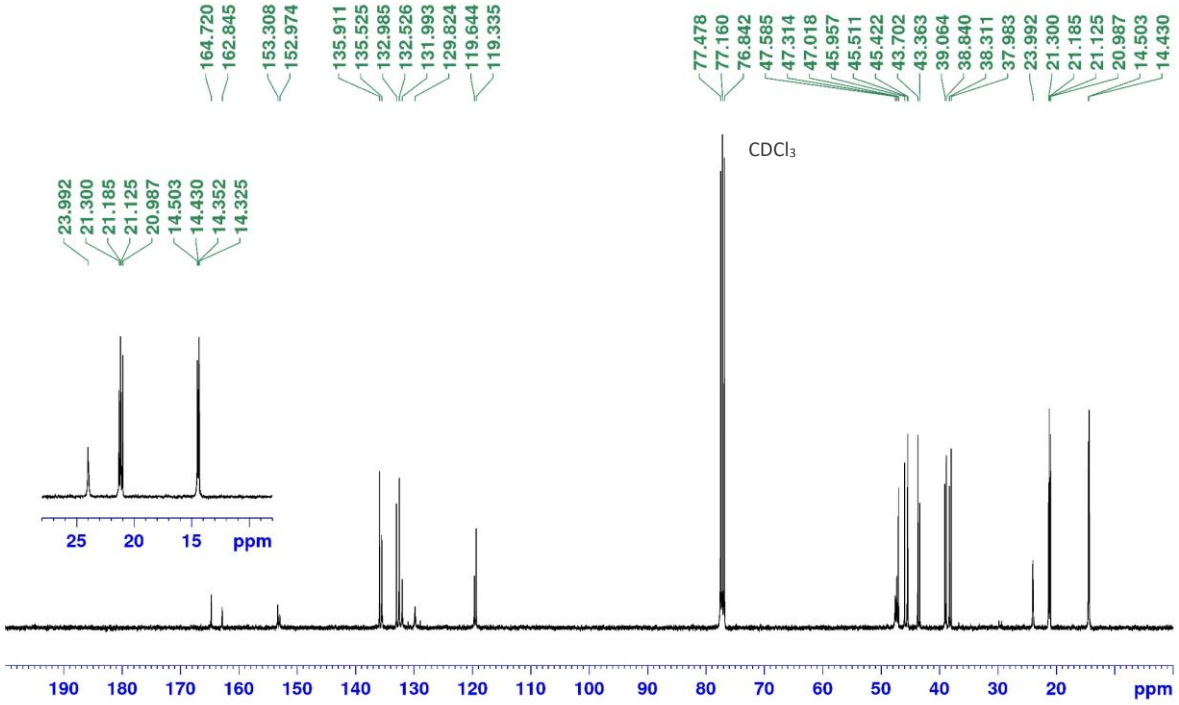
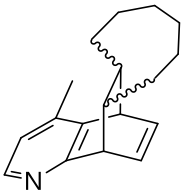


Figure S26. ^{13}C NMR (100 MHz) spectrum of **9d** in $CDCl_3$.



