Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Controlled Photorelease of Alkynoic Acids and their Decarboxylative Deprotection for Copper-Catalyzed Azide/Alkyne Cycloaddition

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Materials and Methods

Materials. The reagents and solvents of the highest purity available were used as purchased, or they were purified/dried using the standard methods when necessary. All glassware was oven-dried prior to use. Purification procedures were performed using silica gel columns or recrystallization. Flash column chromatography was performed using silica gel Merck 60 (230–400 mesh).

Methods. In the spectroscopy measurements, the lowest possible intensity of incident light was used; the spectroscopic identification of the samples was carried out after each measurement to ensure that no unwanted photodegradation processes occurred. All measurements were accomplished using fresh solutions prepared in the dark. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ on 75, 125, 300 and 700 MHz spectrometers. ^{1}H chemical shifts are reported in ppm relative to the tetramethylsilane signal (TMS, δ = 0.00 ppm), using the residual solvent signal as an internal reference. ^{13}C NMR chemical shifts are reported in ppm relative to the $CDCl_3$ signal as an internal standard. High resolution mass spectra (HRMS) were recorded using an ESI technique. Absorption spectra and the molar absorption coefficients were obtained on a UV-vis spectrometer with matched 1.0- or 0.1-cm quartz cells. Molar absorption coefficients were determined from the absorption spectra: The average values were obtained from three independent measurements with solutions of different concentrations. No dependence of the molar absorption coefficient on the solution concentration was observed in the range of 1×10^{-3}–1×10^{-6} M.

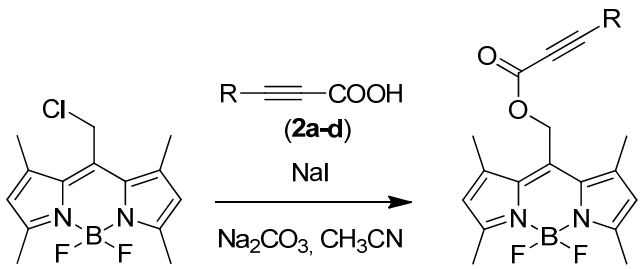
Synthetic Procedures

8-Chloromethyl-4,4'-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (1). This compound was prepared using a slightly modified procedure described in the literature.[1, 2] Chloroacetyl chloride (0.57 mL, 7.17 mmol, 1 equiv.) was added dropwise to the solution of 2,4-dimethylpyrrole (1.62 mL, 15.7 mmol, 2.2 equiv.) in dry dichloromethane (120 mL) at 0 °C under nitrogen. The reaction mixture was stirred at 22 °C for 8 h and then cooled to 0 °C. Triethylamine (2.5 mL, 17.9 mmol, 2.5 equiv.) and after 5 min $BF_3{\cdot}Et_2O$ (46%, 4.8 mL, 17.9 mmol, 2.5 equiv.) were added. The reaction mixture was stirred at 22 °C for 8 h. Aq. HCl (10%, 50 mL) was added, and the crude mixture was extracted with dichloromethane

(3 × 40 mL). The collected organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated to dryness under reduced pressure. The product was purified by flash chromatography on silica gel (cyclohexane/dichloromethane, 6 : 4 → 1 : 1). Yield 1.08 g (51%). Red solid. The spectroscopic data are in good agreement with those from the literature.[1, 2]

Synthesis of *meso*-Methyl BODIPY Propiolates 3a–d (General Procedure)

Chloride **1** (1 equiv.) was dissolved in acetonitrile, and the corresponding carboxylic acid (1.1 equiv.), Na_2CO_3 (1.2 equiv.) and a catalytic amount of NaI (0.1 equiv.) were added. The reaction mixture was stirred at the given temperature until the starting material was consumed (TLC). After the reaction completion, the mixture was filtered and the organic material was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with water (20 mL), dried over anhydrous magnesium sulfate, filtered and concentrated to dryness under reduced pressure. The compounds were purified by flash chromatography on silica gel or by recrystallization.



1 **3a-d**

4,4'-Difluoro-1,3,5,7-tetramethyl-8-(((3-phenylpropynoyl)oxy)methyl)-4-bora-3a,4a-diaza-*s*-indacene (3a). The title compound was prepared according to the general procedure from **1** (50 mg, 0.17 mmol), phenylpropiolic acid (21 mg, 0.19 mmol), Na_2CO_3 (21 mg, 0.20 mmol) and NaI (3 mg, 0.017 mmol) in acetonitrile (5 mL); the reaction time: 12 h. Purified by flash chromatography (hexane/ethyl acetate, 5 : 1). Yield 55 mg (80%). Red solid. Mp: 178.4–180.2 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ (ppm) 7.58 (d, J = 7.4 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 2H), 6.10 (s, 2H), 5.45 (s, 2H), 2.54 (s, 6H), 2.41 (s, 6H) (Figure S1). ^{13}C NMR (175 MHz, $CDCl_3$): δ (ppm) 157.2, 153.7, 141.8, 133.4, 132.9, 132.2, 131.2, 128.9, 122.7,

119.3, 88.3, 79.8, 59.2, 15.9, 14.9 (Figure S2). HRMS-ESI *m/z*: $[M]^+$ calcd for $C_{23}H_{21}BF_2N_2O_2Na$ 429.1560, found 429.1562 (Figure S13).

4,4'-Difluoro-8-(((3-(4-methoxyphenyl)propynoyl)oxy)methyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (3b). The title compound was prepared according to the general procedure from **1** (100 mg, 0.34 mmol), 3-(4-methoxyphenyl)propiolic acid[3] (65 mg, 0.37 mmol), Na_2CO_3 (43 mg, 0.40 mmol) and NaI (5 mg, 0.034 mmol) in acetonitrile (10 mL); the reaction time: 12 h. Purified by recrystallization from hexane containing a small amount of dichloromethane. Yield 140 mg (95%). Red solid. Mp: 108.4−182.0 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ (ppm) 7.53 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.10 (s, 2H), 5.43 (s, 2H), 3.83 (s, 3H), 2.54 (s, 6H), 2.40 (s, 6H) (Figure S3). ^{13}C NMR (175 MHz, $CDCl_3$): δ (ppm) 162.0, 157.0, 153.9, 141.9, 135.5, 133.0, 132.4, 122.7, 114.5, 111.2, 89.1, 79.4, 59.0, 55.6, 15.9, 14.9 (Figure S4). HRMS-ESI *m/z*: $[M]^+$ calcd for $C_{24}H_{23}BF_2N_2O_3Na$ 459.1666, found 459.1668 (Figure S14).

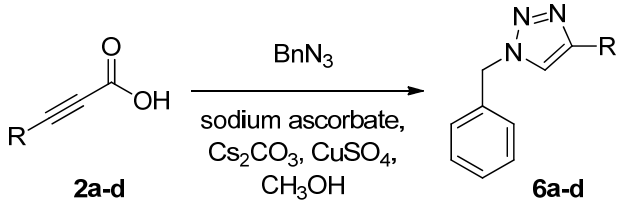
4,4'-Difluoro-8-((hex-2-ynoyloxy)methyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (3c). The title compound was prepared according to the general procedure from **1** (150 mg, 0.51 mmol), 2-hexynoic acid (68 mg, 0.61 mmol), Na_2CO_3 (64 mg, 0.61 mmol) and NaI (8 mg, 0.051 mmol) in acetonitrile (15 mL); the reaction time was 12 h. Purified by recrystallization from hexane/dichloromethane (1 : 10). Yield 145 mg (77%). Red solid. Mp: 127.5−128.4 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ (ppm) 6.08 (s, 2H), 5.36 (s, 2H), 2.53 (s, 6H), 2.37 (s, 6H), 2.31 (t, J = 7.2 Hz, 2H), 1.60 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H) (Figure S5). ^{13}C NMR (175 MHz, $CDCl_3$): δ (ppm) 157.0, 153.3, 141.9, 133.1, 132.4 122.7, 91.6, 72.4, 59.0, 21.1, 20.8, 15.8, 14.8, 13.6 (Figure S6). HRMS-ESI *m/z*: $[M]^+$ calcd for $C_{20}H_{23}BF_2N_2O_2Na$ 395.1717, found 395.1719 (Figure S15).

8-((3-(Cyclopropyl)propynoyloxy)methyl)-4,4'-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (3d). The title compound was prepared according to the general procedure from **1** (100 mg, 0.34 mmol), 3-cyclopropyl-2-propynoic acid (41 mg, 0.37 mmol), Na_2CO_3 (43 mg, 0.40 mmol) and NaI (5 mg, 0.034 mmol) in acetonitrile (10 mL); the reaction time: 12 h. Purified by recrystallization from hexane/dichloromethane (10 : 1). Yield 98 mg (79%). Red solid. Mp: 183.0−184.7 °C. ^{1}H NMR (700 MHz, $CDCl_3$): δ (ppm) 6.08 (s, 2H), 5.34 (s, 2H), 2.53 (s, 6H), 2.36 (s, 6H), 1.39-1.35 (m, 1H), 0.97-0.91 (m, 4H) (Figure S7). ^{13}C NMR (175 MHz, $CDCl_3$): δ (ppm) 157.0, 153.6, 141.8, 133.0, 132.4, 122.5, 95.5, 67.8, 58.8, 15.9,

14.8, 9.7, 0.34 (Figure S8). HRMS-ESI *m/z*: $[M]^+$ calcd for $C_{20}H_{21}BF_2N_2O_2Na$ 393.1560, found 393.1564 (Figure S16).

Preparation of Triazoles 6a–d (General Procedure)

The corresponding carboxylic acid (1 equiv.), sodium ascorbate (1.2 equiv.), Cs_2CO_3 (0.75 equiv.), $CuSO_4 \cdot 5H_2O$ (1 equiv.) and benzyl azide[4] (1.1 equiv.) were dissolved in methanol. The reaction mixture was stirred at 60 °C until the starting material was consumed (TLC). The mixture was then filtered and concentrated to dryness under reduced pressure. Then, the organic material was dissolved with diethyl ether (3 x 10 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated to dryness under reduced pressure.



2a-d **6a-d**

1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (6a). The title compound was prepared according to the general procedure for synthesis of triazoles from phenylpropiolic acid (82 mg, 0.56 mmol), sodium ascorbate (133 mg, 0.67 mmol), Cs_2CO_3 (140 mg, 0.43 mmol), $CuSO_4 \cdot 5H_2O$ (140 mg, 0.56 mmol) and benzyl azide (82 mg, 0.62 mmol) in methanol (4 mL); the reaction time: 30 min. Yield 112 mg (85%). White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.82-7.79 (m, 2H), 7.66 (s, 1H), 7.42-7.31 (m, 8H), 5.57 (s, 2H) (Figure S9). The spectroscopic data are in good agreement with those from the literature.[5]

1-Benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (6b). The title compound was prepared according to the general procedure for synthesis of triazoles from 3-(4-methoxyphenyl)propiolic acid (99 mg, 0.56 mmol), sodium ascorbate (133 mg, 0.67 mmol), Cs_2CO_3 (140 mg, 0.43 mmol), $CuSO_4 \cdot 5H_2O$ (140 mg, 0.56 mmol) and benzyl azide (82 mg, 0.62 mmol) in methanol (4 mL); the reaction time 30 min. Yield 106 mg (95%). Light yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$): δ (ppm) 7.72 (d, J = 8.8 Hz, 2H), 7.57 (s, 1H), 7.42-7.29 (m, 5H), 6.93 (d, J = 8.8 Hz, 2H), 5.56 (s, 2H), 3.83 (s, 3H) (Figure S10). The spectroscopic data are in good agreement with those from the literature.[6]

1-Benzyl-4-propyl-1*H*-1,2,3-triazole (6c). The title compound was prepared according to the general procedure for synthesis of triazoles from 2-hexynoic acid (112 mg, 0.56 mmol), sodium ascorbate (133 mg, 0.67 mmol), Cs_2CO_3 (140 mg, 0.43 mmol), $CuSO_4{\cdot}5H_2O$ (140 mg, 0.56 mmol) and benzyl azide (82 mg, 0.62 mmol) in methanol (4 mL); the reaction time: 30 min. Yield 93 mg (83%). White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.37-7.35 (m, 3H), 7.25-7.24 (m, 2H), 7.18 (s, 1H), 5.49 (s, 2H), 2.66 (t, J = 7.4 Hz, 2H), 1.67 (m, 2H), 0.94 (t, J = 7.0 Hz, 3H) (Figure S11). The spectroscopic data are in good agreement with those from the literature.[7]

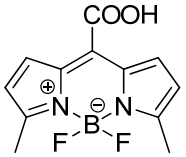
1-Benzyl-4-cyclopropyl-1*H*-1,2,3-triazole (6d). The title compound was prepared according to the general procedure for synthesis of triazoles from 3-cyclopropylpropiolic acid (62 mg, 0.56 mmol), sodium ascorbate (133 mg, 0.67 mmol), Cs_2CO_3 (140 mg, 0.43 mmol), $CuSO_4{\cdot}5H_2O$ (140 mg, 0.56 mmol) and benzyl azide (82 mg, 0.62 mmol) in methanol (4 mL); the reaction time: 30 min. Yield 108 mg (97%). Colorless oil. ^{1}H NMR (700 MHz, $CDCl_3$): δ (ppm) 7.40-7.33 (m, 3H), 7.25-7.23 (m, 2H), 7.14 (s, 1H), 5.46 (s, 2H), 1.96-1.87 (m, 1H), 0.95-0.89 (m, 2H), 0.87-0.79 (m, 2H) (Figure S12). The spectroscopic data are in good agreement with those from the literature.[6]

Photochemical Experiments

Irradiation in the UV Cuvettes. A solution of the given compound (3.0 mL) in a matched 1.0 or 0.1 cm quartz PTFE screw-cap fluorescence cuvettes equipped with a stir bar (a 1.0 cm cuvette only) was irradiated with a light source (LEDs emitting at the selected wavelength: λ_{max} = 525 nm; power 120 mW). The reaction progress was monitored by HPLC (a reverse phase column, methanol/H_2O/0.1% formic acid).

