

3D Coumarin systems based on [2.2]paracyclophane: synthesis, spectroscopic characterization and chiroptical properties

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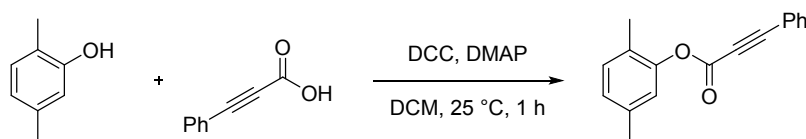
Supporting Information

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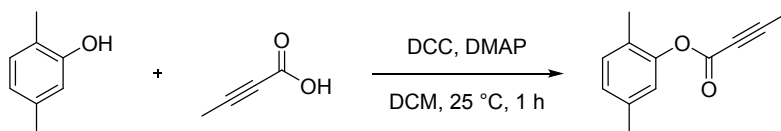
Synthesis of model compounds 7a,b

Synthesis of 2,5-dimethylphenyl 3-phenylpropiolate (**Compound S1**)



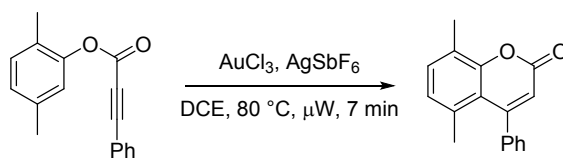
Phenylpropionic acid (125 mg, 0.859 mmol, 1.05 eq.), DMAP (15 mg, 0.123 mmol, 0.15 eq.) and 2,5-dimethylphenol (100 mg, 0.103 mL, 0.819 mmol, 1 eq.) were dissolved in dry DCM (15 mL) under an Argon atmosphere. DCC (1 M, 0.982 mL, 0.982 mmol, 1.2 eq.) was added turning the reaction mixture yellow and cloudy. The reaction was stirred at rt for 1 h, followed by filtration through a plug of silica gel with DCM washings. The crude material was then concentrated under reduced pressure and purified by silica gel column chromatography (eluent = DCM/Cy 4:6) to yield compound **S1** (181 mg, 0.723 mmol, 88 %) as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.67 – 7.61 (m, 2H), 7.52 – 7.45 (m, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.15 (d, J = 7.7 Hz, 1H), 7.01 (d, J = 7.7 Hz, 1H), 6.93 (s, 1H), 2.35 (s, 3H), 2.23 (s, 3H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 152.3 (C), 148.5 (C), 137.1 (C), 133.2 (2CH), 131.0 (CH), 130.9 (CH), 128.6 (2CH), 127.3 (CH), 126.8 (C), 122.2 (CH), 119.3 (C), 88.4 (C), 80.2 (C), 20.8 (CH_3), 15.7 (CH_3) ppm. IR (neat): 2216, 1724, 1508, 1490, 1444, 1282, 1240, 1180, 1000, 912, 757 cm^{-1} . HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{15}\text{O}_2$: 251.1067; found: 251.1066.

Synthesis of 2,5-dimethylphenyl but-2-ynoate (**Compound S2**)



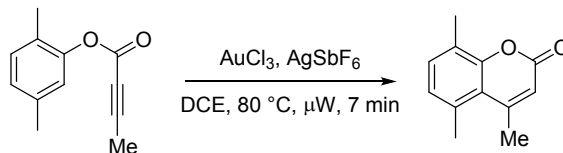
2-Butynoic acid (72.3 mg, 0.859 mmol, 1.05 eq.), DMAP (15 mg, 0.123 mmol, 0.15 eq.) and 2,5-dimethylphenol (100 mg, 0.819 mmol, 1 eq.) were dissolved in dry DCM (15 mL) under an Argon atmosphere. DCC (1 M in DCM, 0.982 mL, 0.982 mmol, 1.2 eq.) was added turning the mixture cloudy. The reaction was stirred at rt for 1 h, followed by filtration through a plug of silica gel with DCM washings. The crude material was concentrated under reduced pressure and purified by silica gel column chromatography (eluent = DCM/Cy 3:7) to afford compound **S2** (123 mg, 0.653 mmol, 80 %) as a colorless oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.11 (d, J = 7.7 Hz, 1H), 6.97 (d, J = 7.7 Hz, 1H), 6.86 (s, 1H), 2.32 (s, 3H), 2.16 (s, 3H), 2.07 (s, 3H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 151.9 (C), 148.4 (C), 137.0 (C), 130.9 (CH), 127.2 (CH), 126.7 (C), 122.2 (CH), 87.7 (C), 72.1 (C), 20.8 (CH_3), 15.7 (CH_3), 3.9 (CH_3) ppm. IR (neat): 2233, 1725, 1508, 1251, 1229, 1203, 1106, 1042, 886, 810, 741 cm^{-1} . HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{13}\text{O}_2$: 189.0910; found: 189.0912.

