Supporting Information

Terminal-oxidant-free Photocatalytic C–H Alkylation of Heteroarenes with Alkylsilicates as Alkyl Radical Precursors

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1. General

Mes-Acr^{+}, TFA, 4CzIPN, $(NH_4)_2S_2O_8$, Et_3N, Et_4NBr, 4-methylquinoline (**4**), 2-methylquinoline, quinoline, 2-phenylquinoline, 4-chloroquinoline, 4-bromoquinoline, methyl isoquinoline-3-carboxylate, 5-bromoisoquinoline, 5-nitroisoquinoline, phenanthridine, benzothiazole, benzimidazole, 4-hydroxyquinazoline, 3,6-dichloropyridazine, 4-(trifluoromethyl)pyridine, 5,7-dichloro-4-(4-fluorophenoxy)quinoline, fasudil hydrochloride and quinine were commercially available and used without further purification. 4-Methoxyquinoline,[1] potassium [18-crown-6] bis(catecholato)cyclohexylsilicate (**1a**) [2] and 3,3,3',3'-tetrakis(trifluoromethyl)-1,1'(3*H*,3'*H*)-spirobi-[2,l-benzoxasilole] (**3**)[3] were synthesized according to the reported literature. Distilled water, dehydrated CH_3CN, CH_2Cl_2, THF and diethyl ether were used for solvent. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. 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. Photocatalytic alkylation was 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 (Figure S1). Gram scale photocatalytic alkylation was carried out in a round-bottom flask with a septum (300 mL) (Figure S2). All NMR spectra were measured on Unity Inova-400 instrument (Varian Inc., 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) (δ = 0), $CHCl_3$ (δ = 7.26) and acetone (δ = 2.05) served as an internal standard for ^{1}H NMR spectra, and acetone was used as an internal standard (δ = 206.26) for ^{13}C NMR spectra. CF_3COOH (δ =76.55) was as used as an external standard for ^{19}F NMR spectra. Tetramethylsilane (TMS) (δ = 0) was used as an external standard for ^{29}Si NMR spectra. The redox potential of alkylsilicate **2** was determined by differential pulse voltammetry (DPV) analysis using the ALS electrochemical analyzer (ALS612E). Stern-Volmer fluorescence quenching experiments were run using the Jasco's spectrofluorometer (FP-6500).

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[1] X. Huang, J. Brubaker, W. Zhou, P. J. Biju, L. Xiao, N. Shao, Y. Huang, L. Dong, Z. Liu, R. Bitar, A. Buevich, J. Jung, S. L. Peterson, J. W. Butcher, J. Close, M. Martinez, R. N. MacCoss, H. Zhang, S. Crawford, K. D. McCormick, R. Aslanian, R. Nargund, C. Correll, F. Gervais, H. Qiu, X. Yang, C. Garlisi, D. Rindgen, K. M. Maloney, P. Siliphaivanh, A. Palani, *ACS Med. Chem. Lett.*, 2018, **9**, 679–684.

[2] V. Corcé, L.-M. Chamoreau, E. Derat, J.-P. Goddard, C. Ollivier, L. Fensterbank, *Angew. Chem. Int. Ed*., 2015, **54**, 11414–11418.

[3] H. Lenormand, J.-P. Goddard, L. Fensterbank, *Org. Lett.*, 2013, **15**, 748–751.

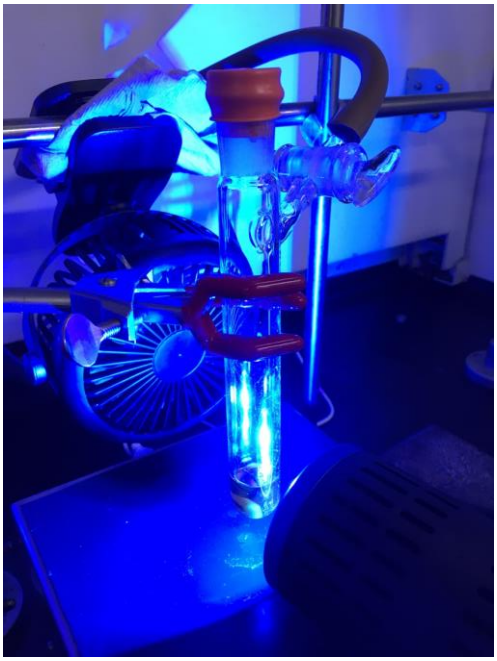


Figure S1. Reaction set up (0.1 mmol or 0.2 mmol scale)

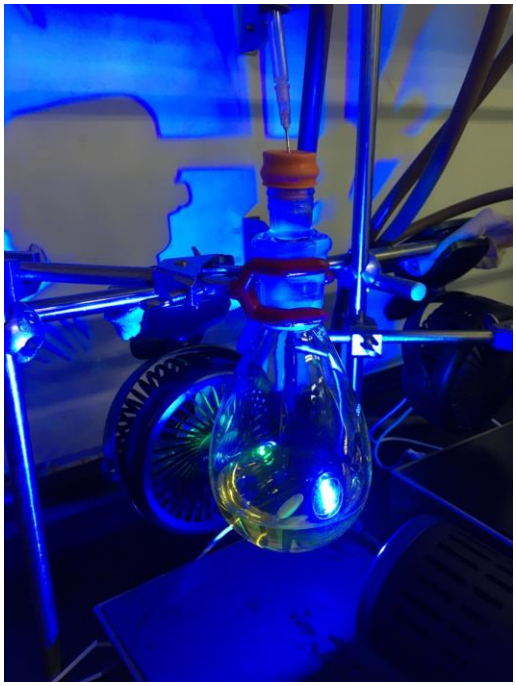
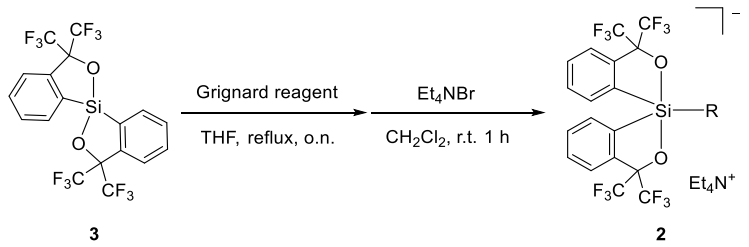


Figure S2. Reaction set up (gram scale).

2. General procedure for silicate synthesis

Procedure A:

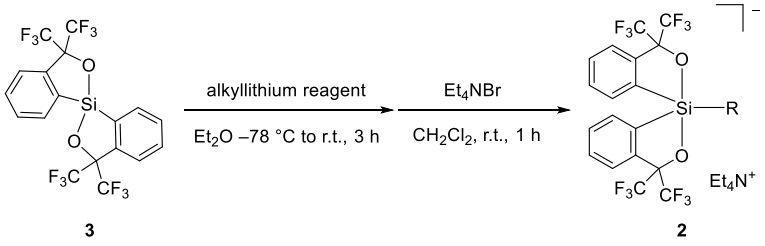
Magnesium turnings (4.0 equiv) were activated by addition of single chip of I_2 (20–30 mg) and heating under vacuum for 5 min in double neck round bottom flask. Then dry THF (5.0 mL/1 mmol of **3**) was added to the reaction flask under inert atmosphere. Alkyl bromide (3.0 equiv) was added and reaction mixture was heated at 60 °C for 15-20 min. 3,3,3',3'-Tetrakis(trifluoromethyl)-1,1'(3*H*,3'*H*)-spirobi-[2,l-benzoxasilole] (**3**) (1.0 eq.) in dry THF (5 mL/mmol of **3**) was added to the solution of the Grignard reagent in double neck round bottom flask under inert atmosphere and the reaction mixture was refluxed overnight. Subsequent hydrolysis was achieved by the cautious addition of EtOH (10 mL) at 0 °C. The solution was filtered and evaporated under reduced pressure to give a colorless oil. CH_2Cl_2 (20 mL) and Et_4NBr (3.0-5.0 eq.) were added to the oil and the mixture was stirred for 1 hour. The reaction mixture was washed with water (20 mL × 3), dried over Na_2SO_4 and evaporated to get crude product. Recrystallization of the crude product with CH_2Cl_2/hexane afforded alkylsilicate (**2**).



Scheme S1.

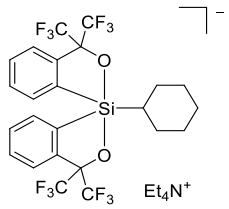
Procedure B:[4]

In a 100 mL flask, 3,3,3',3'-tetrakis(trifluoromethyl)-1,1'(3*H*,3'*H*)-spirobi-[2,l-benzoxasilole] (**3**) (1.0 equiv) was dissolved in Et_2O (5 mL/mmol of **3**). The solution was stirred and alkyllithium reagent (1.1-3.0 equiv) was added at –78 °C. After 15 min at –78 °C, the mixture was stirred for 3 hours at room temperature. The mixture was quenched with EtOH (10 mL) at 0 °C and evaporated under reduced pressure to give a colorless oil. CH_2Cl_2 (20 mL) and Et_4NBr (3.0-5.0 equiv) were added to the oil and the mixture was stirred for 1 hour. The reaction mixture was washed with water (20 mL × 3), dried over Na_2SO_4 and evaporated to get crude product. Recrystallization of the crude product with CH_2Cl_2/hexane afforded alkylsilicate (**2**).



Scheme S2.

[4] This procedure is based on the following paper. W. H. Stevenson, S. Wilson, J. C. Martin, W. B. Farnham, *J. Am. Chem. Soc*., 1985, **107**, 6340–6352.



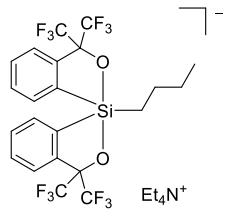
2a

tetraethylammonium bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolate(2-)-*C*^{2},*O*]cyclohexylsilicate (2a)

Following the general procedure A, reaction of **3** (2.06 g, 4.02 mmol) gave the title compound (2.22 g, 76%, colorless solid).

Cyclohexyl bromide (1.47 mL, 12.0 mmol), magnesium turnings (0.414 g, 17.0 mmol), Et_4NBr (4.22 g, 20.1 mmol).

^{1}H NMR (400 MHz, acetone-d_6): δ 8.24 (d, J = 6.8 Hz, 2H), 7.44 (d, J = 6.8 Hz, 2H), 7.29-7.21 (m, 4H), 3.51 (q, J = 7.2 Hz, 8H), 1.80-1.79 (m, 1H), 1.60-1.46 (m, 4H), 1.42-1.38 (m, 12H), 1.08-0.84 (m, 6H); ^{13}C NMR (100 MHz, acetone-d_6): δ 146.5, 142.0, 138.7, 128.4, 128.3, 126.0 (q, J = 286.9 Hz), 125.7 (q, J = 287.8 Hz), 123.8, 82.7 (sept, J = 27.8 Hz), 53.0, 34.1, 30.1, 29.4, 28.4, 7.6; ^{19}F NMR (376 MHz, acetone-d_6): δ –74.3 (q, J = 9.8 Hz), –75.6 (q, J = 9.8 Hz); ^{29}Si NMR (79 MHz, acetone-d_6): δ –63.9; HRMS (ESI, negative) *m/z* calcd for $C_{24}H_{19}F_{12}O_2Si$ [M–Et_4N]$^-$: 595.0968, found: 595.0940; mp: 195-200 °C..



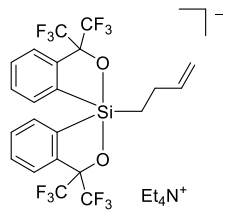
2c

tetraethylammonium bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolate(2-)-*C*^{2},*O*]butylsilicate (2c)

Following the general procedure B, reaction of **3** (1.02 g, 1.99 mmol) gave the title compound (1.25 g, 90%, colorless solid).

1.55 M ^{n}BuLi in hexane (1.42 mL, 2.20 mmol), Et_4NBr (0.868 g, 4.13 mmol).

^{1}H NMR (400 MHz, acetone-d_6): δ 8.25 (d, J = 6.8 Hz, 2H), 7.45 (d, J = 6.0 Hz, 2H), 7.30-7.22 (m, 4H), 3.51 (q, J = 7.2 Hz, 8H), 1.58-1.55 (m, 1H), 1.44-1.38 (m, 12H), 1.14-1.13 (m, 3H), 0.75-0.71 (m, 5H); ^{13}C NMR (100 MHz, acetone-d_6): δ 146.7, 142.0, 138.5, 128.6, 128.5, 125.9 (q, J = 289.6 Hz), 125.7 (q, J = 286.5 Hz), 124.0, 82.7 (sept, J = 27.9 Hz), 53.0, 28.2, 27.7, 23.8, 14.4, 7.6; ^{19}F NMR (376 MHz, acetone-d_6): δ –75.2 (q, J = 9.8 Hz), –75.6 (q, J = 9.4 Hz); ^{29}Si NMR (79 MHz, acetone-d_6): δ –64.2; HRMS (ESI, negative) *m/z* calcd for $C_{22}H_{17}F_{12}O_2Si$ [M–Et_4N]$^-$: 569.0812, found: 569.0812; mp: 181-184 °C.



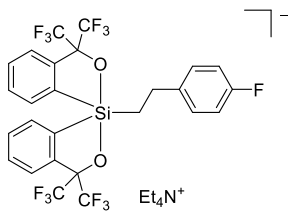
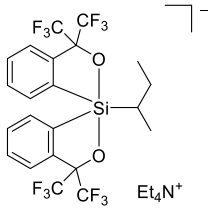
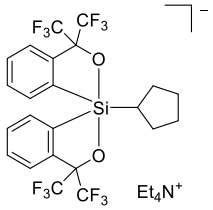
2d

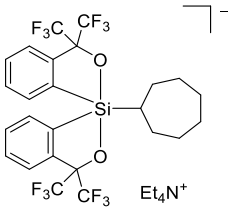
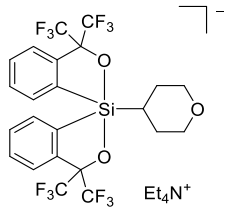
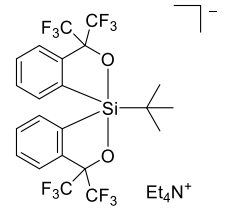
tetraethylammonium bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolate(2-)-*C*^{2},*O*]butenylsilicate (2d)

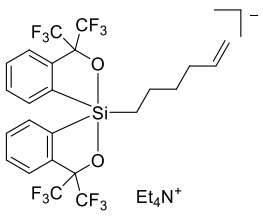
Following the general procedure A, reaction of **3** (0.512 g, 0.998 mmol) gave the title compound (0.618 g, 89%, colorless solid).

Cyclopropylmethyl bromide (0.291 mL, 3.00 mmol), magnesium turnings (0.140 g, 5.77 mmol), Et_4NBr (1.06 g, 5.05 mmol).

^{1}H NMR (400 MHz, acetone-d_6): δ 8.25 (d, J = 6.8 Hz, 2H), 7.47 (d, J = 6.4 Hz, 2H), 7.32-7.24 (m, 4H), 5.82-5.73 (m, 1H), 4.74 (d, J = 17.2 Hz, 1H), 4.59 (d, J = 10.0 Hz, 1H), 3.50 (q, J = 6.8 Hz, 8H), 2.37-2.31 (m, 1H), 1.89-1.81 (m, 1H), 1.41-1.38 (m, 12H), 0.89-0.76 (m, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 146.2, 145.6, 142.0, 138.4, 128.7, 128.6, 125.9 (q, J = 288.9 Hz), 125.7 (q, J = 285.9 Hz), 124.0, 110.8, 82.7 (sept, J = 27.9 Hz), 53.0, 30.7, 23.4, 7.6; ^{19}F NMR (376 MHz, acetone-d_6): δ –75.3 (q, J = 9.4 Hz), –75.7 (q, J = 9.4 Hz); ^{29}Si NMR (79 MHz, acetone-d_6): δ –64.8; HRMS (ESI, negative) *m/z* calcd for $C_{22}H_{15}F_{12}O_2Si$ [M–Et_4N]$^-$: 567.0661, found: 567.0655; mp: 160-163 °C.

 **2e**	**tetraethylammonium bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolate(2-)-*C*^{2},*O*]-2-(4-fluorophenyl)ethylsilicate (2e)** Following the general procedure A, reaction of **3** (0.513 g, 1.00 mmol) gave the title compound (0.611 g, 80%, colorless solid). 1-(2-bromoethyl)-4-fluorobenzene (0.420 mL, 3.00 mmol), magnesium turnings (0.0926 g, 3.81 mmol), Et_4NBr (0.630 g, 3.00 mmol), LiCl (0.153 g, 3.61 mmol) ^{1}H NMR (400 MHz, acetone-d_6): δ 8.22 (d, J = 6.8 Hz, 2H), 7.58 (d, J = 6.4 Hz, 2H), 7.45-7.35 (m, 4H), 7.10-7.02 (m, 2H), 6.91 (t, J = 8.8 Hz, 2H), 3.19-3.00 (m, 8H), 2.91 (dt, J = 4.4, 13.6 Hz, 1H) 2.34-2.23 (t, J = 13.8 Hz, 1H), 1.39-0.88 (m, 14H); ^{13}C NMR (100 MHz, acetone-d_6): δ 162.5, 161.3 (d, J = 237.8 Hz), 145.9, 145.4 (d, J = 2.9 Hz), 142.0, 138.5, 129.9 (d, J = 7.5 Hz), 128.8, 125.9 (q, J = 290.9 Hz), 125.6 (q, J = 286.4 Hz), 124.1, 115.1 (d, J = 20.8 Hz), 82.7 (sept, J = 27.9 Hz), 52.9, 31.9, 27.5, 7.6; ^{19}F NMR (376 MHz, CD_3CN): δ –75.3 (q, J = 10.2 Hz), –75.7 (q, J = 9.0 Hz), –121.1; ^{29}Si NMR (79 MHz, acetone-d_6): δ –65.5; HRMS (ESI, negative) *m/z* calcd for $C_{26}H_{16}F_{13}O_2Si$ [M–Et_4N]$^-$: 635.0701, found: 635.0717; mp: 167-170 °C.
 **2f**	**tetraethylammonium bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolate(2-)-*C*^{2},*O*]-*sec*-butylsilicate (2f)** Following the general procedure B, reaction of **3** (1.00 g, 1.96 mmol) gave the title compound (0.566 g, 41%, colorless solid) as mixture of two diastereomers. 1.00 M ^{s}BuLi in hexane (2.20 mL, 2.20 mmol), Et_4NBr (0.852 g, 4.05 mmol). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.27 (d, J = 6.4 Hz, 2H), 7.43 (d, J = 6.4 Hz, 2H), 7.28-7.23 (m, 4H), 3.50-3.34 (m, 8H), 1.71-1.61 (m, 1H), 1.38 (br s, 12H), 0.91-0.74 (m, 8H); ^{13}C NMR (100 MHz, acetone-d_6): δ 146.6, 142.0, 138.8, 128.4, 128.3, 125.9 (q, J = 286.9 Hz), 125.7 (q, J = 287.8 Hz), 124.0, 82.7 (sept, J = 27.9 Hz), 52.9, 29.8, 29.4, 27.8, 26.6, 16.85, 16.78, 15.0, 14.7, 7.5; ^{19}F NMR (376 MHz, acetone-d_6): δ –74.5 (q, J = 9.8 Hz), –75.4 (q, J = 9.4 Hz), –75.6 (q, J = 9.0 Hz); ^{29}Si NMR (79 MHz, acetone-d_6): δ –64.5; HRMS (ESI, negative) *m/z* calcd for $C_{22}H_{17}F_{12}O_2Si$ [M–Et_4N]$^-$: 569.0809, found: 569.0812; mp: 139-143 °C.
 **2g**	**tetraethylammonium bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolate(2-)-*C*^{2},*O*]cyclopentylsilicate (2g)** Following the general procedure A, reaction of **3** (1.03 g, 2.01 mmol) gave the title compound (0.743 g, 52%, colorless solid). Cyclopentyl bromide (0.643 mL, 6.00 mmol), magnesium turnings (0.230 g, 9.44 mmol), Et_4NBr (1.34 g, 6.39 mmol). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.28 (d, J = 6.8 Hz, 2H), 7.45 (d, J = 5.6 Hz, 2H), 7.32-7.23 (m, 4H), 3.52 (q, J = 7.2 Hz, 8H), 1.78-1.50 (m, 2H), 1.43-1.24 (m, 17H), 1.22-1.08 (m, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 146.9, 142.0, 138.6, 128.5, 128.3, 126.0 (q, J = 286.9 Hz), 125.7 (q, J = 287.9 Hz), 123.7, 82.8 (sept, J = 27.9 Hz), 53.0, 34.2, 27.6, 27.4, 7.6; ^{19}F NMR (376 MHz, acetone-d_6): δ –74.5 (q, J = 9.8 Hz), –75.5 (q, J = 9.8 Hz); ^{29}Si NMR (79 MHz, acetone-d_6): δ –63.3;

	HRMS (ESI, negative) *m/z* calcd for $C_{23}H_{17}F_{12}O_2Si$ $[M–Et_4N]^–$: 581.0792, found: 581.0812; mp: 135-139 °C.
 **2h**	**tetraethylammonium bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolate(2-)-*C*^{2},*O*]cycloheptylsilicate (2h)** Following the general procedure A, reaction of **3** (0.517 g, 1.01 mmol) gave the title compound (0.514 g, 69%, colorless solid). Cycloheptyl bromide (0.406 mL, 3.00 mmol), magnesium turnings (0.104 g, 4.29 mmol), Et_4NBr (0.741 g, 3.52 mmol). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.26 (d, J = 6.8 Hz, 2H), 7.44 (d, J = 6.4 Hz, 2H), 7.30-7.21 (m, 4H), 3.50 (q, J = 7.2 Hz, 8H), 1.89-1.85 (m, 2H), 1.62-1.28 (m, 20H), 1.12-1.02 (m, 1H), 0.94-0.92 (m, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 146.6, 142.1, 138.9, 128.5, 128.4, 126.0 (q, J = 287.1 Hz), 125.7 (q, J = 287.5 Hz), 123.9, 82.7 (sept, J = 28.1 Hz), 53.0, 35.1, 31.6, 31.35, 31.30, 31.2, 29.4, 28.6, 7.6; ^{19}F NMR (376 MHz, acetone-d_6): δ –74.4 (q, J = 9.4 Hz), –75.6 (q, J = 9.8 Hz); ^{29}Si NMR (79 MHz, acetone-d_6): δ –61.9; HRMS (ESI, negative) *m/z* calcd for $C_{25}H_{21}F_{12}O_2Si$ $[M–Et_4N]^–$: 609.1119, found: 609.1125; mp: 212-217 °C.
 **2i**	**tetraethylammonium bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolate(2-)-*C*^{2},*O*]-4-tetrahydropyranylsilicate (2i)** Following the general procedure A, reaction of **3** (1.03 g, 2.00 mmol) gave the title compound (1.43 g, 98%, colorless solid). 4-bromotetrahydropyrane (0.675 mL, 6.00 mmol), magnesium turnings (0.205 g, 8.44 mmol), Et_4NBr (1.30 g, 6.18 mmol). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.23 (d, J = 6.4 Hz, 2H), 7.46 (d, J = 6.0 Hz, 2H), 7.34-7.24 (m, 4H), 3.74-3.68 (m, 2H), 3.50 (q, J = 7.6 Hz, 8H), 3.20-3.01 (m, 2H), 1.91-1.72 (m, 1H), 1.69-1.51 (m, 1H), 1.47-1.12 (m, 14H), 1.10-0.99 (m, 1H); ^{13}C NMR (100 MHz, acetone-d_6): δ 145.9, 142.0, 138.6, 128.6, 128.5, 125.8 (q, J = 286.8 Hz), 125.5 (q, J = 287.7 Hz), 123.9, 82.7 (sept, J = 28.0 Hz), 71.2, 70.8, 53.0, 31.2, 7.6; ^{19}F NMR (376 MHz, acetone-d_6): δ –74.4 (q, J = 9.4 Hz), –75.7 (q, J = 9.8 Hz); ^{29}Si NMR (79 MHz, acetone-d_6): δ –65.2; HRMS (ESI, negative) *m/z* calcd for $C_{23}H_{17}F_{12}O_3Si$ $[M–Et_4N]^–$: 597.0760, found: 597.0761; mp: 140-145 °C.
 **2j**	**tetraethylammonium bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolate(2-)-*C*^{2},*O*]-*tert*-butylsilicate (2j)** Following the general procedure B, reaction of **3** (3.07 g, 6.00 mmol) gave the title compound (3.68 g, 88%, colorless solid) as mixture of two stereoisomers. 1.61 M ^{t}BuLi in hexane (11.2 mL, 18.0 mmol), Et_4NBr (5.04 g, 24.0 mmol). ^{1}H NMR (400 MHz, acetone-d_6): major isomer: δ 8.26 (d, J = 7.2 Hz, 2H), 7.41 (d, J = 6.8 Hz, 2H), 7.31-7.18 (m, 4H), 3.44 (q, J = 7.6 Hz, 8H), 1.37-1.34 (m, 12H), 0.82 (s, 9H), minor isomer: 7.97 (d, J = 6.8 Hz, 2H), 7.46 (d, J = 6.8 Hz, 2H), 7.31-7.18 (m, 4H), 3.44 (q, J = 7.6 Hz, 8H), 1.37-1.34 (m, 12H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, acetone-d_6): δ 152.4, 147.5, 141.9, 140.0, 138.6, 136.7, 128.2, 127.9, 127.6, 126.9, 126.0 (q, J = 286.9 Hz), 125.8 (q, J = 290.3 Hz), 125.3

	(q, J = 284.9 Hz), 125.2 (q, J = 287.5 Hz), 124.4, 123.3, 82.7 (sept, J = 27.9 Hz), 81.0 (sept, J = 28.5 Hz), 52.9, 31.8, 31.1, 24.0, 22.1, 7.6; ^{19}F NMR (376 MHz, acetone-d_6): δ –72.8 (q, J = 9.8 Hz), –74.0 (q, J = 8.3 Hz), –75.2 (q, J = 9.8 Hz), –75.8 (br q, J = 9.0 Hz); ^{29}Si NMR (79 MHz, acetone-d_6): δ –60.9, –62.6; HRMS (ESI, negative) *m/z* calcd for $C_{22}H_{17}F_{12}O_2Si$ $[M–Et_4N]^-$: 569.0803, found: 569.0812; mp: 259-260 °C.
 **2b**	**tetraethylammonium bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolate(2-)-*C*^{2},*O*]-hexenylsilicate (2b)** Following the general procedure A, reaction of **3** (0.514 g, 1.00 mmol) gave the title compound (0.402 mL, 72%, colorless solid). 6-bromo-1-hexene (0.402 mL, 3.00 mmol), magnesium turnings (0.154 g, 6.31 mmol), Et_4NBr (1.05 g, 4.98 mmol). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.25 (d, J = 6.8 Hz, 2H), 7.46 (d, J = 6.4 Hz, 2H), 7.31-7.23 (m, 4H), 5.79-5.69 (m, 1H), 4.87 (d, J = 17.6 Hz, 1H), 4.77 (d, J = 10.8 Hz, 1H), 3.50 (q, J = 7.2 Hz, 8H), 1.90-1.89 (m, 2H), 1.40-1.04 (m,16H), 0.77-0.74 (m, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 146.6, 142.1, 140.8, 138.5, 128.6, 128.5, 126.0 (q, J = 289.3 Hz), 125.7 (q, J = 286.3 Hz), 124.0, 113.8, 82.8 (sept, J = 28.2 Hz), 53.0, 34.6, 34.5, 25.7, 24.0, 7.6; ^{19}F NMR (376 MHz, acetone-d_6): δ –75.2 (q, J = 9.4 Hz), –75.6 (q, J = 9.4 Hz); ^{29}Si NMR (79 MHz, acetone-d_6): δ –64.3; HRMS (ESI, negative) *m/z* calcd for $C_{24}H_{19}F_{12}O_2Si$ $[M–Et_4N]^-$: 595.0968, found: 595.0968; mp: 107-108 °C.

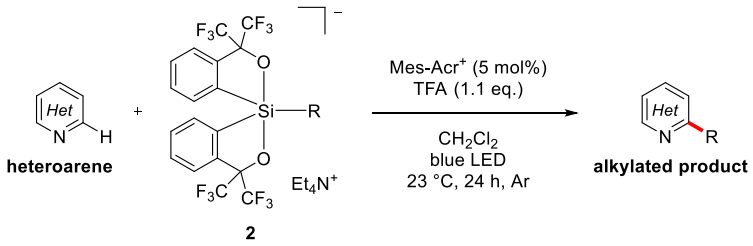
3. Optimization of the C–H alkylation of heteroaromatic compounds

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. 4-Methylquinoline (**4**) (0.1 mmol), cyclohexylsilicate (**2a**) (0.12 mmol), photocatalyst (0.005 mmol), oxidant (0.2 mmol), TFA (0.11 mmol) and solvent (4 mL) were added to the tube, and photoirradiation was carried out with stirring for 24 hours. The Schlenk tube was connected to an argon line during the reaction. The alkylated product was observed by ^{1}H NMR analysis. After the reaction, $NaHCO_3$ *sat*. (20 mL) was added. The obtained organic compounds were extracted with CH_2Cl_2 (3 × 20 mL). Evaporation of the solvents gave a crude material, and yield of **5** was determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

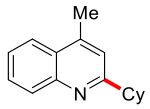
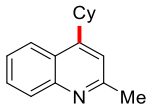
4. Procedure of the C–H alkylation of heteroaromatic compounds

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. The heteroaromatic substrate (0.2 mmol), alkylsilicate **2** (0.24 mmol), Mes-Acr$^+$ (0.01 mmol), TFA (0.22 mmol) and solvent (4 mL) were added to the tube, and photoirradiation was carried out with stirring for 24 hours. The Schlenk tube was connected to an argon line during the reaction. The alkylated product was observed by ^{1}H NMR analysis. After the reaction, Et_3N (0.4 mmol) was added to the solution. Evaporation of the solvents gave a crude material, which was purified with flash chromatography or GPC to give desired product.

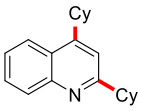
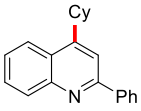
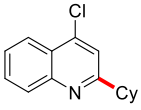
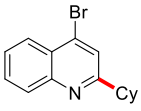
Note: The present photocatalytic alkylation stops before completion when the large-scale reactions were carried out in a sealed flask.



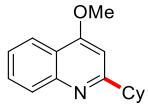
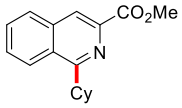
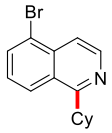
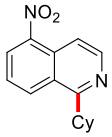
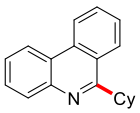
Scheme 3.

 **5**	**2-cyclohexyl-4-methylquinoline (5)**[5] Reaction of 4-methylquinoline (**4**) (29 mg, 0.20 mmol) gave the title compound (32 mg, 72%, colorless liquid). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 6.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.21 (s, 1H), 3.10-2.84 (m, 1H), 2.71 (s, 3H), 2.06-2.00 (m, 2H), 1.97-1.87 (m, 2H), 1.80-1.77 (m, 1H), 1.67-1.58 (m, 2H), 1.51-1.42 (m, 2H), 1.38-1.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 147.7, 144.3, 129.6, 129.0, 127.2, 125.5, 123.7, 120.3, 47.7, 32.9, 26.7, 26.2, 19.0.
 **6**	**2-methyl-4-cyclohexylquinoline (6)**[6] Reaction of 2-methylquinoline (31 mg, 0.21 mmol) gave the title compound (48 mg, 98%, colorless oil). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.19 (s, 1H), 3.30 (br s, 1H), 2.75 (s, 3H), 2.04-1.78 (m, 5H), 1.56-1.51 (m, 4H), 1.37-1.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 153.4, 148.2, 129.6, 128.8, 125.3, 125.2, 122.9, 118.4, 38.9, 33.6, 27.0, 26.4, 25.6.

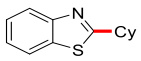
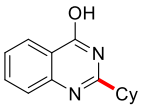
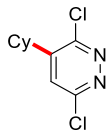
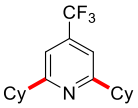
[5] H. Zhao, J. Jin, *Org. Lett*., 2019, **21**, 6179–6184.

 **7**	**2,4-dicyclohexylquinoline (7)**[6] Reaction of quinoline (26 mg, 0.20 mmol) gave the title compound (49 mg, 83%, yellow oil). CH_2Cl_2: 4 mL ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.21 (s, 1H), 3.30 (br s, 1H), 2.89 (t, *J* = 11.8 Hz, 1H), 2.12-1.72 (m, 10H), 1.72-1.28 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 153.5, 148.2, 130.0, 128.7, 125.8, 125.3, 122.9, 115.9, 48.0, 39.1, 33.8, 33.0, 27.1, 26.7, 26.5, 26.3.
 **8**	**2-phenyl-4-cyclohexylquinoline (8)**[6] Reaction of 2-phenylquinoline (39 mg, 0.19 mmol) gave the title compound (41 mg, 76%, colorless solid). CH_2Cl_2: 4 mL ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.6 Hz, 1H), 8.15-8.13 (m, 2H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.75 (s, 1H), 7.71-7.67 (m, 1H), 7.54-7.50 (m, 3H), 7.47-7.45 (m, 1H), 3.40-3.34 (m, 1H), 2.09-2.06 (m, 2H), 1.97-1.94 (m, 2H), 1.89-1.85 (m, 1H), 1.67-1.52 (m, 4H), 1.41-1.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 154.0, 148.7, 140.4, 130.8, 129.2, 129.1, 128.882, 128.878, 127.7, 126.0, 123.0, 115.6, 39.2, 33.8, 27.1, 26.4.
 **9**	**4-chloro-2-cyclohexylquinoline (9)**[6] Reaction of 4-chloroquinoline (33 mg, 0.20 mmol) gave the title compound (43 mg, 88%, colorless oil). CH_2Cl_2: 4 mL ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.43 (s, 1H), 2.89 (t, *J* = 12.0 Hz, 1H), 2.04-2.01 (m, 2H), 1.91-1.88 (m, 2H), 1.81-1.78 (m, 1H), 1.66-1.56 (m, 2H), 1.51-1.41 (m, 2H), 1.38-1.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 148.8, 142.8, 130.3, 129.4, 126.7, 125.3, 124.0, 119.9, 47.5, 32.8, 26.6, 26.1.
 **10**	**4-bromo-2-cyclohexylquinoline (10)**[7] Reaction of 4-bromoquinoline (40 mg, 0.19 mmol) gave the title compound (36 mg, 64%, yellow oil). CH_2Cl_2: 4 mL ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.63 (s, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 2.91-2.85 (m, 1H), 2.04-2.01 (m, 2H), 1.91-1.88 (m, 2H), 1.81-1.78 (m, 1H), 1.68-1.57 (m, 2H), 1.51-1.41 (m, 2H), 1.37-1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 148.6, 134.3, 130.3, 129.5, 127.0, 126.7, 126.6, 123.8, 47.4, 32.8, 26.6, 26.1.

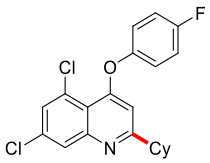
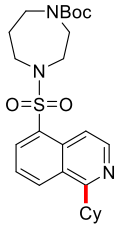
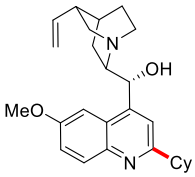
[6] X.-Y. Zhang, W.-Z. Weng, H. Liang, H. Yang, B. Zhang, *Org. Lett*., 2018, **20**, 4686–4690.

 **11**	**4-methoxy-2-cyclohexylquinoline (11)**[6] Reaction of 4-methoxyquinoline (36 mg, 0.22 mmol) gave the title compound (28 mg, 52%, colorless oil). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 6.8 Hz, 1H), 7.42 (t, *J* = 6.8 Hz, 1H), 6.65 (s, 1H), 4.04 (s, 3H), 2.87 (tt, *J* = 8.8, 3.2 Hz, 1H), 2.05-2.02 (m, 2H), 1.91-1.88 (m, 2H), 1.81-1.78 (m, 1H), 1.67-1.57 (m, 2H), 1.52-1.42 (m, 2H), 1.39-1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 162.5, 148.8, 129.7, 128.5, 124.8, 121.6, 120.4, 98.0, 55.5, 48.4, 33.0, 26.7, 26.2.
 **12**	**methyl 1-cyclohexylisoquinoline-3-carboxylate (12)**[6] Reaction of methyl isoquinoline-3-carboxylate (36 mg, 0.19 mmol) gave the title compound (37 mg, 71%, colorless solid). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.28-8.26 (m, 1H), 7.95-7.93 (m, 1H), 7.72-7.69 (m, 2H), 4.03 (s, 3H), 3.60-3.54 (m, 1H), 1.99-1.80 (m, 7H), 1.59-1.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 166.2, 140.8, 136.1, 130.2, 129.2, 129.1, 127.8, 125.1, 122.5, 52.8, 42.1, 32.3, 26.9, 26.2.
 **13**	**5-bromo-1-cyclohexylisoquinoline (13)**[7] Reaction of 5-bromoisoquinoline (42 mg, 0.20 mmol) gave the title compound (39 mg, 67%, yellow oil). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 6.0 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 6.8 Hz, 1H), 7.86 (d, *J* = 5.6 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 3.54 (t, *J* = 11.4 Hz, 1H), 1.98-1.92 (m, 4H), 1.87-1.78 (m, 3H), 1.57-1.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 143.4, 135.6, 133.5, 127.6, 127.2, 124.6, 122.7, 117.8, 41.9, 32.8, 27.0, 26.3.
 **14**	**5-nitro-1-cyclohexylisoquinoline (14)**[6] Reaction of 5-nitroisoquinoline (34 mg, 0.19 mmol) gave the title compound (25 mg, 51%, colorless oil). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 6.0 Hz, 1H), 8.58 (d, *J* = 8.4 Hz, 1H), 8.43 (d, *J* = 7.2 Hz, 1H), 8.22 (d, *J* = 6.0 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 3.57 (t, *J* = 11.4 Hz, 1H), 2.06-1.80 (m, 7H), 1.54-1.45 (m, 2H), 1.45-1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 146.1, 145.4, 131.5, 129.0, 127.4, 127.0, 125.3, 113.6, 42.3, 32.9, 26.9, 26.2.
 **15**	**6-cyclohexylphenanthridine (15)**[6] Reaction of phenanthridine (35 mg, 0.20 mmol) gave the title compound (43 mg, 83%, colorless oil). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 7.6 Hz, 1H), 8.30

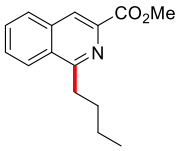
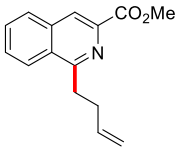
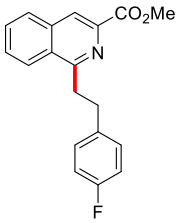
[7] X.-L. Lyu, S.-S. Huang, H.-J. Song, Y.-X. Liu, Q.-M. Wang, *Org. Lett*., 2019, **21**, 5728–5732.

	(d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.72-7.67 (m, 2H), 7.59 (t, *J* = 7.0 Hz, 1H), 3.63-3.57 (m, 1H), 2.09-1.71 (m, 7H), 1.62-1.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 144.0, 133.1, 130.05, 130.02, 128.5, 127.2, 126.2, 125.7, 124.8, 123.4, 122.7, 121.9, 42.1, 32.4, 27.0, 26.4.
 **16**	**2-cyclohexylbenzothiazole (16)**[6] Reaction of benzothiazole (31 mg, 0.23 mmol) gave the title compound (24 mg, 47%, colorless oil). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 3.15-3.08 (m, 1H), 2.21 (d, *J* = 12.0 Hz, 2H), 1.89 (d, *J* = 12.8 Hz, 2H), 1.77 (d, *J* = 12.4 Hz, 1H), 1.70-1.63 (m, 2H), 1.45 (q, *J* = 12.8 Hz, 2H), 1.37-1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.8, 153.2, 134.7, 125.9, 124.6, 122.7, 121.7, 43.6, 33.6, 26.2, 25.9.
 **18**	**2-cyclohexyl-4-hydroxyquinazoline (18)**[8] Reaction of 4-hydroxyquinazoline (29 mg, 0.20 mmol) gave the title compound (29 mg, 64%, colorless solid). CH_3CN/H_2O: 4 mL (1/1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.8 (br s, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 7.79-7.71 (m, 2H), 7.49-7.45 (m, 1H), 2.78-2.72 (m, 1H), 2.08-2.05 (m, 2H), 1.95-1.92 (m, 2H), 1.83-1.74 (m, 3H), 1.51-1.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 160.4, 149.7, 134.8, 127.5, 126.4, 126.3, 120.9, 45.0, 30.6, 26.2, 25.8.
 **19**	**2-cyclohexyl-4-hydroxyquinazoline (19)**[6] Reaction of 3,6-dichloropyridazine (29 mg, 0.20 mmol) gave the title compound (15 mg, 33%, colorless oil). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 2.90-2.84 (m, 1H), 1.98-1.90 (m, 4H), 1.84-1.81 (m, 1H), 1.51-1.41 (m, 2H), 1.37-1.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 156.4, 148.8, 127.2, 40.2, 31.9, 26.3, 25.8.
 **20**	**2,6-dicyclohexyl-4-(trifluoromethyl)pyridine (20)**[6] Reaction of 4-(trifluoromethyl)pyridine (30 mg, 0.21 mmol) gave the title compound (27 mg, 43%, colorless oil). Cyclohexylsilicate (0.32 g, 0.44 mmol), CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 2H), 2.78-2.72 (m, 2H), 1.98-1.95 (m, 4H), 1.87-1.84 (m, 4H), 1.78-1.74 (m, 2H), 1.56-1.38 (m, 8H), 1.33-1.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 138.8 (q, *J* = 32.1 Hz), 123.5 (q, *J* = 271.4 Hz), 113.6, 46.7, 33.0, 26.6, 26.1.

[8] N. Y. Kim, C.-H. Cheon, *Tetrahedron Lett.*, 2014, **55**, 2340-2344.

 **21**	**5,7-dichloro-2-cyclohexyl-4-(4-fluorophenoxy)quinoline (21)**[6] Reaction of 5,7-dichloro-4-(4-fluorophenoxy)quinoline (62 mg, 0.20 mmol) gave the title compound (51 mg, 65%, colorless solid). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.18-7.09 (m, 4H), 6.52 (s, 1H), 2.71-2.66 (m, 1H), 1.89-1.81 (m, 4H), 1.74-1.71 (m, 1H), 1.49-1.23 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 162.4, 160.0 (d, *J* = 242.6 Hz), 151.5, 150.4 (d, *J* = 2.6 Hz), 134.9, 130.0, 128.7, 127.6, 122.1 (d, *J* = 8.3 Hz), 117.2 (d, *J* = 13.6 Hz), 117.0, 105.8, 47.4, 32.5, 26.4, 26.0.
 **22'**	**Compound 22'** 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. Fasudil (29 mg, 0.10 mmol, prepared from commercially available fasudil hydrochloride by washing with sodium hydroxide solution, extraction with CH_2Cl_2, and then concentration in vacuo), cyclohexylsilicate **2a** (88 mg, 0.12 mmol), Mes-Acr$^+$ (2.3 mg, 0.0055 mmol), TFA (24 mg, 0.21 mmol) and CH_2Cl_2 (4 mL) were added to the tube, and photoirradiation was carried out with stirring for 24 hours. To the solution was added K_2CO_3 (approximate 150 mg), and the mixture was vigorously stirred for 5 min. After that, the mixture was filtrated through a pad of Celite and washed with CH_2Cl_2. The filtrate was concentrated in vacuo and the residue was dissolved in CH_2Cl_2 (5 mL). Alkylated compound **22** was observed by ^{1}H NMR analysis. To the solution was added Boc_2O (44 mg, 0.2 mmol) and Et_3N (30 mg, 0.3 mmol), and then the mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo and the residue was purified by flash chromatography and GPC to afford compound **22'** (20 mg, 43% for 2 steps) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.4 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 8.32–8.23 (m, 2H), 7.65 (t, *J* = 6.6 Hz, 1H), 3.57–3.51 (m, 5H), 3.42–3.37 (m, 4H), 1.97–1.95 (m, 6H), 1.88–1.82 (m, 3H), 1.61–1.49 (m, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 155.3, 154.9, 144.1, 135.1, 132.6, 132.3, 130.5, 127.1, 125.3, 115.4, 80.1, 80.0, 50.2, 50.0, 49.5, 49.4, 47.8, 47.5, 46.1, 45.6, 42.2, 32.9, 28.7, 28.5, 28.3, 26.9, 26.3. Spectral data are consistent with those reported in the literature.[9]
 **23**	**Compound 23** 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. Quinine (63 mg, 0.20 mmol), cyclohexylsilicate **2a** (0.18 g, 0.25 mmol), Mes-Acr$^+$ (4.7 mg, 0.011 mmol), TFA (48 mg, 0.42 mmol) and 1,1,1,3,3,3-hexafluoro-2-propanol (4 mL) were added to the tube, and photoirradiation was carried out with stirring for

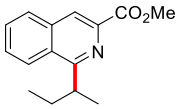
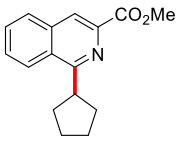
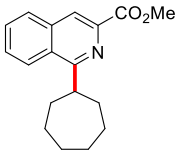
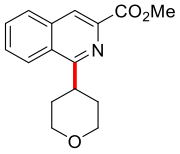
[9] J. Wang, G.-X. Li, G. He, G. Chen, *Asian J. Org. Chem.*, 2018, **7**, 1307–1310.

	24 hours. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (3 mL). To the solution was added K_2CO_3 (approximate 150 mg), the mixture was vigorously stirred for 5 min. The mixture was filtrated through a pad of Celite and washed with CH_2Cl_2. The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography on silica gel to afford compound **23** (39 mg, 49%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.2 Hz, 1H), 7.48 (s, 1H), 7.30 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.19 (d, *J* = 2.0 Hz, 1H), 5.77-5.69 (m, 1H), 5.57 (d, *J* = 2.8 Hz, 1H), 4.98-4.90 (m, 2H), 3.88 (s, 3H), 3.49 (br s, 1H), 3.13- 3.08 (m, 2H), 2.84-2.78 (m, 1H), 2.70-2.67 (m, 2H), 2.27 (br s, 1H), 1.94-1.92 (m, 2H), 1.84-1.73 (m, 6H), 1.56-1.25 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 157.3, 147.7, 144.0, 142.0, 131.3, 125.2, 121.1, 116.8, 114.5, 101.4, 72.4, 60.0, 57.3, 55.8, 47.5, 43.5, 40.1, 33.0, 28.1, 27.7, 26.6, 26.2, 21.5. Spectral data are consistent with those reported in the literature.[10]
 **24**	**methyl 1-butylisoquinoline-3-carboxylate (24)**[11] Reaction of methyl isoquinoline-3-carboxylate (37 mg, 0.20 mmol) and *n*butylsilicate **2c** (0.17 g, 0.24 mmol) gave the title compound (28 mg, 58%, pale yellow solid). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.22 (d, *J* = 7.2 Hz, 1H), 7.96-7.94 (m, 1H), 7.76-7.70 (m, 2H), 4.05 (s, 3H), 3.38 (t, *J* = 8.0 Hz, 2H), 1.88-1.81 (m, 2H), 1.57-1.47 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 163.4, 140.7, 136.0, 130.6, 129.4, 129.0, 128.5, 125.8, 123.0, 53.0, 35.8, 32.4, 23.2, 14.1.
 **25**	**methyl 1-(but-3-en-1-yl)isoquinoline-3-carboxylate (25)**[12] Reaction of methyl isoquinoline-3-carboxylate (36 mg, 0.19 mmol) and butenylsilicate **2d** (0.17 g, 0.24 mmol) gave the title compound (19 mg, 41%, colorless solid). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.22 (d, *J* = 7.2 Hz, 1H), 7.98-7.96 (m, 1H), 7.76-7.73 (m, 2H), 6.04-5.94 (m, 1H), 5.13 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.03 (d, *J* = 10.4 Hz, 1H), 4.05 (s, 3H), 3.48 (t, *J* = 8.0 Hz, 2H), 2.67-2.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 162.3, 140.7, 137.8, 136.0, 130.7, 129.5, 129.1, 128.5, 125.6, 123.1, 115.3, 53.0, 35.0, 33.9.
 **26**	**methyl 1-(2-(4-fluorophenyl))ethylisoquinoline-3-carboxylate (26)** Reaction of methyl isoquinoline-3-carboxylate (37 mg, 0.19 mmol) and 2-(4-fluorophenyl)ethyl silicate **2e** (0.19 g, 0.24 mmol) gave the title compound (40 mg, 67%, yellow solid). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.2

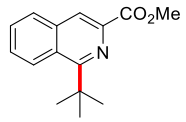
[10] G.-X. Li, C. A. Morales-Rivera, Y. Wang, F. Gao, G. He, P. Liu, G. Chen, *Chem. Sci.*, 2016, **7**, 6407–6412

[11] C. D. Gilmore, K. M. Allan, B. M. Stoltz, *J. Am. Chem. Soc*., 2008, **130**, 1558–1559.

[12] J. K. Matsui, D. N. Primer, G. A. Molander, *Chem. Sci*., 2017, **8**, 3512–3522.