Photorelease of Alkynoates. The chemical yields of photorelease of the compound **2** from **3** under irradiation at λ_{irr} = 525 nm (LEDs; power 120 mW) in degassed (purging by argon) methanol solutions ($c \approx 1 \times 10^{-4}$ M) were determined by HPLC in 5 min intervals.

Determination of Quantum Yields. The quantum yields of the photoproduct **2** formation in both aerated and degassed (purging with argon) methanol solutions were determined at λ_{irr} = 505 nm (LEDs; power 120 mW) using the BODIPY derivative **7**[8] as an actinometer dissolved in



7

aqueous phosphate buffered saline (I = 0.1 M, pH = 7.4) according to the published procedure.[8] The actinometer absorbance was maintained above 2 to ensure that all photons were absorbed. In order to keep the proper concentration of irradiated starting material due to calibration by HPLC ($c \approx 1 \times 10^{-4}$ M), the absorbance of irradiated sample in a 1 cm cuvette was maintained also above 2. All quantum yield measurements were repeated at least 5 times with independently prepared samples.

Decarboxylation and Click Reactions

Procedure for Decarboxylation of Acids 2. The stock solution ($c = 1.4 \times 10^{-1}$ M) of **2a** in methanol (15 mL) was prepared. Sodium ascorbate (0.5 g, 2.5 mmol), Cs_2CO_3 (0.52 g, 1.6 mmol) and $CuSO_4 \cdot 5H_2O$ (0.53 g, 2.1 mmol) were added to the solution in a 25 mL round-bottom flask. The mixture was heated at 60 °C. The progress of the reaction was monitored by HPLC. Degassing the solvent did not have any effect on the reaction conversion. See Table S1 for the data from the reaction optimization: The best selected conditions are shown in red.

The rate constant of Decarboxylation of 2a. An aliquot (0.1 mL) of the reaction mixture obtained by the same procedure as described above was diluted to the total of 10 mL with methanol, and HPLC analyses were carried out in 10 min intervals to obtain the rate constant of $k = 6.4 \times 10^{-3}$ $M^{-1} s^{-1}$ (Figure S17).

Procedure for a Tandem Photorelease/Decarboxylation/Click Process (A General Procedure). The photoreactor for this experiment was based on a 250 mL flask containing a degassed solution of **3** rotating slowly to make a thin film which was irradiated by a white high-power LED (100 W). This method, inspired by the reported equipment based on a rotary evaporator,[9] helps to reduce an internal filter effect of solutes possessing high molar absorption coefficients. Thus, the solution of **3** (c ~10^{-3}–10^{-4} M) in methanol (100 mL) was degassed by a freeze-pump-thaw technique (3 cycles), and the solution in the rotating flask was irradiated using a white light until the complete conversion of the starting material was achieved to give **2**, and the sample was concentrated to dryness under reduced pressure. The resulting solid mass containing **2** (1 equiv.), sodium ascorbate (2 equiv.), Cs_2CO_3 (0.75 equiv.), $CuSO_4 \cdot 5H_2O$ (1 equiv.) and benzyl azide (1.2 equiv.) were dissolved in methanol (c ~1×10^{-4} M). The reaction mixture was stirred at 60 °C until the starting material (**2**) was

consumed (TLC). The mixture was then filtered and the overall yield of the triazole **6** (over 3 steps) was determined by HPLC.

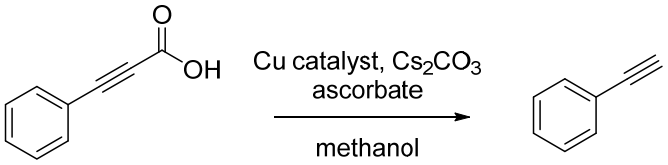
Tandem Photorelease/Decarboxylation/Click Process from 3a. The solution of **3a** (*c* = 1.1 × 10^{-3} M) in methanol (100 mL) was irradiated for 4 h to give **2a** in 88% yield. After solvent removal, the isolated product **2a** (14.1 mg, 0.096 mmol), sodium ascorbate (38 mg, 0.193 mmol), Cs_2CO_3 (24 mg, 0.073 mmol), $CuSO_4{\cdot}5H_2O$ (24 mg, 0.096 mmol) and benzyl azide (15 mg, 0.116 mmol) were dissolved in methanol (0.7 mL). The reaction mixture was stirred at 60 °C for 2 h. The overall yield of the triazole **6a** was 84%.

Tandem Photorelease/Decarboxylation/Click Process from 3b. The solution of **3b** (*c* = 4.7 × 10^{-4} M) in methanol (100 mL) was irradiated for 3 h to give **2b** in 86% yield. After solvent removal, the isolated product **2b** (7.1 mg, 0.04 mmol), sodium ascorbate (16 mg, 0.081 mmol), Cs_2CO_3 (10 mg, 0.031 mmol), $CuSO_4{\cdot}5H_2O$ (10 mg, 0.04 mmol) and benzyl azide (6.4 mg, 0.049 mmol) were dissolved in methanol (0.3 mL). The reaction mixture was stirred at 60 °C for 2 h. The overall yield of the triazole **6b** was 79%.

Tandem Photorelease/Decarboxylation/Click Process from 3c. The solution of **3c** (*c* = 6.65 × 10^{-4} M) in methanol (100 mL) was irradiated for 16 h to give **2c** in 81% yield. After solvent removal, the isolated product **2c** (6 mg, 0.054 mmol), sodium ascorbate (21 mg, 0.108 mmol), Cs_2CO_3 (13 mg, 0.040 mmol), $CuSO_4{\cdot}5H_2O$ (13 mg, 0.054 mmol) and benzyl azide (9 mg, 0.065 mmol) were dissolved in methanol (0.4 mL). The reaction mixture was stirred at 60 °C for 2 h. The overall yield of the triazole **6c** was 78%.

Tandem Photorelease/Decarboxylation/Click Process from 3d. The solution of **3d** (*c* = 1.24 × 10^{-3} M) in methanol (100 mL) was irradiated for 12 h to give **2d** in 79% yield. . After solvent removal, the isolated product **2d** (11 mg, 0.098 mmol), sodium ascorbate (39 mg, 0.195 mmol), Cs_2CO_3 (24 mg, 0.073 mmol), $CuSO_4{\cdot}5H_2O$ (24mg, 0.098 mmol) and benzyl azide (16 mg, 0.117 mmol) were dissolved in methanol (0.7 mL). The reaction mixture was stirred at 60 °C for 2 h. The overall yield of the triazole **6d** was 75%.

Table S1. Optimization of the reaction conditions of decarboxylation of alkynoic acids



2a **5a**

c_2/M [1 equiv.]	Cu catalyst [equiv.]	ascorbate [equiv.]	Cs_2CO_3 [equiv.]	T / °C	reaction time [conversion of **2a**]
7×10^{-2}	CuI [0.2]	0	0.5	60	7 h [complete]
		0.4		60[b]	7 h [complete]
		0		22	days [complete]
		0.4		22[b]	days [complete]
7×10^{-5}	CuI [0.2]	0		60	days [complete]
7×10^{-5}	CuI [1]	0		60	510 min [6%]
7×10^{-3}	CuI [0.2]	0		60	100 min [7%]
7×10^{-2}	CuI [1]	0		60	260 min [19%]
7×10^{-5}	CuI [1]	1		60	120 min [0%]
7×10^{-5}	$CuSO_4 \cdot 5H_2O$ [1]	1.2	0.5	60	120 min [30%]
1.4×10^{-1}	$CuSO_4 \cdot 5H_2O$ [1]	1.2	0.5	60	11 min [complete]
7×10^{-4}	$CuSO_4 \cdot 5H_2O$ [1]	1.2	0.5	60	48 h [complete]
1.4×10^{-1}	$CuSO_4 \cdot 5H_2O$ [0.2]	0.24	0.5	60	>48 h [complete]
1.4×10^{-1}	$CuSO_4 \cdot 5H_2O$ [1]	1.2	0.76	60	4.5 h [complete]
1.4×10^{-1}	$CuSO_4 \cdot 5H_2O$ [1]	1.2	0	60	<35 min [complete]
1.4×10^{-1}	$CuSO_4 \cdot 5H_2O$ [1]	1.2	0	22	215 min [88%]

[a] The reaction was monitored as the reaction conversion of the starting acid **2** (HPLC); determination of the yield of **5a** was not possible because it degraded under the HPLC conditions used. For the procedure, see page S7 and the main text. c_2 = the starting concentration of **2** as a 1-molar equivalent used in the reaction. The best conditions for the reaction are shown in red. [b] Degassed by purging with nitrogen.

