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Tetrahydrofluorenyl rhodium complexes: positive impact of *p*-methoxybenzyl substituent on catalytic annulation reactions

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Experimental details and procedures

Complex **2** was synthesized by modified our own preparation method.[S1]

Preparation of complex 2 by one-pot synthesis starting from 1,2,3,4-tetrahydrofluorene

Reagent Bu^{t}ONa (54 mg, 0.59 mmol, 1 equiv.) was added to a solution of 1,2,3,4-tetrahydrofluorene (100 mg, 0.59 mmol, 1 equiv) in THF (3 ml), and the reaction mixture was stirred at 40 °C for 0.5 h (oil bath). Then *p*-anysaldehyde (240 mg, 1.77 mmol, 3 equiv.) was added, and the reaction was stirred for additional 2 h. Then AcOH (1 ml) was added, and the reaction was stirred for 0.5 h. The reaction was cooled, diluted with water, and the product was extracted with dichloromethane (2 × 10 ml) and dried with anhydrous sodium sulfate. The solvent was evaporated and the product was purified with column chromatography (SiO_2, 1 × 10 cm). The first colored band eluted with hexane contains 9-(4-methoxybenzylidene)-2,3,4,9-tetrahydro-1*H*-fluorene, which was recrystallized from methanol. Then an ethanolic solution (5 ml) of 9-(4-methoxybenzylidene)-2,3,4,9-tetrahydro-1*H*-fluorene (137 mg, 0.48 mmol, 1 equiv) was added to a solution (5 ml) of $RhCl_3 \cdot 3H_2O$ (126 mg, 0.48 mmol, 1 equiv) in the same solvent, and the reaction mixture was stirred at 80 °C for 6 h (oil bath). The hot solution was poured into hexane, the resulting residue was dried in vacuo and the complex was extracted with dichloromethane (2 × 5 ml). The combined dichloromethane extracts were reduced to the quarter of the volume and the complex was precipitated with hexane (20 ml). The precipitated red-brown solid of the chloride complex $[(\eta^5\text{-9-PMB-tetrahydrofluorenyl})RhCl_2]_2$ (136 mg) was dried and mixed with anhydrous NaI (864 mg, 5.76 mmol, 20 equiv counting for 60% yield at previous stage) in acetone (10 ml). The reaction mixture was stirred vigorously at room temperature for 2 days (no inert atmosphere required). The solvent was evaporated *in vacuo* and the residue was extracted with dichloromethane (5 × 5 ml). The combined solution was dried, the resulting residue was washed with Et_2O (2 × 10 ml). The complex was twice reprecipitated from dichloromethane with hexane. The precipitate was dried. The total yield of **2** in three step is 172 mg (45%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.77 – 7.66 (m, 2H), 7.64 – 7.58 (m, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.94 (dd, *J* = 116.2, 15.2 Hz, 2H), 3.69 (s, 3H), 3.26 – 3.17 (m, 1H), 2.61 – 2.52 (m, 1H), 2.47 – 2.40 (m, 2H, overlapped with dmso signal), 1.91 – 1.80 (m, 2H), 1.73 – 1.57 (m, 2H) ppm (*cf.* Ref.[S1]).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 158.0, 134.4, 131.5, 129.7, 129.3, 127.5, 123.6, 114.2, 112.6 (d, *J* = 5.6 Hz), 107.4 (d, *J* = 4.0 Hz), 100.1 (d, *J* = 4.5 Hz), 84.9 (d, *J* = 6.9 Hz), 55.0, 29.2, 22.9, 21.1, 21.0, 20.2 ppm.

Preparation of complex 4

Complex **2** (97 mg, 0.15 mmol, 1 equiv), Na_2CO_3 (159 mg, 1.50 mmol, 10 equiv), and cyclooctadiene (33.5 mg, 0.31 mmol, 2.05 equiv.), ethanol (2 ml) were placed in a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred at 80 °C for 4 h (oil bath). The solvent was removed in vacuo and the residue was extracted with pentane (3 × 10 ml). Then pentane was evaporated, and the residue was purified by column chromatography (SiO_2, 1× 10 cm). The complex was rapidly eluted with a mixture of pentane : dichloromethane (8:1). The yellow band was collected and the solvent was evaporated. The yield of **4** is 48 mg (64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 7.9 Hz, 1H), 7.09 – 6.94 (m, 5H), 6.75 (d, *J* = 8.1 Hz, 2H), 3.74 (s, 3H), 3.58 – 3.45 (m, 2H), 3.45 – 3.33 (m, 4H), 3.01 – 2.89 (m, 1H), 2.60 – 2.51 (m, 1H), 2.49 – 2.40 (m, 1H), 2.28 – 2.18 (m, 1H), 2.01 – 1.67 (m, 12H) ppm (*cf*. Ref.[S1]).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.9, 132.7, 130.2, 129.1, 122.0, 121.2, 118.0, 116.7, 113.8, 110.8 (d, *J* = 2.7 Hz), 110.3(d, *J* = 2.0 Hz), 72.5 (d, *J* = 13.4 Hz), 71.2 (d, *J* = 13.7 Hz), 55.3, 29.1, 24.2, 23.5, 23.3, 20.4. Several signals of quaternary carbon atoms in the indenyl moiety were not observed in ^{13}C{^{1}H} NMR because of their low intensity.

Preparation of complex 5

Complex **2** (32 mg, 0.05 mmol, 1 equiv), CpTl (17.5 mg, 0.065 mmol, 1.3 equiv), and MeCN (1 ml) were placed in a Schlenk tube equipped with a stir bar. The reaction mixture was refluxed (an oil bath) and stirred for 8 h. After cooling to room temperature, the solvent was removed *in vacuo*. The residue was extracted with water and the resulting solution was treated with an excess of an aqueous solution of KPF_6. The yellow precipitate was centrifuged, washed with water, and dried *in vacuo*. Re-precipitation from CH_2Cl_2 with petroleum ether gave complex **5** as a pale yellow solid. The yield is 25 mg (83%)

^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.91 – 7.86 (m, 1H), 7.75 – 7.69 (m, 1H), 7.50 – 7.44 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 7.7 Hz, 2H), 5.64 (s, 5H), 4.23 (dd, *J* = 58.8, 15.4 Hz, 2H), 3.69 (s, 3H), 3.18 – 3.05 (m, 1H), 2.92 – 2.72 (m, 2H), 2.42 – 2.31 (m, 1H), 1.99 – 1.71 (m, 4H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6): δ = 158.0, 130.9, 130.2, 130.0, 129.5, 122.8, 114.2, 88.1 (d, *J* = 6.9 Hz), 55.0, 29.5, 21.89, 21.87, 21.6, 21.3 ppm. Several signals of quaternary carbon atoms in the ligand were not observed in ^{13}C{^{1}H} NMR because of their low intensity

HRMS (ESI, *m*/*z*) calcd. for $C_{26}H_{26}ORh$ $[M\text{-}PF_6]^+$: 457.1038, found: 457.1037.

General procedure for isocoumarin preparation

Carboxylic acid (0.25 mmol, 1 equiv), alkyne (0.25 mmol, 1 equiv), complex **2** (3.2 mg, 1 mol %), AgOAc (63 mg, 0.375 mmol, 1 equiv), and MeOH (2 ml) were placed in a Schlenk tube equipped with a stir bar. The reaction mixture was stirred at 90°C (an oil bath) for 10 h. Then, the formed precipitate was centrifuged, the solvent was removed in vacuo, and the residue was chromatographed on silica (1 × 15 cm). The first colorless band containing unreacted alkyne was eluted with petroleum ether. The second band was eluted with a mixture of petroleum ether and dichloromethane.

3,4-Diphenyl-1*H*-isochromen-1-one. Colorless crystals. Yield: 59 mg (80%). Eluent: petroleum ether/CH_2Cl_2 (2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.36 – 7.30 (m, 2H), 7.28 – 7.15 (m, 6H) ppm (*cf*. Ref.[S2]). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 162.3, 151.0, 138.9, 134.7, 134.4, 133.0, 131.3, 129.6, 129.3, 129.1, 129.0, 128.2, 128.2, 127.9, 125.4, 120.5, 117.0 ppm.

3,4-Diethyl-1*H*-isochromen-1-one. Colorless solid. Yield: 49 mg (97%). Eluent: petroleum ether/CH_2Cl_2 (6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 7.9, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 2.67 – 2.58 (m, 4H), 1.27 (t, *J* = 7.5 Hz, 3H), 1.19 (t, *J* = 7.5 Hz, 3H) ppm (*cf*. Ref.[S2]). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 163.1, 155.1, 137.9, 134.7, 130.0, 127.2, 122.6, 121.0, 113.2, 24.2, 19.4, 14.4, 12.7 ppm.

5-Methoxy-3,4-diphenyl-1*H*-isochromen-1-one. Colorless solid. Yield: 53 mg (67%). Eluent: petroleum ether/CH_2Cl_2 (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.23–7.18 (m, 5H), 7.17–7.09 (m, 6H), 3.32 (s, 3H) ppm (*cf*. Ref.[S3]). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 162.4, 156.3, 151.1, 137.8, 133.7, 130.8 (2C), 129.7 (2C), 129.2, 128.6, 127.8, 127.7 (2C), 127.5 (2C), 126.8, 122.2, 122.1, 117.7, 115.6, 56.1 ppm.

7-Methoxy-3,4-diphenyl-1*H*-isochromen-1-one. Colorless solid. Yield: 26 mg (30%). Eluent: petroleum ether/CH_2Cl_2 (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 2.7 Hz, 1H), 7.41–7.39 (m, 2H), 7.34–7.28 (m, 2H), 7.26–7.10 (m, 8H), 3.93 (s, 3H) ppm (*cf*. Ref.[S3]). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 162.5, 159.6, 149.1, 134.6, 133.1 (2C), 132.7, 131.3, 129.19 (2C), 129.16 (2C),128.8, 128.2, 128.0 (2C), 127.2, 124.3, 121.7, 116.9, 110.0, 56.0 ppm.

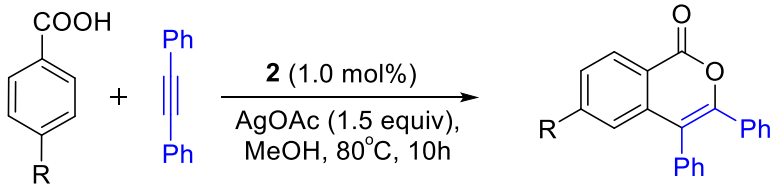
3,4-Diethyl-5-methoxy-1*H*-isochromen-1-one. Colorless solid. Yield: 38 mg (65%). Eluent: petroleum ether/CH_2Cl_2 (3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 3.89 (s, 3H), 2.83 (q, *J* = 7.2 Hz, 2H), 2.60 (q, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.15 (t, *J* = 7.3 Hz, 3H) ppm (*cf*. Ref.[S3]). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 163.1, 155.8, 154.3, 127.9, 124.3, 122.9, 122.0, 116.4, 113.4, 55.9, 24.2, 22.0, 15.6, 12.9 ppm.

3,4-Diethyl-7-methoxy-1*H*-isochromen-1-one. Colorless solid. Yield: 19 mg (33%). Eluent: petroleum ether/CH_2Cl_2 (3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 2.8 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 7.32 (dd, *J* = 8.9, 2.8 Hz, 1H), 3.90 (s, 3H), 2.68–2.55 (m, 3H), 1.27 (t, *J* = 7.5 Hz,

4H), 1.18 (t, *J* = 7.5 Hz, 3H) ppm (*cf*. Ref.[S3]). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 163.3, 158.7, 153.1, 131.6, 124.4, 124.3, 122.1, 113.1, 110.3, 55.9, 24.0, 19.6, 14.6, 12.8 ppm.

Additional examples

Complex **2** proved to be better catalyst for annulation of 4-substituted benzoic acids compared with **1**. A particularly dramatic difference in catalytic performance was observed for the CF_3 derivative.



R = OMe (yield 96% *vs*. 94% for **1**);
R = CF_3 (yield 87% *vs*. traces for **1**)

6-Methoxy-3,4-diphenyl-1*H*-isochromen-1-one. White solid. Yield: 78 mg (96%). Eluent: petroleum ether/CH_2Cl_2 (3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 8.8 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.33 – 7.28 (m, 2H), 7.26 – 7.13 (m, 5H), 7.04 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.57 (d, *J* = 1.5 Hz, 1H), 3.74 (s, 3H) ppm (*cf*. Ref.[S4]). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 164.8, 162.1, 151.6, 141.3, 134.5, 133.1, 132.0, 131.3, 129.4, 129.2, 129.0, 128.3, 127.9, 116.9, 115.8, 113.8, 108.6, 77.2, 55.6 ppm.

3,4-Diphenyl-6-trifluoromethyl-1*H*-isochromen-1-one. Pale yellow solid. Yield: 79 mg (87%). Eluent: petroleum ether/CH_2Cl_2 (3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 8.3 Hz, 1H), 7.74 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.48 – 7.42 (m, 4H), 7.36 – 7.30 (m, 2H), 7.28 – 7.20 (m, 5H) ppm (*cf*. Ref.[S5]). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 160.3, 152.6, 139.5, 136.4(q, *J* = 32.1 Hz), 133.4, 132.5, 131.2, 130.7, 129.6, 129.4, 128.8, 128.1, 124.9, 124.5 - 124.4 (m), 122.9, 122.53, (q, *J* = 3.8), 116.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -63.35 ppm.

General procedure for naphthalene preparation

Carboxylic acid (0.25 mmol, 1 equiv), alkyne (0.5 mmol, 2 equiv), complex **2** (3.2 mg, 1 mol %), $Cu(OAc)_2$ (90.5 mg, 0.5 mmol, 2 equiv), and *o*-xylene (1 ml) were placed in a Schlenk tube equipped with a stir bar. The reaction mixture was stirred at 160 °C (an oil bath) for 10 h. Then, the formed precipitate was centrifuged, the solvent was removed in vacuo, and the residue was chromatographed on silica (1 × 15 cm). The first colorless band containing unreacted alkyne was eluted with petroleum ether. The second band was eluted with a mixture of petroleum ether and dichloromethane.

1,2,3,4-Tetraphenylnaphthalene. White solid. Yield: 89 mg (89%). Eluent: petroleum ether/CH_2Cl_2 (9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 – 7.71 (m, 2H), 7.50 – 7.43 (m, 2H), 7.35 – 7.26 (m, 10H), 6.97 – 6.88 (m, 10H) ppm (*cf*. Ref.[S2]). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 140.6, 139.7, 139.0, 138.5, 132.1, 131.4, 127.7, 127.1, 126.7, 126.5, 126.0, 125.5 ppm.

1,2,3,4-Tetraethylnaphthalene. Colorless oil. Yield: 59 mg (96%). Eluent: petroleum ether/CH_2Cl_2 (15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23−8.20 (m, 2H), 7.61−7.57 (m, 2H), 3.32−3.24 (m, 4H), 3.06−2.98 (m, 4H), 1.51−1.41 (m, 12H) ppm (*cf*. Ref.[S2]). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 137.9, 135.5, 131.1, 124.7, 124.6, 22.9, 21.9, 16.0, 15.7 ppm.

Preparation of indole derivative

Acetanilide (13.5 mg, 0.1 mmol, 1 equiv), complex **2** (1.3 mg, 1 mol%), $AgSbF_6$ (3.5 mg, 10 mol%), $Cu(OAc)_2$ (2 mg, 10 mol%), diphenylacetylene (0.1 mmol), and acetone (1 ml) were placed in a Schlenk tube equipped with a stir bar. The reaction mixture was stirred at room temperature for 50 h. Then, the solvent was removed *in vacuo*, and the residue was chromatographed on SiO_2 (1 × 15 cm). The first colorless band containing unreacted alkyne was eluted with petroleum ether. The second band was eluted with a mixture of petroleum ether and dichloromethane (4:1) to give a product.

1-(2,3-Diphenyl-1*H*-indol-1-yl)ethan-1-one. White crystals. Yield: 15 mg (50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.42 – 7.25 (m, 11H), 2.05 (s, 3H) ppm (*cf*. Ref.[S6]). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 171.6, 136.9, 135.1, 133.2, 133.1, 130.9, 130.1, 129.4, 128.7, 128.3, 127.0, 125.6, 123.9, 123.5, 119.7, 116.3, 28.0 ppm.

General procedure for dihydroisoquinolone preparation

Benzohydroxamic acid pivalate (22 mg, 0.1 mmol, 1 equiv), alkene (0.25 mmol, 2.5 equiv), complex **2** (1.9 mg, 1.5 mol %), CF_3COOAg (1.7 mg, 7.5 mol%), CsOAc (0.5 mg, 25 mol%), and CH_2Cl_2 (1 ml) were placed in a Schlenk tube equipped with a stir bar. The reaction mixture was stirred at room temperature for 1 h. Then, the resulting mixture was transferred on chromatography column with silica (1 × 15 cm). The first colorless band containing unreacted alkene was eluted with pure dichloromethane. The second band, containing a product was eluted with a dichloromethane and ethyl acetate mixture (3:1).

1,3,4,4a,5,10b-Hexahydro-1,4-methanophenanthridin-6(2*H*)-one. White crystals. Yield: 21.3 mg (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.32–7.19 (m, 2H), 6.22 (br s, 1H), 3.81 (d, *J* = 8.9 Hz, 1H), 3.12 (d, *J* = 8.8 Hz, 1H), 2.32 (s, 1H), 2.24 (s, 1H), 1.69–1.62 (m, 3H), 1.57–1.48 (m, 1H), 1.37–1.29 (m, 1H), 1.18 (d, *J* = 10.5 Hz, 1H) ppm (*cf*. Ref.[S7]). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 163.9, 140.5, 132.5, 128.6, 127.5, 126.5, 126.0, 58.4, 47.9, 46.4, 44.3, 32.5, 30.2, 25.8 ppm.

3-Phenyl-3,4-dihydroisoquinolin-1(2*H*)-one. White crystals. Yield: 21 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.45 – 7.35 (m, 5H), 7.19 (d, *J* = 7.0 Hz, 1H), 5.99 (s, 1H), 4.93 – 4.80 (m, 1H), 3.28 – 3.03 (m, 2H) ppm. (*cf*. Ref.[S7]). ^{13}C{^{1}H} NMR

(101 MHz, $CDCl_3$): δ = 166.4, 141.0, 137.6, 132.6, 129.1 (2C), 128.5, 128.3, 128.2, 127.4 (2C), 126.5 (2C), 56.3, 37.6 ppm.

Preparation of isoquinolinium salt

Complex **2** (1.3 mg, 1 mol %), $Cu(OAc)_2$ (40 mg, 0.2 mmol, 2 equiv), NaOAc (8.2 mg, 0.1 mmol, 1 equiv), $AgBF_4$·dioxane solvate (5.6 mg, 20 mol%), diphenylacetylene (18 mg, 0.1 mmol, 1 equiv), *p*-anysaldehyde (14 mg, 0.1 mmol, 1 equiv), *p*-toluidine (16 mg, 0.15 mmol, 1.5 equiv), and MeOH (2 ml) were placed in a Schlenk tube equipped with a stir bar. The reaction mixture was stirred at 80°C (an oil bath) for 16 h. After cooling to room temperature, the solution was treated with saturated aqueous solution of KPF_6 and stirred for additional hour. Then the product was extracted with CH_2Cl_2 (2 × 10 ml). The organic phase was dried under sodium sulfate and the solvent was evaporated. The product was chromatographed on neutral alumina (1 × 15 cm) using a mixture of petroleum ether/CH_2Cl_2 (1:1) as an eluent. The first colored band contains the product.

