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Synthesis and photophysical activity of 6-substituted isocoumarins

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General information

All reactions were carried out in an argon atmosphere using distilled solvents. The catalysts $[Cp^*RhCl_2]_2$ [S1] and $(PPh_3)_2PdCl_2$ [S2] were prepared as described in the literature. All other reagents were purchased from Acros or Aldrich and used as received. Column chromatography was carried out using Macherey-Nagel silica gel 60 (particle size 0.04−0.063 mm). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 400 and 101, respectively. Chemical shifts are given in ppm using residual solvent signals as internal standards. HRMS (ESI) spectra were recorded using a TripleTOF 5600+ mass spectrometer (SCIEX) equipped with electrospray ionization. Infrared spectra were recorded on an FSM-2202 (INFRASPEC) instrument.

Absorption and fluorescence spectroscopy

Absorption spectra were recorded on an Agilent Cary 300 double-beam UV-vis spectrophotometer in a standard 1 cm quartz cell (Helma QS with PTFE stopper). Fluorescence spectra were recorded on an Agilent Cary Eclipse spectrofluorometer at 20±1°C in a standard 1 cm quartz cell. The observed fluorescence was detected at a right angle to the excitation beam. Fluorescence spectra were corrected for the non-uniformity of detector spectral sensitivity and normalized to the excitation light intensity derived from the values of the calibrated built-in reference sensor. Phenanthrene (PQY = 0.125 ± 0.007) in ethanol was used as a reference to measure the luminescence quantum yield [S3]. The luminescence quantum yields were calculated using the equation:

$$\varphi_i = \varphi_0 \frac{(1 - 10^{-D_0}) \cdot S_i \cdot n_i^2}{(1 - 10^{-D_i}) \cdot S_0 \cdot n_0^2}$$

where φ_i and φ_0 are the luminescence quantum yields of the studied solution and the standard compound, respectively; D_i and D_0 are the absorbance of the studied solution and the standard, respectively; S_i and S_0 are the areas underneath the curves of the luminescence spectra of the studied solution and the standard, respectively; and n_i and n_0 are the refractive indices of the solvents of the studied solution and the standard compound (n_i = 1.4246 for DCM; n_0 = 1.3614 for EtOH).

To detect the enhancement effect of AIE, diluted solutions ($1 \cdot 10^{-5}$ M) were prepared by diluting highly concentrated THF solutions ($1 \cdot 10^{-3}$ M) with the required amount of THF and water.

To measure absorption and emission spectra in other solvents, diluted solutions ($1 \cdot 10^{-5}$ M) were prepared by diluting highly concentrated CH_2Cl_2 solutions ($1 \cdot 10^{-3}$ M) with the required solvent. Because of the low concentration of CH_2Cl_2, we were unable to subtract its absorption from the UV spectrum with good accuracy.

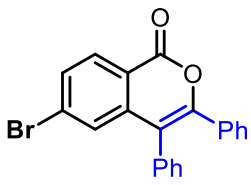
Synthesis of isocoumarin 1 *via* Rh^{III}-catalyzed C−H activation/annulation of *p*-bromobenzoic acid with tolane

p-Bromobenzoic acid (1.0 equiv., 2.0 mmol, 402 mg), tolane (1.0 equiv., 2.0 mmol, 356 mg), catalyst $[Cp^*RhCl_2]_2$ (2 mol% by Rh, 0.02 mmol, 12.4 mg), oxidant AgOAc (2.0 equiv., 4.0 mmol, 668 mg) were dissolved in methanol (15 mL) in a dried 25 mL Schlenk flask equipped with a magnetic stir bar. The reaction mixture was stirred at 60°C under argon for 6h and then cooled to room temperature. Then the insoluble metal Ag^0, reduced during the reaction, was separated by centrifugation. The solvent was removed *in vacuo*, and the residue was chromatographed on a silica column (~ 1 × 15 cm). Petroleum ether was used as the first eluent to remove an excess of unreacted alkyne, then the desired product was

eluted with petroleum ether/dichloromethane (2:1). Removal of the solvent *in vacuo* gave the desired isocoumarin derivative **1** as a yellow powder. Yield: 734 mg (97%).

Characterization of the isocoumarin 1

6-Bromo-3,4-diphenyl-1*H*-isochromen-1-one (1)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.32 – 7.28 (m, 3H), 7.25 – 7.16 (m, 5H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.60, 152.20, 140.41, 133.52, 132.51, 131.45, 131.17, 131.09 (2C), 130.46, 129.29 (2C), 129.25, 129.21 (2C), 128.45, 128.02, 127.90 (2C), 119.08, 115.92 ppm.

IR (CCl_4): ν = 1742 (C=O), 1718 (C=O), 1592 (C-C arom), 1473 (C-C arom), 964 (C-Br), 548 (C-Br) cm^{-1}.

HRMS (ESI, *m*/*z*) calcd. for $C_{21}H_{13}BrO_2$ $[M]^+$: 377.0172, found: 377.0176.

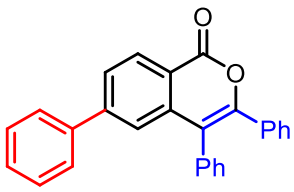
General procedure for Pd^0-catalyzed Suzuki cross-coupling of arylboronic acids with isocoumarin 1

Isocoumarin **1** (1.0 equiv., 1.5 mmol, 564 mg), the corresponding arylboronic acid (or its anhydride) (1.0 equiv., 1.5 0.5 mmol, respectively), catalyst $(PPh_3)_2PdCl_2$ (1 mol%, 0.015 mmol, 10.5 mg) and $NaHCO_3$ (2.9 equiv., 4.4 mmol, 370 mg) were dissolved in Pr^iOH/H_2O (3:1; 40 mL) in a dried 100 mL flask equipped with a magnetic stir bar. The reaction mixture was stirred at 100^{o}C under argon for 16 h and then cooled to room temperature. Then the precipitate was separated by centrifugation. The solvent was removed *in vacuo*, and the residue was chromatographed on a silica column (~ 1 × 15 cm). Petroleum ether was used first, then the desired product was eluted with petroleum ether/dichloromethane (gradient ratio from 2:1 to 1:2). Removal of the solvent *in vacuo* gave the desired isocoumarin derivatives **2**.

Characterization of isocoumarins 2a-f

3,4,6-Triphenyl-1*H*-isochromen-1-one (2a)

Starting from **1** and phenylboronic acid anhydride, the desired product **2a** was isolated as a colorless powder (472 mg, 84% yield).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.44 – 7.27 (m, 11H), 7.25 – 7.17 (m, 3H) ppm.

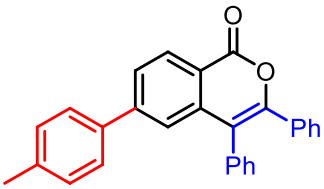
^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.22, 151.32, 147.46, 139.67, 139.28, 134.21, 132.92, 131.23 (2C), 130.16, 129.24 (2C), 129.12 (2C), 128.99 (2C), 128.96, 128.56, 128.20, 127.85 (2C), 127.42 (2C), 127.17, 123.59, 119.14, 117.01 ppm.

IR (CCl_4): ν = 1738 (C=O), 1609 (C-C arom), 1477 (C-C arom) cm^{-1}.

HRMS (ESI, *m*/*z*) calcd. for $C_{27}H_{18}O_2$ $[M+H]^+$: 375.1380, found: 375.1384.

3,4-Diphenyl-6-(*p*-tolyl)-1*H*-isochromen-1-one (2b)

Starting from **1** and *p*-tolylboronic acid, the desired product **2b** was isolated as a colorless powder (285.5 mg, 49% yield).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.42 – 7.33 (m, 8H), 7.30 – 7.28 (m, 2H), 7.23 – 7.17 (m, 5H), 2.37 (s, 3H) ppm.

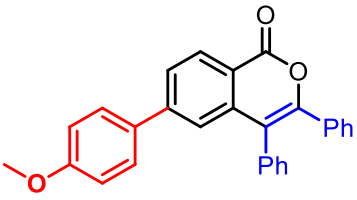
^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.18, 151.25, 147.39, 139.26, 138.63, 136.79, 134.28, 132.98, 131.23 (2C), 130.10, 129.69 (2C), 129.23 (2C), 129.06 (2C), 128.90, 128.13, 127.81 (2C), 127.24 (2C), 126.94, 123.30, 118.91, 117.02, 21.11 ppm.

IR (CCl_4): ν = 1737 (C=O), 1607 (C-C arom), 1480 (C-C arom) cm^{-1}.

HRMS (ESI, *m*/*z*) calcd. for $C_{28}H_{20}O_2[M+H]^+$: 389.1536, found: 389.1537.

6-(4-Methoxyphenyl)-3,4-diphenyl-1*H*-isochromen-1-one (2c)

Starting from **1** and 4-methoxyphenylboronic acid, the desired product **2c** was isolated as a colorless powder (340 mg, 56% yield).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 6.1 Hz, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.42 – 7.39 (m, 5H), 7.33 – 7.26 (m, 5H), 7.23 – 7.15 (m, 3H), 6.91 (d, J = 6.6 Hz, 2H), 3.79 (s, 3H) ppm.

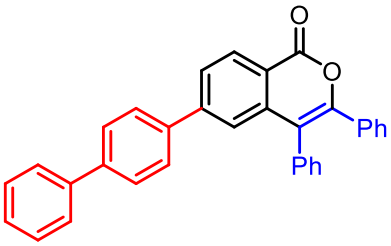
^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.18, 160.17, 151.24, 146.96, 139.27, 134.31, 133.00, 131.93, 131.24 (2C), 130.11, 129.23 (2C), 129.07 (2C), 128.90, 128.51 (2C), 128.14, 127.82 (2C), 126.61, 122.81, 118.58, 117.02, 114.44 (2C), 55.35 ppm.

IR (CCl_4): ν = 2837 (C-H, OMe), 1737 (C=O), 1606 (C-C arom), 1480 (C-C arom) cm^{-1}.

HRMS (ESI, *m*/*z*) calcd. for $C_{28}H_{20}O_3[M+H]^+$: 405.1485, found: 405.1487.

6-([1,1'-Biphenyl]-4-yl)-3,4-diphenyl-1*H*-isochromen-1-one (2d)

Starting from **1** and [1,1'-biphenyl]-4-ylboronic acid, the desired product **2d** was isolated as a yellowish powder (466 mg, 69% yield).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.59 – 7.55 (m, 4H), 7.45 – 7.39 (m, 6H), 7.37 – 7.29 (m, 5H), 7.23 – 7.14 (m, 3H) ppm.

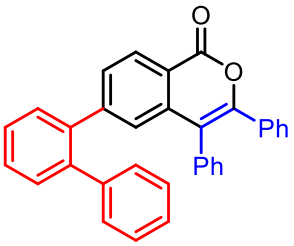
^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.92, 141.48, 140.21, 139.34, 138.46, 134.24, 132.94, 131.24 (2C), 130.21, 129.24 (2C), 129.11 (2C), 128.95, 128.86 (2C), 128.20, 127.84 (2C), 127.77 (2C), 127.69 (2C), 127.65, 127.34, 127.02 (2C), 126.96, 123.41, 119.18, 116.97 ppm.

IR (CCl_4): ν = 1738 (C=O), 1607 (C-C arom), 1478 (C-C arom) cm^{-1}.

HRMS (ESI, *m*/*z*) calcd. for $C_{33}H_{22}O_2$ $[M+H]^+$: 451.1693, found: 451.1692.

6-([1,1'-Biphenyl]-2-yl)-3,4-diphenyl-1*H*-isochromen-1-one (2e)

Starting from **1** and [1,1'-biphenyl]-2-ylboronic acid, the desired product **2e** was isolated as a yellowish powder (453 mg, 67% yield).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, J = 8.2 Hz, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.30 – 7.13 (m, 11H), 7.05 – 7.03 (m, 2H), 6.89 (s, 1H), 6.78 (d, J = 7.2 Hz, 2H) ppm.

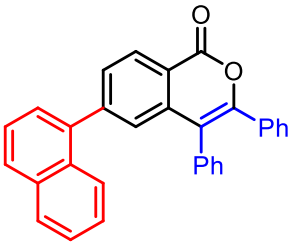
^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.22, 150.95, 148.01, 140.74, 139.09, 137.88, 133.82, 132.92, 131.03 (2C), 130.87, 130.27, 129.90 (2C), 129.66, 129.50, 129.22 (2C), 128.92 (2C), 128.84, 128.47, 128.26(2C), 127.76 (2C), 127.71 (2C), 127.37, 126.73, 118.55, 116.84 ppm. The signal of one carbon atom in ^{13}C {^{1}H} NMR could not be detected, possibly due to signal overlap.

IR (CCl_4): ν = 1736 (C=O), 1717 (C=O), 1609 (C-C arom), 1487 (C-C arom) cm^{-1}.

HRMS (ESI, *m*/*z*) calcd. for $C_{33}H_{22}O_2$ $[M+H]^+$: 451.1693, found: 451.1688.

6-(Naphthalen-1-yl)-3,4-diphenyl-1*H*-isochromen-1-one (2f)

Starting from **1** and naphthalen-1-ylboronic acid, the desired product **2f** was isolated as a yellowish powder (311 mg, 52% yield).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, J = 8.3 Hz, 1H), 7.94 (s, 1H), 7.87 – 7.81 (m, 3H), 7.57 (d, J = 6.8 Hz, 1H), 7.50 – 7.47 (m, 3H), 7.44 – 7.39 (m, 3H), 7.34 – 7.29 (m, 4H), 7.23 – 7.14 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.39, 147.42, 139.34, 136.95, 134.23, 133.36, 133.06, 132.95, 131.25 (2C), 130.22, 129.25 (2C), 129.12 (2C), 128.96, 128.78, 128.36, 128.22, 127.85 (2C), 127.64, 127.37, 126.68 (2C), 126.63, 125.08, 123.81, 119.18, 117.02 ppm. The signal of one carbon atom in ^{13}C {^{1}H} NMR could not be detected, possibly due to signal overlap.

IR (CCl_4): ν = 1740 (C=O), 1717 (C=O), 1608 (C-C arom), 1473 (C-C arom) cm^{-1}.

HRMS (ESI, *m*/*z*) calcd. for $C_{31}H_{20}O_2$[M+H]$^+$: 425.1536, found: 425.1536.

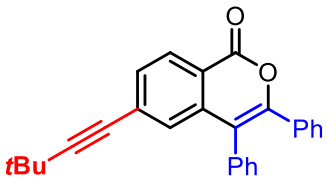
General procedure for Pd^0-catalyzed Sonogashira cross-coupling of terminal alkynes with isocoumarin 1

Isocoumarin **1** (1.0 equiv., 1.0 mmol, 376 mg), the corresponding alkyne (1.05 equiv., 1.05 mmol), catalyst $(PPh_3)_2PdCl_2$ (5 mol%, 0.05 mmol, 37.8 mg), CuI (15 mol%, 0.15 mmol, 28.0 mg) and triethylamine (8.6 equiv., 8.6 mmol, 1.19 ml) were dissolved in THF (15 mL) in a dried 50 mL flask equipped with a magnetic stir bar. The reaction mixture was stirred at 100^{o}C under argon for 10 h and then cooled to room temperature. The solvent was removed *in vacuo*, and the residue was chromatographed on a silica column (~ 1 × 15 cm). Petroleum ether/dichloromethane was used as an eluent (gradient ratio from 2:1 to 1:2). Removal of the solvent *in vacuo* gave the desired isocoumarin derivatives **3**.

Characterization of isocoumarins 3a and 3b

6-(3,3-Dimethylbut-1-yn-1-yl)-3,4-diphenyl-1*H*-isochromen-1-one (3a)

Starting from **1** and *tert*-butylacetylene, the desired product **3a** was isolated as a yellowish powder (208 mg, 55% yield).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, J = 8.3 Hz, 1H), 7.49 (d, J = 8.2 Hz, 1H), 7.43 – 7.40 (m, 3H), 7.31 – 7.16 (m, 8H), 1.27 (s, 9H) ppm.

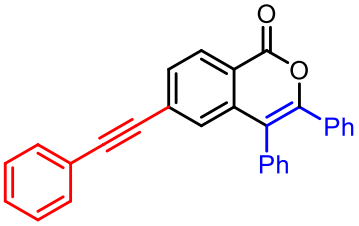
^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.87, 151.43, 138.65, 133.99, 132.85, 131.40, 131.28 (2C), 130.89, 129.33, 129.23 (2C), 129.10 (2C), 128.97, 128.17, 127.82 (2C), 127.66, 118.94, 116.46, 103.29, 78.58, 30.72 (3C), 28.08 ppm.

IR (CCl_4): ν = 1741 (C=O), 1602 (C-C arom), 1481 (C-C arom) cm^{-1}.

HRMS (ESI, *m*/*z*) calcd. for $C_{27}H_{22}O_2$ [M+H]$^+$: 379.1693, found: 379.1695.

3,4-Diphenyl-6-phenylethynyl-1*H*-isochromen-1-one (3b)

Starting from **1** and phenylacetylene, the desired product **3b** was isolated as a yellowish powder (243 mg, 61% yield).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 5.9 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.43 – 7.41 (m, 3H), 7.33 – 7.26 (m, 8H), 7.24 – 7.15 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.68, 151.63, 138.85, 133.91, 132.78, 132.47, 131.77 (2C), 131.25 (2C), 130.95, 129.90, 129.57, 129.23 (2C), 129.19 (2C), 129.06, 129.03, 128.42 (2C), 128.27, 127.97, 127.86 (2C), 122.22, 119.50, 116.37, 93.51, 88.44 ppm.

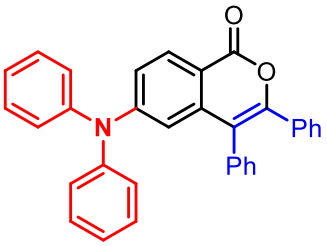
IR (CCl_4): ν = 1739 (C=O), 1718 (C=O), 1603 (C-C arom), 1492 (C-C arom) cm^{-1}.

HRMS (ESI, *m*/*z*) calcd. for $C_{29}H_{18}O_2$ [M+H]$^+$: 399.1380, found: 399.1378.