Synthesis of 5,8-dimethyl-4-phenyl-2H-chromen-2-one (Compound 7a)



A G10 Anton Paar microwave vial was charged with AuCl₃ (4.93 mg, 0.0162 mmol, 0.08 eq.), and AgSbF₆ (11.5 mg, 0.0336 mmol, 0.17 eq.). The tube was sealed, then evacuated and refilled with argon three times. DCE (2 mL) was then added and the resulting mixture was stirred at rt for 5 min. Compound **S1** (50 mg, 0.2 mmol, 1 eq.) in DCE (2 mL) was finally added. The solution was irradiated in a microwave reactor at 80 °C for 7 min. At the end of the reaction, TLC showed no traces of starting material. The crude product was purified over silica gel column chromatography using EtOAc/Cy 1:9 as the eluent. Compound **7a** (26 mg, 0.104 mmol, 52 %) was isolated as an amorphous white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.43 (dd, *J* = 4.2, 2.2 Hz, 3H), 7.30 – 7.21 (m, 3H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.23 (s, 1H), 2.45 (s, 3H), 1.77 (s, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 160.3 (C), 157.0 (C), 153.2 (C), 139.7 (C), 134.8 (C), 132.6 (CH), 128.7 (CH), 128.6 (2CH), 127.6 (CH), 127.4 (2CH), 124.5 (C), 117.6 (C), 117.0 (CH), 23.3 (CH₃), 15.9 (CH₃) ppm. IR (neat): 1728, 1583, 1445, 1407, 1346, 1268, 1184, 1059, 903, 866, 817, 781, 740 cm⁻¹. HRMS (ESI): *m/z* [M+Na]⁺ calcd for C₁₇H₁₄O₂Na: 273.0886; found: 273.0885.

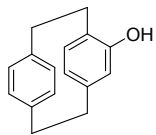
Synthesis of 4,5,8-trimethyl-2H-chromen-2-one (Compound 7b)



A G10 Anton Paar microwave vial was charged with AuCl₃ (6.55 mg, 0.0216 mmol, 0.08 eq.), and AgSbF₆ (15.4 mg, 0.0447 mmol, 0.17 eq.). The tube was sealed, then evacuated and refilled with argon three times. DCE (1 mL) was then added and the resulting mixture was stirred at rt for 5 min. Compound **S2** (50 mg, 0.266 mmol, 1 eq.) in DCE (2 mL) was finally added. The solution was irradiated in a microwave reactor at 80 °C for 7 min. At the end of the reaction, TLC showed no traces of starting material. The crude product was purified over silica gel column chromatography using EtOAc/Cy 3:7 as the eluent. Compound **7b** (34 mg, 0.181 mmol, 68 %) was isolated as an amorphous white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.25 – 6.16 (m, 1H), 2.67 (s, 3H), 2.60 (d, *J* = 1.1 Hz, 3H), 2.39 (s, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 160.4 (C), 154.5 (C), 153.2 (C), 134.1 (C), 132.2 (CH), 127.6 (CH), 124.8 (C), 118.9 (C), 116.2 (CH), 25.2 (CH₃), 24.3 (CH₃), 16.0 (CH₃) ppm. IR (neat): 1703, 1585, 1411, 1206, 1136, 1064, 920, 819 cm⁻¹. HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₂H₁₃O₂: 189.0910; found: 189.0909.