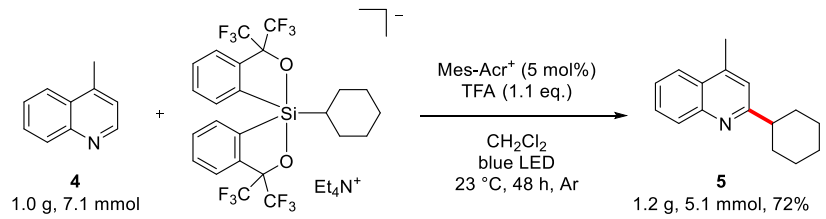
	Hz, 1H), 7.77-7.68 (m, 2H), 7.27-7.23 (m, 2H), 6.97 (t, J = 8.8 Hz, 2H), 4.06 (s, 3H), 3.68-3.64 (m, 2H), 3.20 (t, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 161.6, 161.5 (d, J = 242.2 Hz), 140.7, 137.3 (d, J = 3.3 Hz), 136.0, 130.7, 130.0 (d, J = 7.9 Hz), 129.6, 129.1, 128.5, 125.3, 123.2, 115.3 (d, J = 21.0 Hz), 53.0, 37.3, 34.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ –117.3; HRMS (ESI, positive) *m/z* calcd for $C_{19}H_{17}FNO_2$ $[M+H]^+$: 310.1238, found: 310.1237; mp: 108-110 °C; IR (KBr): 1713, 1509, 1450, 1329, 1297, 1249, 1218, 987, 837, 747 cm^{-1}.
 **27**	**methyl 1-(*sec*-butyl)isoquinoline-3-carboxylate (27)**[13] Reaction of methyl isoquinoline-3-carboxylate (36 mg, 0.19 mmol) and ^{s}butylsilicate **2f** (0.17 g, 0.24 mmol) gave the title compound (33 mg, 71%, colorless oil). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.28 (d, J = 6.8 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.74-7.69 (m, 2H), 4.03 (s, 3H), 3.76-3.68 (m, 1H), 2.12-2.05 (m, 1H), 1.85-1.78 (m, 1H), 1.46 (d, J = 6.8 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 166.5, 140.8, 136.1, 130.2, 129.1, 128.4, 125.1, 122.5, 52.8, 38.7, 29.5, 19.9, 12.6. (One peak is missing.)
 **28**	**methyl 1-cyclopentylisoquinoline-3-carboxylate (28)**[14] Reaction of methyl isoquinoline-3-carboxylate (37 mg, 0.20 mmol) and cyclopentylsilicate **2g** (0.17 g, 0.24 mmol) gave the title compound (41 mg, 81%, colorless oil). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.30-8.28 (m, 1H), 7.95-7.93 (m, 1H), 7.74-7.68 (m, 2H), 4.02-3.99 (m, 4H), 2.20-2.18 (m, 4H), 1.95-1.94 (m, 2H), 1.80-1.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 165.1, 140.5, 136.0, 130.3, 129.1, 129.0, 128.7, 125.6, 122.6, 52.8, 43.9, 32.6, 26.0.
 **29**	**methyl 1-cycloheptylisoquinoline-3-carboxylate (29)**[14] Reaction of methyl isoquinoline-3-carboxylate (36 mg, 0.19 mmol) and cycloheptylsilicate **2h** (0.18 g, 0.24 mmol) gave the title compound (35 mg, 63%, colorless oil). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.28-8.24 (m, 1H) 7.96-7.92 (m, 1H), 7.74-7.68 (m, 2H), 4.02 (s, 3H), 3.76-3.72 (m, 1H), 2.12-2.07 (m, 4H), 1.94-1.91 (m, 2H), 1.79-1.69 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 167.0, 140.6, 136.2, 130.2, 129.2, 129.1, 127.6, 125.3, 122.5, 52.8, 44.2, 34.3, 28.2, 27.7.
 **30**	**methyl 1-(4-tetrahydropyranyl)isoquinoline-3-carboxylate (29)**[13] Reaction of methyl isoquinoline-3-carboxylate (37 mg, 0.20 mmol) and 4-tetrahydropyranylsilicate **2i** (0.17 g, 0.24 mmol) gave the title compound (35 mg, 66%, colorless solid). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.30-8.25 (m, 1H), 8.00-7.95 (m, 1H),

[13] G.-X. Li, X. Hu, G. He, G. Chen, *ACS Catal*., 2018, **8**, 11847–11853.

	7.78-7.70 (m, 2H), 4.19 (dd, *J* = 11.2, 2.4 Hz, 2H), 4.03 (s, 3H), 3.89-3.78 (m, 1H), 3.77-3.65 (m, 2H), 2.42-2.28 (m, 2H), 1.90 (d, *J* = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 163.9, 140.8, 136.2, 130.4, 129.4, 129.3, 127.7, 124.6, 122.9, 68.2, 52.8, 39.3, 32.0
 **31**	**methyl 1-(*tert*-butyl)isoquinoline-3-carboxylate (31)**[13] Reaction of methyl isoquinoline-3-carboxylate (37 mg, 0.20 mmol) and ᵗbutylsilicate **2j** (0.17 g, 0.24 mmol) gave the title compound (29 mg, 60%, colorless solid). CH_2Cl_2: 4 mL ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 6.8 Hz, 1H), 8.41 (s, 1H), 7.98-7.96 (m, 1H), 7.72-7.66 (m, 2H), 4.03 (s, 3H), 1.70 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 167.0, 139.4, 137.3, 129.9, 129.6, 128.1, 127.8, 127.5, 123.3, 52.7, 40.4, 31.2.

5. Procedure of gram scale photocatalytic alkylation.

A 300 mL flask equipped with a magnetic stirring bar and a septum, was dried under vacuum with heating. After the flask was cooled to room temperature, it was purged with argon. 4-Methylquinoline (**4**) (1.02 g, 7.13 mmol), cyclohexylsilicate **2a** (6.08 g, 8.38 mmol), Mes-Acr$^+$ (0.145 g, 0.353 mmol), TFA (0.867 g, 7.61 mmol) and CH_2Cl_2 (80 mL) were added to the flask, and photoirradiation was carried out with stirring for 48 hours. The flask was connected to an argon line during the reaction. After the reaction, Et_3N (1.95 mL, 14.0 mmol) was added to the solution. Evaporation of the solvents gave a crude material, which was purified with flash chromatography to give desired product **5** (1.15 g, 72%).



Scheme S4. Gram scale synthesis of **5**.

6. Stern-Volmer quenching experiment

Stern-Volmer fluorescence quenching experiments were run with freshly prepared 5.0×10^{-5} M solutions of Mes-Acr^+ in CH_2Cl_2 under an argon atmosphere using Jasco's spectrofluorometer (FP-6500). Concentration of an additive (**Q**: silicate **2a**, 2-cyclohexyl-2,3-dihydrobenzo[*d*]thiazole (**16'**), spirosilane **3**, benzothiazole+TFA, benzothiazole, TFA) was between 0 M and 0.025 M. The solution was irradiated at 429 nm, and fluorescence was measured at 510 nm. The fluorescence intensity was measured three times in the presence and absence of the additives (Tables S1-S6), and their ratio was plotted based on the Stern–Volmer expression as shown in eq S1 (Figure S3).

Table S1. Luminescence quenching data for Mes-Acr^+ and silicate **2a**.

I_{obs}					
Run 1	Run 2	Run 3	average	I_0/I_{obs}	silicate **2a** (M)
545	542	544	544	1	0
126	124	127	126	4.30	0.005
80.8	81.3	82.3	81.4	6.68	0.01
63.5	64.1	64.5	64.0	8.49	0.015
55.4	55.0	55.4	55.2	9.84	0.02
46.2	47.0	47.3	46.8	11.6	0.025

Table S2. Luminescence quenching data for Mes-Acr^+ and **16'**.

I_{obs}					
Run 1	Run 2	Run 3	average	I_0/I_{obs}	**16'** (M)
555	550	561	555	1	0
342	342	344	343	1.62	0.005
246	246	247	246	2.25	0.01
191	191	192	191	2.89	0.015
156	155	156	155	3.56	0.02
128	128	128	128	4.32	0.025

Table S3. Luminescence quenching data for Mes-Acr$^+$ and benzothiazole+TFA.

I_{obs}					
Run 1	Run 2	Run 3	average	I_0/I_{obs}	benzothiazole+TFA (M)
566	565	565	565	1	0
545	547	547	546	1.03	0.005
548	549	551	549	1.02	0.01
527	528	529	528	1.07	0.015
544	547	545	545	1.03	0.02
533	535	537	535	1.05	0.025

Table S4. Luminescence quenching data for Mes-Acr$^+$ and spirosilane (**3**).

I_{obs}					
Run 1	Run 2	Run 3	average	I_0/I_{obs}	spirosilane **3** (M)
551	553	551	552	1	0
562	561	563	562	0.98	0.005
559	561	561	560	0.98	0.01
560	560	560	560	0.98	0.015
567	569	568	568	0.97	0.02
585	583	582	583	0.94	0.025

Table S5. Luminescence quenching data for Mes-Acr$^+$ and benzothiazole.

I_{obs}					
Run 1	Run 2	Run 3	average	I_0/I_{obs}	benzothiazole (M)
569	571	565	568	1	0
518	518	519	518	1.09	0.005
514	512	513	513	1.10	0.01
502	502	500	501	1.13	0.015
484	485	483	484	1.17	0.02
469	468	469	469	1.21	0.025

Table S6. Luminescence quenching data for Mes-Acr^{+} and TFA.

I_{obs}					
Run 1	Run 2	Run 3	average	I_0/I_{obs}	TFA (M)
573	571	570	571	1	0
569	569	569	569	1.00	0.005
589	587	587	588	0.97	0.01
571	572	572	572	0.99	0.015
573	571	571	572	0.99	0.02
572	574	573	573	0.99	0.025

$$\frac{I_0}{I_{obs}} = 1 + t_0 k_q [Q] \qquad (S1)$$

I_0: the intensity of fluorescence without the additive

I_{obs}: the intensity of fluorescence in the presence of the additive

t_0: the lifetime of the excited state of Ru(II) without the additive

k_q: the quencher rate coefficient

[**Q**]: the concentration of the additive

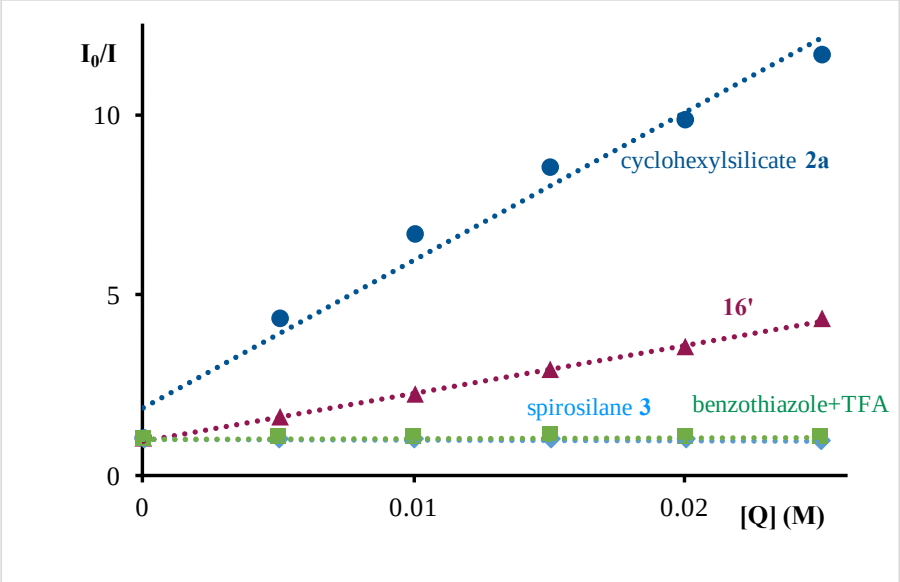
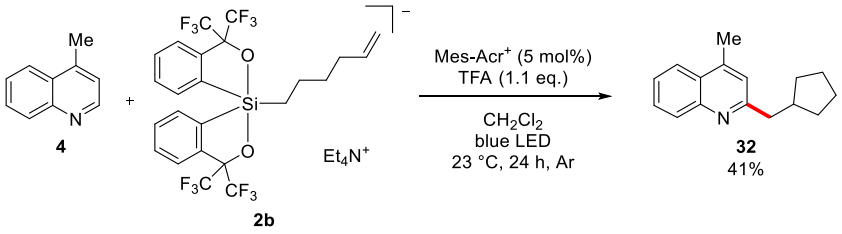


Figure S3.

7. A radical clock experiment

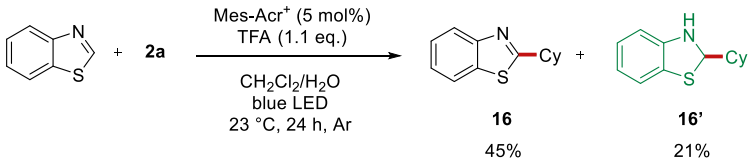
A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the tube to 23 °C, it was purged with argon gas. 4-Methylquinoline (**4**) (28 mg, 0.20 mmol), alkylsilicate **2b** (0.18 g, 0.24 mmol), Mes-Acr$^+$ (5.8 mg, 0.013 mmol), TFA (26 mg, 0.23 mmol) and CH_2Cl_2 (4 mL) were added to the tube, and photoirradiation was carried out with stirring for 24 hours. The Schlenk tube was connected to an argon line during the reaction. After the reaction, Et_3N (40 mg, 0.40 mmol) was added to the solution. Evaporation of the solvents gave a crude material, which was purified with flash chromatography to give desired product **32** (18 mg, 41%) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.69-7.65 (m, 1H), 7.52-7.48 (m, 1H), 7.14 (s, 1H), 2.93 (d, J = 7.2 Hz, 2H), 2.68 (s, 3H), 2.36 (quin, J = 7.6 Hz, 1H), 1.75-1.66 (m, 4H), 1.55-1.52 (m, 2H), 1.32-1.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4, 147.9, 144.0, 129.5, 129.1, 126.9, 125.5, 123.7, 122.6, 45.3, 40.9, 32.7, 25.1, 18.9. Spectral data are consistent with those reported in the literature.[14]



Scheme S5.

8. Observation of an intermediate

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. Benzothiazole (13 mg, 0.095 mmol), cyclohexylsilicate (**2a**) (91 mg, 0.13 mmol), Mes-Acr$^+$ (2.7 mg, 0.0066 mmol), TFA (13 mg, 0.11 mmol) and CH_2Cl_2/H_2O (1/1, 4 mL) were added to the tube, and photoirradiation was carried out with stirring for 24 hours. The obtained organic compounds were extracted with CH_2Cl_2 (3 × 20 mL). Evaporation of the solvents gave a crude material, and yields of **16** and **16'** were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.



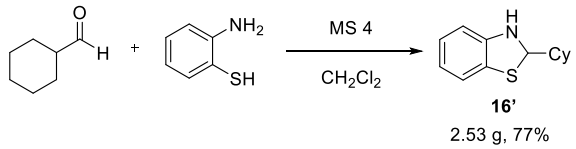
Scheme S6. Observation of the intermediate.

[14] J. Dong, X. Lyu, Z. Wang, X. Wang, H. Song, Y. Liu, Q. Wang, *Chem. Sci*., 2019, **10**, 976–982.

9. Dehydrogenation reaction

Synthesis of 2-cyclohexyl-2,3-dihydrobenzo[*d*]thiazole (16'):

To a stirred solution of cyclohexanecarboxaldehyde (2.52 g, 22.5 mmol) in dichloromethane (22.5 ml) was added 4Å molecular sieves (15.0 g). 2-Aminothiophenol (1.88 g, 15.0 mmol) was added dropwise to the mixture and stirred at room temperature for 2 h. After completion of the reaction, the reaction mixture was filtered to remove the molecular sieves. The solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the desired product **16'** (2.53 g, 77%) as colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, J = 6.8 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.67 (t, J = 6.4 Hz, 1H), 6.56 (d, J = 7.6 Hz, 1H), 5.06 (d, J = 6.8 Hz, 1H), 4.11 (br s, 1H), 1.85-1.82 (m, 1H), 1.77-1.74 (m, 3H), 1.68-1.64 (m, 2H), 1.24-0.94 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 127.1, 125.0, 121.6, 120.2, 109.9, 74.1, 45.3, 29.3, 29.1, 26.3, 25.80, 25.79; HRMS (ESI, positive) *m/z* calcd for $C_{13}H_{18}NS$ $[M+H]^+$: 220.1154, found: 220.1153; mp: 83-85 °C; IR (KBr): 3362, 2925, 2850, 1579, 1475, 1405, 1305, 1232, 1205, 734 cm^{-1}.

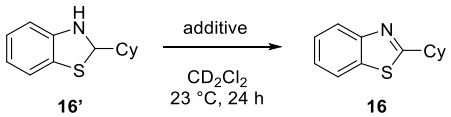


Scheme S7.

Dehydrogenation reaction:

2-Cyclohexyl-2,3-dihydrobenzo[*d*]thiazole **16'** (0.02 mmol), an additive (silicate **2a**, spirosilane **3**, TFA, Mes-Acr$^+$) (0.02 mmol) and CD_2Cl_2 (0.7 mL) were added to an NMR tube. It was purged with argon gas. Yield of **16** was determined by ^{1}H NMR analysis.

Table 7.



entry	additive	yield of **16**[a]
1	cyclohexylsilicate **2a** (1.0 eq.)	0
2	spirosilane **3** (1.0 eq.)	0
3	TFA (1.0 eq.)	0
4	Mes-Acr (5 mol%)	0
5[b]	Mes-Acr (5 mol%)	38
6[b]	Mes-Acr (5 mol%), TFA (1.0 eq.)	100

[a] Yields are determined by ^{1}H NMR spectroscopy. [b] Blue light was irradiated.

10. Computational study of photocatalytic dehydrogenation

Density functional theory (DFT) calculations were conducted at the (U)B3LYP/6-311G+(d,p) level to gain insight into the reaction mechanism of photocatalytic dehydrogenation of intermediate **II** as solvated molecules using the PCM method considering solvation by CH_2Cl_2 using the Gaussian 09 program.[15] The natural population analysis (NPA) analysis was conducted using the Gaussian 16 program.[16] We chose 2-methylbenzothiazoline **S1** as a model intermediate. Stern-Volmer experiments indicate that the radical cation of **S1** could be generated by the excited state of the photocatalyst (Figure S3). The NPA analysis revealed that **S1** has more negative hydrogen atom and radical cation of **S1** has more positive hydrogen atom than that in methane (Figure S4). These observations are consistent with previous reports that hydrogen atom in **S1** reacts as hydride[17] and radical cation of a nitrogen-containing compound easily deprotonates the alpha position of the nitrogen atom.[18] Based on such the reactivity and DFT calculations, an energy profile of a plausible reaction mechanism for dehydrogenation of **S1** to give **S4** is shown in Figure S5a. In the proposed reaction mechanism, hydrogen molecule is formed together with protonated 2-methylbenzothiazole **S2** and radical **S3** from **S1** and its radical cation. Sum of calculated Gibbs free energy of hydrogen molecule, protonated 2-methylbenzothiazole **S2** and radical **S3** is only 5.7 kcal/mol higher than that of **S1** and its radical cation. Proton transfer from **S2** to **S3**, which is thermodynamically favored by 12.0 kcal/mol, gives desired product **S4** and radical cation of **S1**. Resulting radical cation of **S1** would be quenched by reduced photocatalyst or react with other **S1** again. TFA would facilitate protonation of **S3** and **S4**, which makes the dehydrogenation process irreversible (Figure S5b).

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[15] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[16] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[17] C. Zhu, T. Akiyama, *Org. Lett*., 2009, **11**, 4180–4183.

[18] G. W. Dombrowski, J. P. Dinnocenzo, *J. Org. Chem.*, 2005, **70**, 3791–3800.

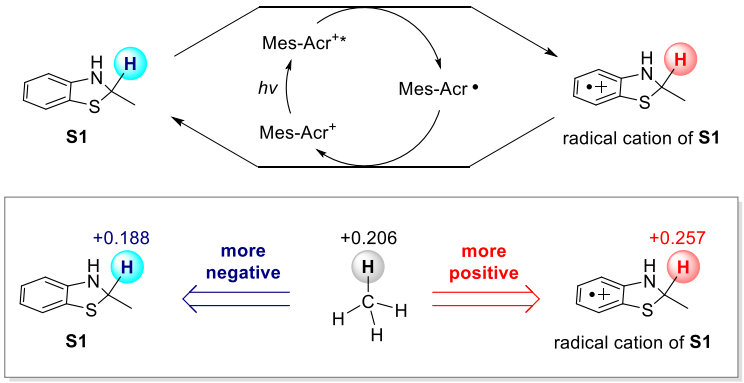

Figure S4.

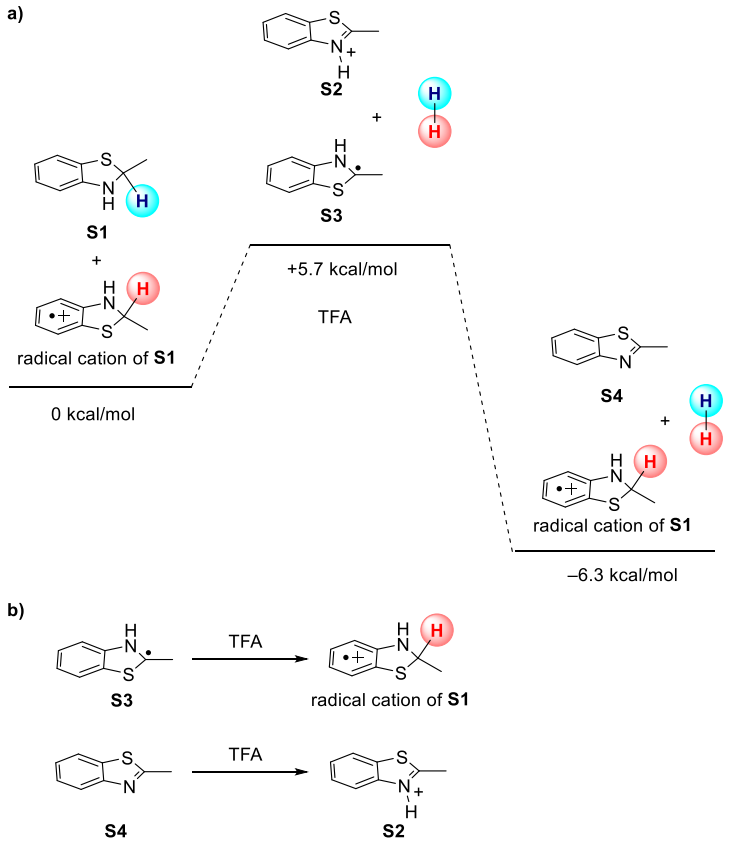

Figure S5

Cartesian Coordinates:

S1

C	-2.86572400	-0.58209500	0.01946500
C	-1.67803400	-1.32556000	0.00493600
C	-0.46509500	-0.65326500	-0.00066000
C	-0.41033600	0.75169800	0.01502000
C	-1.59364400	1.48822100	0.02282000
C	-2.81796400	0.81095800	0.02539100

H	-3.81980900	-1.09572500	0.01840100
H	-1.70778600	-2.40892100	-0.00706000
H	-1.56248800	2.57227300	0.03296400
H	-3.73898800	1.38277600	0.02842900
N	0.88904700	1.26140400	0.08615900
H	1.01093700	2.20363500	-0.26501100
S	1.17549600	-1.35059200	0.02839300
C	1.89842900	0.31324100	-0.40030800
C	3.26344900	0.53001500	0.22876500
H	3.20400700	0.46164600	1.31641200
H	1.97751500	0.35052100	-1.49429900
H	3.63830600	1.52183200	-0.04104600
H	3.98055800	-0.20767500	-0.13876000

E = -763.34109432 a.u.

Radical cation of **S1**

C	-2.79042200	-0.59989000	0.19711700
C	-1.62910000	-1.34934600	0.12081800
C	-0.41733800	-0.67467600	-0.04283200
C	-0.38824800	0.75669700	-0.12985600
C	-1.58456400	1.50511800	-0.04550200
C	-2.76346400	0.81831300	0.11496900
H	-3.74138600	-1.10218700	0.32199100
H	-1.65611400	-2.42913400	0.18363300
H	-1.55634200	2.58552900	-0.10692100
H	-3.69542400	1.36551600	0.18011300
N	0.84862400	1.24740600	-0.28517000
H	1.02657400	2.24158600	-0.37265700
S	1.16871200	-1.35905800	-0.15644900
C	1.95514700	0.30716400	-0.36887600
C	3.05536800	0.58156100	0.65344300
H	2.66074100	0.55558400	1.66942900
H	2.36196200	0.32565500	-1.38503600
H	3.84520900	-0.16370900	0.55357300
H	3.49074400	1.56459300	0.45956900

E = -763.14697163 a.u.

S2

C	-2.82258900	-0.57246400	0.00702500
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C	-0.44457700	-0.65762100	0.00266700
C	-0.39915900	0.74294400	-0.00194700
C	-1.56380600	1.51097000	-0.00223500
C	-2.77341200	0.83192000	0.00282000
H	-3.78390700	-1.07094900	0.01036100
H	-1.70269100	-2.41797500	0.00888200
H	-1.52043300	2.59294600	-0.00599800
H	-3.69737300	1.39630900	0.00327700
N	0.91898600	1.19844300	-0.01126500
H	1.15315100	2.18681500	-0.01401100
S	1.18771900	-1.31305100	-0.00875900
C	1.85922400	0.26650100	-0.01253600
C	3.31593200	0.55554200	0.01663800
H	3.66296900	0.57773700	1.05431000
H	3.52434300	1.52387700	-0.43955800
H	3.87451400	-0.21653600	-0.51115800

E = -762.57739220 a.u.

S3

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C	-1.65653100	-1.32472700	0.03484600
C	-0.44246500	-0.65337500	-0.00941600
C	-0.38948200	0.75468600	-0.02469200
C	-1.57345000	1.49826600	-0.01016100
C	-2.79171800	0.81840900	0.03588200
H	-3.79515200	-1.08766400	0.09422500
H	-1.68830100	-2.40777700	0.04749000
H	-1.54173500	2.58163700	-0.03173300
H	-3.71380900	1.38824400	0.04890100
N	0.90311100	1.23493400	-0.04355100
H	1.09505300	2.21688100	-0.18067600
S	1.19570000	-1.33983600	-0.03773800
C	1.91373600	0.28413600	-0.27517400
C	3.30653600	0.56291700	0.19036600
H	3.38746900	0.58857400	1.28913400
H	3.64654700	1.53052800	-0.19116000

H	3.99816000	-0.19626400	-0.18044200

E = -762.69717794 a.u.

H_2

H	0.00000000	0.00000000	0.37225700
H	0.00000000	0.00000000	-0.37225700

E = -1.17970042 a.u.

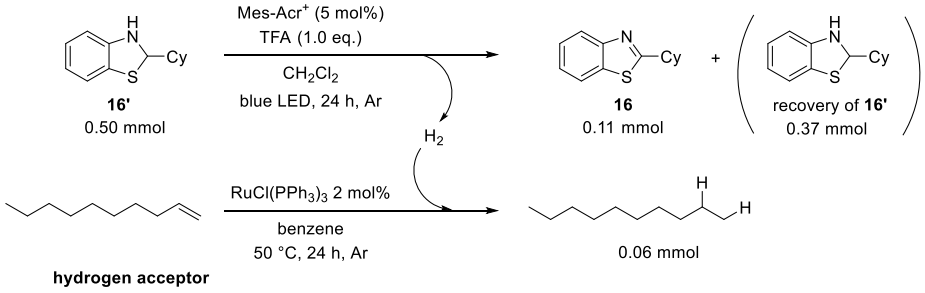
S4

C	-2.80995400	-0.55685500	0.00001700
C	-1.64707000	-1.32098700	0.00002700
C	-0.42245900	-0.65184800	-0.00000100
C	-0.35130500	0.75913900	-0.00002700
C	-1.53317000	1.51034300	-0.00002700
C	-2.75313800	0.84624700	-0.00000200
H	-3.77279500	-1.05444400	0.00002800
H	-1.69502800	-2.40307700	0.00002800
H	-1.47958500	2.59260800	-0.00003800
H	-3.67430400	1.41721600	-0.00000700
N	0.93391500	1.28698800	0.00003200
S	1.20396700	-1.30503000	-0.00002300
C	1.83520200	0.36096300	0.00002200
C	3.30956100	0.60507600	0.00001800
H	3.78056800	0.16349100	0.88217200
H	3.49383600	1.67914000	0.00037400
H	3.78041700	0.16417100	-0.88257000

E = -762.14638788 a.u.

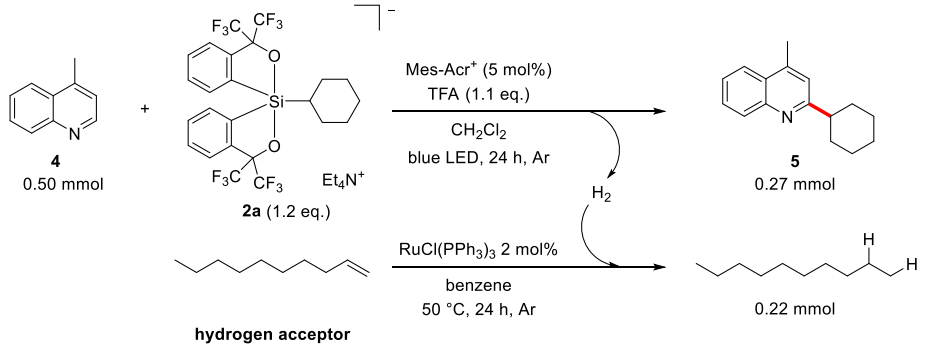
11. Detection of hydrogen gas

Formation of H_2 from **16'** was confirmed by the following experiment of Ru-catalyzed hydrogenation of 1-decene. An H-type flask was used, in which two test tubes were connected with a glass tube. In a left tube, under argon atmosphere, Mes-Acr$^+$ (5.0 mol %), **16'** (0.50 mmol), TFA (0.50 mmol) and dichloromethane (3.5 mL) were placed. In a right flask, under argon atmosphere, $RhCl(PPh_3)_3$ (2.0 mol %), 1-decene (1.0 mmol), and benzene (3 mL) were placed. The H-type flask was sealed. The mixture in the left flask was stirred and irradiated at room temperature for 24 h, while the mixture in the right flask was stirred at 50 °C. Formation of 0.11 mmol of dehydrogenated product **16** and recovery of 0.37 mmol of **16'** was observed by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The yield of decane was determined by GC analysis using dodecane as an internal standard. In the right flask, 0.06 mmol of decane was produced, which means at least 0.06 mmol of H_2 was evolved from 0.11 mmol of **16'** in the left flask and transferred to the right flask.



Scheme S8.

Formation of H_2 in the photocatalytic alkylation of lepidine (**4**) and cyclohexylsilicate **2a** was confirmed by the following experiment of Ru-catalyzed hydrogenation of 1-decene. An H-type flask was used, in which two test tubes were connected with a glass tube. In a left tube, under argon atmosphere, Mes-Acr$^+$ (5.0 mol %), **4** (0.50 mmol), **2a** (0.60 mmol), TFA (0.55 mmol) and dichloromethane (3.5 mL) were placed. In a right flask, under argon atmosphere, $RhCl(PPh_3)_3$ (2.0 mol %), 1-decene (1.0 mmol), and benzene (3 mL) were placed. The H-type flask was sealed. The mixture in the left flask was stirred and irradiated at room temperature for 24 h, while the mixture in the right flask was stirred at 50 °C. Formation of 0.27 mmol of alkylated product **5** was observed by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The yield of decane was determined by GC analysis using dodecane as an internal standard. In the right flask, 0.22 mmol of decane was produced, which means at least 0.22 mmol of H_2 was evolved in the left flask and transferred to the right flask.

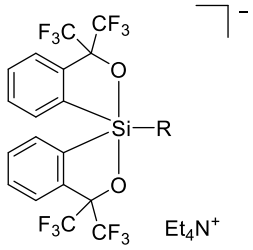


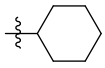
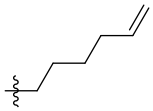
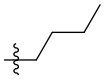
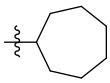
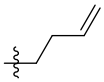
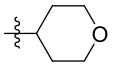
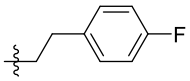
Scheme 9.

12. Electrochemical property of alkylsilicates

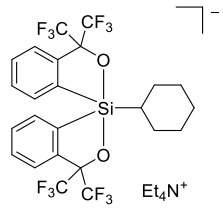
The redox potentials of alkylsilicate **2** were determined by differential pulse voltammetry (DPV) analysis, which are summarized in Table S8. Substrate concentration was 1 mM, and 50 mM solution of Bu_4NBF_4 in CH_3CN was used for solvent. A glassy carbon working electrode, a platinum counter electrode, an $Ag/AgNO_3$ reference electrode were used. We measured the redox potential with respect to the $[FeCp_2]/[FeCp_2]^+$ couple, which was converted to saturated calomel electrode (SCE) by adding 0.469 V.[19] Voltammograms of DPV and cyclic voltammetry (CV) are shown in Figures S6-S15.

Table S8.



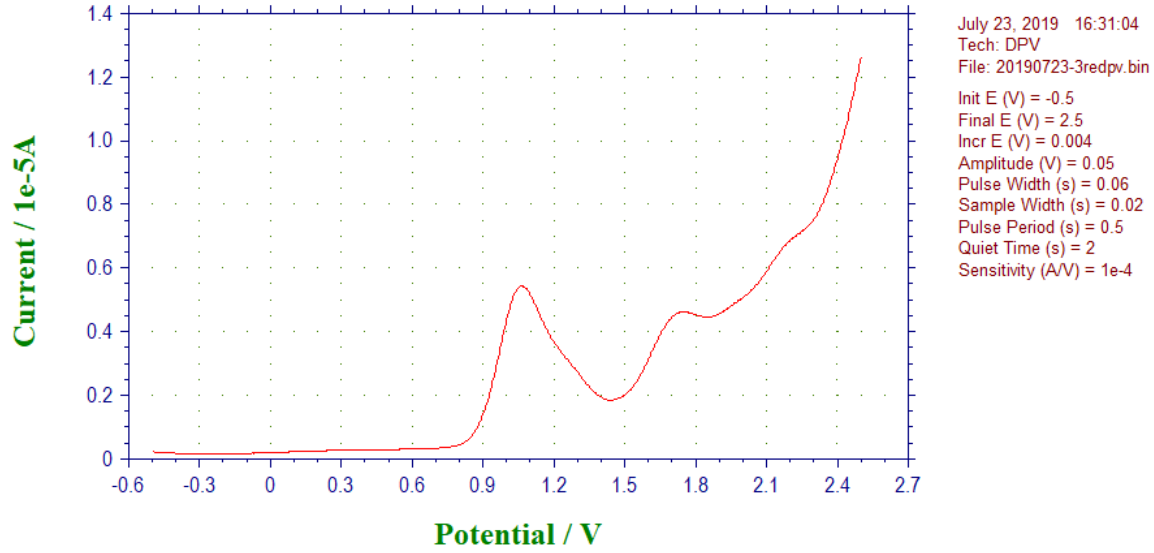
	alkylsilicate	oxidation potential (V vs. SCE)		alkylsilicate	oxidation potential (V vs. SCE)
2a	R = 	+1.47	**2f**	R = 	+1.33
2b	R = 	+1.51	**2g**	R = 	+1.42
2c	R = 	+1.64	**2h**	R = 	+1.28
2d	R = 	+1.53	**2i**	R = 	+1.32
2e	R = 	+1.48	**2j**	R = 	+1.04 +1.28

[19] 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.



2a

DPV



CV

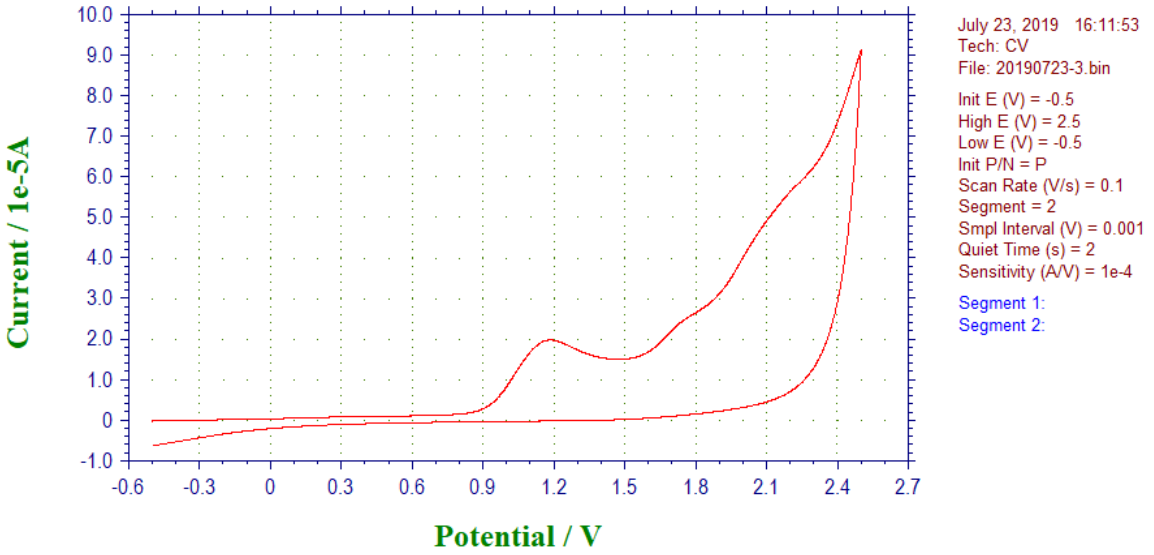
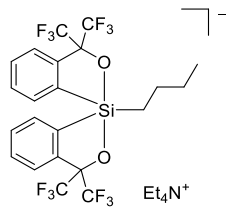
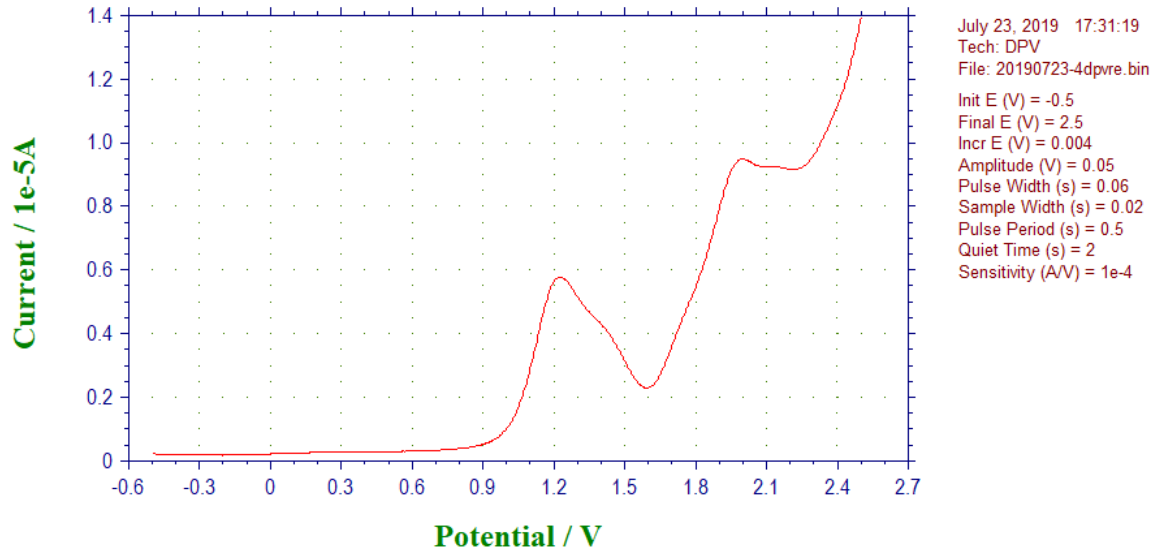


Figure S6



2c

DPV



CV

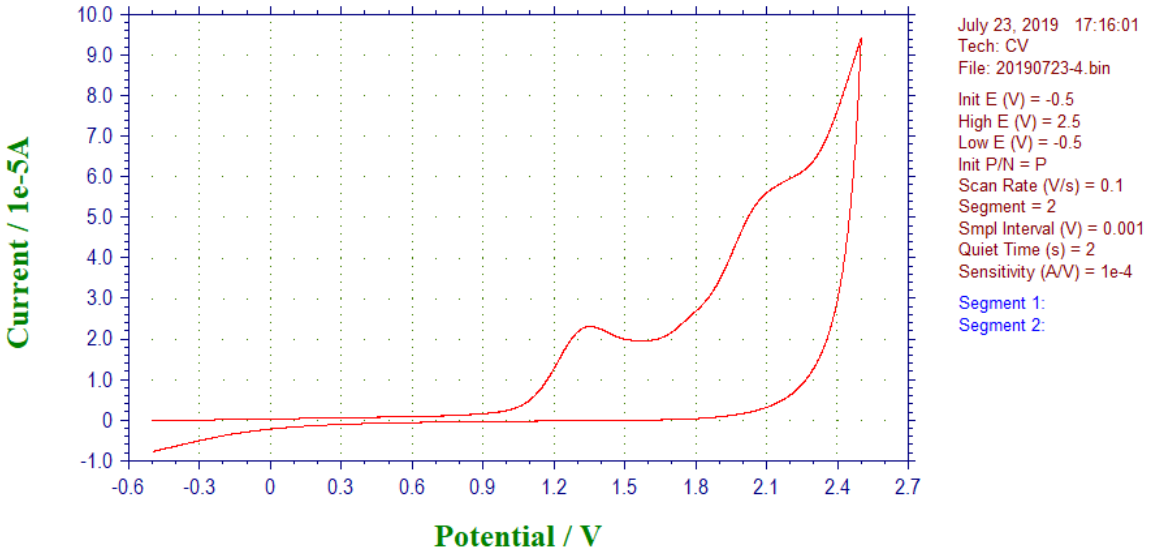
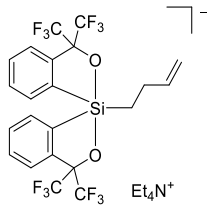
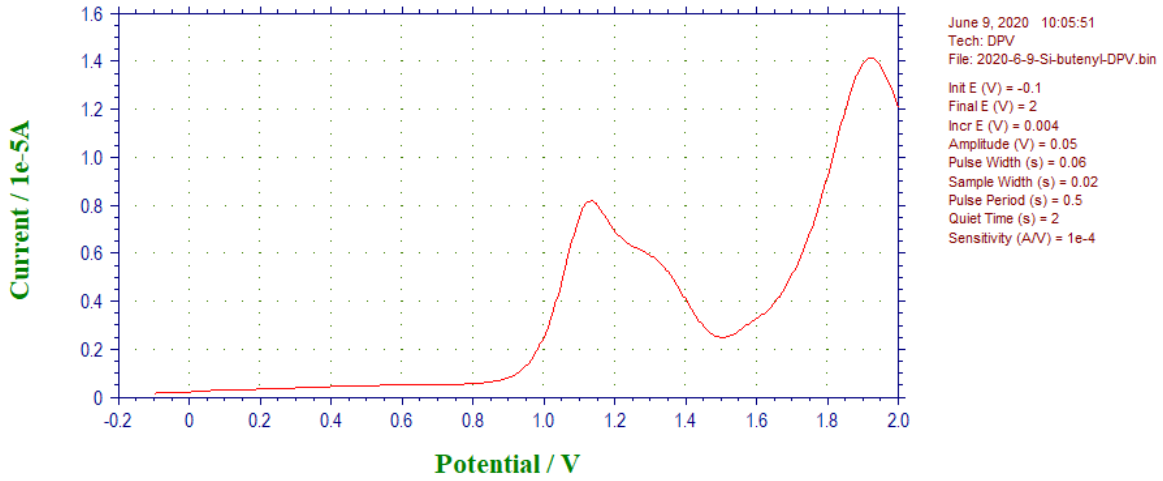


Figure S7



2d

DPV



CV

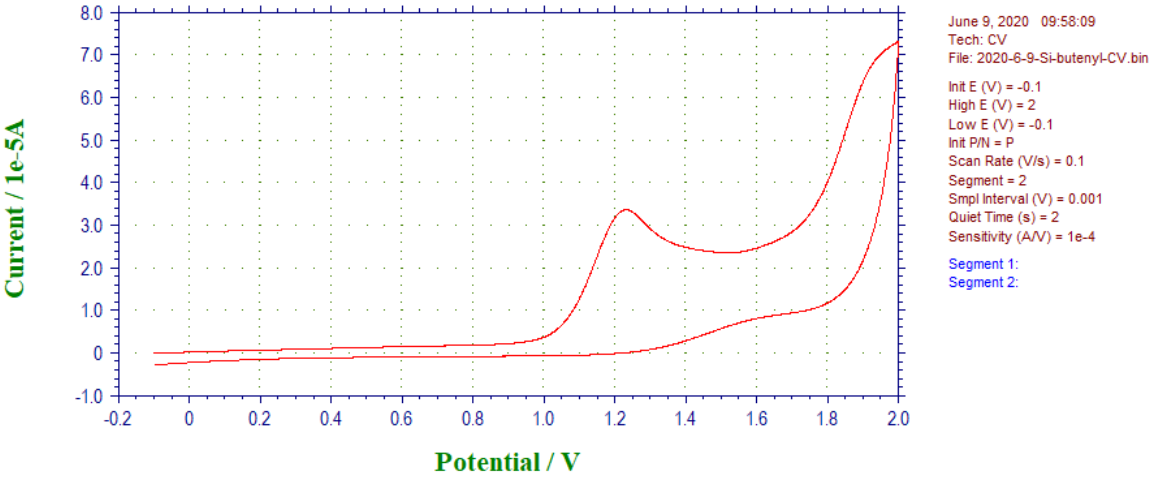
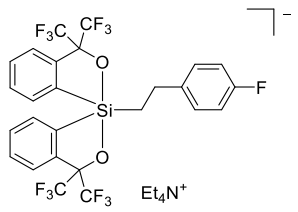
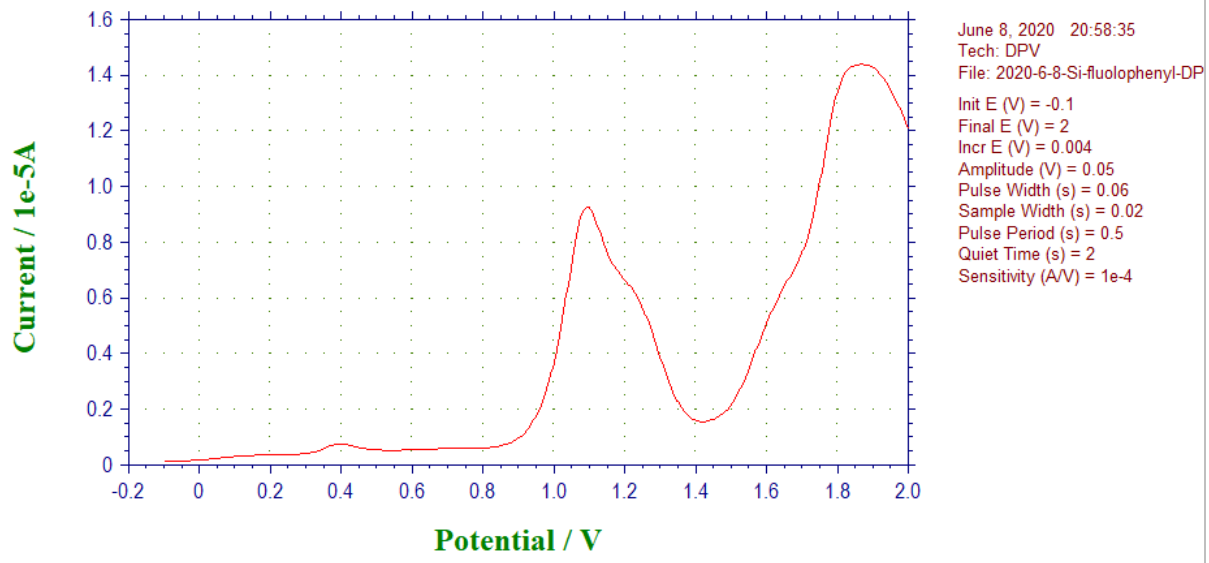


Figure S8



2e

DPV



CV

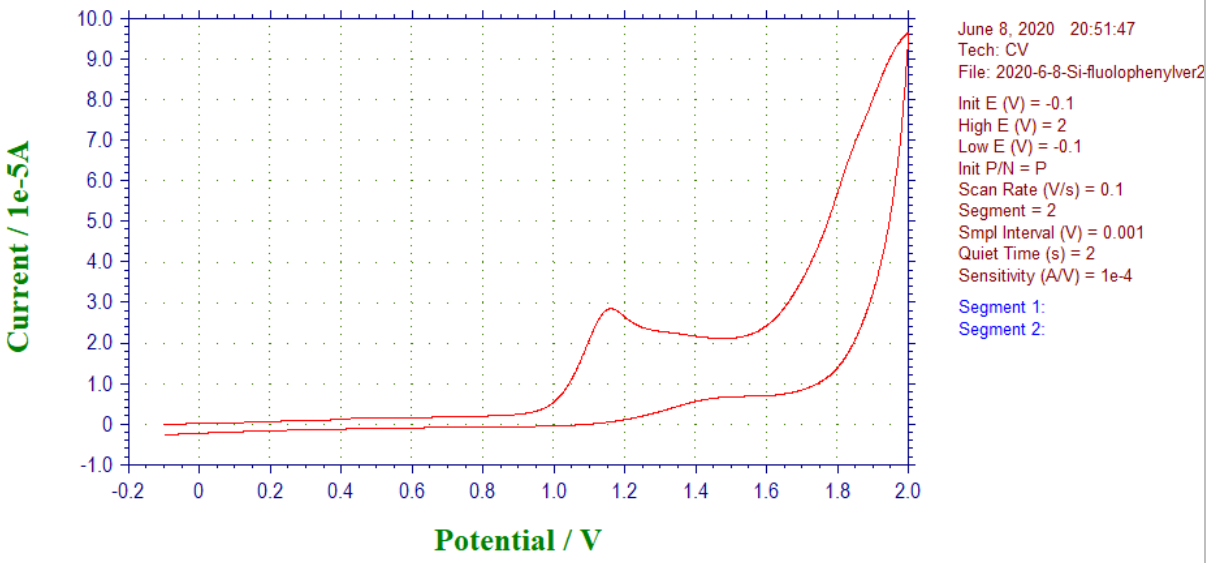
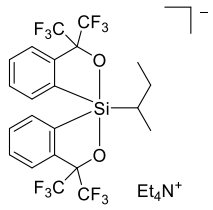
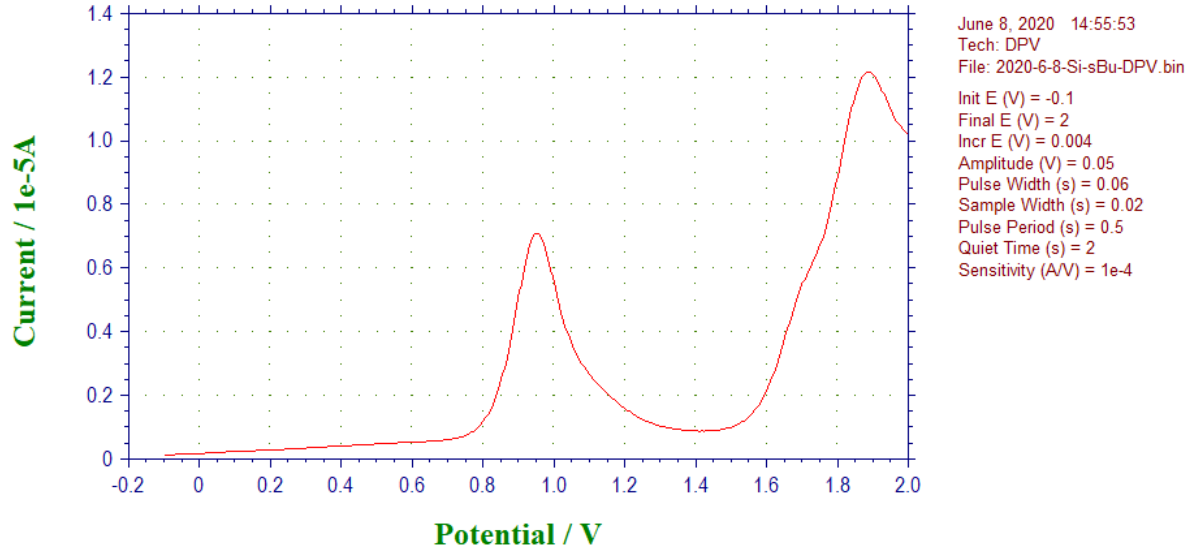