Pd^0-catalyzed Buchwald–Hartwig cross-coupling reaction of diphenylamine with isocoumarin 1

Isocoumarin **1** (1.0 equiv., 1.0 mmol, 376 mg), diphenylamine (1.05 equiv., 1.05 mmol, 177 mg), pre-catalyst $Pd(OAc)_2$ (5 mol%, 0.05 mmol, 11.3 mg) and ligand RuPhos (10 mol%, 0.10 mmol, 46.7 mg) were dissolved in 1,4-dioxane (15 mL) in a dried 50 mL flask equipped with a magnetic stir bar. The reaction mixture was stirred at 110°C under argon for 16 h and then cooled to room temperature. The solvent was removed *in vacuo*, and the residue was chromatographed on a silica column (~ 15 cm). Petroleum ether/dichloromethane was used as an eluent (gradient ratio from 2:1 to 1:2). Removal of the solvent *in vacuo* gave the desired isocoumarin derivative **4** as a colorless powder. Yield: 368 mg (79%).

6-Diphenylamino-3,4-diphenyl-1*H*-isochromen-1-one (4)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 9.0 Hz, 1H), 7.31 – 7.22 (m, 6H), 7.20 – 7.03 (m, 15H), 6.56 (s, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.96, 153.30, 151.13, 145.75, 140.25, 134.26, 133.21, 130.94 (2C), 130.85, 129.60 (4C), 129.25 (2C), 128.78, 128.63 (2C), 127.77 (2C), 127.68, 126.18 (4C), 125.13 (2C), 119.51, 116.74, 114.02, 112.40 ppm. The signal of one carbon atom in ^{13}C {^{1}H} NMR could not be detected, possibly due to signal overlap.

IR (CCl_4): ν = 1730 (C=O), 1589 (C-C arom), 1494 (C-C arom) cm^{-1}.

HRMS (ESI, *m*/*z*) calcd. for $C_{33}H_{23}NO_2$ [M+H]$^+$: 466.1802, found: 466.1797.

NMR spectra

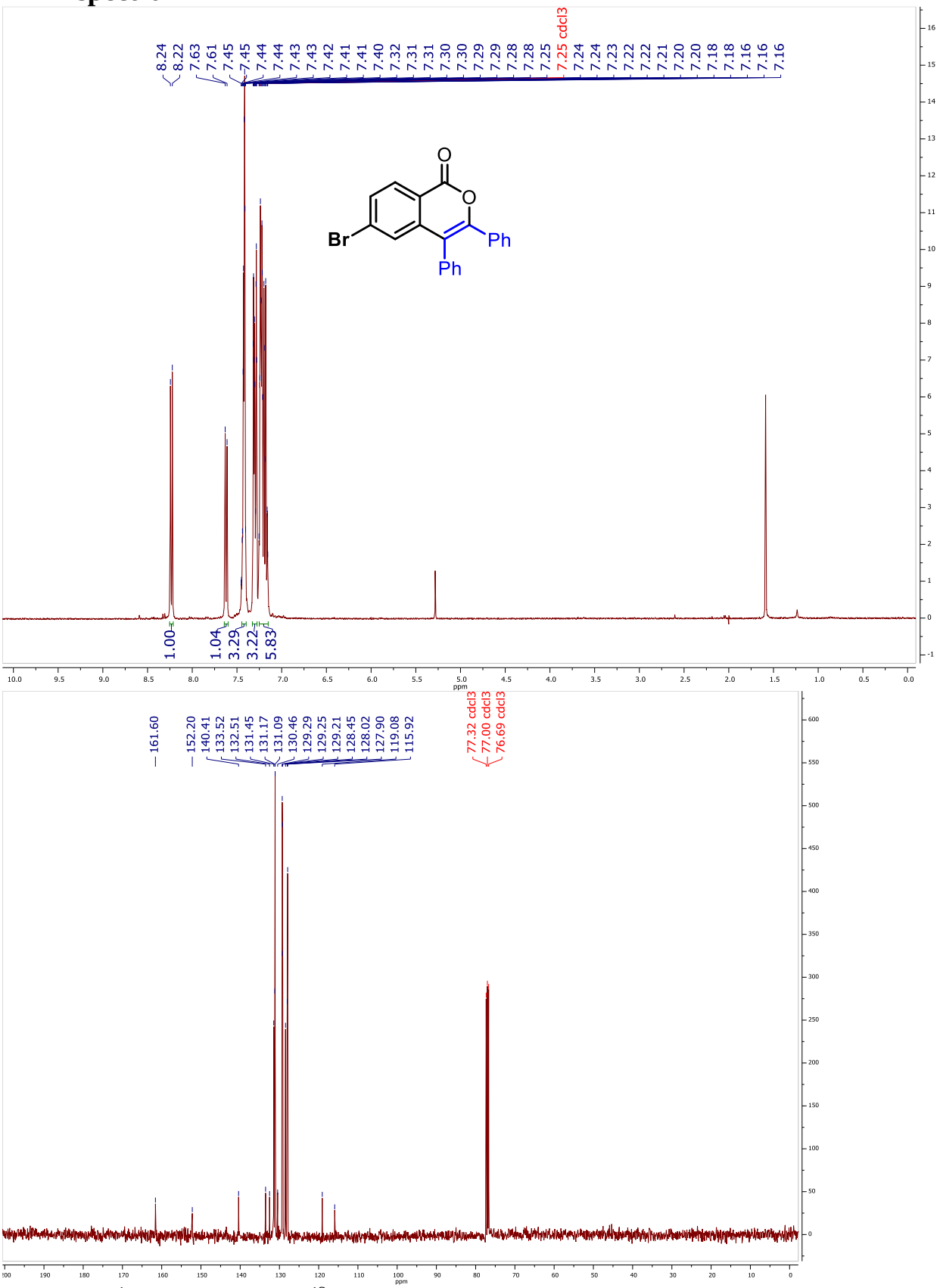


Figure S1. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 6-bromo-3,4-diphenyl-1*H*-isochromen-1-one (**1**) in $CDCl_3$.

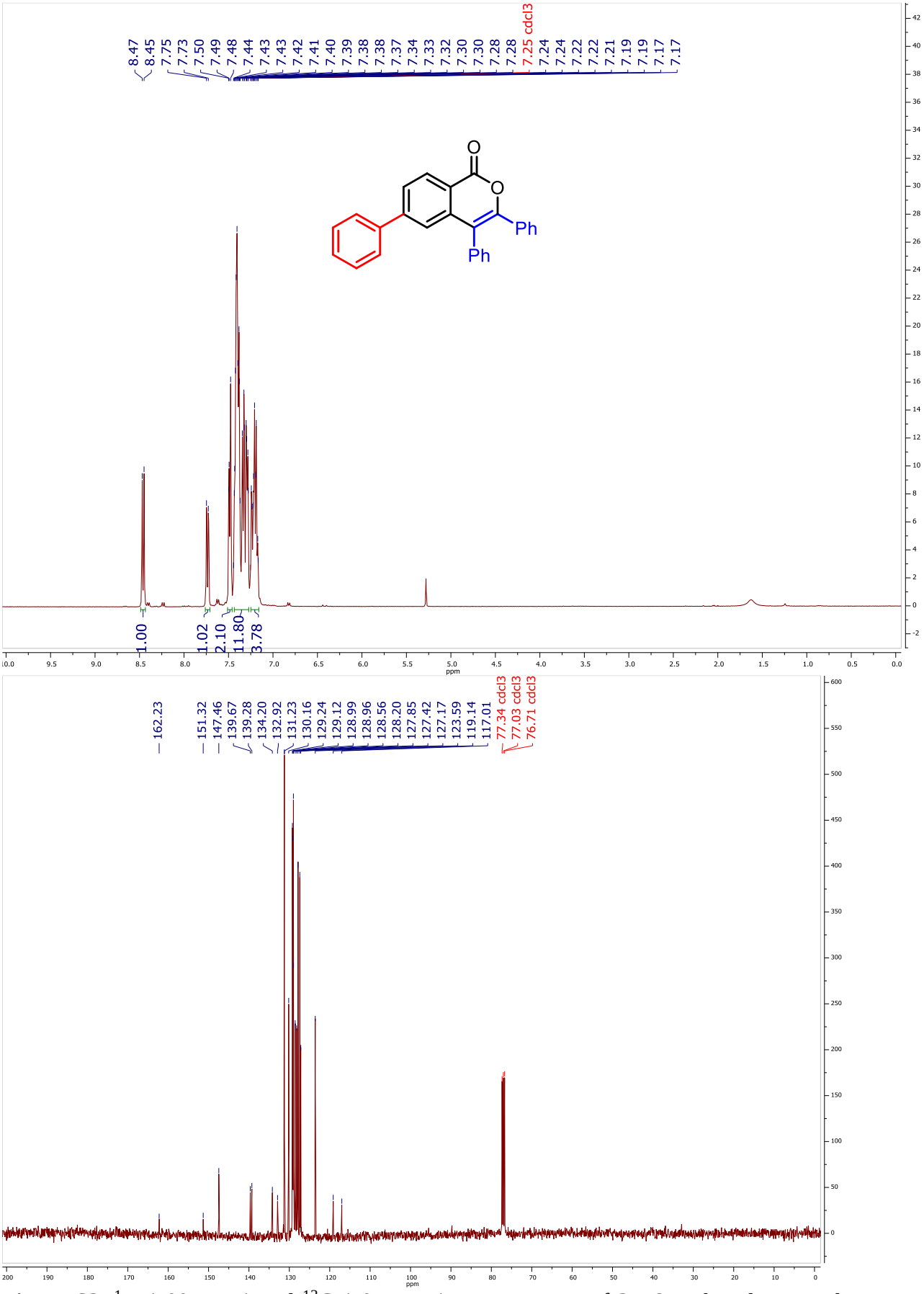


Figure S2. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 3,4,6-triphenyl-1*H*-isochromen-1-one (**2a**) in $CDCl_3$.

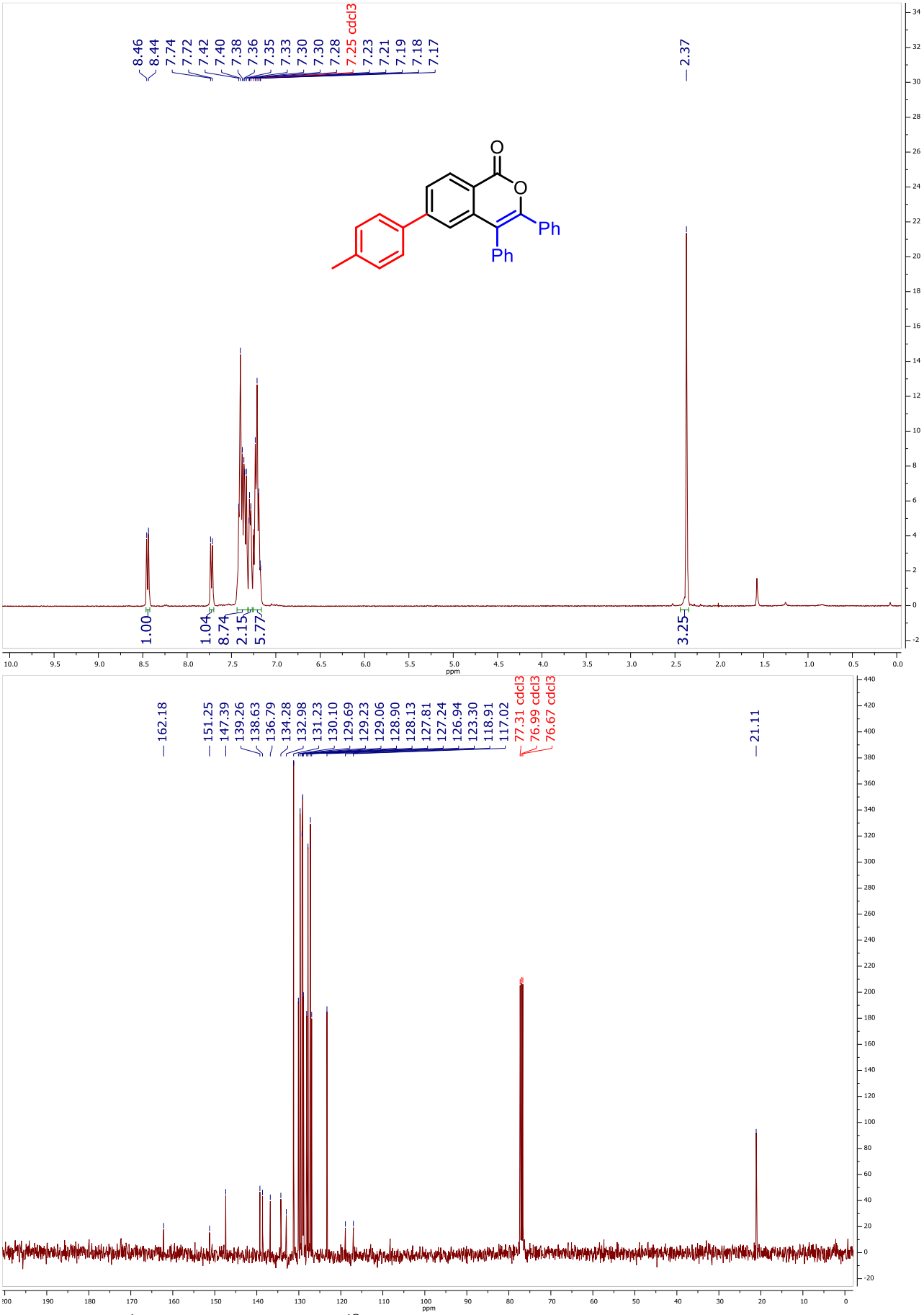


Figure S3. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 3,4-diphenyl-6-(*p*-tolyl)-1*H*-isochromen-1-one (**2b**) in $CDCl_3$.

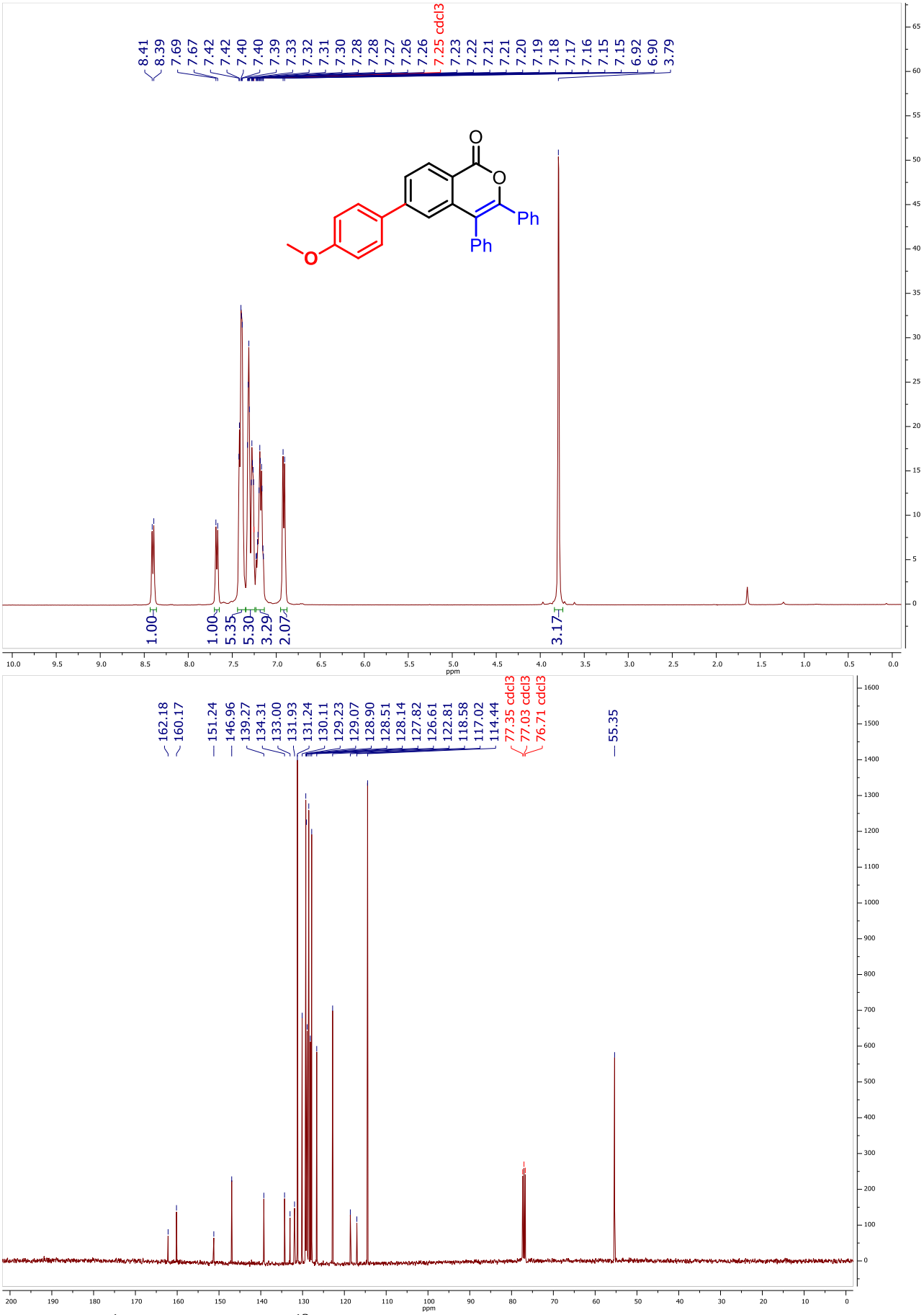


Figure S4. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 6-(4-methoxyphenyl)-3,4-diphenyl-1*H*-isochromen-1-one (**2c**) in $CDCl_3$.