Figure S1: ^{1}H NMR (700 MHz, $CDCl_3$): **3a**

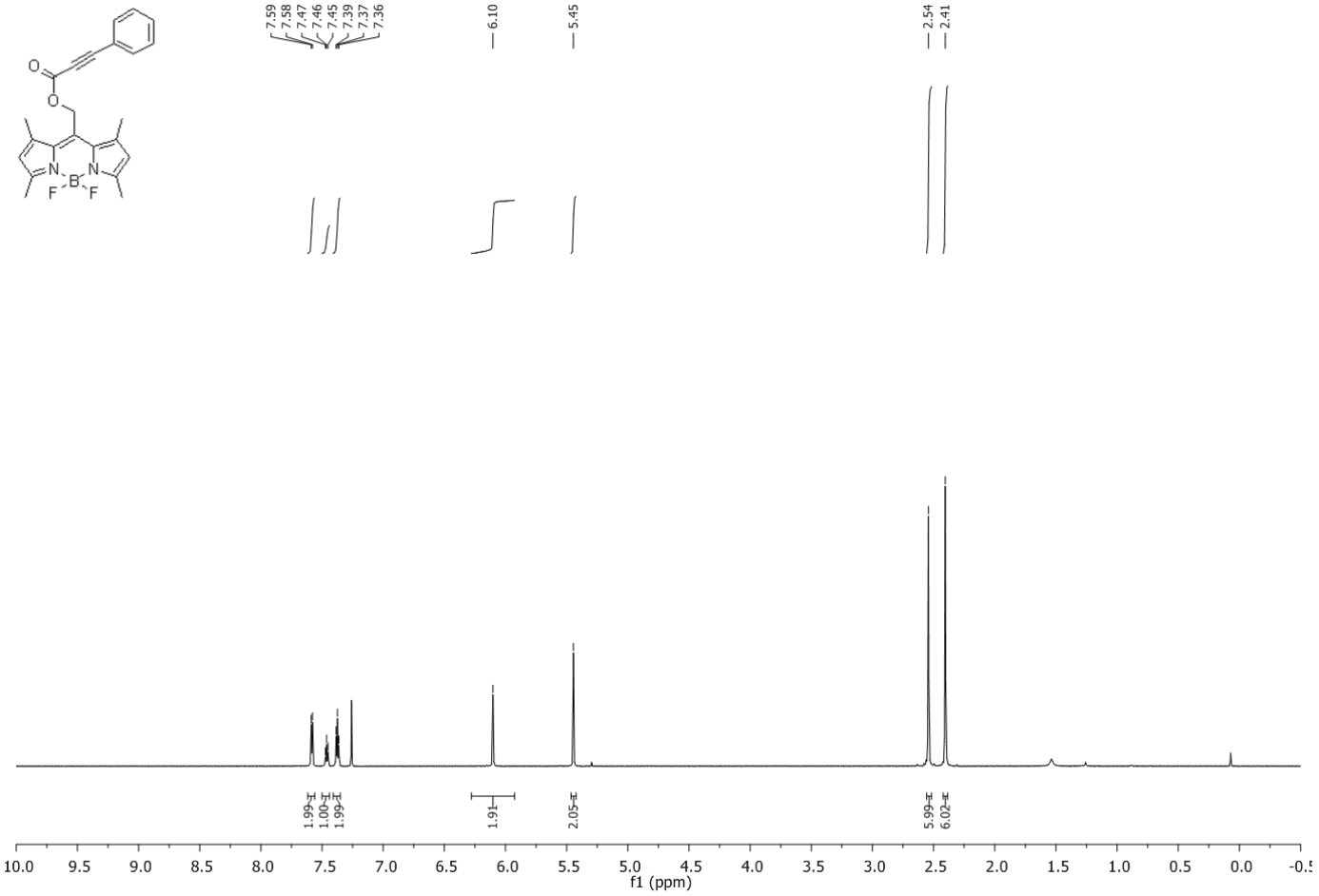


Figure S2: ^{13}C NMR (175 MHz, $CDCl_3$): **3a**

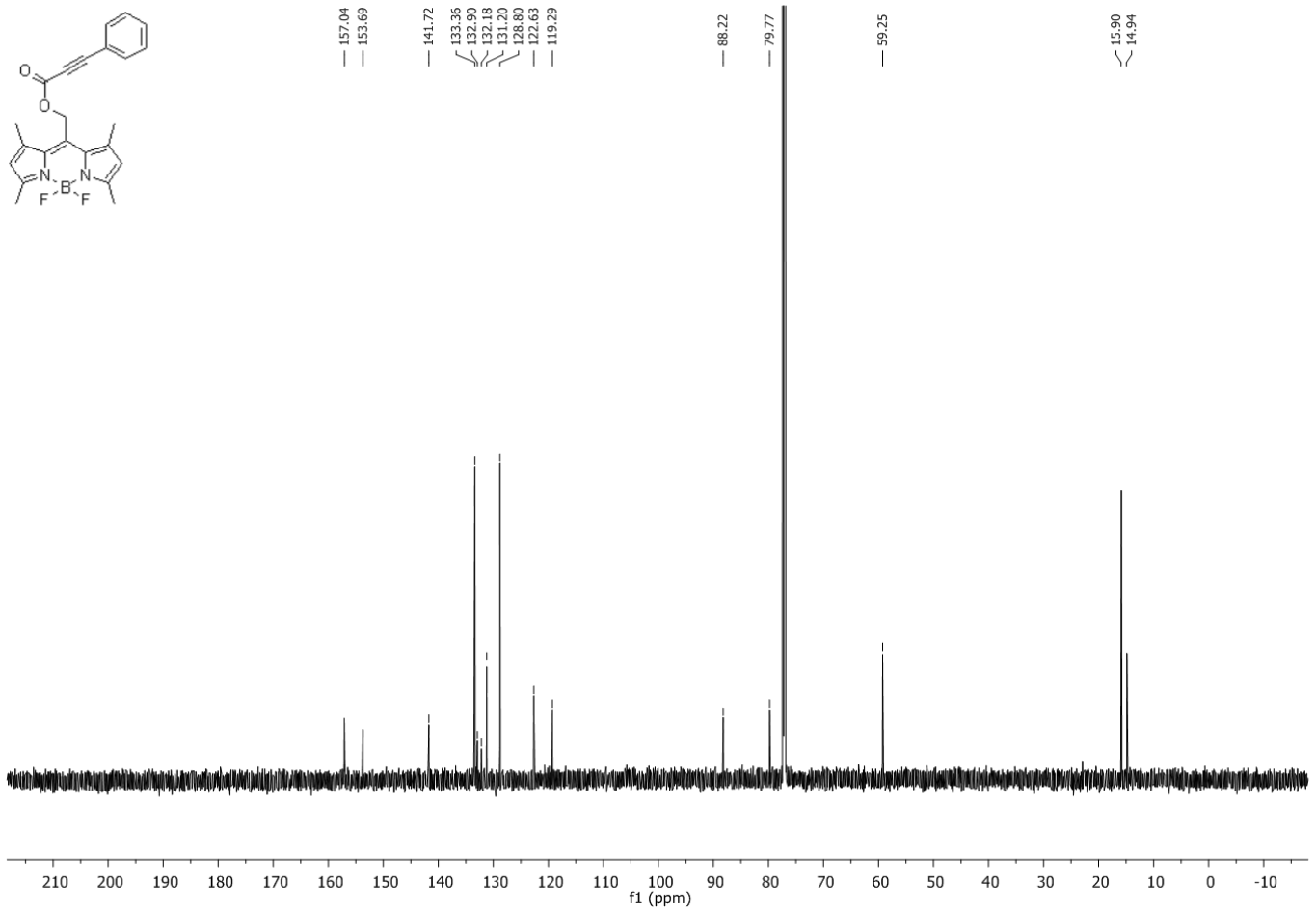


Figure S3: ^{1}H NMR (700 MHz, $CDCl_3$): **3b**

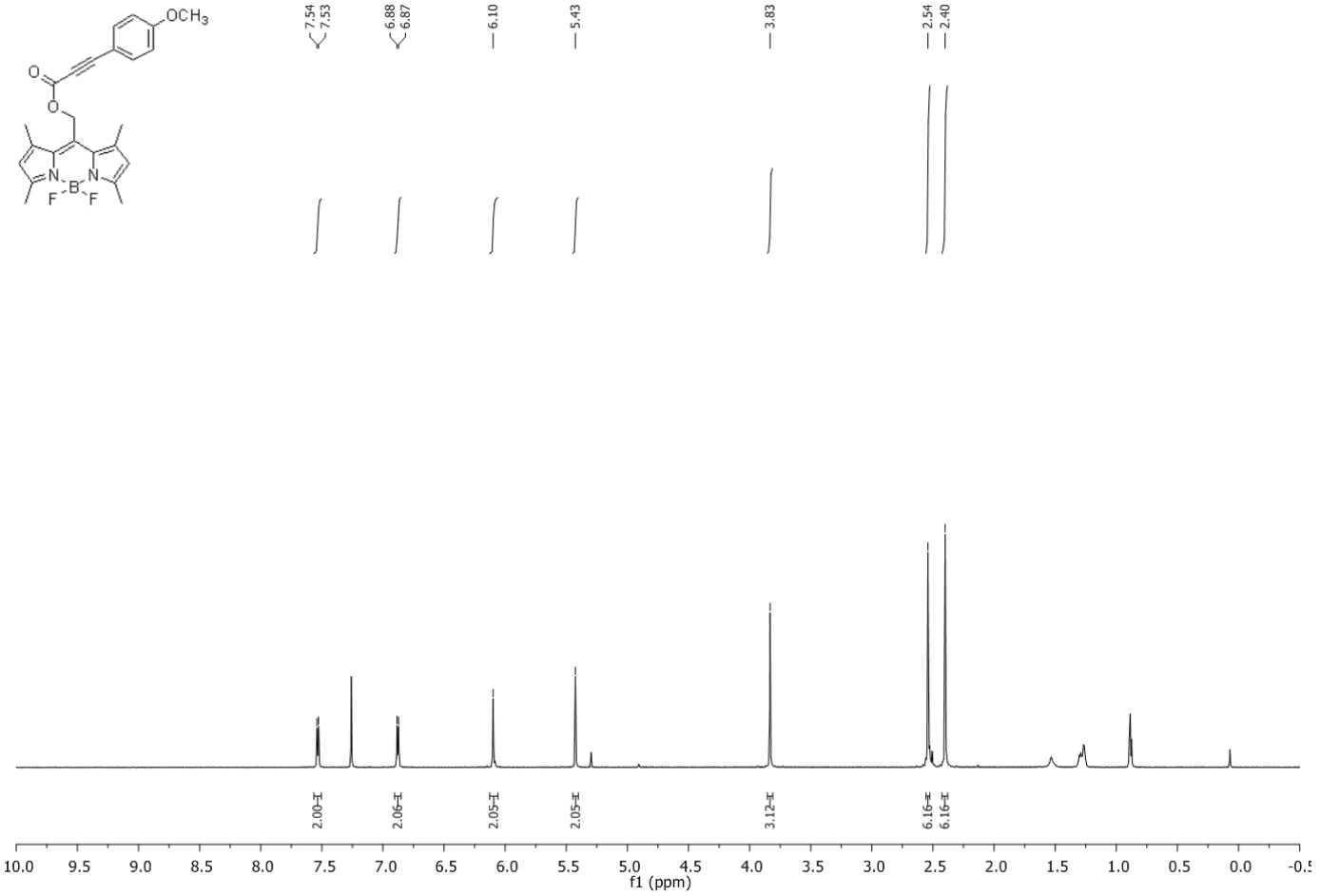


Figure S4: ^{13}C NMR (175 MHz, $CDCl_3$): **3b**

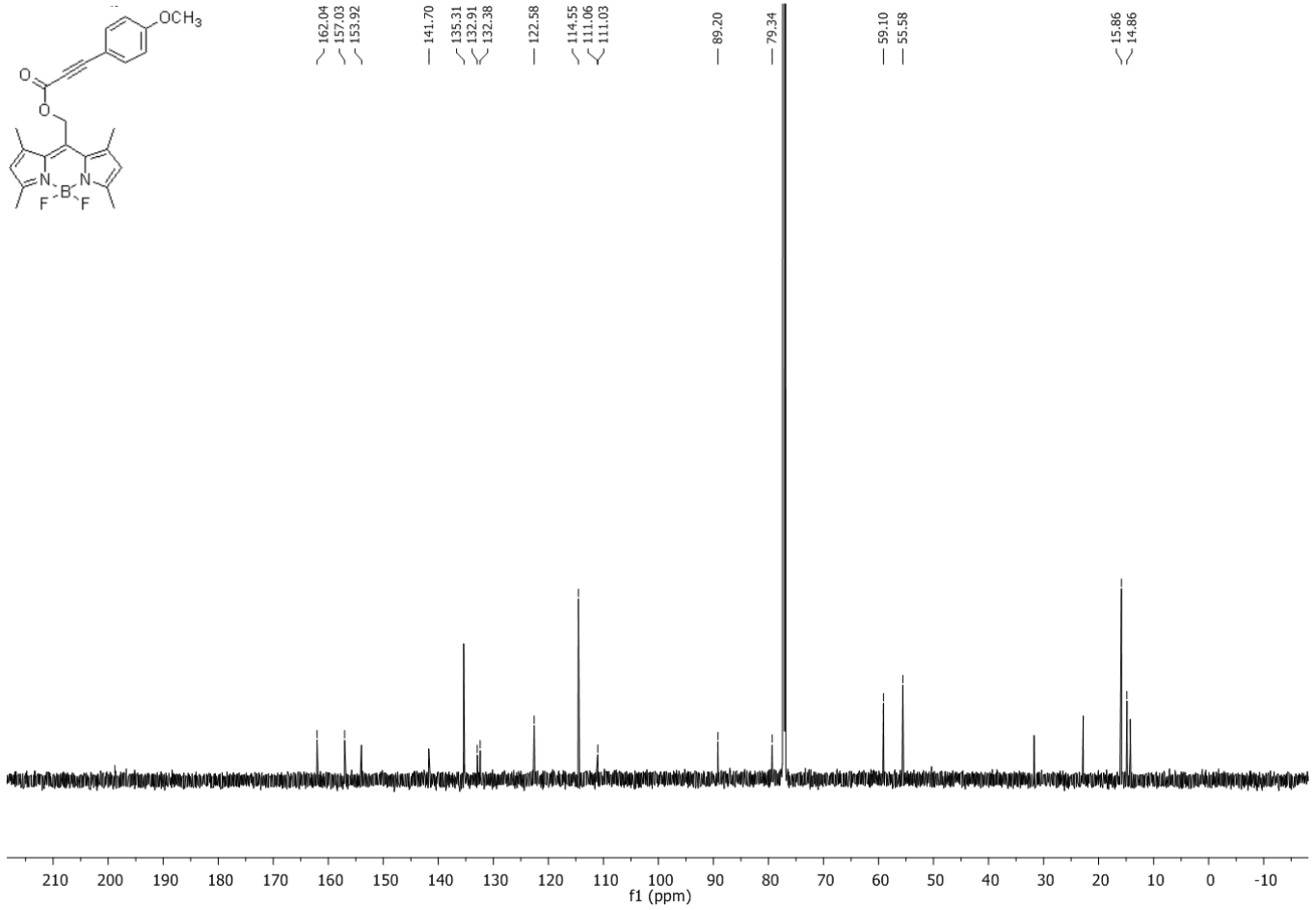


Figure S5: ^{1}H NMR (700 MHz, $CDCl_3$): **3c**

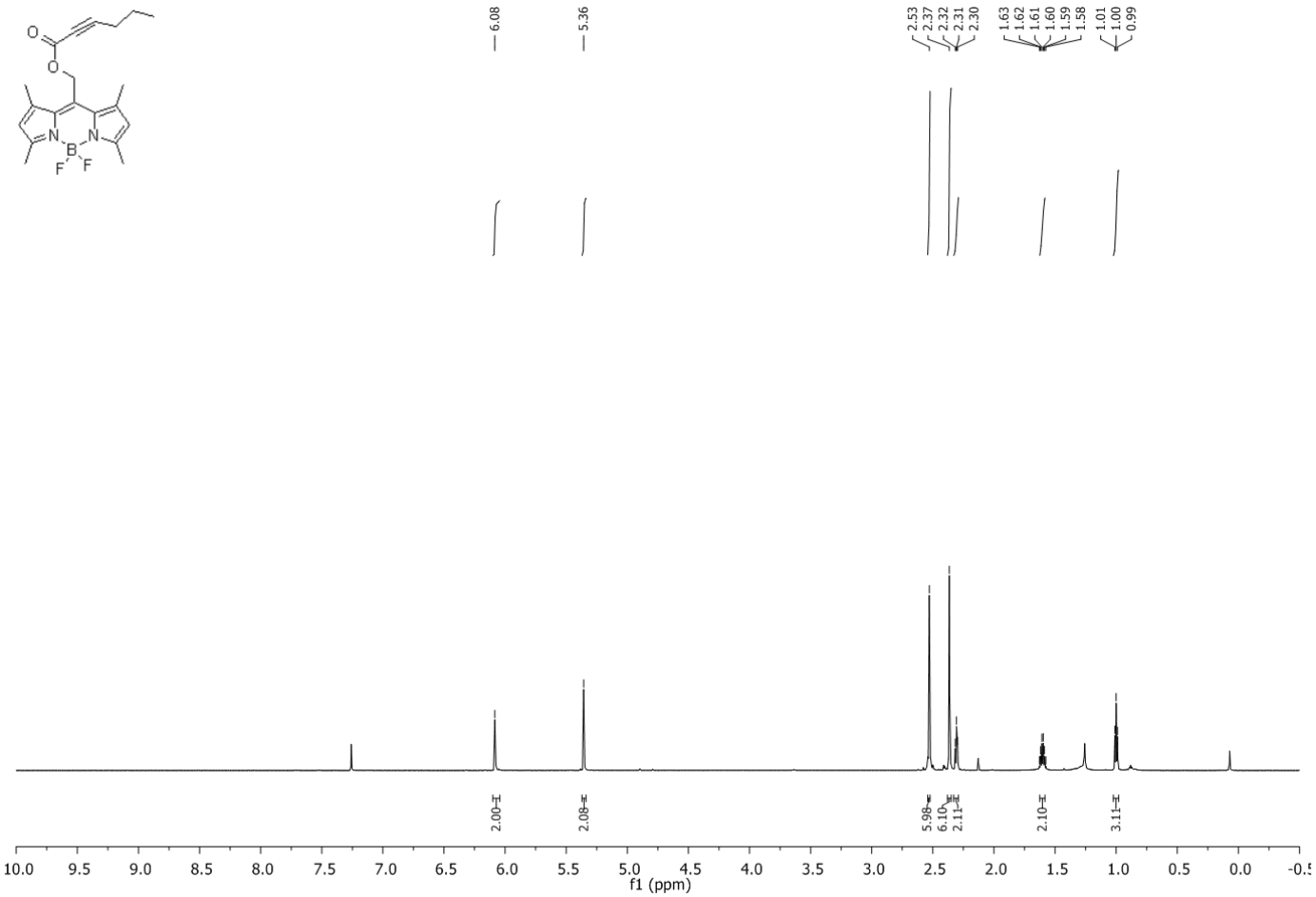


Figure S6: ^{13}C NMR (175 MHz, $CDCl_3$): **3c**

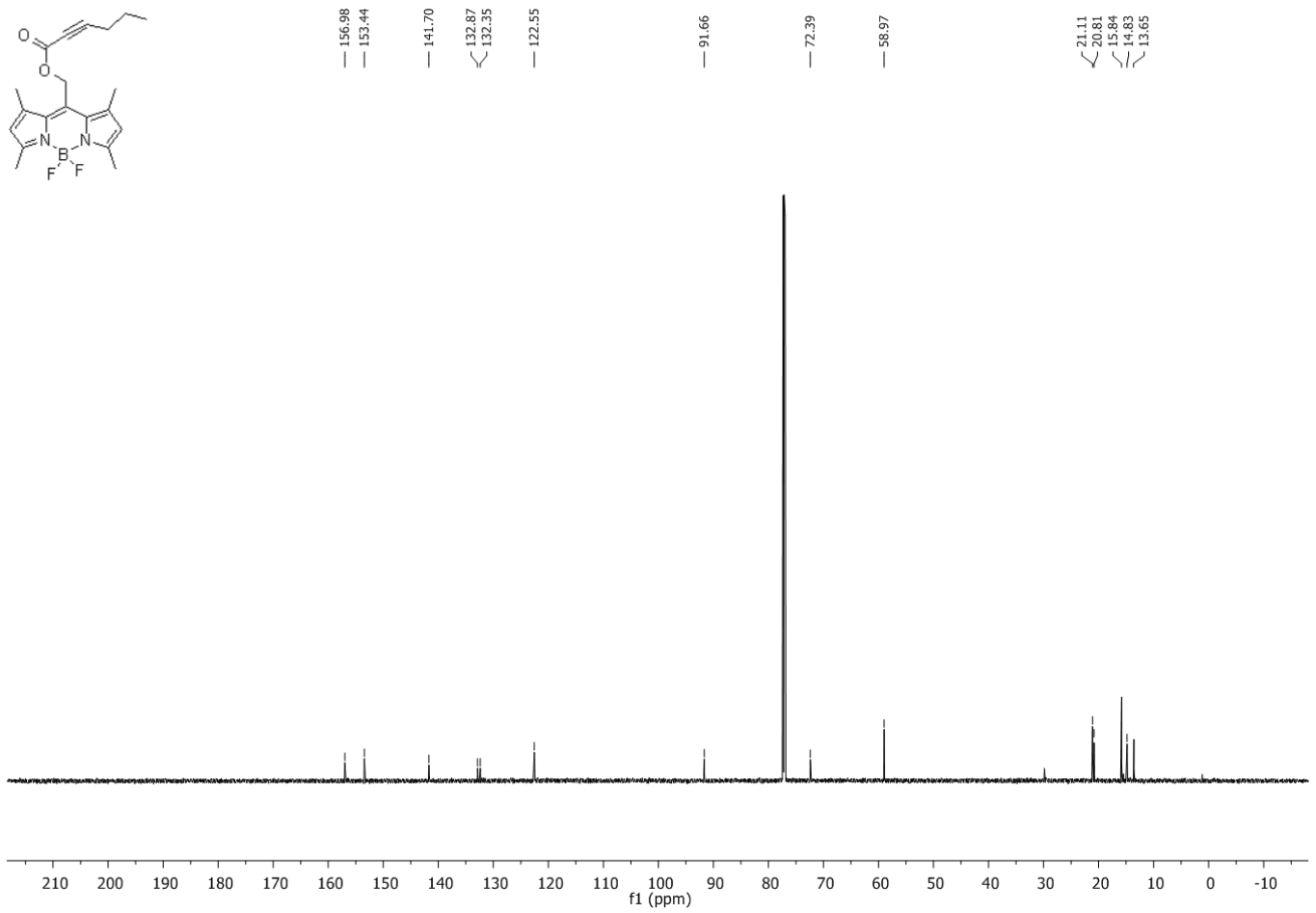