Figure S9



2f

DPV



CV

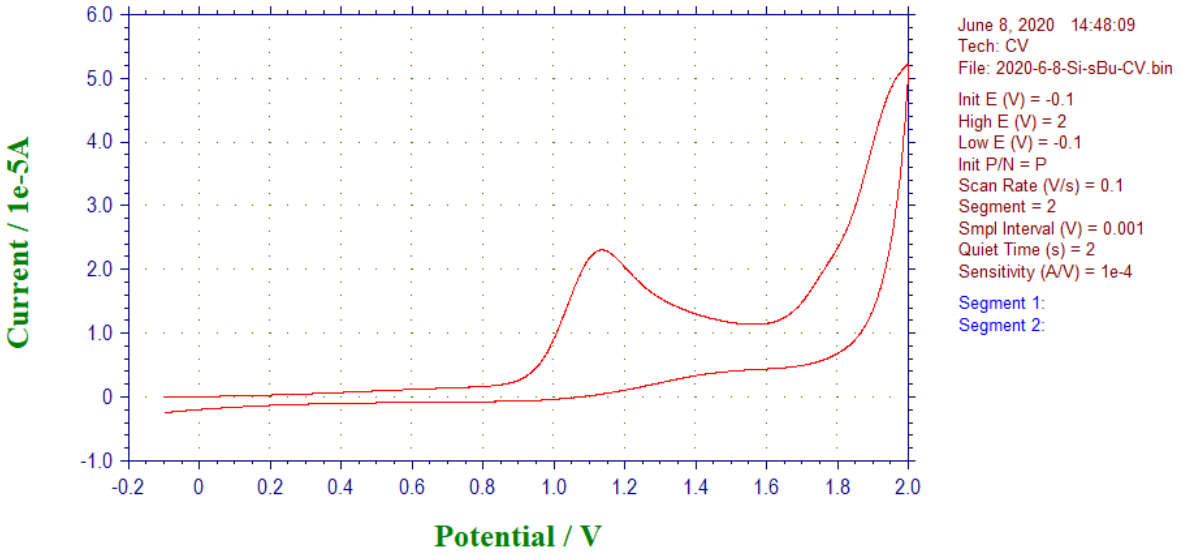
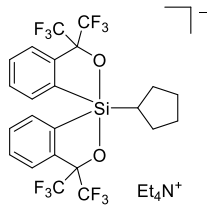
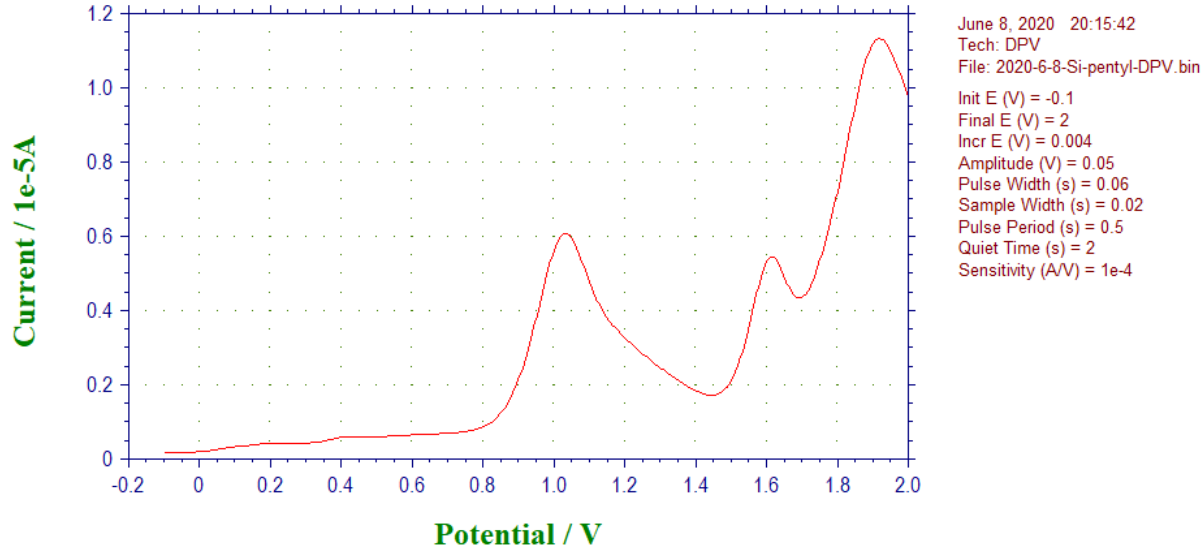


Figure S10



2g

DPV



CV

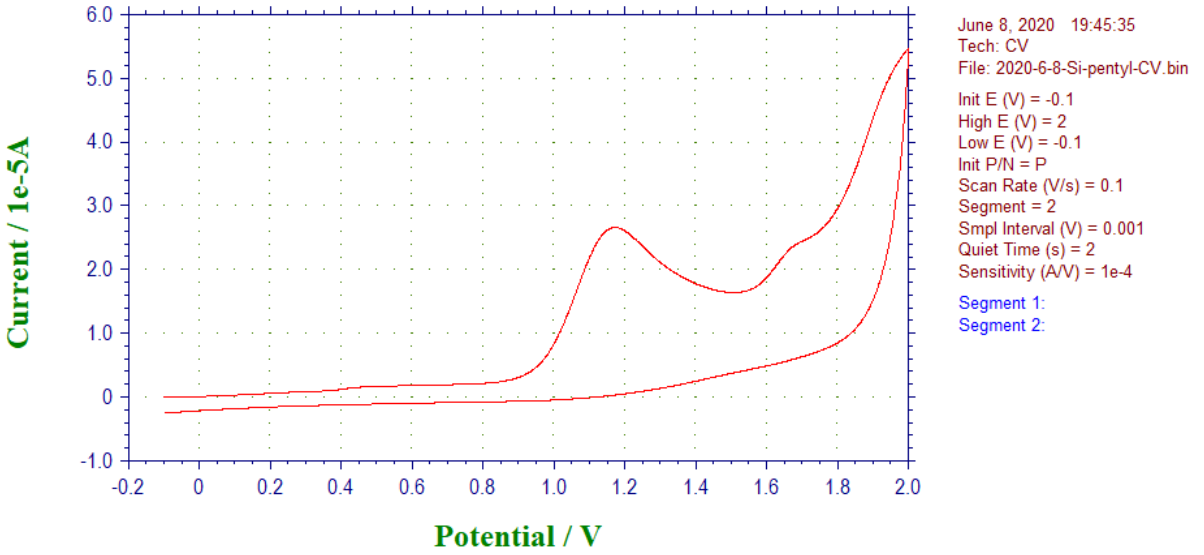
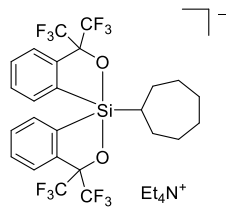
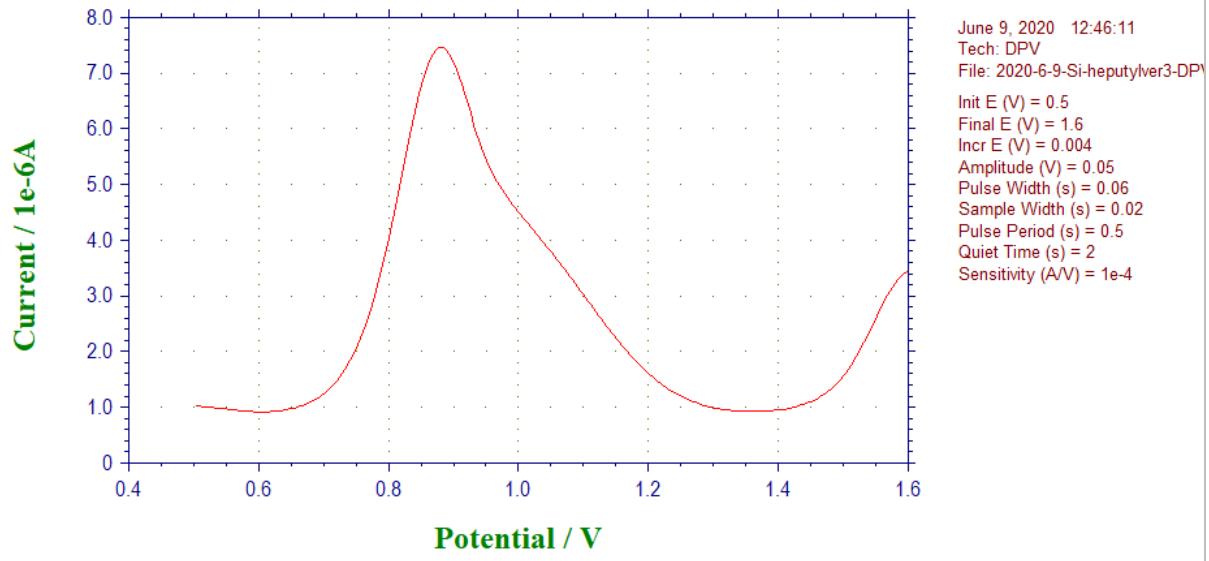


Figure S11



2h

DPV



CV

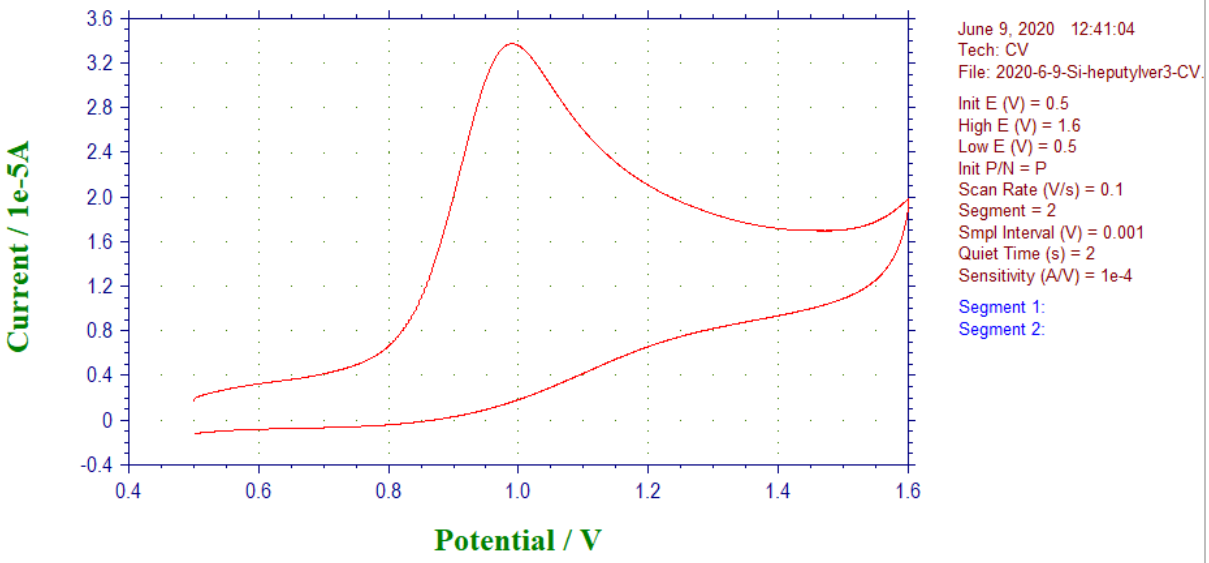
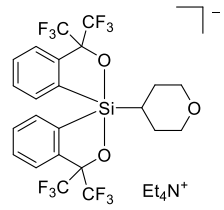
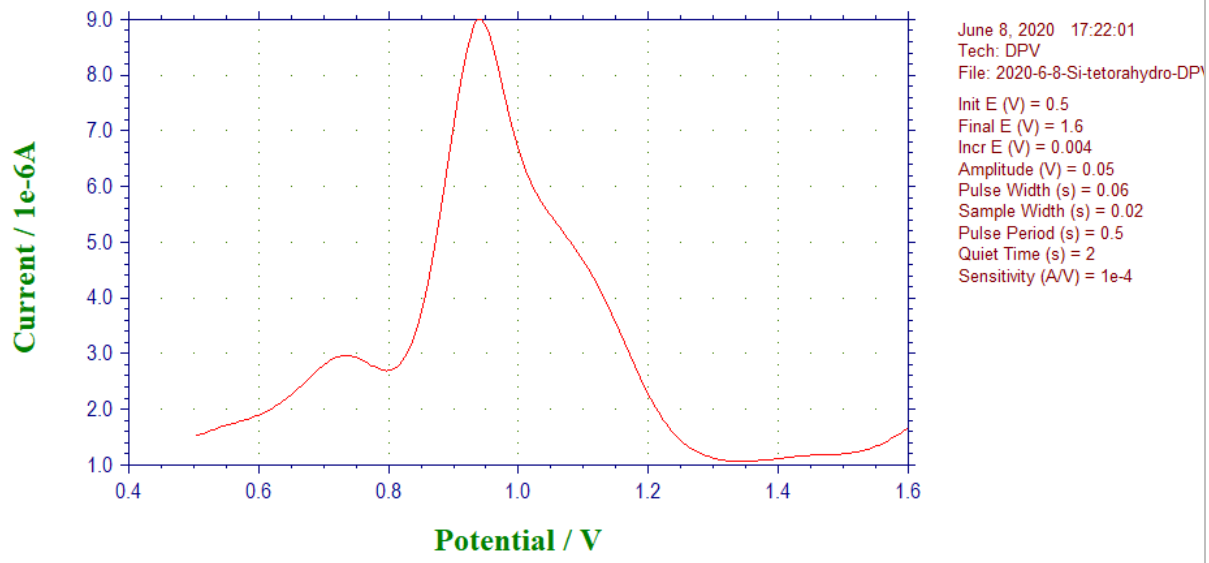


Figure S12



2i

DPV



CV

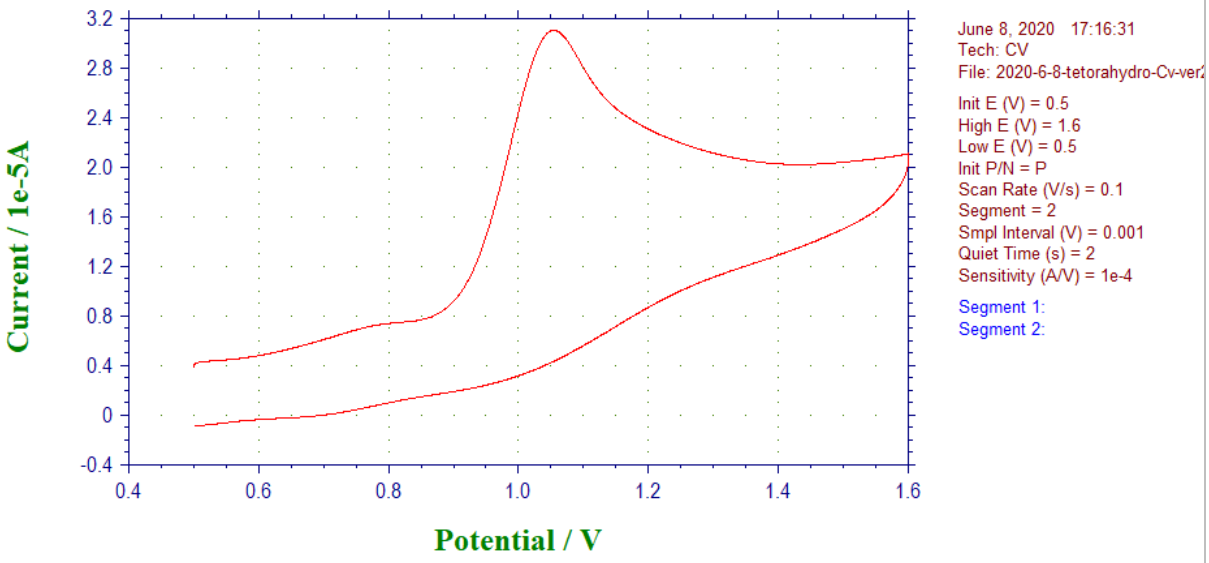
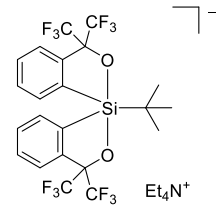
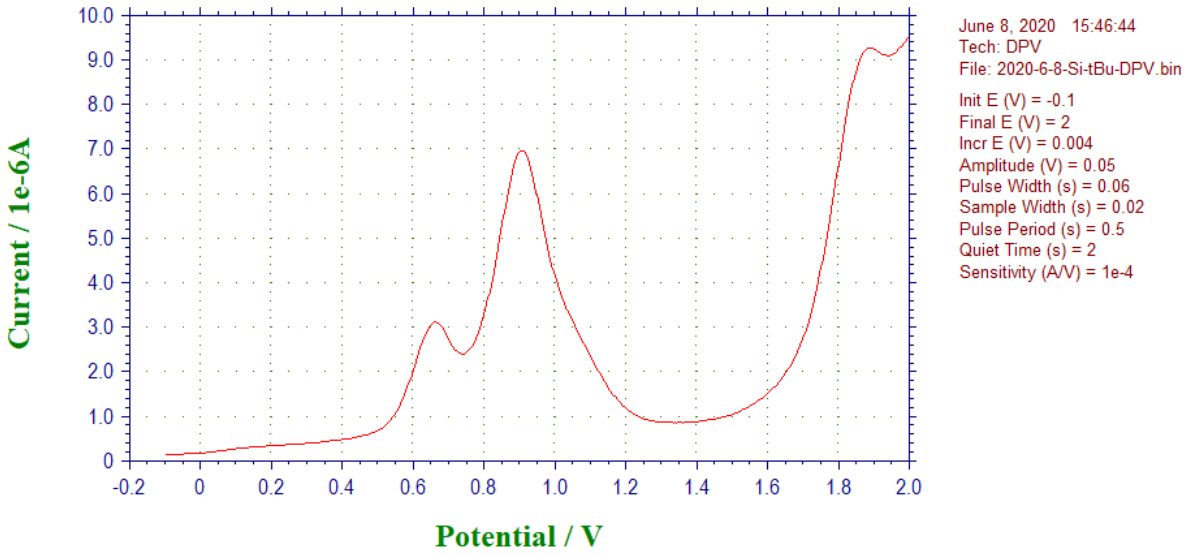


Figure S13



2j

DPV



CV

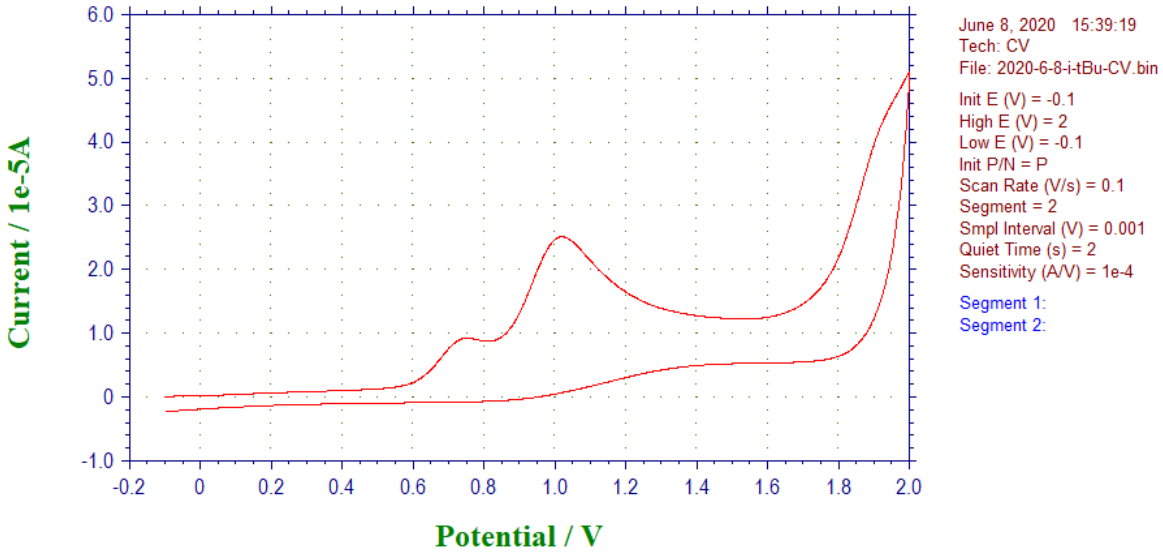
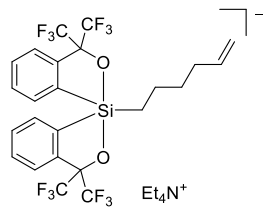
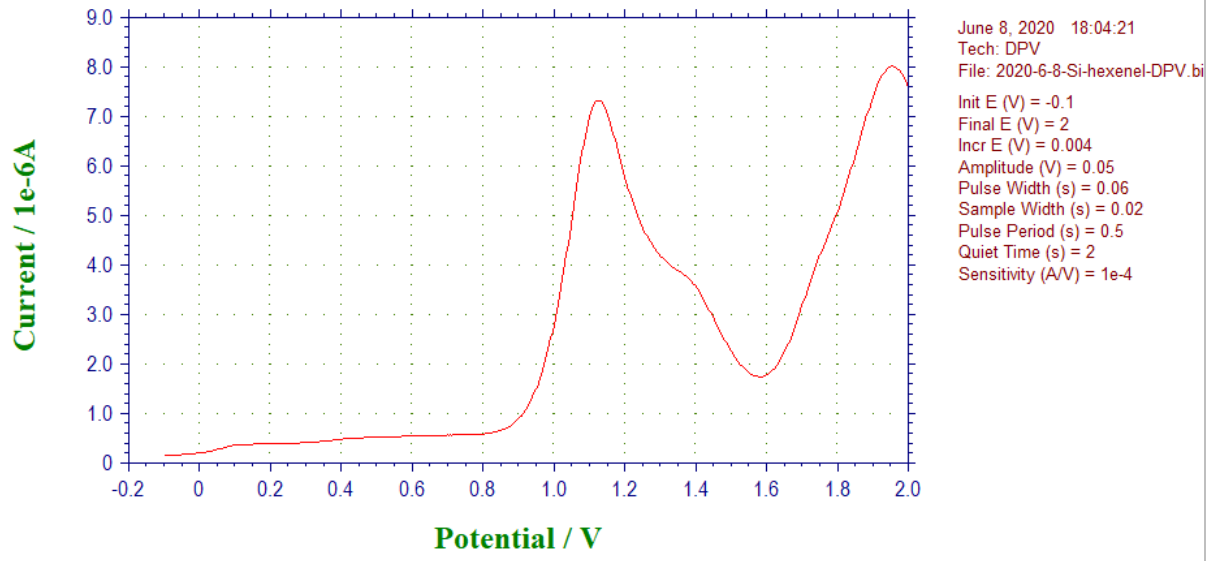


Figure S14



2b

DPV



CV

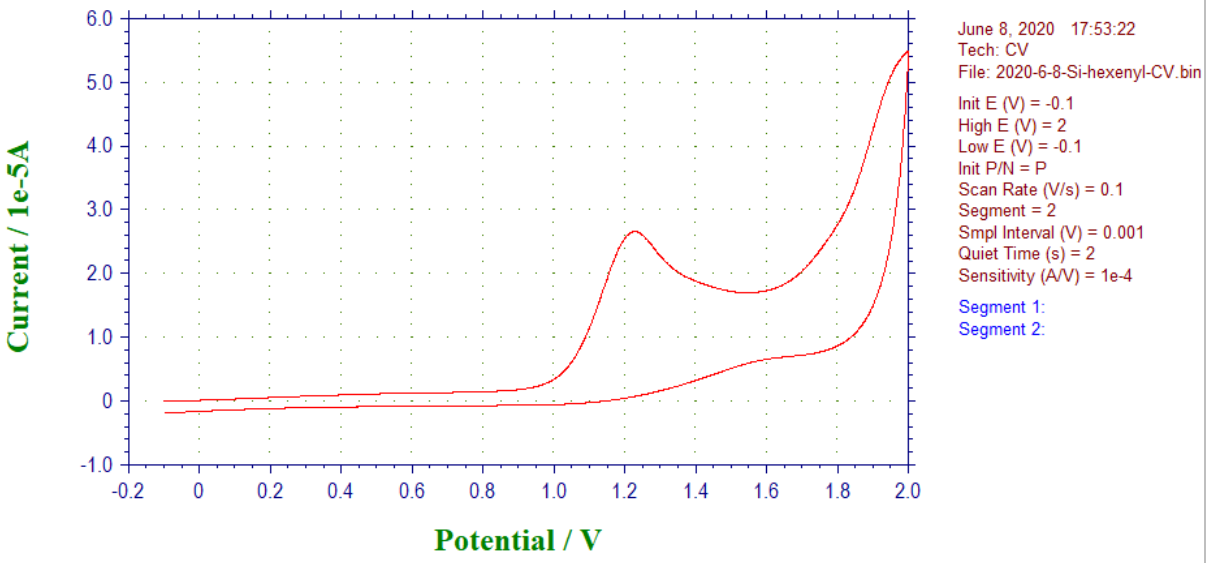
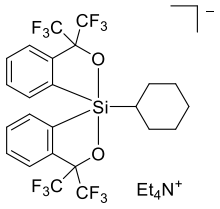


Figure S15

13. NMR spectra



2a

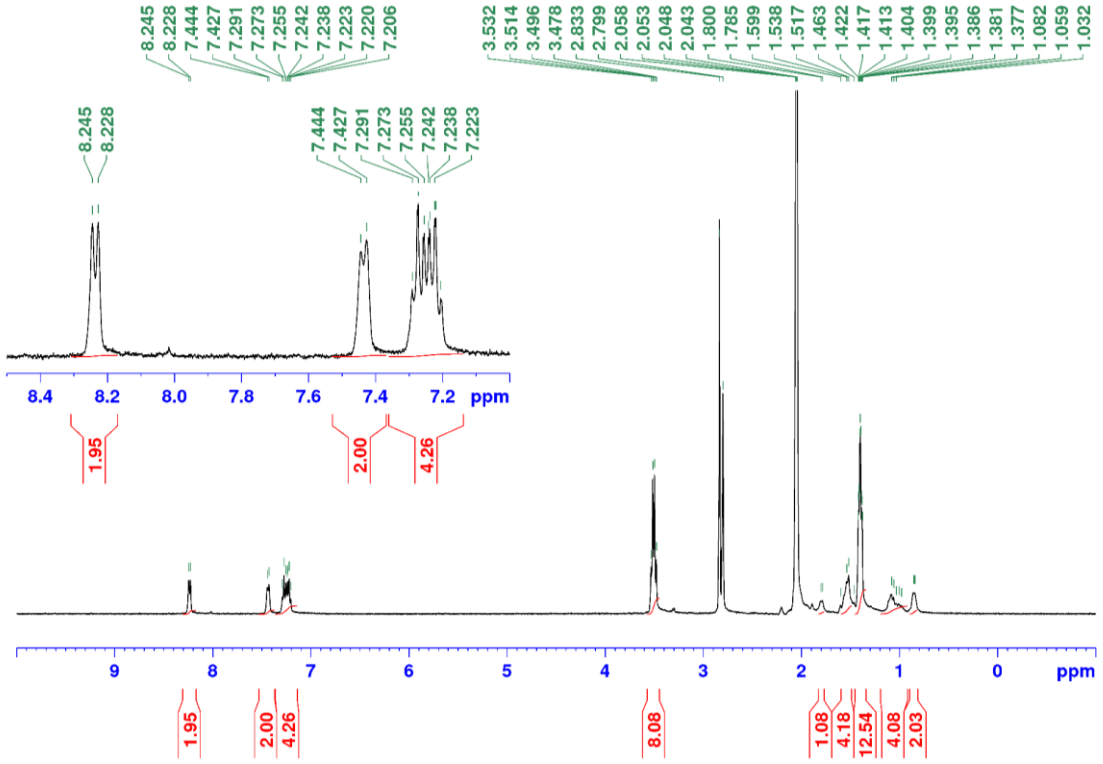
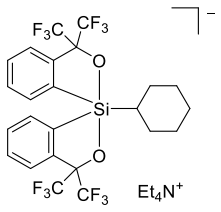


Figure S16. ^{1}H NMR (400 MHz) spectrum of **2a** in acetone-d_6.



2a

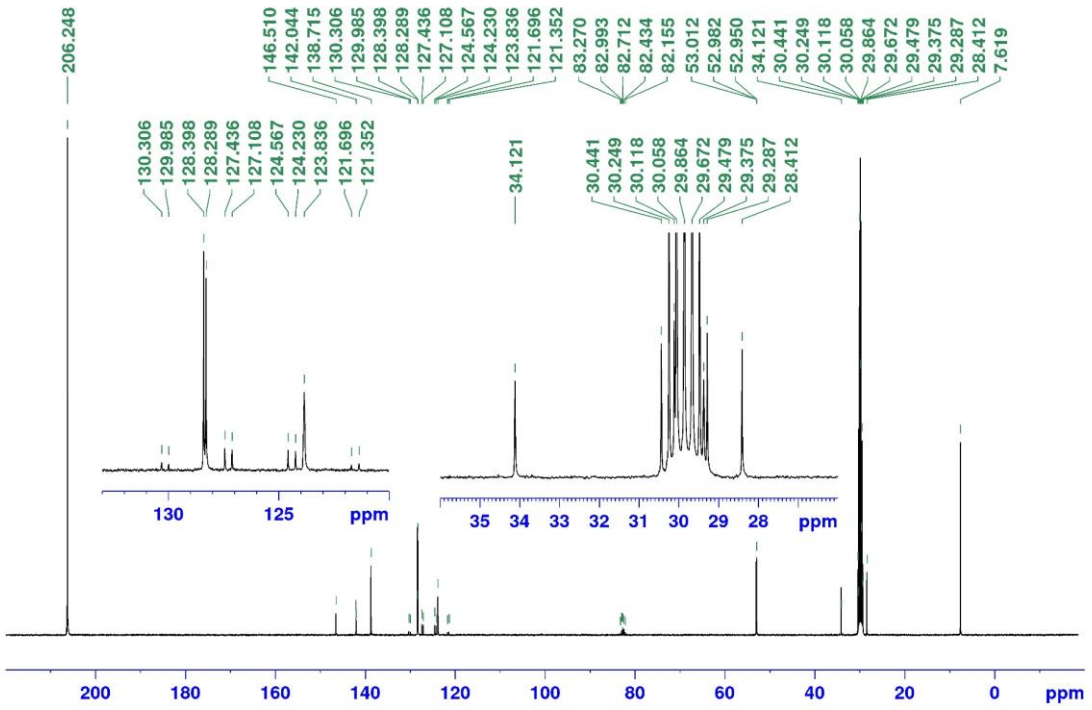
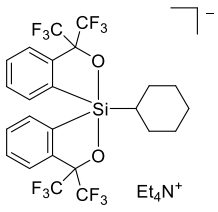


Figure S17. ^{13}C NMR (100 MHz) spectrum of **2a** in acetone-d_6.



2a

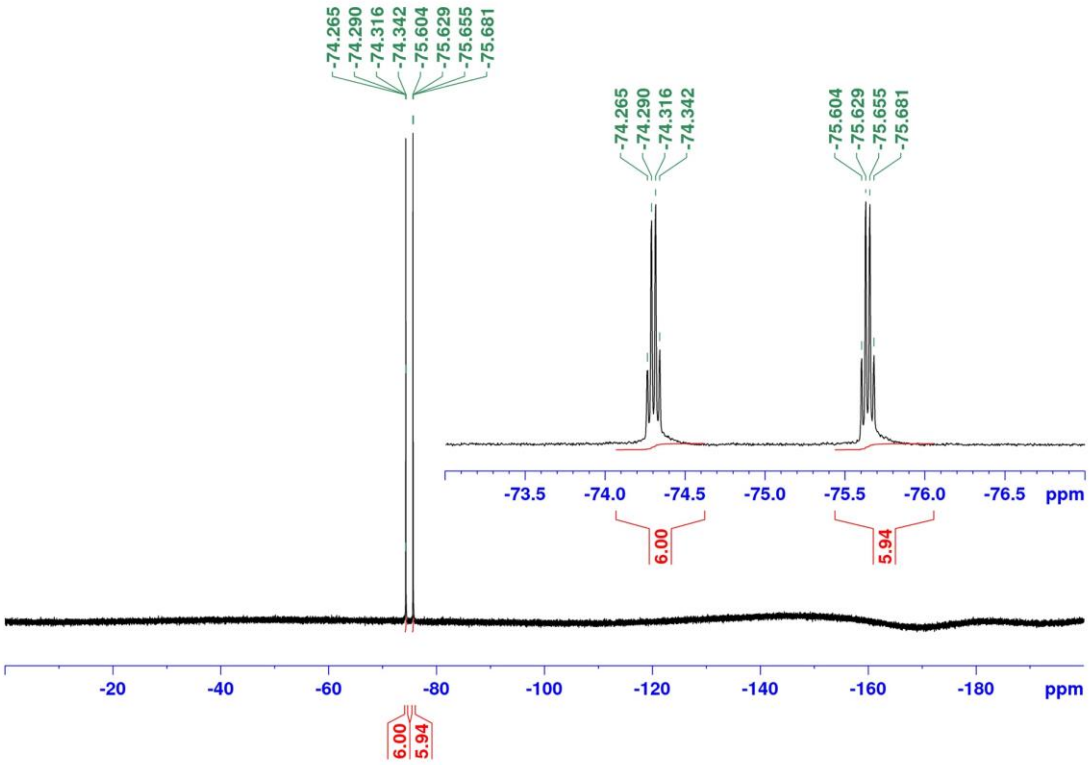
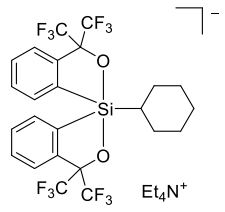


Figure S18. ^{19}F NMR (376 MHz) spectrum of **2a** in acetone-d_6.



2a

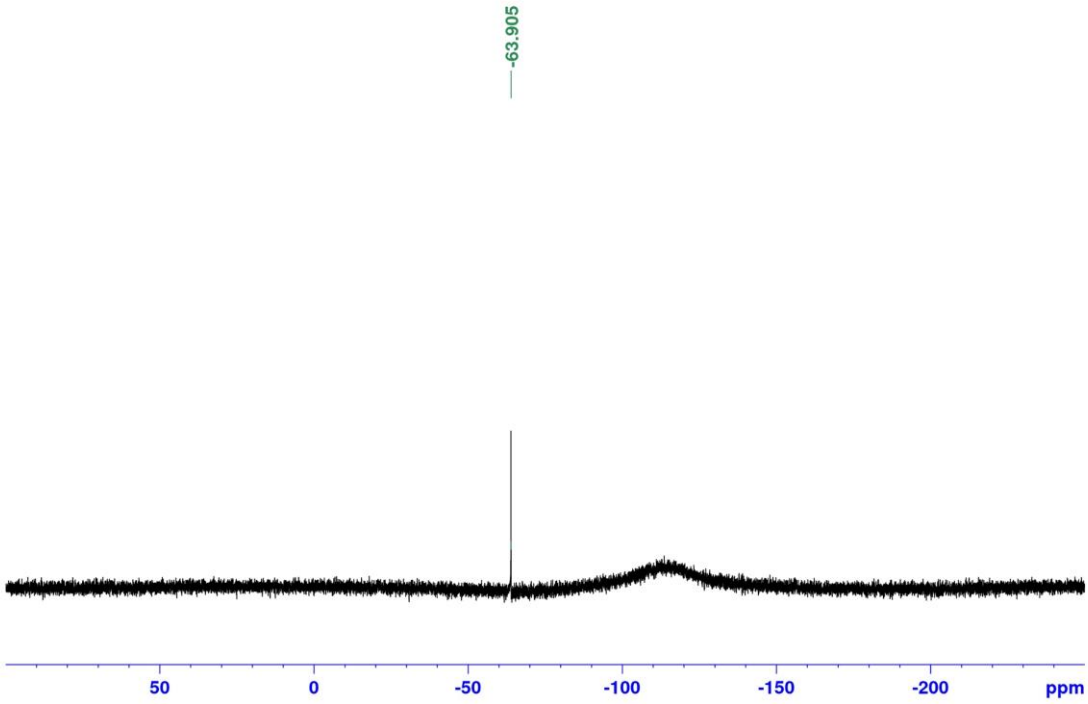
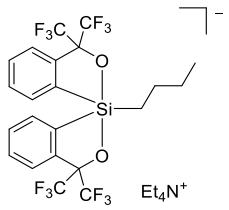


Figure S19. ^{29}Si NMR (79 MHz) spectrum of **2a** in acetone-d_6.



2c

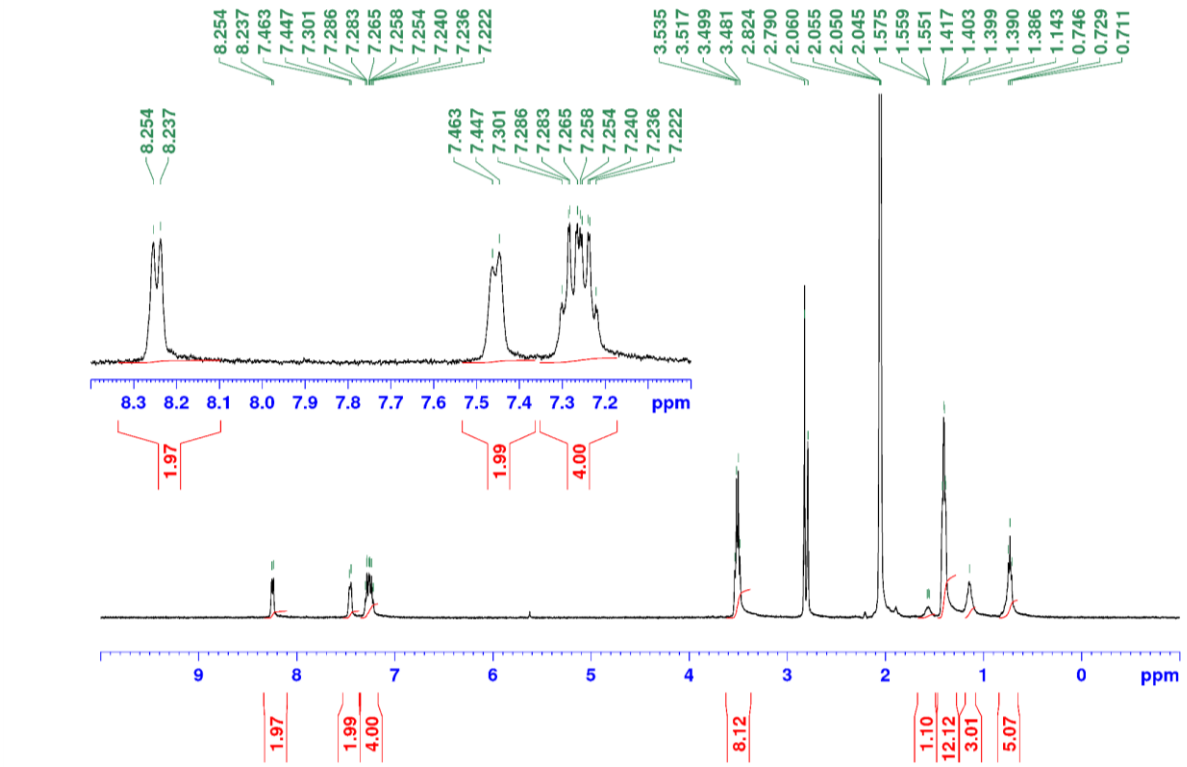
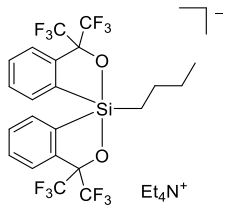


Figure S20. ^{1}H NMR (400 MHz) spectrum of **2c** in acetone-d_6.



2c

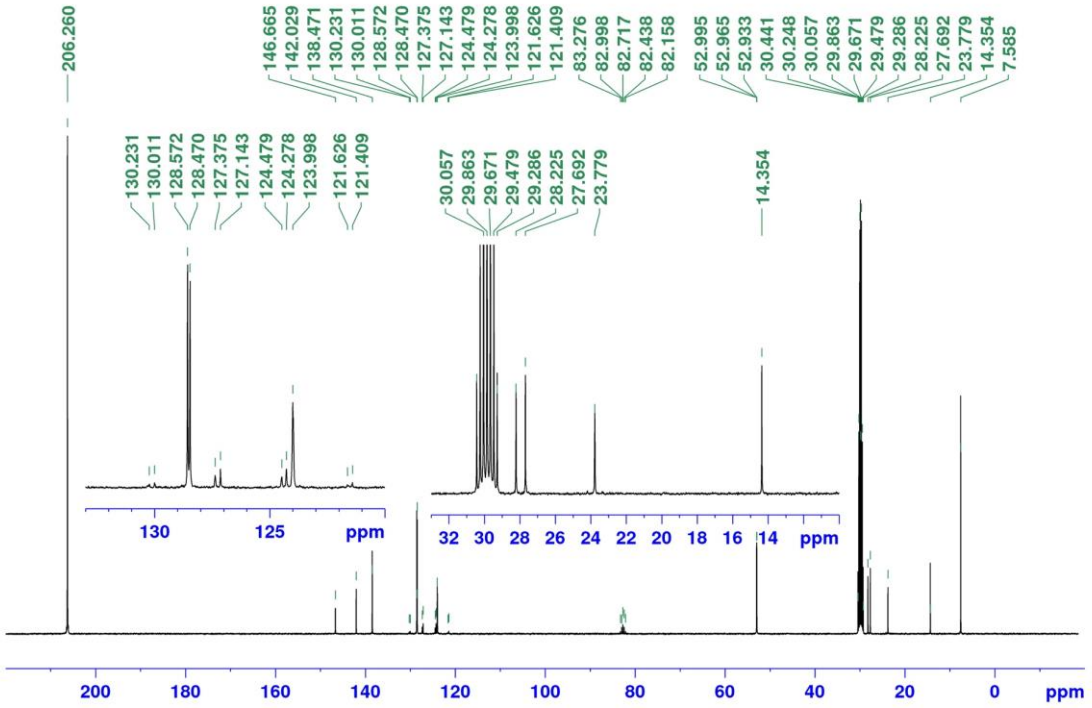
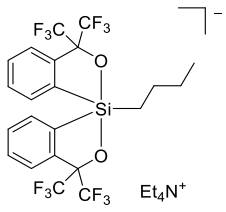


Figure S21. ^{13}C NMR (100 MHz) spectrum of **2c** in acetone-d_6.



2c

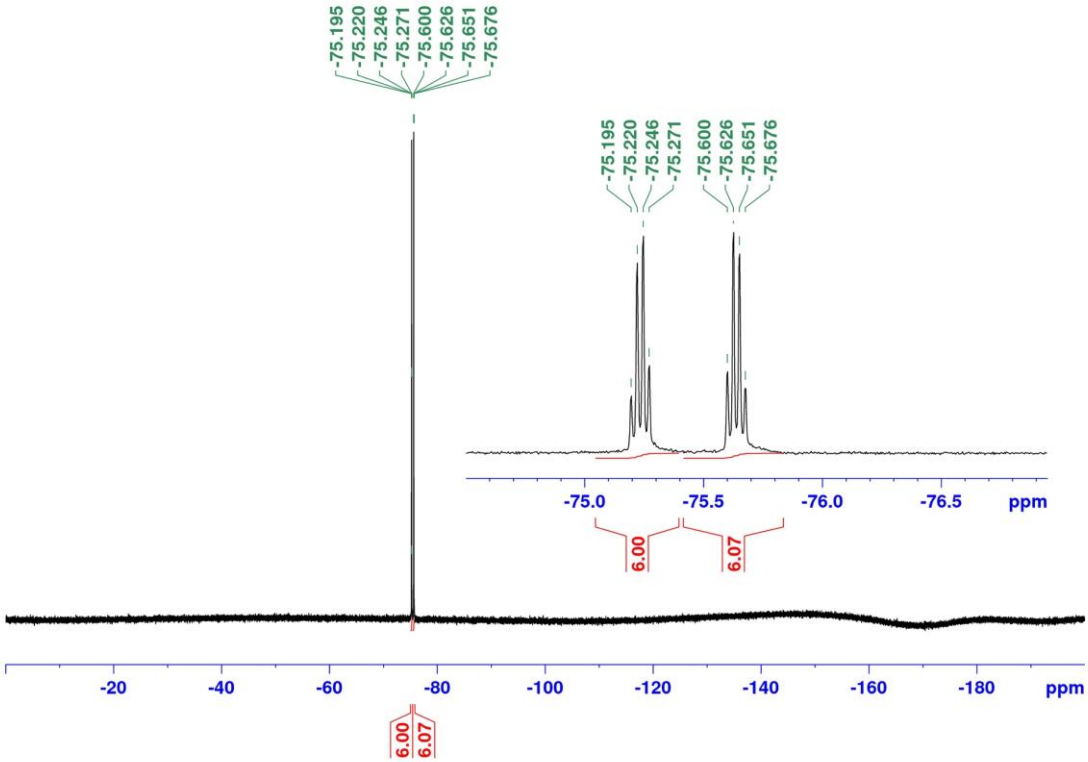
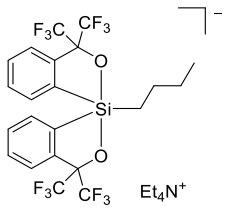


Figure S22. ^{19}F NMR (376 MHz) spectrum of **2c** in acetone-d_6.



2c

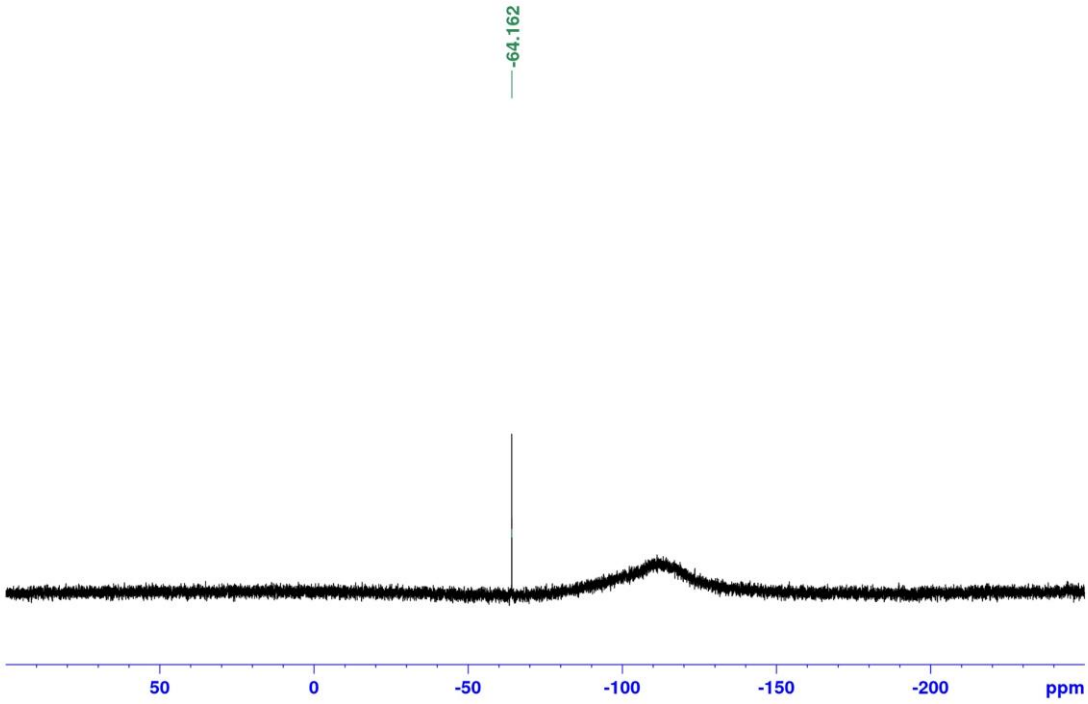
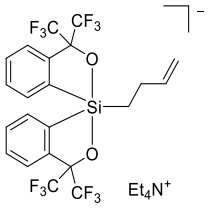


Figure S23. ^{29}Si NMR (79 MHz) spectrum of **2c** in acetone-d_6.



2d

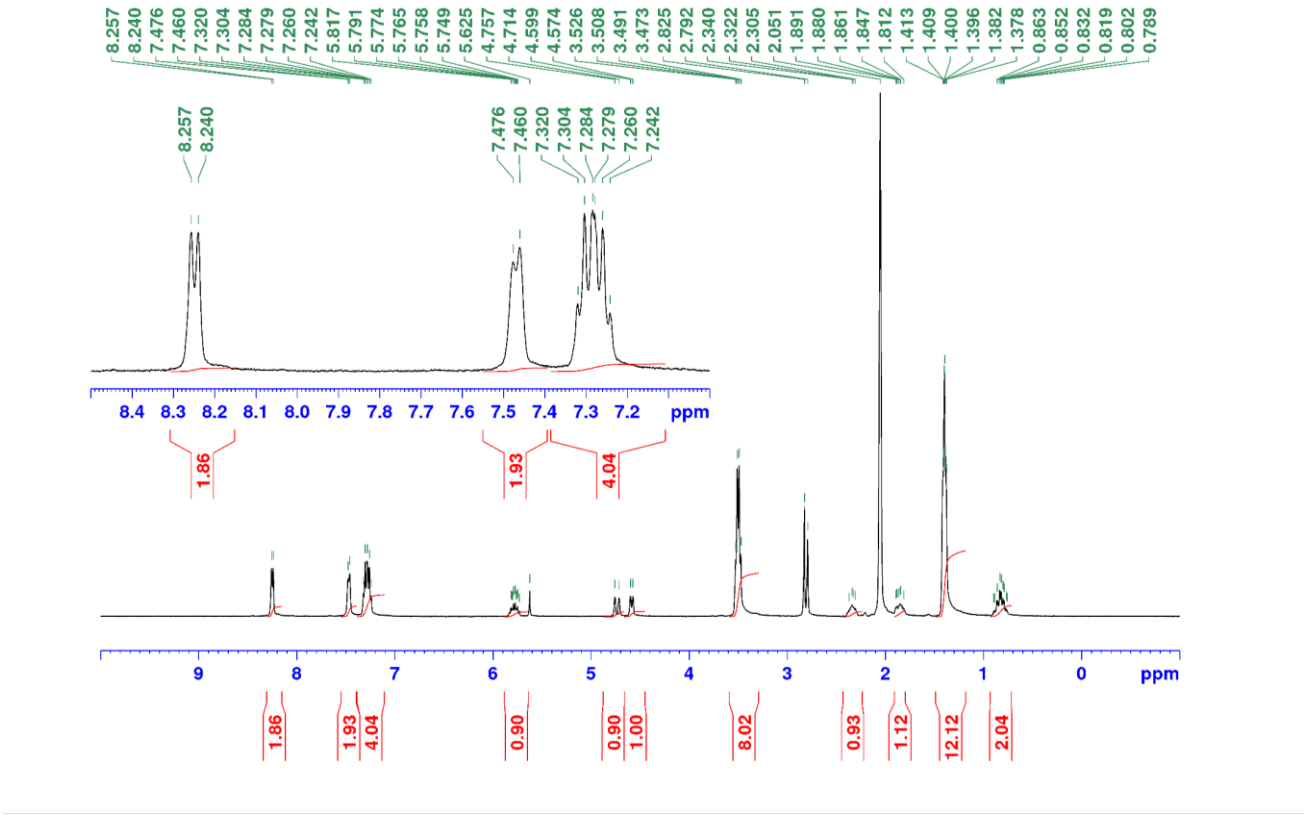
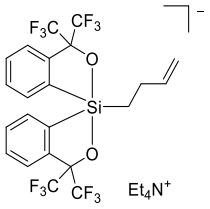


Figure S24. ^{1}H NMR (400 MHz) spectrum of **2d** in acetone-d_6.