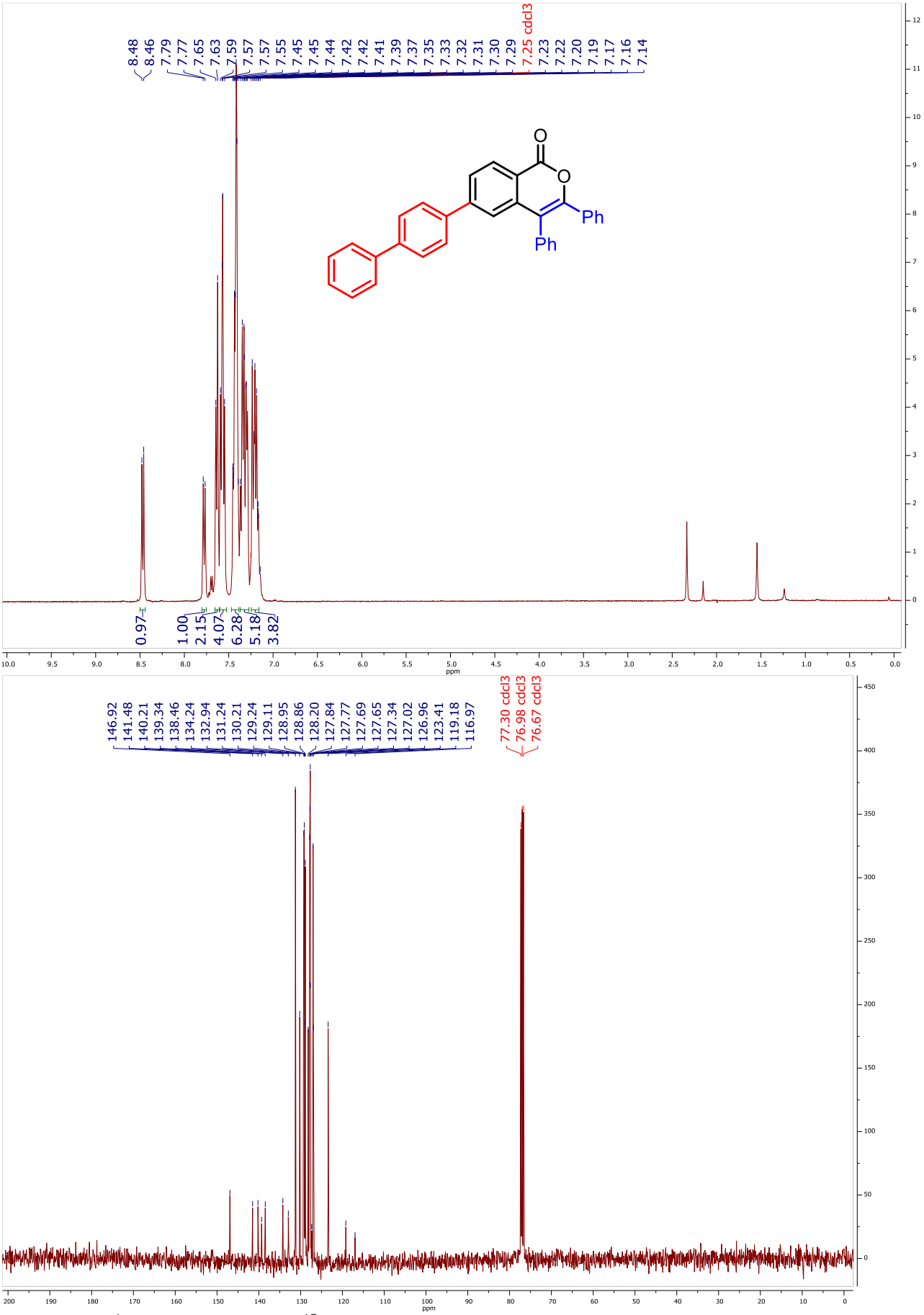


Figure S5. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 6-([1,1'-biphenyl]-4-yl)-3,4-diphenyl-1*H*-isochromen-1-one (**2d**) in $CDCl_3$.

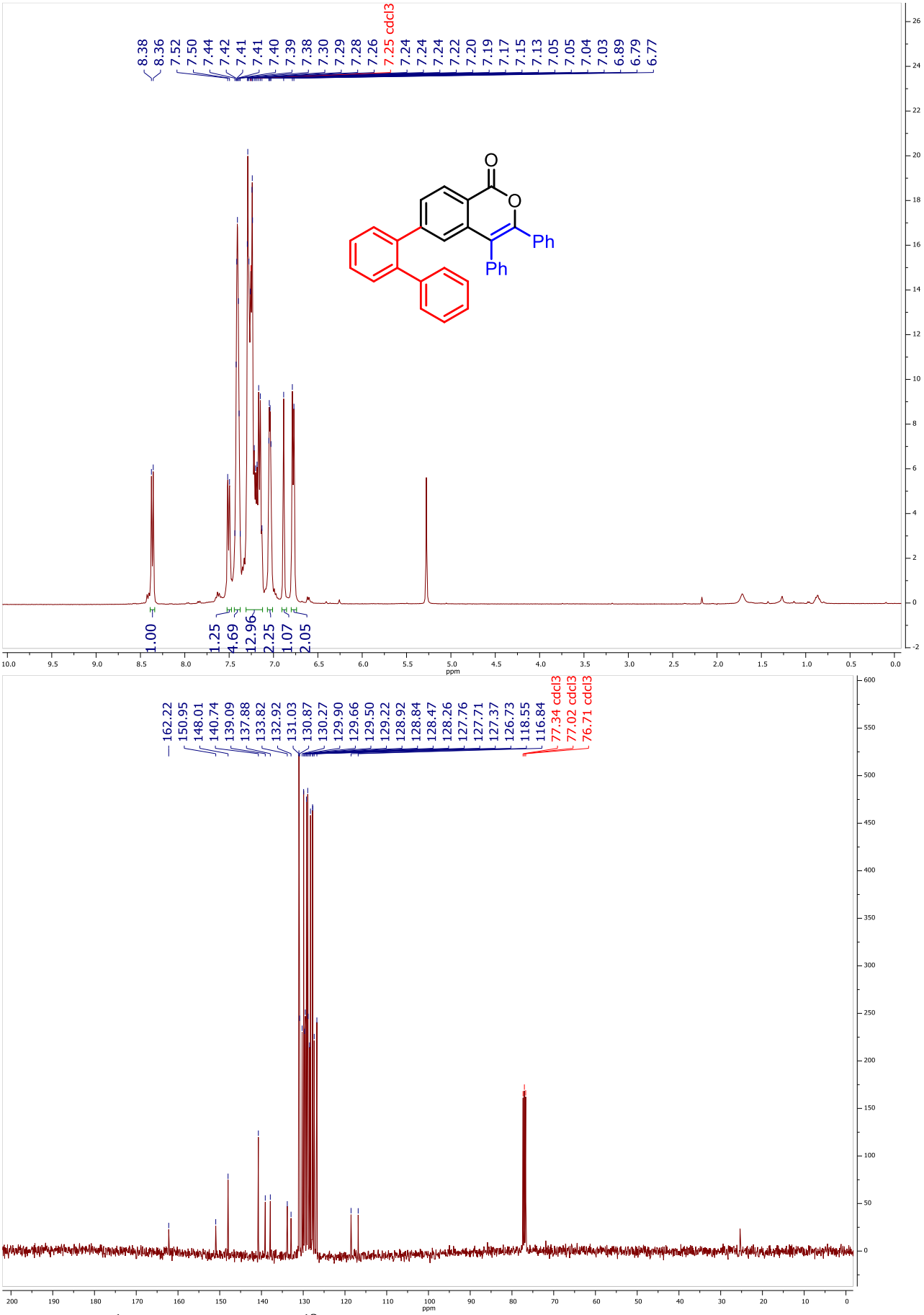


Figure S6. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 6-([1,1'-biphenyl]-2-yl)-3,4-diphenyl-1*H*-isochromen-1-one (**2e**) in $CDCl_3$.

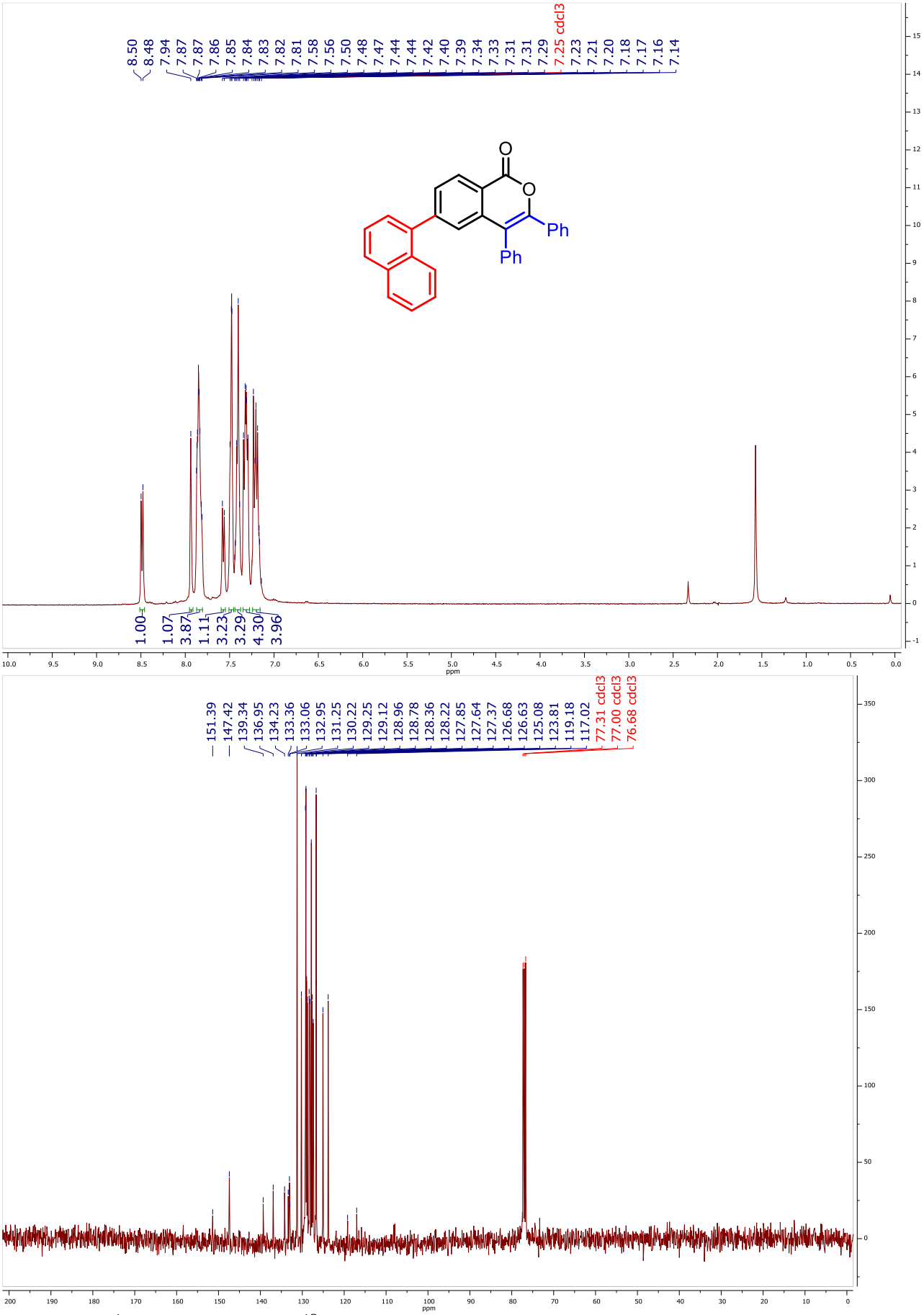


Figure S7. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 6-(naphthalen-1-yl)-3,4-diphenyl-1*H*-isochromen-1-one (**2f**) in $CDCl_3$.

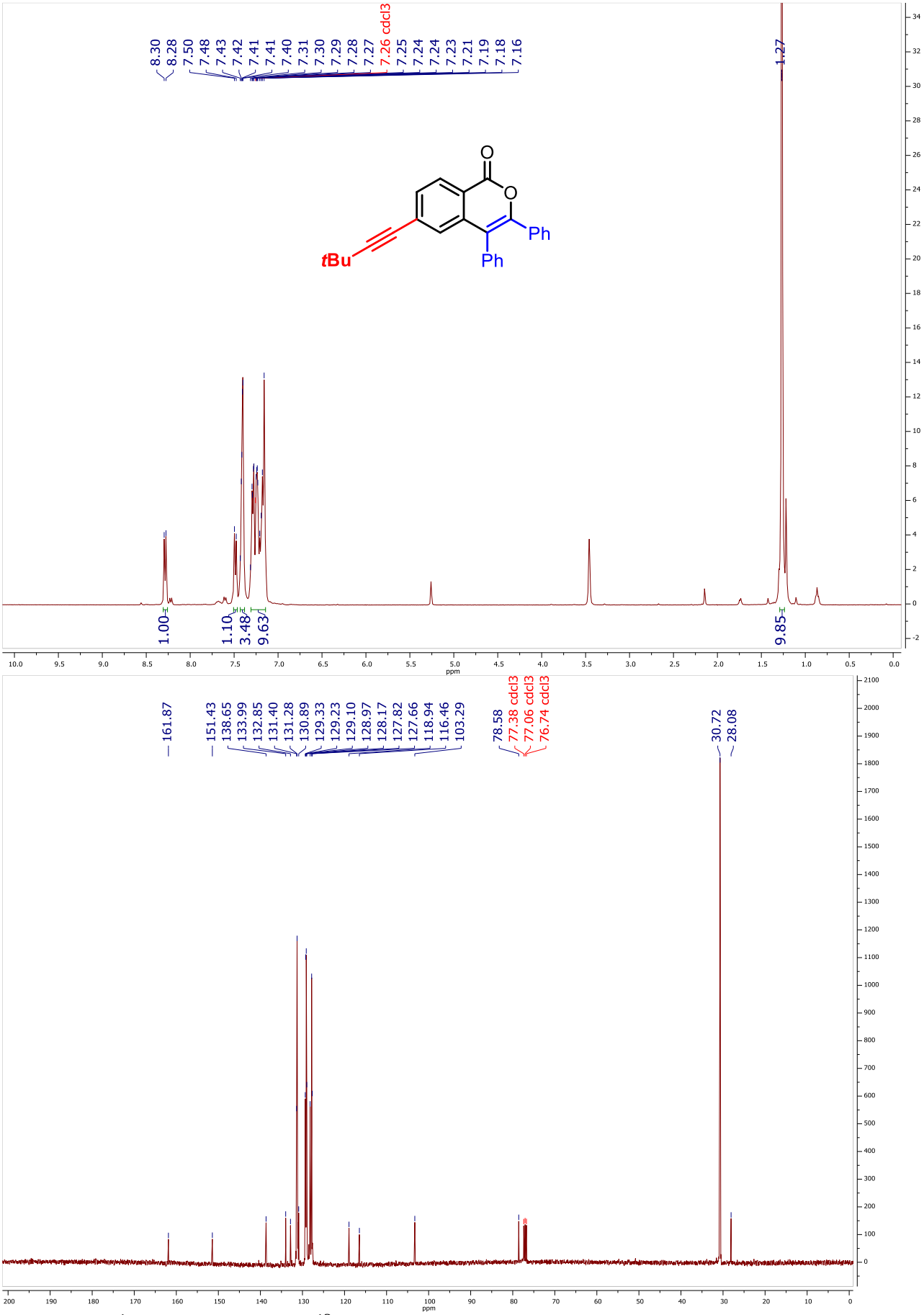


Figure S8. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 6-(3,3-dimethylbut-1-yn-1-yl)-3,4-diphenyl-1*H*-isochromen-1-one (**3a**) in $CDCl_3$.

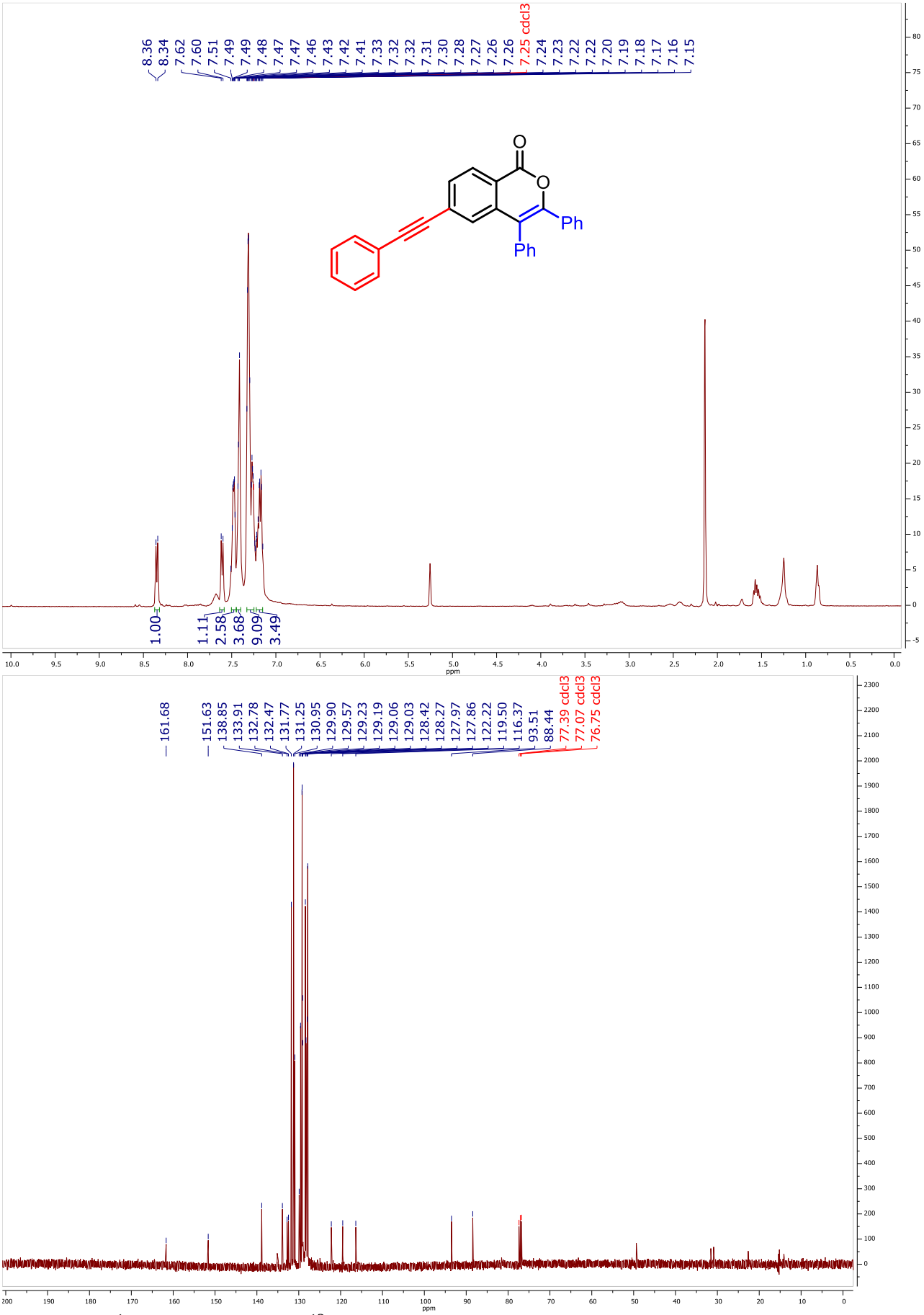


Figure S9. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 3,4-diphenyl-6-(phenylethynyl)-1*H*-isochromen-1-one (**3b**) in $CDCl_3$.