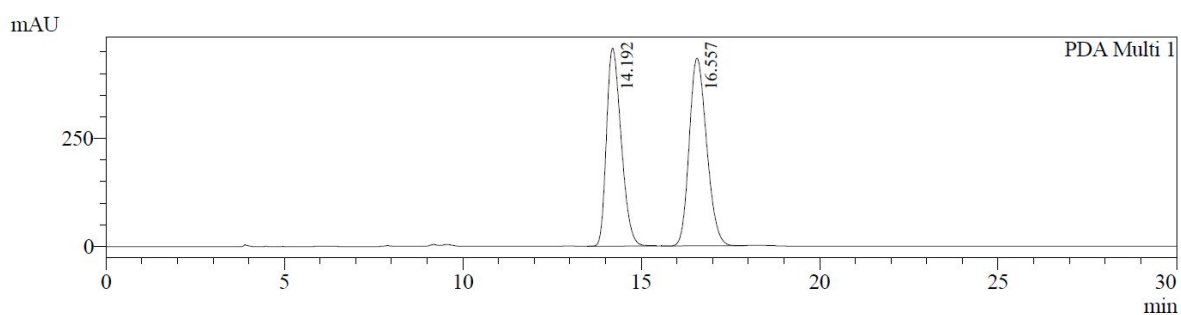
HPLC analyses

(*Sp*)- and (*Rp*)-4-hydroxy-[2.2]paracyclophane (**compound 3a**)



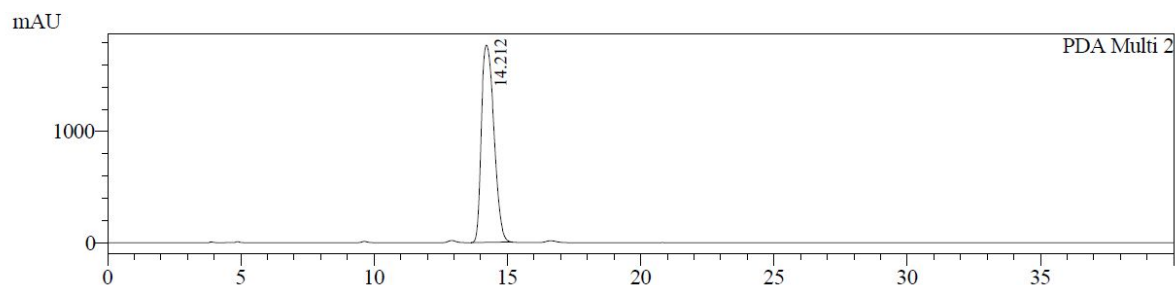
HPLC conditions: Column = Chiralcel OD (250 x 4,6 mm); eluent = *n*-heptane/*i*-PrOH (9:1); T = 25 °C; flow = 1 mL/min; λ = 250 nm.

HPLC analysis of racemic (\pm)-**3a** ($t_{R\text{ }Sp}$ = 14.2 min; $t_{R\text{ }Rp}$ = 16.6 min)



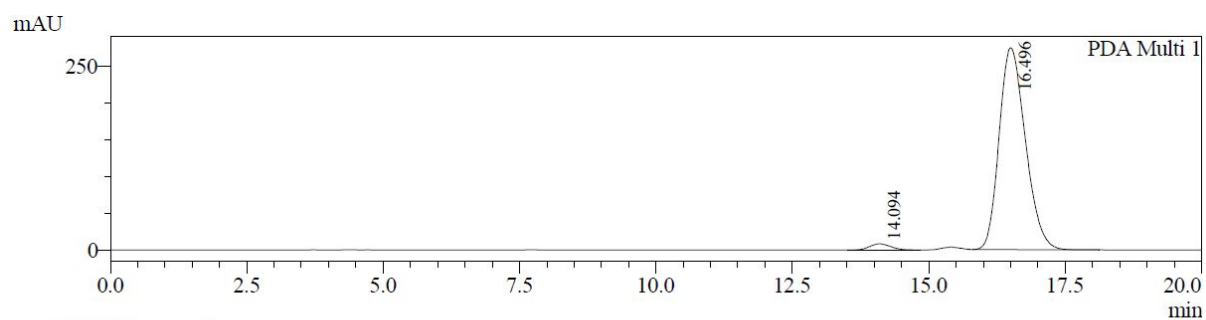
Peak#	Ret. Time	Area	Height	Area %
1	14.192	13118690	458235	47.068
2	16.557	14753166	434523	52.932
Total				100.000

HPLC analysis of (*Sp*)-**3a** ($t_{R\text{ }Sp}$ = 14.2 min)



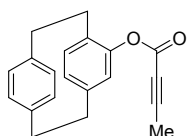
Peak#	Ret. Time	Area	Height	Area %
1	14.212	58211481	1775008	100.000
Total				100.000