Figure S7: ^{1}H NMR (700 MHz, $CDCl_3$): **3d**

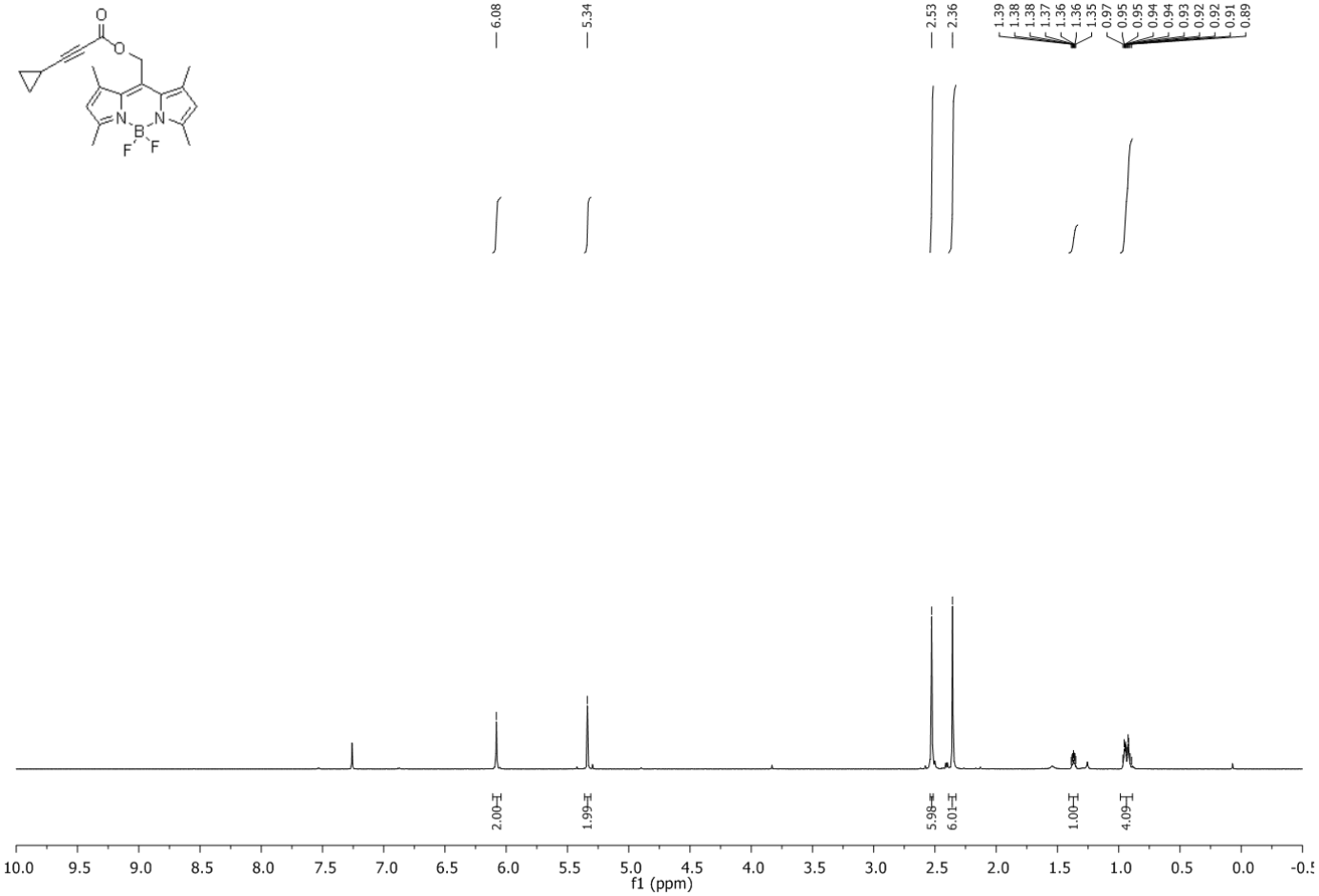


Figure S8: ^{13}C NMR (175 MHz, $CDCl_3$): **3d**

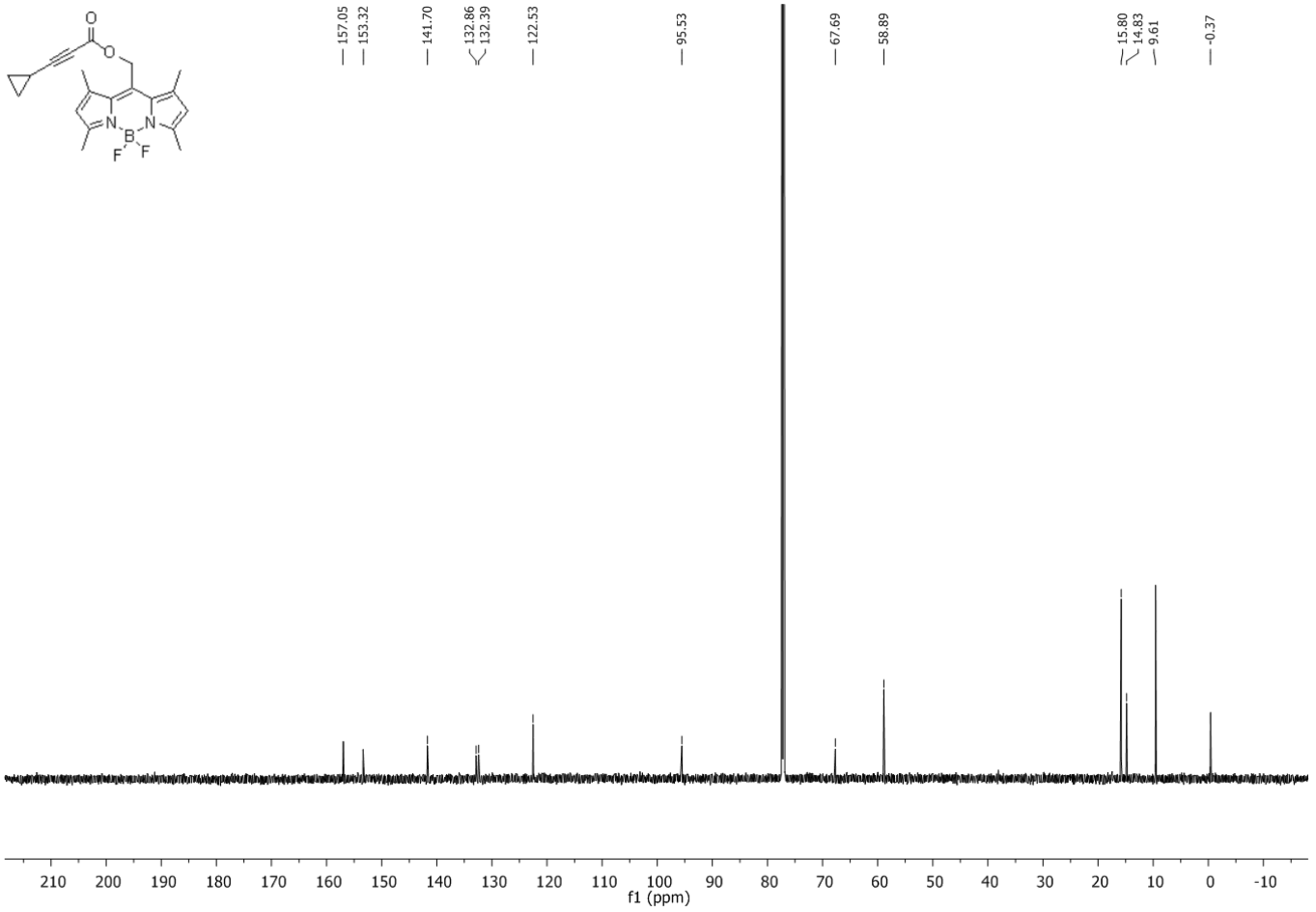


Figure S9: ^{1}H NMR (300 MHz, $CDCl_3$): **6a**

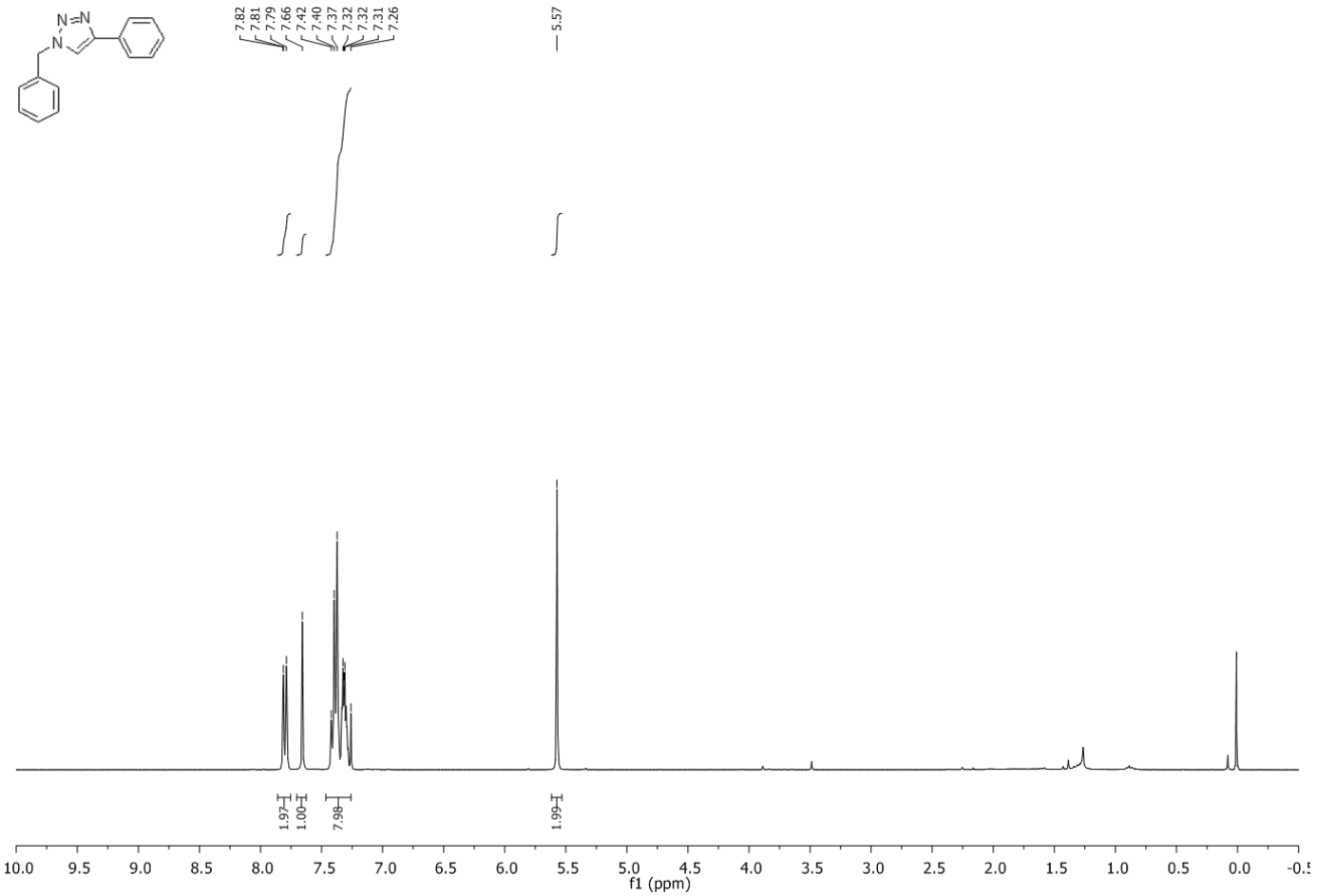


Figure S10: ^{1}H NMR (300 MHz, $CDCl_3$): **6b**

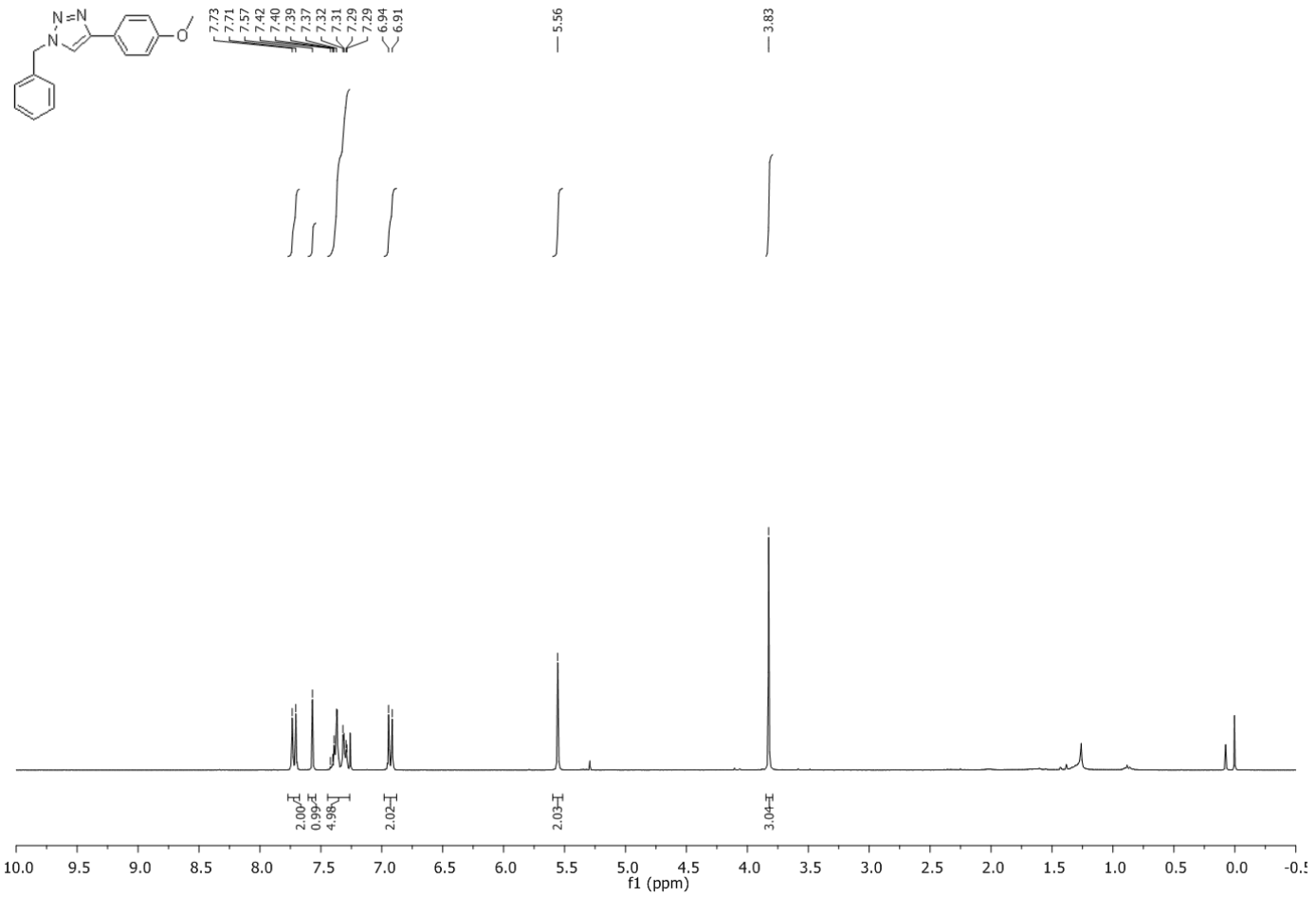


Figure S11: ^{1}H NMR (300 MHz, $CDCl_3$): **6c**

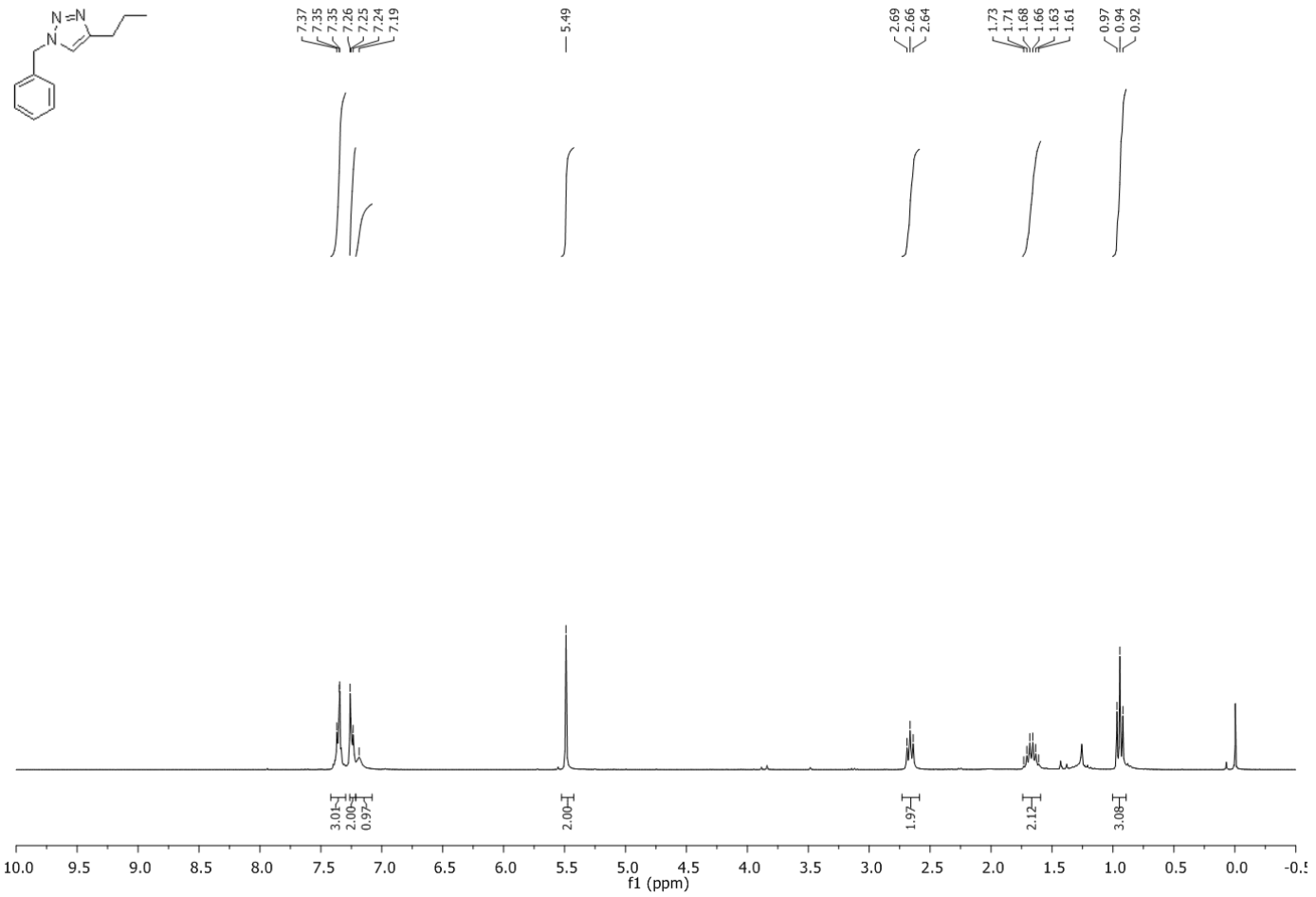


Figure S12: ^{1}H NMR (300 MHz, $CDCl_3$): **6d**