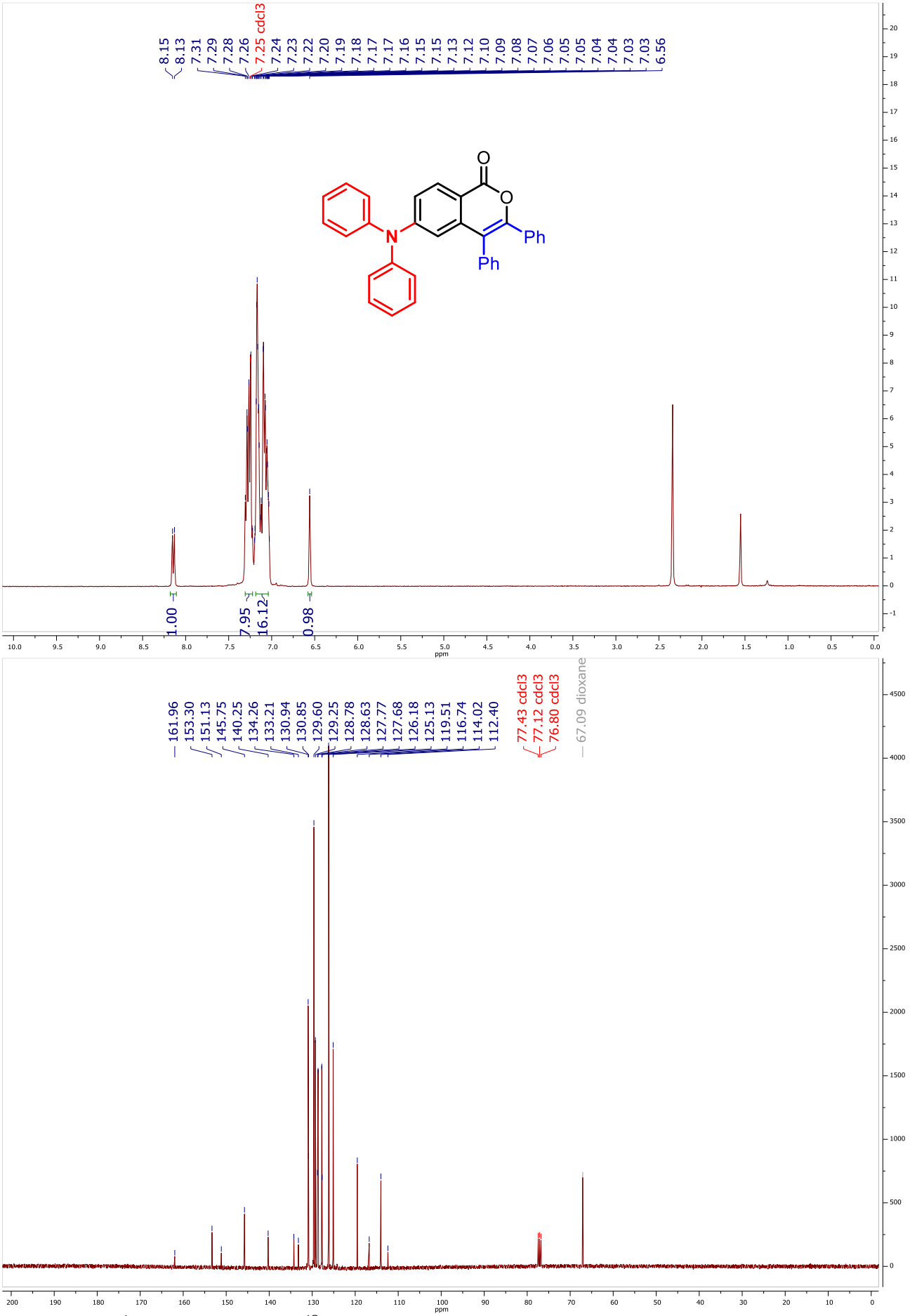


Figure S10. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of 6-(diphenylamino)-3,4-diphenyl-1*H*-isochromen-1-one (**4**) in $CDCl_3$.

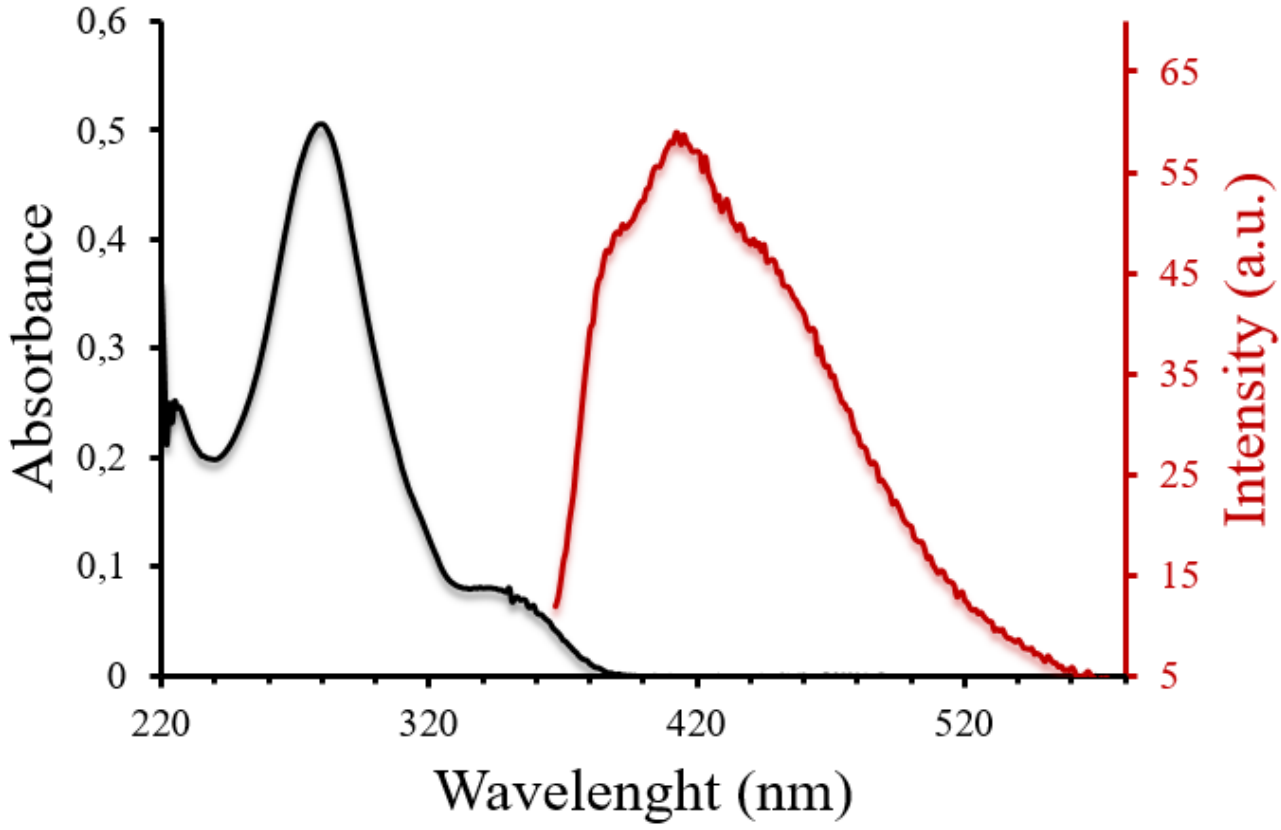


Figure S11. Absorption (C = $1.7 \cdot 10^{-5}$ M) and fluorescence (C = $1.7 \cdot 10^{-5}$ M, λex = 355 nm) spectra of 3,4,6-triphenyl-1*H*-isochromen-1-one (**2a**) in CH_2Cl_2.

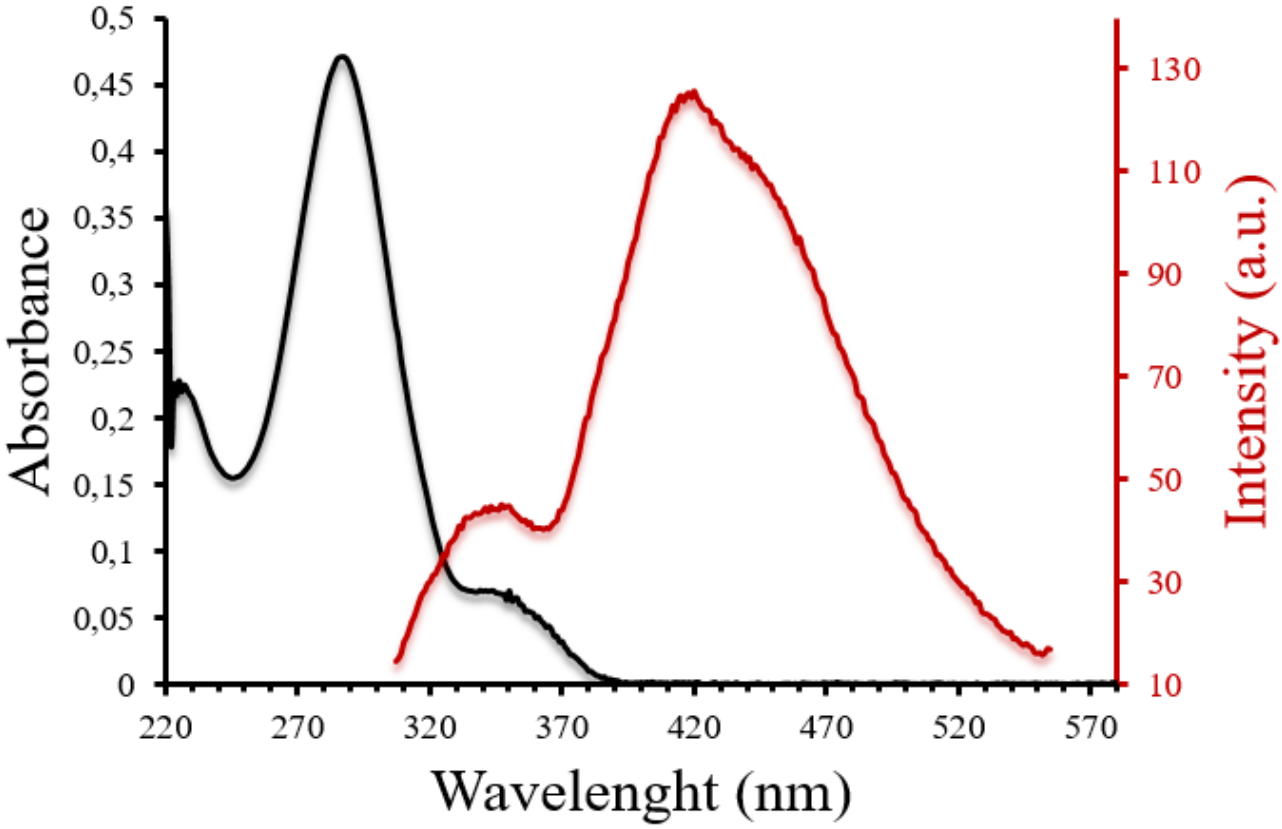


Figure S12. Absorption (C = $1.6 \cdot 10^{-5}$ M) and fluorescence (C = $1.6 \cdot 10^{-5}$ M, λex = 287 nm) spectra of 3,4-diphenyl-6-(*p*-tolyl)-1*H*-isochromen-1-one (**2b**) in CH_2Cl_2.

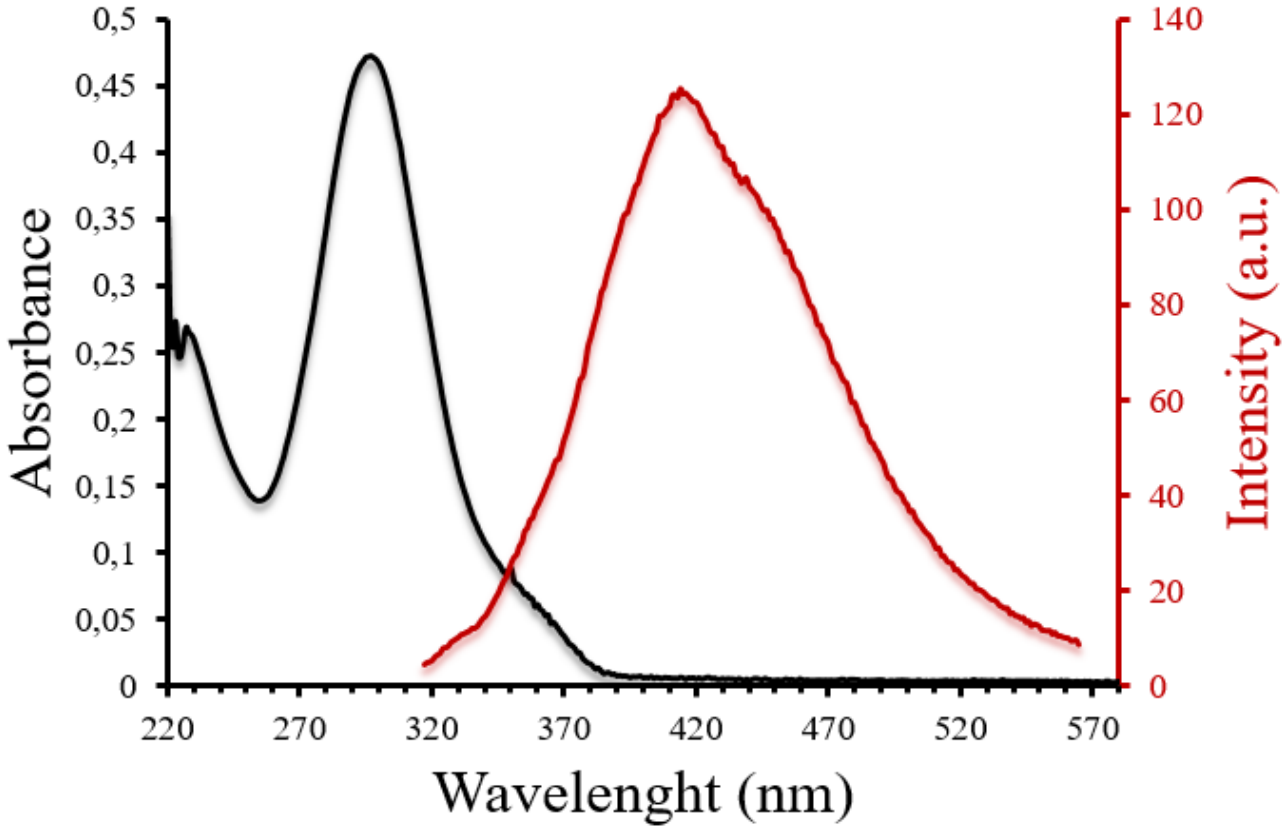


Figure S13. Absorption (C = $1.6 \cdot 10^{-5}$ M) and fluorescence (C = $1.6 \cdot 10^{-5}$ M, λex = 297 nm) spectra of 6-(4-methoxyphenyl)-3,4-diphenyl-1*H*-isochromen-1-one (**2c**) in CH_2Cl_2.

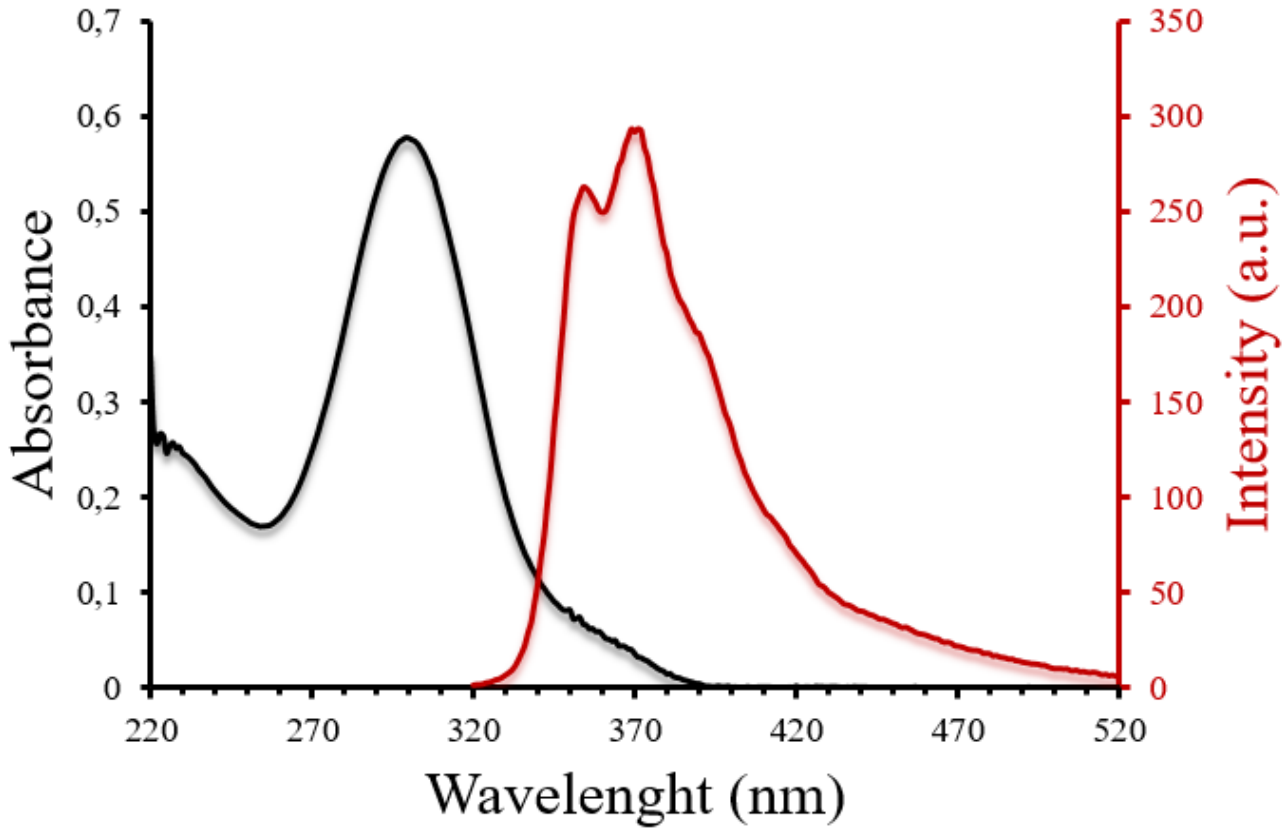


Figure S14. Absorption (C = $1.5 \cdot 10^{-5}$ M) and fluorescence (C = $1.5 \cdot 10^{-5}$ M, λex = 300 nm) spectra of 6-([1,1'-biphenyl]-4-yl)-3,4-diphenyl-1*H*-isochromen-1-one (**2d**) in CH_2Cl_2.