2d

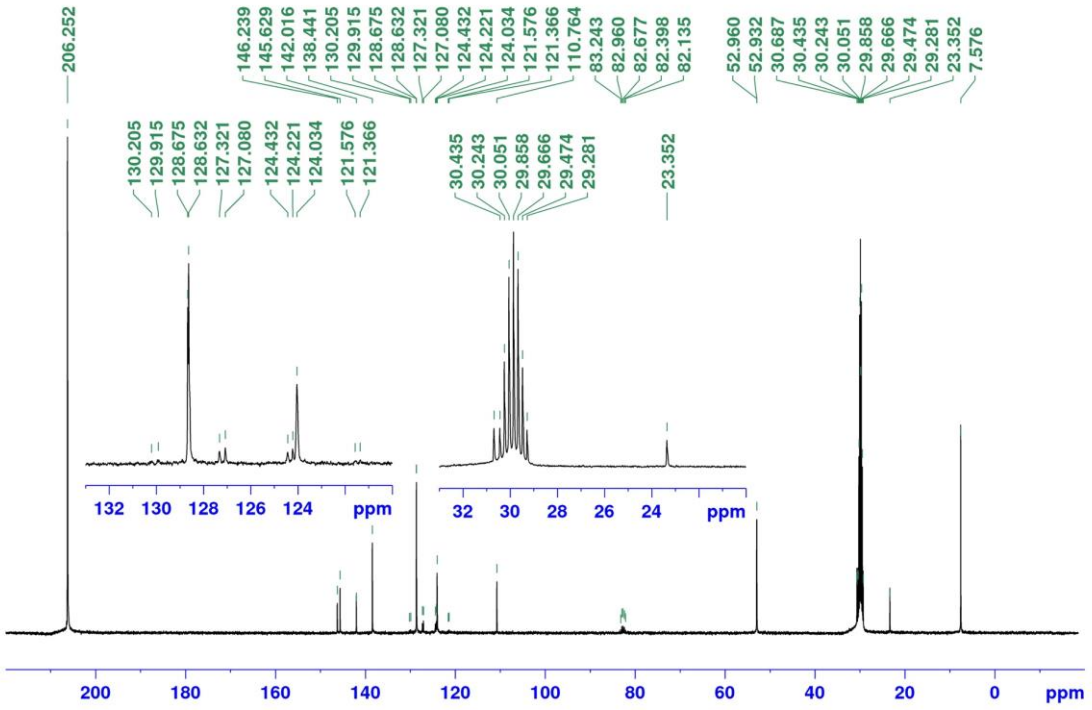
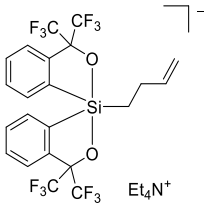


Figure S25. ^{13}C NMR (100 MHz) spectrum of **2d** in acetone-d_6.



2d

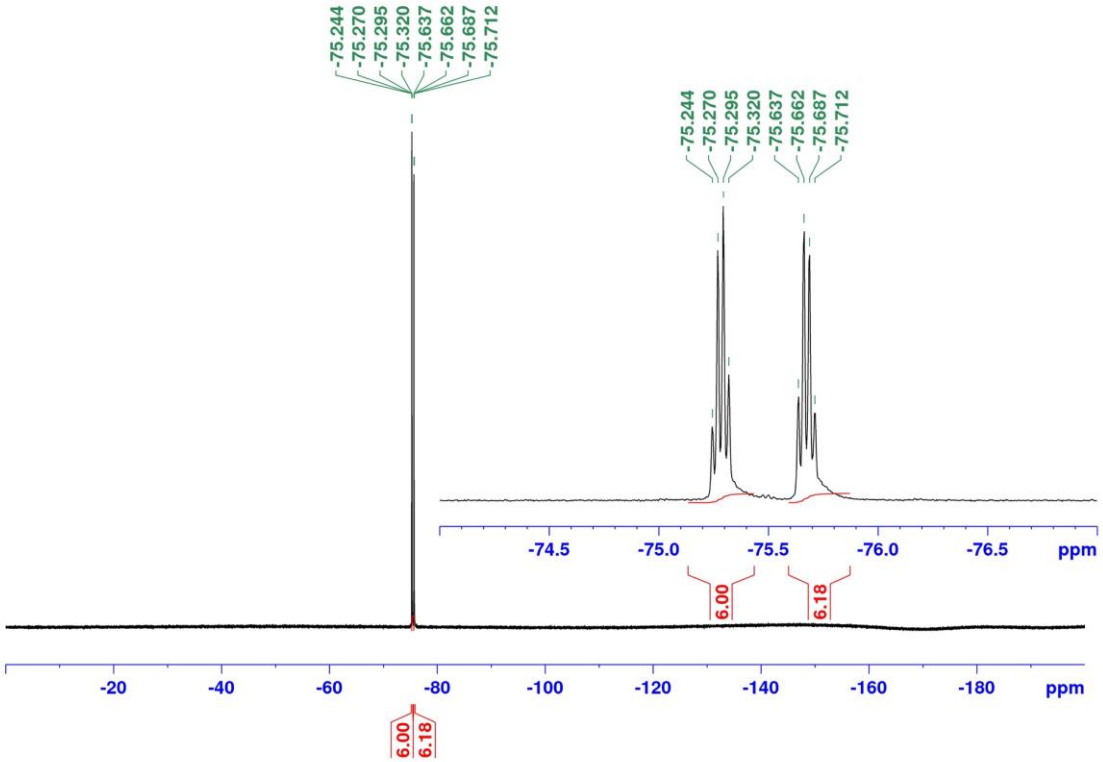
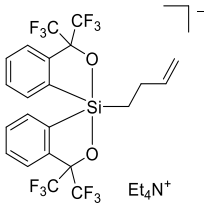


Figure S26. ^{19}F NMR (376 MHz) spectrum of **2d** in acetone-d_6.



2d

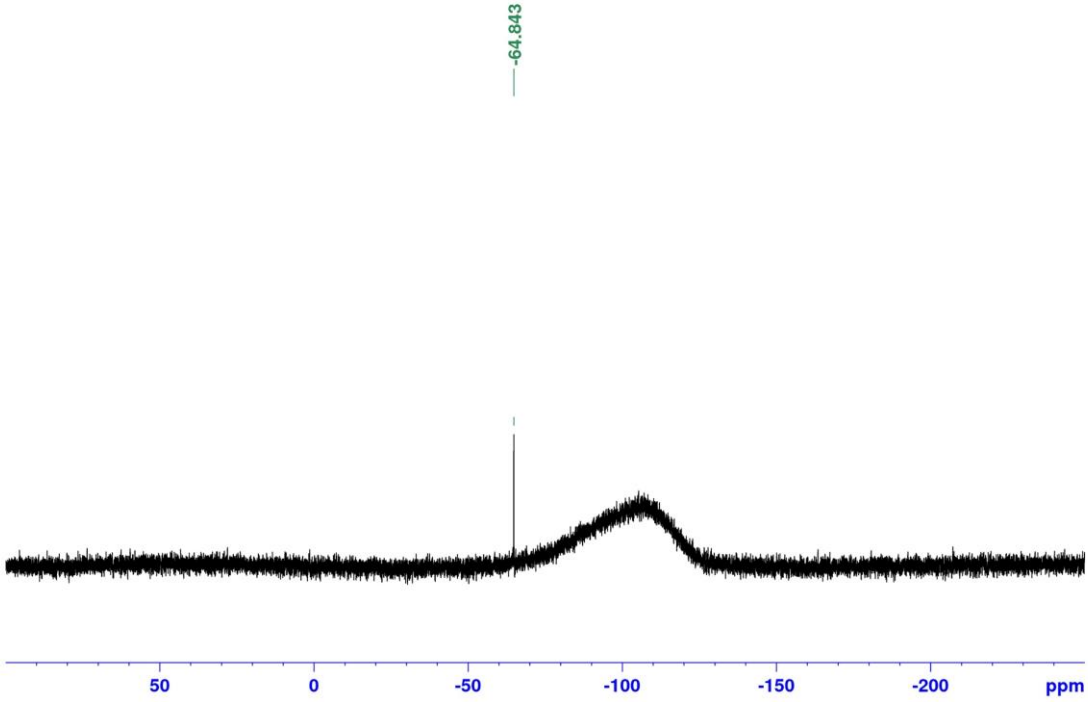
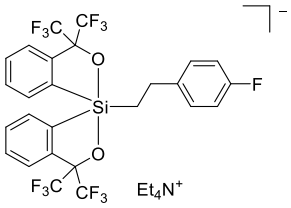


Figure S27. ^{29}Si NMR (79 MHz) spectrum of **2d** in acetone-d_6.



2e

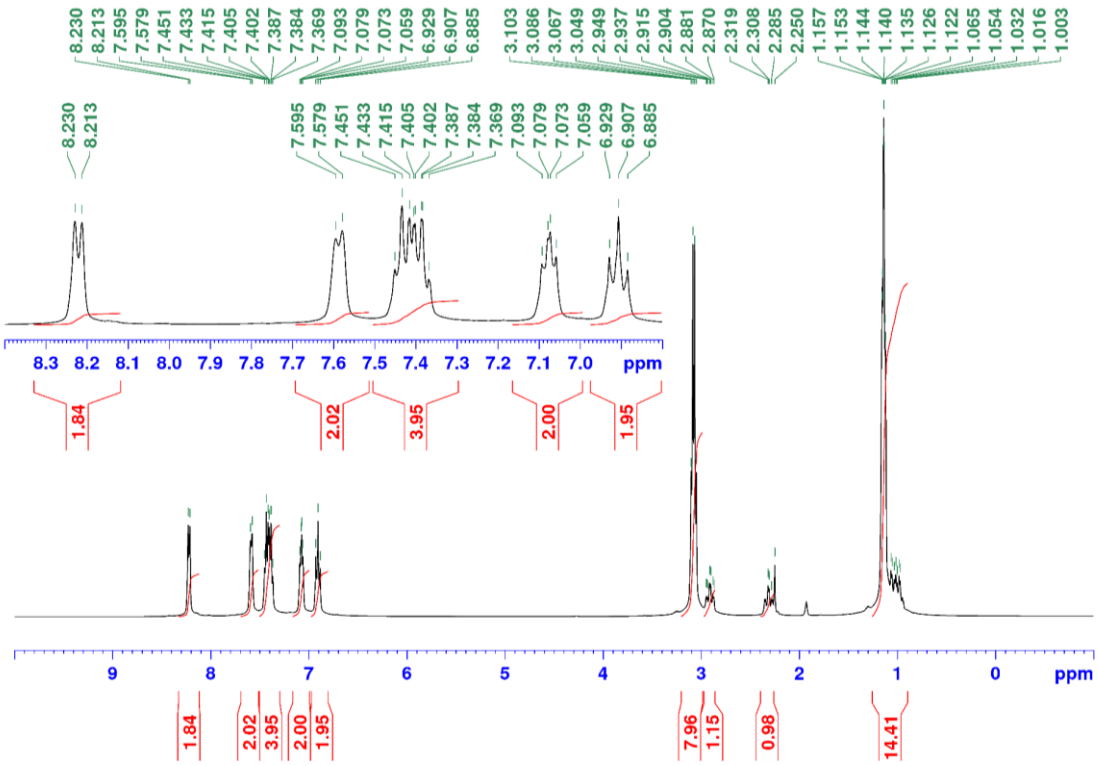
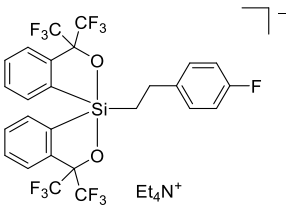


Figure S28. ^{1}H NMR (400 MHz) spectrum of **2e** in acetone-d_6.



2e

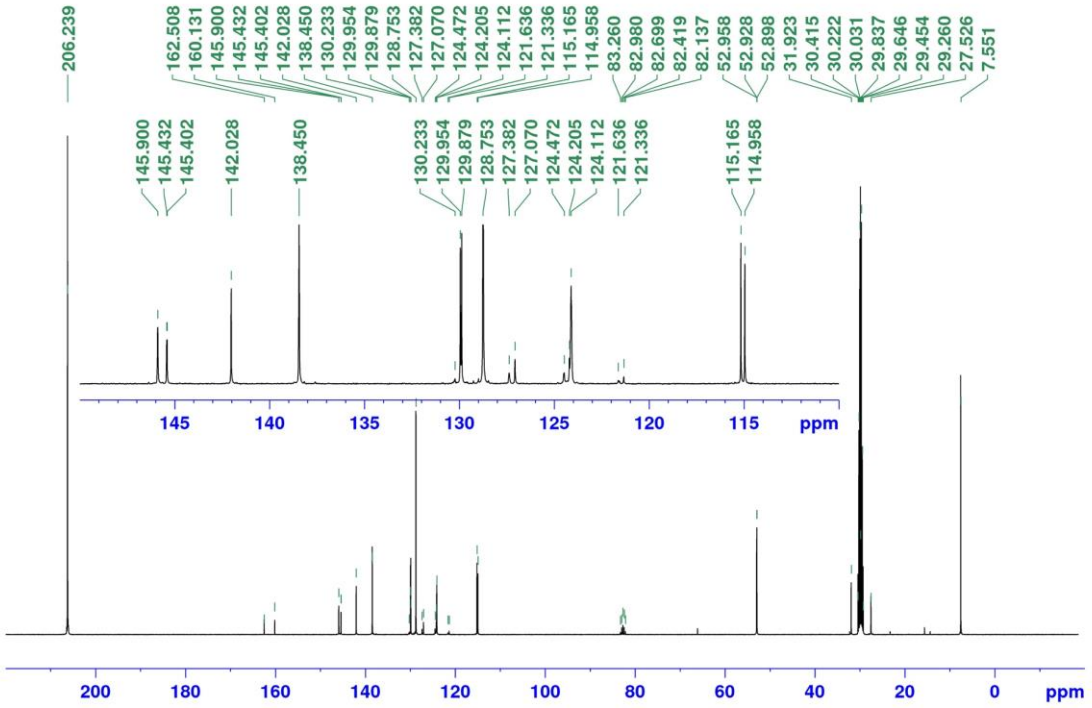
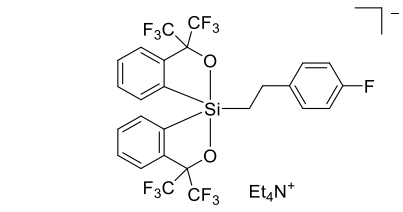


Figure S29. ^{13}C NMR (100 MHz) spectrum of **2e** in acetone-d_6.



2e

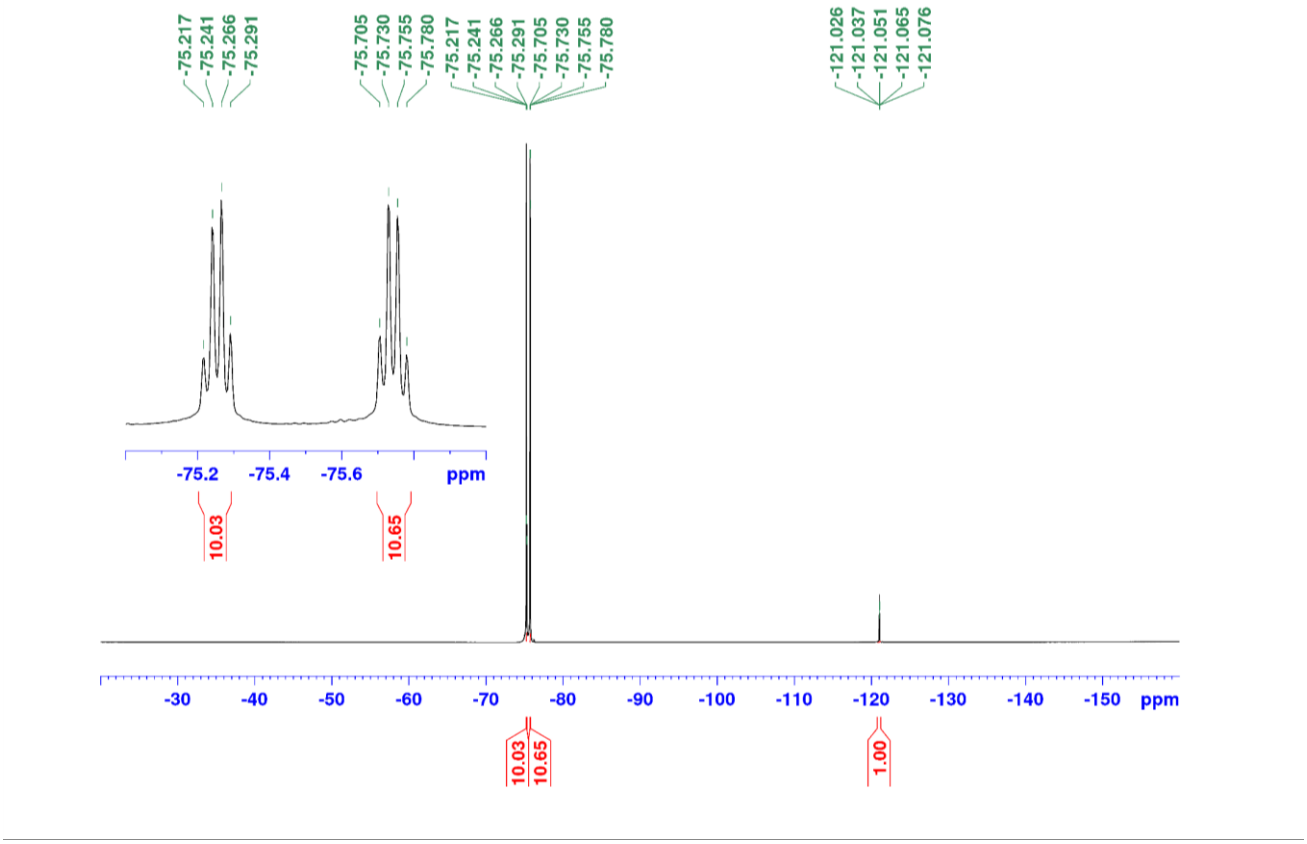
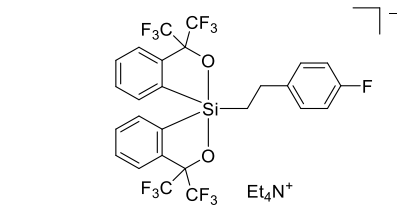


Figure S30. ^{19}F NMR (376 MHz) spectrum of **2e** in CD_3CN.



2e

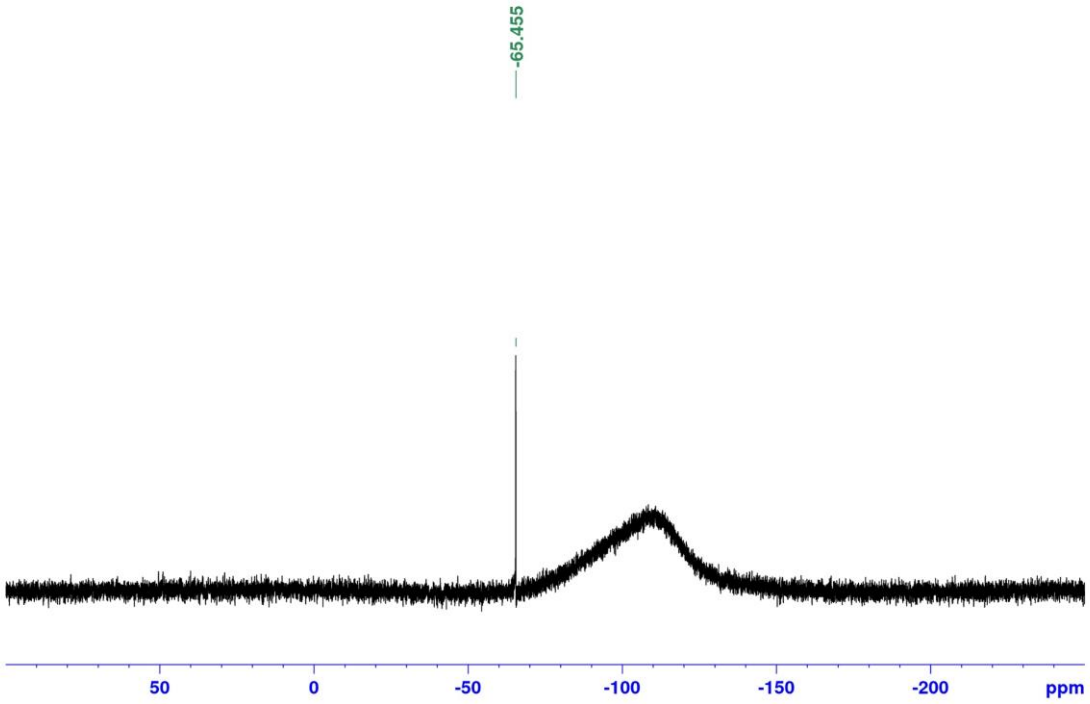
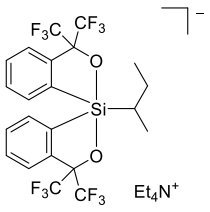


Figure S31. ^{29}Si NMR (79 MHz) spectrum of **2e** in acetone-d_6.



2f

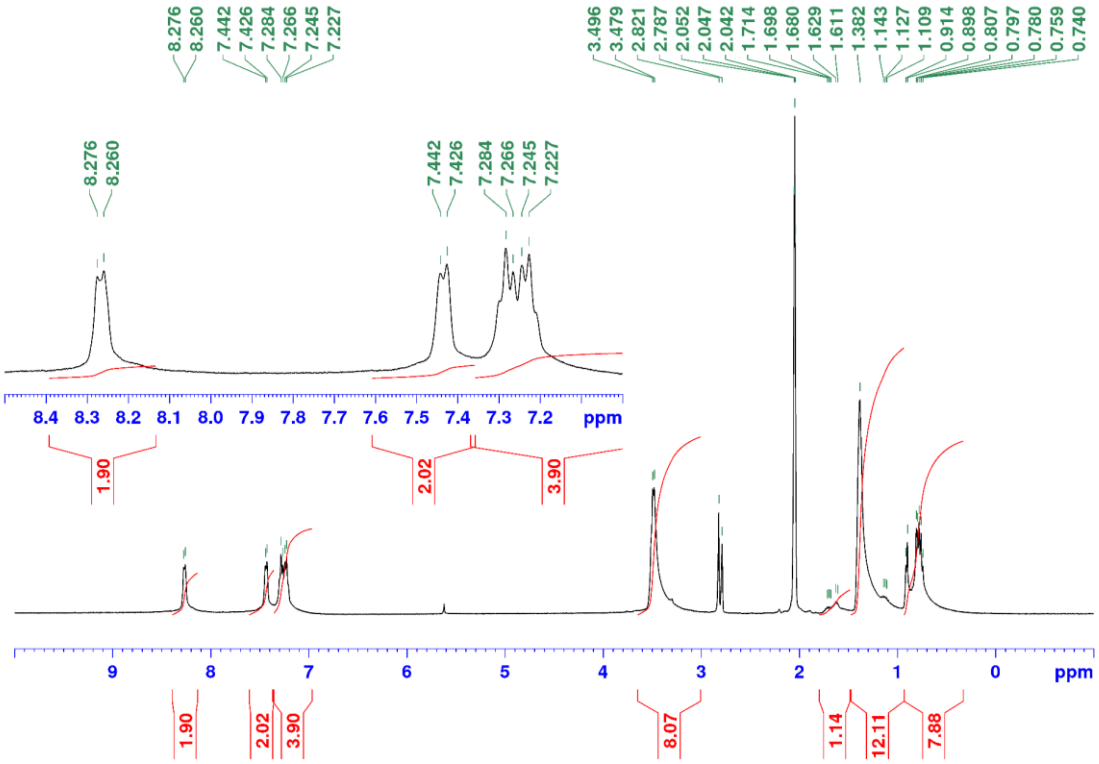
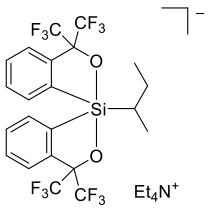


Figure S32. ^{1}H NMR (400 MHz) spectrum of **2f** in acetone-d_6.



2f

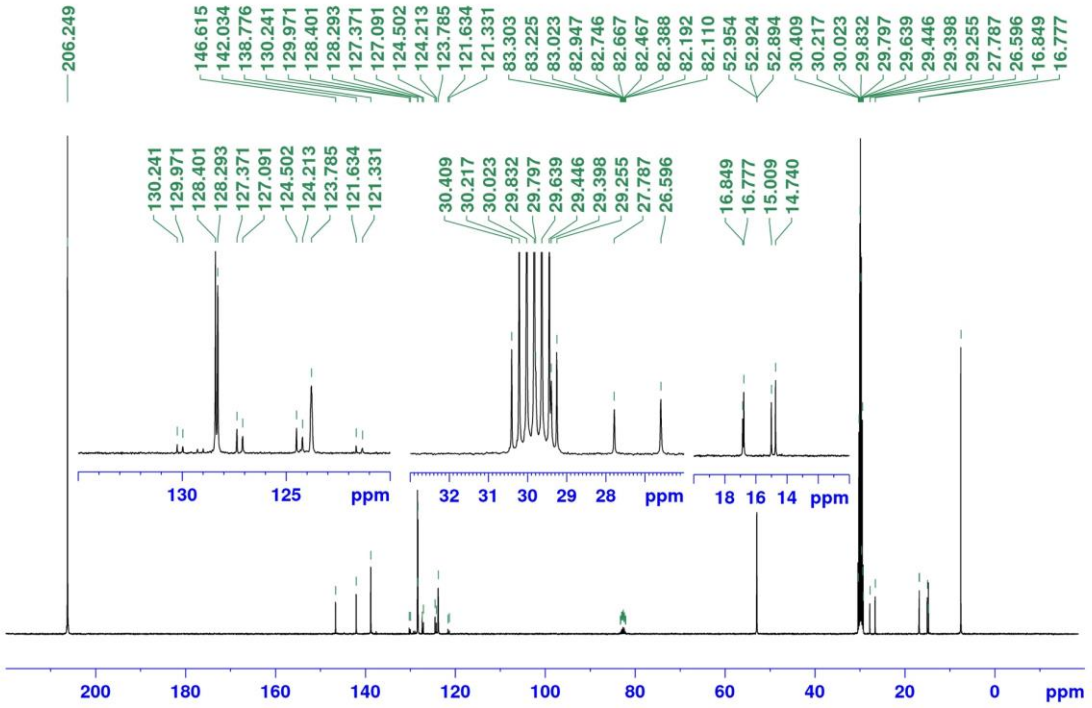
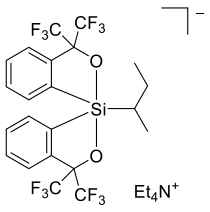


Figure S33. ^{13}C NMR (100 MHz) spectrum of **2f** in acetone-d_6.



2f

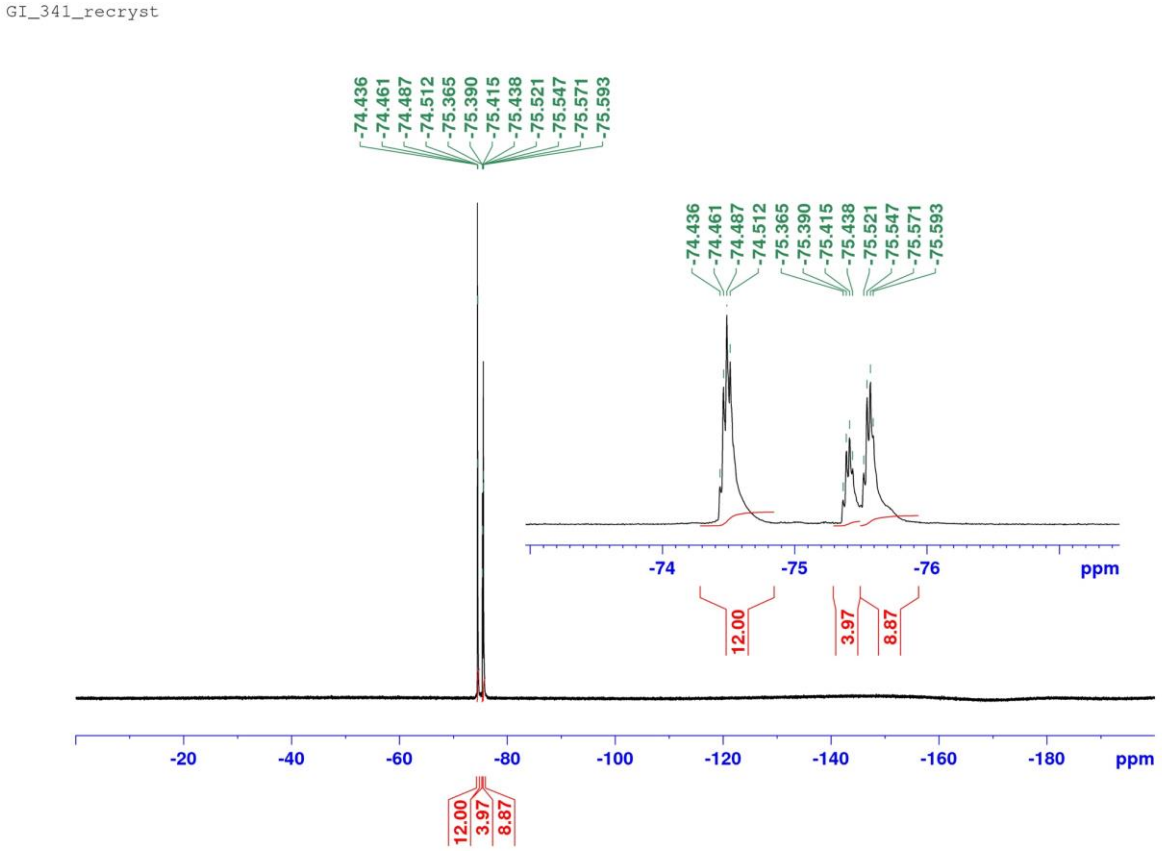
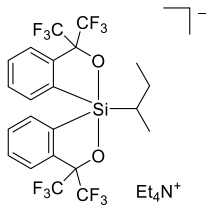


Figure S34. ^{19}F NMR (376 MHz) spectrum of **2f** in acetone-d_6.



2f

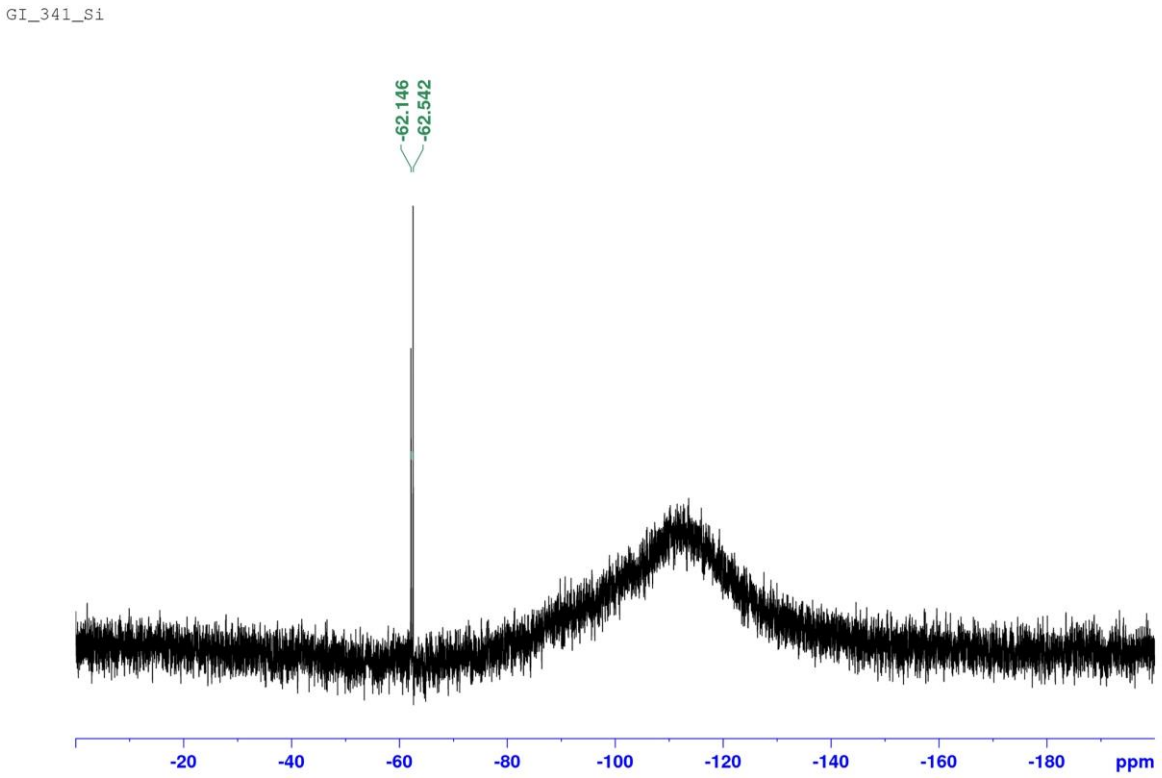
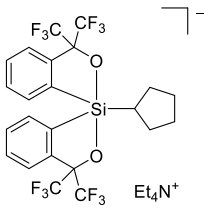


Figure S35. ^{29}Si NMR (79 MHz) spectrum of **2f** in acetone-d_6.



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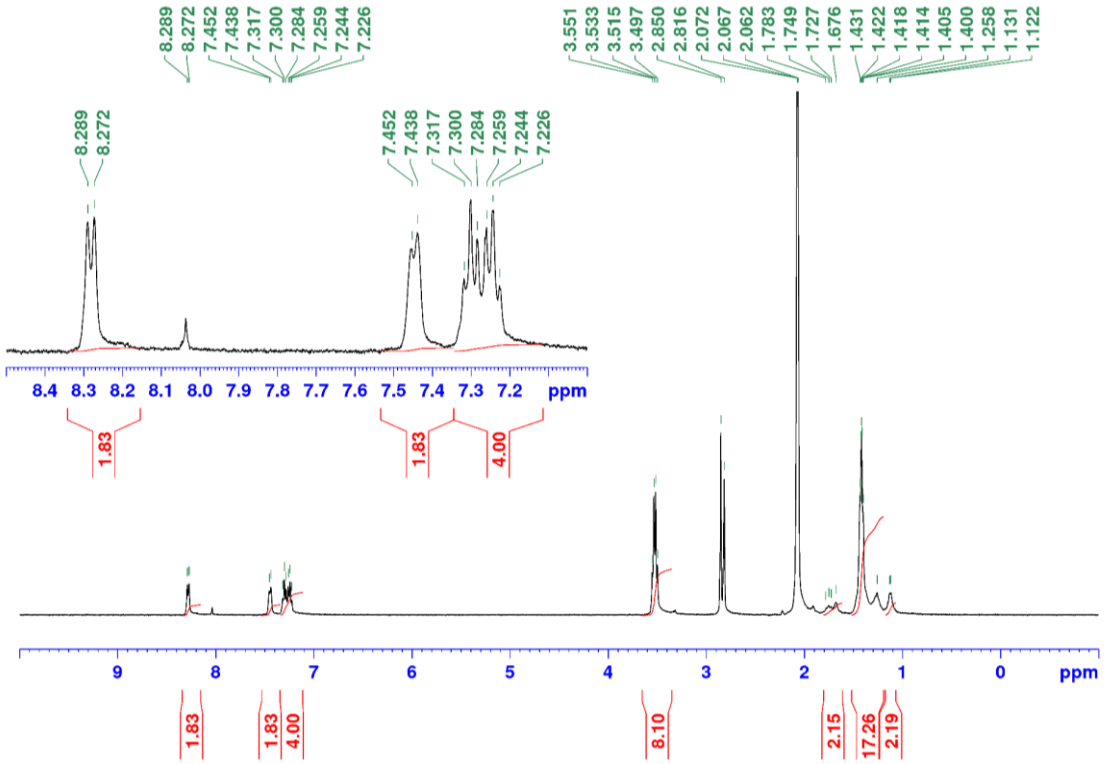
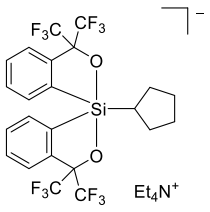


Figure S36. ^{1}H NMR (400 MHz) spectrum of **2g** in acetone-d_6.



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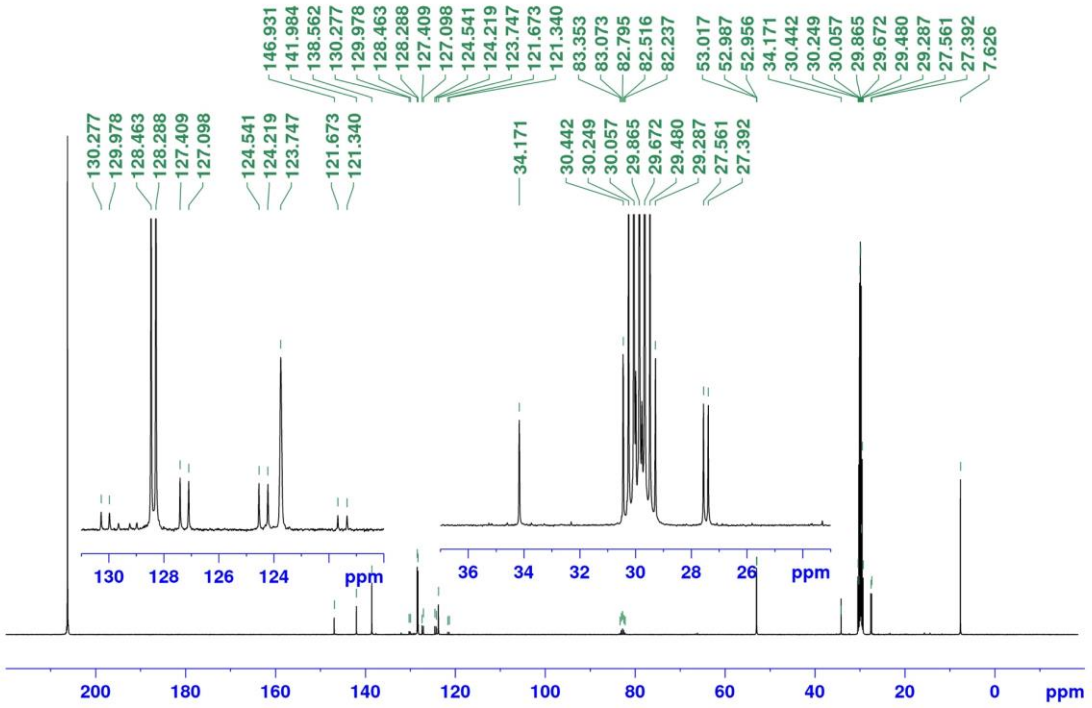
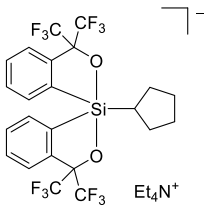


Figure S37. ^{13}C NMR (100 MHz) spectrum of **2g** in acetone-d_6.



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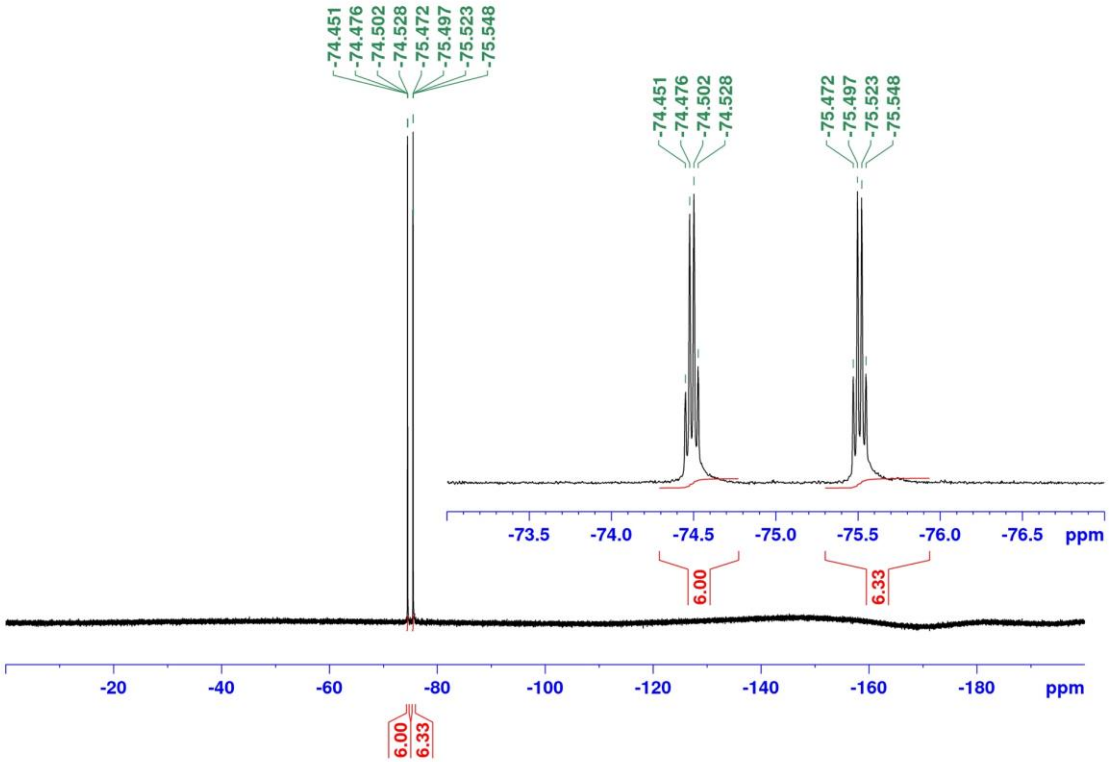
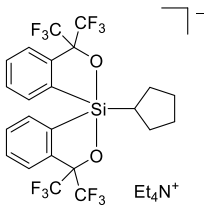


Figure S38. ^{19}F NMR (376 MHz) spectrum of **2g** in acetone-d_6.



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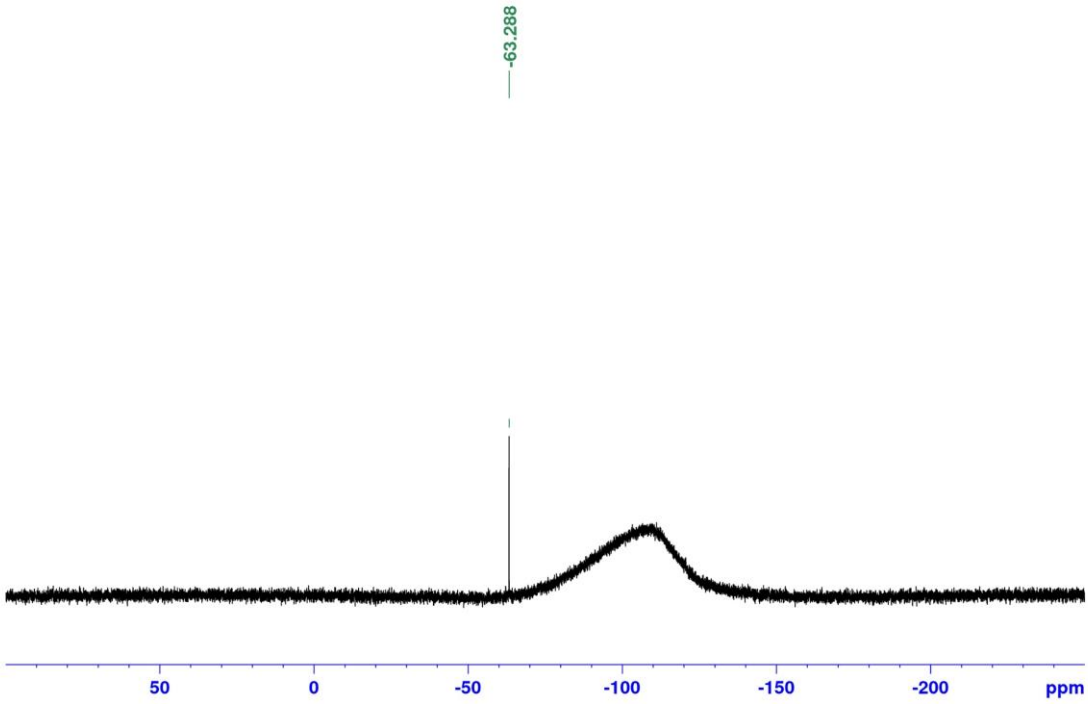
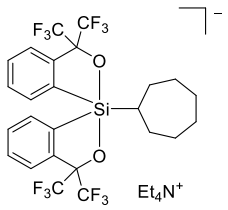


Figure S39. ^{29}Si NMR (79 MHz) spectrum of **2g** in acetone-d_6.



2h

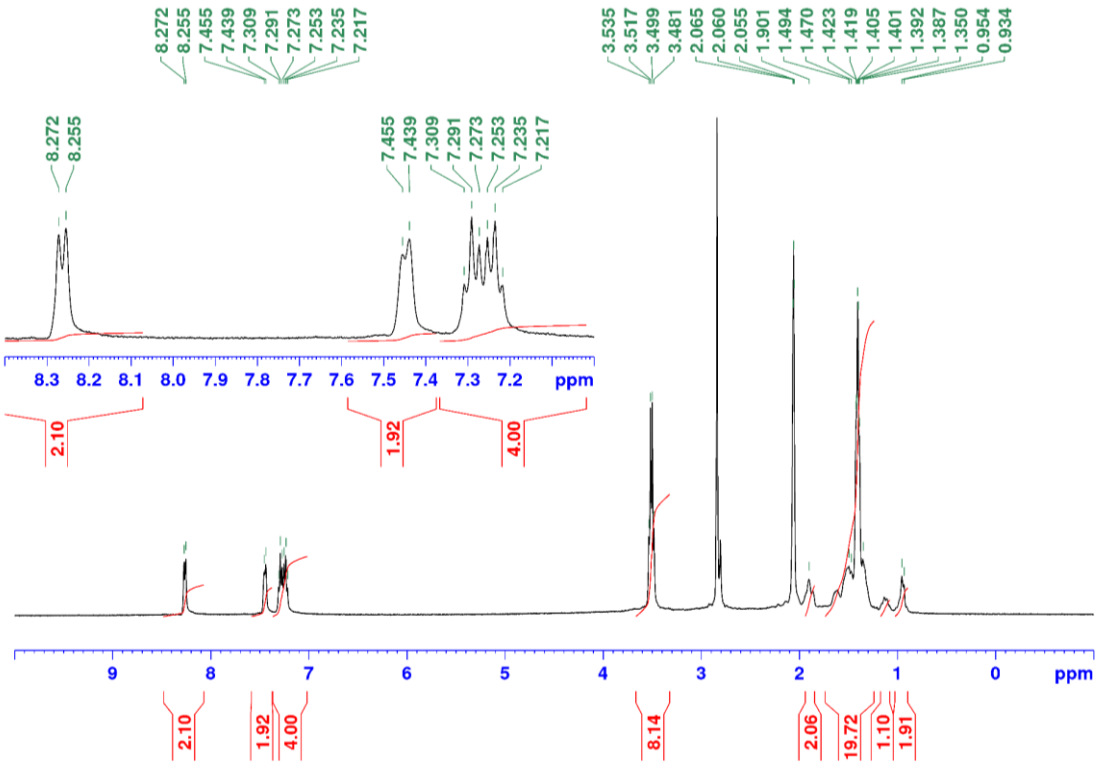
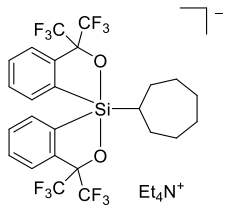


Figure S40. ^{1}H NMR (400 MHz) spectrum of **2h** in acetone-d_6.



2h

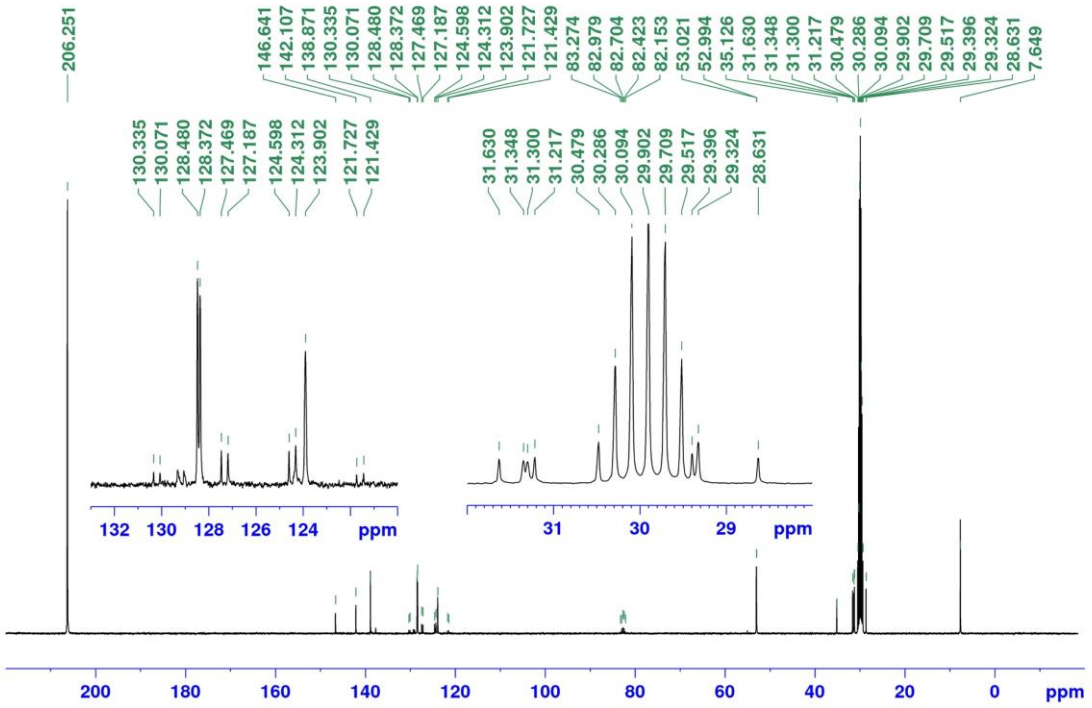
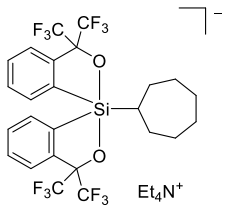


Figure S41. ^{13}C NMR (100 MHz) spectrum of **2h** in acetone-d_6.