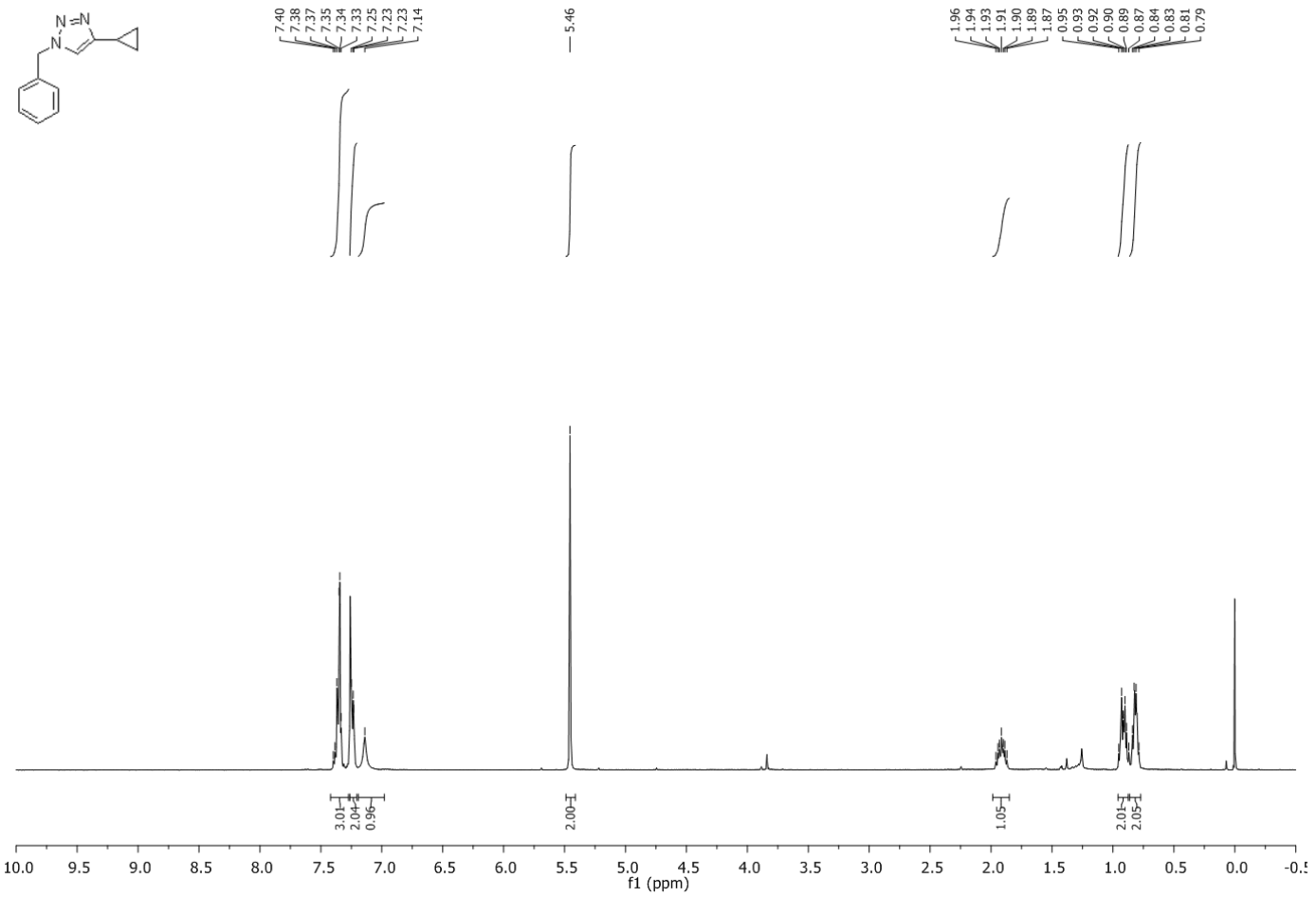


Figure S13: HRMS (ESI+): **3a**

ESI$^+$ (MMI): nitrogen flow 5 L/min, gas temperature 325°C, nebulizer 45 psi, skimmer 65 V, vaporizer 200°C, fragmentor 100 V, dissolved in Methanol

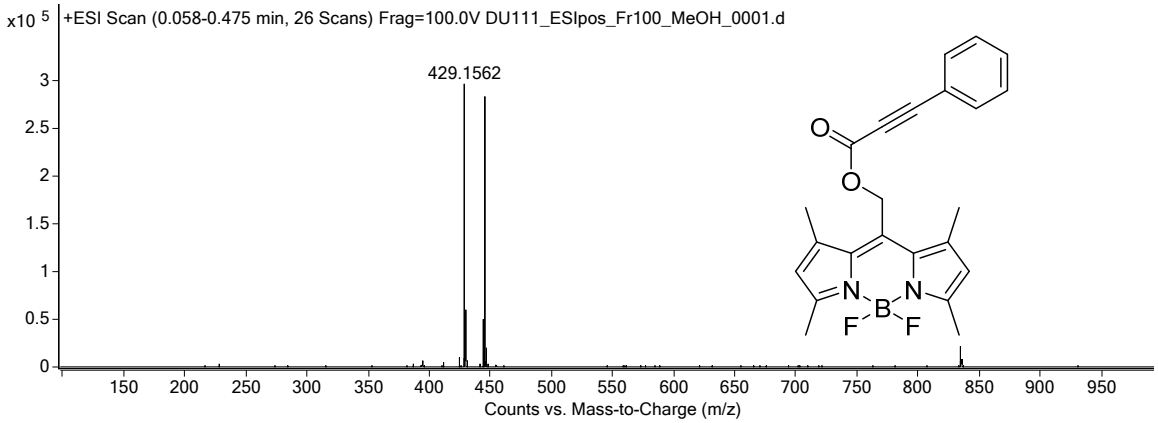


Figure S14: HRMS (ESI+): **3b**

ESI$^+$ (MMI): nitrogen flow 5 L/min, gas temperature 325°C, nebulizer 45 psi, skimmer 65 V, vaporizer 200°C, fragmentor 60 V, dissolved in Methanol

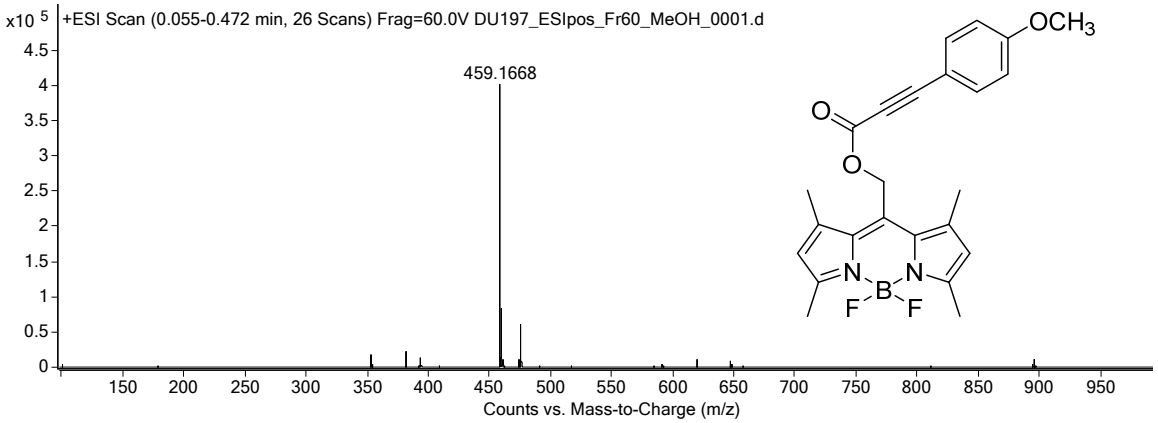


Figure S15: HRMS (ESI+): **3c**