6-Methoxy-3,4-diphenyl-2-(*p*-tolyl)isoquinolin-2-ium hexafluorophosphate. Pale yellow solid. Yield: 39 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (s, 1H), 8.45 (d, *J* = 9.1 Hz, 1H), 7.44 (d, *J* = 9.1 Hz, 1H), 7.24−7.28 (m, 5H), 7.17−7.21 (m, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.96−7.06 (m, 5H), 6.83 (s, 1H), 3.77 (s, 3H), 2.22 (s, 3H) ppm (*cf*. Ref.[S4]). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 167.2, 148.8, 144.6, 141.8, 140.5, 139.8, 137.0, 134.1, 133.7, 131.6, 131.2, 130.4, 130.1, 129.1, 128.7, 128.0, 126.7, 124.1, 122.7, 105.2, 56.3, 21.2 ppm.

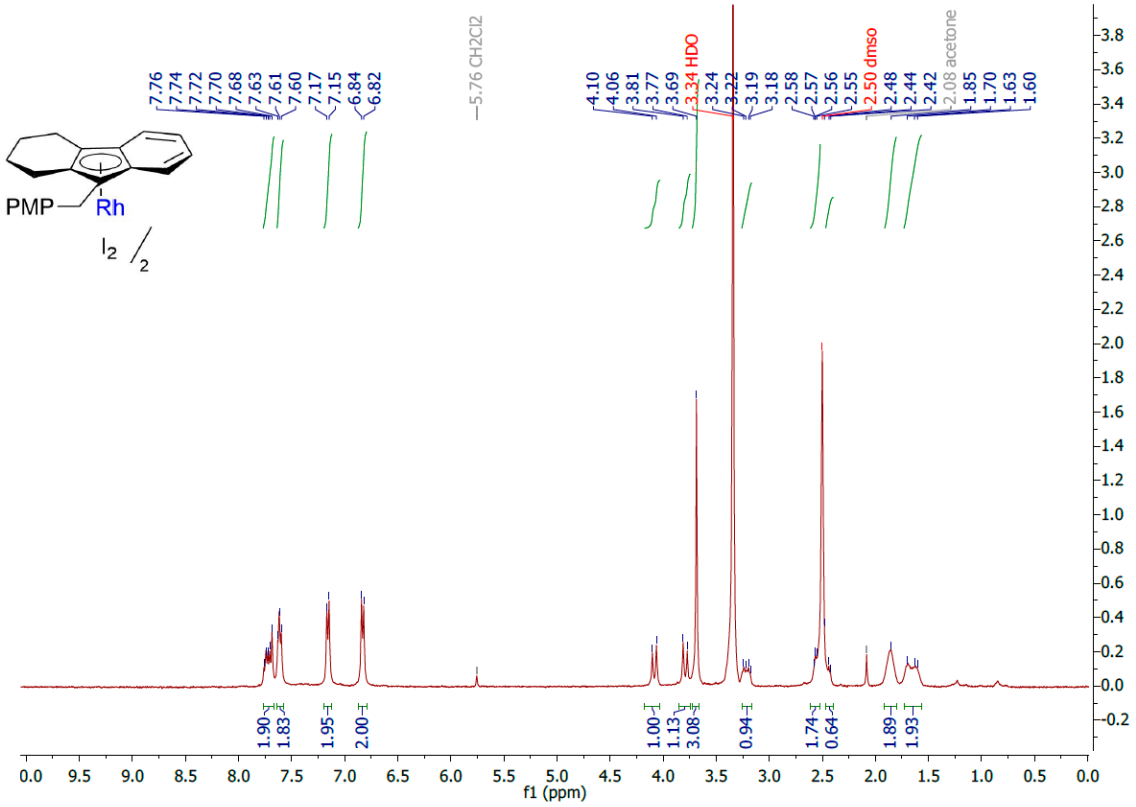
Preparation of thiophene derivative

Dimethyl acetylenedicarboxylate (29 mg, 0.2 mmol, 1 equiv), complex **4** (1 mg, 1 mol%), elemental sulfur (6.5 mg, 0.2 mmol, 2 equiv), *o*-xylene were placed in a Schlenk tube equipped with a stir bar. The reaction mixture was stirred at 150°C (an oil bath) for 8 h. Then, the solvent was removed in vacuo, and the residue was chromatographed on SiO_2 (1 × 15 cm). The product was eluted with a mixture of dichloromethane and ethyl acetate (1:1).

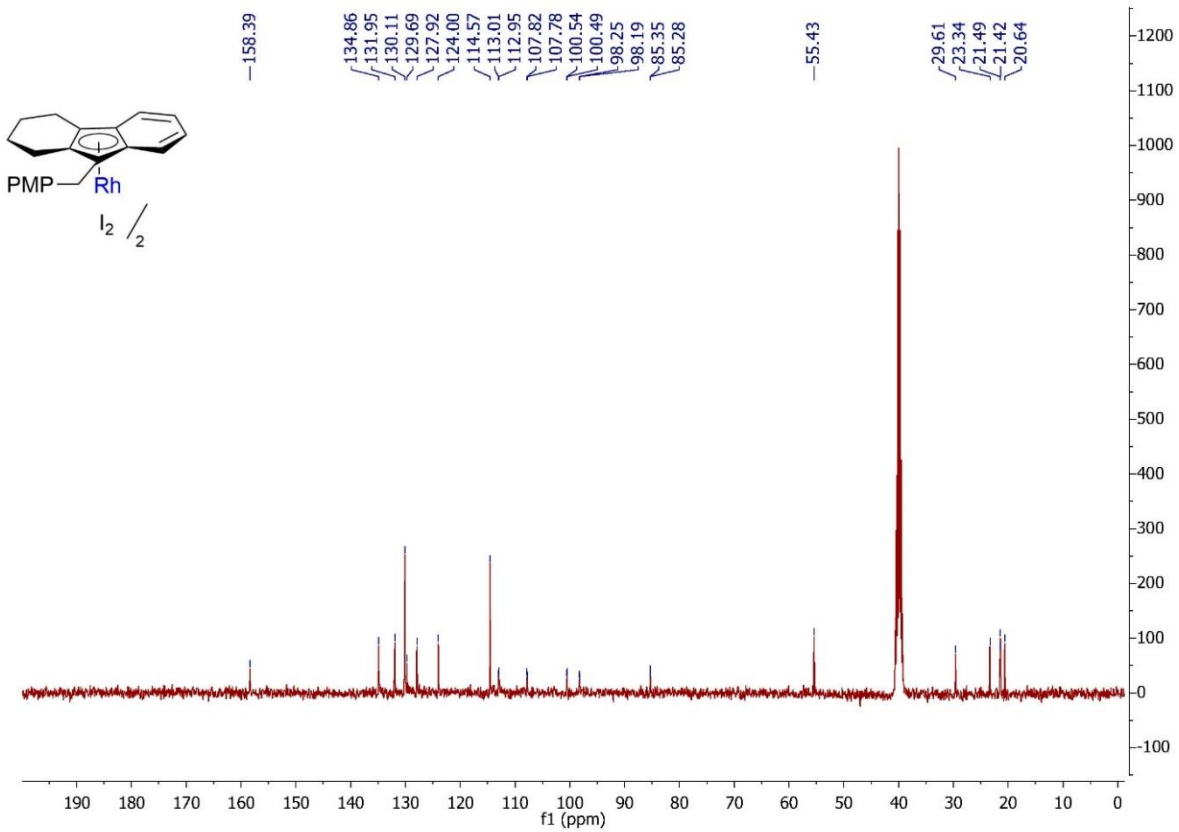
Tetramethyl thiophene-2,3,4,5-tetracarboxylate. Pale red solid. Yield: 25 mg (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 12H) ppm (*cf*. Ref.[S8]). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 163.0, 160.4, 137.1, 136.2, 53.4 ppm.

Copies of NMR Spectra

^{1}H NMR (400 MHz) spectrum of **2** in DMSO-d_6



^{13}C{^{1}H} NMR (101 MHz) spectrum of **2** in DMSO-d_6



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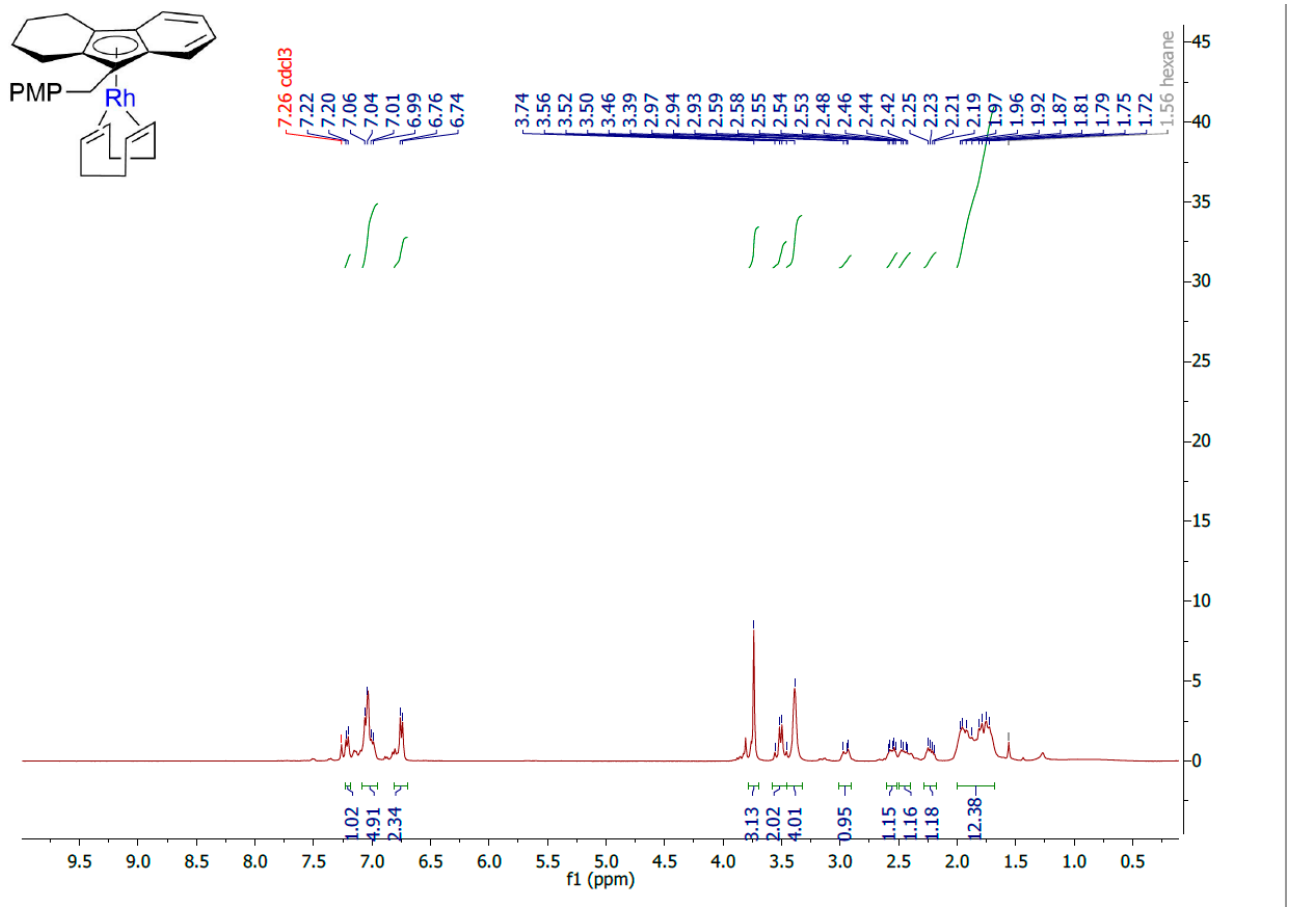
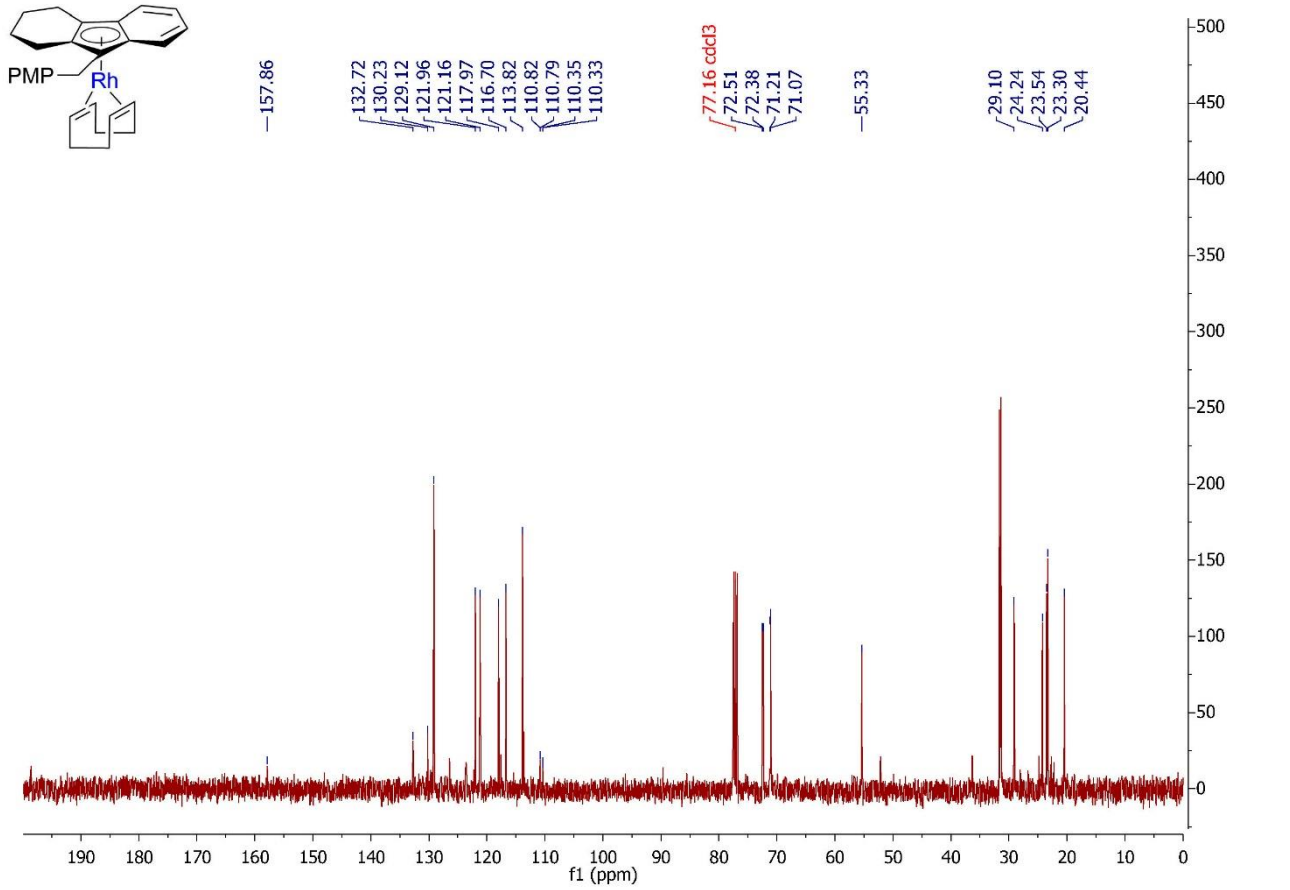
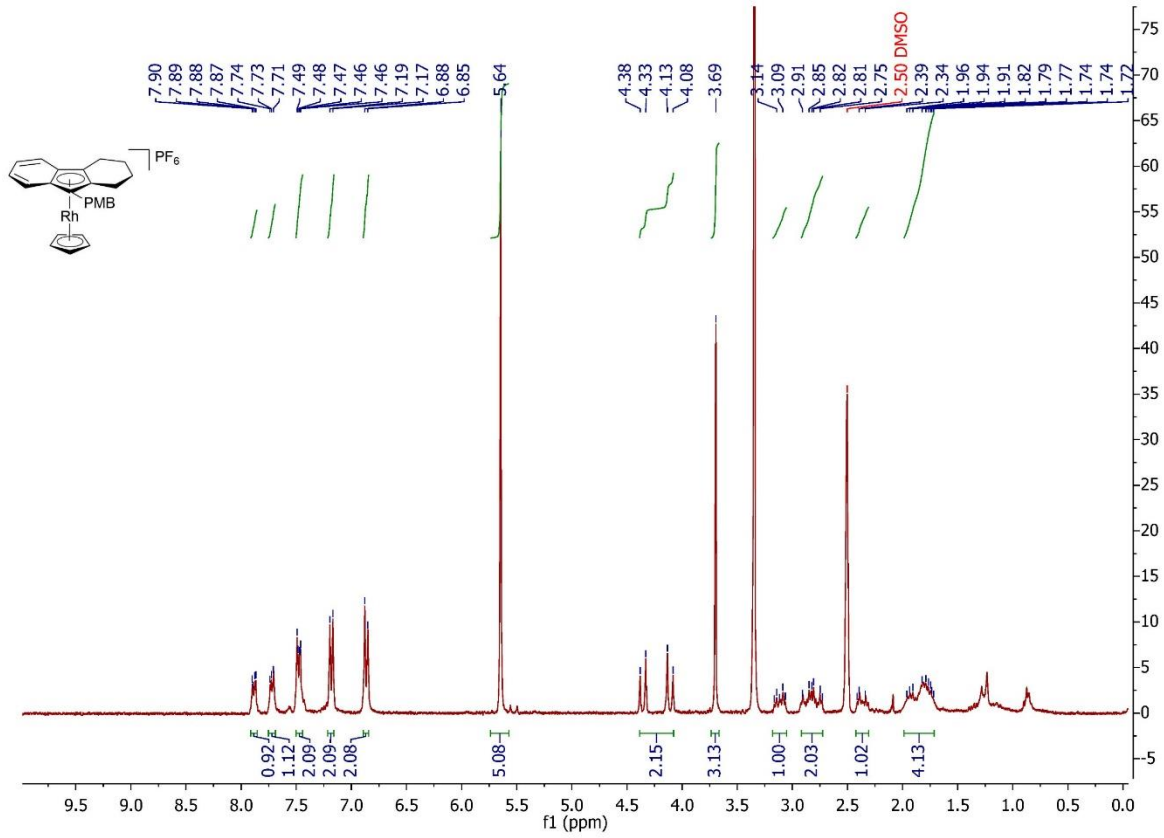


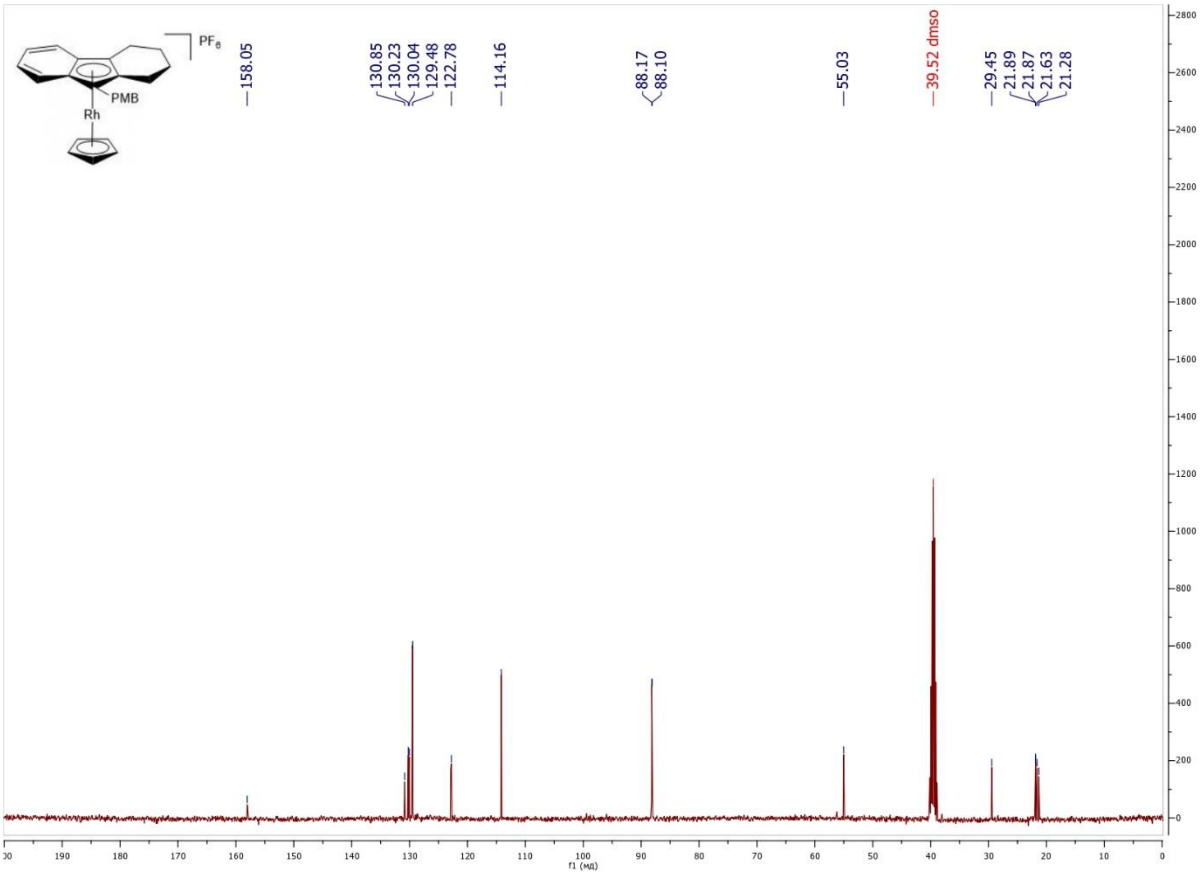
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4** in $CDCl_3$