HPLC analysis of (*Rp*)-**3a** ($t_{R\ Sp} = 16.4$ min)



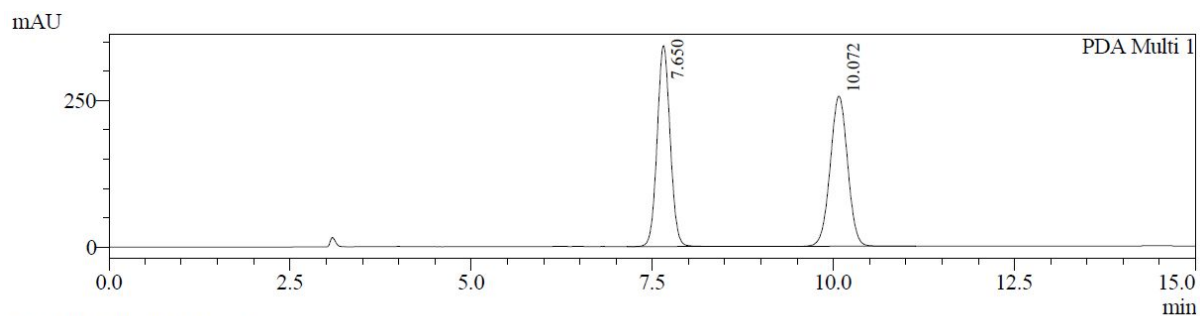
Peak#	Ret. Time	Area	Height	Area %
1	14.094	229824	8448	2.438
2	16.496	9195468	274369	97.562
Total		9425292	282817	100.000

(*Sp*)- and (*Rp*)-Tricyclo[8.2.2.2[^]{4,7}]hexadeca-1(12),4(16),5,7(15),10,13-hexaen-5-yl but-2-ynoate (**compound 2b**)



HPLC Conditions: Column = Chiralcel AD (250 x 4,6 mm); eluent = *n*-heptane/*i*-PrOH (9:1); T = 25 °C; flow = 1 mL/min; λ = 254 nm.

HPLC analysis of racemic (\pm)-**2b** ($t_{R\ P} = 7.7$ min; $t_{R\ Sp} = 10.1$ min)

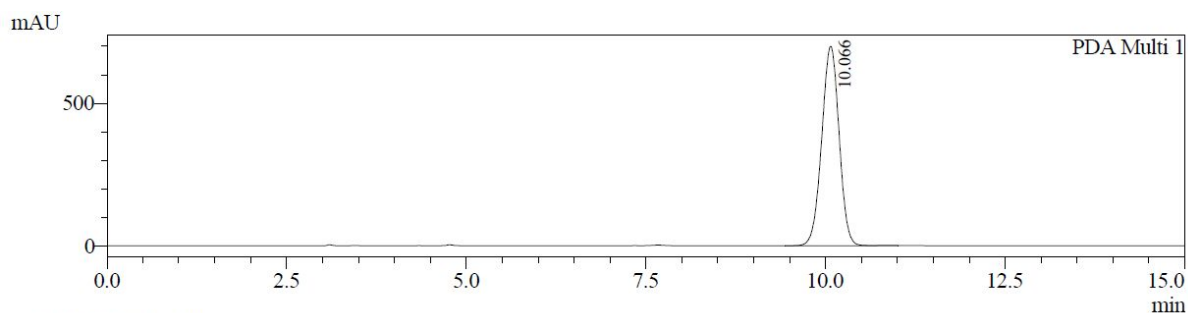


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.650	4284102	49.949
2	10.072	4292908	50.051
Total		8577010	100.000

HPLC analysis of (*Sp*)-**2b** ($t_{R\ Sp} = 10.1$ min)