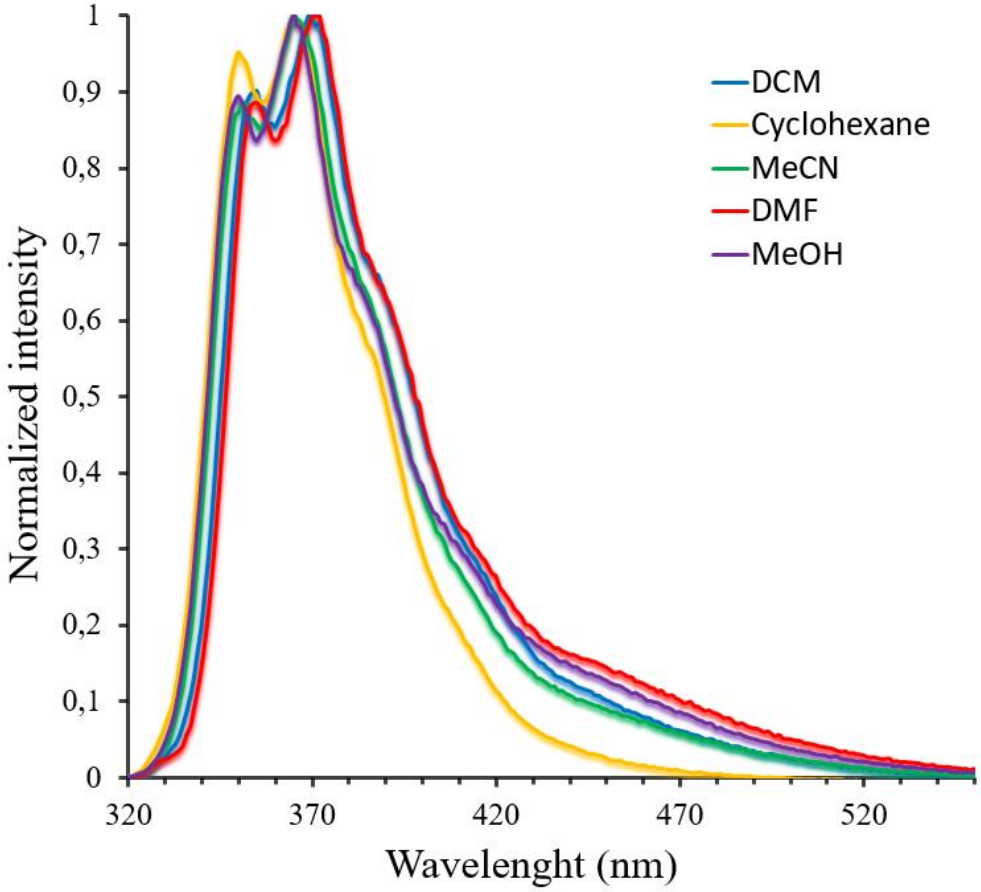


Figure S15. Fluorescence (C = $1.5 \cdot 10^{-5}$ M, λ_{ex} = 300 nm) spectra of 6-([1,1'-biphenyl]-4-yl)-3,4-diphenyl-1*H*-isochromen-1-one (**2d**) in different solvents.

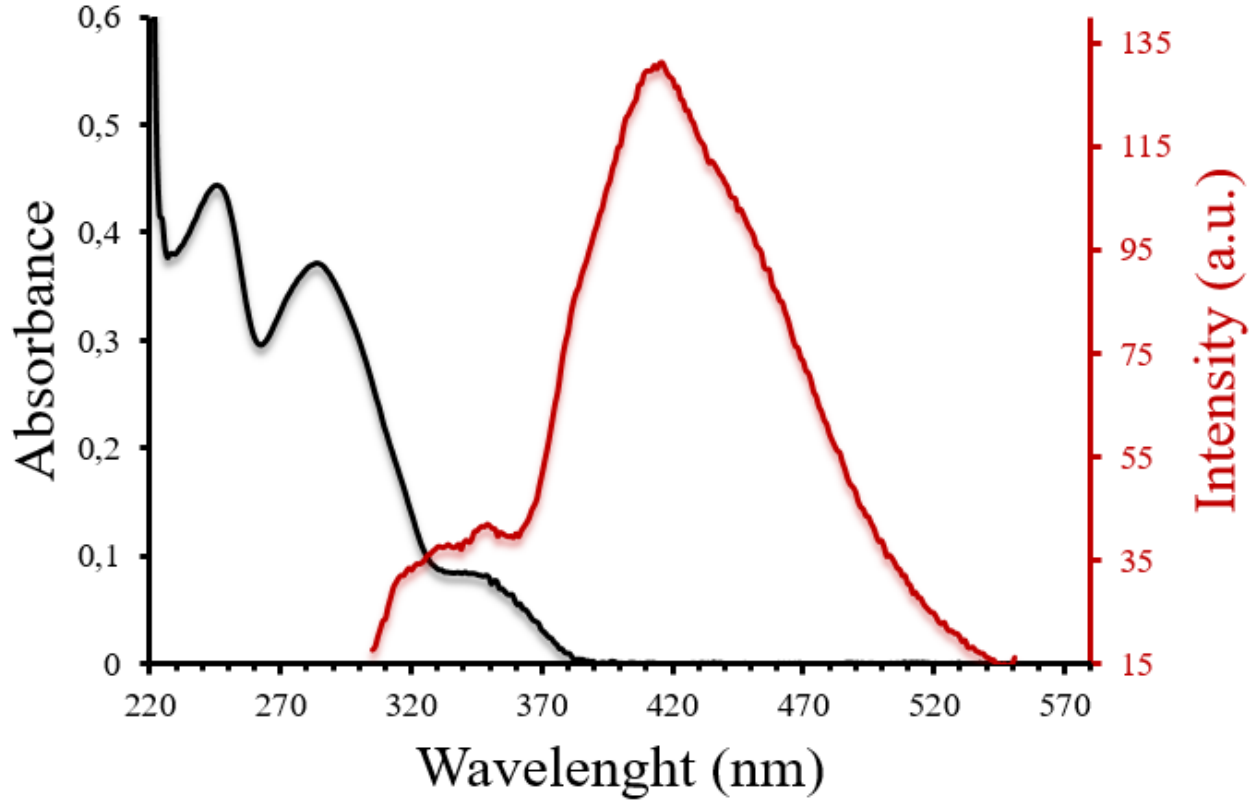


Figure S16. Absorption (C = $2.3 \cdot 10^{-5}$ M) and fluorescence (C = $2.3 \cdot 10^{-5}$ M, λex = 285 nm) spectra of 6-([1,1'-biphenyl]-2-yl)-3,4-diphenyl-1*H*-isochromen-1-one (**2e**) in CH_2Cl_2.

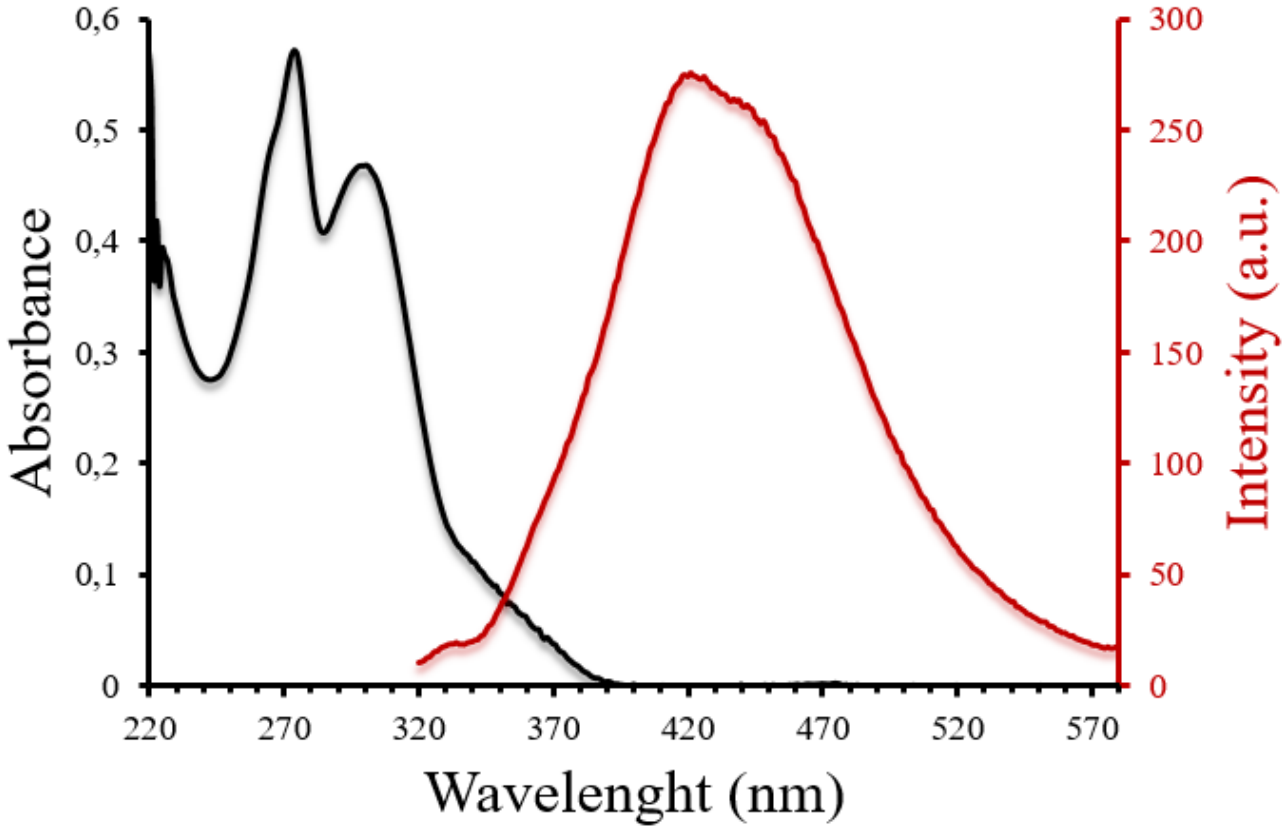


Figure S17. Absorption (C = $2.4 \cdot 10^{-5}$ M) and fluorescence (C = $2.4 \cdot 10^{-5}$ M, λex = 300 nm) spectra of 6-(naphthalen-1-yl)-3,4-diphenyl-1*H*-isochromen-1-one (**2f**) in CH_2Cl_2.

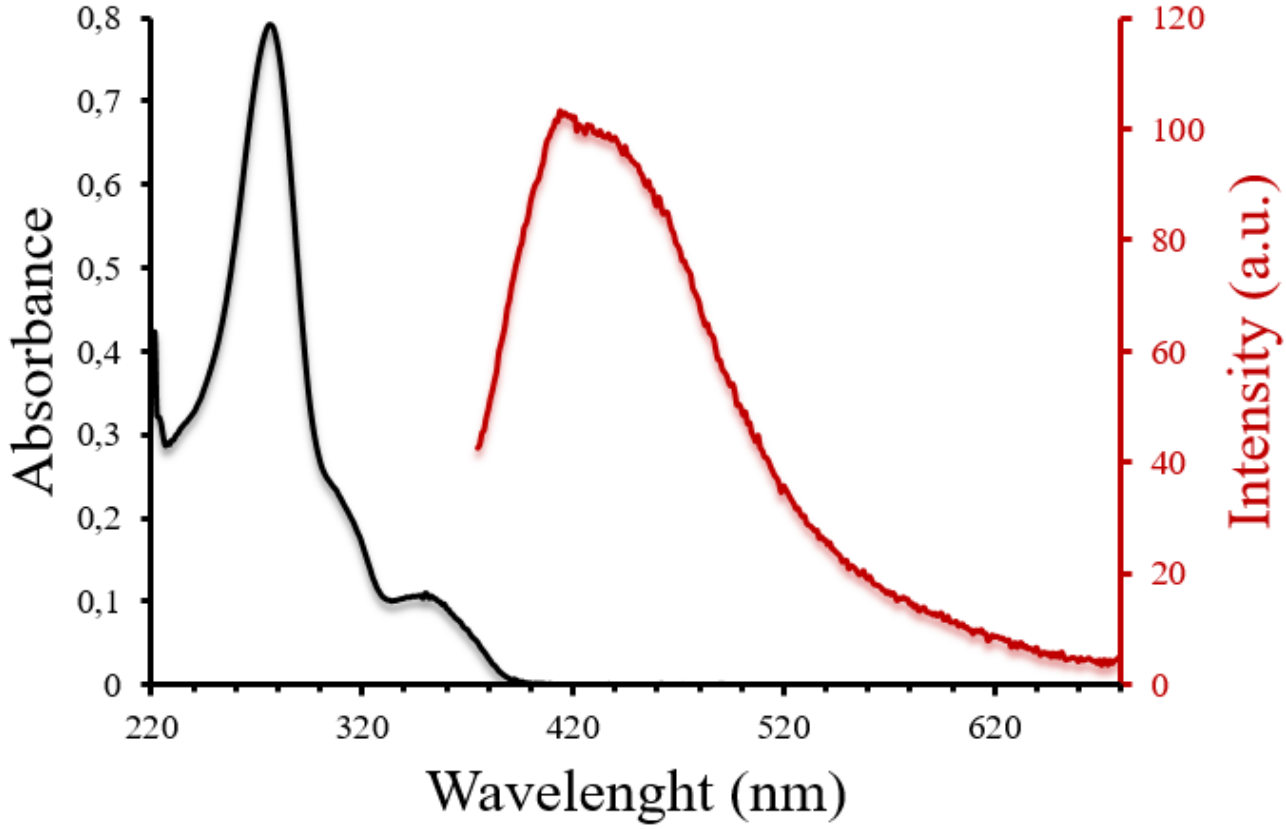


Figure S18. Absorption (C = $2.5 \cdot 10^{-5}$ M) and fluorescence (C = $2.5 \cdot 10^{-5}$ M, λ_{ex} = 350 nm) spectra of 6-(3,3-dimethylbut-1-yn-1-yl)-3,4-diphenyl-1*H*-isochromen-1-one (**3a**) in CH_2Cl_2.

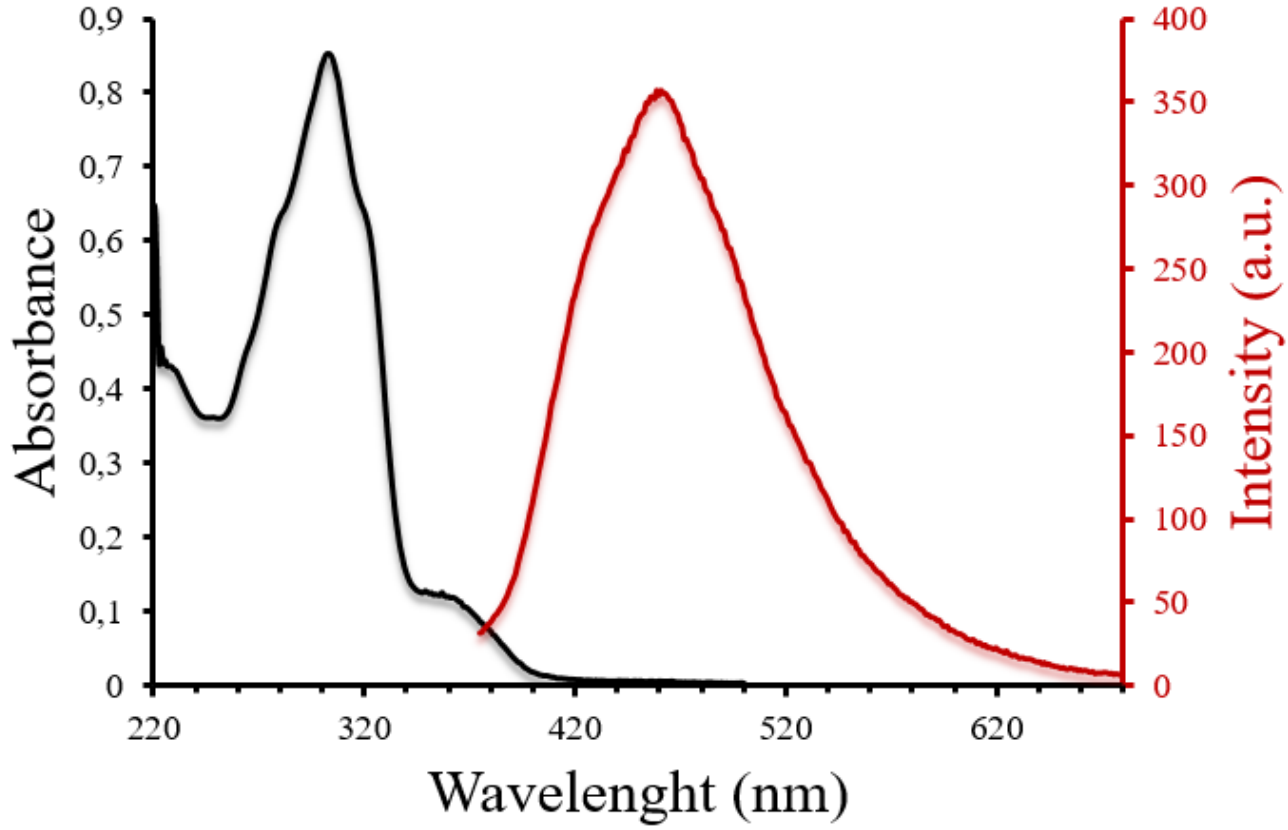


Figure S19. Absorption (C = $2.3 \cdot 10^{-5}$ M) and fluorescence (C = $2.3 \cdot 10^{-5}$ M, λex = 300 nm) spectra of 3,4-diphenyl-6-(phenylethynyl)-1*H*-isochromen-1-one (**3b**) in CH_2Cl_2.