2h

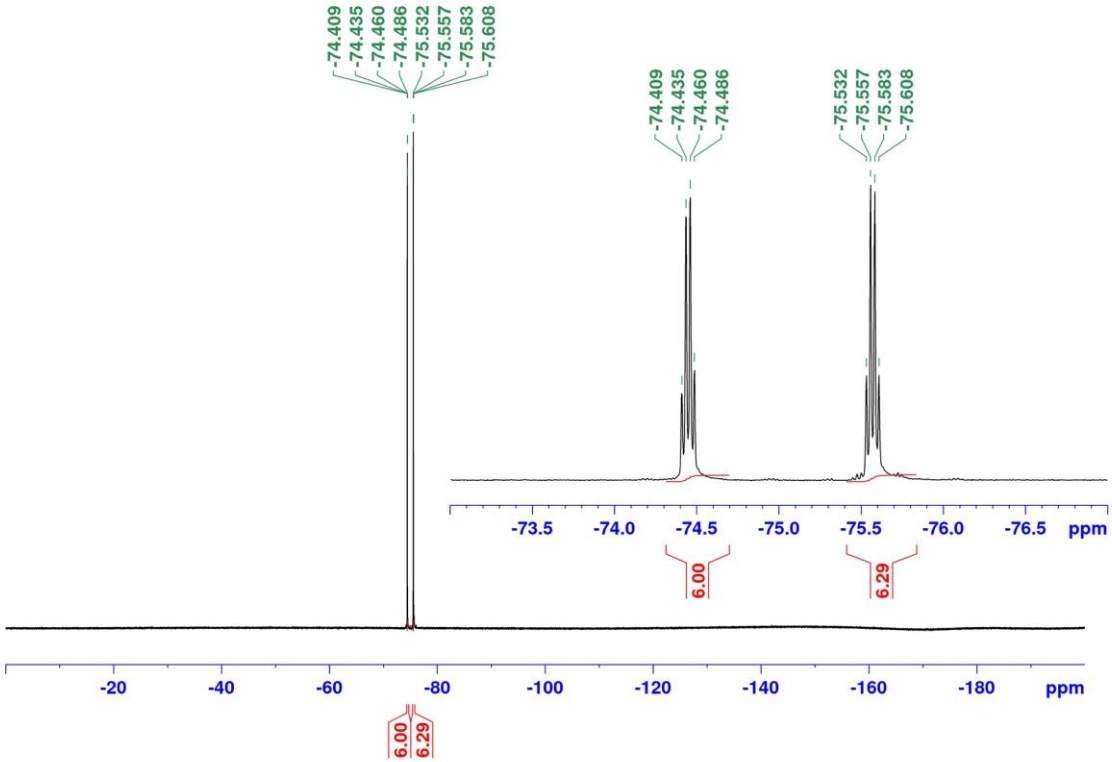
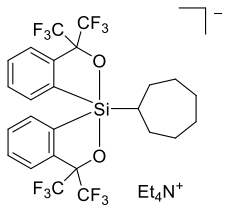


Figure S42. ^{19}F NMR (376 MHz) spectrum of **2h** in acetone-d_6.



2h

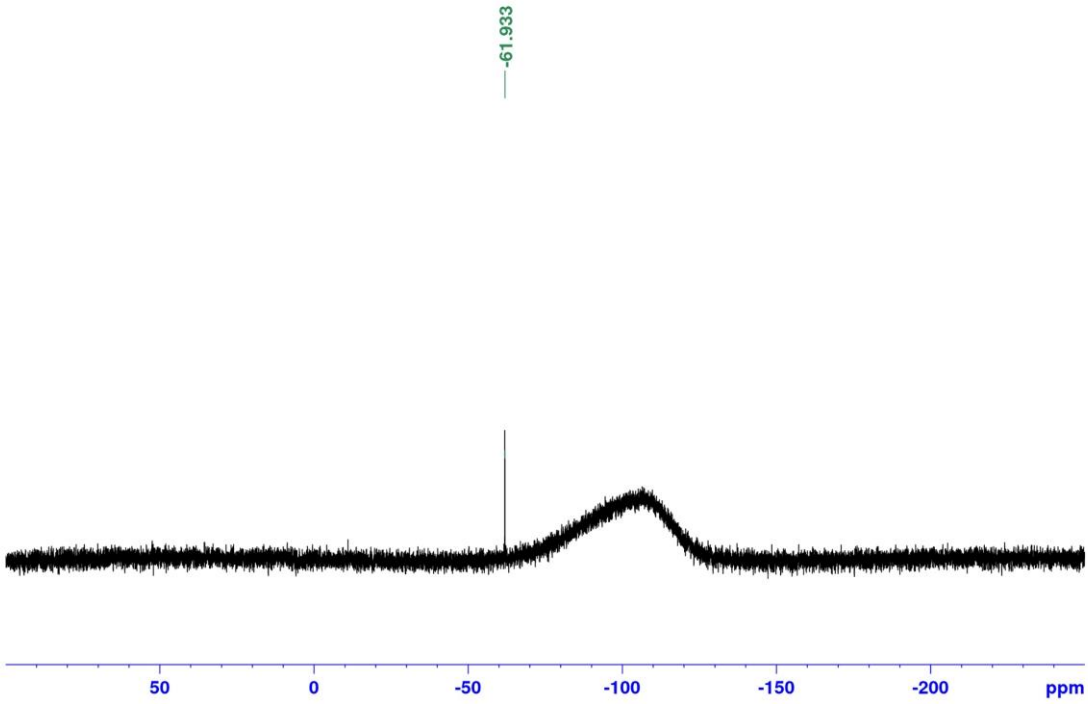
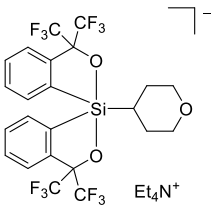


Figure S43. ^{29}Si NMR (79 MHz) spectrum of **2h** in acetone-d_6.



2i

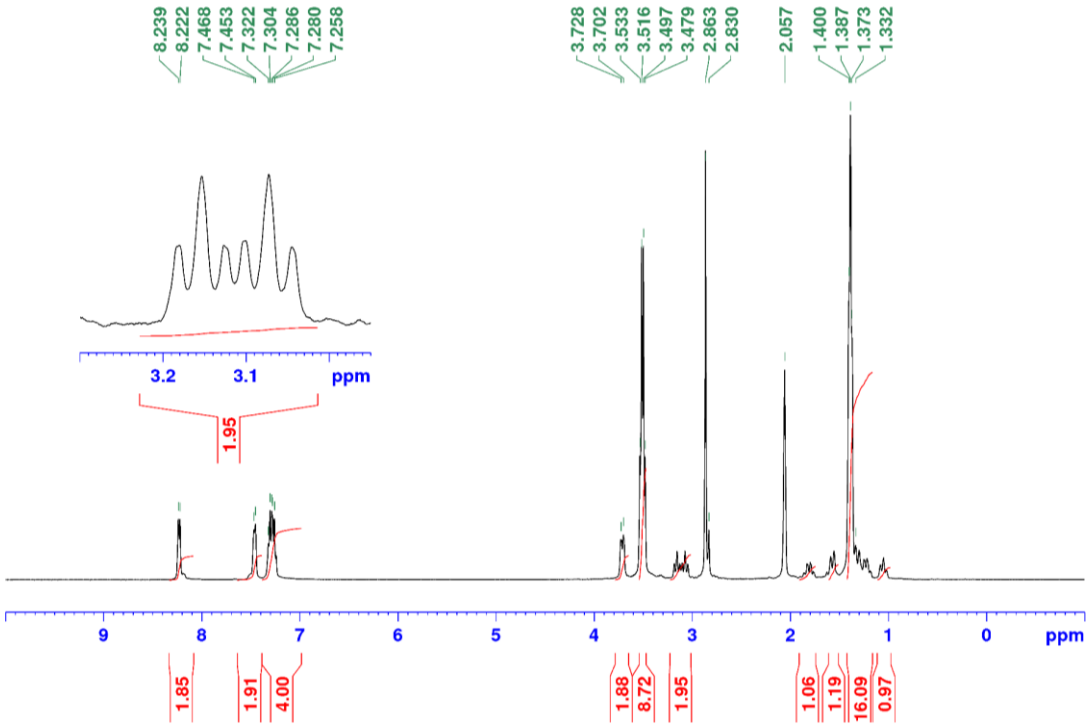
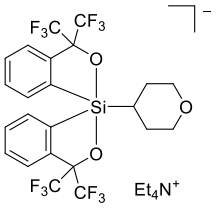


Figure S44. ^{1}H NMR (400 MHz) spectrum of **2i** in acetone-d_6.



2i

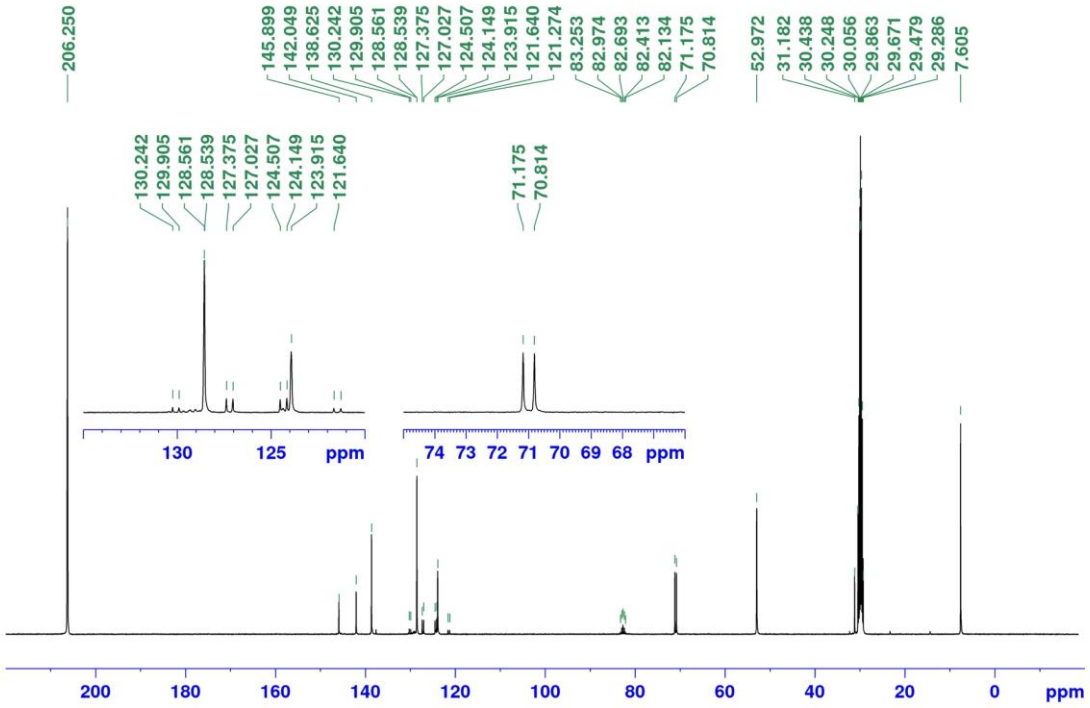
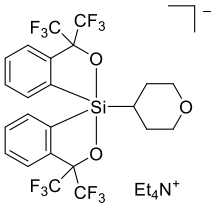


Figure S45. ^{13}C NMR (100 MHz) spectrum of **2i** in acetone-d_6.



2i

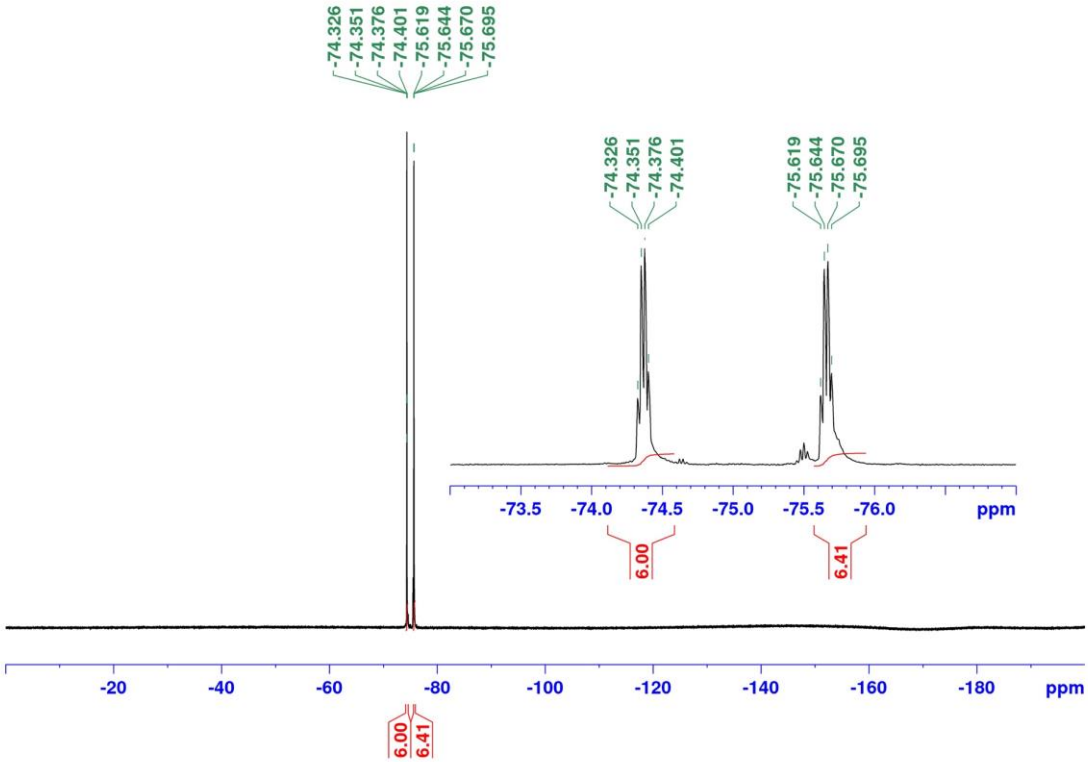
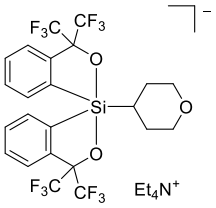


Figure S46. ^{19}F NMR (376 MHz) spectrum of **2i** in acetone-d_6.



2i

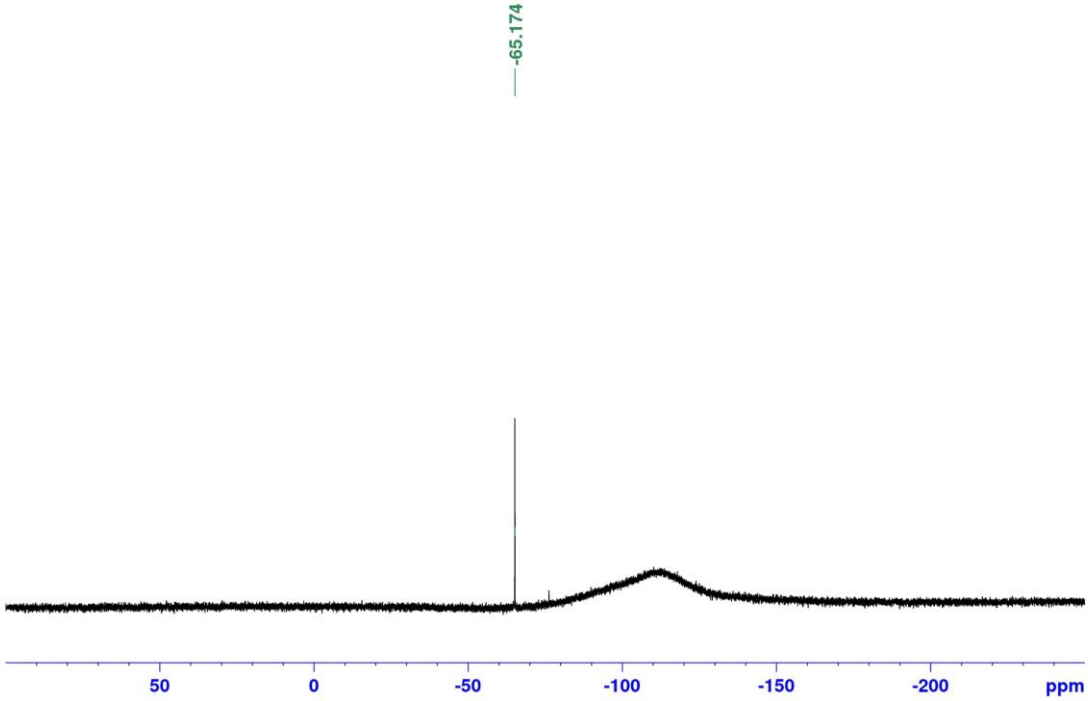
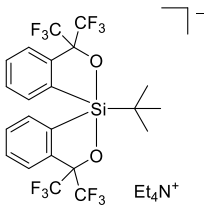


Figure S47. ^{29}Si NMR (79 MHz) spectrum of **2i** in acetone-d_6.



2j

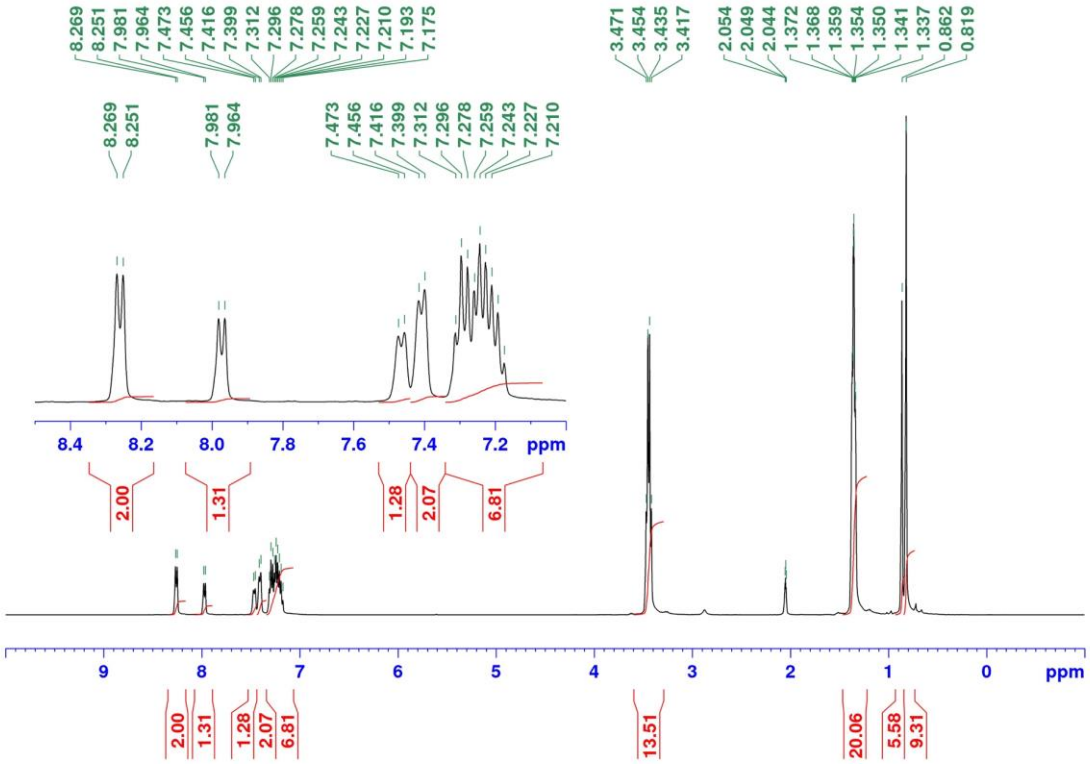
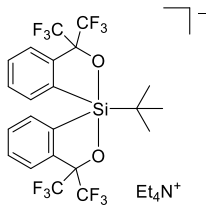


Figure S48. ^{1}H NMR (400 MHz) spectrum of **2j** in acetone-d_6.



2j

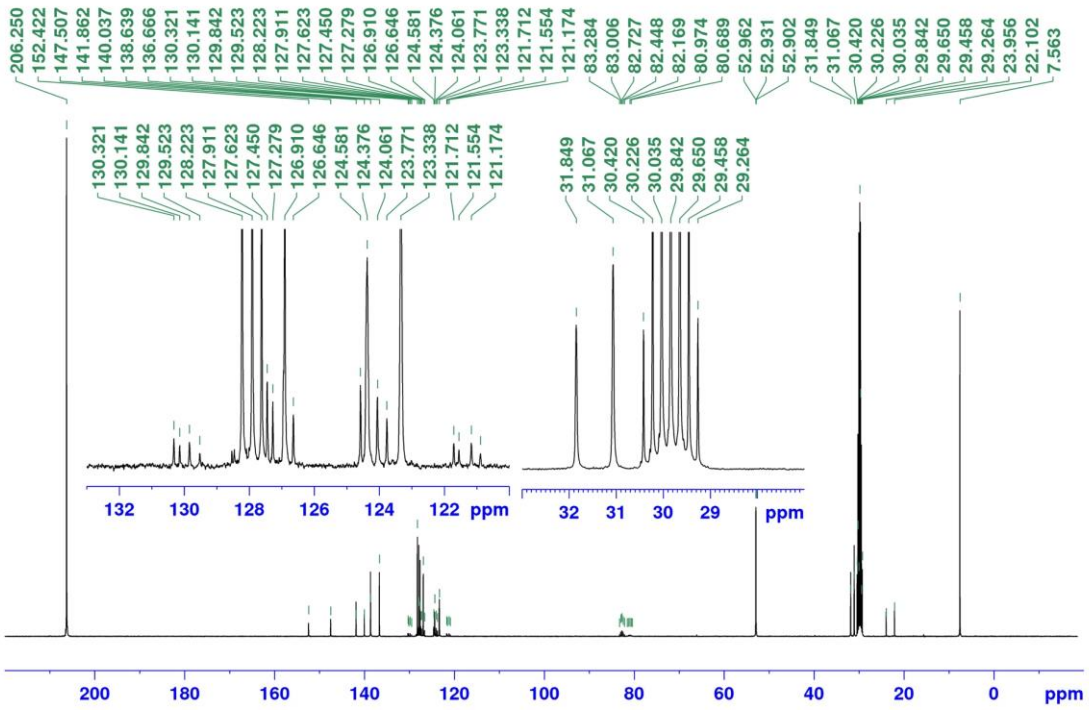
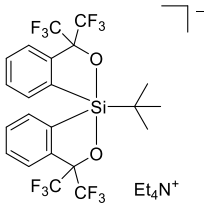


Figure S49. ^{13}C NMR (100 MHz) spectrum of **2j** in acetone-d_6.



2j

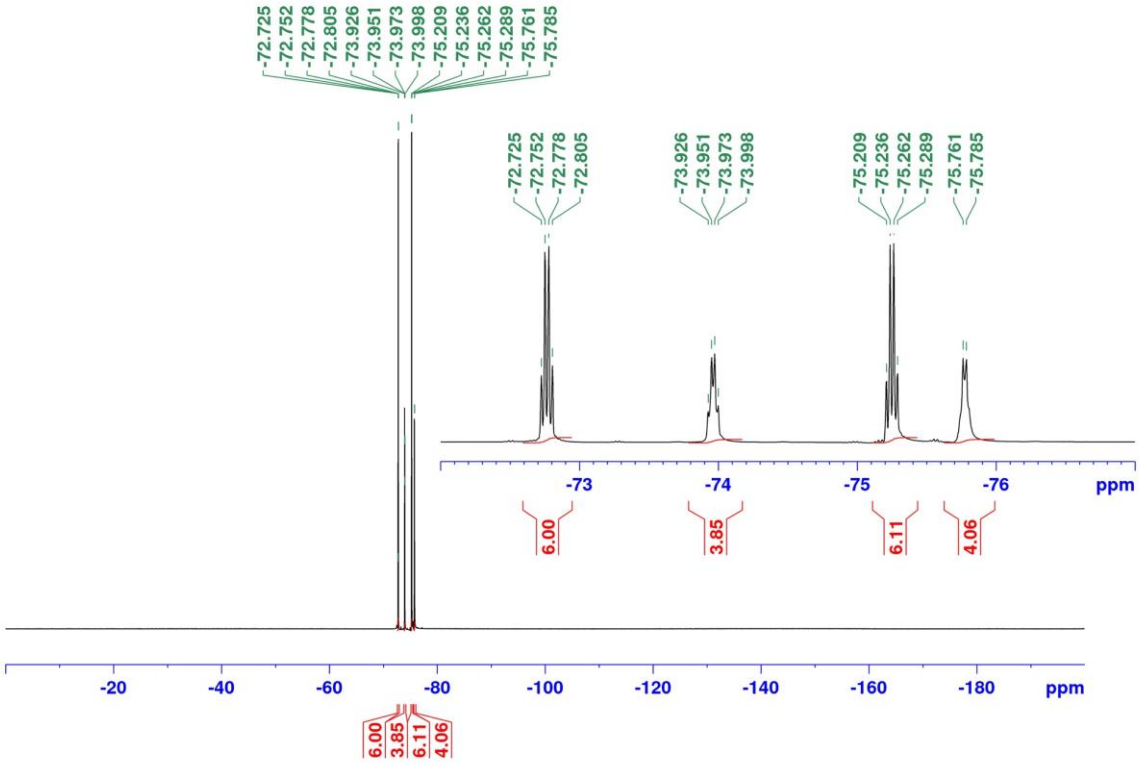
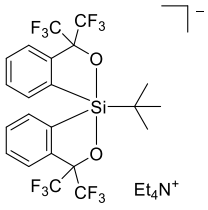


Figure S50. ^{19}F NMR (376 MHz) spectrum of **2j** in acetone-d_6.



2j

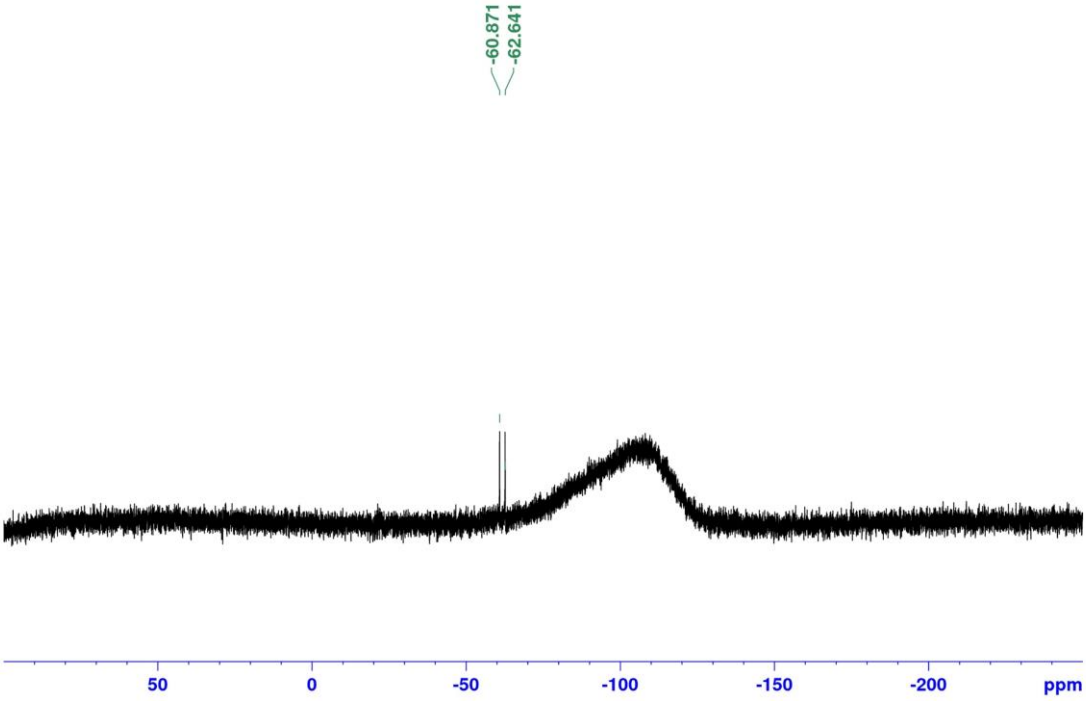
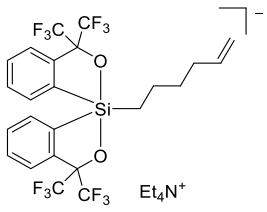


Figure S51. ^{29}Si NMR (79 MHz) spectrum of **2j** in acetone-d_6.



2b

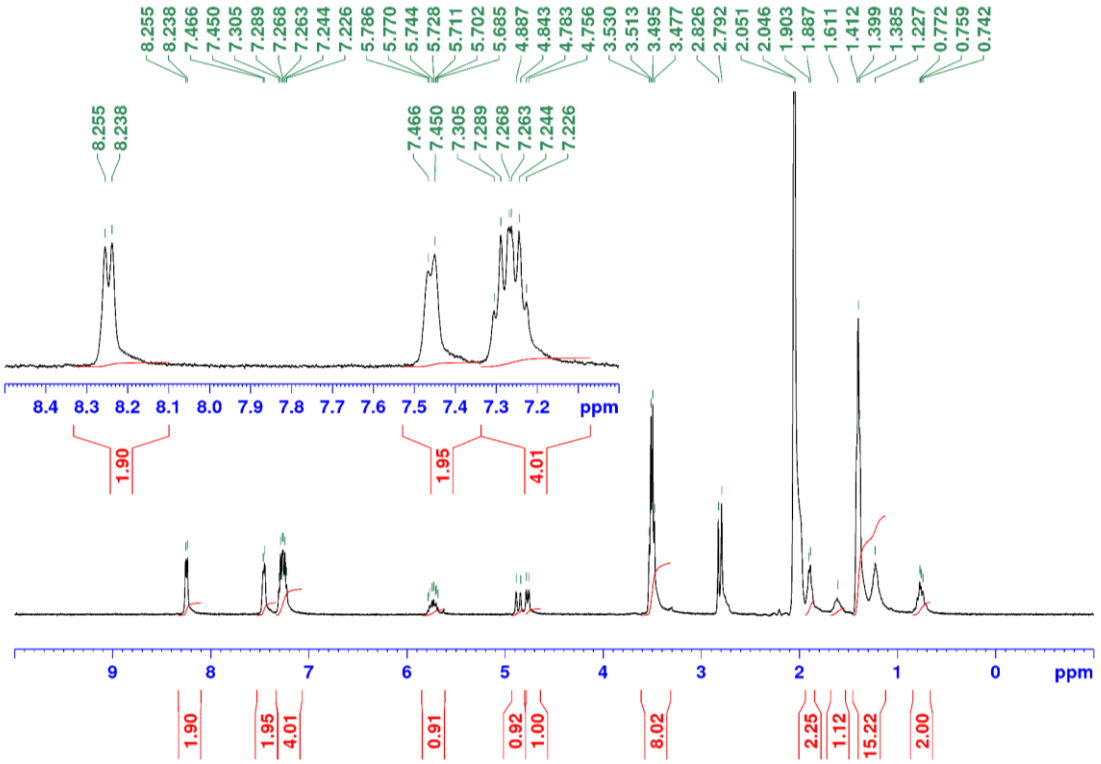
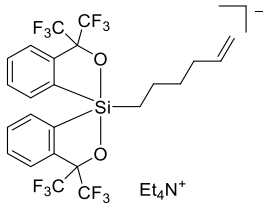


Figure S52. ^{1}H NMR (400 MHz) spectrum of **2b** in acetone-d_6.



2b

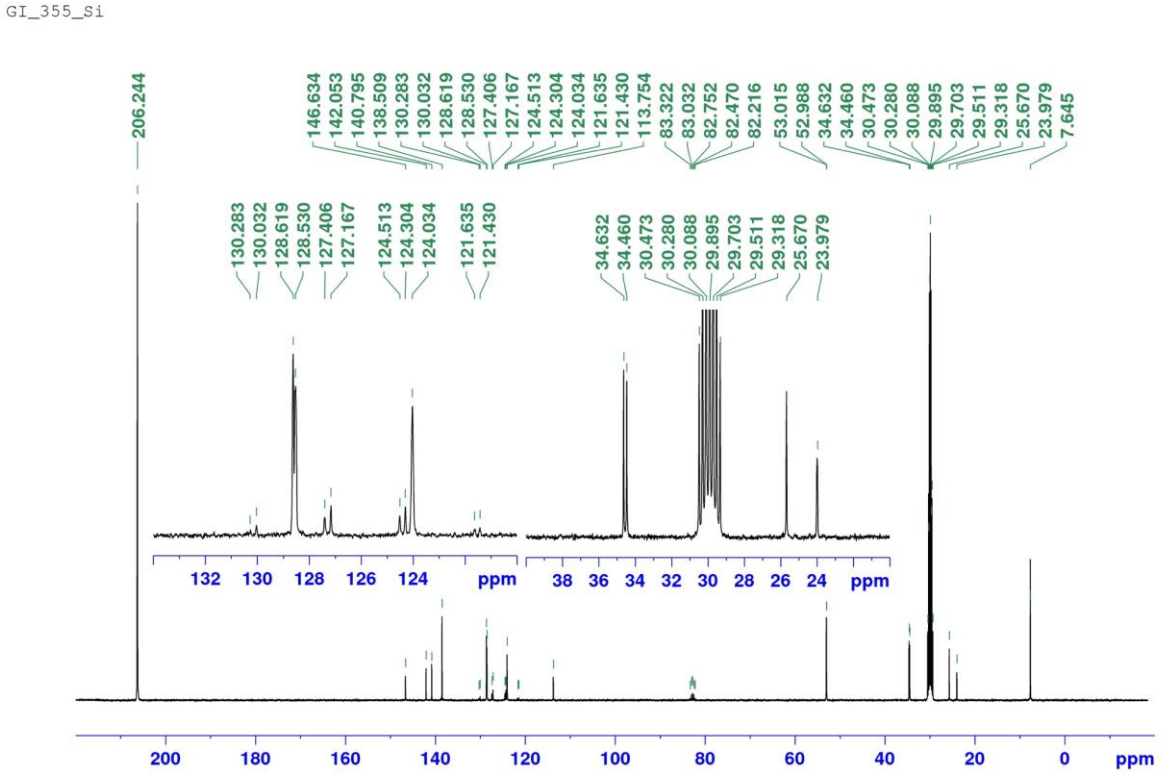
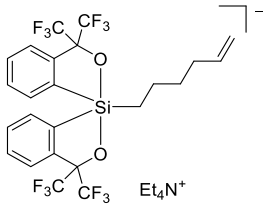


Figure S53. ^{13}C NMR (100 MHz) spectrum of **2b** in acetone-d_6.



2b

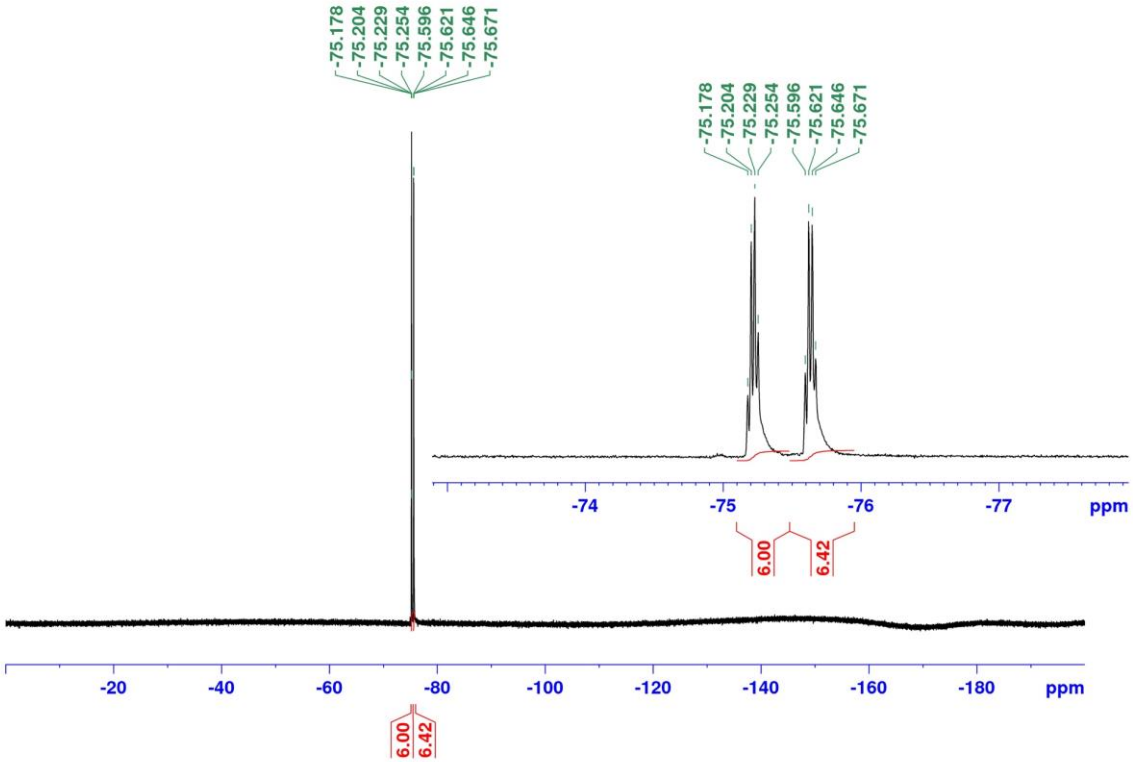
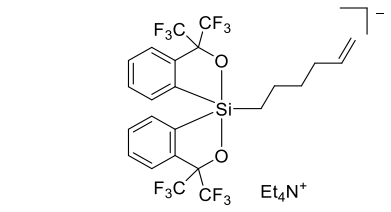


Figure S54. ^{19}F NMR (376 MHz) spectrum of **2b** in acetone-d_6.



2b

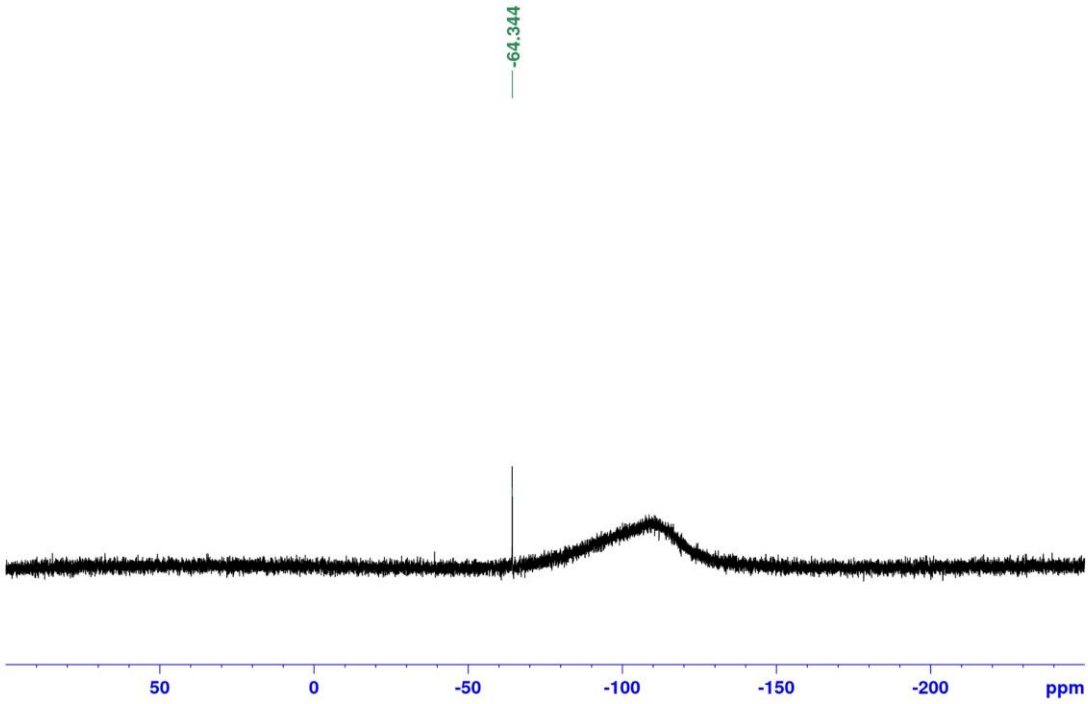


Figure S55. ^{29}Si NMR (79 MHz) spectrum of **2b** in acetone-d_6.

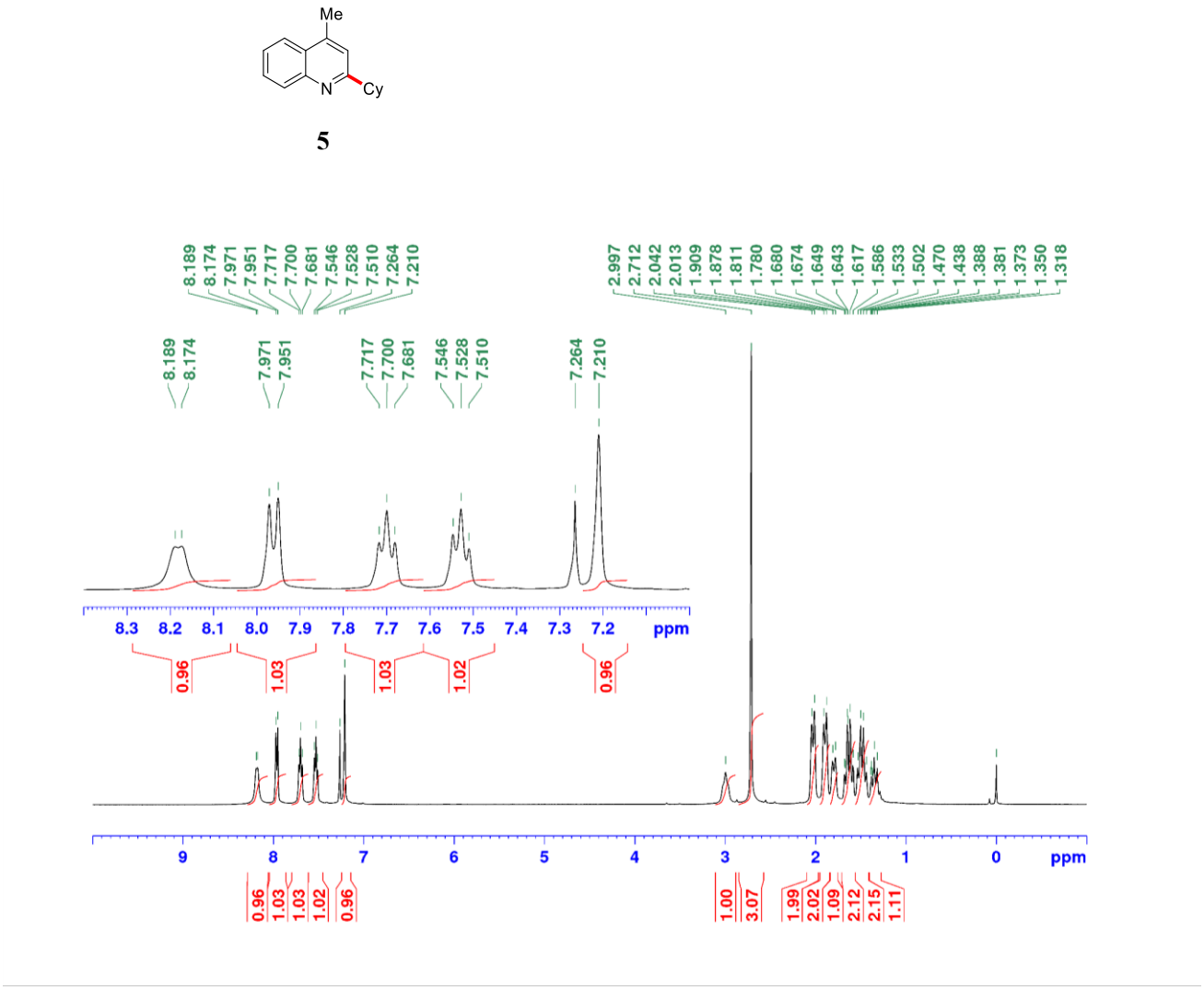
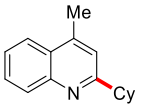


Figure S56. ^{1}H NMR (400 MHz) spectrum of **5** in $CDCl_3$.



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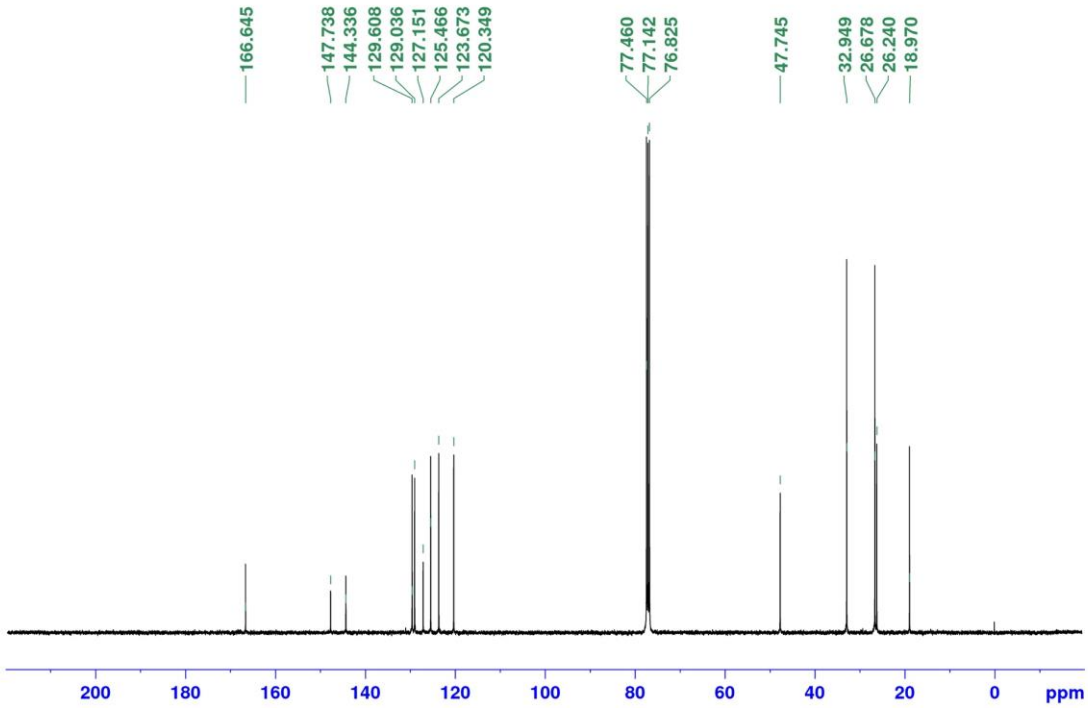


Figure S57. ^{13}C NMR (100 MHz) spectrum of **5** in $CDCl_3$.

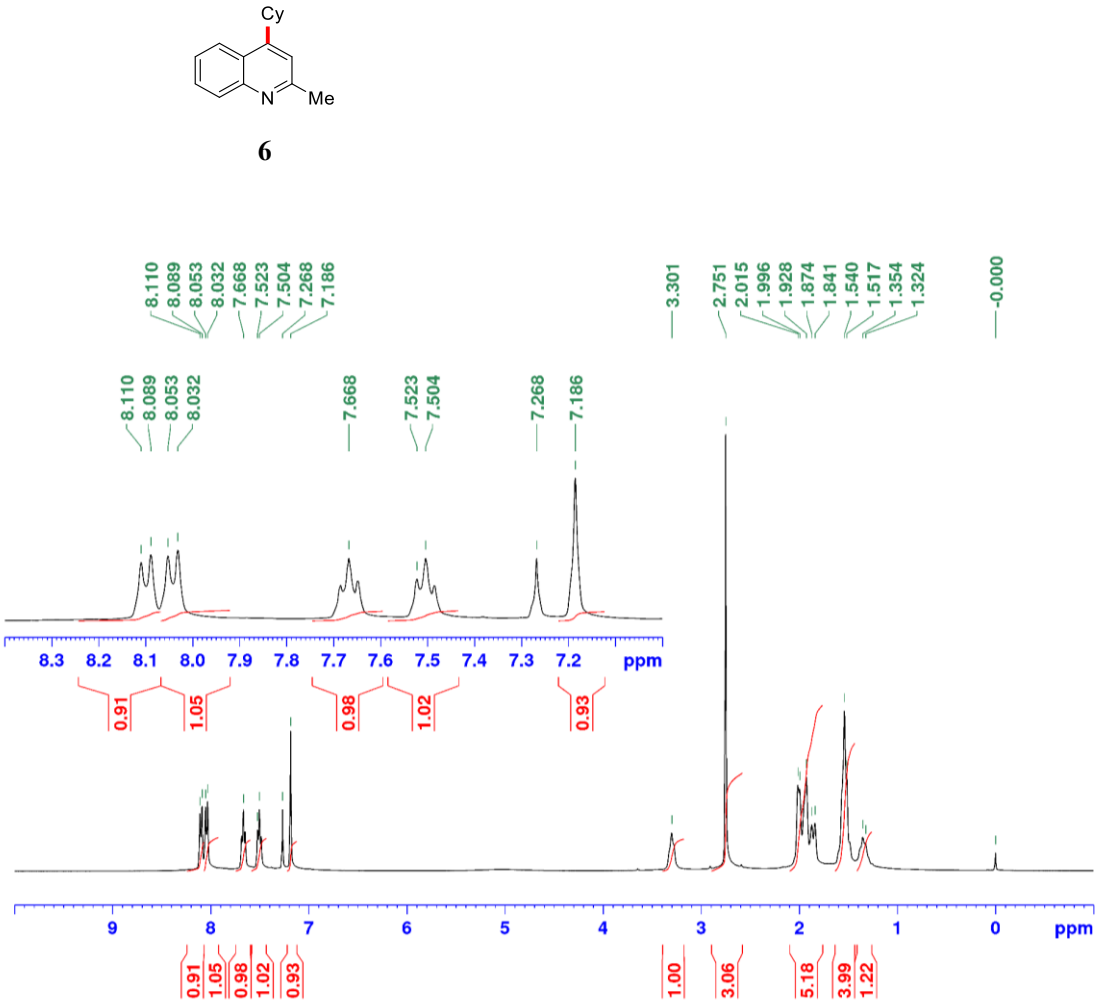


Figure S58. ^{1}H NMR (400 MHz) spectrum of **6** in $CDCl_3$.