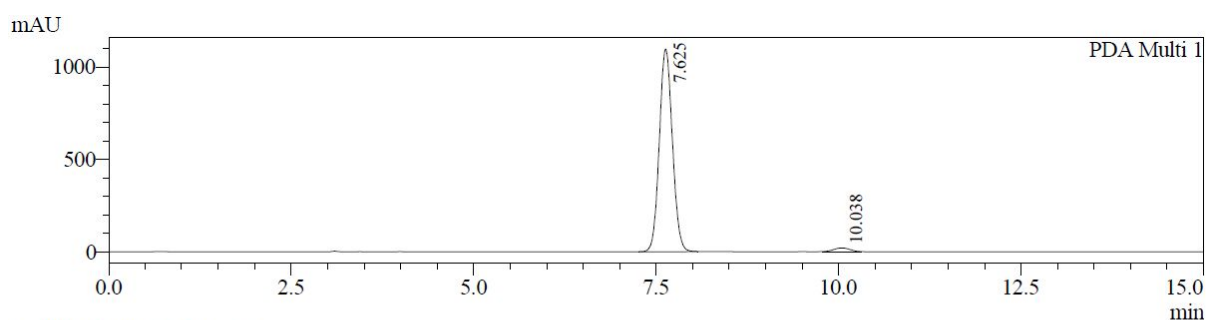


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.066	11792270	100.000
Total		11792270	100.000

HPLC analysis of (*Rp*)-**2b** ($tr_{Rp} = 7.6$ min; $tr_{Sp} = 10.0$ min)

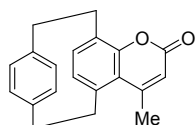


PeakTable

PDA Ch1 254nm 4nm

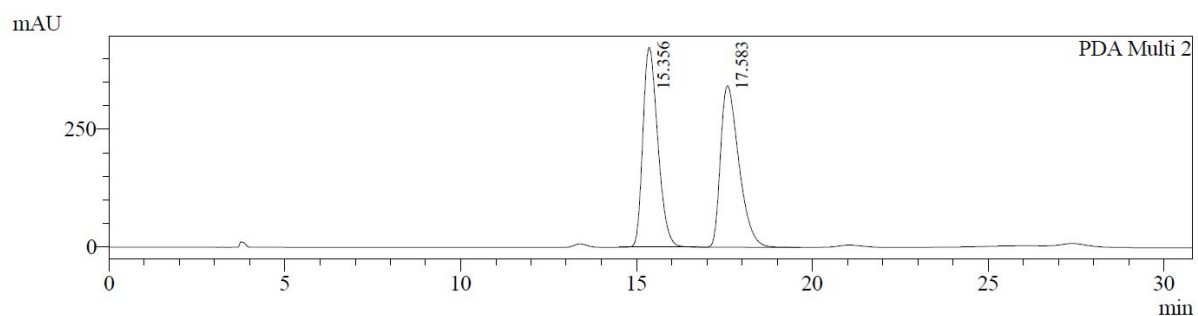
Peak#	Ret. Time	Area	Area %
1	7.625	13682204	97.796
2	10.038	308399	2.204
Total		13990603	100.000

(*Sp*)- and (*Rp*)-15-ethyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (**Compound 1b**)



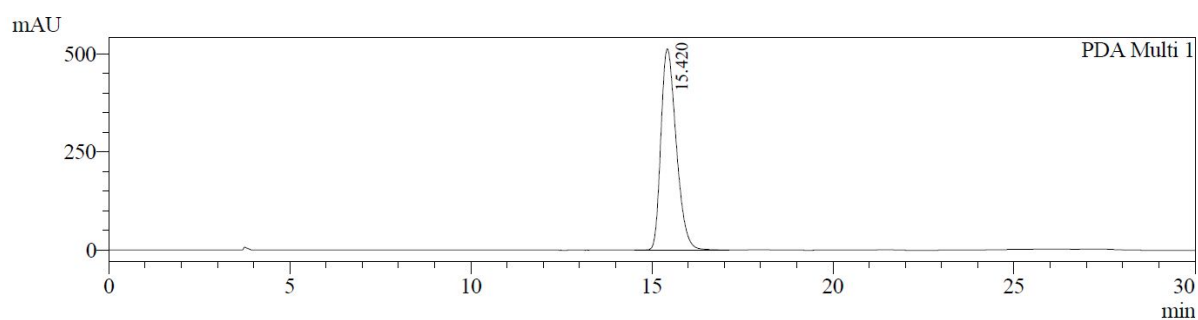
HPLC conditions: Column = Chiralcel OD (250 x 4,6 mm); eluent = *n*-heptane/*i*-PrOH (9:1); T = 25 °C; flow = 1 mL/min; λ = 250 nm.