ESI+ (MMI): nitrogen flow 5 L/min, gas temperature 325°C, nebulizer 45 psi, skimmer 65 V, vaporizer 200°C, fragmentor 80 V, dissolved in Methanol

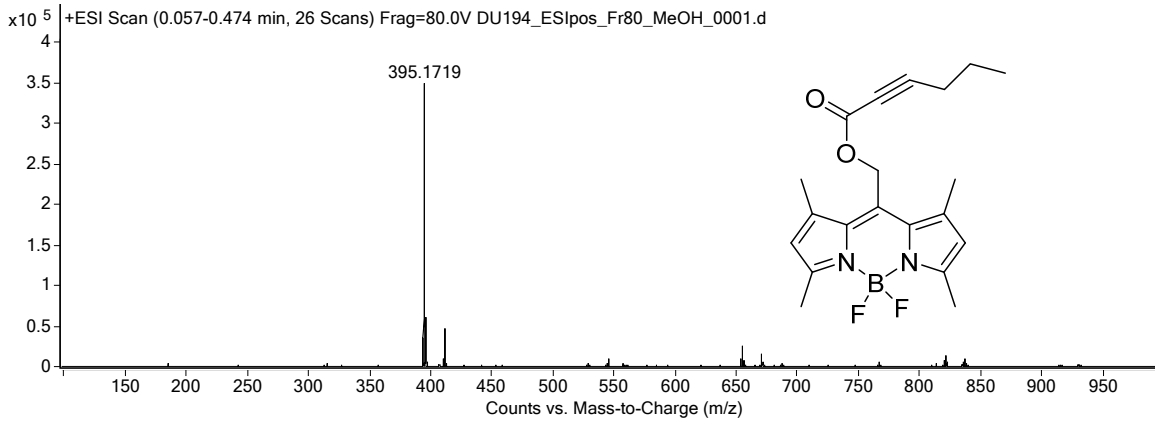


Figure S16: HRMS (ESI+): **3d**

ESI+ (MMI): nitrogen flow 5 L/min, gas temperature 325°C, nebulizer 45 psi, skimmer 65 V, vaporizer 200°C, fragmentor 60 V, dissolved in Methanol

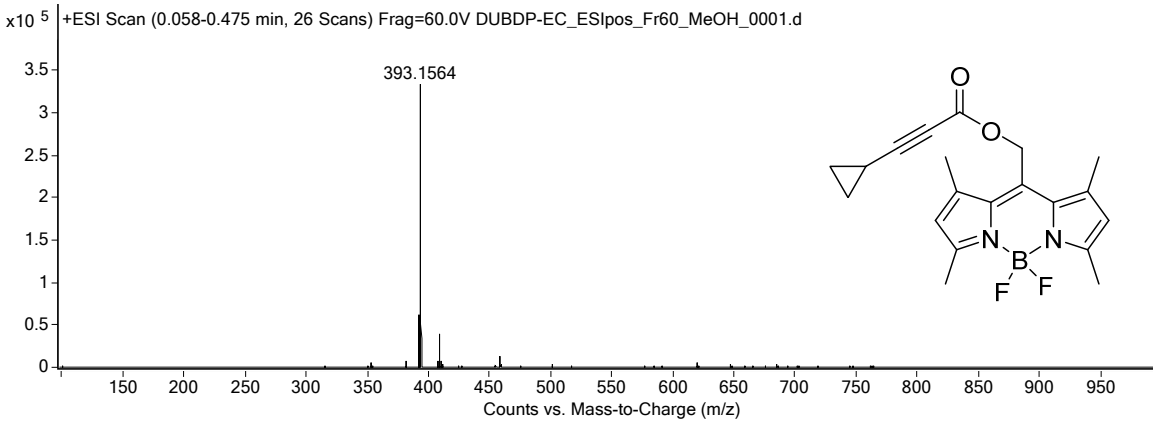


Figure S17. Kinetics of **2a** decarboxylation (see page S7; $k = 6.4 \times 10^{-3}$ M^{-1} s^{-1}). The data (black dots) are fitted with the second-order kinetics (red dots).