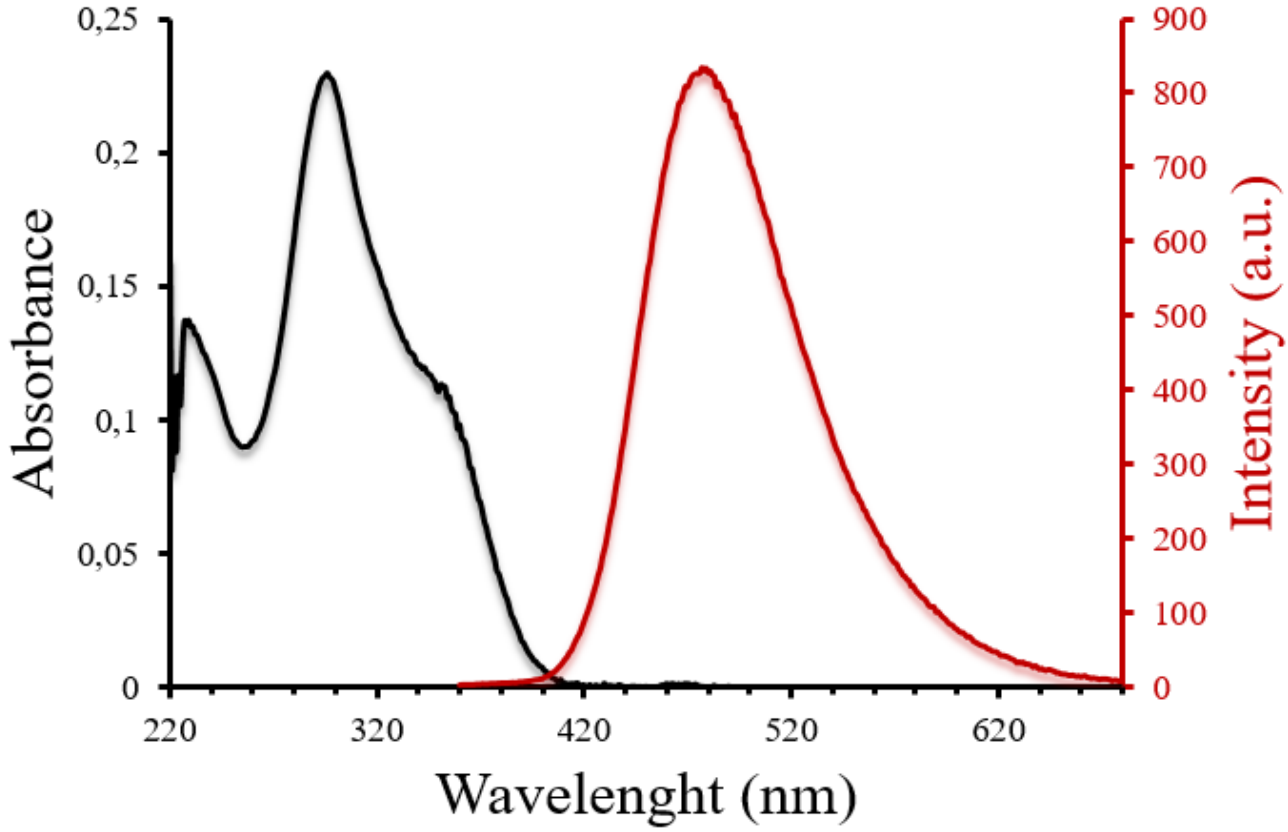


Figure S20. Absorption (C = $0.7 \cdot 10^{-5}$ M) and fluorescence (C = $0.7 \cdot 10^{-5}$ M, λ_{ex} = 350 nm) spectra of 6-(diphenylamino)-3,4-diphenyl-1*H*-isochromen-1-one (**4**) in CH_2Cl_2.

DFT Calculations

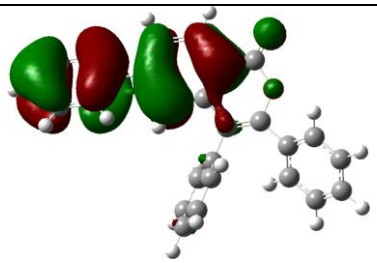
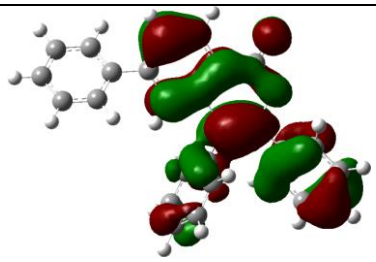
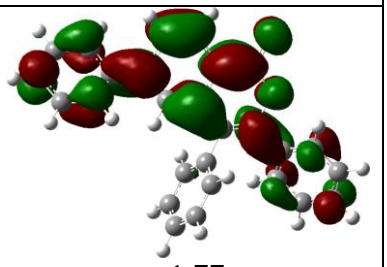
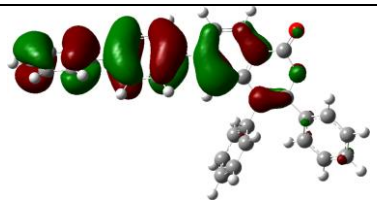
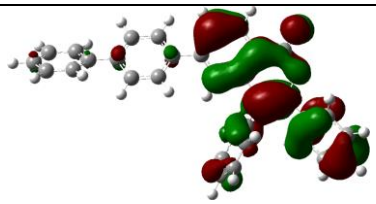
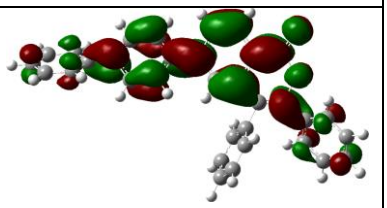
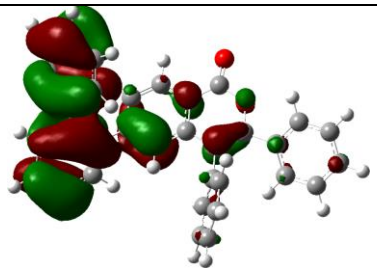
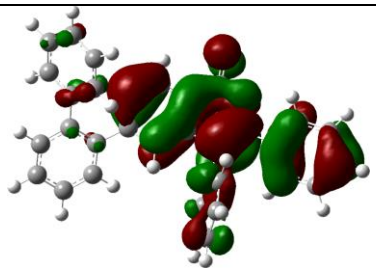
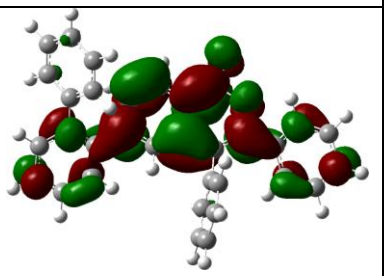
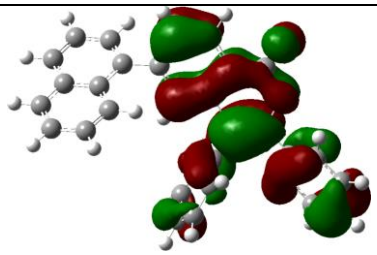
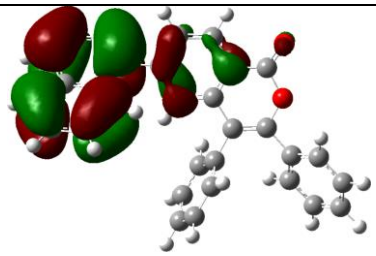
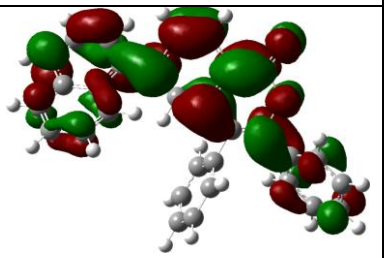
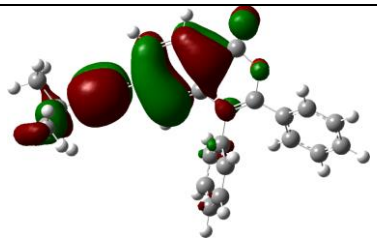
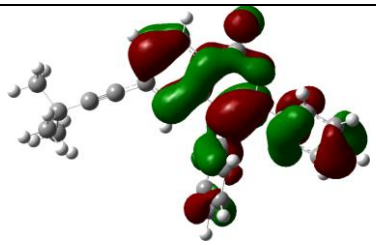
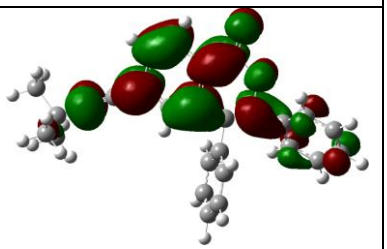
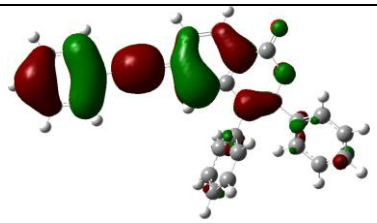
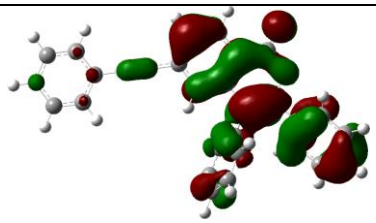
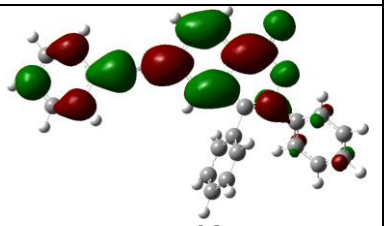
Geometry optimizations at the S_0 minimum were performed without constraints at the B3LYP/6-31G(d) level using the Gaussian 09 software (revision D.01) [S4] with corrections for solvation in dichloromethane (PCM model). The optimized geometry was verified to have no negative frequencies. Then, at the same level, TD-DFT was adopted to estimate the energies of the vertical excitations based on the optimized S_0 geometries (Table S1). The selected MOs responsible for excitation are shown in Table S2. The first 10 singlet and triplet excited states were considered. The geometries of the excited state S_1 were optimized using TDA-DFT method [S5] at the B3LYP/6-31G(d) level.

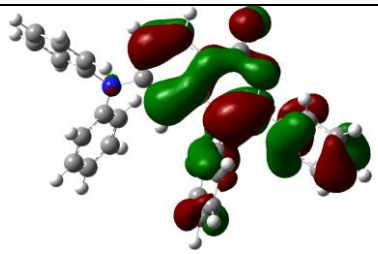
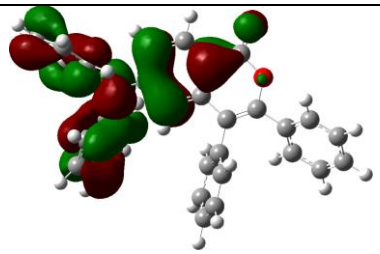
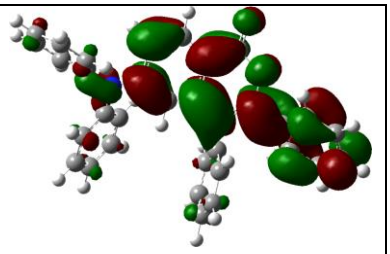
Table S1. Analysis of the long-wavelength absorption bands of compounds **2a**, **2d-f**, **3a**,**b**, and **4** by TD-DFT calculations at the B3LYP/6-31G(d) level with corrections for solvation in dichloromethane (PCM model).

Compound	Calculated absorption maxima ($S_0 \rightarrow S_1$) / oscillator strength / Main MOs responsible for excitation[a]
2a	344 nm / 0.2164 / HOMO-1 → LUMO (2%), HOMO → LUMO (93%)
2d	348 nm / 0.2214 / HOMO-1 → LUMO (12%), HOMO → LUMO (83%)
2e	341 nm / 0.2053 / HOMO-1 → LUMO (2%), HOMO → LUMO (92%)
2f	346 nm / 0.3309 / HOMO-1 → LUMO (51%), HOMO → LUMO (46%)
3a	349 nm / 0.2037 / HOMO-1 → LUMO (3%), HOMO → LUMO (93%)
3b	368 nm / 0.1580 / HOMO-1 → LUMO (12%), HOMO → LUMO (84%)
4	369 nm / 0.1324 / HOMO → LUMO (92%)

[a] Values in parentheses give the percentage contribution of the corresponding orbitals to the total transition.

Table S2. Selected molecular orbitals of **2a**, **2d-f**, **3a**,**b**, and **4** at the B3LYP/6-31G(d) level (isovalue = 0.02 a.u.). Energies of the orbitals are given in eV.

Compound	HOMO-1	HOMO	LUMO
2a	 −6.47	 −5.90	 −1.77
2d	 −6.07	 −5.91	 −1.83
2e	 −6.26	 −5.88	 −1.72
2f	 −5.91	 −5.89	 −1.77
3a	 −6.49	 −5.93	 −1.84
3b	 −6.13	 −5.94	 −2.08

4	 −5.84	 −5.39	 −1.54

Cartesian coordinates and energies optimized at B3LYP/6-31G(d)

2a
S_0 E = –1190.20043807 Hartree
ZPVE = 0.370693 Hartree
Thermal correction to Gibbs Free Energy = 0.317690 Hartree

6	2.777956000	-2.318161000	0.026118000
6	2.812485000	-0.905133000	0.019322000
6	1.604666000	-0.201544000	-0.005656000
6	0.360548000	-0.860426000	-0.025369000
6	0.359662000	-2.275307000	-0.001059000
6	1.568305000	-2.988973000	0.020199000
6	-0.912985000	-0.144917000	-0.051435000
6	-2.066224000	-0.871588000	-0.051921000
8	-2.046246000	-2.249565000	-0.003135000
6	-0.897813000	-3.013096000	0.027120000
8	-1.031816000	-4.220679000	0.073207000
6	-0.922365000	1.349397000	-0.009009000
6	-3.465475000	-0.389516000	-0.084825000
6	-0.473802000	2.104114000	-1.105246000
6	-0.470649000	3.499115000	-1.054603000
6	-0.911273000	4.160444000	0.094376000
6	-1.351894000	3.419074000	1.192893000
6	-1.354606000	2.024220000	1.142477000
6	-4.443444000	-1.071394000	0.662237000
6	-5.772520000	-0.653583000	0.639655000
6	-6.152127000	0.441163000	-0.140610000
6	-5.191940000	1.112882000	-0.900778000
6	-3.859688000	0.703332000	-0.875389000
1	3.705493000	-2.879933000	0.068453000
1	1.625212000	0.881120000	-0.033960000
1	-0.134958000	1.594308000	-2.003331000
1	-0.126338000	4.068089000	-1.913866000
1	-0.909240000	5.246218000	0.133587000
1	-1.692158000	3.925684000	2.091921000

1	-1.696218000	1.450165000	1.999137000
1	-4.155387000	-1.927475000	1.263073000
1	-6.512451000	-1.185847000	1.230829000
1	-7.189216000	0.764227000	-0.161282000
1	-5.480466000	1.954951000	-1.523642000
1	-3.127771000	1.223762000	-1.481758000
1	1.530962000	-4.072800000	0.045719000
6	4.109330000	-0.180949000	0.041574000
6	4.252521000	1.022394000	0.754543000
6	5.225859000	-0.684059000	-0.649134000
6	5.471256000	1.699566000	0.776060000
6	6.443630000	-0.004803000	-0.629884000
6	6.571775000	1.189310000	0.083333000
1	3.411284000	1.416230000	1.317563000
1	5.133477000	-1.599847000	-1.225913000
1	5.562605000	2.623009000	1.341308000
1	7.291306000	-0.406401000	-1.178315000
1	7.521221000	1.717132000	0.099967000

S_1 E = – 1190.08292938 Hartree

6	2.732144000	-2.292509000	-0.211371000
6	2.830425000	-0.881297000	-0.024601000
6	1.619296000	-0.179152000	0.170284000
6	0.369364000	-0.808343000	0.169643000
6	0.310083000	-2.251350000	0.065696000
6	1.521189000	-2.952985000	-0.159353000
6	-0.884107000	-0.092388000	0.235291000
6	-2.078900000	-0.855919000	0.357425000
8	-2.021836000	-2.154684000	0.748490000
6	-0.890817000	-2.970699000	0.301945000
8	-1.129309000	-4.164605000	0.229794000
6	-0.931892000	1.374611000	0.180154000
6	-3.429437000	-0.406382000	0.087339000
6	-0.224448000	2.098676000	-0.806710000
6	-0.273268000	3.488706000	-0.835687000
6	-1.002266000	4.188577000	0.132291000
6	-1.698231000	3.488241000	1.122989000
6	-1.677779000	2.098089000	1.140296000
6	-4.515401000	-1.129181000	0.652977000
6	-5.824421000	-0.739009000	0.416793000
6	-6.097613000	0.360206000	-0.410120000
6	-5.043052000	1.062322000	-1.006253000

6	-3.727417000	0.690194000	-0.768190000
1	3.637460000	-2.876413000	-0.346800000
1	1.657719000	0.896321000	0.291509000
1	0.325278000	1.559260000	-1.570427000
1	0.254300000	4.028992000	-1.615992000
1	-1.030143000	5.274045000	0.111826000
1	-2.257865000	4.027931000	1.881019000
1	-2.211304000	1.556943000	1.914644000
1	-4.304577000	-1.978359000	1.291478000
1	-6.640710000	-1.289234000	0.875300000
1	-7.125128000	0.656859000	-0.599318000
1	-5.251762000	1.892258000	-1.674648000
1	-2.927508000	1.212728000	-1.276413000
1	1.483795000	-4.034020000	-0.249802000
6	4.123617000	-0.185731000	-0.045274000
6	4.317025000	1.037924000	0.637030000
6	5.230826000	-0.712730000	-0.749877000
6	5.543559000	1.696380000	0.611085000
6	6.457006000	-0.053569000	-0.770701000
6	6.625800000	1.157598000	-0.091982000
1	3.505324000	1.461616000	1.221223000
1	5.119672000	-1.634720000	-1.312904000
1	5.658518000	2.631330000	1.153968000
1	7.284275000	-0.483562000	-1.330005000
1	7.583001000	1.670946000	-0.109510000