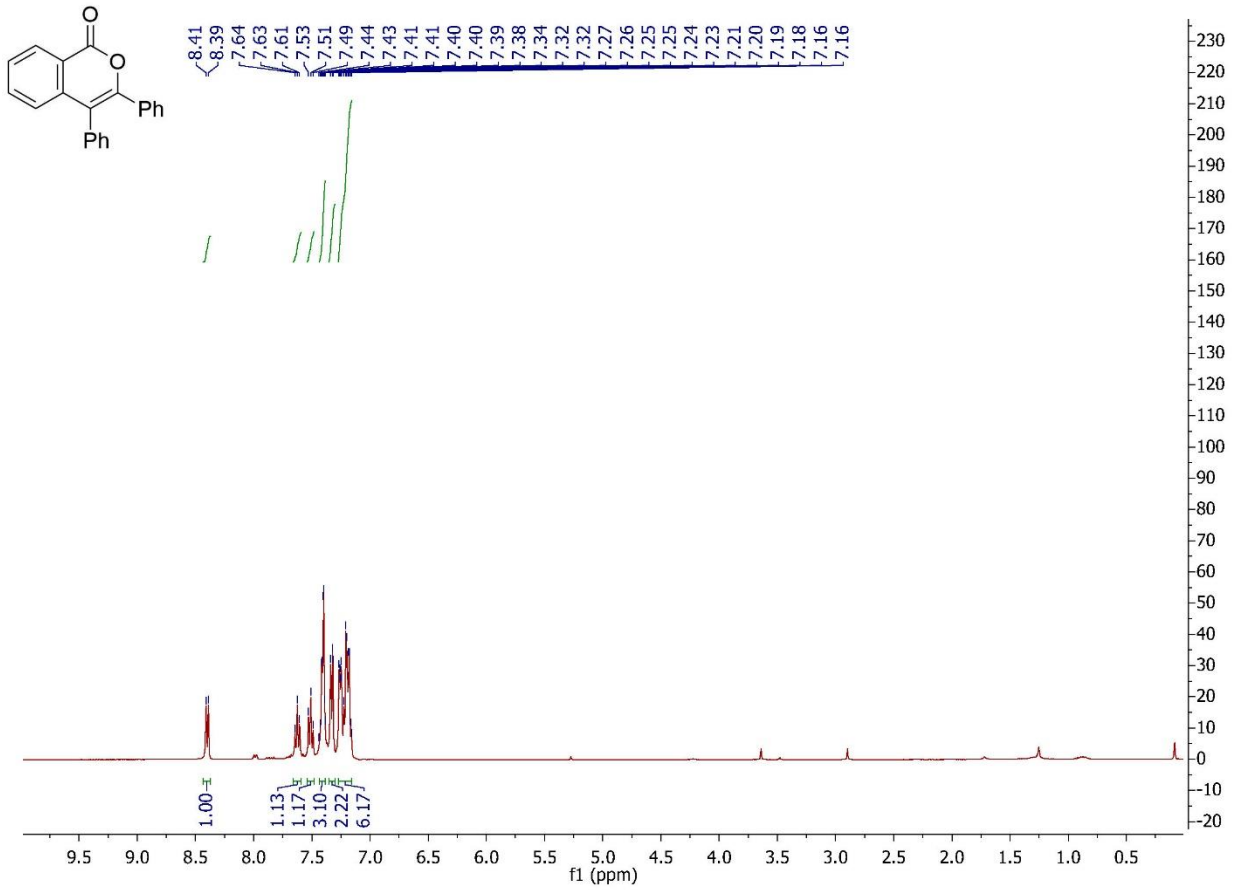
^{1}H NMR (400 MHz) spectrum of **5** in DMSO-d_6



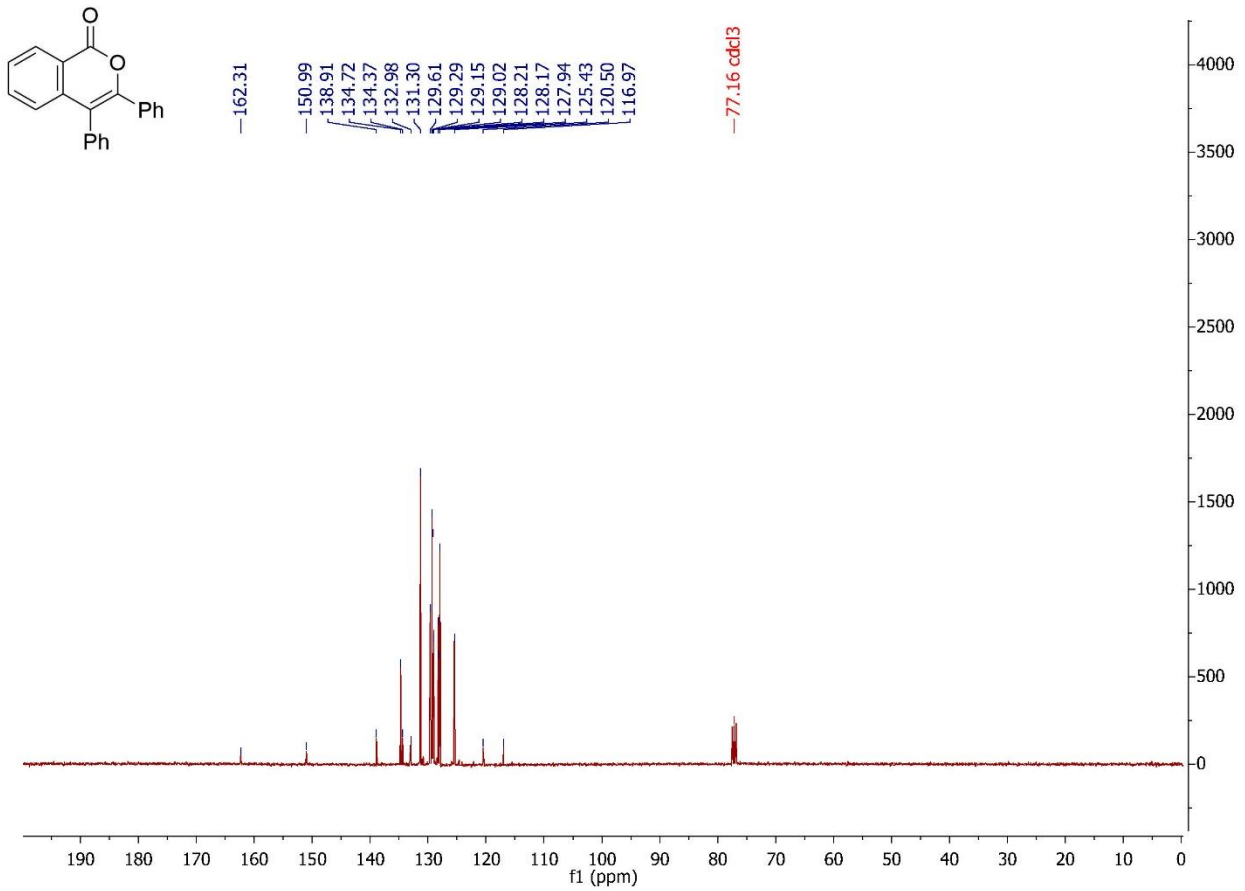
^{13}C{^{1}H} NMR (101 MHz) spectrum of **5** in DMSO-d_6



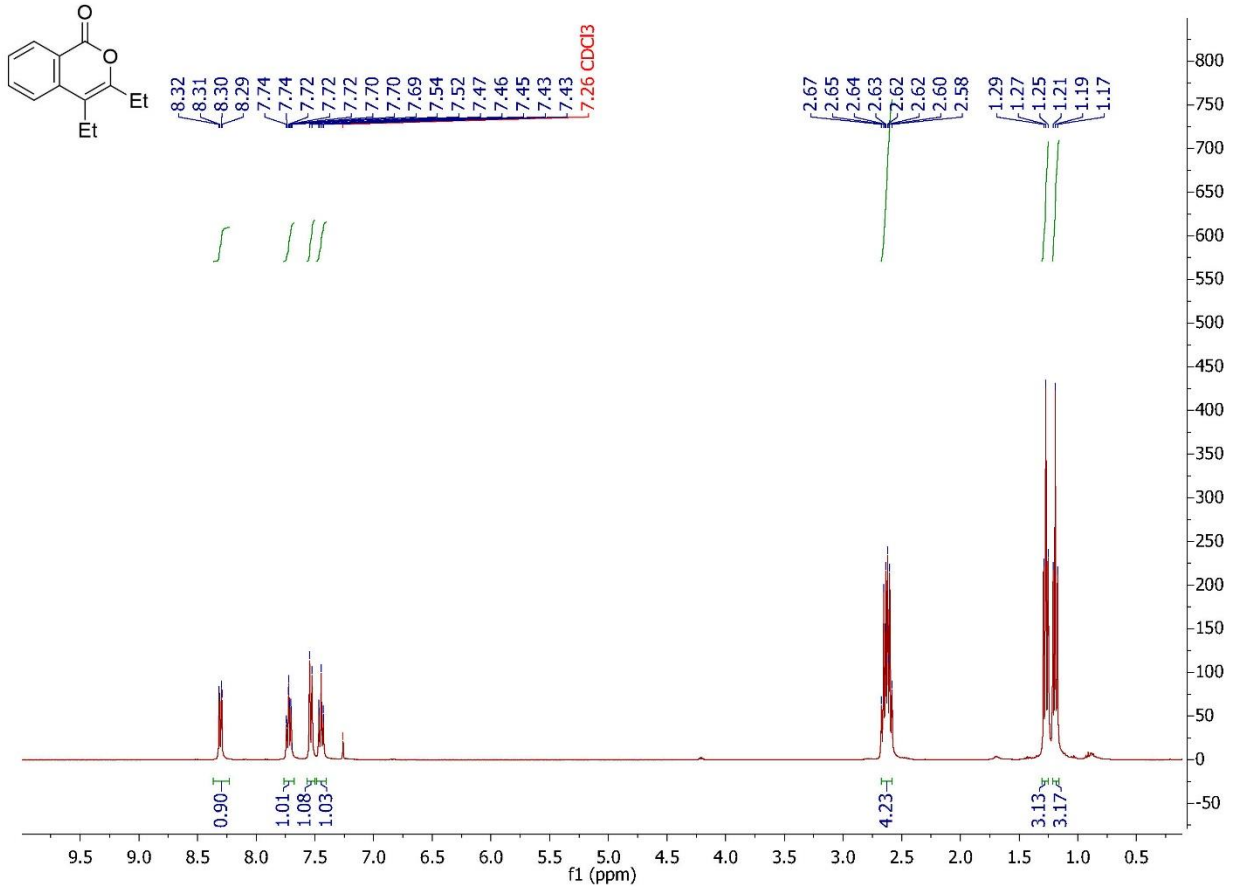
^{1}H NMR (400 MHz) spectrum of **3,4-diphenyl-1*H*-isochromen-1-one** in $CDCl_3$



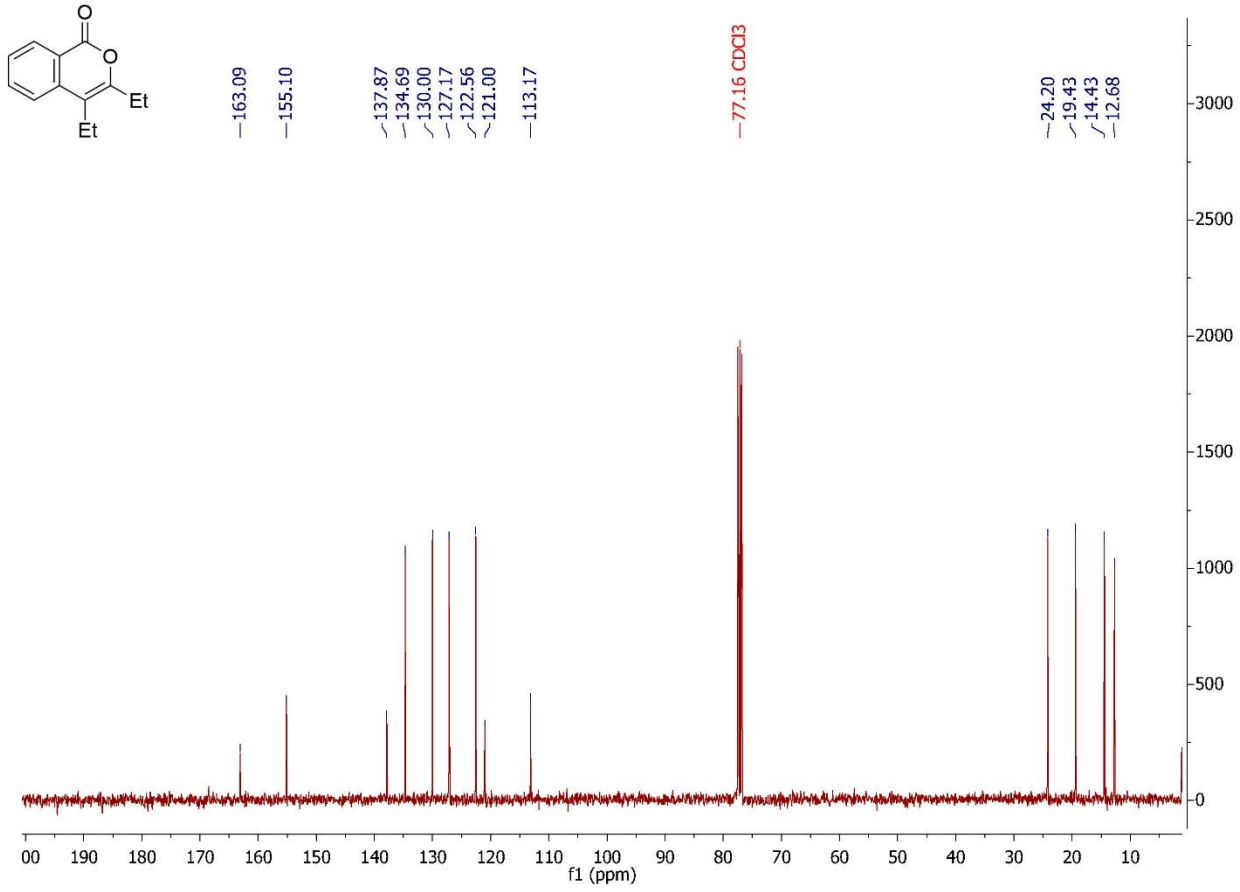
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3,4-diphenyl-1*H*-isochromen-1-one** in $CDCl_3$



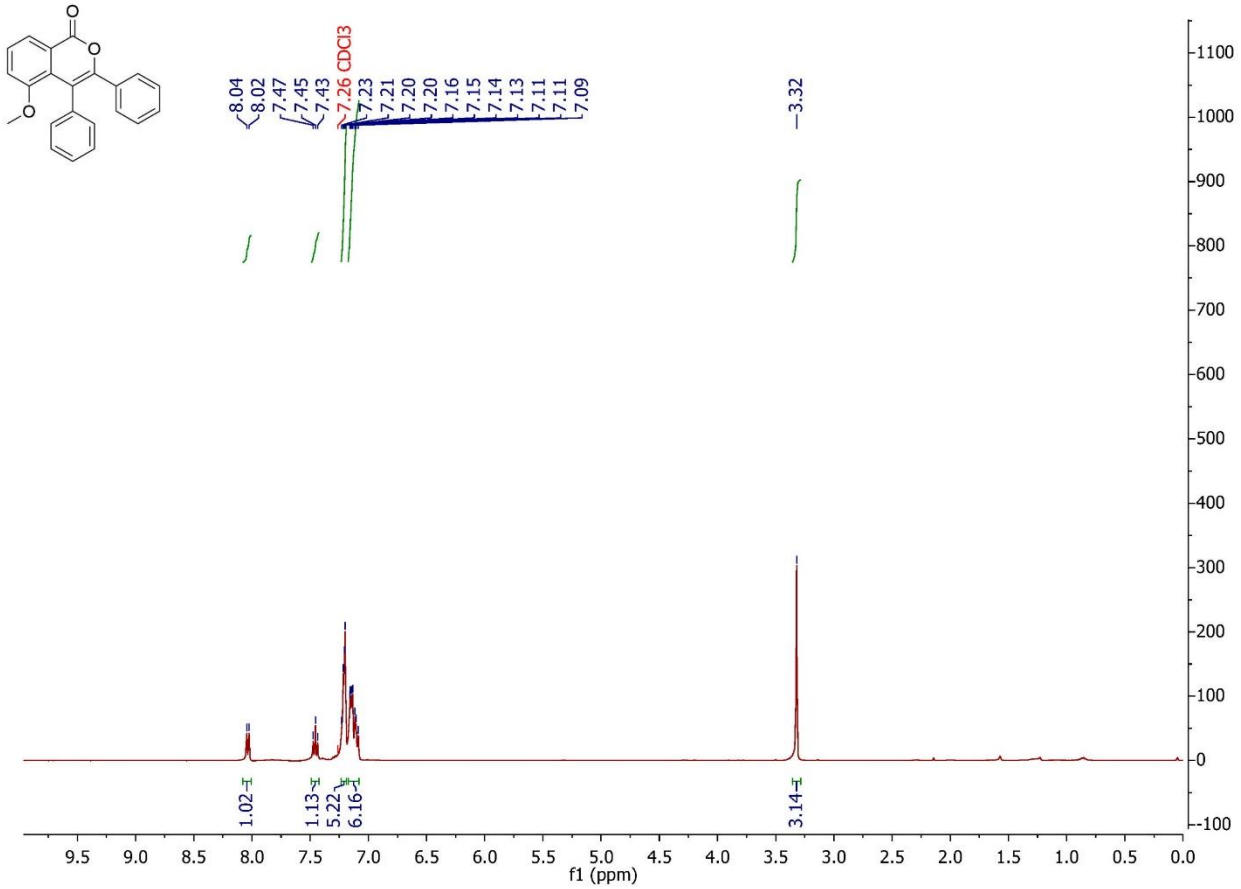
^{1}H NMR (400 MHz) spectrum of **3,4-diethyl-1*H*-isochromen-1-one** in $CDCl_3$