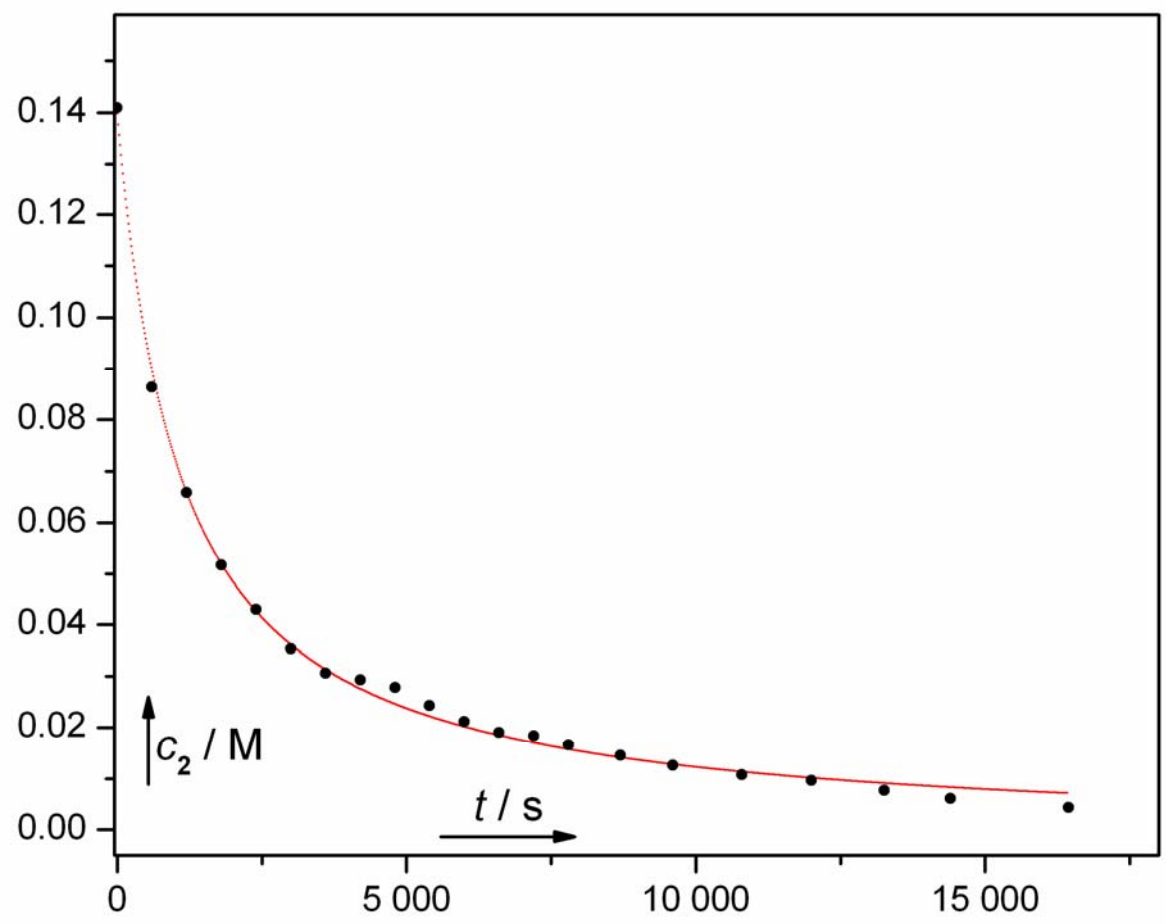
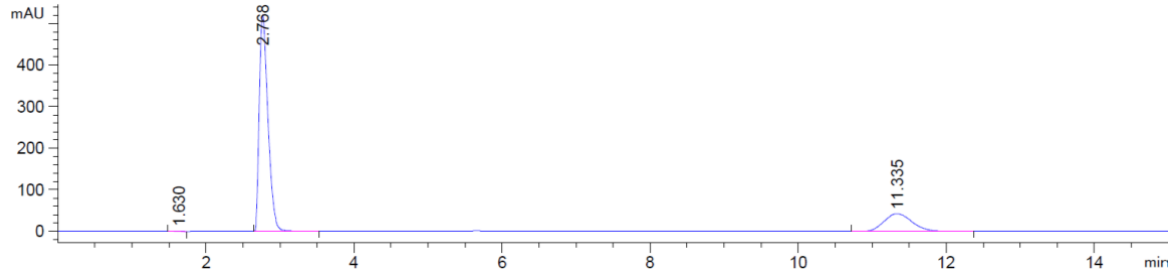


Figure S18. The comparison of HPLC chromatograms of **3a** (c = 1.5 × 10^{-4} M; retention time = 11.335 min) and an excess of **2a** (c = 5.21 × 10^{-4} M; retention time = 2.768 min): (a) Before irradiation; (b) After irradiation at 525 nm for 20 minutes (the resulting concentration of **2a** was 2.01 × 10^{-4} M).

(a)



(b)

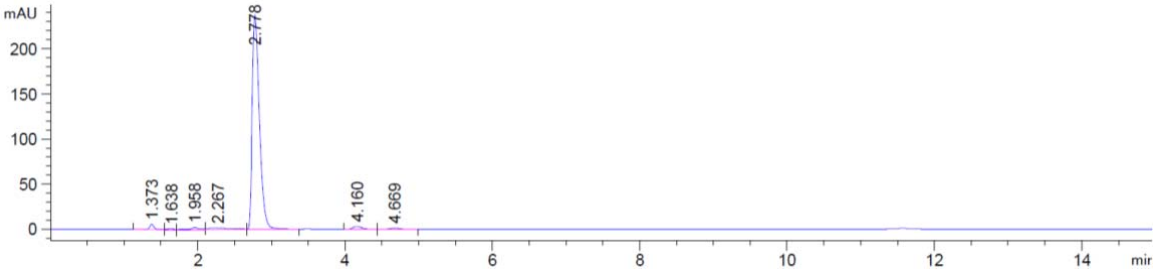
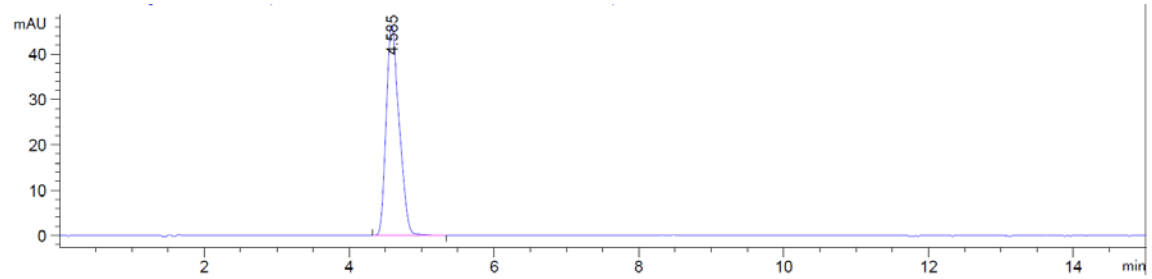
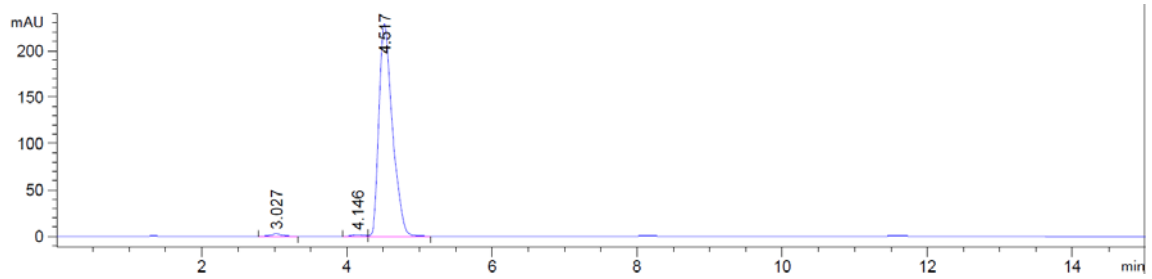


Figure S19: The comparison of HPLC chromatograms of methoxy-*meso*-methyl BODIPY **4** (retention time = 4.5 min): (a) the standard **4** from the previous work;[1] (b) **4** produced by irradiation of **3a**; (b) **4** produced by irradiation of **3b**. (Additional peaks are the products of further photodegradation).

(a)



(b)



(c)

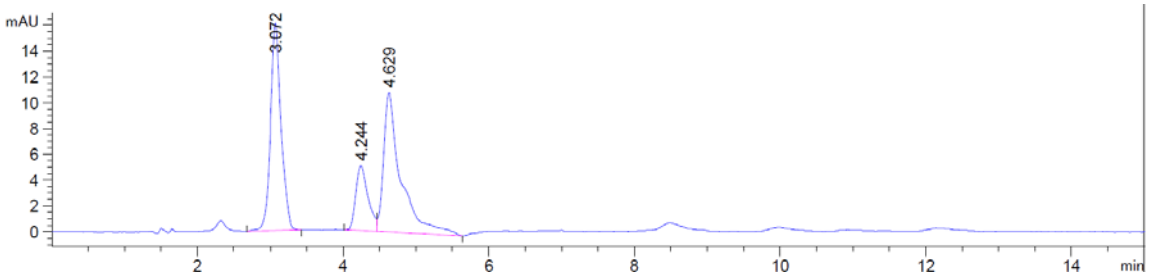


Figure S20. Irradiation of **3b** in methanol at 525 nm for 20 min (red line: the initial spectrum; blue line: the end spectrum (the intermediate **4**)).

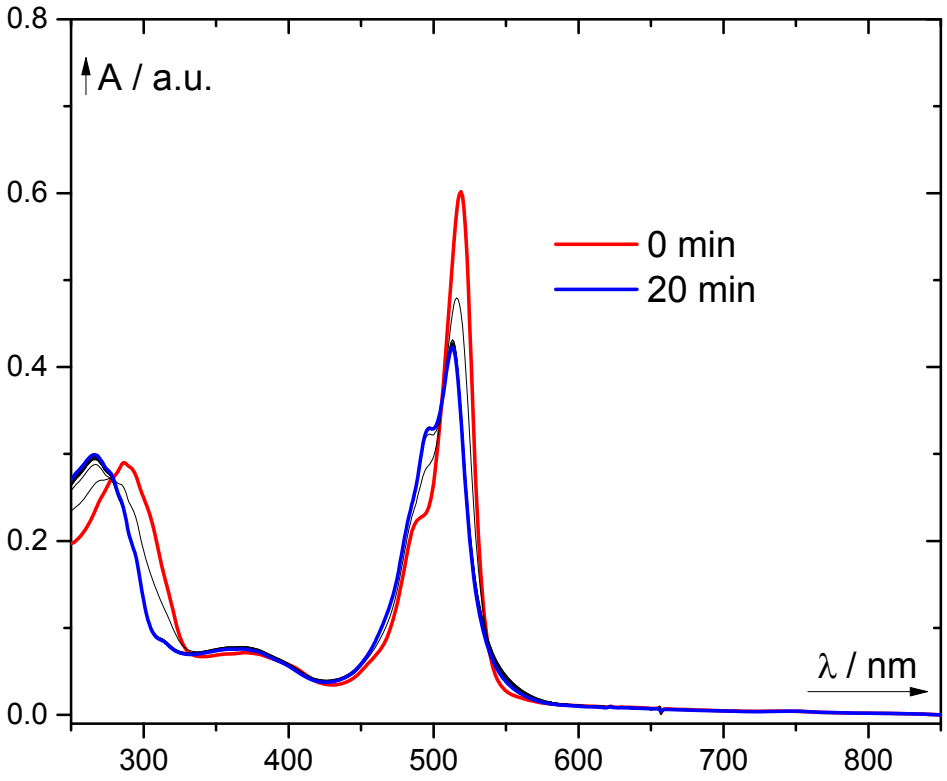


Figure S21. Irradiation of **3c** in methanol at 525 nm for 30 min (red line: the initial spectrum; blue line: the end spectrum (the intermediate **4**)).