2d

S_0 E = –1421.25936377 Hartree
ZPVE = 0.451657 Hartree
Thermal correction to Gibbs Free Energy = 0.391829 Hartree

6	-0.675268000	2.950794000	0.077513000
6	-0.972868000	1.569145000	0.035450000
6	0.083535000	0.653844000	-0.006781000
6	1.428343000	1.069814000	-0.009108000
6	1.692998000	2.458709000	0.048800000
6	0.638144000	3.384181000	0.087626000
6	2.545843000	0.129869000	-0.050870000
6	3.814586000	0.627822000	-0.034290000
8	4.051360000	1.984154000	0.045647000
6	3.065659000	2.947873000	0.093556000
8	3.422706000	4.107830000	0.166838000
6	2.273001000	-1.340115000	-0.042560000

6	5.099715000	-0.105505000	-0.077969000
6	1.718445000	-1.976079000	-1.165301000
6	1.449506000	-3.345726000	-1.146016000
6	1.725567000	-4.098885000	-0.002234000
6	2.269136000	-3.474426000	1.122460000
6	2.537748000	-2.104737000	1.103434000
6	6.188178000	0.373318000	0.674236000
6	7.417377000	-0.281987000	0.639930000
6	7.587078000	-1.416910000	-0.156643000
6	6.517925000	-1.889427000	-0.921170000
6	5.284206000	-1.241428000	-0.884552000
1	-1.481473000	3.674939000	0.134600000
1	-0.136462000	-0.405186000	-0.063414000
1	1.506082000	-1.395155000	-2.059007000
1	1.026297000	-3.823645000	-2.025278000
1	1.516462000	-5.164948000	0.012576000
1	2.482846000	-4.052267000	2.017509000
1	2.958811000	-1.621452000	1.980563000
1	6.064093000	1.259312000	1.287677000
1	8.243942000	0.096428000	1.234805000
1	8.546835000	-1.925167000	-0.186490000
1	6.644810000	-2.761591000	-1.556380000
1	4.468250000	-1.609589000	-1.495163000
1	0.876620000	4.441170000	0.139664000
6	-2.380010000	1.098279000	0.037474000
6	-2.751714000	-0.084086000	0.700624000
6	-3.387646000	1.819987000	-0.625424000
6	-4.071232000	-0.525358000	0.698547000
6	-4.706587000	1.376385000	-0.628643000
6	-5.079664000	0.193619000	0.033290000
1	-2.003328000	-0.657748000	1.239513000
1	-3.135406000	2.730651000	-1.160890000
1	-4.319167000	-1.451702000	1.208395000
1	-5.461556000	1.967318000	-1.138897000
6	-6.487539000	-0.278364000	0.030394000
6	-7.040923000	-0.909661000	1.158688000
6	-7.305083000	-0.106042000	-1.100876000
6	-8.363397000	-1.352488000	1.155826000
6	-8.627633000	-0.548597000	-1.103783000
6	-9.163253000	-1.173927000	0.024638000
1	-6.438357000	-1.032129000	2.054278000
1	-6.894022000	0.356260000	-1.993905000

1	-8.771491000	-1.830398000	2.042426000
1	-9.237774000	-0.411613000	-1.992566000
1	-10.193576000	-1.518709000	0.022506000

S_1 E = –1421.14317867 Hartree

6	0.670479000	2.942179000	0.067479000
6	1.008330000	1.555738000	-0.011466000
6	-0.087932000	0.649462000	-0.084515000
6	-1.419344000	1.062240000	-0.051198000
6	-1.722873000	2.473615000	-0.026754000
6	-0.635838000	3.383460000	0.048631000
6	-2.534046000	0.133781000	-0.053907000
6	-3.848594000	0.652383000	-0.126372000
8	-4.076694000	1.961490000	-0.364940000
6	-3.042910000	2.965675000	-0.187306000
8	-3.461705000	4.110359000	-0.212411000
6	-2.307445000	-1.319823000	-0.014528000
6	-5.089519000	-0.086774000	0.047961000
6	-1.503312000	-1.905237000	0.989160000
6	-1.287562000	-3.279420000	1.008644000
6	-1.838951000	-4.092853000	0.012249000
6	-2.623640000	-3.526018000	-0.997120000
6	-2.870269000	-2.157316000	-1.004287000
6	-6.264823000	0.407903000	-0.576938000
6	-7.474887000	-0.251802000	-0.427829000
6	-7.559803000	-1.398997000	0.373701000
6	-6.420128000	-1.877940000	1.029554000
6	-5.198731000	-1.236575000	0.873470000
1	1.461258000	3.684904000	0.094222000
1	0.117751000	-0.410683000	-0.144675000
1	-1.084929000	-1.278386000	1.769508000
1	-0.689501000	-3.718456000	1.801384000
1	-1.658871000	-5.163683000	0.024266000
1	-3.044517000	-4.152523000	-1.777631000
1	-3.472686000	-1.718287000	-1.792556000
1	-6.198881000	1.295402000	-1.194692000
1	-8.358949000	0.124636000	-0.933342000
1	-8.511819000	-1.906699000	0.496851000
1	-6.489624000	-2.745281000	1.678781000
1	-4.338564000	-1.590204000	1.426647000
1	-0.852918000	4.446696000	0.061583000
6	2.388803000	1.090002000	-0.017785000

6	2.748676000	-0.208520000	-0.465523000
6	3.459635000	1.910692000	0.424191000
6	4.064808000	-0.644481000	-0.470213000
6	4.773129000	1.467959000	0.420461000
6	5.123055000	0.176165000	-0.027005000
1	1.985702000	-0.883862000	-0.839841000
1	3.256369000	2.909049000	0.798587000
1	4.276482000	-1.655127000	-0.809022000
1	5.552044000	2.147656000	0.755312000
6	6.525285000	-0.292358000	-0.029878000
6	6.986120000	-1.217069000	-0.989042000
6	7.451881000	0.169325000	0.927134000
6	8.307766000	-1.660097000	-0.989551000
6	8.774560000	-0.270403000	0.923731000
6	9.212291000	-1.189268000	-0.033903000
1	6.307341000	-1.571877000	-1.759346000
1	7.124793000	0.860616000	1.698618000
1	8.634937000	-2.367993000	-1.746960000
1	9.463562000	0.098697000	1.679275000
1	10.242954000	-1.533150000	-0.035616000

2e

S_0 E = –1421.25242549 Hartree

ZPVE = 0.451285 Hartree

Thermal correction to Gibbs Free Energy = 0.391586 Hartree

6	-2.120698000	1.199362000	-1.320324000
6	-1.903450000	-0.112894000	-0.843718000
6	-0.606710000	-0.503588000	-0.502523000
6	0.488728000	0.375719000	-0.616125000
6	0.236544000	1.688466000	-1.078205000
6	-1.063719000	2.084252000	-1.432113000
6	1.849976000	-0.006207000	-0.249812000
6	2.840251000	0.922478000	-0.372068000
8	2.571681000	2.202671000	-0.808544000
6	1.321726000	2.657835000	-1.173816000
8	1.234516000	3.814106000	-1.539545000
6	2.108402000	-1.370292000	0.304779000
6	4.284229000	0.783513000	-0.077209000
6	2.016306000	-2.508426000	-0.512921000
6	2.239890000	-3.782022000	0.012909000
6	2.553707000	-3.937290000	1.365330000
6	2.640227000	-2.812550000	2.188656000

6	2.416302000	-1.539040000	1.662951000
6	4.976124000	1.870810000	0.487449000
6	6.339504000	1.779833000	0.760374000
6	7.039793000	0.608769000	0.461031000
6	6.365835000	-0.469486000	-0.116885000
6	5.000339000	-0.385729000	-0.385110000
1	-3.120813000	1.509829000	-1.602757000
1	-0.442215000	-1.506309000	-0.125887000
1	1.776909000	-2.392110000	-1.566758000
1	2.170935000	-4.651717000	-0.634795000
1	2.727779000	-4.928474000	1.774822000
1	2.879702000	-2.925110000	3.242533000
1	2.481615000	-0.666372000	2.306646000
1	4.438849000	2.785520000	0.714308000
1	6.855248000	2.626050000	1.205596000
1	8.103655000	0.539466000	0.670158000
1	6.905172000	-1.378264000	-0.368938000
1	4.493967000	-1.223812000	-0.849145000
1	-1.217922000	3.095456000	-1.793436000
6	-3.021161000	-1.097328000	-0.762150000
6	-4.261911000	-0.816002000	-0.136701000
6	-2.839998000	-2.346363000	-1.380912000
6	-5.274005000	-1.789450000	-0.185858000
6	-3.853525000	-3.301748000	-1.411225000
6	-5.082399000	-3.017748000	-0.815577000
1	-1.893548000	-2.552858000	-1.872546000
1	-6.219026000	-1.581510000	0.308011000
1	-3.685672000	-4.255002000	-1.904389000
1	-5.884749000	-3.750094000	-0.830281000
6	-4.537751000	0.443306000	0.614849000
6	-3.680292000	0.890075000	1.634353000
6	-5.704586000	1.180900000	0.353016000
6	-3.977898000	2.040874000	2.364021000
6	-6.000065000	2.335523000	1.079415000
6	-5.137432000	2.769958000	2.087779000
1	-2.781758000	0.324764000	1.863232000
1	-6.376355000	0.853211000	-0.435991000
1	-3.304738000	2.365904000	3.152821000
1	-6.903496000	2.896189000	0.854720000
1	-5.366817000	3.667975000	2.654832000

S_1 E = –1421.13534147 Hartree

6	2.038545000	-1.104578000	-1.247639000
6	1.865509000	0.206911000	-0.712133000
6	0.612116000	0.568556000	-0.229093000
6	-0.503301000	-0.312467000	-0.264766000
6	-0.260931000	-1.669053000	-0.704054000
6	1.003291000	-2.018008000	-1.218157000
6	-1.827804000	0.043788000	0.125392000
6	-2.811520000	-1.016863000	0.086034000
8	-2.373579000	-2.307309000	0.276139000
6	-1.220443000	-2.713265000	-0.451179000
8	-1.141535000	-3.898851000	-0.712001000
6	-2.208007000	1.387638000	0.566103000
6	-4.210835000	-0.902542000	-0.164656000
6	-1.773748000	2.555547000	-0.106567000
6	-2.148438000	3.817967000	0.340625000
6	-2.956069000	3.956484000	1.475718000
6	-3.405162000	2.815256000	2.147735000
6	-3.052818000	1.549434000	1.692729000
6	-5.059141000	-2.039134000	0.032972000
6	-6.422984000	-1.954327000	-0.180194000
6	-7.007451000	-0.751361000	-0.612898000
6	-6.194194000	0.366648000	-0.842370000
6	-4.825542000	0.304561000	-0.630909000
1	3.000243000	-1.391068000	-1.659038000
1	0.490045000	1.553122000	0.206477000
1	-1.184070000	2.460496000	-1.011998000
1	-1.819891000	4.698675000	-0.203813000
1	-3.242658000	4.944458000	1.824129000
1	-4.035096000	2.913230000	3.027233000
1	-3.399035000	0.667993000	2.222924000
1	-4.616398000	-2.967588000	0.372292000
1	-7.046437000	-2.827684000	-0.009115000
1	-8.078969000	-0.693125000	-0.780866000
1	-6.634100000	1.290680000	-1.207522000
1	-4.214199000	1.165887000	-0.865410000
1	1.156033000	-3.034656000	-1.566805000
6	2.979353000	1.193341000	-0.711778000
6	4.293956000	0.886622000	-0.270807000
6	2.723372000	2.481868000	-1.216564000
6	5.289464000	1.871909000	-0.382711000
6	3.721257000	3.449177000	-1.306183000
6	5.017728000	3.139513000	-0.893985000

1	1.724772000	2.710266000	-1.578021000
1	6.290139000	1.640883000	-0.028169000
1	3.489302000	4.431507000	-1.708289000
1	5.810297000	3.879652000	-0.959940000
6	4.668774000	-0.412709000	0.359515000
6	3.936573000	-0.942731000	1.435940000
6	5.809700000	-1.107919000	-0.076221000
6	4.329826000	-2.130933000	2.051268000
6	6.201090000	-2.299426000	0.536339000
6	5.462073000	-2.815882000	1.602792000
1	3.060773000	-0.413028000	1.798435000
1	6.384056000	-0.716746000	-0.911798000
1	3.752861000	-2.519862000	2.886069000
1	7.082032000	-2.824883000	0.177264000
1	5.765769000	-3.743061000	2.081056000

2f

S_0 E = –1343.84059320 Hartree
ZPVE = 0.417509 Hartree
Thermal correction to Gibbs Free Energy = 0.361071 Hartree

6	1.851736000	2.856496000	-0.015620000
6	2.060091000	1.476595000	0.202900000
6	0.953439000	0.624808000	0.257786000
6	-0.361104000	1.106514000	0.100474000
6	-0.535420000	2.490872000	-0.135715000
6	0.570942000	3.352406000	-0.187088000
6	-1.533203000	0.236197000	0.151628000
6	-2.764162000	0.792654000	-0.030759000
8	-2.911621000	2.140942000	-0.281076000
6	-1.869401000	3.040973000	-0.350725000
8	-2.148282000	4.201579000	-0.581118000
6	-1.351792000	-1.236594000	0.333021000
6	-4.090517000	0.135301000	-0.019964000
6	-0.917270000	-1.762687000	1.560481000
6	-0.734920000	-3.137389000	1.720299000
6	-0.979268000	-4.005913000	0.653745000
6	-1.403844000	-3.491974000	-0.573450000
6	-1.585544000	-2.117346000	-0.733575000
6	-5.080769000	0.575944000	-0.917205000
6	-6.345064000	-0.009715000	-0.921948000
6	-6.648780000	-1.033934000	-0.021929000
6	-5.678599000	-1.465424000	0.885554000

6	-4.409995000	-0.887552000	0.889170000
1	2.706205000	3.523854000	-0.068255000
1	1.109432000	-0.430869000	0.444323000
1	-0.730452000	-1.091179000	2.394432000
1	-0.404063000	-3.528711000	2.678409000
1	-0.837715000	-5.075931000	0.778053000
1	-1.591909000	-4.160591000	-1.409075000
1	-1.914478000	-1.720138000	-1.689731000
1	-4.852675000	1.376805000	-1.612440000
1	-7.094154000	0.336397000	-1.628599000
1	-7.635934000	-1.487675000	-0.023197000
1	-5.910575000	-2.249839000	1.600482000
1	-3.671638000	-1.221228000	1.608619000
1	0.399502000	4.407285000	-0.373168000
6	3.441641000	0.964417000	0.428130000
6	3.996933000	-0.121372000	-0.334417000
6	4.209576000	1.560843000	1.415965000
6	5.320436000	-0.581747000	-0.014753000
6	5.512678000	1.106906000	1.719592000
6	6.053190000	0.049932000	1.025656000
1	3.786927000	2.379321000	1.991918000
1	6.076297000	1.592092000	2.511339000
1	7.051283000	-0.313458000	1.257619000
6	3.318815000	-0.741962000	-1.421617000
1	2.334953000	-0.385887000	-1.705854000
6	3.895992000	-1.775459000	-2.127230000
6	5.882197000	-1.655526000	-0.758398000
1	6.881449000	-1.997309000	-0.499714000
6	5.186999000	-2.246166000	-1.788800000
1	3.357576000	-2.229135000	-2.954751000
1	5.629089000	-3.064563000	-2.350118000

S_1 E = –1343.72379301 Hartree

6	-1.708980000	2.835037000	-0.275585000
6	-2.018961000	1.442133000	-0.277672000
6	-0.977402000	0.533847000	-0.082802000
6	0.367345000	0.945757000	0.089582000
6	0.626043000	2.365334000	0.206363000
6	-0.426173000	3.276648000	-0.015493000
6	1.480904000	0.052092000	0.150851000
6	2.765640000	0.652387000	0.418567000
8	2.790120000	1.825919000	1.130552000

6	1.879290000	2.849888000	0.711923000
8	2.245766000	3.996036000	0.894201000
6	1.358802000	-1.397305000	-0.027245000
6	4.051706000	0.189825000	-0.001686000
6	0.580193000	-1.966704000	-1.063185000
6	0.479977000	-3.347053000	-1.201634000
6	1.137850000	-4.197629000	-0.305632000
6	1.916378000	-3.654178000	0.721302000
6	2.040532000	-2.275418000	0.850945000
6	5.227302000	0.802751000	0.534820000
6	6.487633000	0.368686000	0.164103000
6	6.640216000	-0.676286000	-0.762556000
6	5.503476000	-1.271827000	-1.325303000
6	4.232065000	-0.852840000	-0.964837000
1	-2.507982000	3.555056000	-0.423979000
1	-1.202247000	-0.525144000	-0.098113000
1	0.096768000	-1.317533000	-1.785332000
1	-0.105327000	-3.762929000	-2.016590000
1	1.052526000	-5.274850000	-0.414460000
1	2.430290000	-4.307924000	1.420026000
1	2.640193000	-1.858398000	1.653678000
1	5.115329000	1.604961000	1.253734000
1	7.365300000	0.840972000	0.596600000
1	7.632616000	-1.010278000	-1.051264000
1	5.614323000	-2.057885000	-2.067050000
1	3.372345000	-1.291889000	-1.453352000
1	-0.215500000	4.338568000	0.064870000
6	-3.401428000	0.987831000	-0.567635000
6	-4.080347000	-0.003975000	0.228167000
6	-4.062817000	1.535932000	-1.660206000
6	-5.387588000	-0.443704000	-0.178545000
6	-5.354586000	1.113874000	-2.039779000
6	-5.999383000	0.130184000	-1.324714000
1	-3.554071000	2.282273000	-2.264047000
1	-5.825853000	1.557689000	-2.912384000
1	-6.987456000	-0.214306000	-1.619670000
6	-3.543642000	-0.542071000	1.431586000
1	-2.586902000	-0.181469000	1.792347000
6	-4.226035000	-1.493426000	2.160259000
6	-6.058677000	-1.434611000	0.589731000
1	-7.041389000	-1.765356000	0.261949000
6	-5.490938000	-1.957446000	1.729490000

1	-3.793052000	-1.881981000	3.077975000
1	-6.017358000	-2.711629000	2.307958000

3a

S_0 E = –1192.55533731 Hartree
ZPVE = 0.412013 Hartree
Thermal correction to Gibbs Free Energy = 0.354476 Hartree