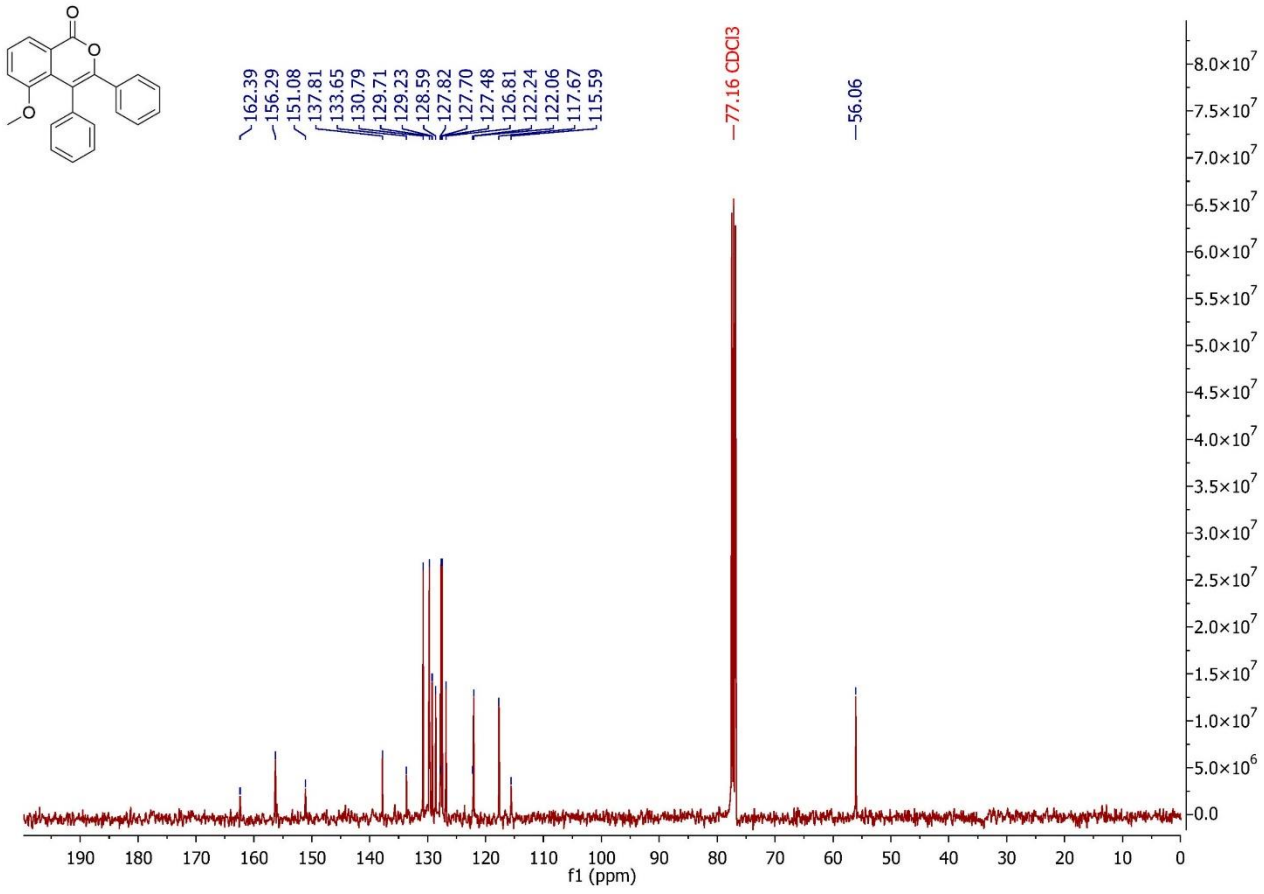
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3,4-diethyl-1*H*-isochromen-1-one** in $CDCl_3$



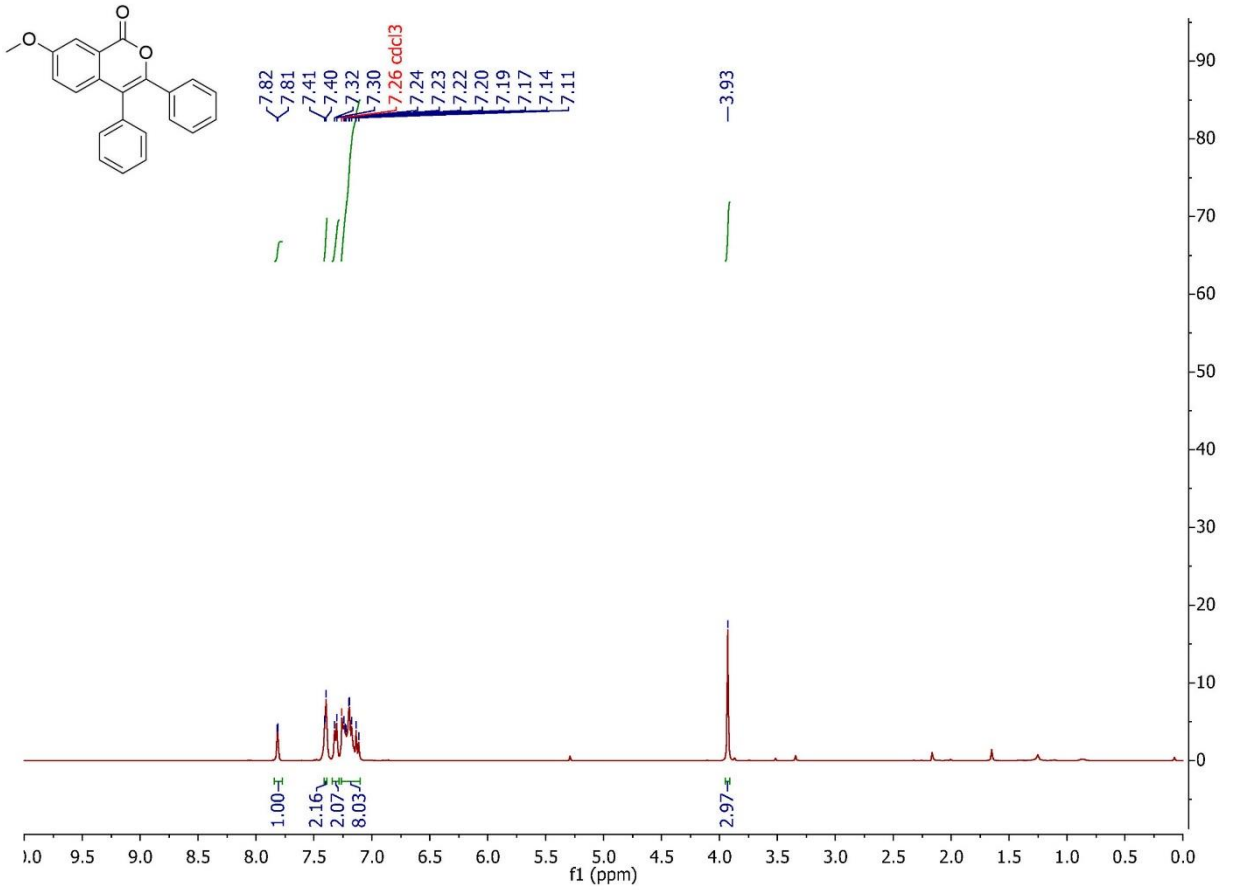
^{1}H NMR (400 MHz) spectrum of **5-methoxy-3,4-diphenyl-1*H*-isochromen-1-one** in $CDCl_3$



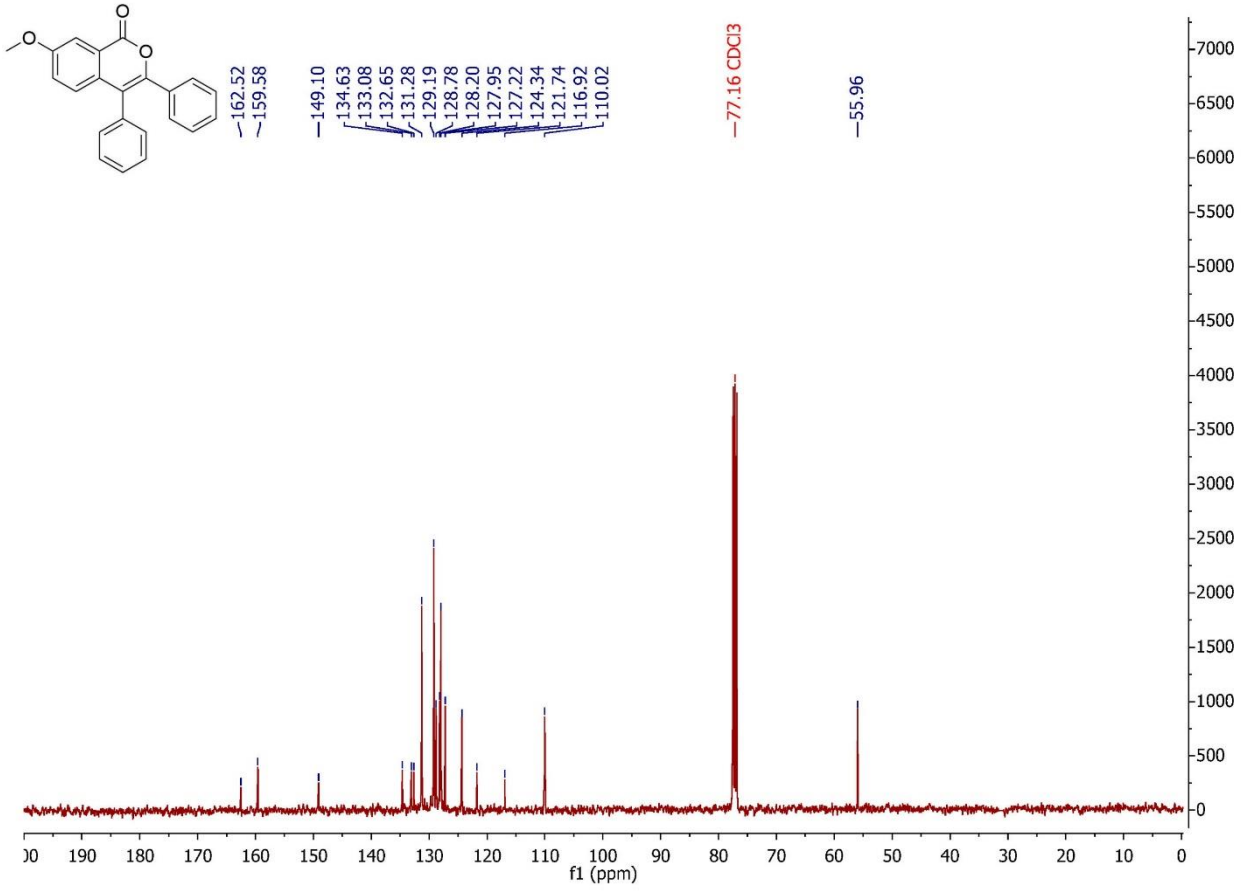
^{13}C{^{1}H} NMR (101 MHz) spectrum of **5-methoxy-3,4-diphenyl-1*H*-isochromen-1-one** in $CDCl_3$



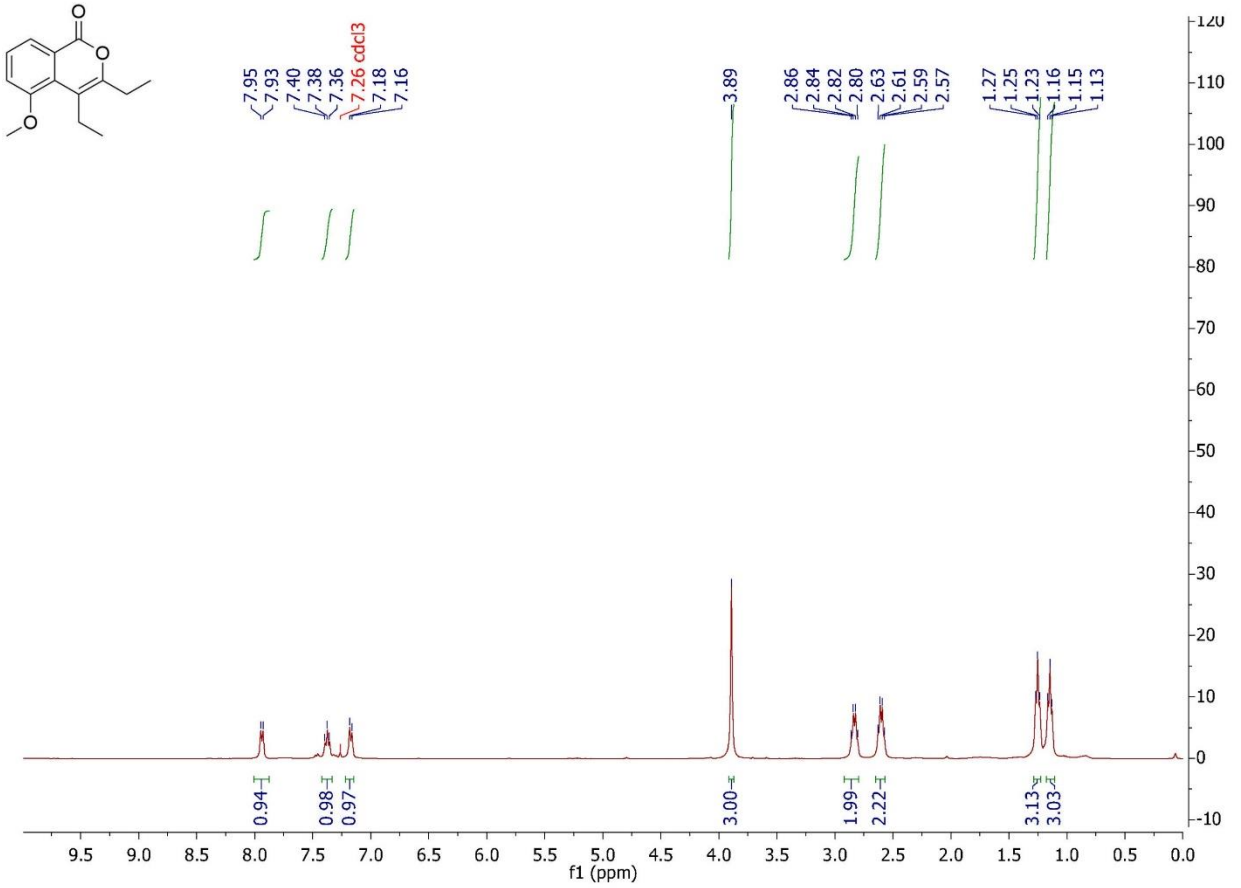
^{1}H NMR (400 MHz) spectrum of **7-methoxy-3,4-diphenyl-1*H*-isochromen-1-one** in $CDCl_3$



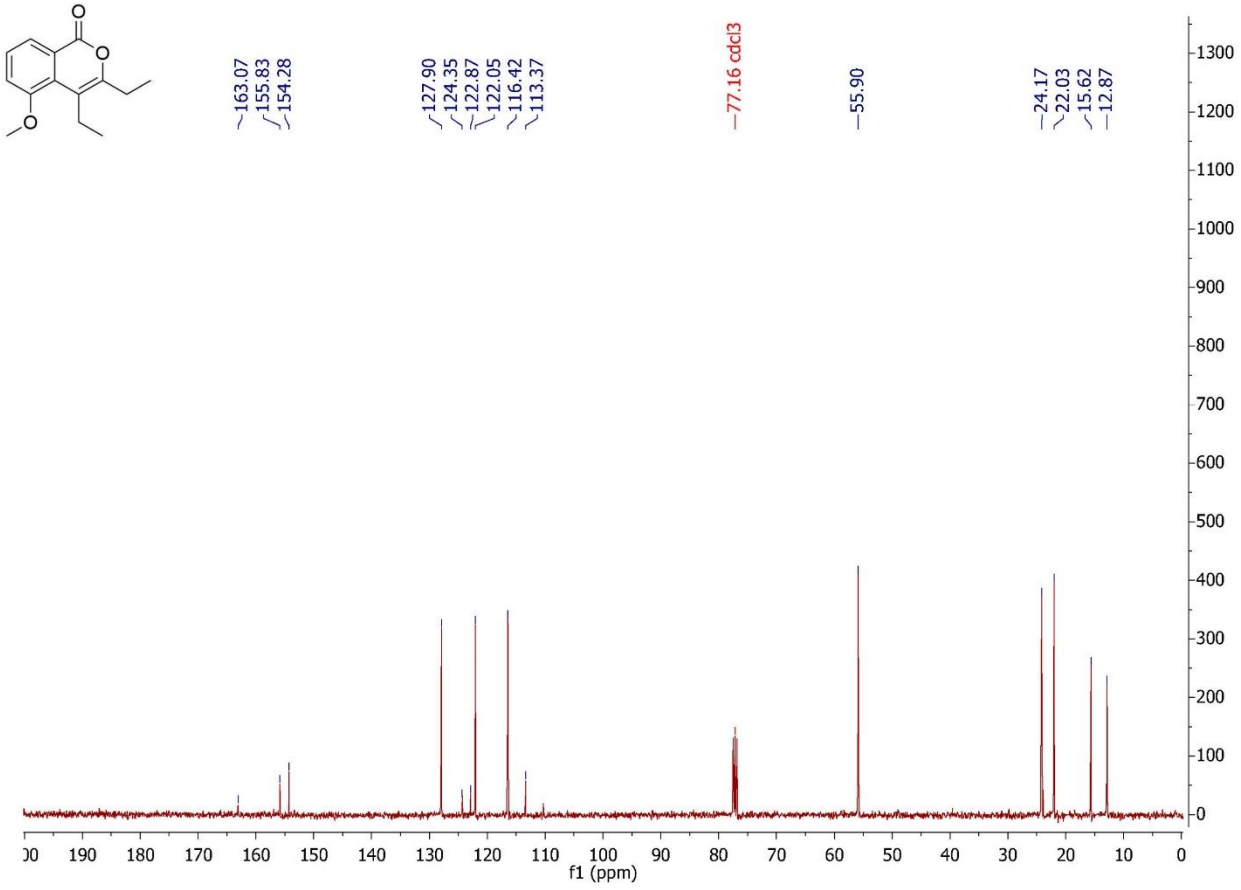
^{13}C{^{1}H} NMR (101 MHz) spectrum of **7-methoxy-3,4-diphenyl-1*H*-isochromen-1-one** in $CDCl_3$



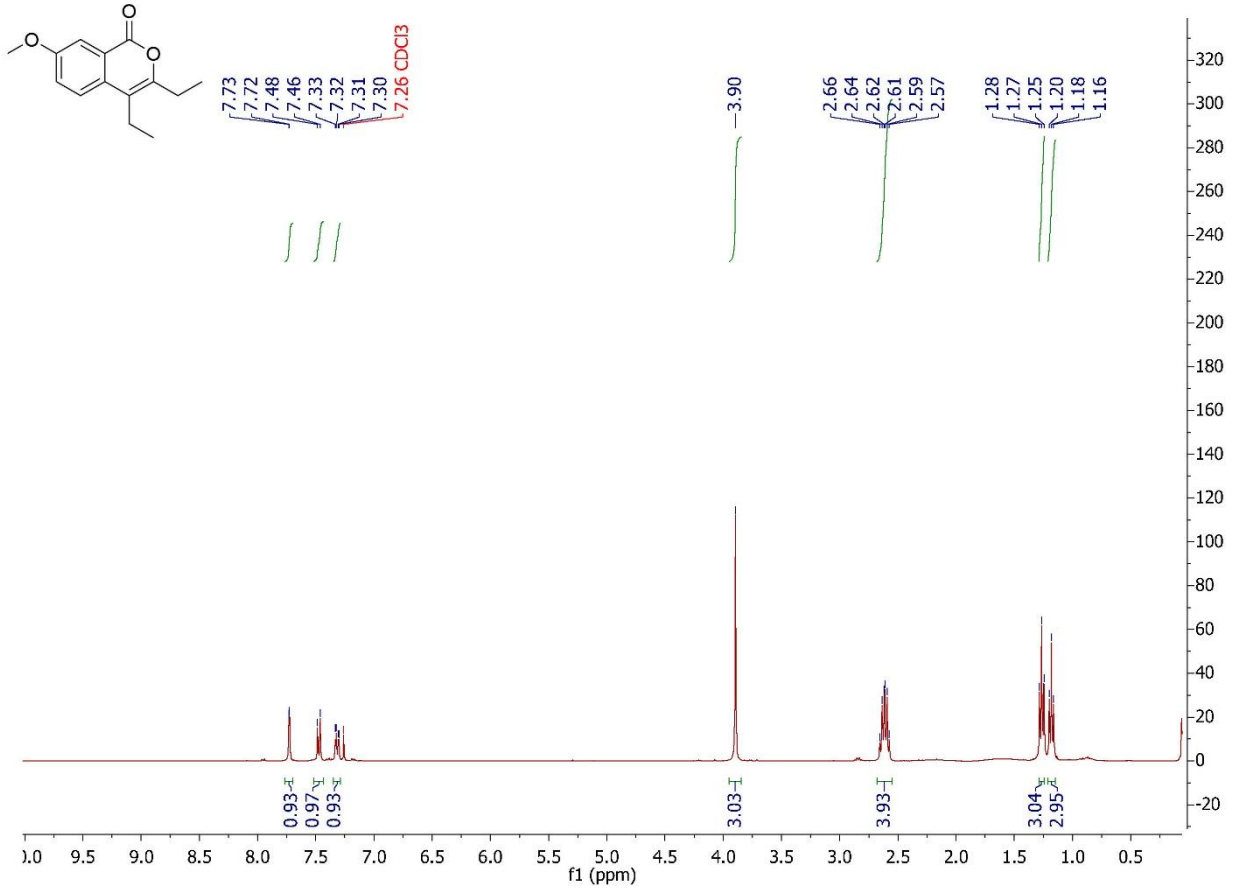
^{1}H NMR (400 MHz) spectrum of **3,4-diethyl-5-methoxy-1*H*-isochromen-1-one** in $CDCl_3$