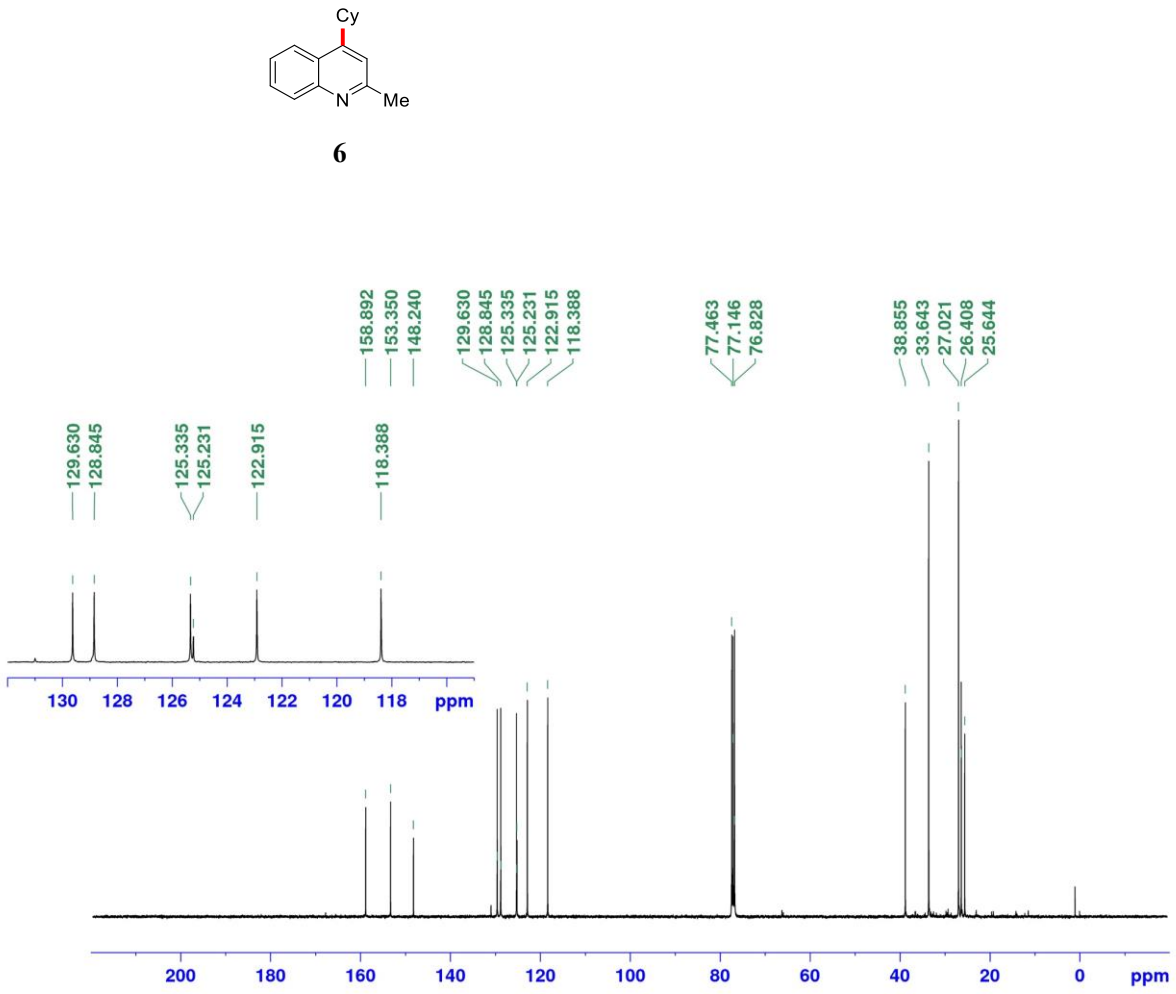


Figure S59. ^{13}C NMR (100 MHz) spectrum of **6** in $CDCl_3$.

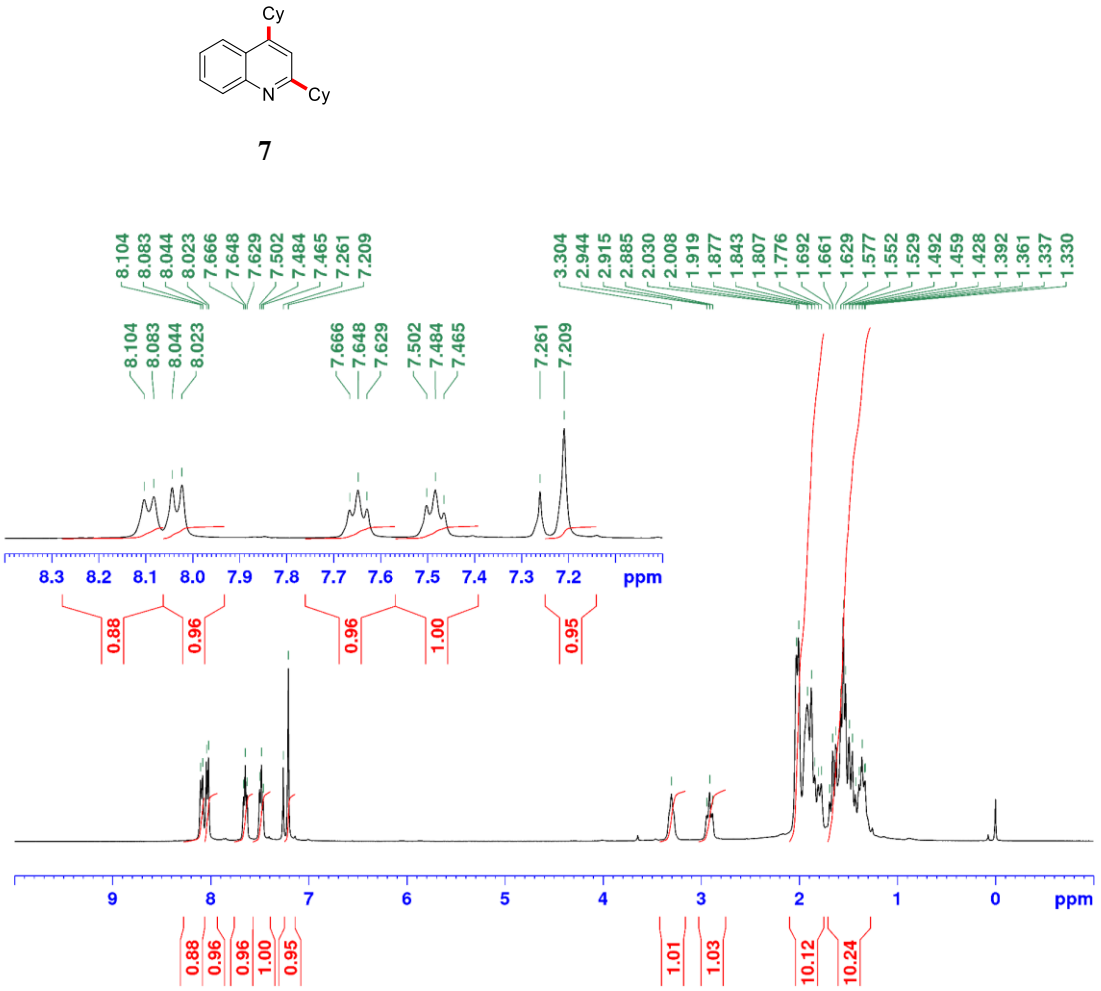
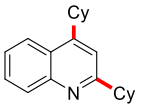


Figure S60. ^{1}H NMR (400 MHz) spectrum of **7** in $CDCl_3$.



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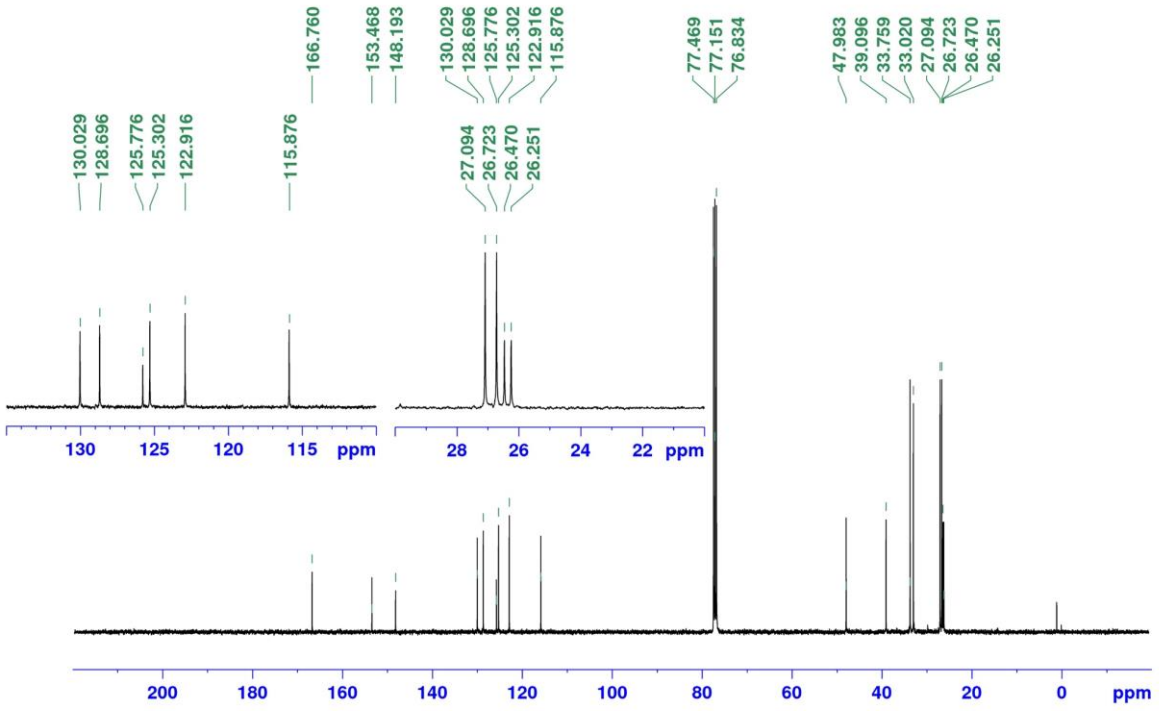


Figure S61. ^{13}C NMR (100 MHz) spectrum of **7** in $CDCl_3$.

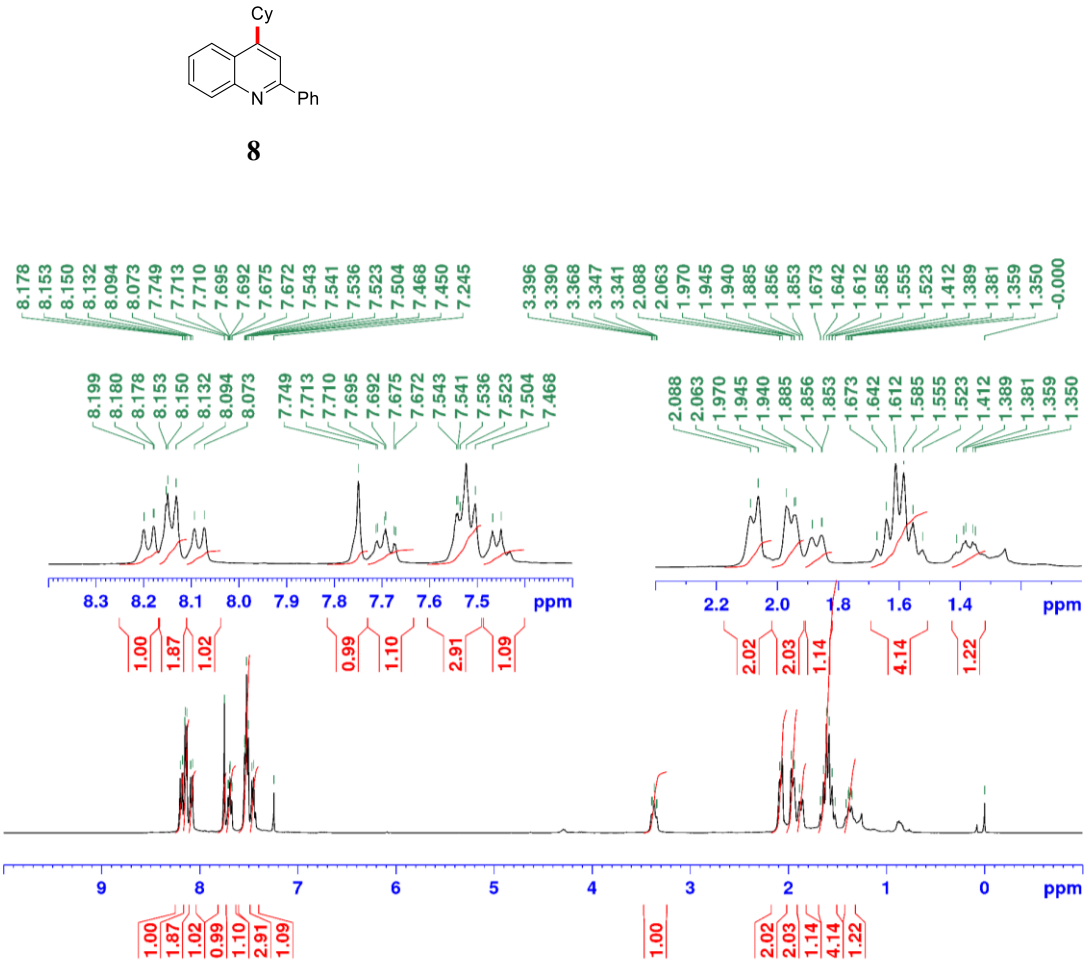
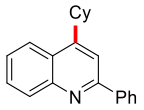


Figure S62. ^{1}H NMR (400 MHz) spectrum of **8** in $CDCl_3$.



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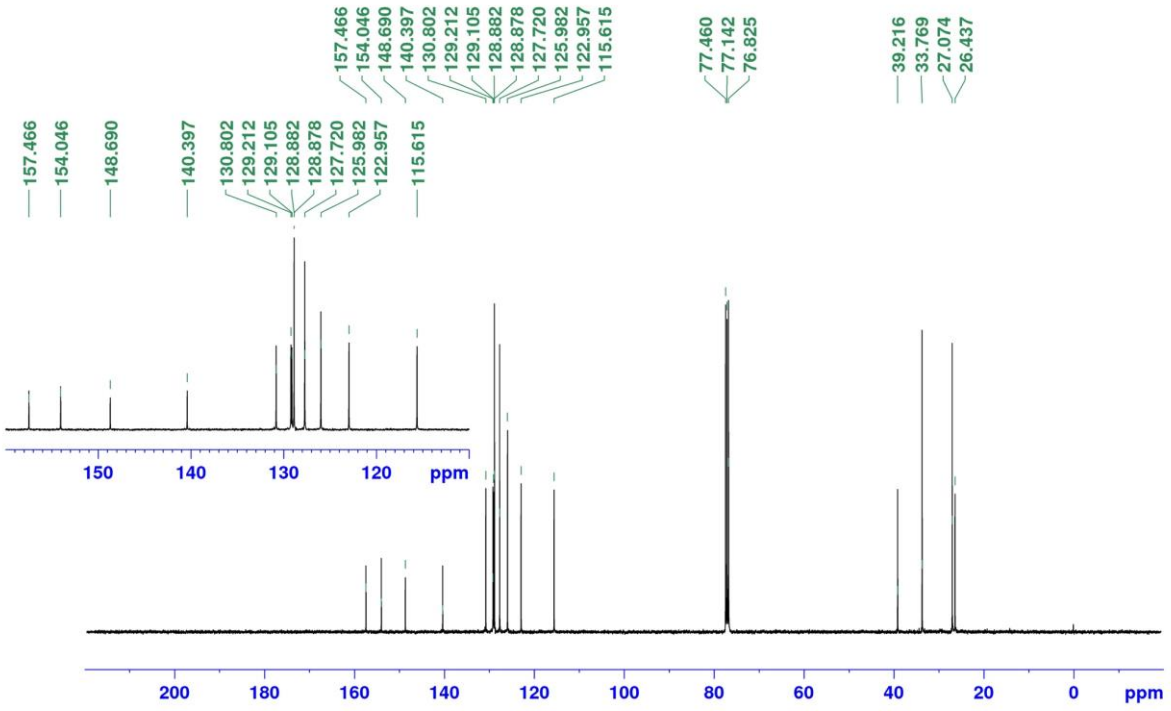
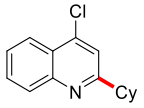


Figure S63. ^{13}C NMR (100 MHz) spectrum of **8** in $CDCl_3$.



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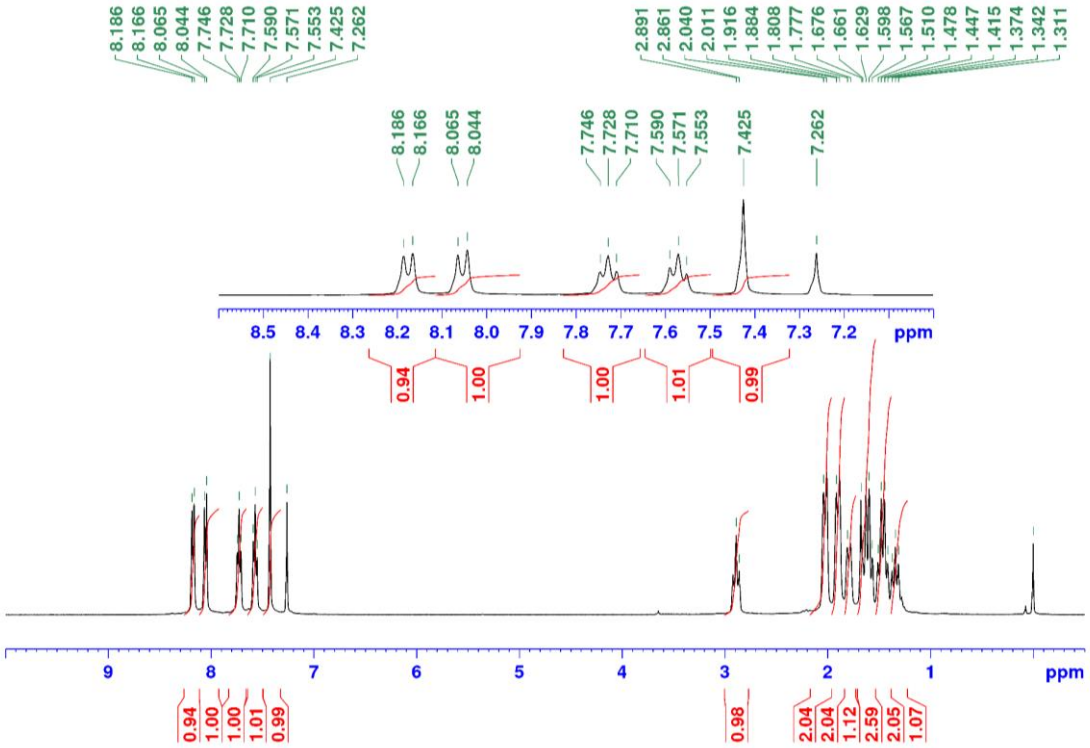
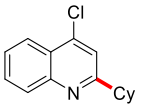


Figure S64. ^{1}H NMR (400 MHz) spectrum of **9** in $CDCl_3$.



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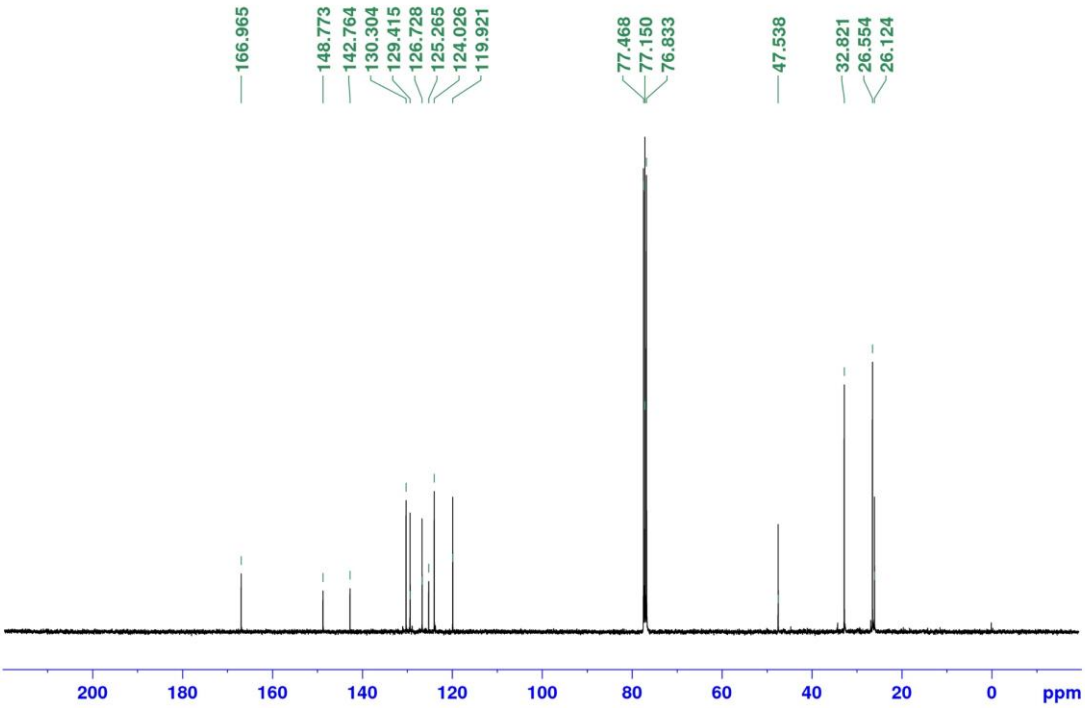
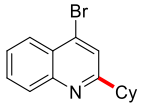


Figure S65. ^{13}C NMR (100 MHz) spectrum of **9** in $CDCl_3$.



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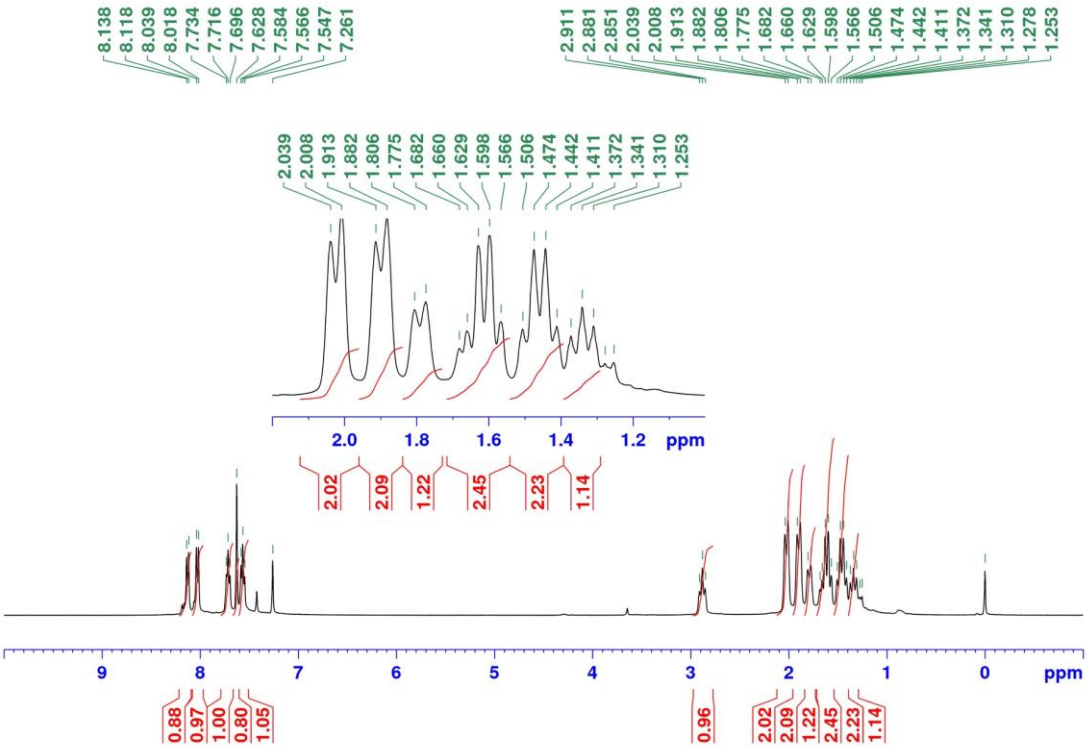
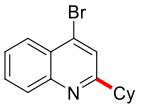


Figure S66. ^{1}H NMR (400 MHz) spectrum of **10** in $CDCl_3$.



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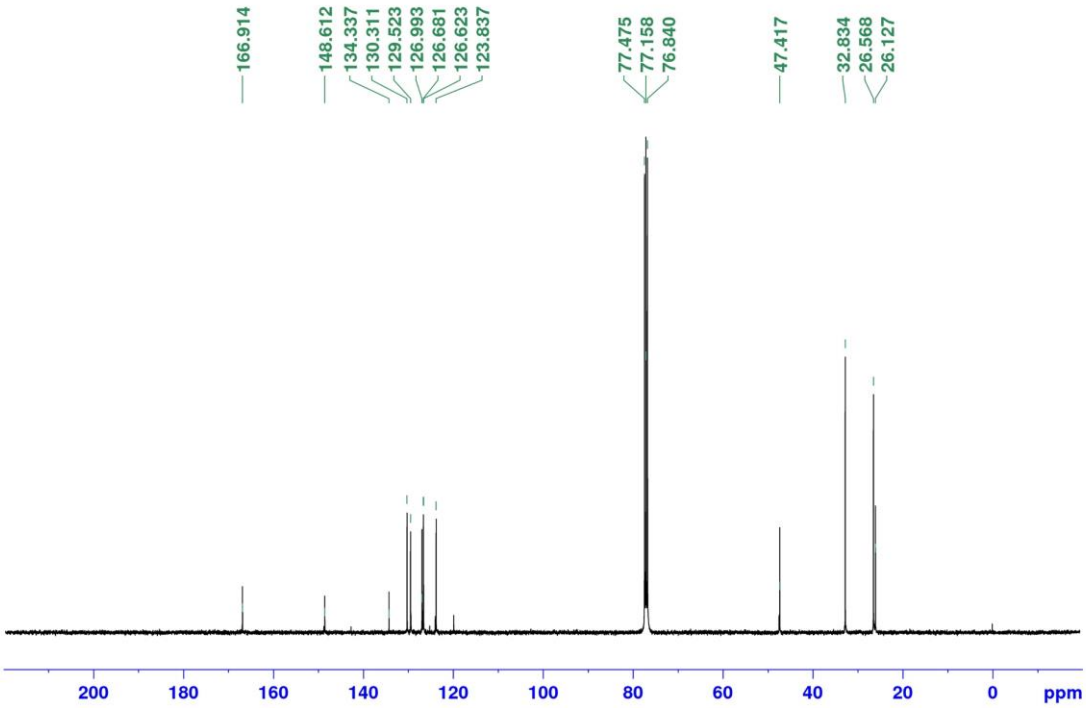


Figure S67. ^{13}C NMR (100 MHz) spectrum of **10** in $CDCl_3$.

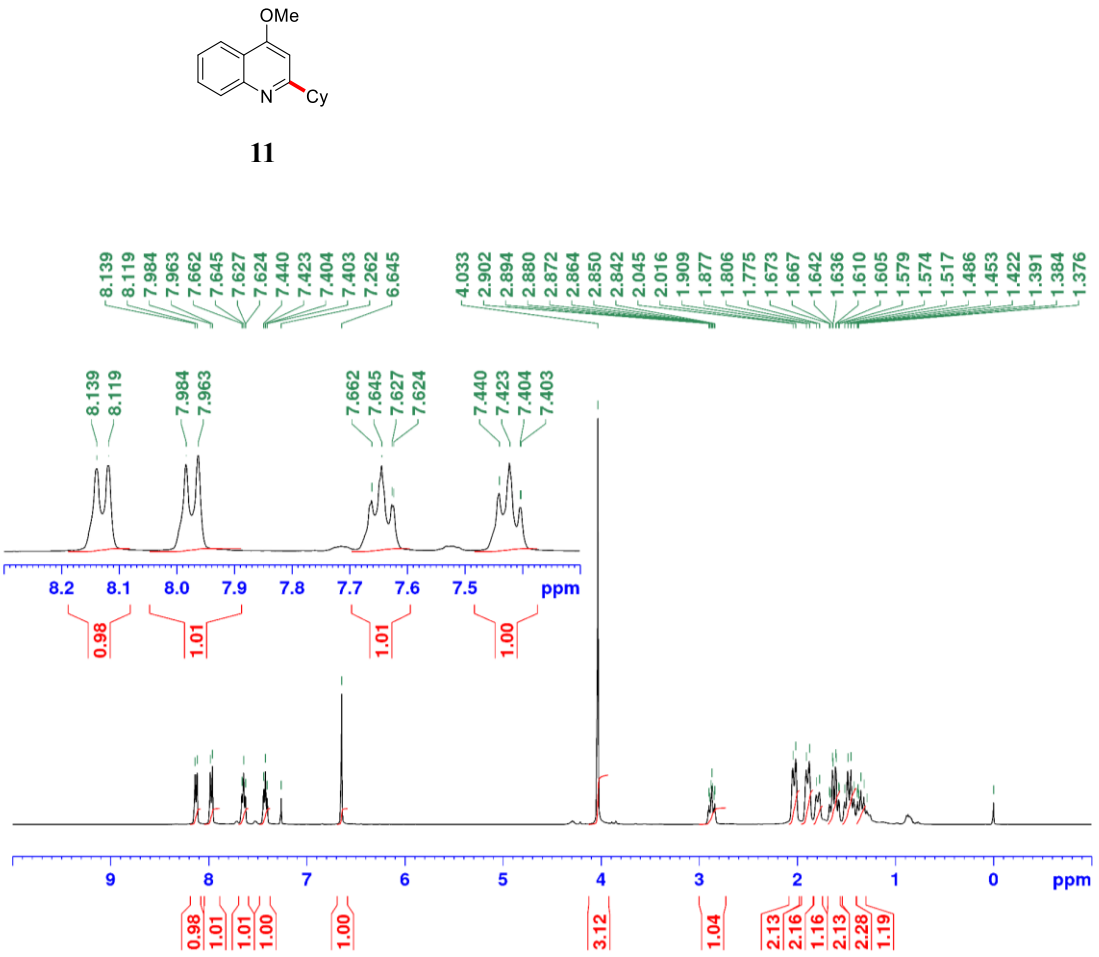
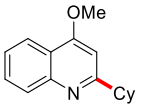


Figure S68. ^{1}H NMR (400 MHz) spectrum of **11** in $CDCl_3$.



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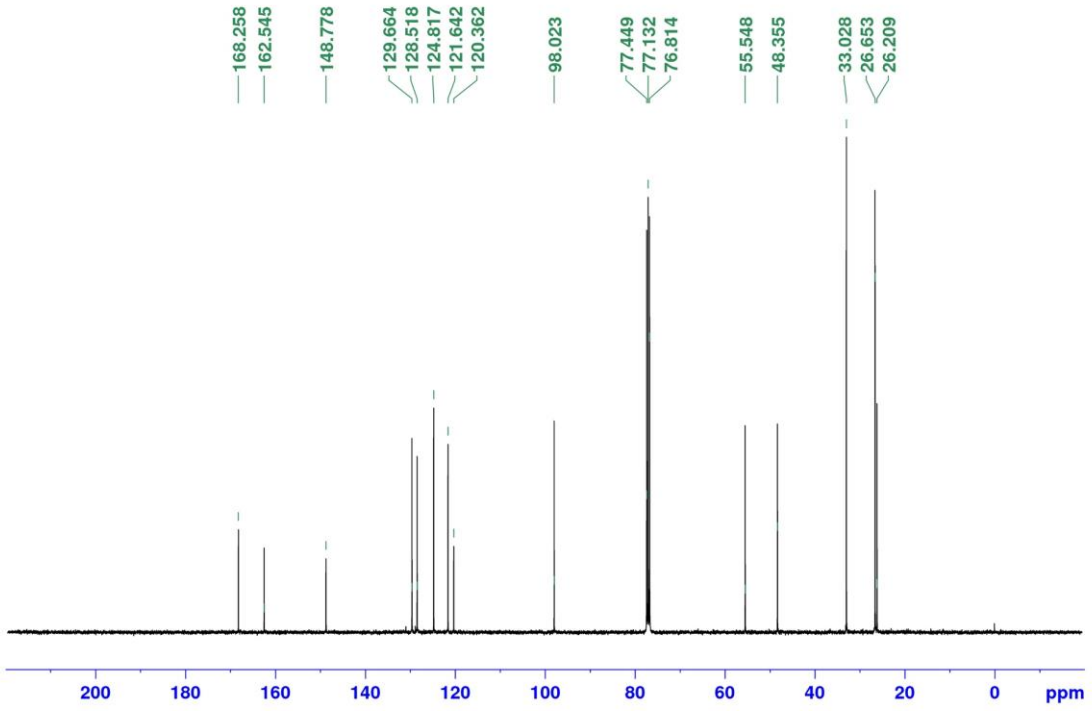
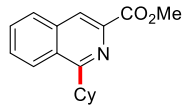


Figure S69. ^{13}C NMR (100 MHz) spectrum of **11** in $CDCl_3$.



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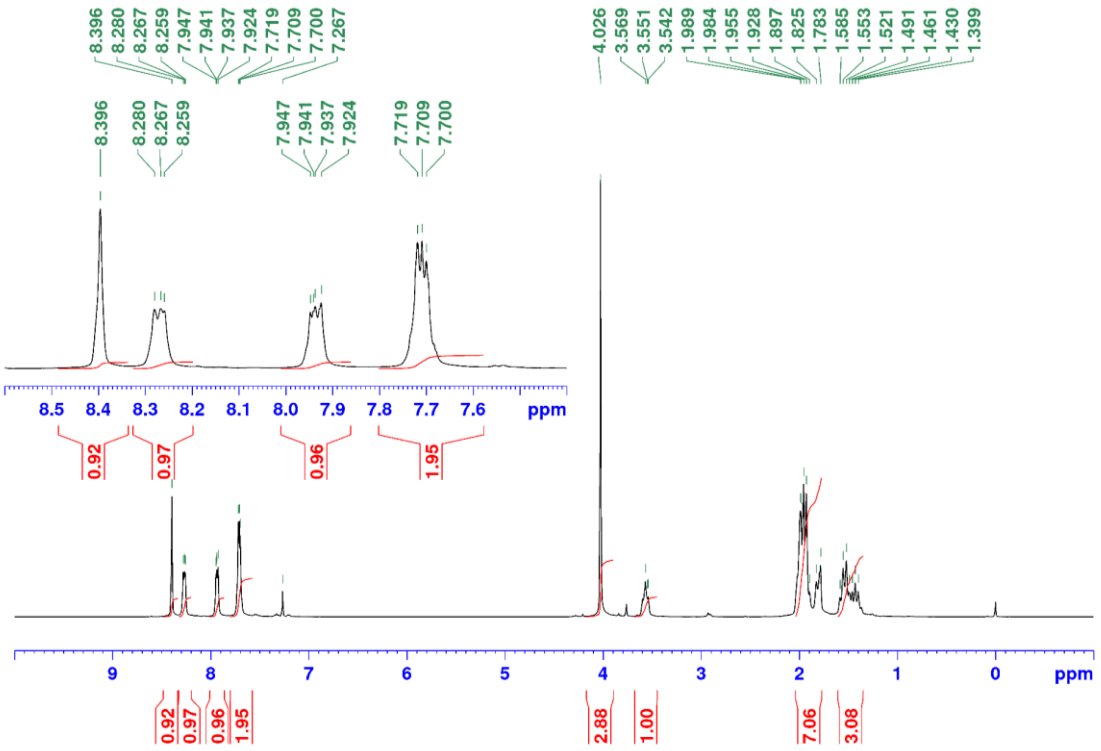
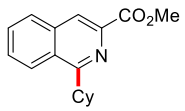


Figure S70. ^{1}H NMR (400 MHz) spectrum of **12** in $CDCl_3$.



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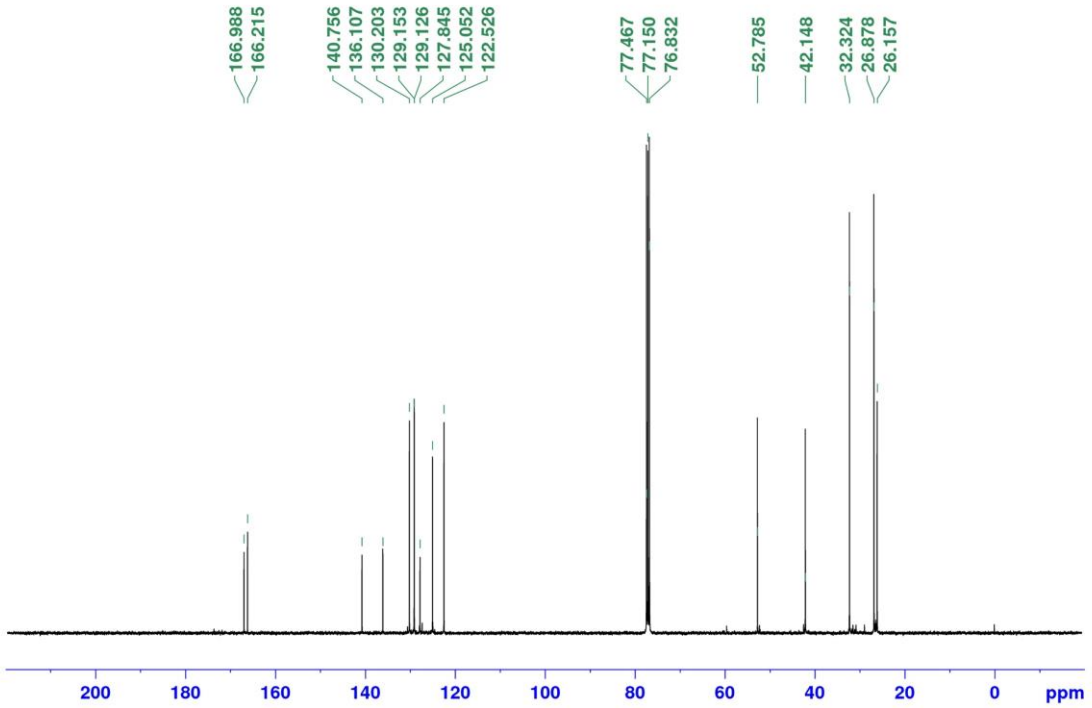
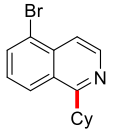


Figure S71. ^{13}C NMR (100 MHz) spectrum of **12** in $CDCl_3$.



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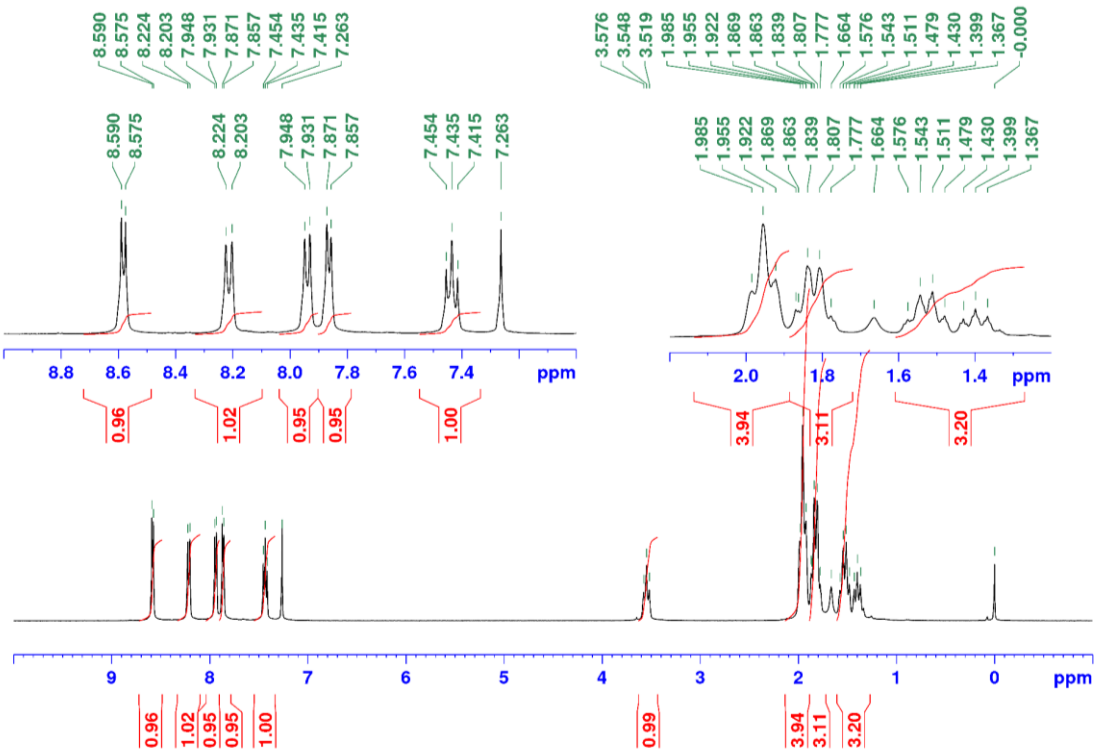
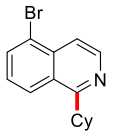


Figure S72. ^{1}H NMR (400 MHz) spectrum of **13** in $CDCl_3$.



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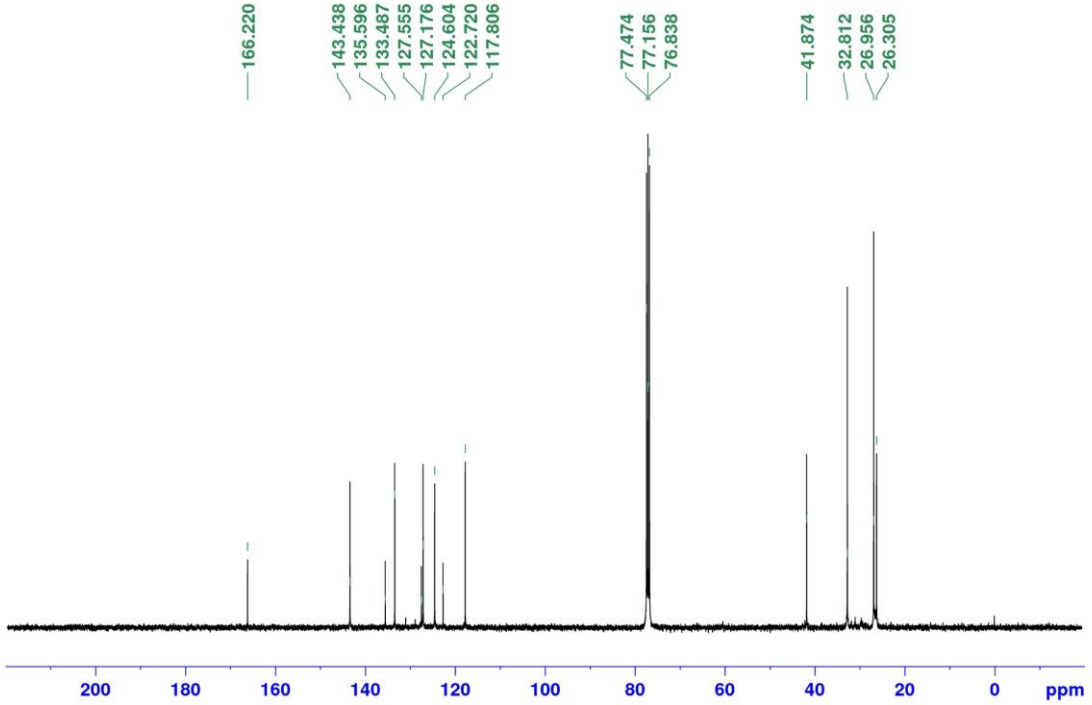


Figure S73. ^{13}C NMR (100 MHz) spectrum of **13** in $CDCl_3$.

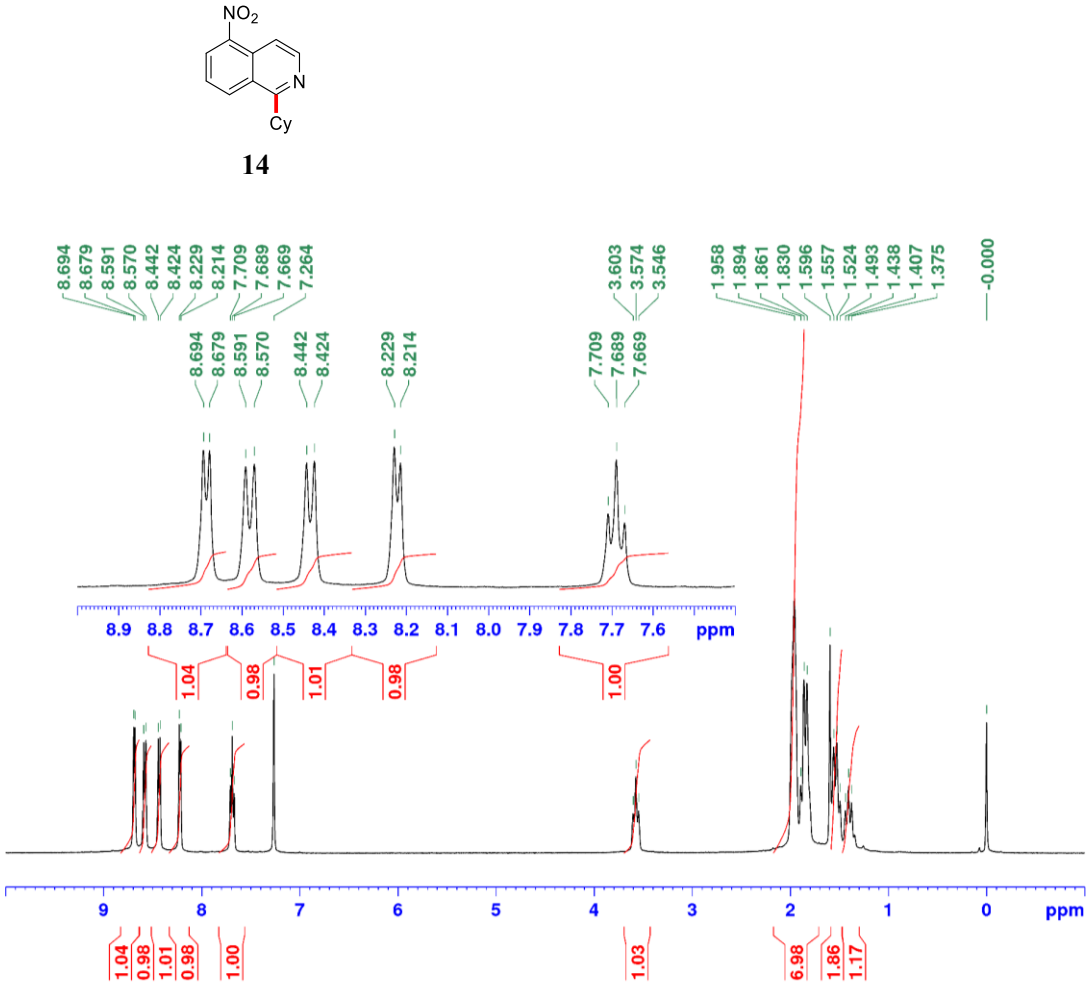
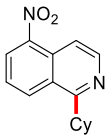


Figure S74. ^{1}H NMR (400 MHz) spectrum of **14** in $CDCl_3$.



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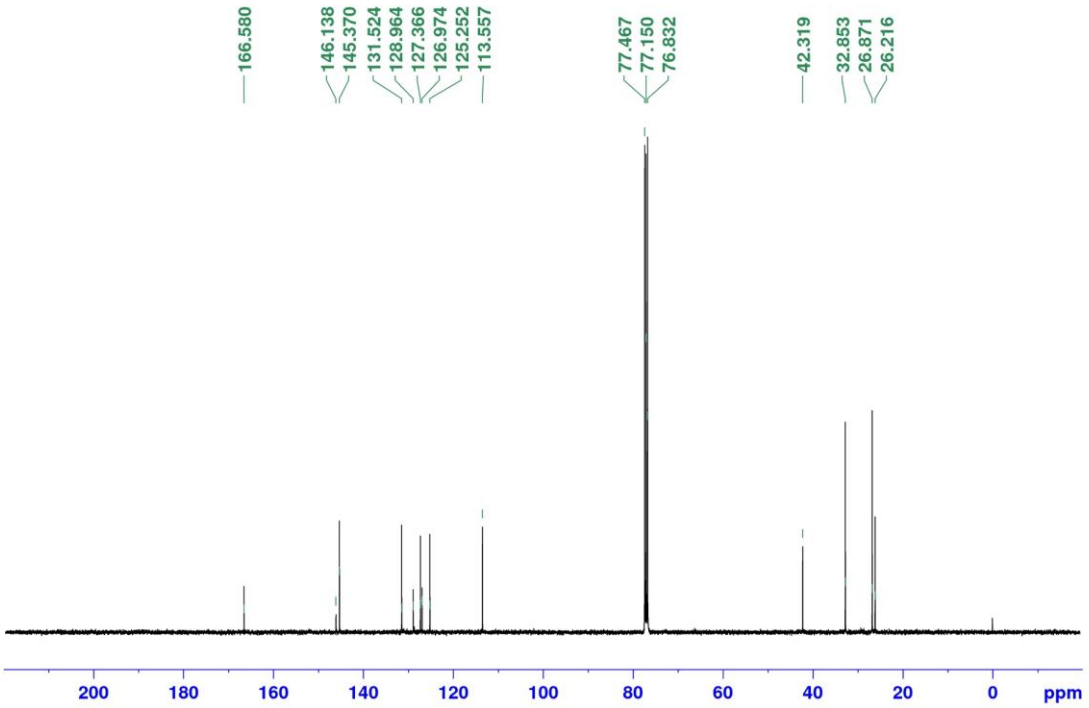
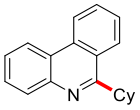


Figure S75. ^{13}C NMR (100 MHz) spectrum of **14** in $CDCl_3$.