HPLC analysis of racemic (\pm)-**1b** (tR_{Sp} = 15.4 min; tR_{Rp} = 17.6 min)



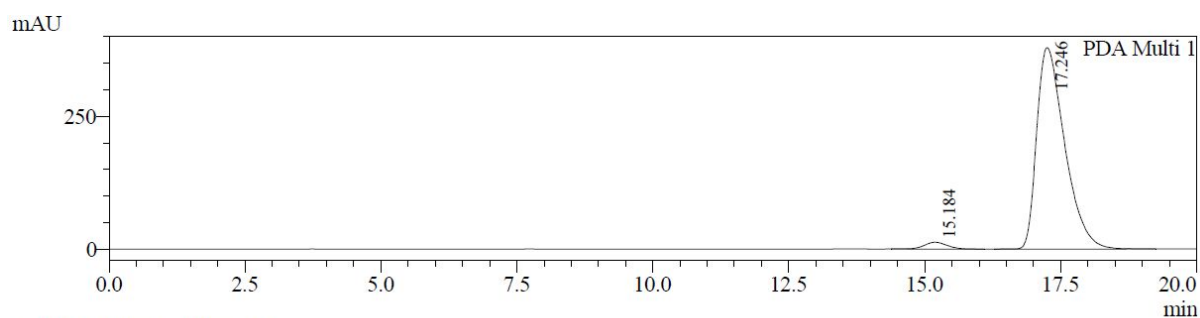
Peak#	Ret. Time	Area	Height	Area %
1	15.356	12526418	424382	50.109
2	17.583	12471809	343073	49.891
Total				100.000

HPLC analysis of (*Sp*)-**1b** (tR_{Sp} = 15.4 min)