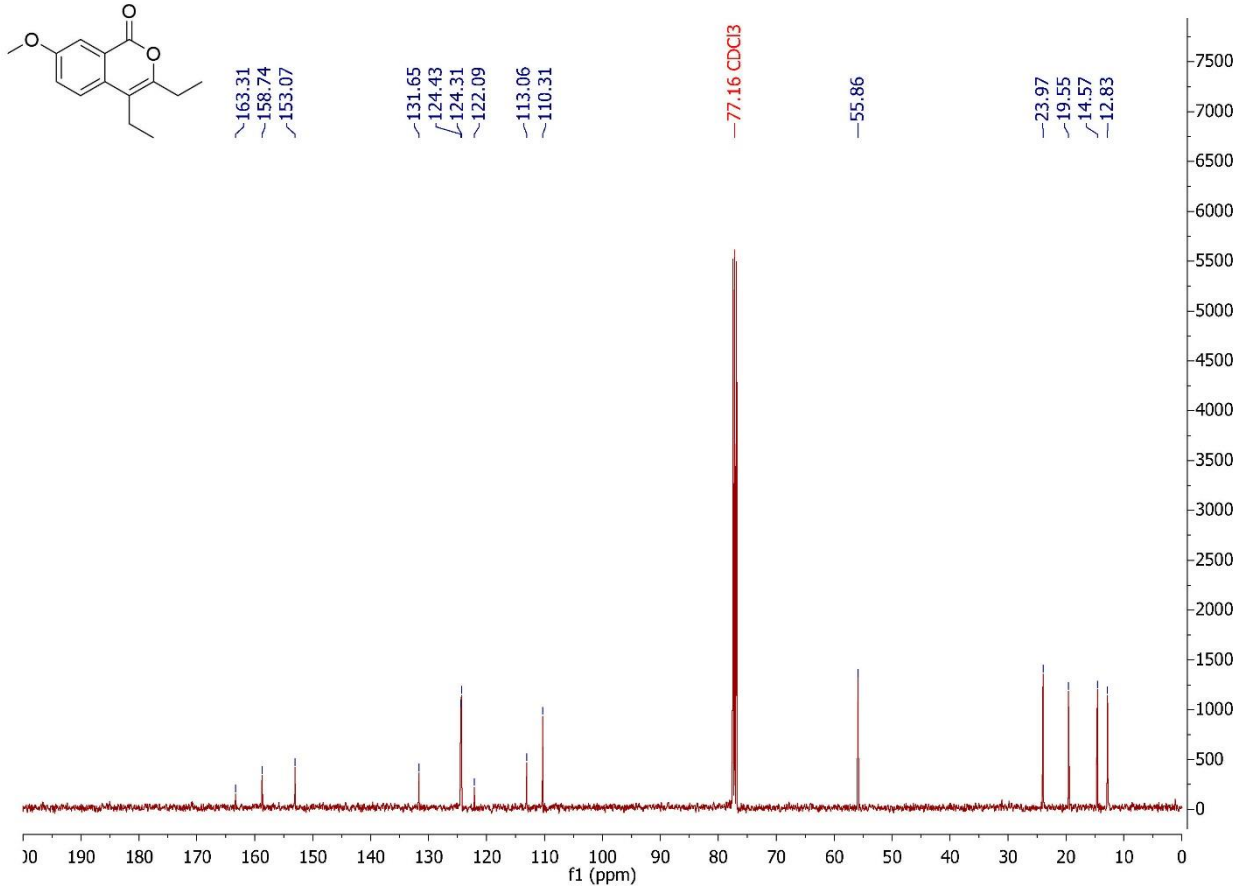
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3,4-diethyl-5-methoxy-1*H*-isochromen-1-one** in $CDCl_3$



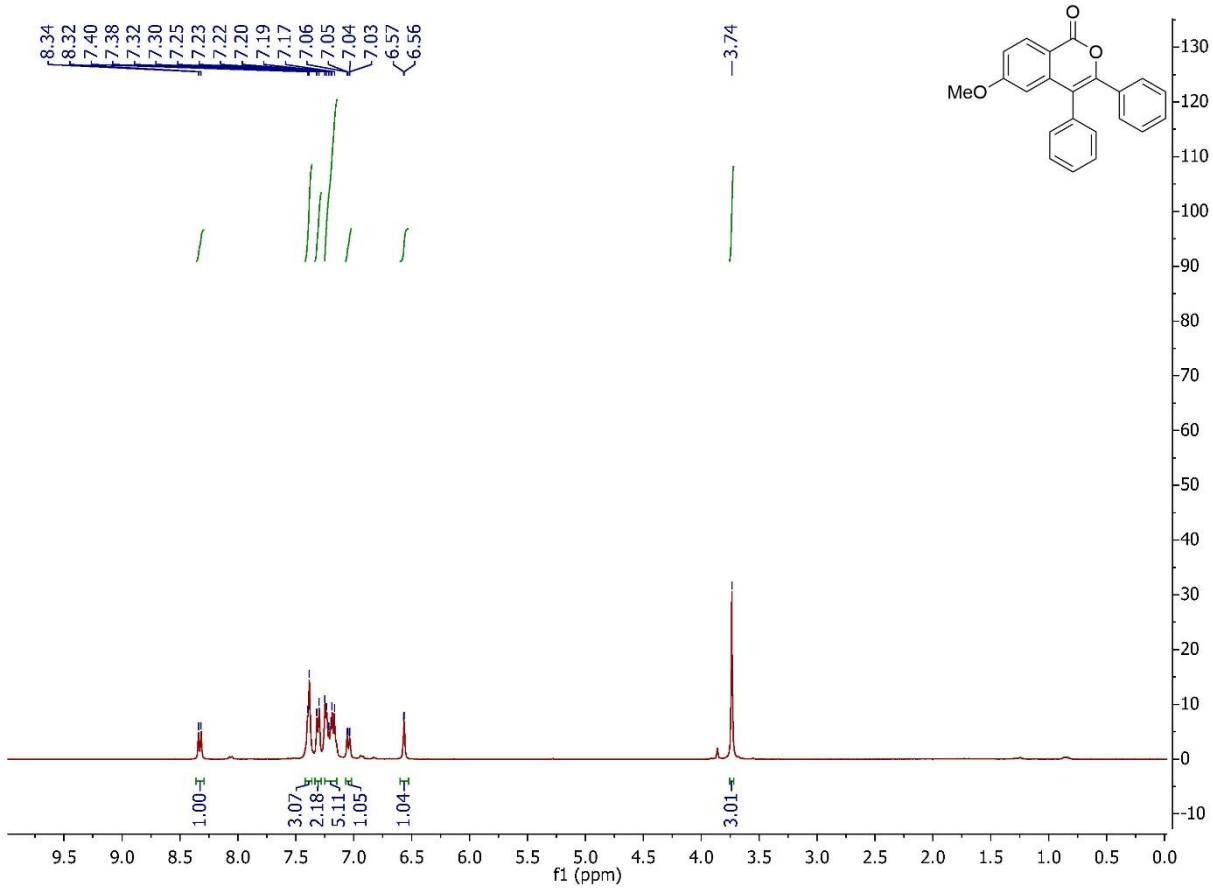
^{1}H NMR (400 MHz) spectrum of **3,4-diethyl-7-methoxy-1*H*-isochromen-1-one** in $CDCl_3$



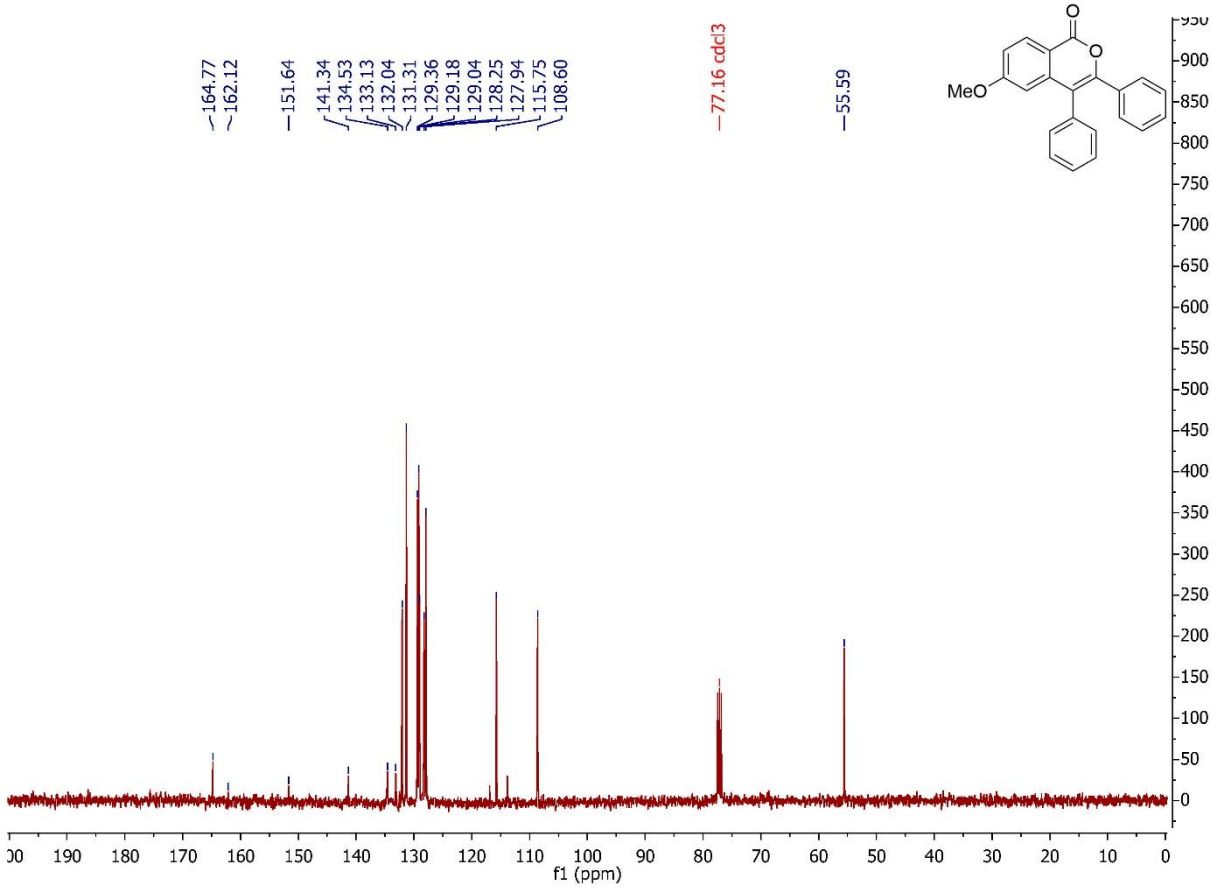
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3,4-diethyl-7-methoxy-1*H*-isochromen-1-one** in $CDCl_3$



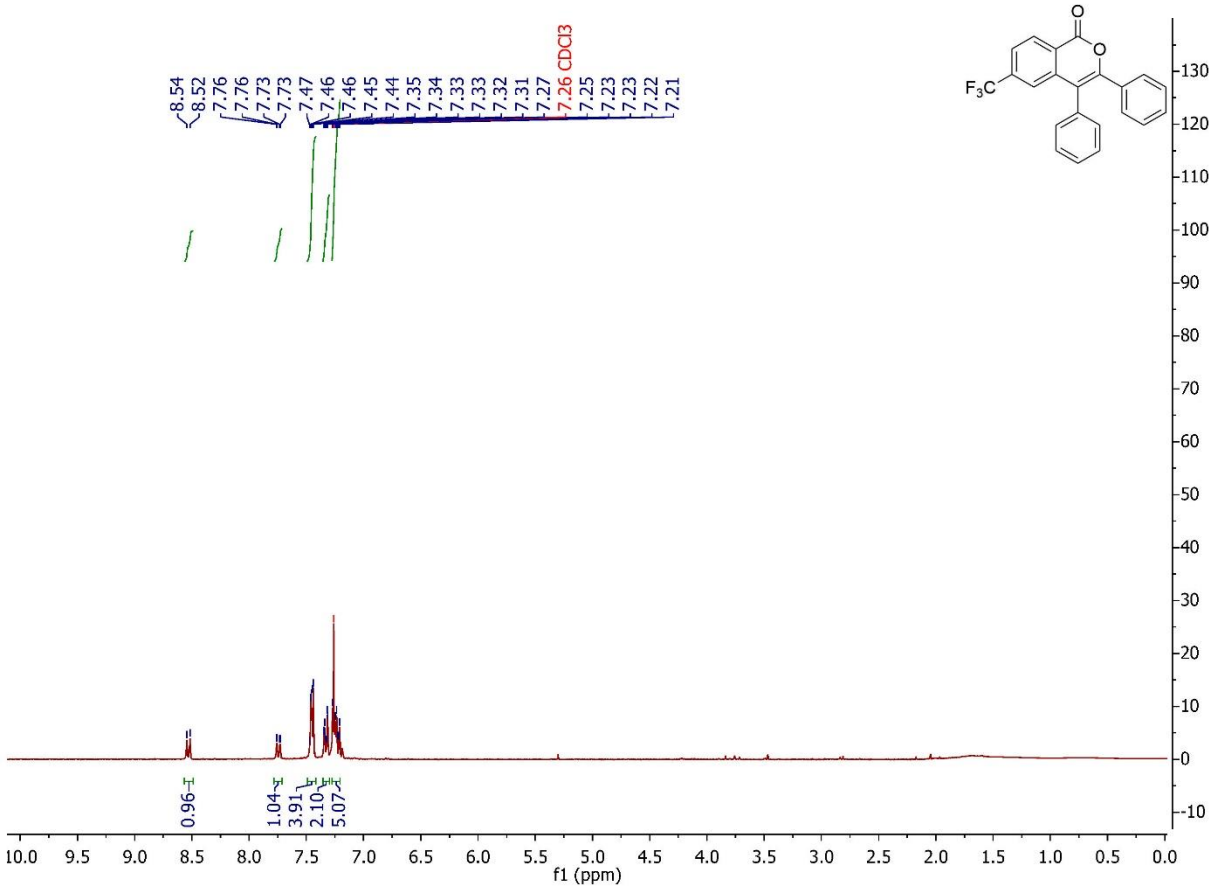
^{1}H NMR (400 MHz) spectrum of **6-methoxy-3,4-diphenyl-1*H*-isochromen-1-one** in $CDCl_3$



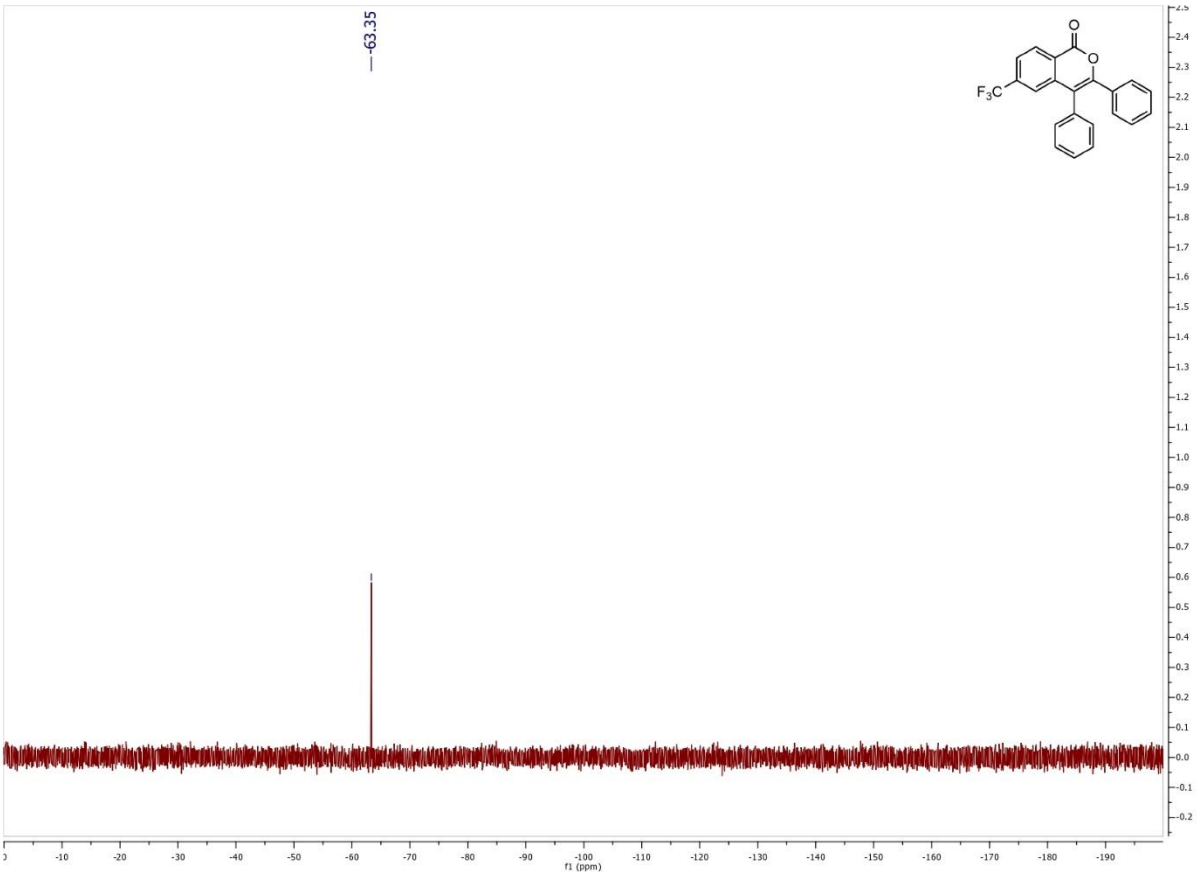
^{13}C{^{1}H} NMR (101 MHz) spectrum of **6-methoxy-3,4-diphenyl-1*H*-isochromen-1-one** in $CDCl_3$