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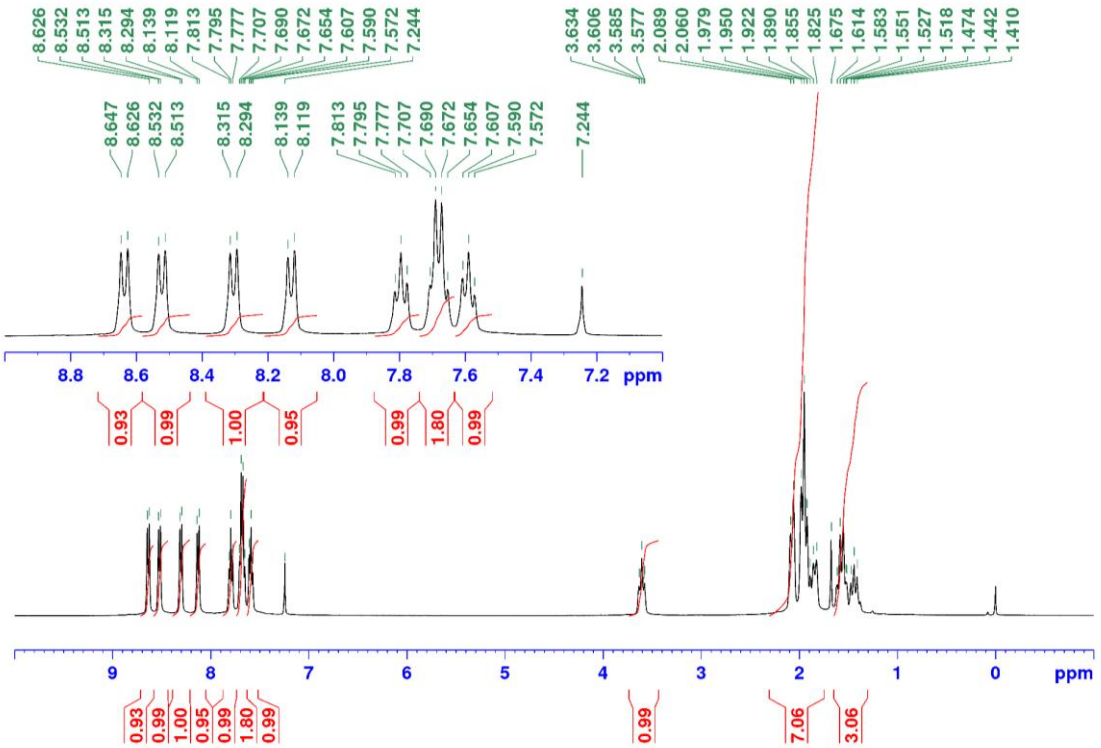
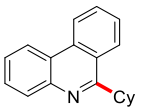


Figure S76. ^{1}H NMR (400 MHz) spectrum of **15** in $CDCl_3$.



15

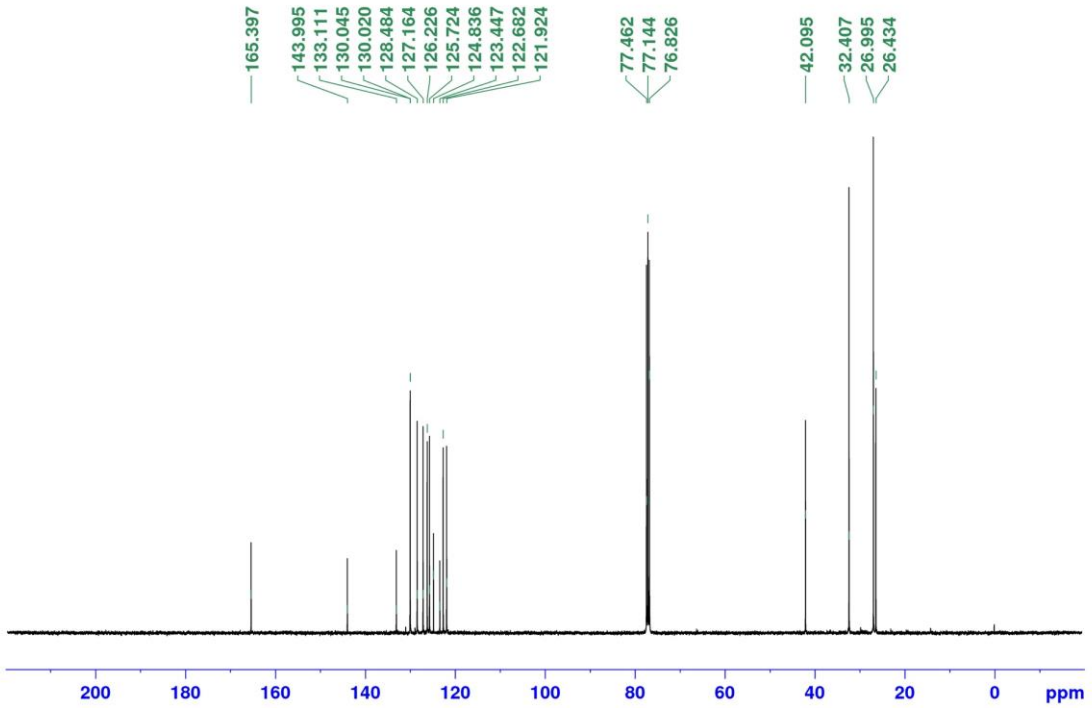
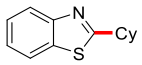


Figure S77. ^{13}C NMR (100 MHz) spectrum of **15** in $CDCl_3$.



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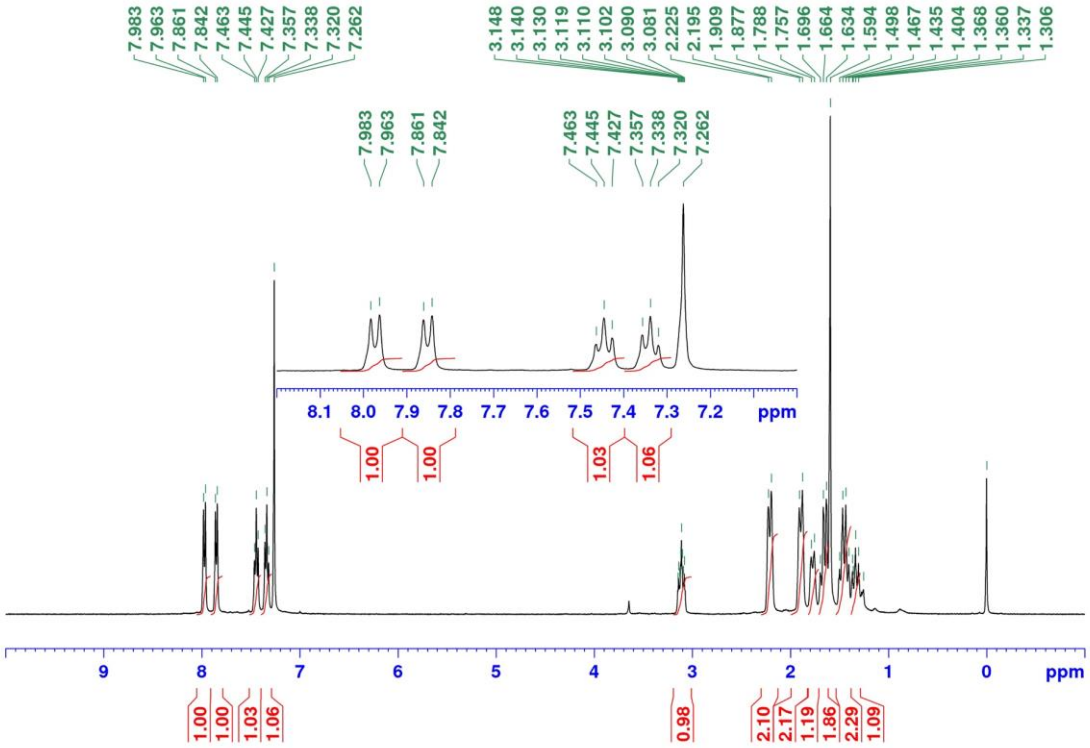
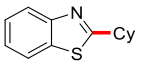


Figure S78. ^{1}H NMR (400 MHz) spectrum of **16** in $CDCl_3$.



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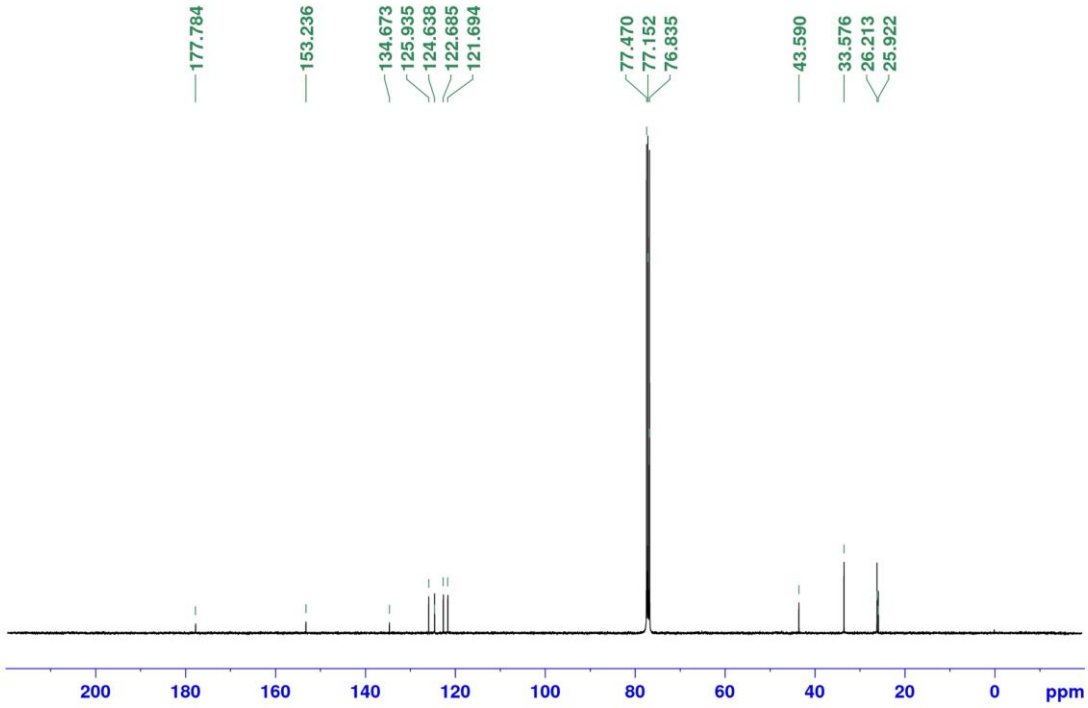
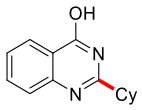


Figure S79. ^{13}C NMR (100 MHz) spectrum of **16** in $CDCl_3$.



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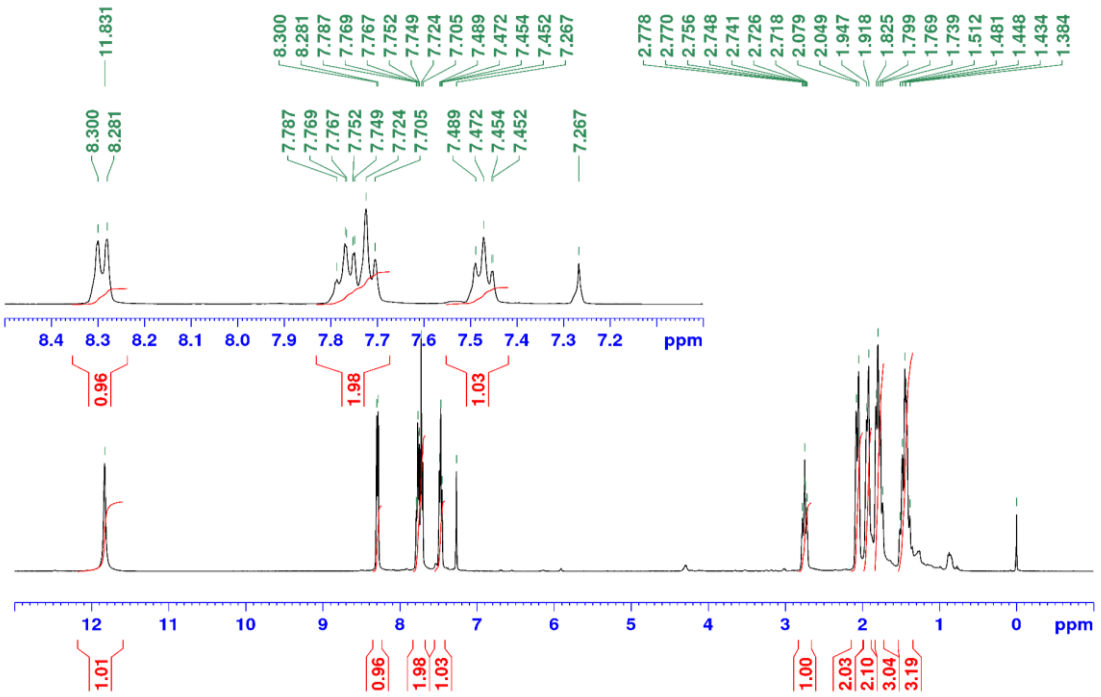
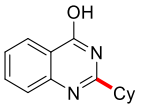


Figure S80. ^{1}H NMR (400 MHz) spectrum of **18** in $CDCl_3$.



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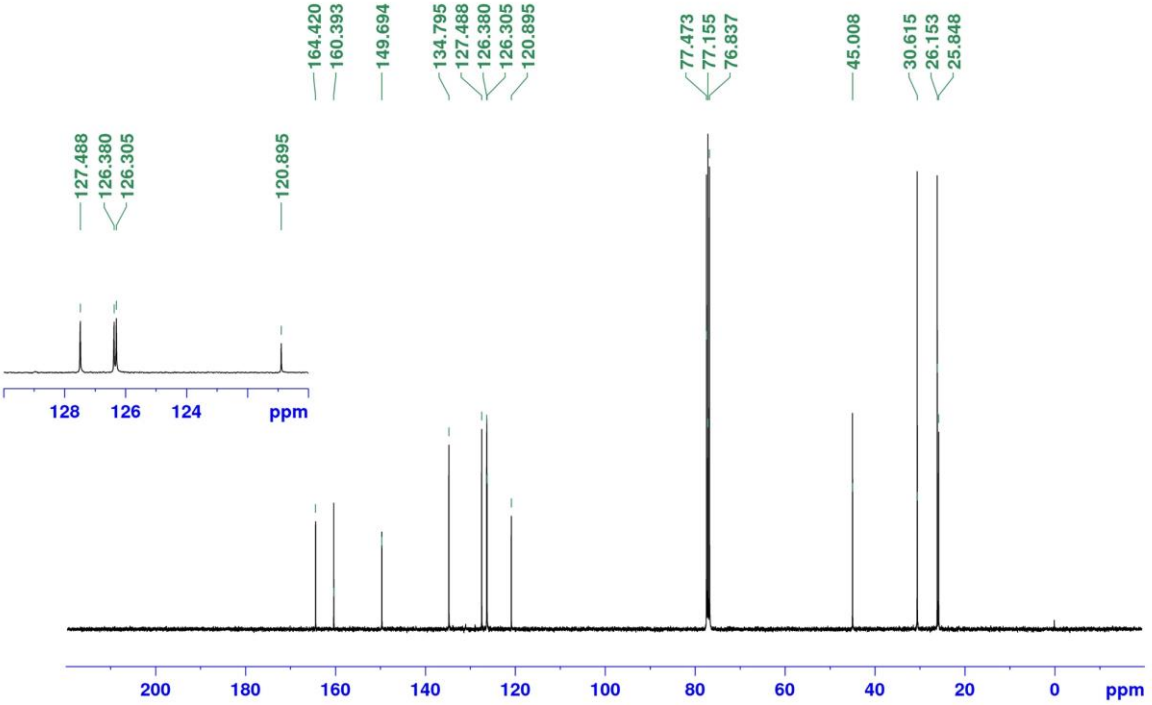
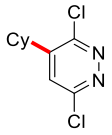


Figure S81. ^{13}C NMR (100 MHz) spectrum of **18** in $CDCl_3$.



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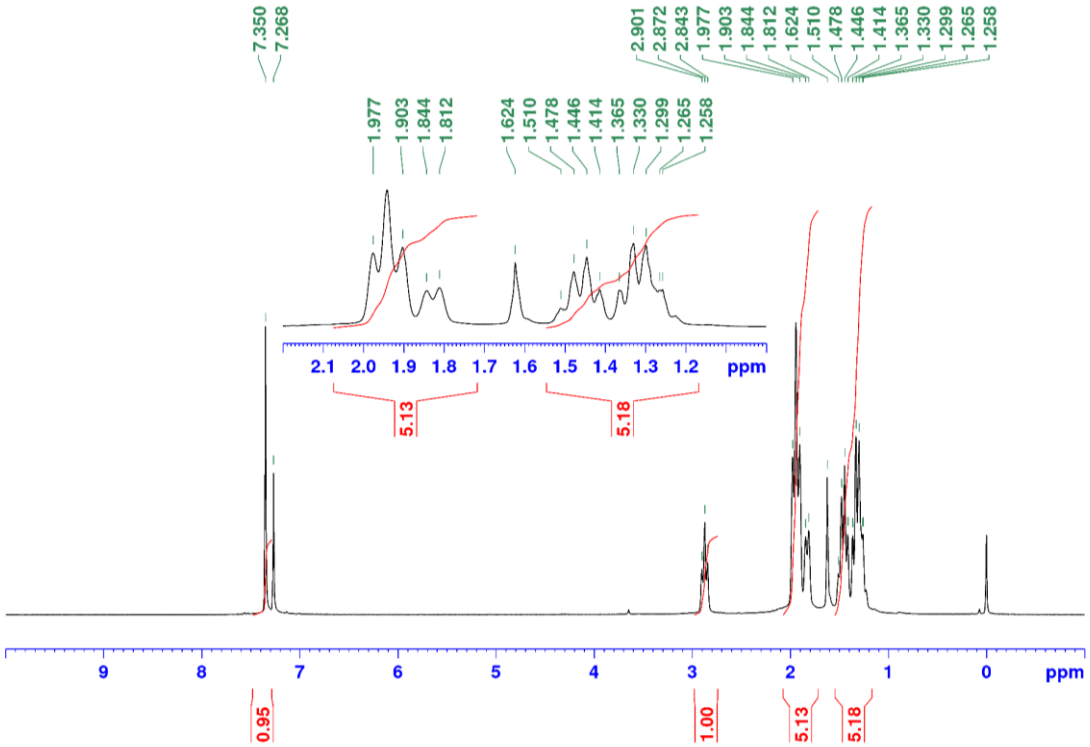
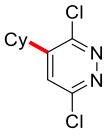


Figure S82. ^{1}H NMR (400 MHz) spectrum of **19** in $CDCl_3$.



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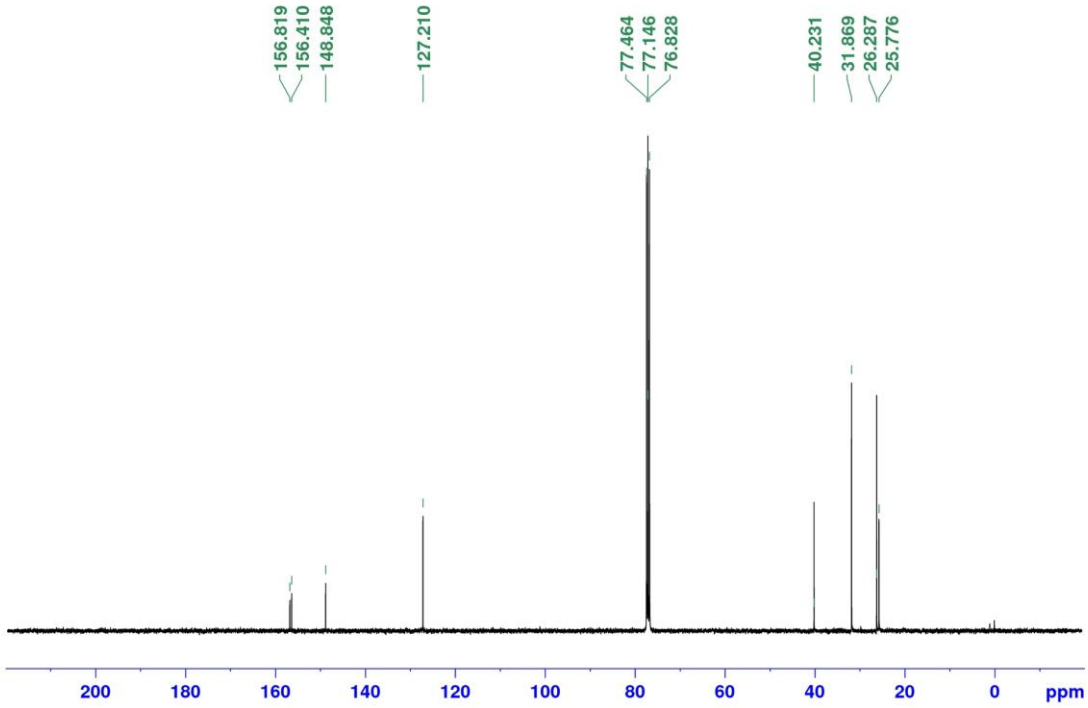
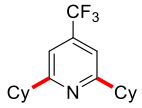


Figure S83. ^{13}C NMR (100 MHz) spectrum of **19** in $CDCl_3$.



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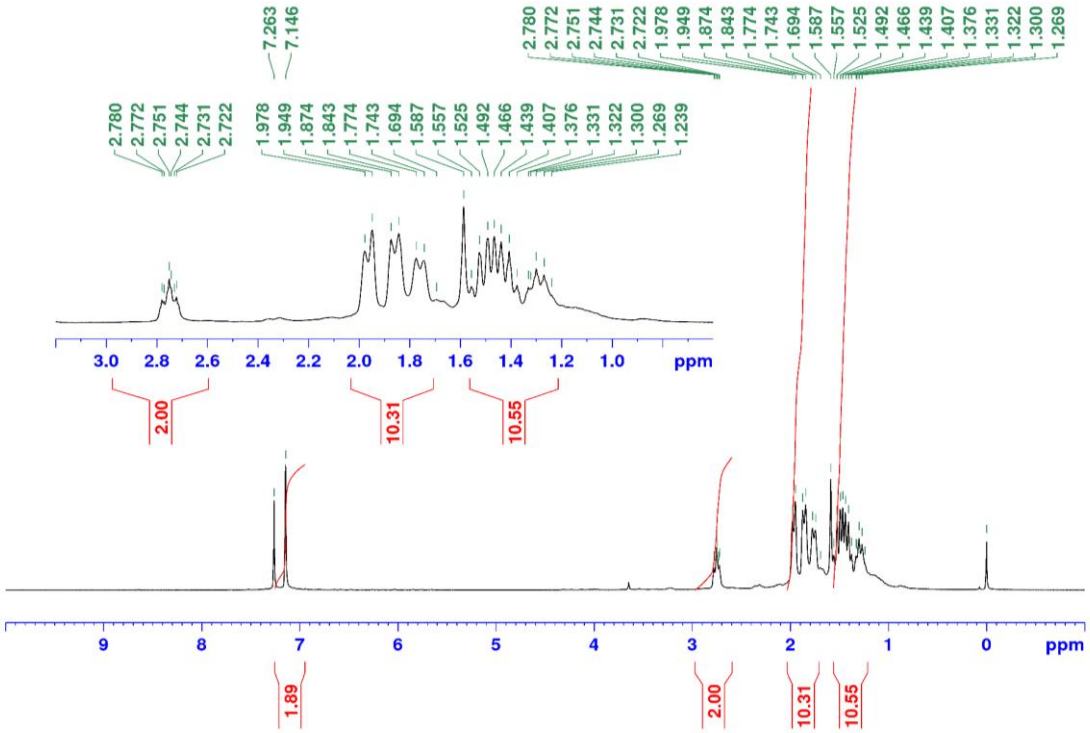
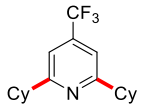


Figure S84. ^{1}H NMR (400 MHz) spectrum of **20** in $CDCl_3$.



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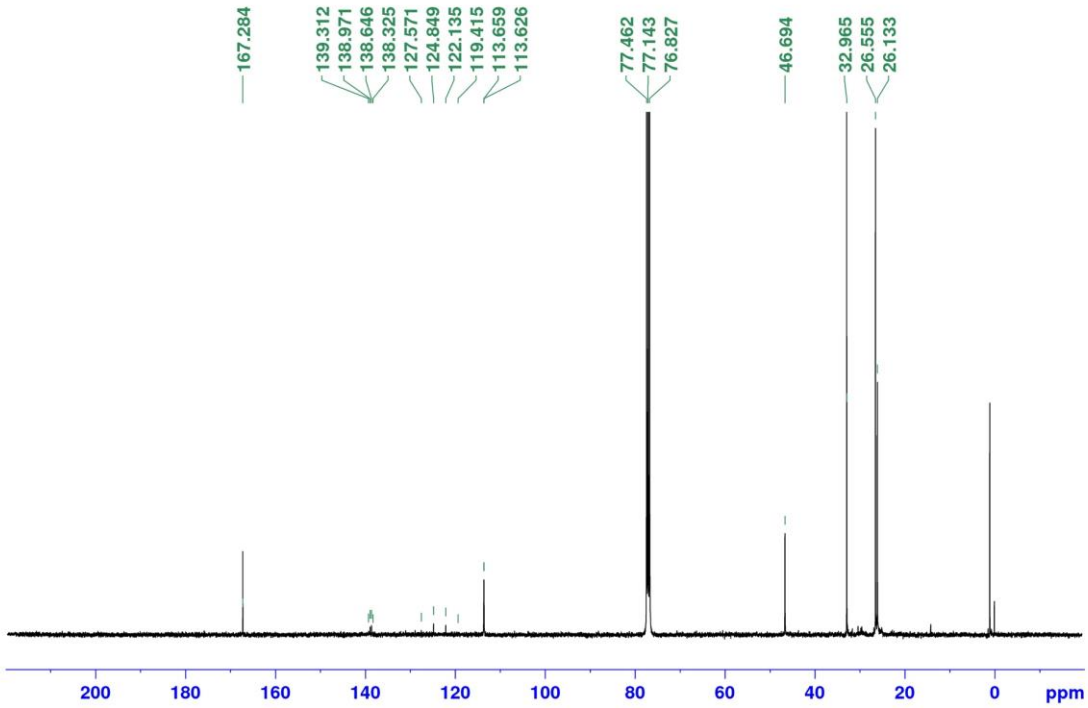
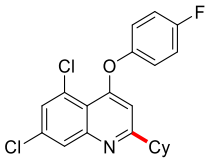


Figure S85. ^{13}C NMR (100 MHz) spectrum of **20** in $CDCl_3$.



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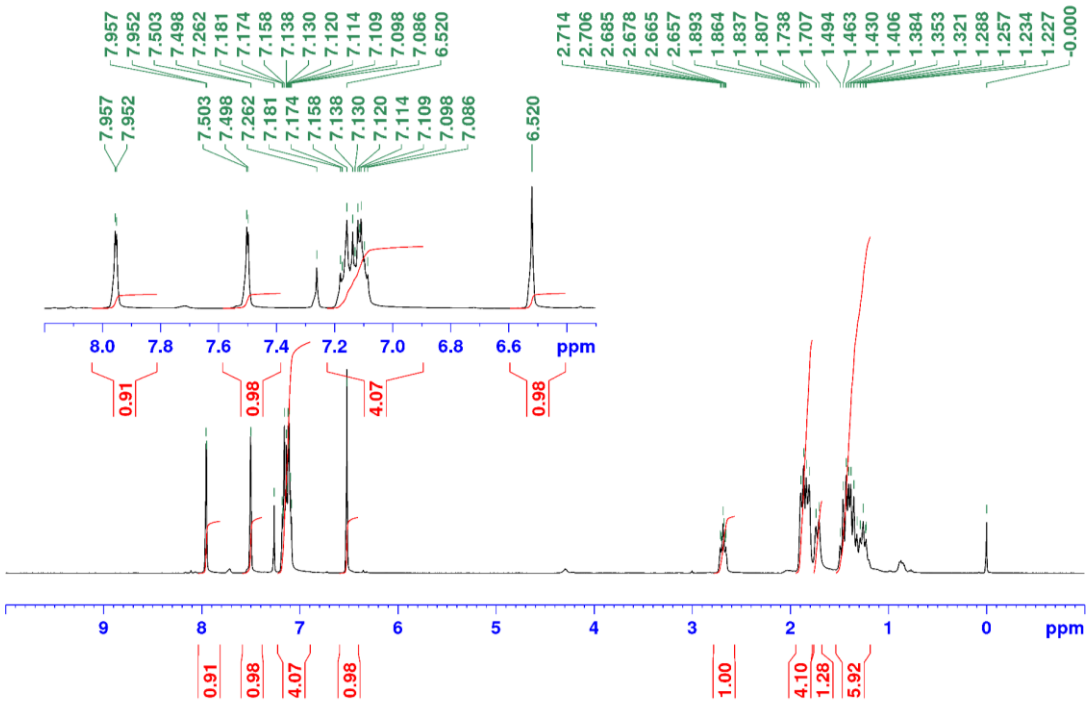
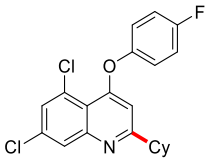


Figure S86. ^{1}H NMR (400 MHz) spectrum of **21** in $CDCl_3$.



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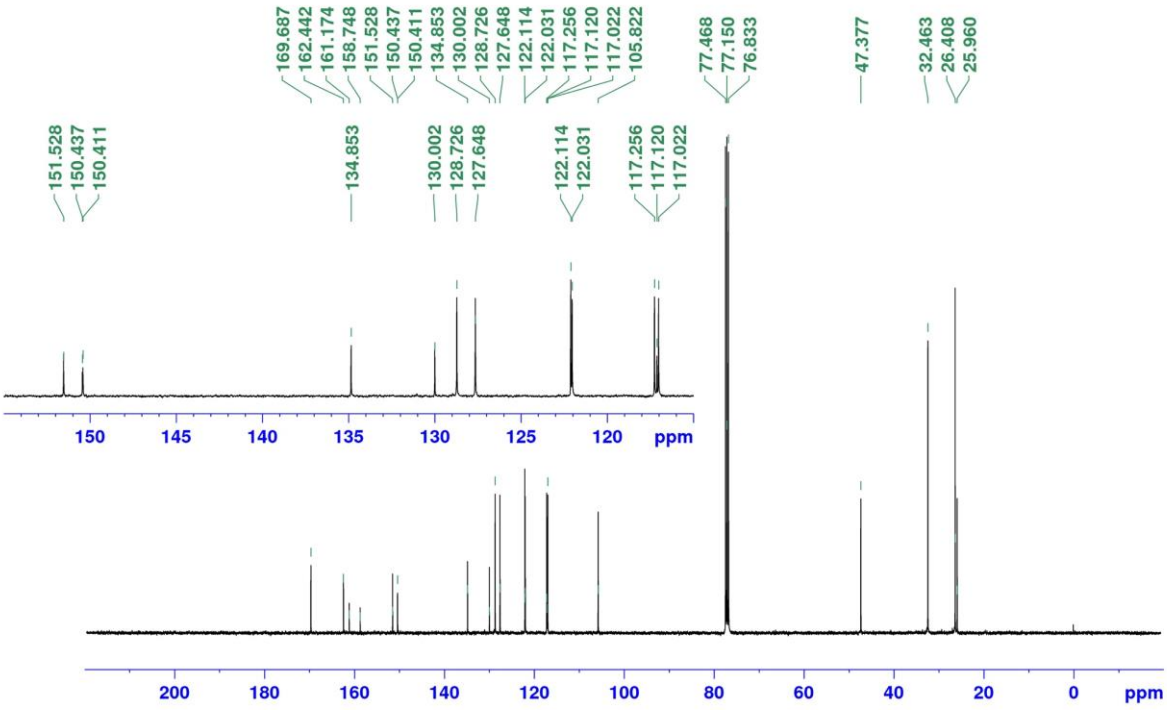
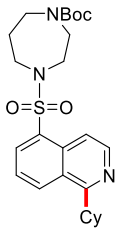


Figure S87. ^{13}C NMR (100 MHz) spectrum of **21** in $CDCl_3$.



22'

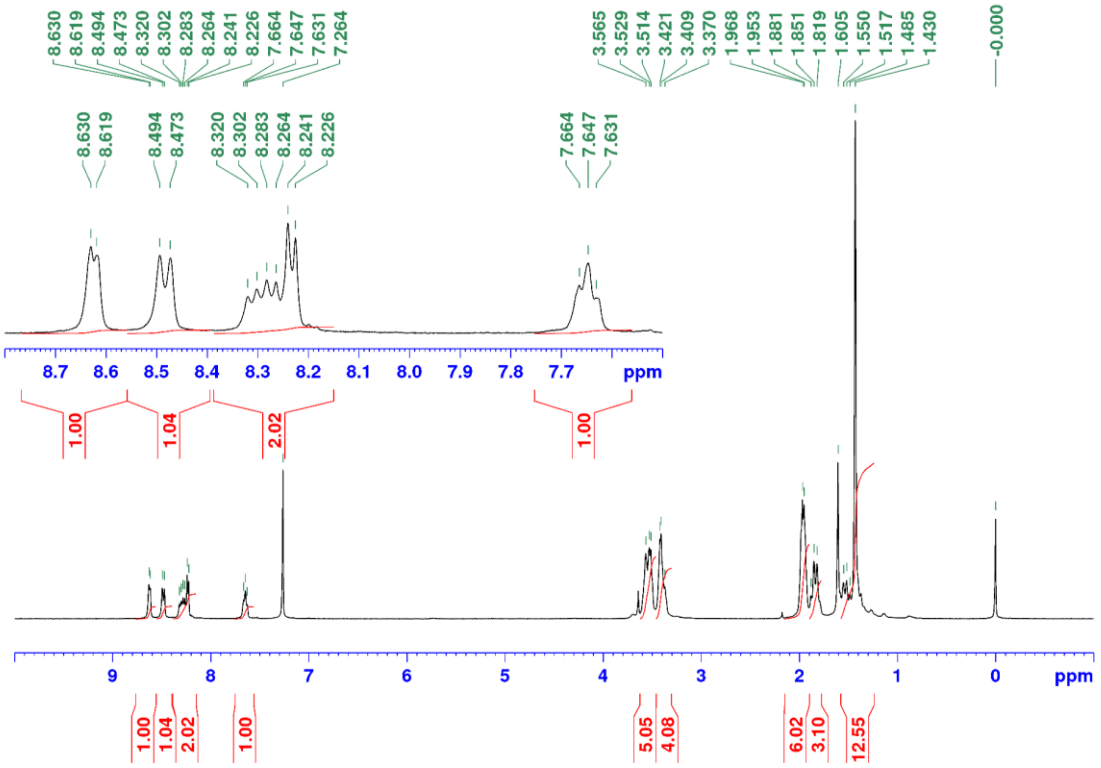


Figure S88. ^{1}H NMR (400 MHz) spectrum of **22'** in $CDCl_3$.

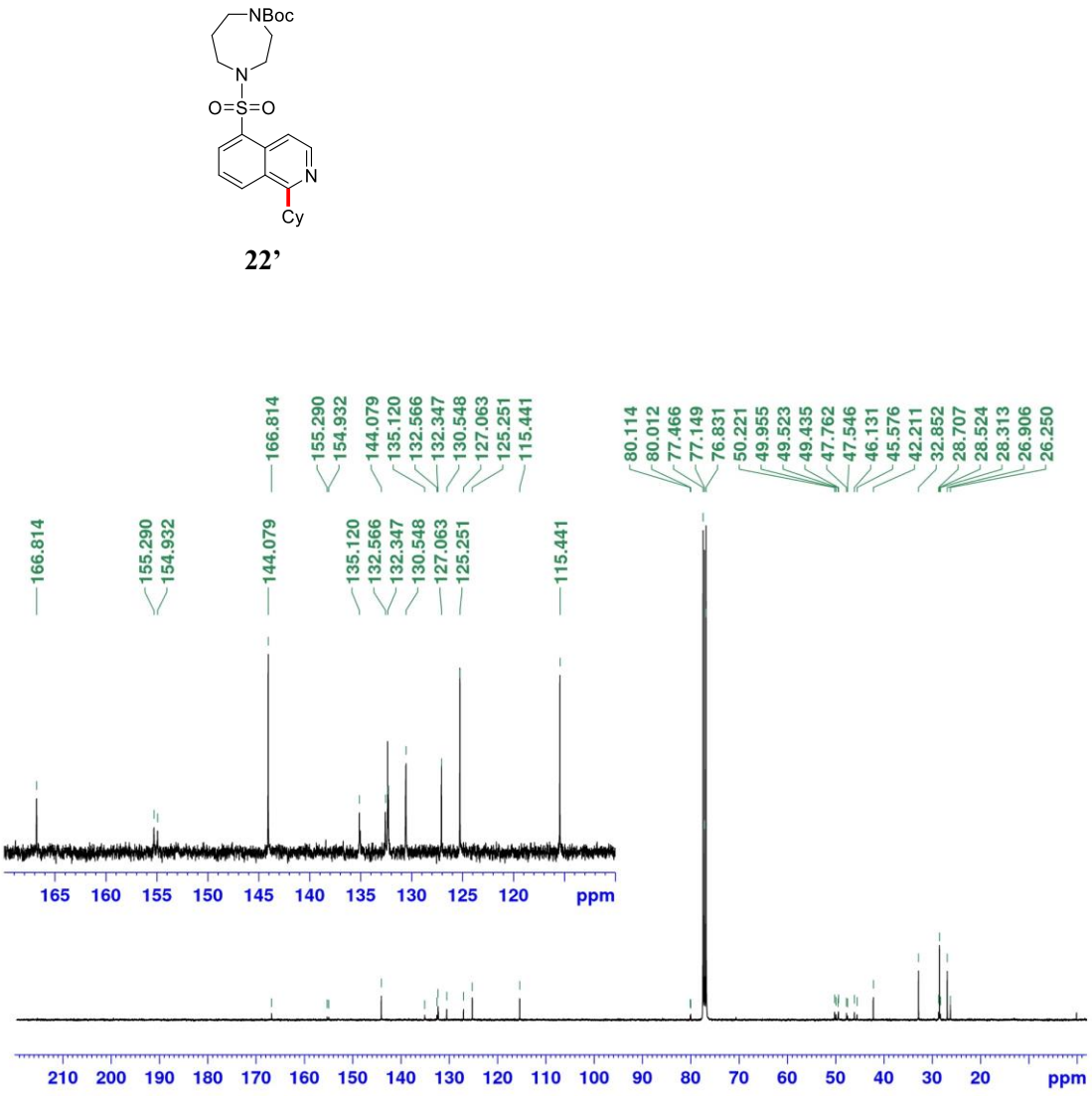
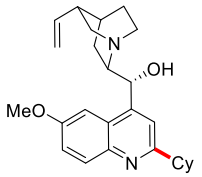


Figure S89. ^{13}C NMR (100 MHz) spectrum of **22'** in $CDCl_3$.



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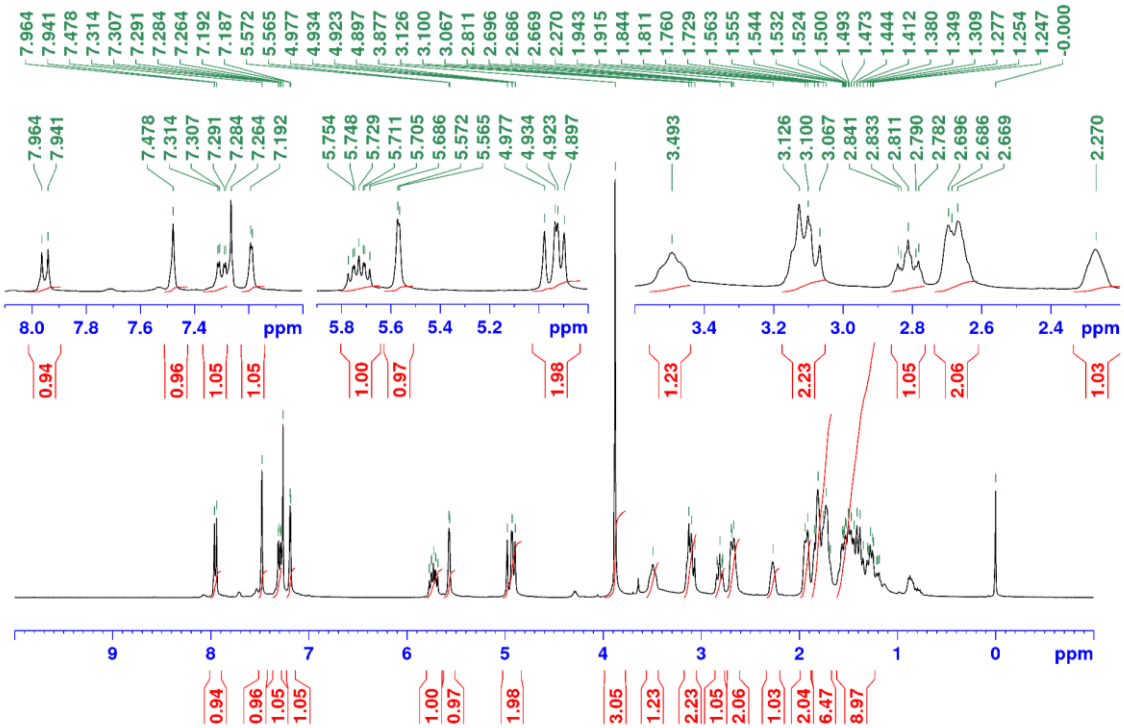
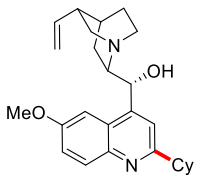


Figure S90. ^{1}H NMR (400 MHz) spectrum of **23** in $CDCl_3$.



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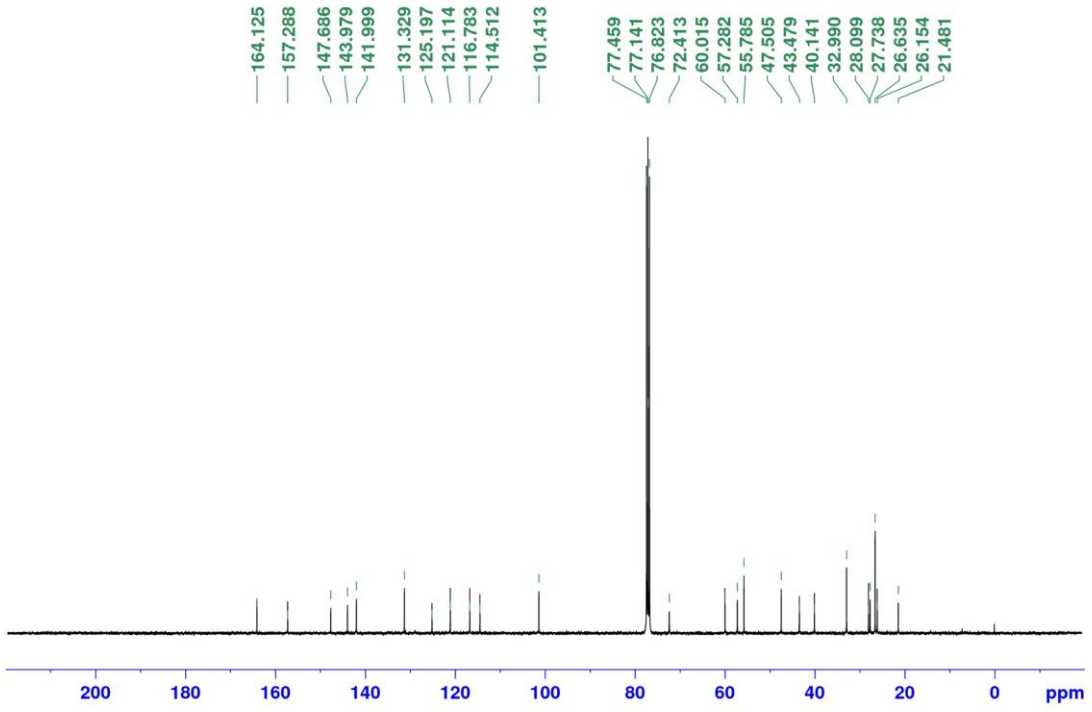
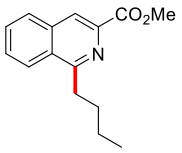


Figure S91. ^{13}C NMR (100 MHz) spectrum of **23** in $CDCl_3$.



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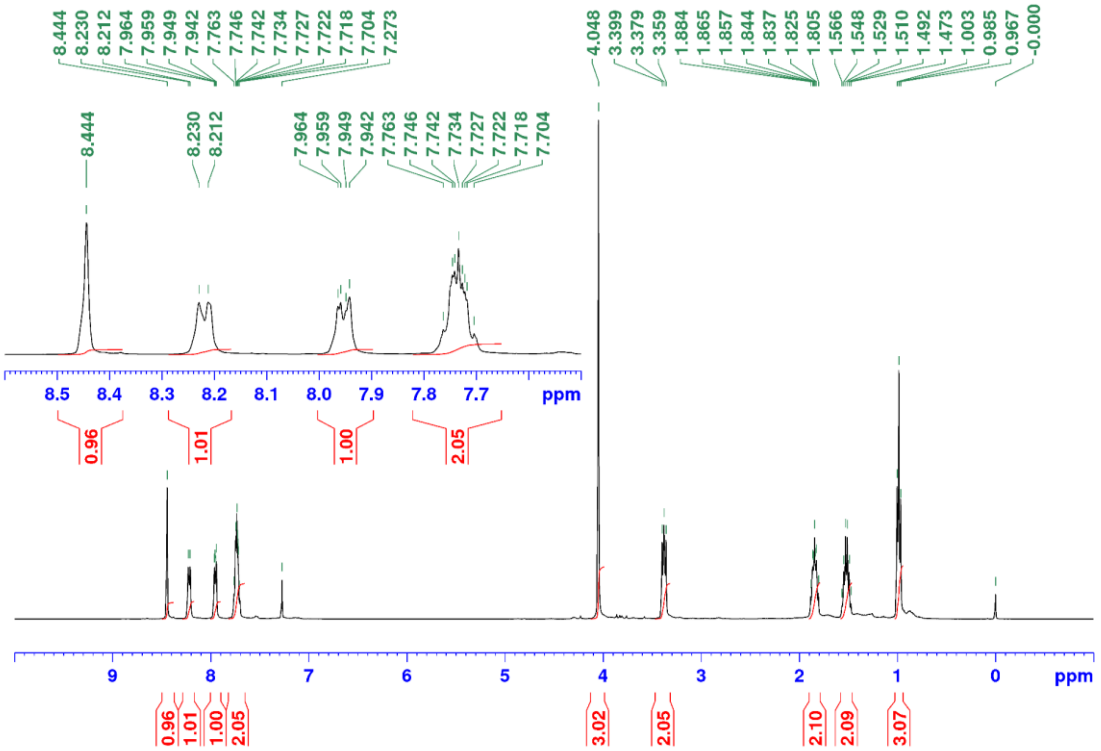
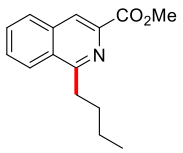


Figure S92. ^{1}H NMR (400 MHz) spectrum of **24** in $CDCl_3$.



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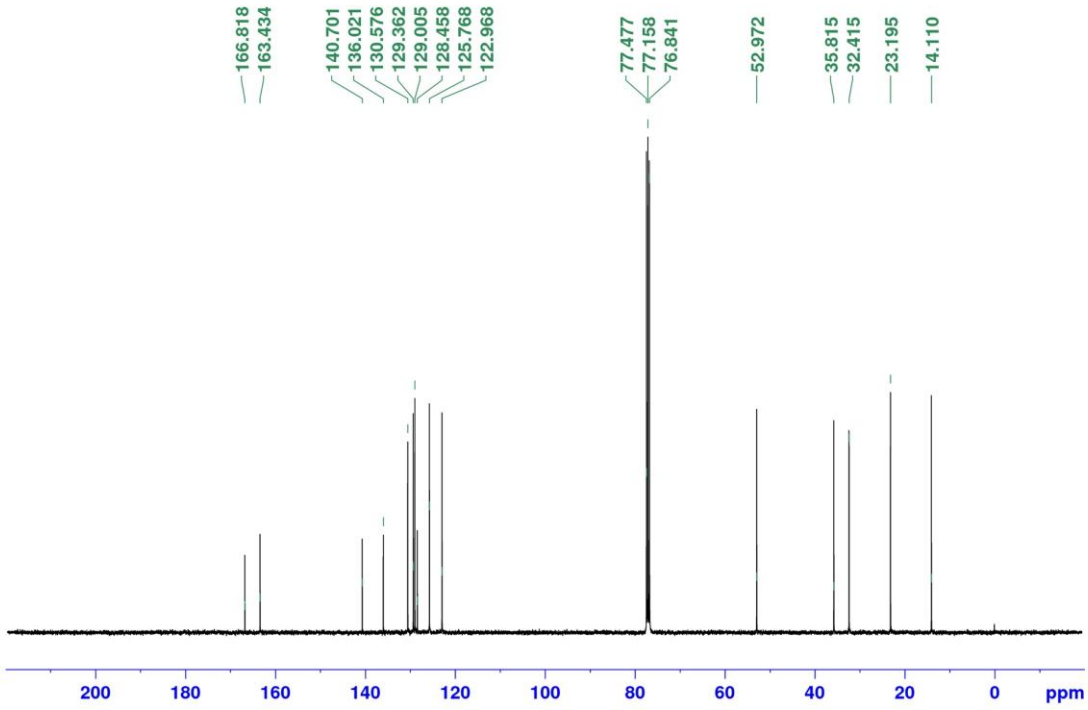
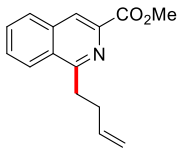


Figure S93. ^{13}C NMR (100 MHz) spectrum of **24** in $CDCl_3$.



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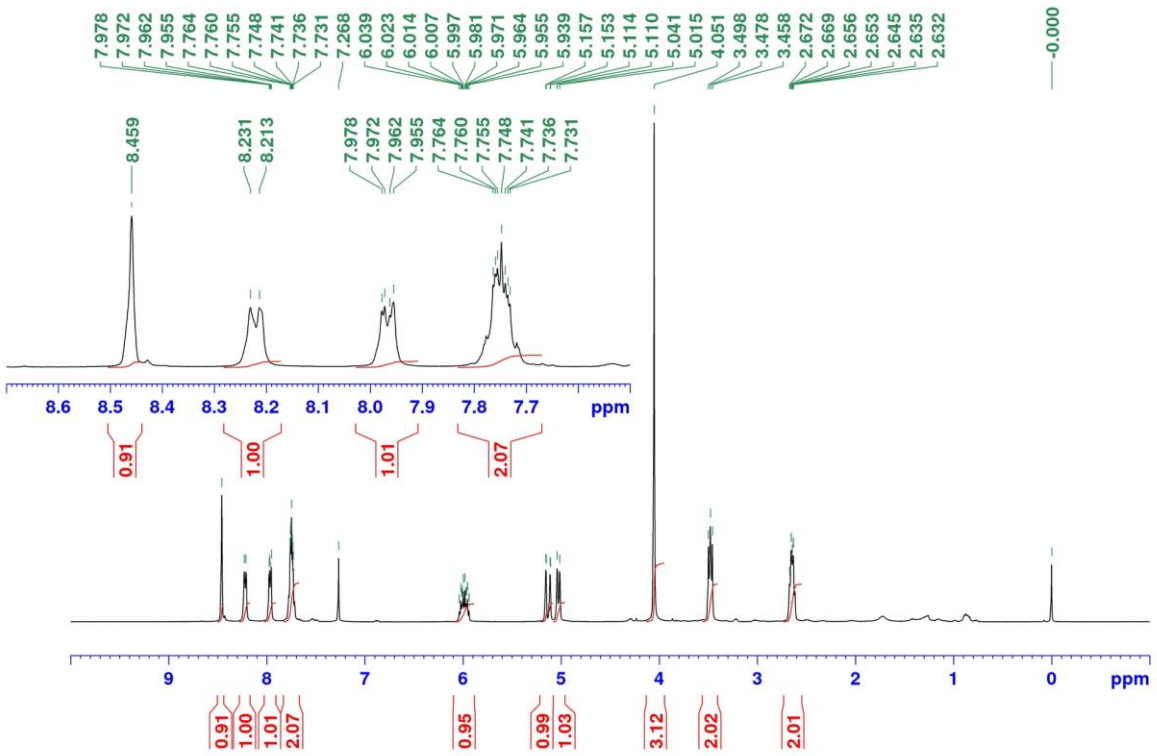
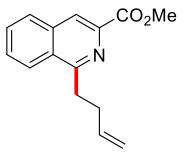


Figure S94. ^{1}H NMR (400 MHz) spectrum of **25** in $CDCl_3$.