Peak#	Ret. Time	Area	Height	Area %
1	15.420	15110599	513352	100.000
Total				100.000

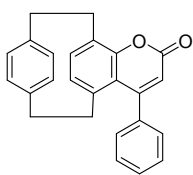
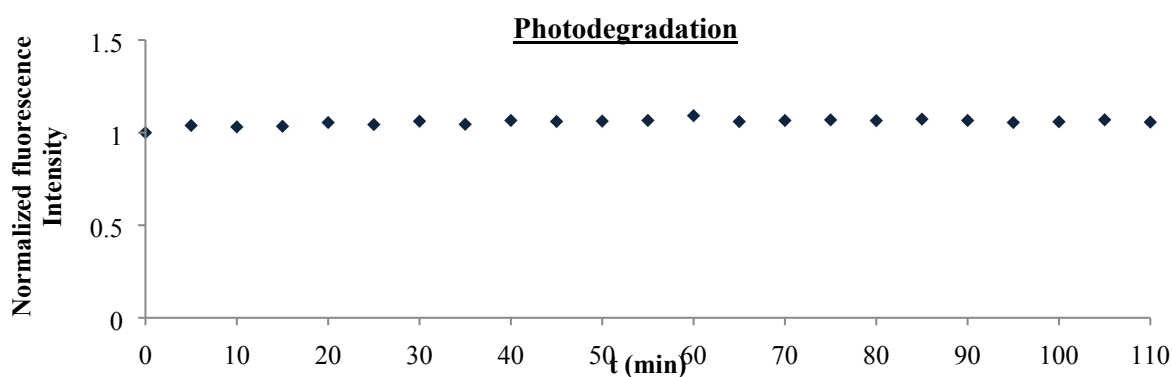
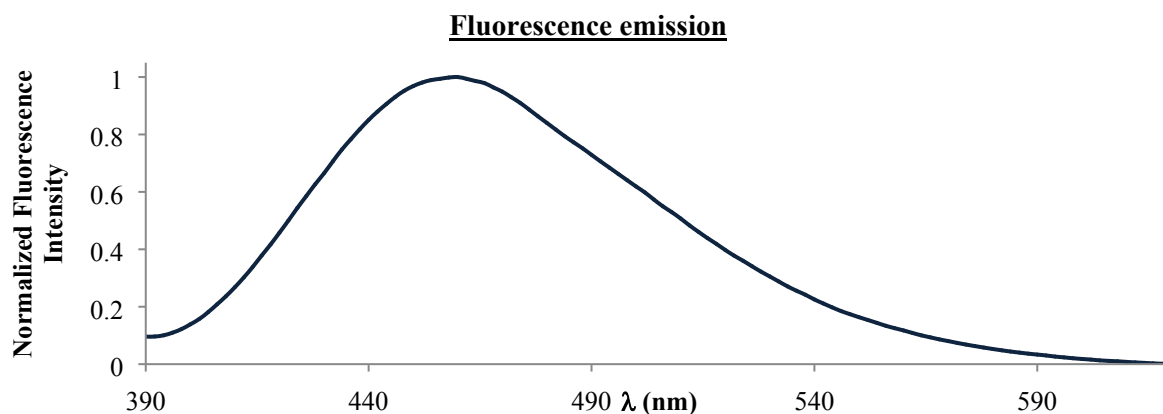
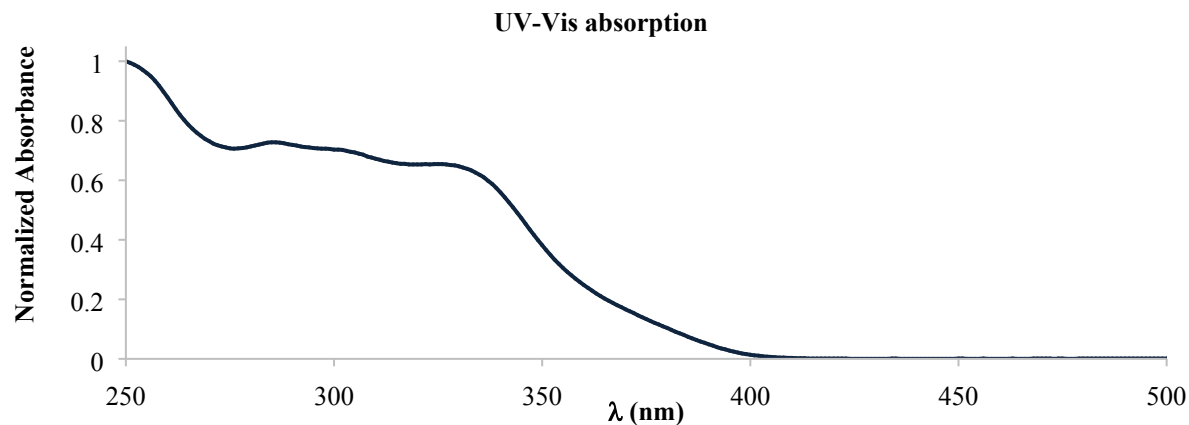
HPLC analysis of (*Rp*)-**1b** (tR_{Rp} = 17.2 min)