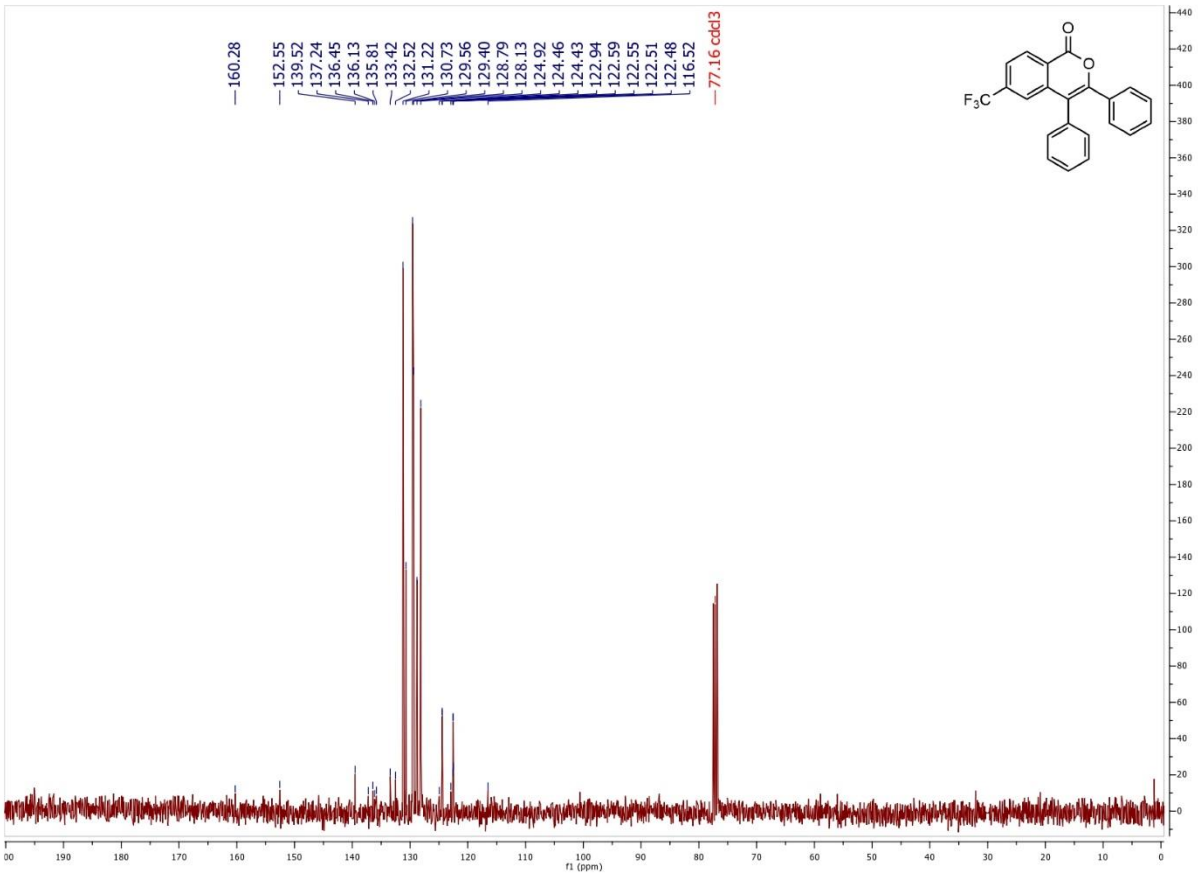
^{1}H NMR (400 MHz) spectrum of **3,4-diphenyl-6-trifluoromethyl-1*H*-isochromen-1-one** in $CDCl_3$



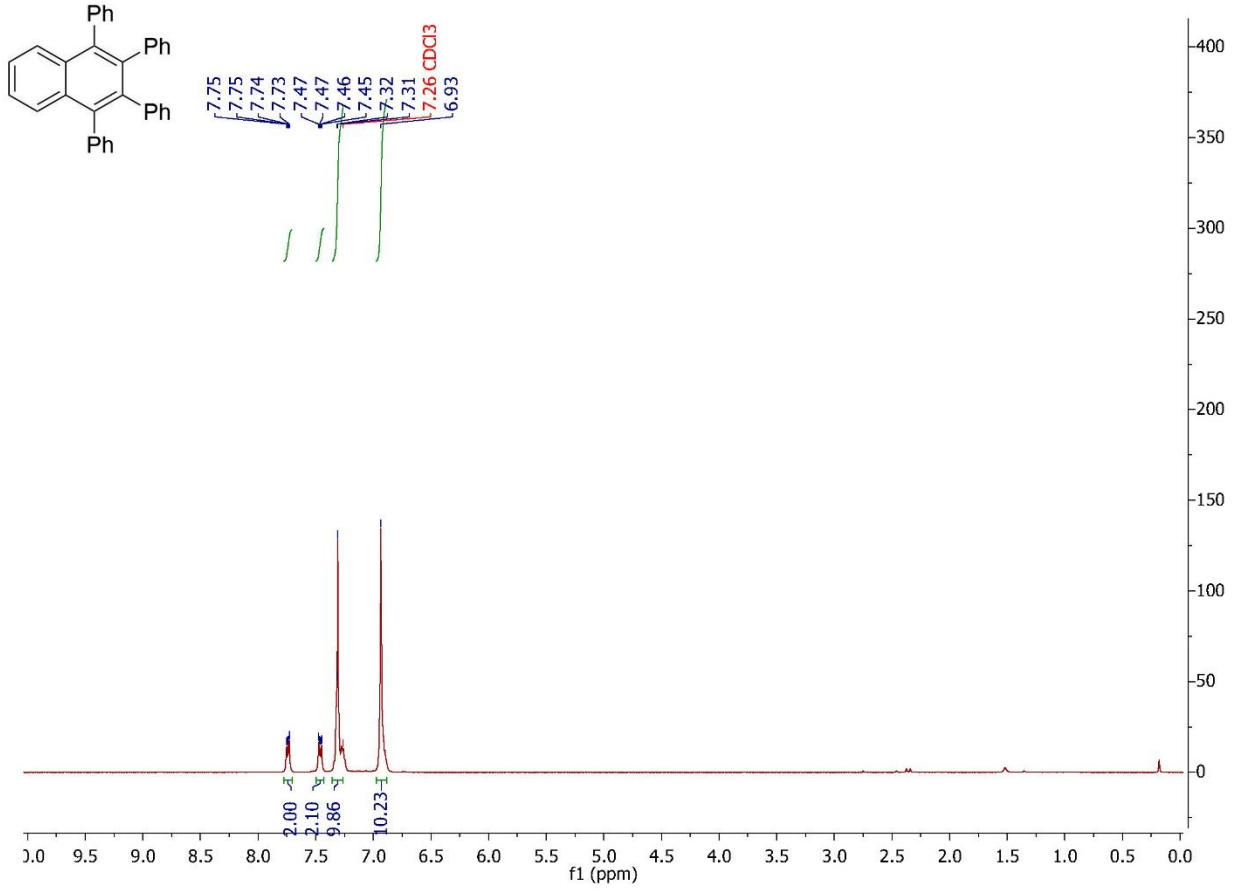
^{19}F NMR (376 MHz) spectrum of **3,4-diphenyl-6-trifluoromethyl-1*H*-isochromen-1-one** in $CDCl_3$



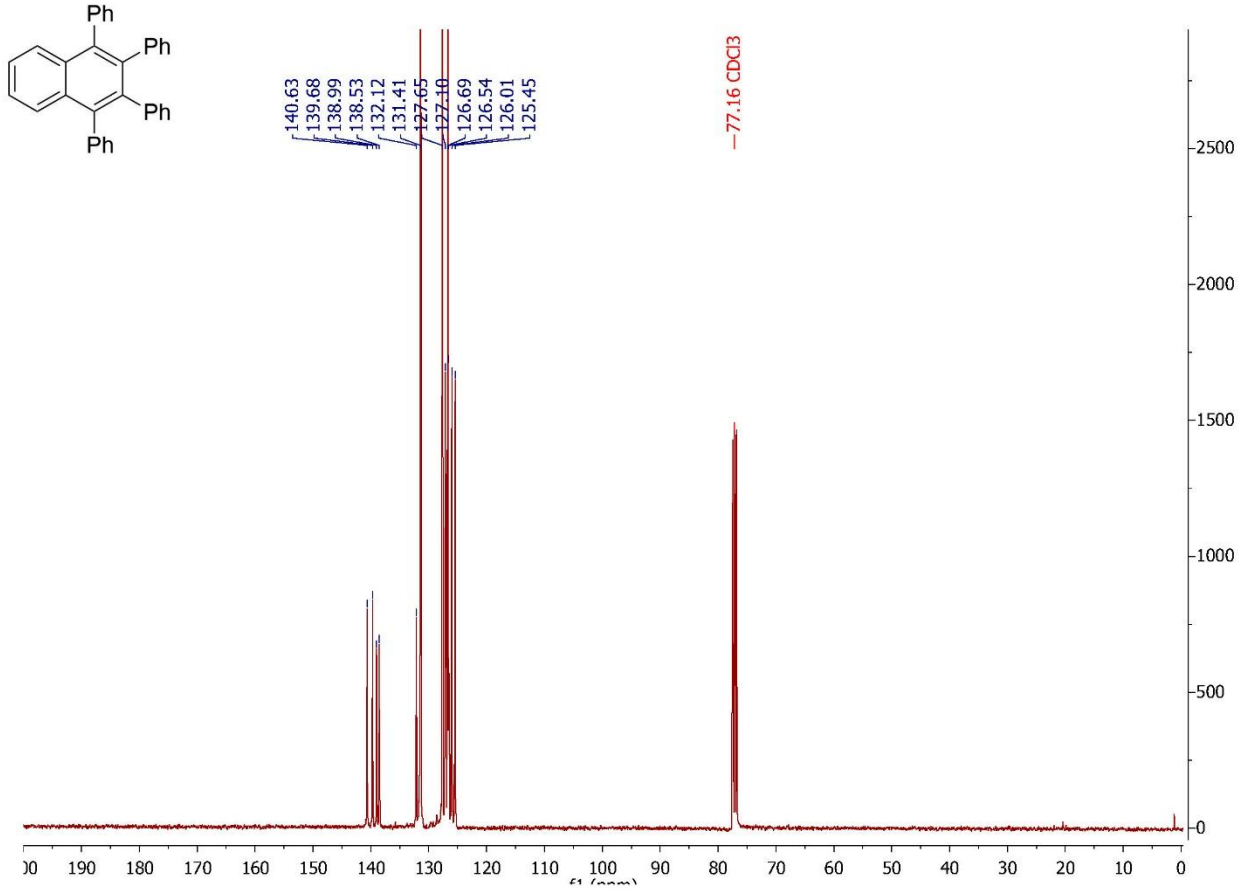
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3,4-diphenyl-6-trifluoromethyl-1*H*-isochromen-1-one** in $CDCl_3$



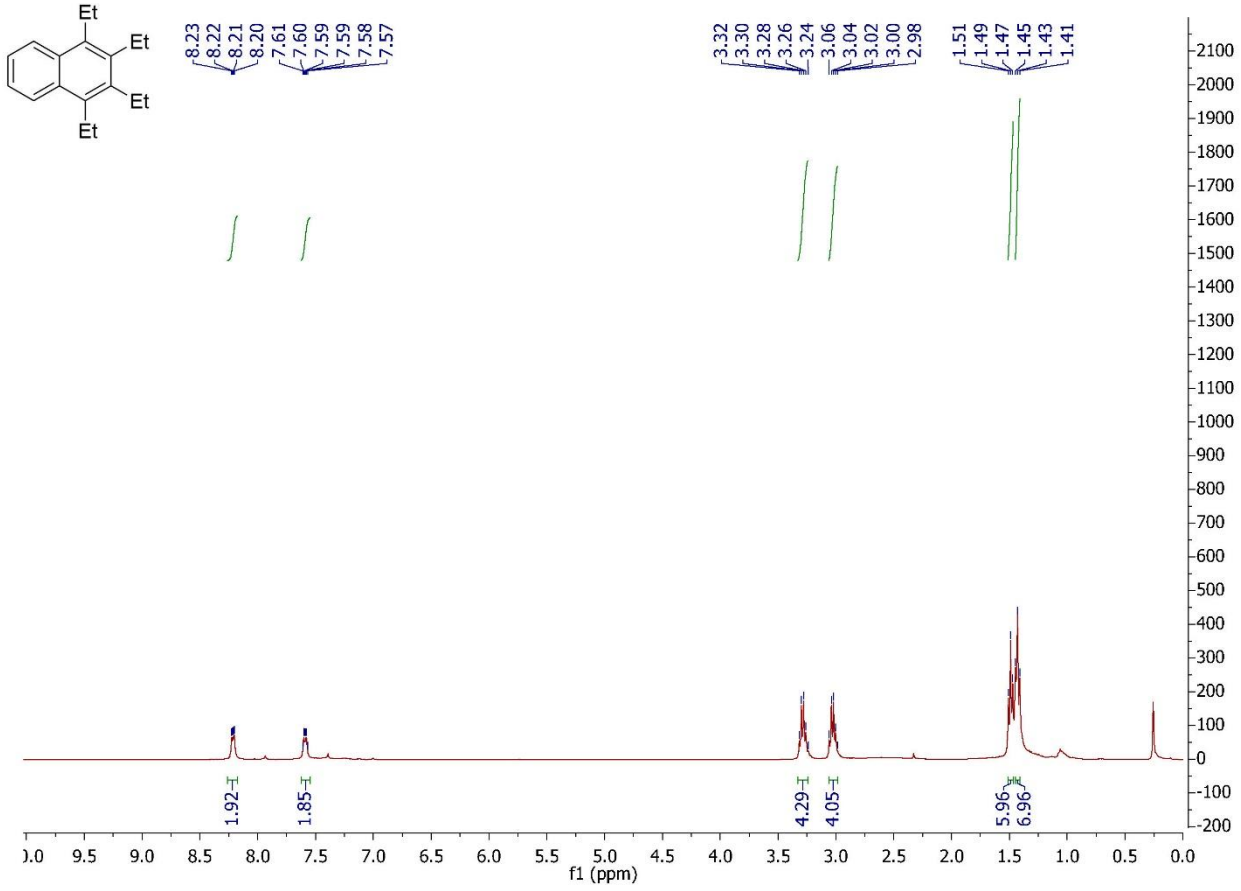
^{1}H NMR (400 MHz) spectrum of **1,2,3,4-tetraphenylnaphthalene** in $CDCl_3$



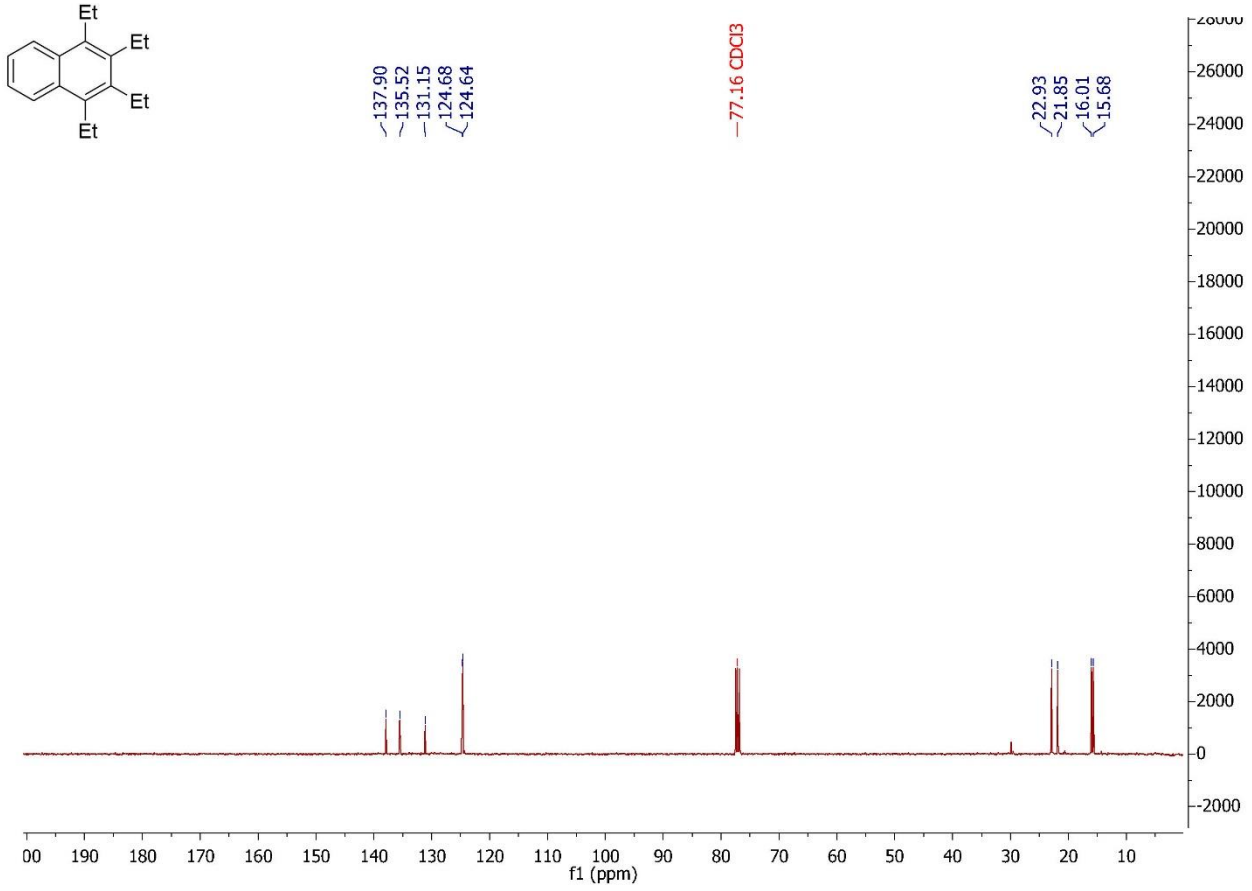
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **1,2,3,4-tetraphenylnaphthalene** in $CDCl_3$



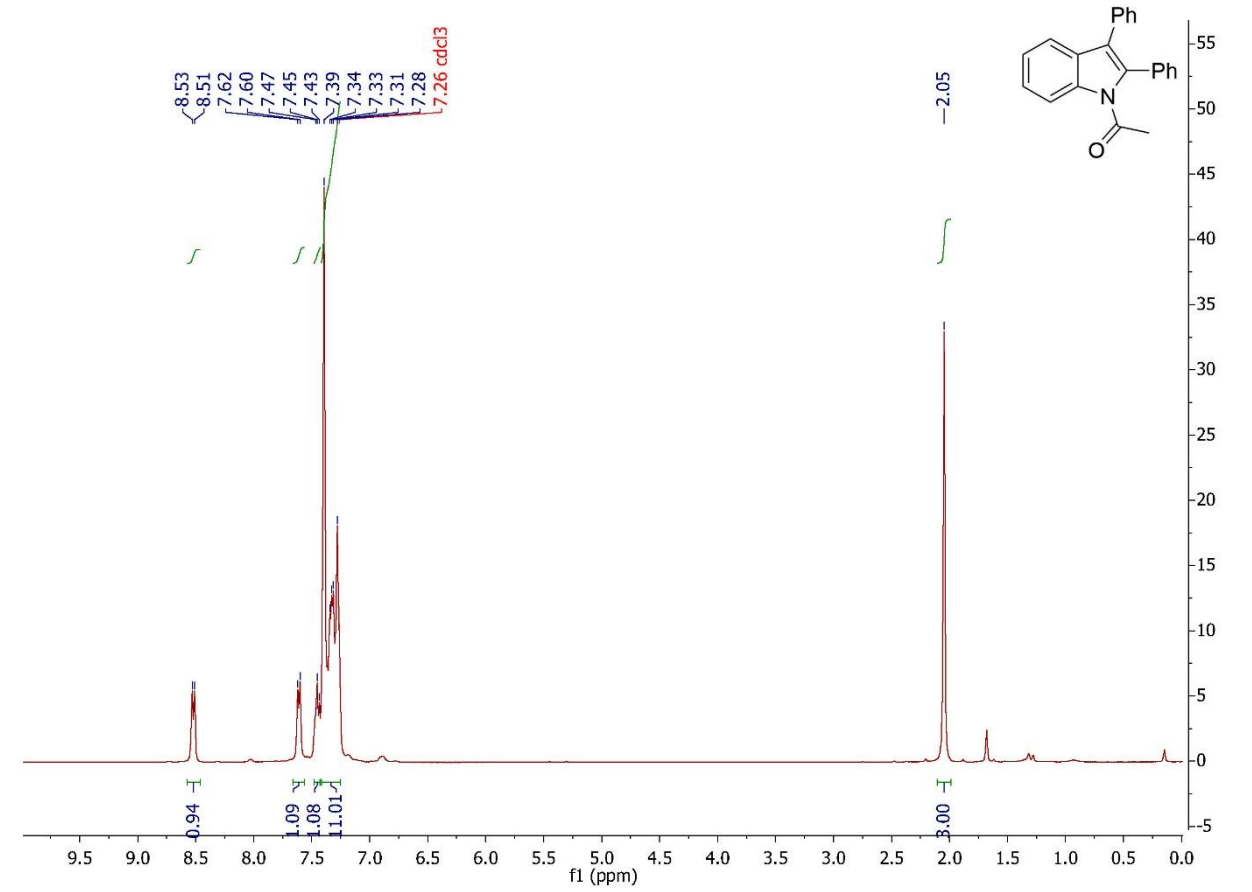
^{1}H NMR (400 MHz) spectrum of **1,2,3,4-tetraethylnaphthalene** in $CDCl_3$