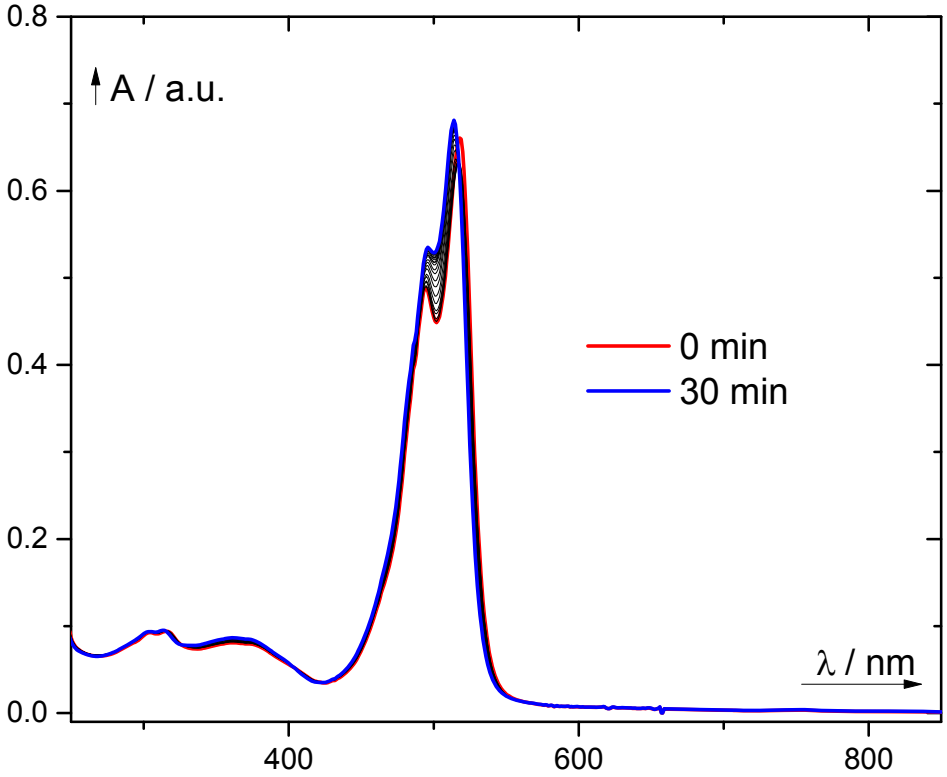


Figure S22. Irradiation of **3d** in methanol at 525 nm for 20 min (red line: the initial spectrum; blue line: the end spectrum (the intermediate **4**)).

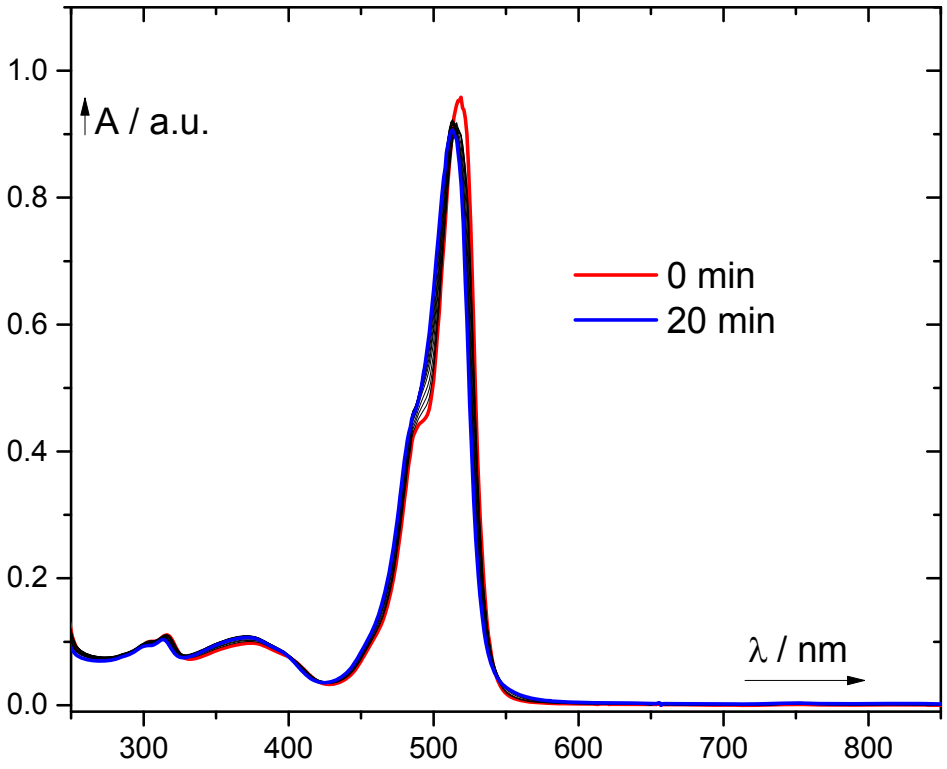
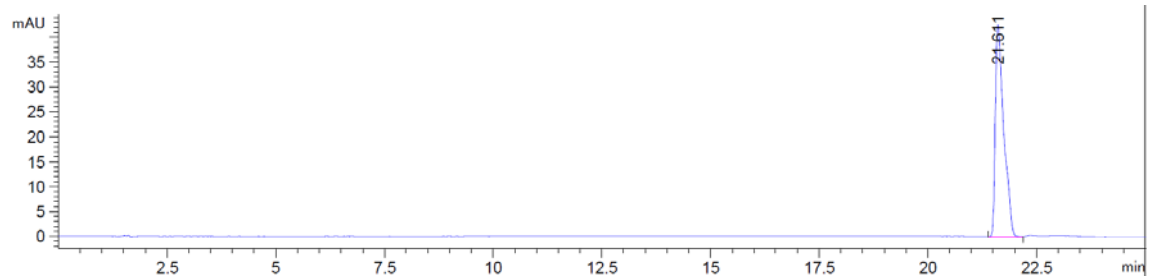
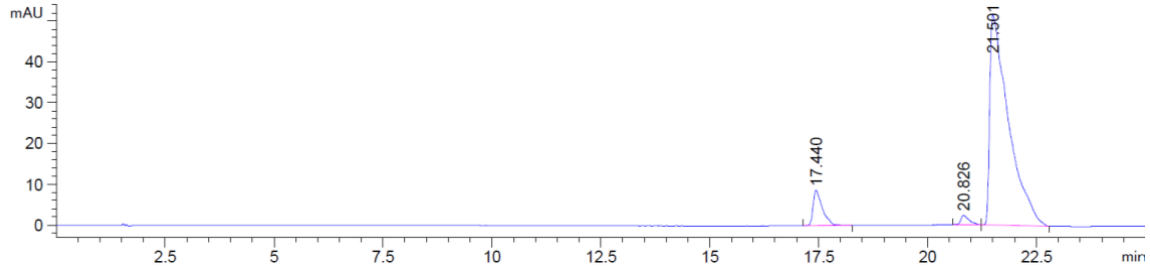


Figure S23. The comparison of HPLC chromatograms of methoxy-*meso*-methyl BODIPY **4** (retention time = 21.6 min): (a) the standard **4** from the previous work;[1] (b) **4** produced by irradiation of **3c**; (c) **4** produced by irradiation of **3d**. (Additional peaks are the products of further photodegradation).

(a)



(b)



(c)

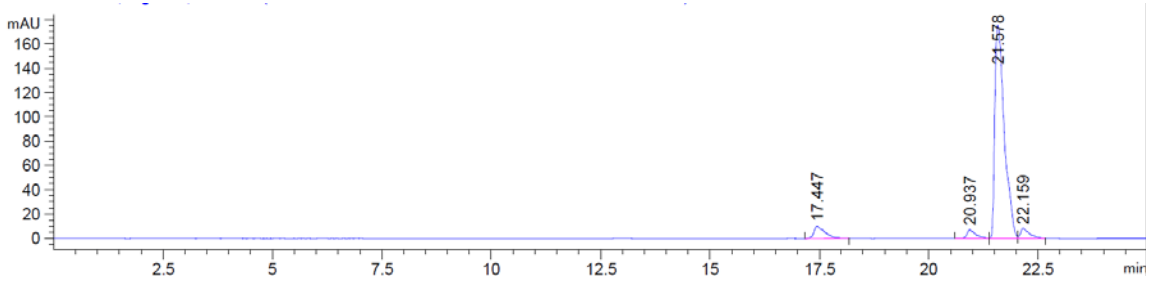
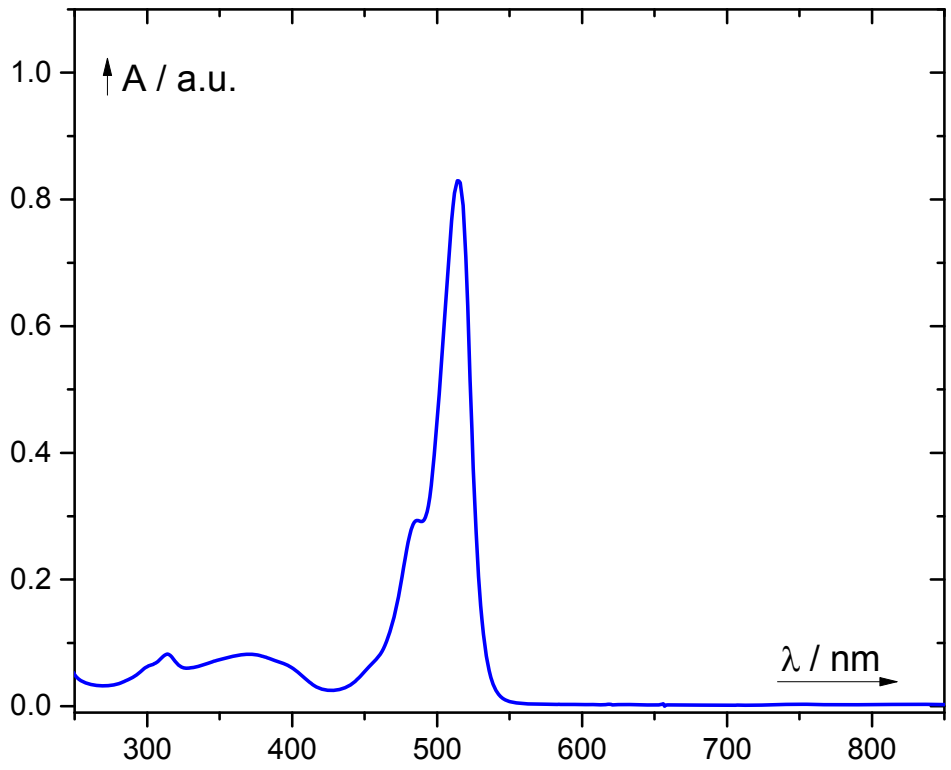


Figure S24: Absorption spectrum of the methoxy-*meso*-methyl BODIPY **4** in methanol.[1]



References

1. T. Slanina, P. Shrestha, E. Palao, D. Kand, J. A. Peterson, A. S. Dutton, N. Rubinstein, R. Weinstain, A. H. Winter and P. Klan, *J. Am. Chem. Soc.*, 2017, **139**, 15168-15175.
2. B. C. Guo, X. J. Peng, A. J. Cui, Y. K. Wu, M. Z. Tian, L. Z. Zhang, X. Q. Chen and Y. L. Gao, *Dyes Pigments*, 2007, **73**, 206-210.
3. K. Park, J.-M. You, S. Jeon and S. Lee, *Eur. J. Org. Chem.*, 2013, **2013**, 1973-1978.
4. F. Liu, Y. Liang and K. N. Houk, *J. Am. Chem. Soc.*, 2014, **136**, 11483-11493.
5. C. Shao, X. Wang, J. Xu, J. Zhao, Q. Zhang and Y. Hu, *J. Org. Chem.*, 2010, **75**, 7002-7005.
6. S. Wang, K. Jia, J. Cheng, Y. Chen and Y. Yuan, *Tetrahedron Lett.*, 2017, **58**, 3717-3721.
7. M. Z. C. Hatit, C. P. Seath, A. J. B. Watson and G. A. Burley, *J. Org. Chem.*, 2017, **82**, 5461-5468.
8. E. Palao, T. Slanina, L. Muchova, T. Solomek, L. Vitek and P. Klan, *J. Am. Chem. Soc.*, 2016, **138**, 126-133.
9. C. A. Clark, D. S. Lee, S. J. Pickering, M. Poliakoff and M. W. George, *Org. Process Res. Dev.*, 2016, **20**, 1792-1798.