9e

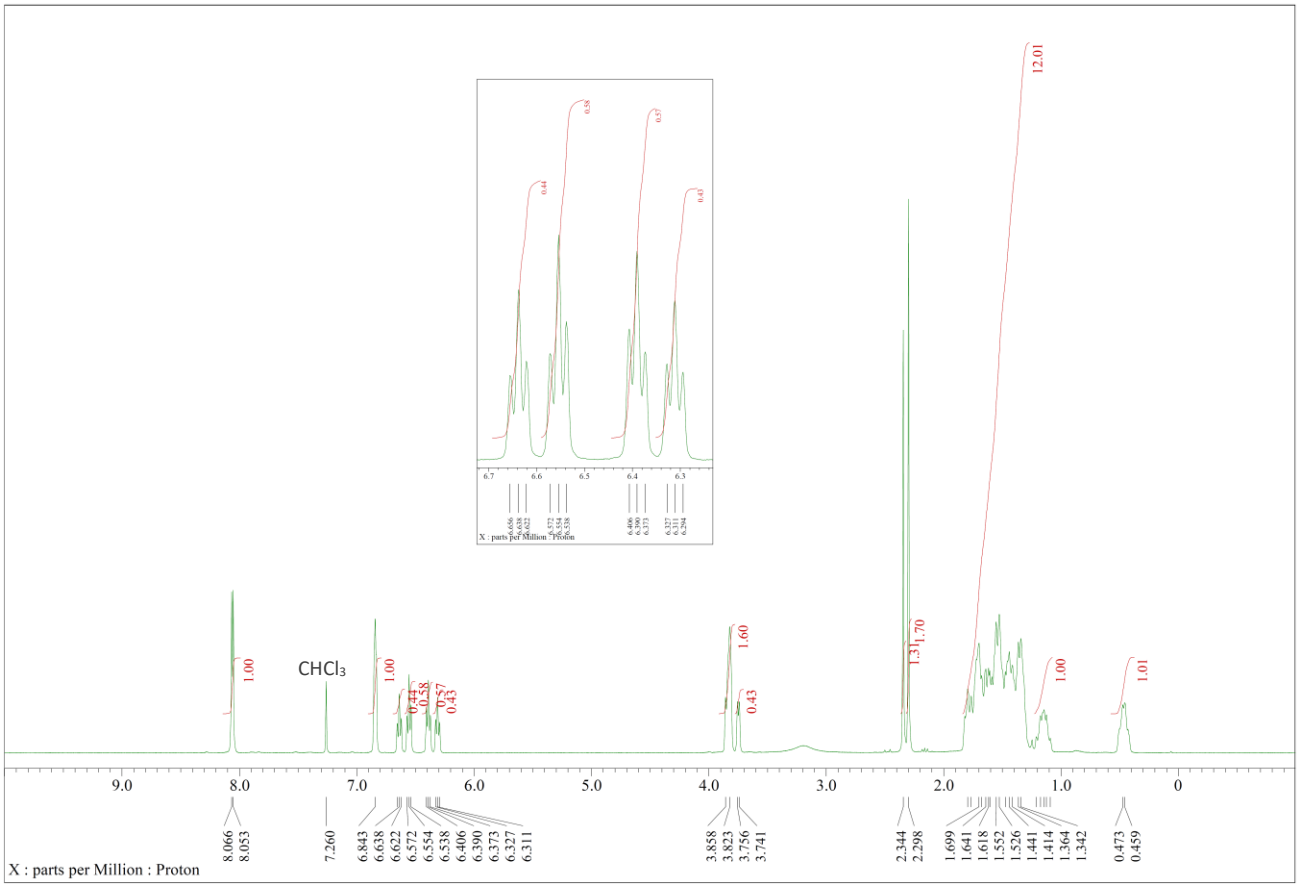
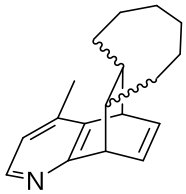


Figure S27. ^{1}H NMR (400 MHz) spectrum of **9e** in $CDCl_3$.



9e

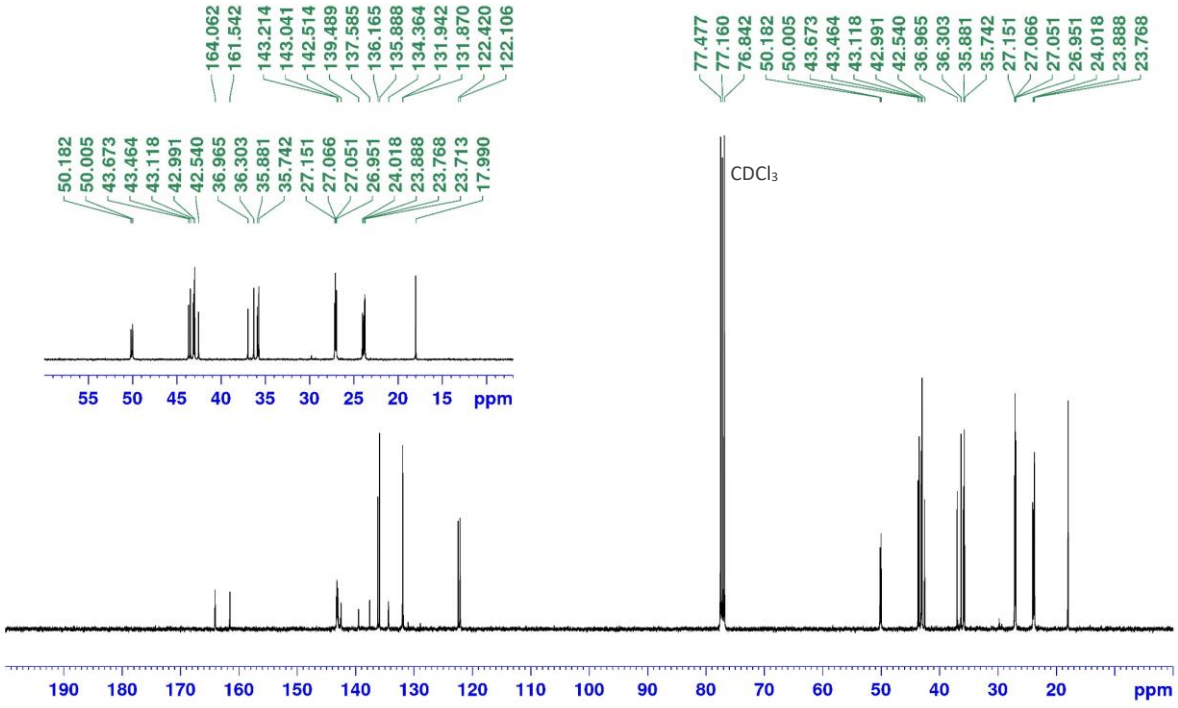
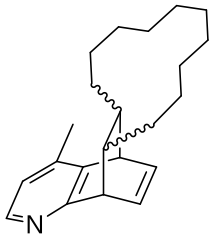