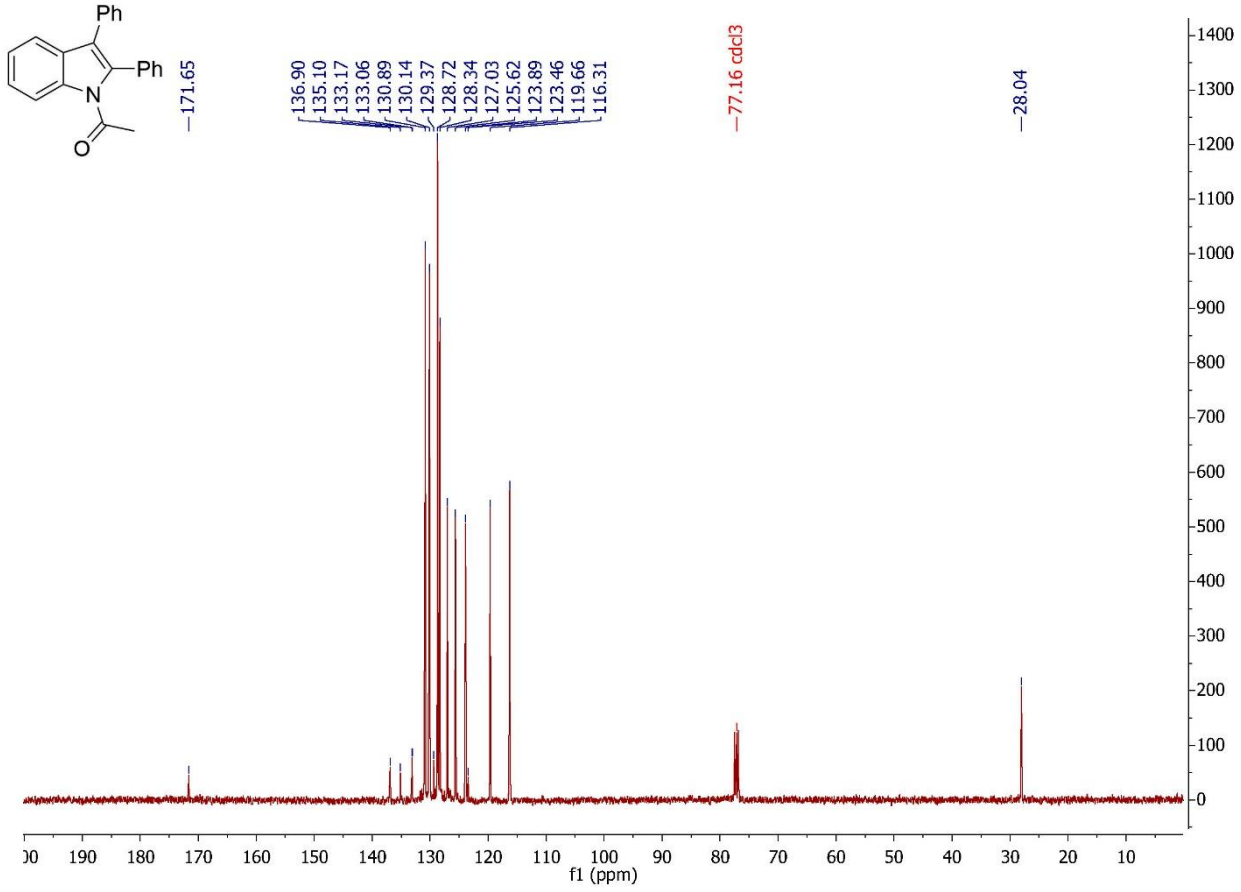
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **1,2,3,4-tetraethylnaphthalene** in $CDCl_3$



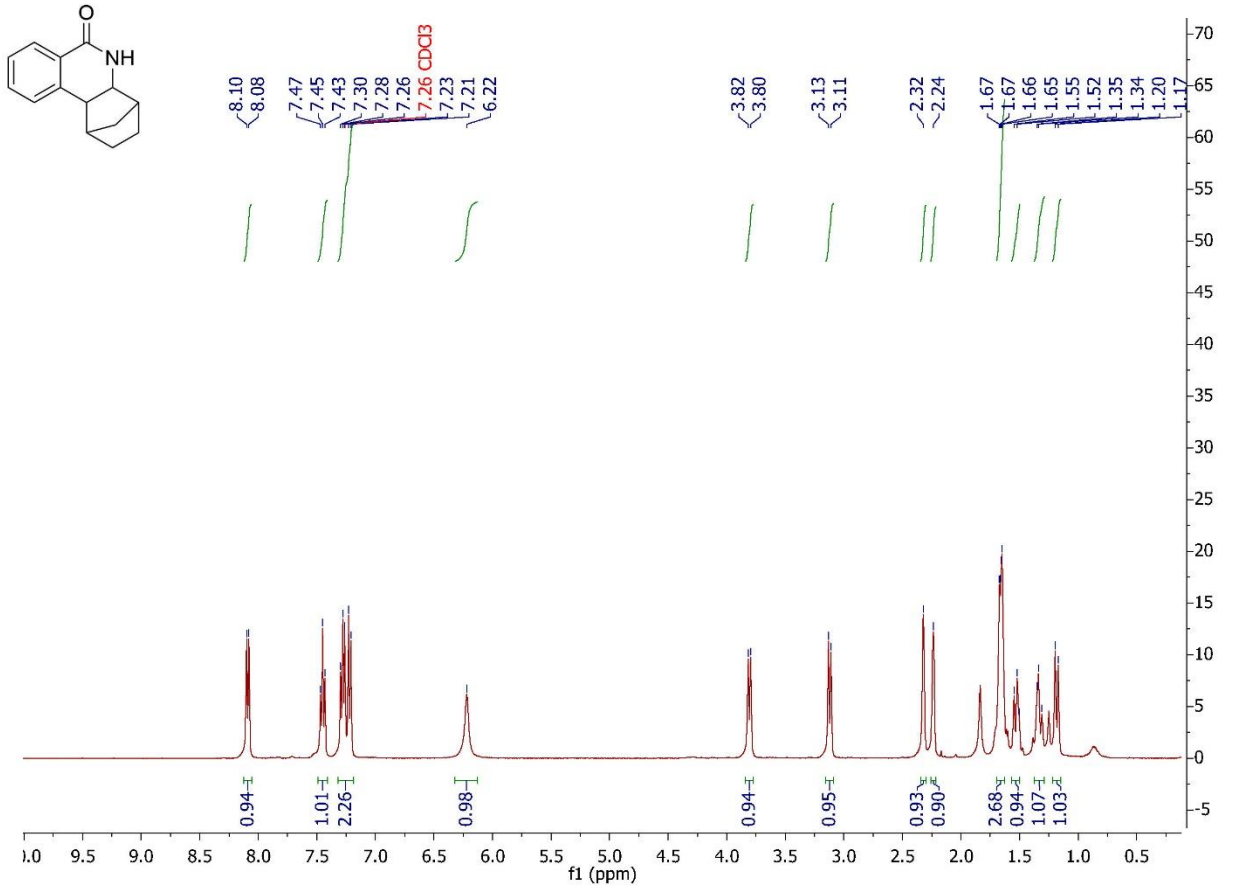
^{1}H NMR (400 MHz) spectrum of **1-(2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one** in $CDCl_3$



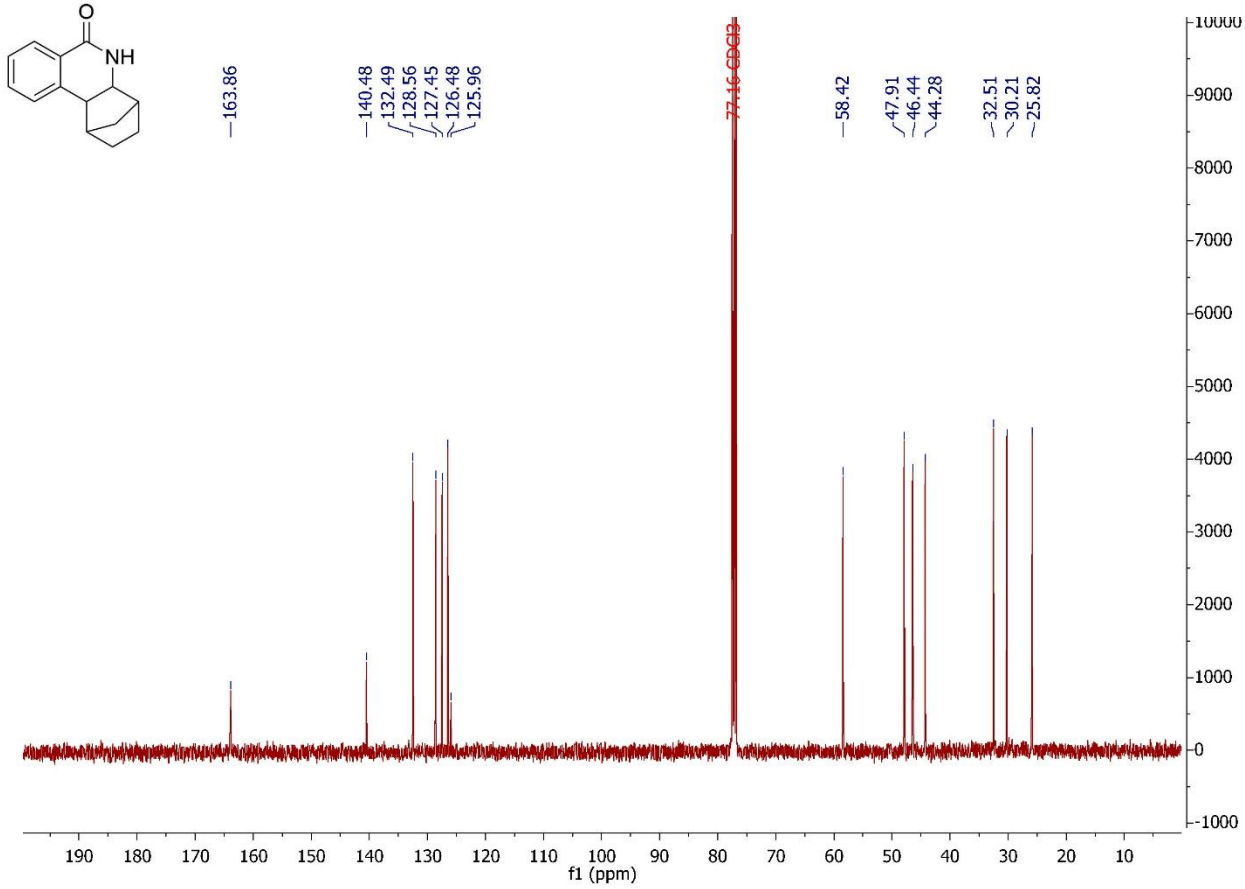
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **1-(2,3-diphenyl-1*H*-indol-1-yl)ethan-1-one** in $CDCl_3$



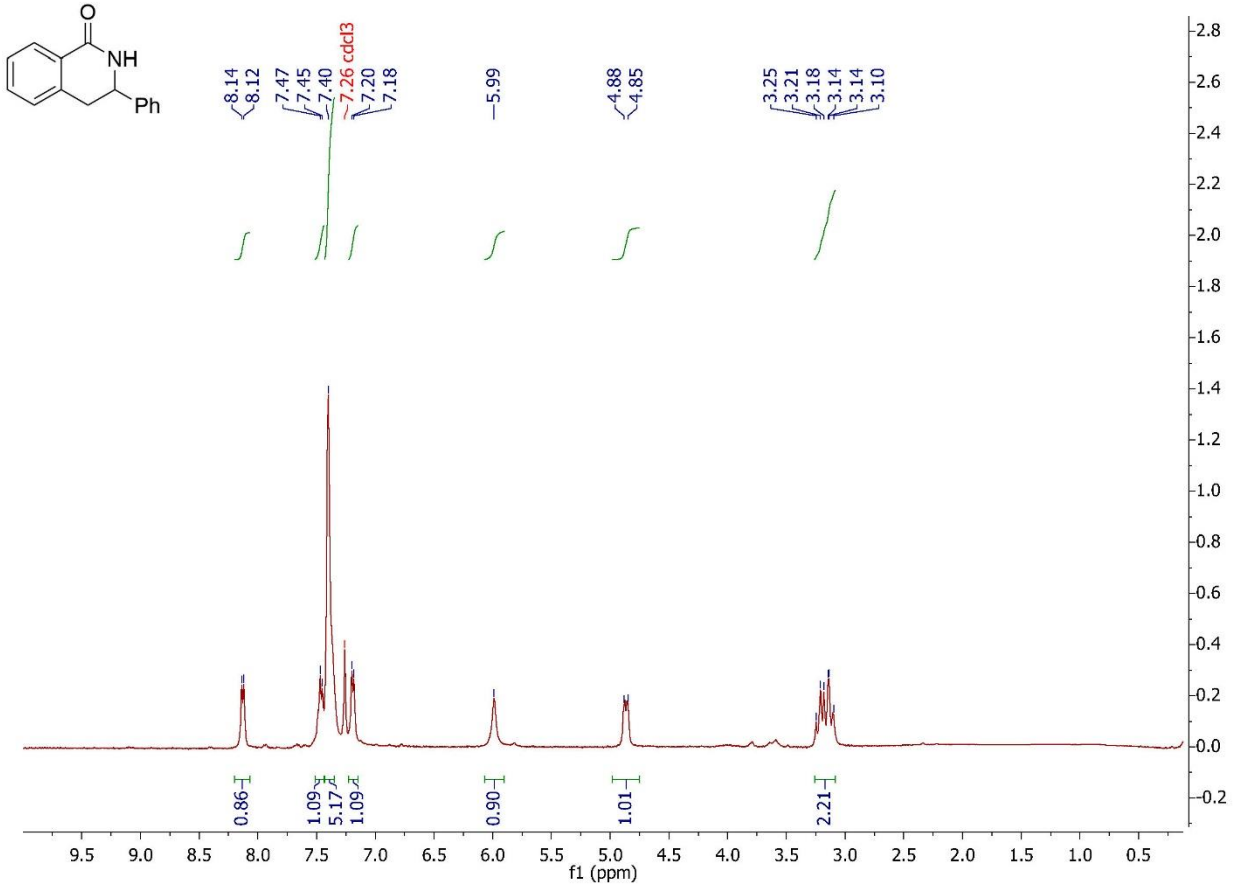
^{1}H NMR (400 MHz) spectrum of **1,3,4,4a,5,10b-hexahydro-1,4-methanophenanthridin-6(2*H*)-one** in $CDCl_3$



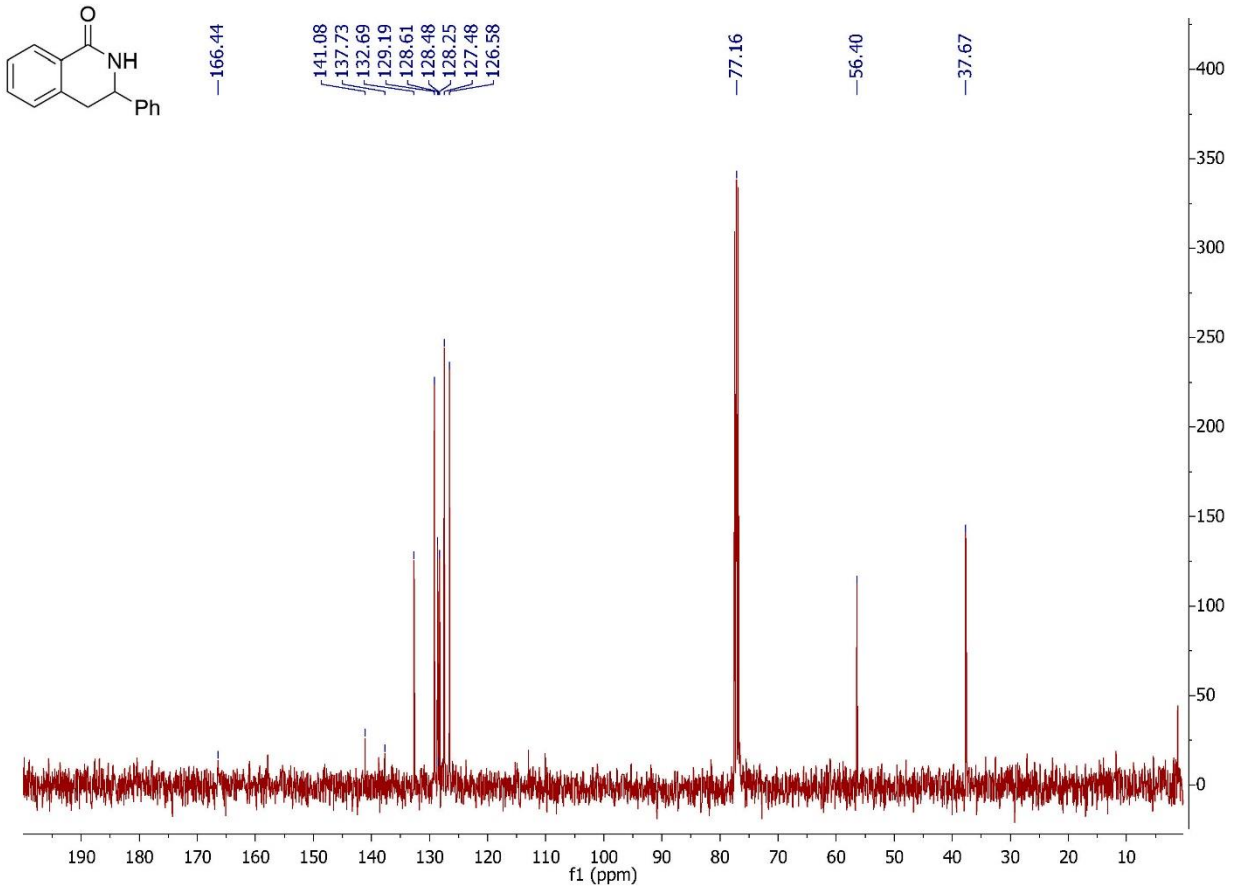
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **1,3,4,4a,5,10b-hexahydro-1,4-methanophenanthridin-6(2*H*)-one** in $CDCl_3$