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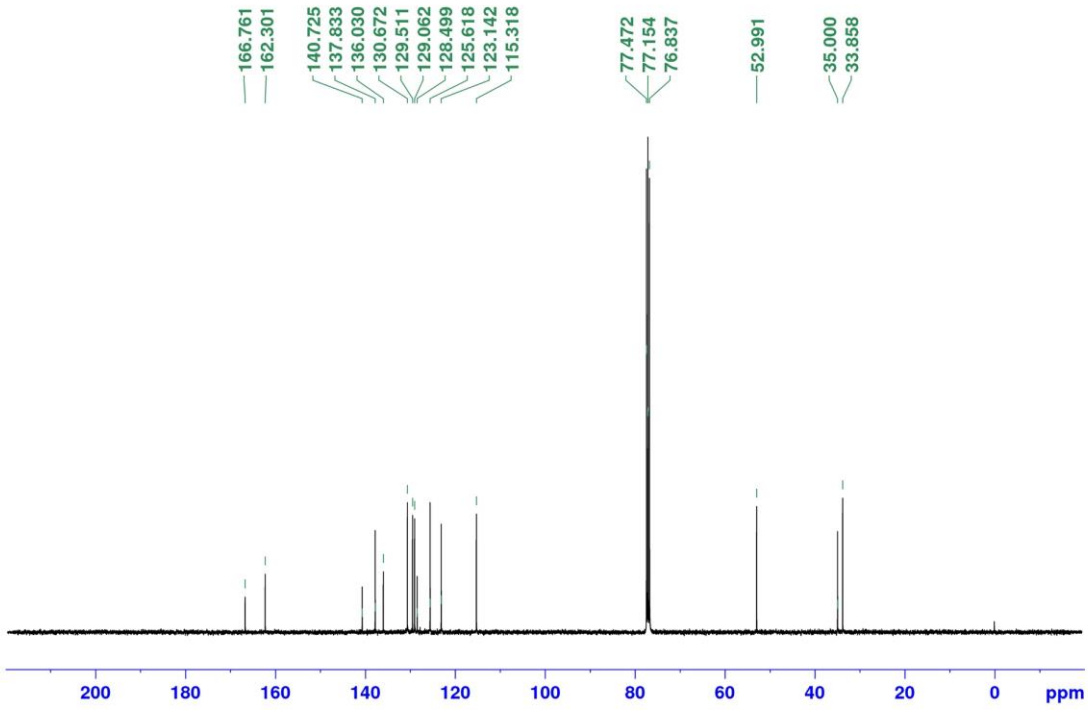
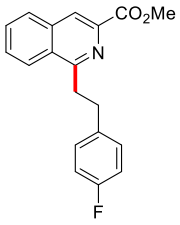


Figure S95. ^{13}C NMR (100 MHz) spectrum of **25** in $CDCl_3$.



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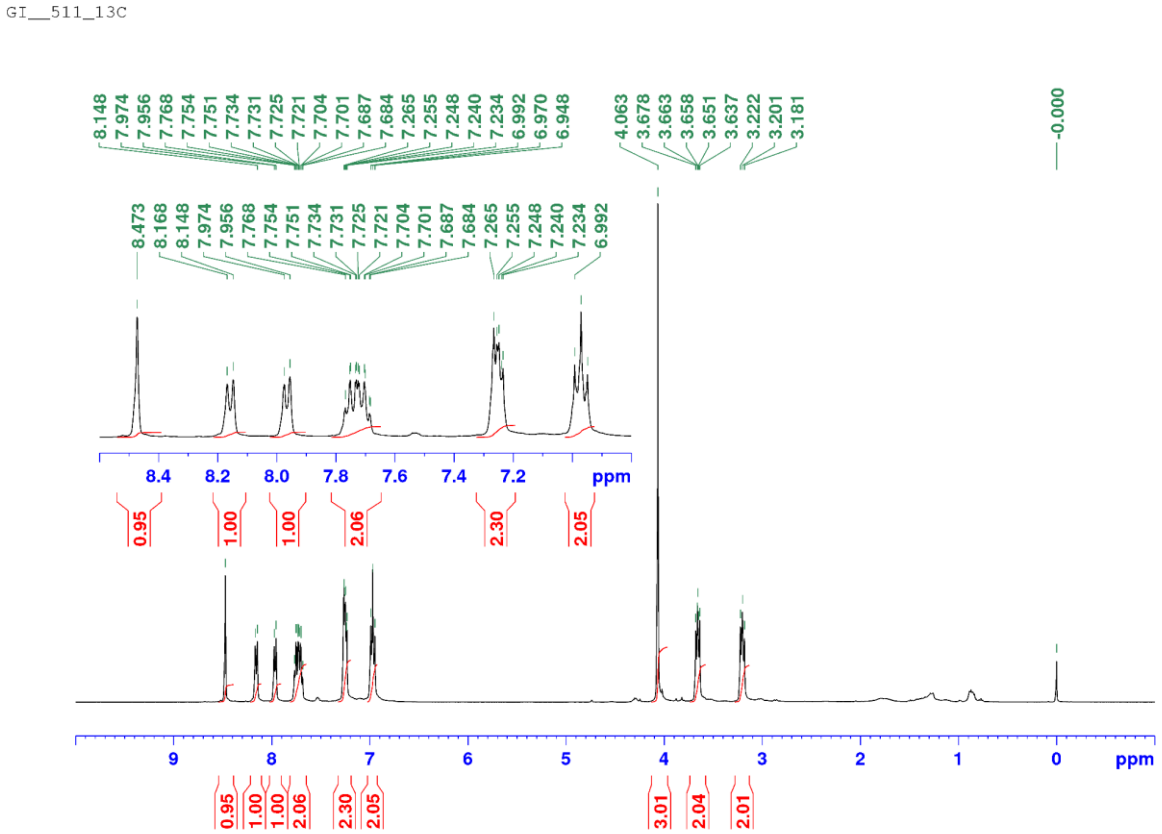
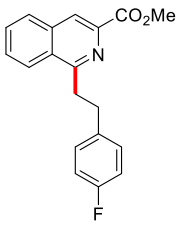


Figure S96. ^{1}H NMR (400 MHz) spectrum of **26** in $CDCl_3$.



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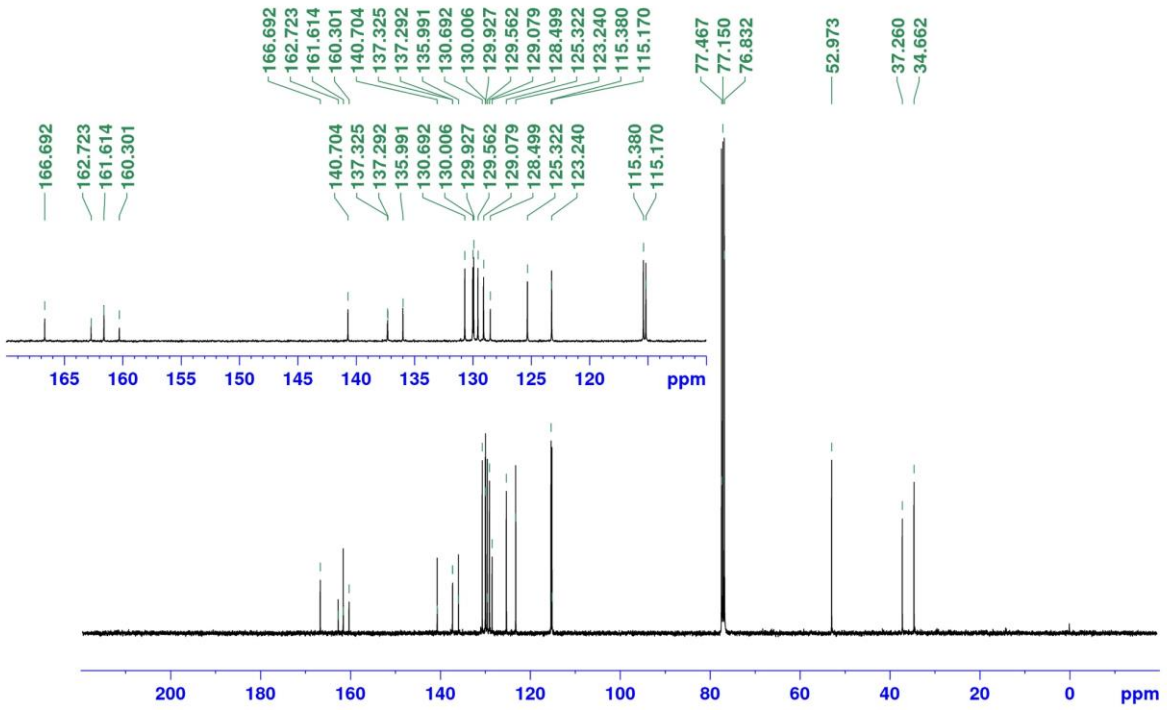
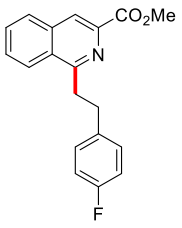


Figure S97. ^{13}C NMR (100 MHz) spectrum of **26** in $CDCl_3$.



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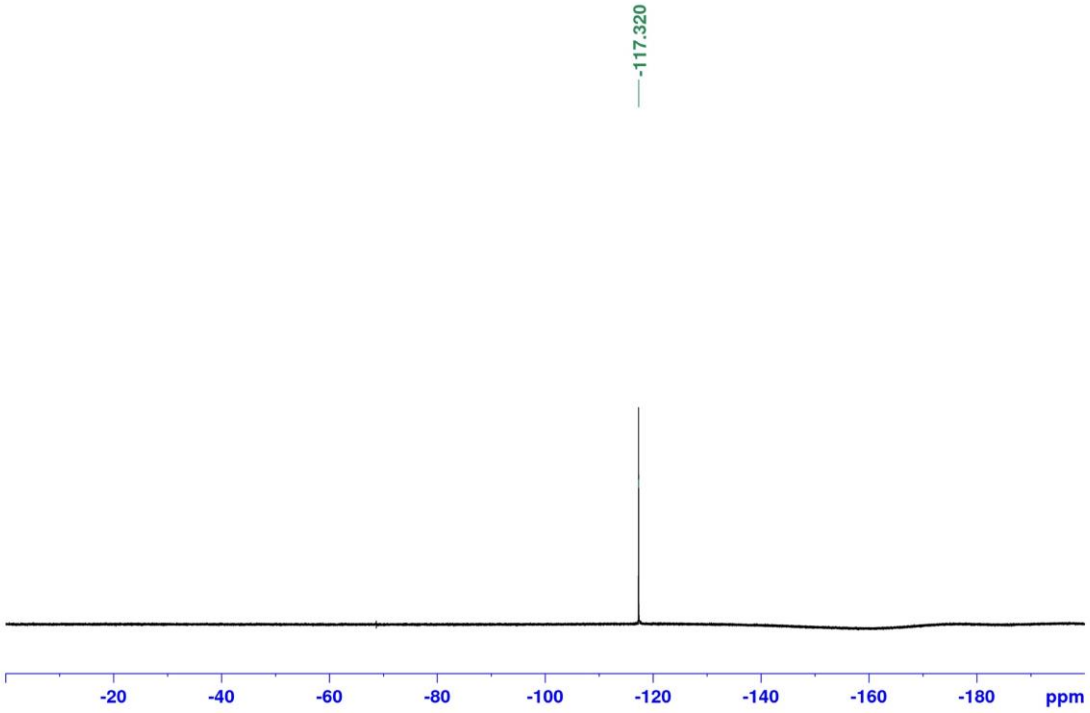
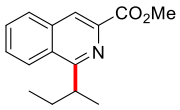


Figure S98. ^{19}F NMR (376 MHz) spectrum of **26** in $CDCl_3$.



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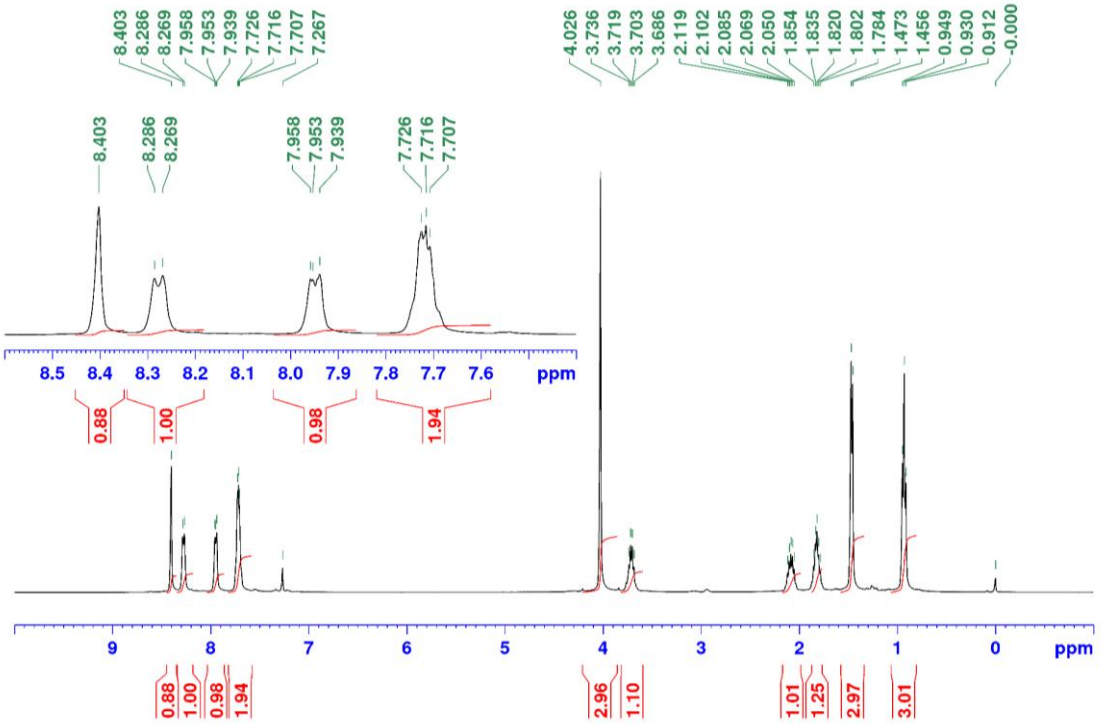
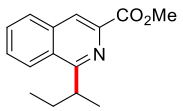


Figure S99. ^{1}H NMR (400 MHz) spectrum of **27** in $CDCl_3$.



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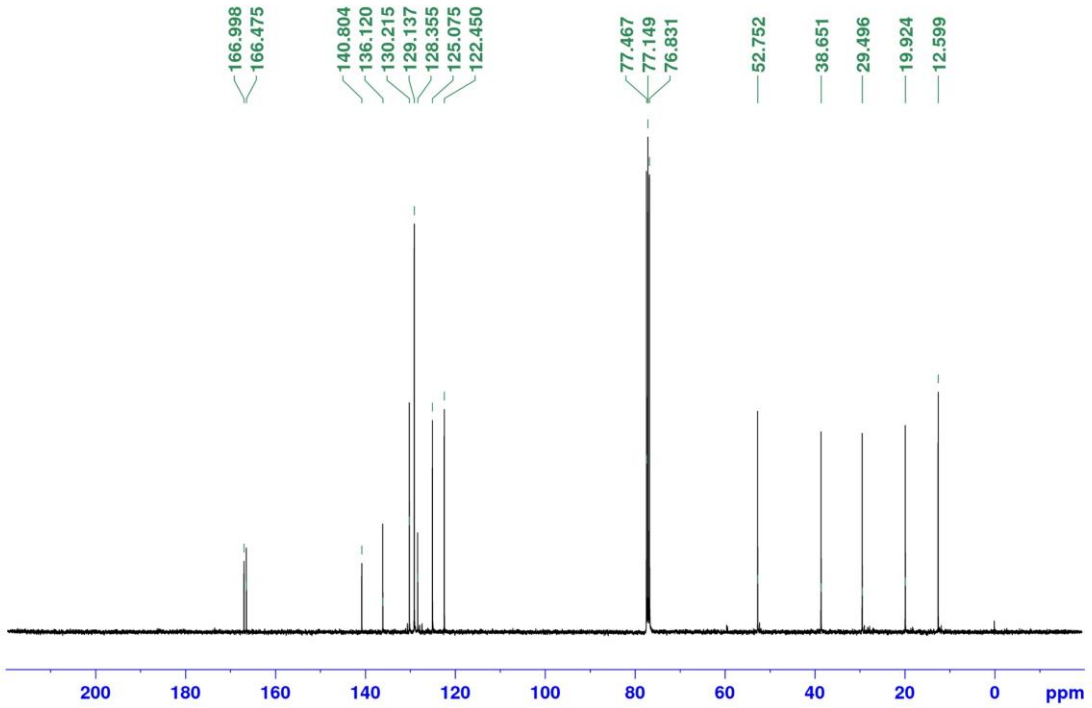
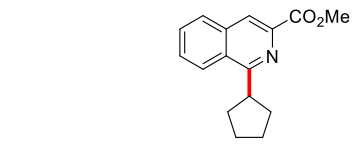


Figure S100. ^{13}C NMR (100 MHz) spectrum of **27** in $CDCl_3$.



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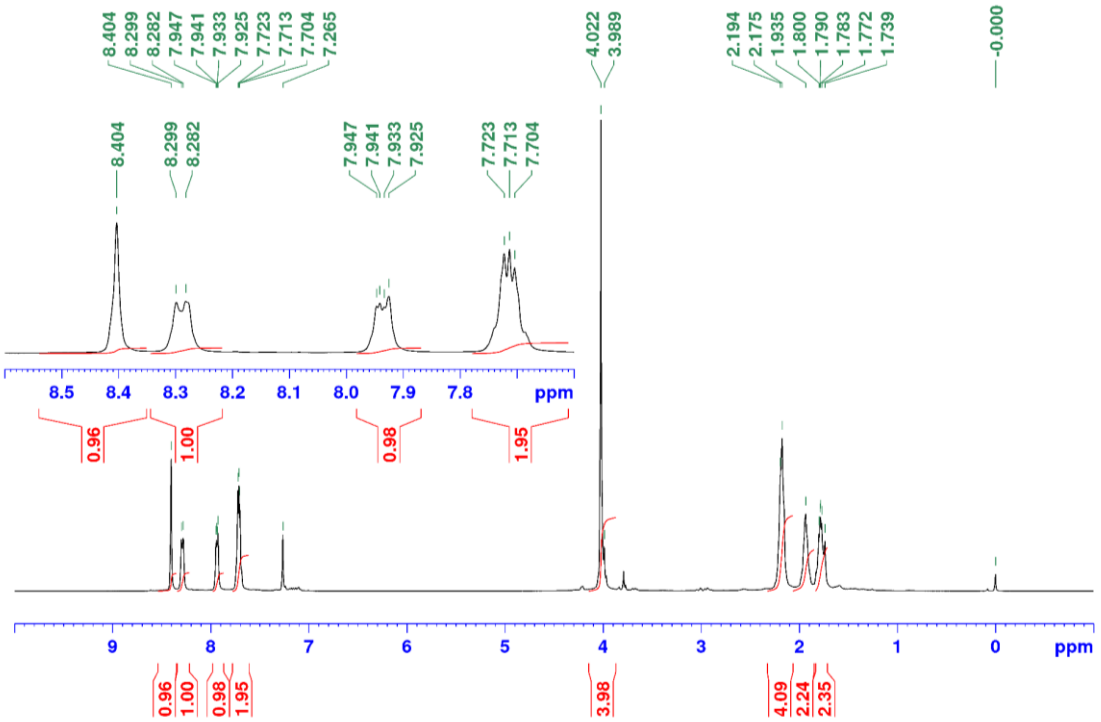
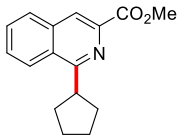


Figure S101. ^{1}H NMR (400 MHz) spectrum of **28** in $CDCl_3$.



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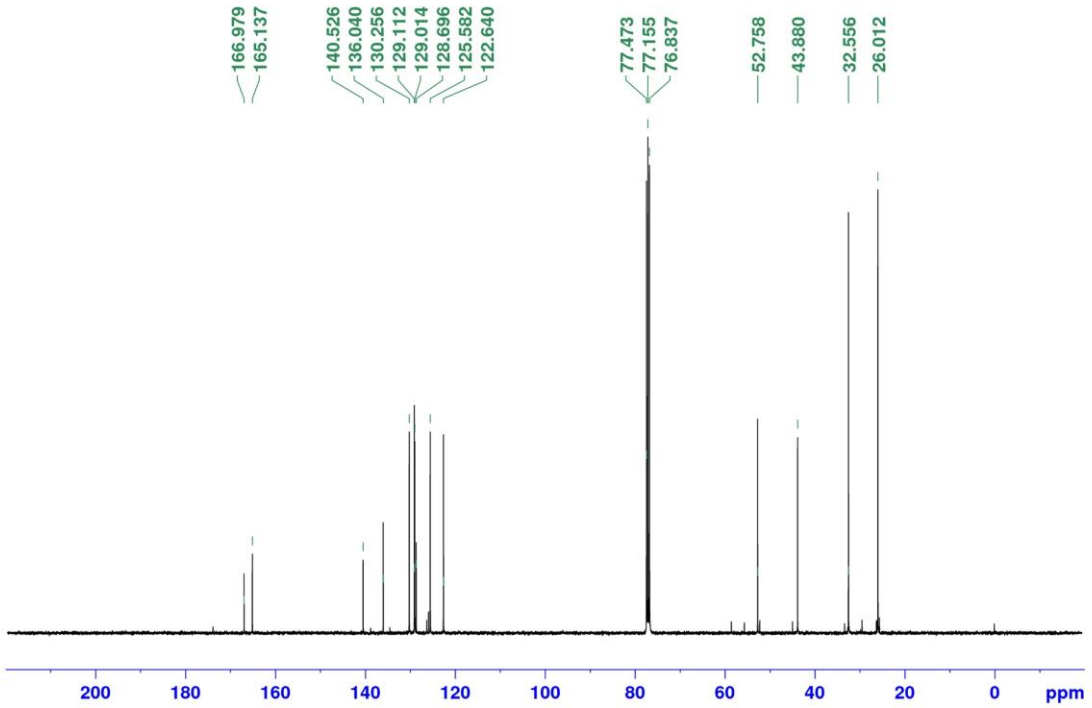
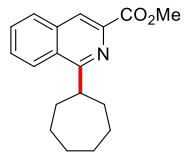


Figure S102. ^{13}C NMR (100 MHz) spectrum of **28** in $CDCl_3$.



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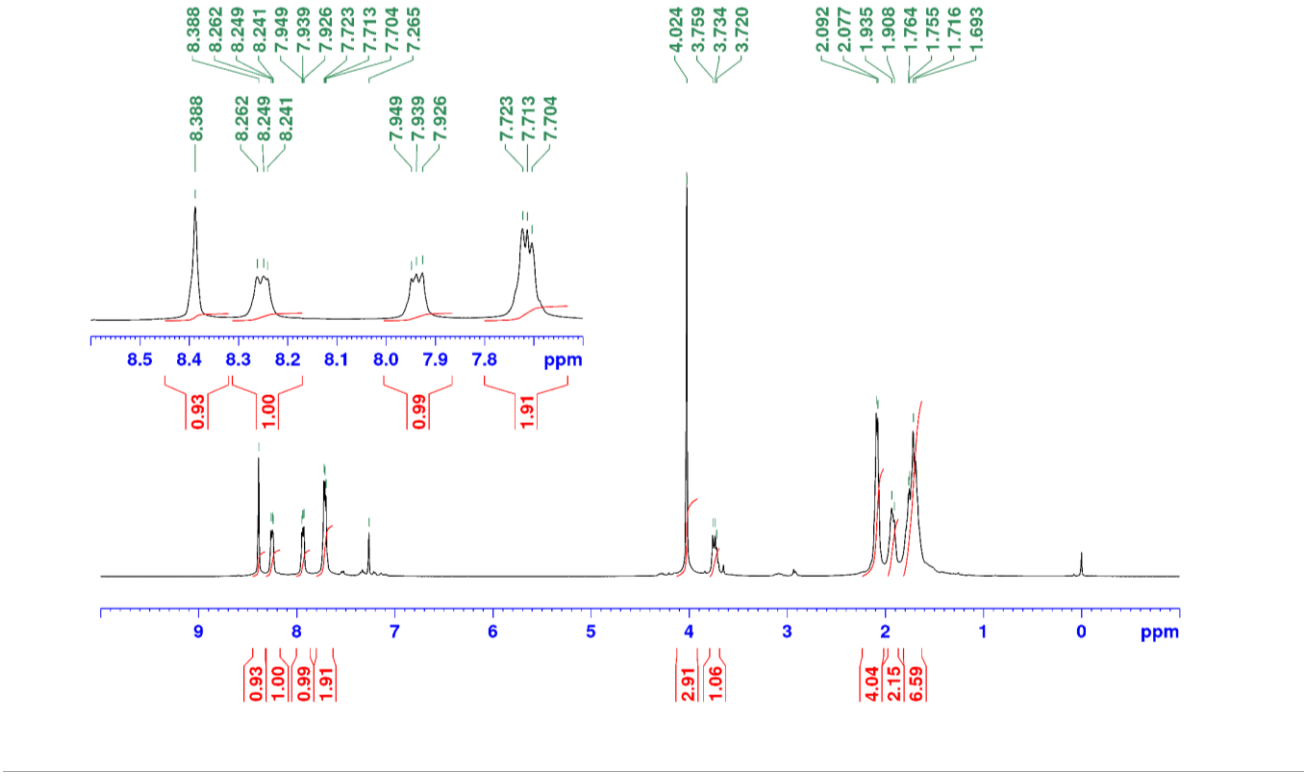
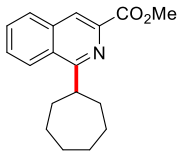


Figure S103. ^{1}H NMR (400 MHz) spectrum of **29** in $CDCl_3$.



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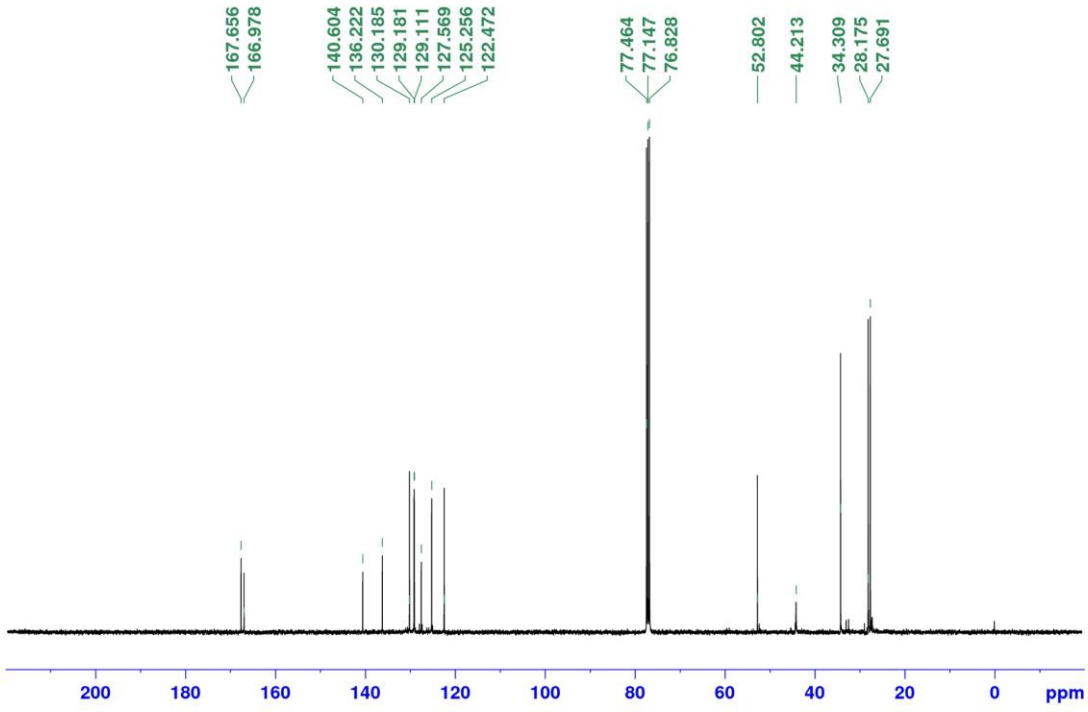
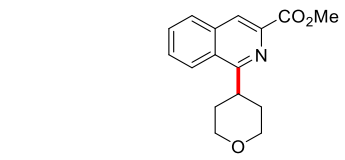


Figure S104. ^{13}C NMR (100 MHz) spectrum of **29** in $CDCl_3$.



30

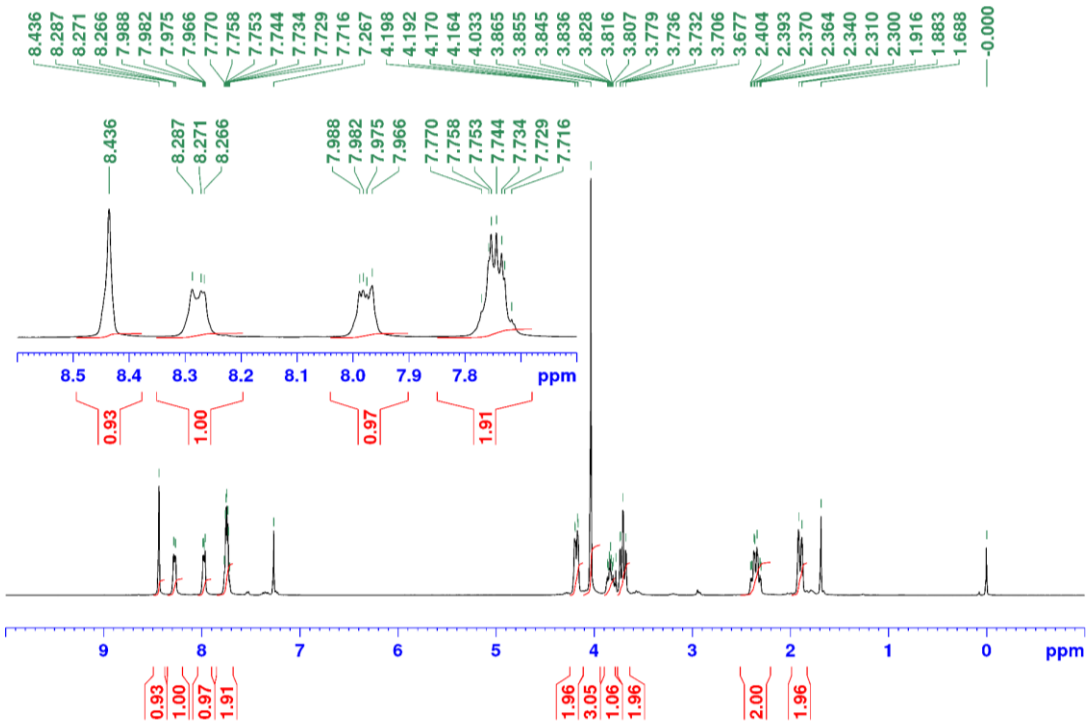
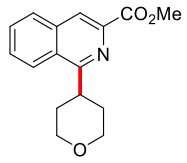


Figure S105. ^{1}H NMR (400 MHz) spectrum of **30** in $CDCl_3$.



30

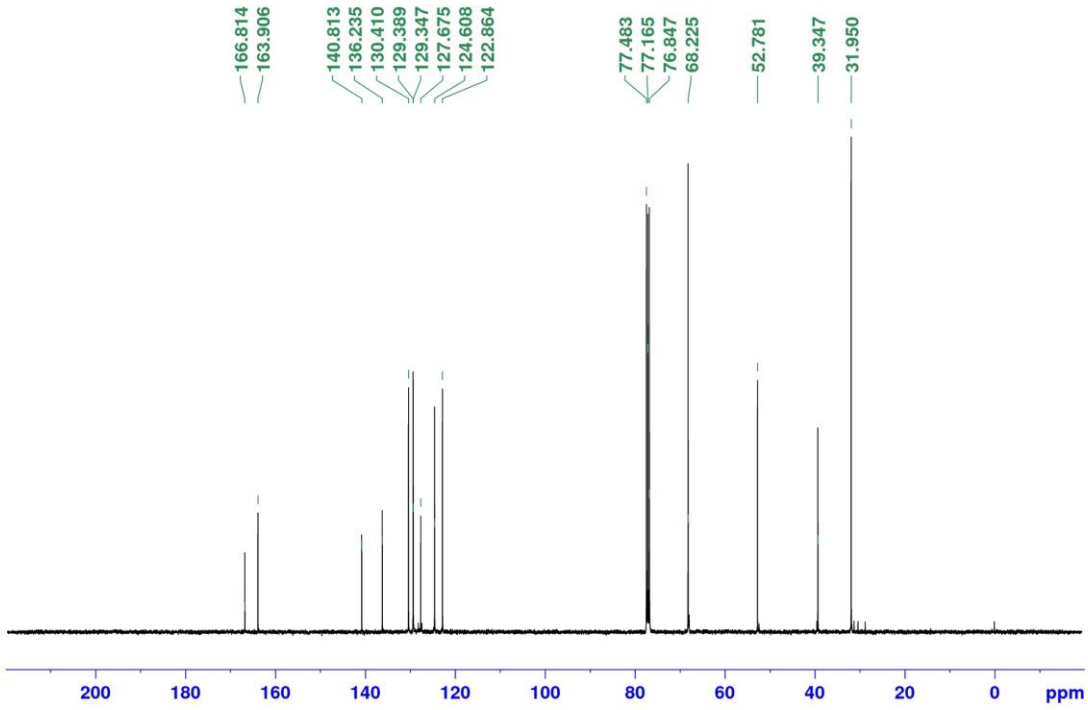
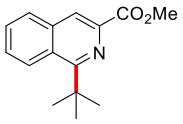


Figure S106. ^{13}C NMR (100 MHz) spectrum of **30** in $CDCl_3$.



31

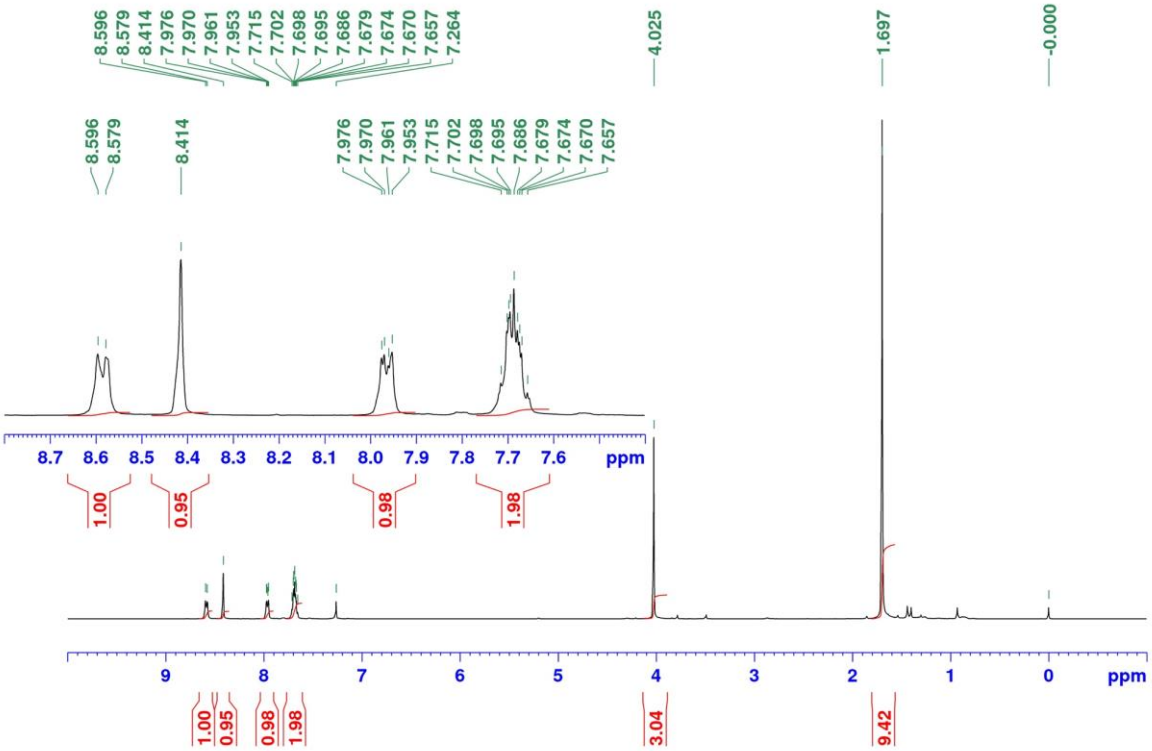
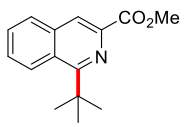


Figure S107. ^{1}H NMR (400 MHz) spectrum of **31** in $CDCl_3$.



31

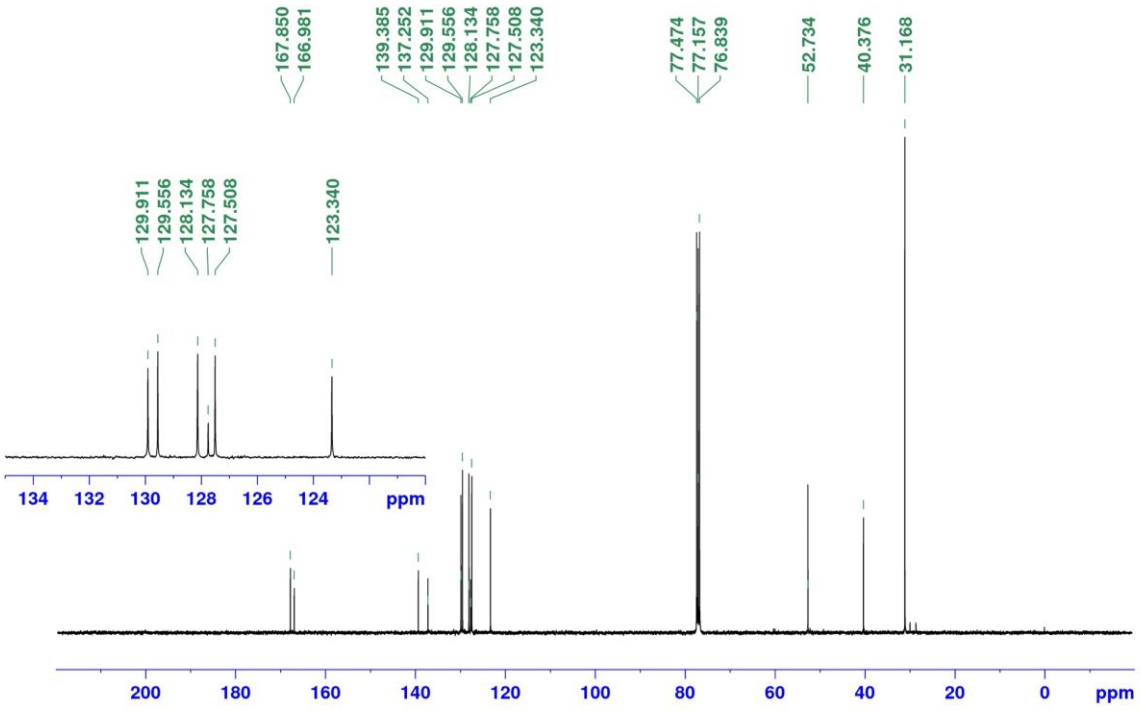
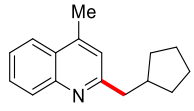


Figure S108. ^{13}C NMR (100 MHz) spectrum of **31** in $CDCl_3$.



32

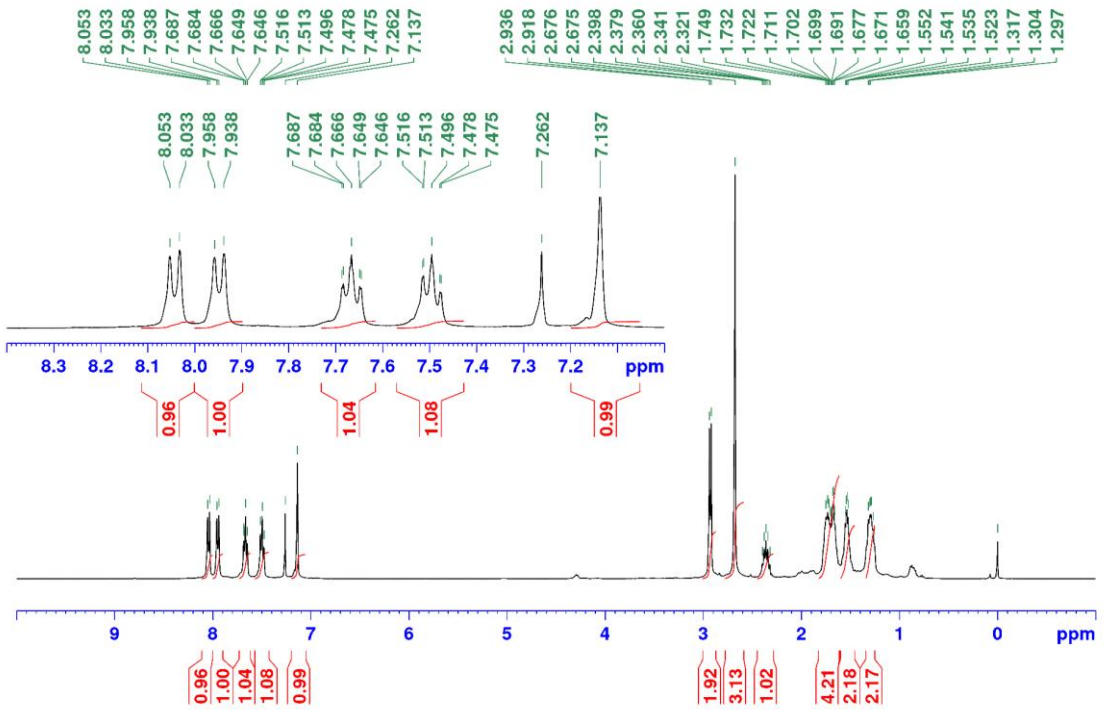
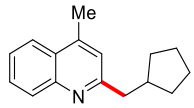


Figure S109. ^{1}H NMR (400 MHz) spectrum of **32** in $CDCl_3$.



32

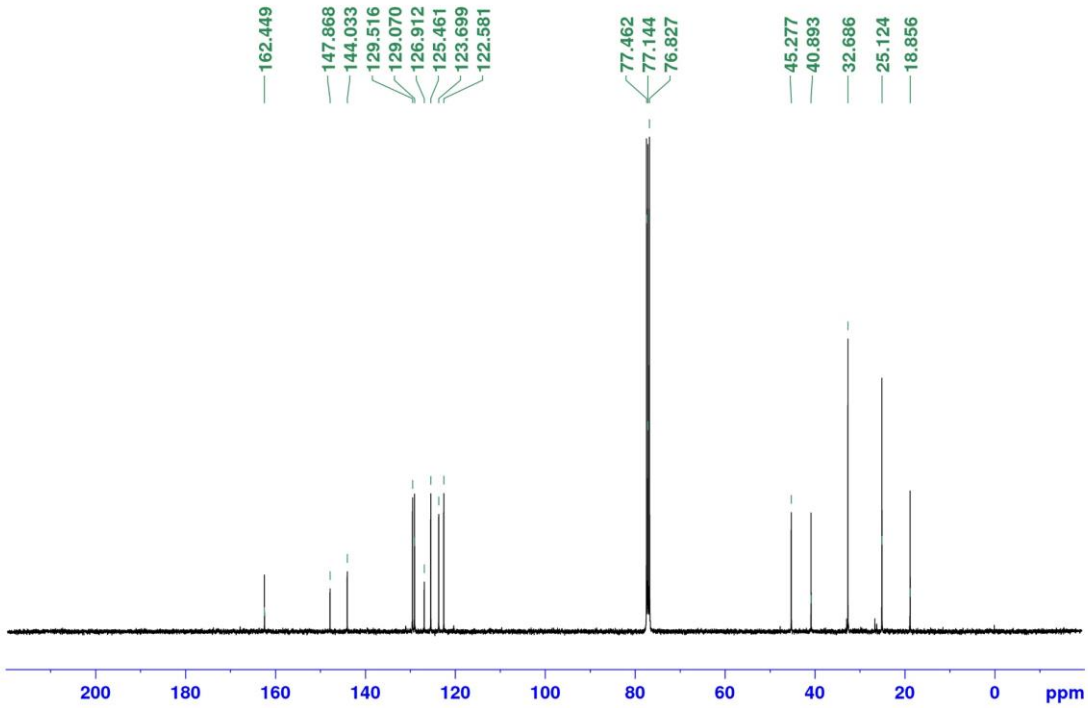
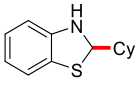


Figure S110. ^{13}C NMR (100 MHz) spectrum of **32** in $CDCl_3$.



16'

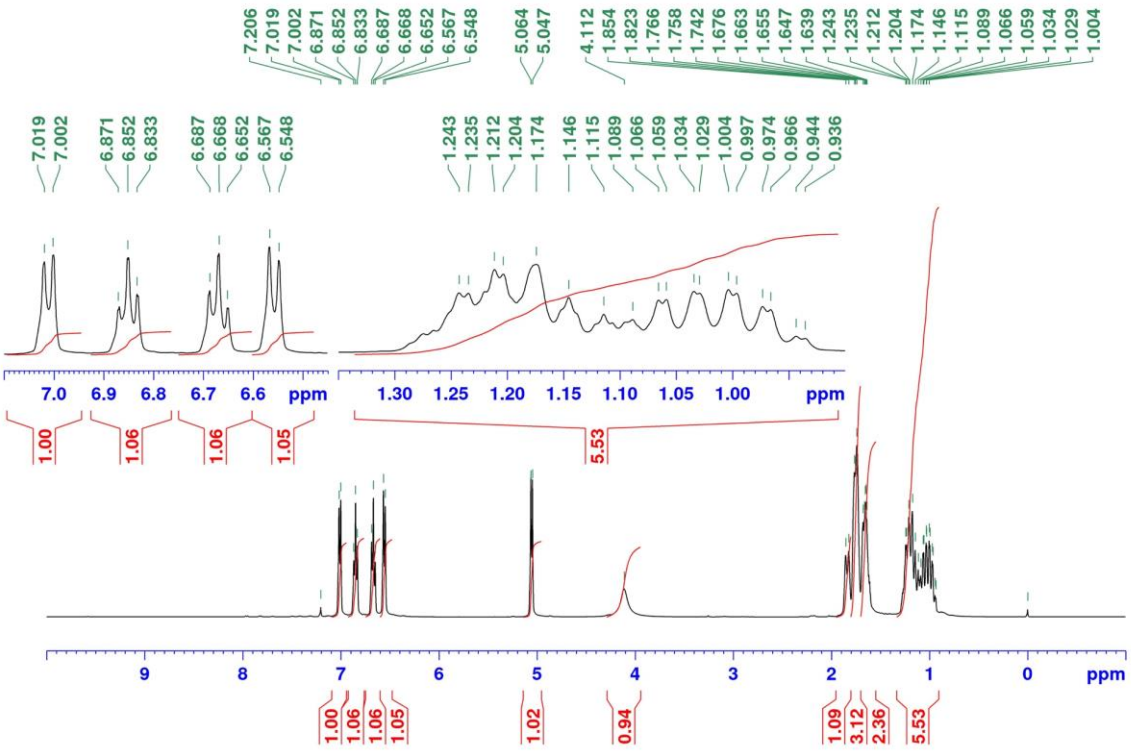
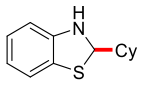


Figure S111. ^{1}H NMR (400 MHz) spectrum of **16'** in $CDCl_3$.



16'

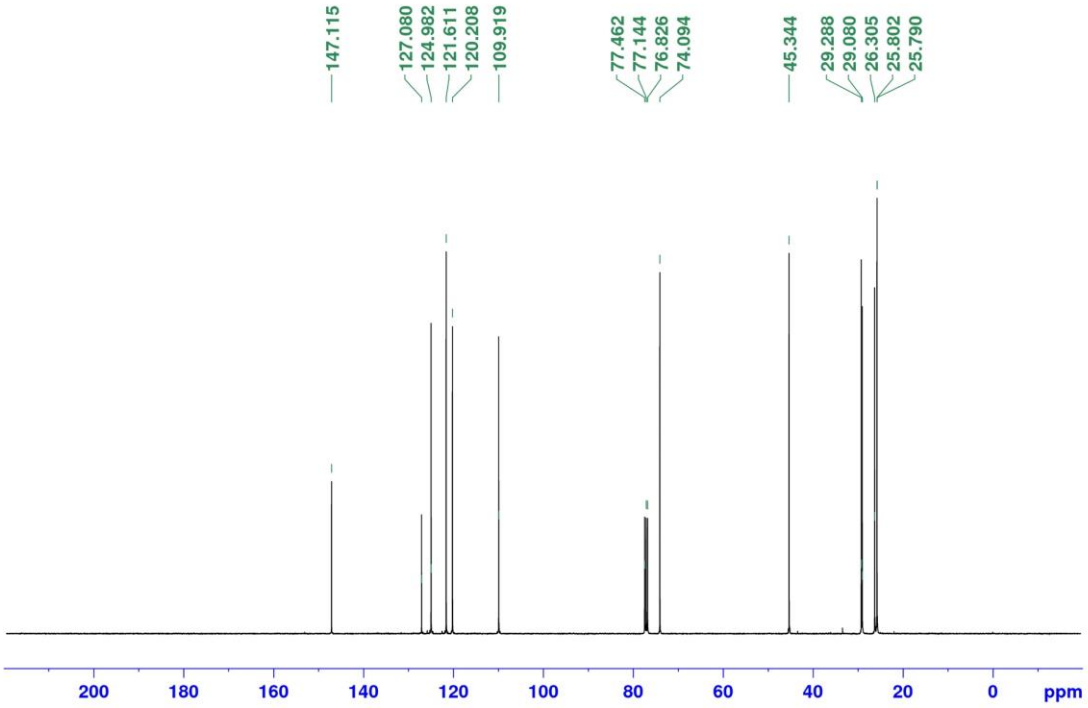


Figure S112. ^{13}C NMR (100 MHz) spectrum of **16'** in $CDCl_3$.