6	2.313498000	-2.601878000	-0.056231000
6	2.438722000	-1.191133000	-0.029982000
6	1.285950000	-0.394772000	-0.027406000
6	0.001233000	-0.967452000	-0.056735000
6	-0.095715000	-2.379914000	-0.066850000
6	1.058619000	-3.180484000	-0.069728000
6	-1.220267000	-0.166074000	-0.051497000
6	-2.420479000	-0.812100000	-0.064696000
8	-2.494782000	-2.188827000	-0.054638000
6	-1.401527000	-3.029601000	-0.051154000
8	-1.617258000	-4.225937000	-0.036880000
6	-1.126575000	1.323412000	0.034595000
6	-3.783103000	-0.233882000	-0.076340000
6	-0.633003000	2.078030000	-1.042184000
6	-0.534439000	3.467485000	-0.950489000
6	-0.922464000	4.122553000	0.220746000
6	-1.406441000	3.380459000	1.300326000
6	-1.505040000	1.991204000	1.208849000
6	-4.803441000	-0.866709000	0.657023000
6	-6.100016000	-0.356356000	0.653635000
6	-6.404741000	0.783845000	-0.093711000
6	-5.402846000	1.407928000	-0.840534000
6	-4.102515000	0.905668000	-0.834084000
1	3.207041000	-3.217002000	-0.059191000
1	1.394954000	0.682388000	-0.002770000
1	-0.334525000	1.573481000	-1.957402000
1	-0.156691000	4.037085000	-1.795157000
1	-0.846100000	5.204007000	0.291913000
1	-1.705963000	3.881993000	2.216514000
1	-1.880397000	1.416374000	2.050698000
1	-4.573724000	-1.757119000	1.232569000
1	-6.873272000	-0.851727000	1.234106000
1	-7.416688000	1.179144000	-0.099406000
1	-5.634028000	2.285273000	-1.438099000
1	-3.337852000	1.390610000	-1.429421000

1	0.941282000	-4.258824000	-0.078502000
6	3.732165000	-0.585847000	-0.003579000
6	4.836040000	-0.079765000	0.017848000
6	6.173524000	0.537966000	0.047225000
6	7.234777000	-0.517936000	-0.341977000
1	7.051433000	-0.906719000	-1.349153000
1	8.232608000	-0.064751000	-0.324247000
1	7.226610000	-1.360057000	0.357958000
6	6.214224000	1.714815000	-0.956750000
1	5.468451000	2.474841000	-0.701366000
1	7.204932000	2.183368000	-0.937596000
1	6.016853000	1.368316000	-1.976584000
6	6.458350000	1.062561000	1.475439000
1	7.452271000	1.523590000	1.508032000
1	5.719603000	1.814207000	1.772542000
1	6.432565000	0.247483000	2.206162000

S_1 E = –1192.43960067 Hartree

6	2.225215000	-2.549204000	-0.351046000
6	2.433879000	-1.157625000	-0.091834000
6	1.315041000	-0.347674000	0.160584000
6	0.004038000	-0.860345000	0.144738000
6	-0.170329000	-2.290906000	-0.011502000
6	0.959090000	-3.092983000	-0.296650000
6	-1.177809000	-0.050866000	0.252460000
6	-2.426937000	-0.753970000	0.338757000
8	-2.416128000	-2.026513000	0.839557000
6	-1.421483000	-2.918060000	0.277785000
8	-1.753598000	-4.086114000	0.184151000
6	-1.135329000	1.413329000	0.274542000
6	-3.723027000	-0.291441000	-0.074128000
6	-0.320954000	2.153977000	-0.614946000
6	-0.293240000	3.543520000	-0.562799000
6	-1.059306000	4.230444000	0.385940000
6	-1.871122000	3.515937000	1.273037000
6	-1.922706000	2.128284000	1.210282000
6	-4.879865000	-1.024301000	0.326956000
6	-6.148123000	-0.604540000	-0.037123000
6	-6.318974000	0.543615000	-0.826290000
6	-5.195762000	1.260480000	-1.258777000
6	-3.918596000	0.856054000	-0.900138000
1	3.083318000	-3.180148000	-0.560716000

1	1.478059000	0.703567000	0.365047000
1	0.249842000	1.631801000	-1.375056000
1	0.320517000	4.094832000	-1.269048000
1	-1.029795000	5.315292000	0.427111000
1	-2.465914000	4.043161000	2.013053000
1	-2.546738000	1.577165000	1.906151000
1	-4.751119000	-1.907817000	0.939905000
1	-7.015354000	-1.169061000	0.293350000
1	-7.315914000	0.866064000	-1.112363000
1	-5.319924000	2.130103000	-1.897711000
1	-3.064389000	1.393085000	-1.290909000
1	0.812677000	-4.159672000	-0.435181000
6	3.744326000	-0.605274000	-0.091136000
6	4.870121000	-0.142354000	-0.091680000
6	6.230707000	0.424712000	-0.086938000
6	7.244973000	-0.673849000	-0.483135000
1	7.030058000	-1.064157000	-1.483575000
1	8.260400000	-0.260620000	-0.485561000
1	7.215043000	-1.509345000	0.224253000
6	6.305824000	1.590693000	-1.102231000
1	5.593687000	2.381780000	-0.844283000
1	7.314042000	2.021571000	-1.102028000
1	6.080002000	1.243164000	-2.115895000
6	6.563317000	0.951763000	1.330032000
1	7.574291000	1.376087000	1.343017000
1	5.858203000	1.732951000	1.633336000
1	6.519010000	0.144701000	2.068875000

3b

S_0 E = –1266.35636743 Hartree
ZPVE = 0.380326 Hartree
Thermal correction to Gibbs Free Energy = 0.322290 Hartree

6	-1.715643000	2.821544000	-0.048547000
6	-1.927313000	1.420128000	-0.027137000
6	-0.826303000	0.552041000	-0.024125000
6	0.490815000	1.044434000	-0.049971000
6	0.674939000	2.448442000	-0.056063000
6	-0.427280000	3.319714000	-0.058007000
6	1.660188000	0.168764000	-0.046029000
6	2.897958000	0.739666000	-0.059330000
8	3.057110000	2.109089000	-0.045760000
6	2.018557000	3.016017000	-0.037816000

8	2.307662000	4.196625000	-0.018672000
6	1.474171000	-1.312055000	0.039059000
6	4.222300000	0.078763000	-0.076145000
6	0.936452000	-2.034438000	-1.038655000
6	0.751214000	-3.415039000	-0.947040000
6	1.095743000	-4.092827000	0.224861000
6	1.623653000	-3.382339000	1.305136000
6	1.808648000	-2.001902000	1.213930000
6	5.282324000	0.647153000	0.653775000
6	6.545624000	0.059351000	0.643239000
6	6.777480000	-1.095542000	-0.107693000
6	5.736278000	-1.656441000	-0.850834000
6	4.468747000	-1.076523000	-0.837316000
1	-2.569228000	3.490885000	-0.051460000
1	-1.001616000	-0.516272000	-0.002444000
1	0.671692000	-1.512385000	-1.954420000
1	0.340086000	-3.960097000	-1.792303000
1	0.951860000	-5.167382000	0.295955000
1	1.890103000	-3.901528000	2.221691000
1	2.217992000	-1.451413000	2.056203000
1	5.109734000	1.548596000	1.232084000
1	7.350050000	0.505901000	1.220940000
1	7.763729000	-1.551064000	-0.118963000
1	5.911165000	-2.544872000	-1.451098000
1	3.673676000	-1.513050000	-1.430310000
1	-0.242496000	4.388463000	-0.063325000
6	-3.251599000	0.897680000	-0.007509000
6	-4.386803000	0.459069000	0.006252000
6	-5.716259000	-0.054403000	0.021328000
6	-5.945791000	-1.445647000	0.043152000
6	-6.820554000	0.822645000	0.013728000
6	-7.246962000	-1.941384000	0.056781000
6	-8.117753000	0.316698000	0.027464000
6	-8.335460000	-1.064116000	0.048914000
1	-5.098161000	-2.123933000	0.049207000
1	-6.647978000	1.894302000	-0.002995000
1	-7.412624000	-3.014846000	0.073492000
1	-8.961356000	1.001067000	0.021373000
1	-9.349002000	-1.454804000	0.059433000

S_1 E = –1266.24539919 Hartree

6	-1.707703000	2.839832000	-0.172811000

6	-1.966339000	1.436051000	-0.066324000
6	-0.832018000	0.567441000	0.037055000
6	0.470459000	1.048171000	0.006781000
6	0.702607000	2.471632000	-0.053513000
6	-0.423623000	3.335587000	-0.157208000
6	1.637595000	0.177820000	0.067436000
6	2.919373000	0.764107000	0.133584000
8	3.084805000	2.092538000	0.280432000
6	1.996687000	3.034033000	0.094116000
8	2.352999000	4.199288000	0.095823000
6	1.486758000	-1.283480000	0.088601000
6	4.199564000	0.074059000	0.032320000
6	0.718579000	-1.950065000	-0.894038000
6	0.574652000	-3.332268000	-0.858577000
6	1.159521000	-4.075026000	0.174275000
6	1.907360000	-3.428812000	1.163943000
6	2.085389000	-2.050912000	1.115605000
6	5.325158000	0.638482000	0.685036000
6	6.567582000	0.028814000	0.599850000
6	6.731732000	-1.134251000	-0.165599000
6	5.640512000	-1.681423000	-0.848712000
6	4.387058000	-1.090829000	-0.754469000
1	-2.549571000	3.521734000	-0.250086000
1	-1.017133000	-0.493279000	0.149956000
1	0.275067000	-1.377799000	-1.701639000
1	0.006504000	-3.834034000	-1.635804000
1	1.033288000	-5.153075000	0.205741000
1	2.352109000	-4.000887000	1.972353000
1	2.656525000	-1.549535000	1.889604000
1	5.197182000	1.539234000	1.273405000
1	7.414785000	0.456851000	1.126721000
1	7.708928000	-1.602051000	-0.239172000
1	5.772053000	-2.562047000	-1.469615000
1	3.562898000	-1.496660000	-1.326701000
1	-0.248337000	4.405104000	-0.208475000
6	-3.267948000	0.923760000	-0.054341000
6	-4.409285000	0.469084000	-0.040731000
6	-5.722438000	-0.052145000	-0.021780000
6	-5.952274000	-1.445160000	0.110558000
6	-6.848528000	0.802447000	-0.133004000
6	-7.247374000	-1.951437000	0.130589000
6	-8.138025000	0.282256000	-0.111584000

6	-8.349674000	-1.095462000	0.020157000
1	-5.100924000	-2.113944000	0.197376000
1	-6.690481000	1.872081000	-0.234978000
1	-7.400288000	-3.022812000	0.233507000
1	-8.986851000	0.955889000	-0.198090000
1	-9.359147000	-1.496165000	0.036456000

4

S_0 E = –1476.59489217 Hartree
ZPVE = 0.467361 Hartree
Thermal correction to Gibbs Free Energy = 0.405008 Hartree

6	1.858744000	-2.259287000	-0.585576000
6	1.838806000	-0.875960000	-0.275214000
6	0.603399000	-0.236492000	-0.093742000
6	-0.608480000	-0.930961000	-0.230635000
6	-0.564878000	-2.316201000	-0.527067000
6	0.674477000	-2.957334000	-0.700110000
6	-1.908141000	-0.288536000	-0.039604000
6	-3.033585000	-1.045085000	-0.181444000
8	-2.965891000	-2.391611000	-0.463795000
6	-1.785571000	-3.092680000	-0.636648000
8	-1.880020000	-4.284732000	-0.866219000
6	-1.971882000	1.148579000	0.365866000
6	-4.449503000	-0.626699000	-0.064317000
6	-1.577590000	2.166873000	-0.517492000
6	-1.626051000	3.506196000	-0.126944000
6	-2.065264000	3.848351000	1.154147000
6	-2.451731000	2.843184000	2.043458000
6	-2.401793000	1.504083000	1.653308000
6	-5.379286000	-1.507864000	0.517524000
6	-6.722496000	-1.152771000	0.625024000
6	-7.164825000	0.080213000	0.139771000
6	-6.253081000	0.953995000	-0.457151000
6	-4.907079000	0.606041000	-0.560090000
1	2.805236000	-2.763272000	-0.741733000
1	0.587219000	0.813595000	0.165632000
1	-1.238980000	1.907215000	-1.516990000
1	-1.321603000	4.281396000	-0.824761000
1	-2.103199000	4.890864000	1.457829000
1	-2.789798000	3.099954000	3.043737000
1	-2.700829000	0.724414000	2.348163000
1	-5.042405000	-2.470290000	0.887698000

1	-7.424452000	-1.841710000	1.086554000
1	-8.212896000	0.355053000	0.219985000
1	-6.590432000	1.907989000	-0.852697000
1	-4.212648000	1.286873000	-1.038280000
1	0.680695000	-4.015468000	-0.939949000
7	3.039054000	-0.160207000	-0.158240000
6	4.238956000	-0.806113000	0.274095000
6	4.238833000	-1.618725000	1.417490000
6	5.434084000	-0.611555000	-0.433120000
6	5.416221000	-2.239229000	1.834616000
6	6.610758000	-1.221530000	0.000659000
6	6.607483000	-2.041572000	1.131930000
1	3.318117000	-1.759073000	1.975355000
1	5.434841000	0.016380000	-1.318650000
1	5.403110000	-2.866986000	2.721355000
1	7.530384000	-1.063380000	-0.555979000
1	7.524398000	-2.520005000	1.463746000
6	3.090969000	1.241045000	-0.440401000
6	3.686892000	2.120196000	0.474443000
6	2.572964000	1.743779000	-1.643315000
6	3.765187000	3.482770000	0.186109000
6	2.639967000	3.109568000	-1.916564000
6	3.238990000	3.984745000	-1.006449000
1	4.087050000	1.732090000	1.405932000
1	2.123669000	1.062340000	-2.359164000
1	4.229859000	4.154170000	0.902925000
1	2.236737000	3.486976000	-2.852308000
1	3.296864000	5.046929000	-1.225945000

S_1 E = –1476.48908667 Hartree

6	1.798384000	-2.176419000	-1.008238000
6	1.795483000	-0.870450000	-0.436838000
6	0.646689000	-0.207491000	-0.079527000
6	-0.639428000	-0.798705000	-0.299356000
6	-0.629721000	-2.137510000	-0.843948000
6	0.568084000	-2.780436000	-1.194648000
6	-1.867645000	-0.163025000	0.018278000
6	-3.072625000	-0.848149000	-0.206185000
8	-3.017888000	-2.202908000	-0.606745000
6	-1.878212000	-2.862758000	-0.977100000
8	-2.007129000	-4.016295000	-1.370463000
6	-1.844705000	1.173215000	0.684492000

6	-4.446088000	-0.407569000	-0.104299000
6	-1.374072000	2.317704000	0.017518000
6	-1.329931000	3.558083000	0.658948000
6	-1.759284000	3.679778000	1.982240000
6	-2.228783000	2.550236000	2.659147000
6	-2.267710000	1.312343000	2.017670000
6	-5.500154000	-1.365503000	-0.051045000
6	-6.832311000	-0.978476000	0.030061000
6	-7.191025000	0.374704000	0.054145000
6	-6.172161000	1.333959000	-0.016780000
6	-4.835947000	0.961942000	-0.097665000
1	2.727418000	-2.653958000	-1.295996000
1	0.718790000	0.777755000	0.365984000
1	-1.049908000	2.232244000	-1.016583000
1	-0.966217000	4.430042000	0.121163000
1	-1.729536000	4.644595000	2.481487000
1	-2.561506000	2.633082000	3.690757000
1	-2.633032000	0.437069000	2.547797000
1	-5.251950000	-2.419945000	-0.069309000
1	-7.602917000	-1.745138000	0.076594000
1	-8.233457000	0.673935000	0.115931000
1	-6.424127000	2.392357000	-0.023310000
1	-4.084576000	1.736051000	-0.182893000
1	0.503327000	-3.780830000	-1.611350000
7	3.073870000	-0.213257000	-0.234914000
6	3.997091000	-0.801647000	0.629328000
6	3.534207000	-1.602683000	1.701618000
6	5.390430000	-0.649166000	0.418702000
6	4.447399000	-2.199216000	2.557033000
6	6.287039000	-1.261216000	1.280420000
6	5.823907000	-2.032415000	2.354959000
1	2.469405000	-1.712043000	1.864659000
1	5.748083000	-0.095574000	-0.441217000
1	4.088322000	-2.794746000	3.389818000
1	7.352575000	-1.157098000	1.104328000
1	6.532168000	-2.510737000	3.023549000
6	3.333721000	0.978885000	-0.922222000
6	4.113308000	1.998559000	-0.327485000
6	2.775030000	1.180152000	-2.205637000
6	4.342005000	3.180753000	-1.018201000
6	3.024787000	2.362483000	-2.884570000
6	3.806755000	3.367495000	-2.297759000

1	4.486333000	1.871973000	0.682094000
1	2.183567000	0.394829000	-2.660271000
1	4.922237000	3.968745000	-0.549380000
1	2.613250000	2.504288000	-3.878486000
1	3.987702000	4.294781000	-2.831649000

References

[S1] C. White, A. Yates and P. M. Maitlis, *Inorg. Synth.*, 1992, **29**, 228.

[S2] H. A. Tayim, A. Bouldoukian and F. Awad, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3799.

[S3] W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, 1968, **72**, 3251.

[S4] Gaussian 09, Revision D.01. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.V.; Bloino, J., Janesko, B.G., Gomperts, R., Mennucci, B., Hratchian, H.P., Ortiz, J.V., Izmaylov, A.F., Sonnenberg, J.L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V.G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery Jr., J.A., Peralta, J.E., Ogliaro, F., Bearpark, M.J., Heyd, J.J., Brothers, E.N., Kudin, K.N., Staroverov, V.N., Keith, T.A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A.P., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Millam, J.M., Klene, M., Adamo, C., Cammi, R., Ochterski, J.W., Martin, R.L., Morokuma, K., Farkas, O., Foresman, J.B., Fox, D.J. Gaussian, Inc., Wallingford CT, **2016**.

[S5] S. Grimme, *J. Chem. Phys*., 2013, **138**, 244104.