Figure S28. ^{13}C NMR (100 MHz) spectrum of **9e** in $CDCl_3$.



9f

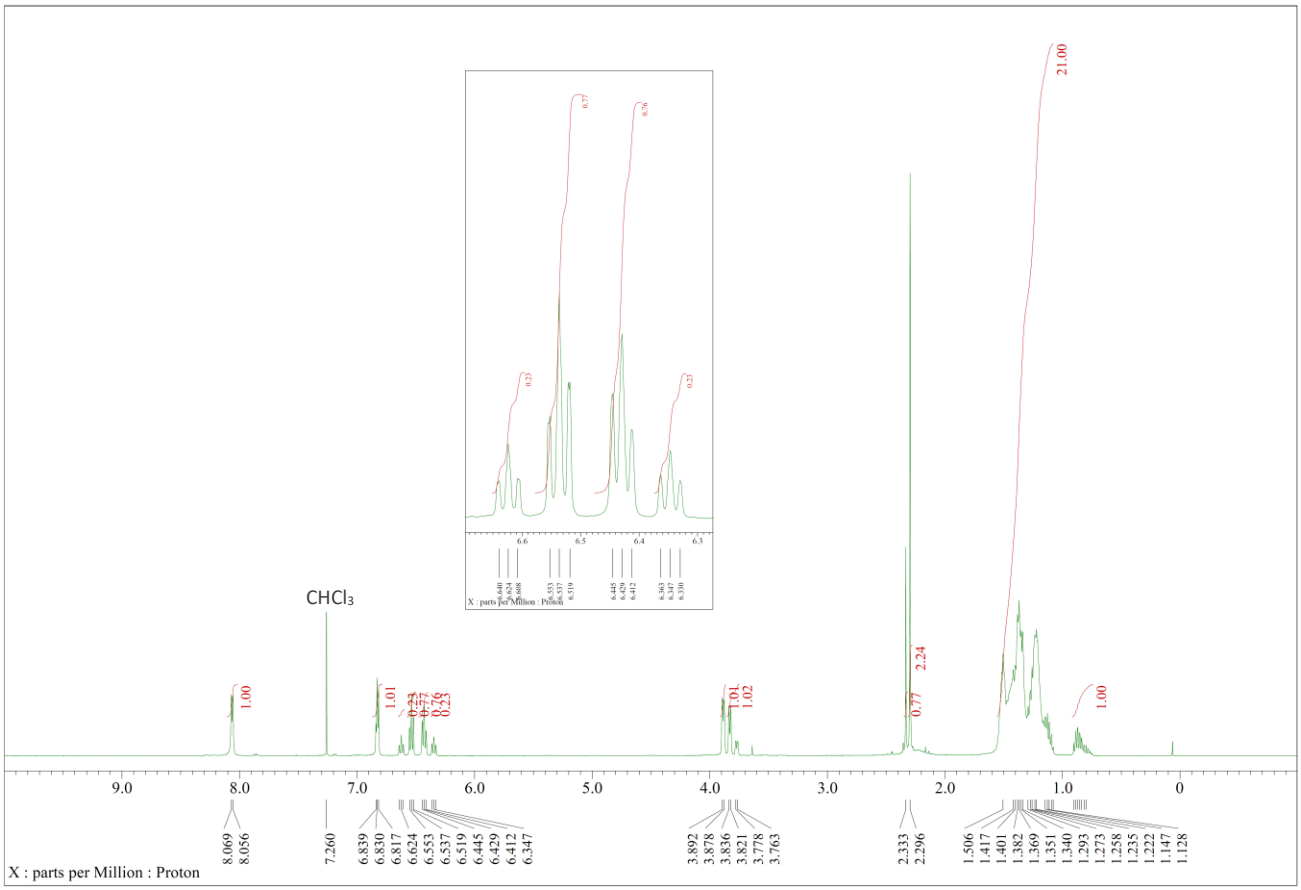
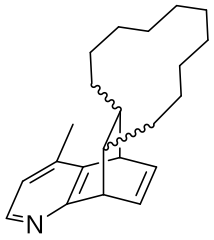


Figure S29. ^{1}H NMR (400 MHz) spectrum of **9f** in $CDCl_3$.