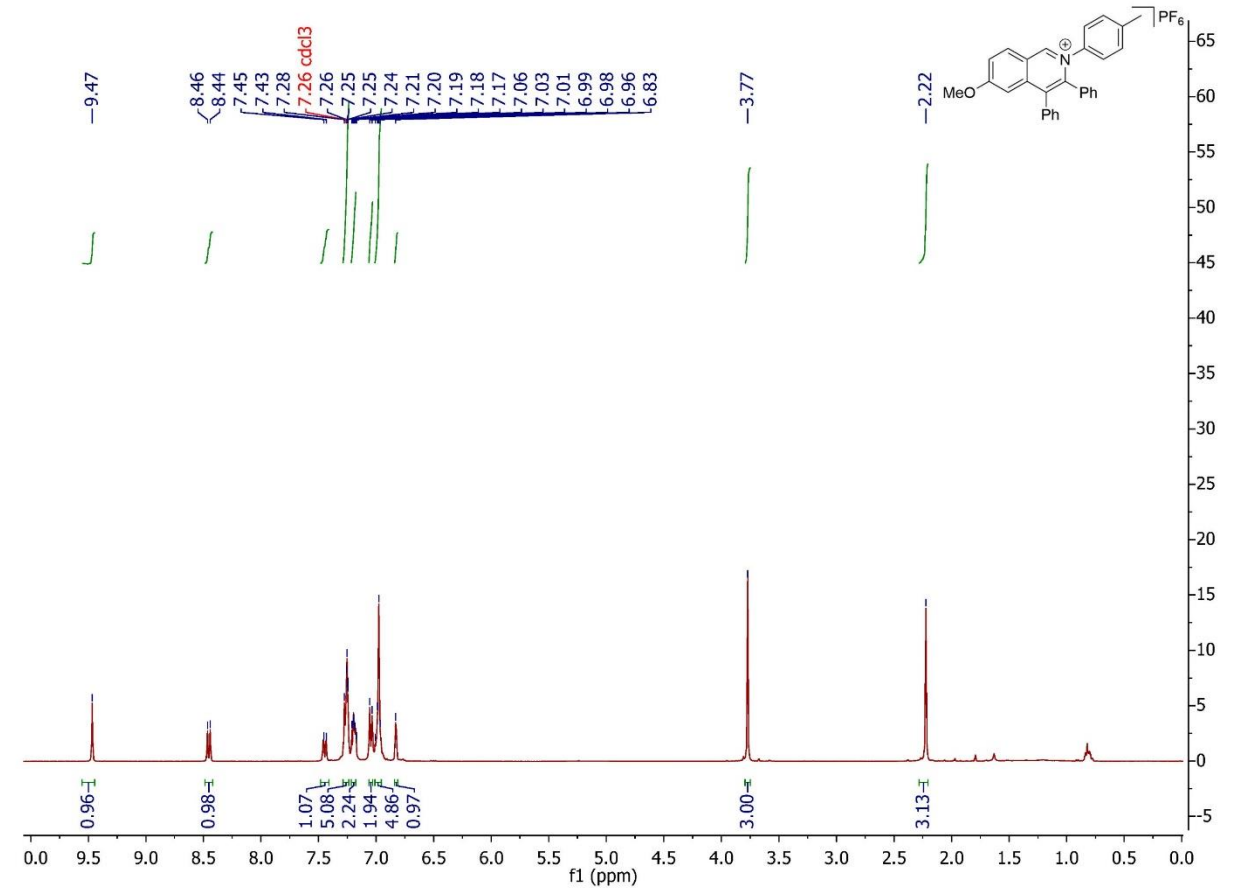
^{1}H NMR (400 MHz) spectrum of **3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one** in $CDCl_3$



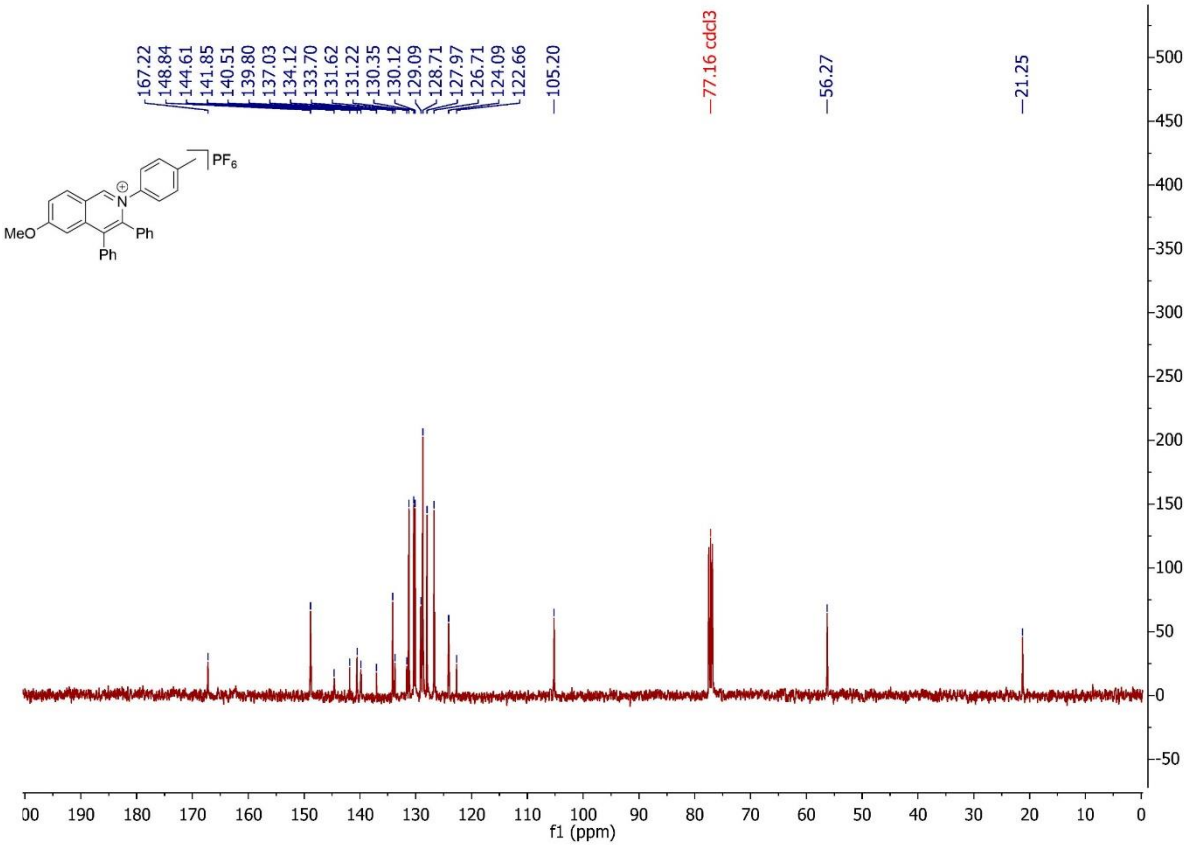
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one** in $CDCl_3$



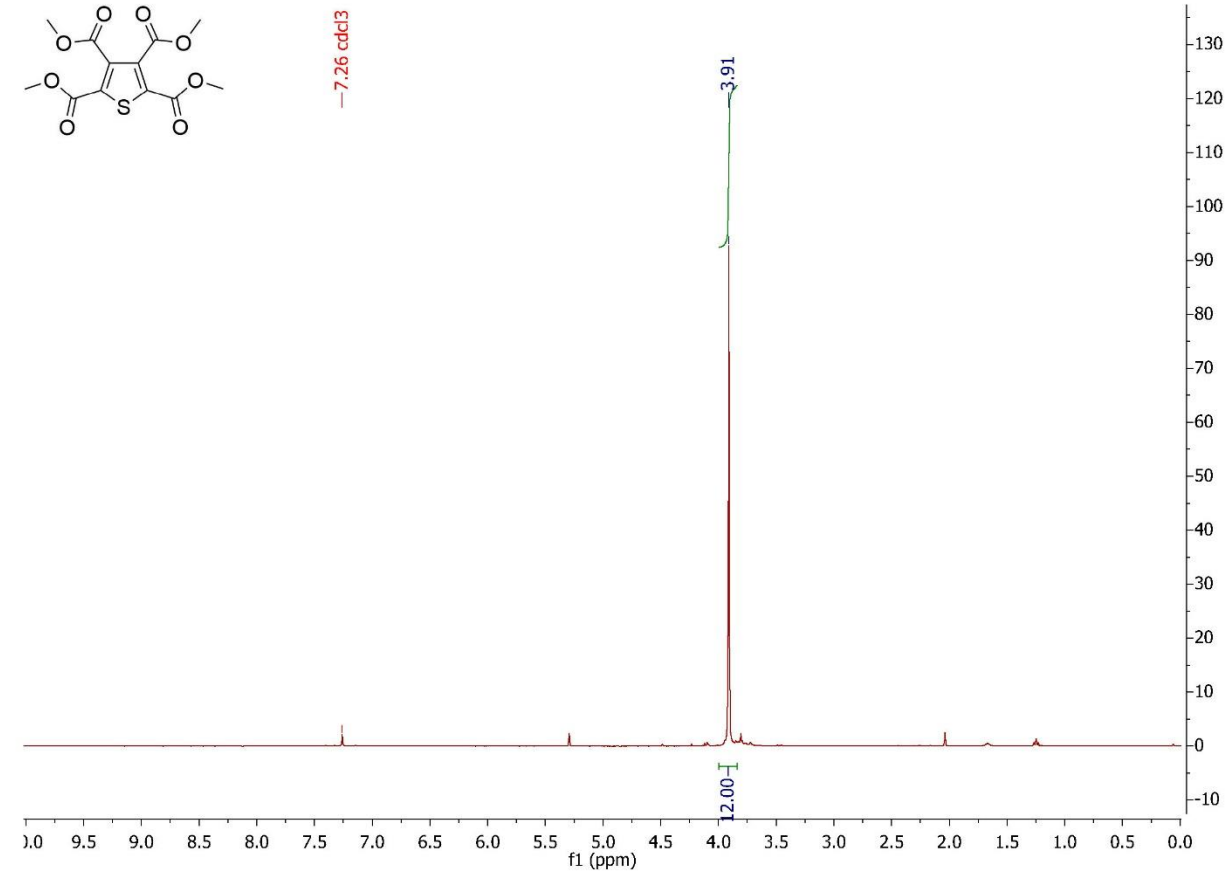
^{1}H NMR (400 MHz) spectrum of **6-methoxy-3,4-diphenyl-2-(*p*-tolyl)isoquinolin-2-ium hexafluorophosphate** in $CDCl_3$



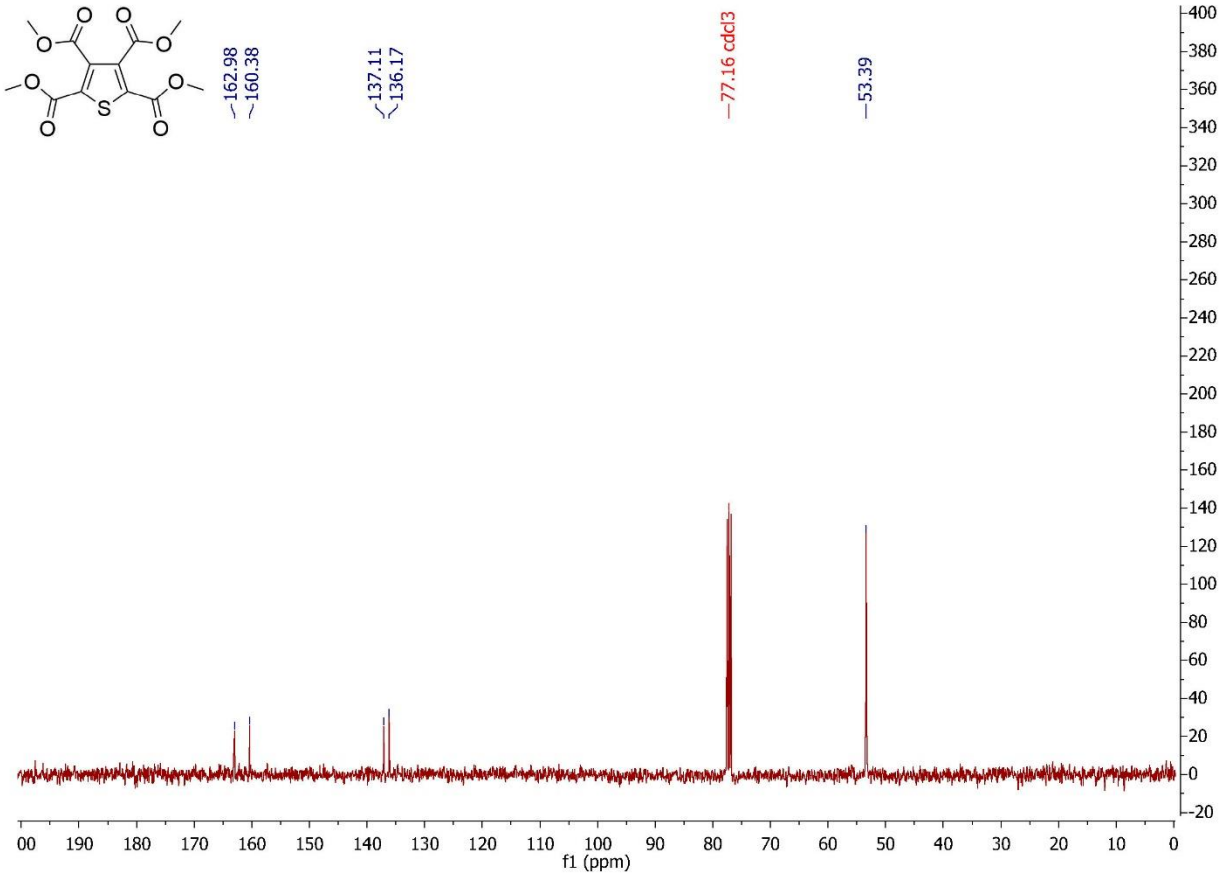
$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **6-methoxy-3,4-diphenyl-2-(*p*-tolyl)isoquinolin-2-ium hexafluorophosphate** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of **tetramethyl thiophene-2,3,4,5-tetracarboxylate** in $CDCl_3$



$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum **tetramethyl thiophene-2,3,4,5-tetracarboxylate** in $CDCl_3$



Computational details

All calculations were performed using ADF 10 program[S9] at the GGABP-D3/TZP level with corrections for solvation in methanol (the COSMO model implemented in the ADF 10 program).

The coordinates of optimized structures

[(Indenyl)RhCp]$^+$

6	3.164415000	8.605388000	4.011406000
1	3.421047000	8.015047000	3.136745000
6	3.944534000	9.689037000	4.557255000
1	4.889244000	10.051071000	4.162793000
1	7.653867000	8.404778000	7.062765000
45	3.810224000	8.048804000	6.109631000
6	3.829732000	5.988346000	6.990273000
1	3.080548000	5.238288000	6.754311000
6	5.122619000	6.119374000	6.356170000
6	5.753376000	5.390681000	5.310231000
1	5.238476000	4.557338000	4.834421000
6	7.128148000	7.582350000	6.579738000
6	3.258430000	10.203149000	5.697349000
1	3.582205000	11.026054000	6.327538000
6	5.816163000	7.226452000	6.998379000
6	4.938400000	7.757226000	8.018768000
6	2.066762000	9.418778000	5.880597000
1	1.326662000	9.554161000	6.664405000
6	7.034923000	5.751349000	4.947315000
1	7.549106000	5.193209000	4.164887000
6	7.716633000	6.838090000	5.577758000
1	8.730594000	7.077333000	5.257545000
6	3.755160000	6.949772000	8.048602000
6	2.001400000	8.446144000	4.819715000
1	1.212109000	7.714894000	4.672670000
1	5.168900000	8.573298000	8.697198000
1	2.927045000	7.065906000	8.741211000

[(1,2,3,4-tetrahydrofluorenyl)RhCp]$^+$

1	3.79604000	7.46233000	10.91720000
2	4.12255000	9.94344000	10.55400000
3	3.89240000	9.25978000	9.725650000
4	2.26016000	8.33466000	10.83970000
5	7.63895000	8.41559000	7.07198000
6	3.81722000	8.03813000	6.10528000
7	3.81918000	5.99491000	6.98754000
8	3.07190000	5.24169000	6.75384000
9	5.11294000	6.12882000	6.35416000
10	5.74821000	5.40371000	5.30909000
11	5.23539000	4.57174000	4.82878000
12	7.11604000	7.59329000	6.58586000
13	3.13122000	8.02881000	10.2441000
14	3.26115000	9.81414000	9.01103000
15	5.80379000	7.23408000	6.99754000
16	4.93071000	7.76039000	8.02774000
17	5.19782000	8.84116000	9.02751000
18	5.90407000	8.43911000	9.77538000
19	5.70001000	9.69485000	8.55265000
20	2.66547000	7.10511000	9.10102000
21	2.40019000	6.11207000	9.49263000
22	1.75309000	7.50199000	8.63327000
23	3.74331000	6.94446000	8.06094000
24	1.99620000	8.45622000	4.83193000
25	1.19955000	7.73015000	4.69866000
26	3.14695000	8.60783000	4.00543000
27	3.38820000	8.01437000	3.12845000
28	3.94452000	9.68213000	4.54396000
29	4.88852000	10.03540000	4.13893000
30	3.27969000	10.20020000	5.69529000

31	3.62132000	11.01940000	6.32079000
32	2.08608000	9.42563000	5.89450000
33	1.36075000	9.56600000	6.69081000
34	7.03058000	5.76662000	4.95062000
35	7.54698000	5.21173000	4.16757000
36	7.70927000	6.85338000	5.58312000
37	8.72280000	7.09517000	5.26414000

[(9-PMB-1,2,3,4-tetrahydrofluorenyl)RhCp]$^{+}$

1	6.178130000	4.616730000	14.106100000
2	2.376800000	11.930700000	11.958200000
3	6.001360000	2.789000000	12.838100000
4	5.867410000	2.846160000	11.761800000
5	7.262480000	2.705530000	13.528800000
6	8.244020000	2.712700000	13.063700000
7	6.105620000	6.454330000	12.853700000
8	3.176190000	7.943850000	12.994000000
9	4.993480000	6.456290000	13.774600000
10	2.997050000	8.950720000	13.960800000
11	3.071750000	8.704920000	15.021700000
12	2.320290000	12.323600000	10.569700000
13	3.273140000	12.113800000	10.062600000
14	2.137120000	13.401600000	10.576300000
15	1.499930000	11.811200000	10.047200000
16	4.949480000	2.733490000	13.817100000
17	3.883700000	2.763680000	13.611100000
18	6.992360000	6.592480000	15.006700000
19	2.634710000	10.606500000	12.227900000
20	7.332630000	6.475440000	13.604100000
21	3.538210000	6.524160000	13.401300000
22	2.925540000	6.193020000	14.249100000
23	3.337790000	5.837030000	12.570400000
24	2.727650000	10.265500000	13.589900000
25	2.588190000	11.043900000	14.340900000
26	7.162590000	6.860530000	17.389900000
27	7.756500000	6.980370000	18.295900000
28	6.991160000	2.642700000	14.924100000
29	7.729890000	2.593270000	15.718700000
30	2.798390000	9.614130000	11.250100000
31	2.716680000	9.849290000	10.190700000
32	3.067920000	8.297300000	11.644400000
33	3.194450000	7.533930000	10.875200000
34	4.927530000	6.721000000	16.388400000
35	3.842520000	6.726350000	16.480900000
36	6.083410000	6.455660000	11.355600000
37	5.270080000	5.821780000	10.977000000
38	5.852850000	7.484600000	11.027200000
39	8.694560000	6.518780000	12.968400000
40	9.214900000	5.565120000	13.138900000
41	9.297900000	7.288900000	13.471200000
42	5.543740000	6.593810000	15.113100000
43	5.738040000	6.860800000	17.496600000
44	5.286260000	6.979270000	18.481100000
45	7.448430000	6.025170000	10.793300000
46	7.589430000	4.945690000	10.969500000
47	7.461070000	6.181240000	9.706240000
48	5.559480000	2.664940000	15.104000000
49	5.040170000	2.633350000	16.057400000
50	8.589560000	6.811890000	11.458500000
51	8.408210000	7.889580000	11.311800000
52	9.549700000	6.582120000	10.976700000
53	7.796500000	6.718940000	16.172400000
54	8.882610000	6.726920000	16.092500000

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