9f

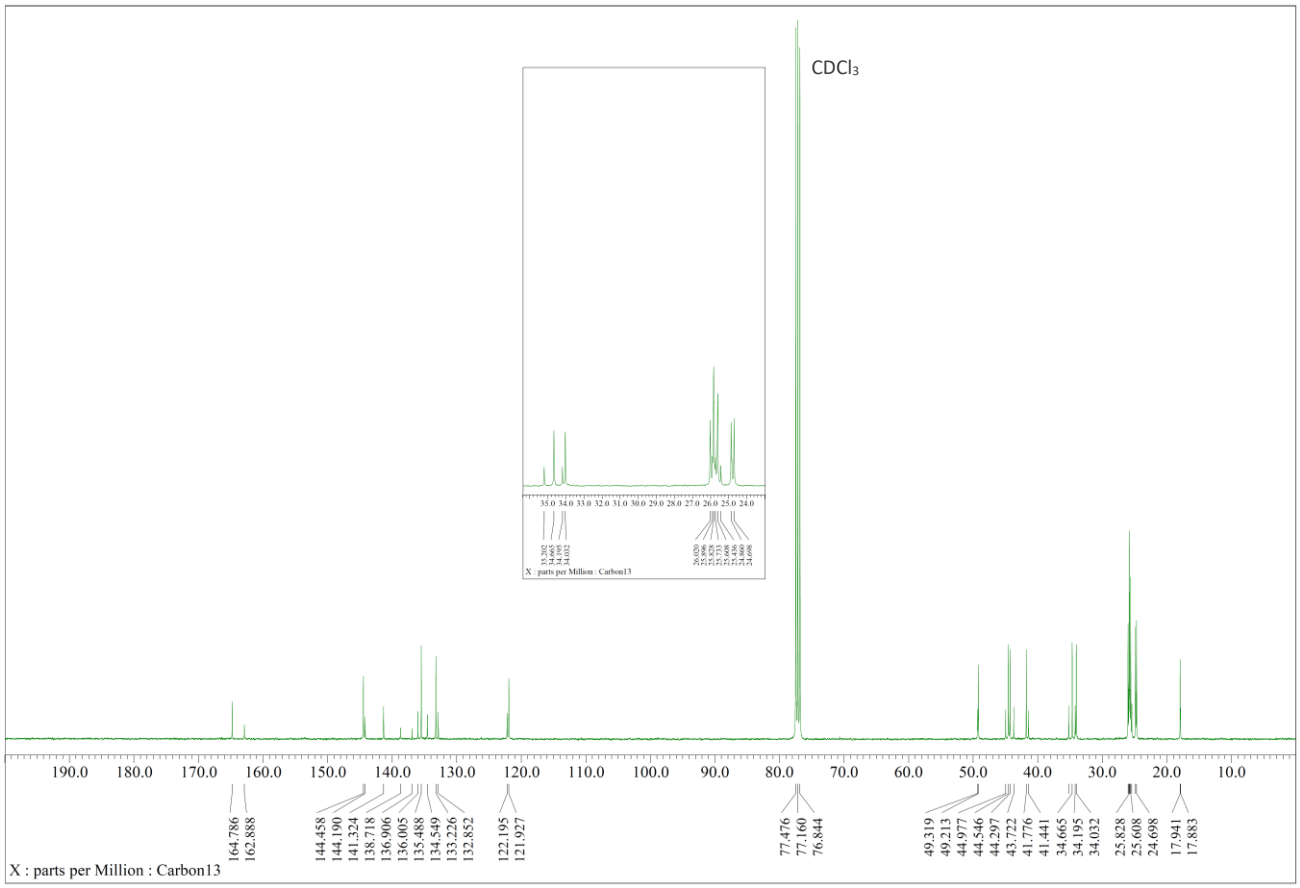


Figure S30. ^{13}C NMR (100 MHz) spectrum of **9f** in $CDCl_3$.