Peak#	Ret. Time	Area	Height	Area %
1	15.184	386353	13085	2.762
2	17.246	13599481	379101	97.238
Total		13985834	392186	100.000

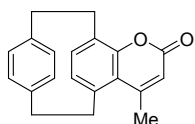
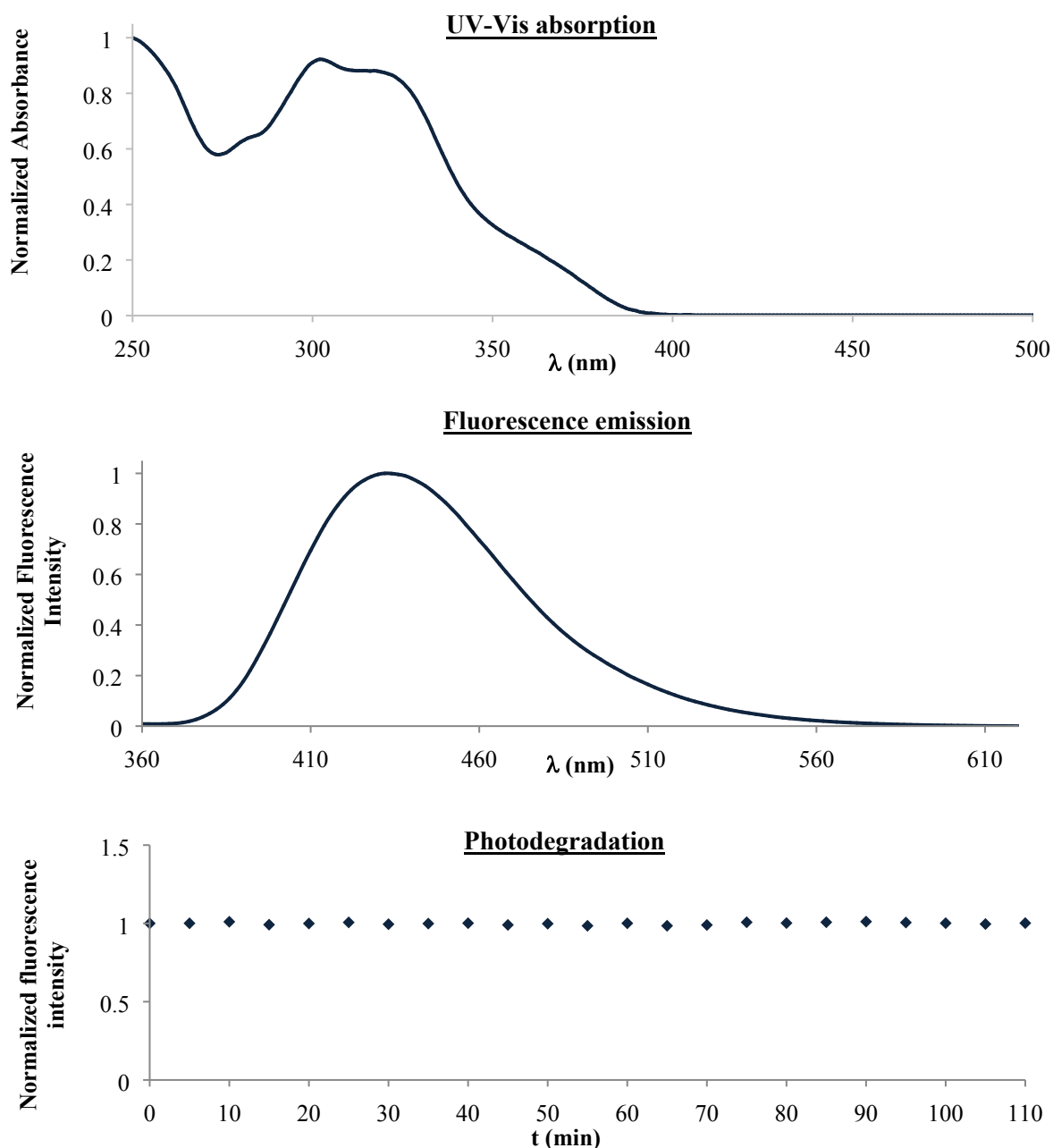
UV-Vis and Fluorescence spectroscopy

15-Phenyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (**Compound** (±)-**1a**)



Absorbance max: 285 nm, 300 nm, 330 nm ($1 \cdot 10^{-4}$ M solution in DCE);
 Emission max: 460 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 340$ nm, $\epsilon_{340\text{nm}} = 5240 \text{ cm}^{-1} \cdot \text{M}^{-1}$ at 10°C). A $1 \cdot 10^{-4}$ M solution of (±)-**1a** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 110 min at 20°C ($\lambda_{\text{ex}} = 340$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 460$ nm) were measured at 5-minute time intervals. QY n.d. (<0.1%).

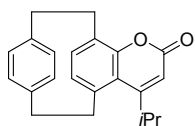
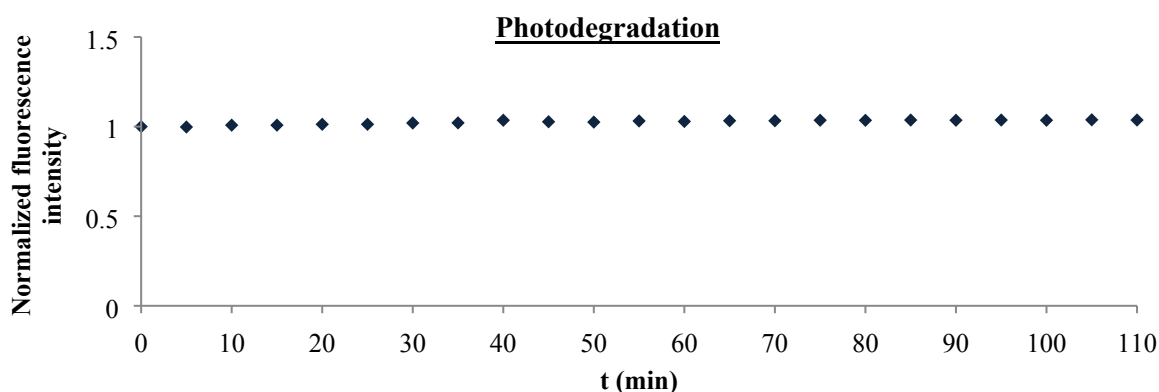
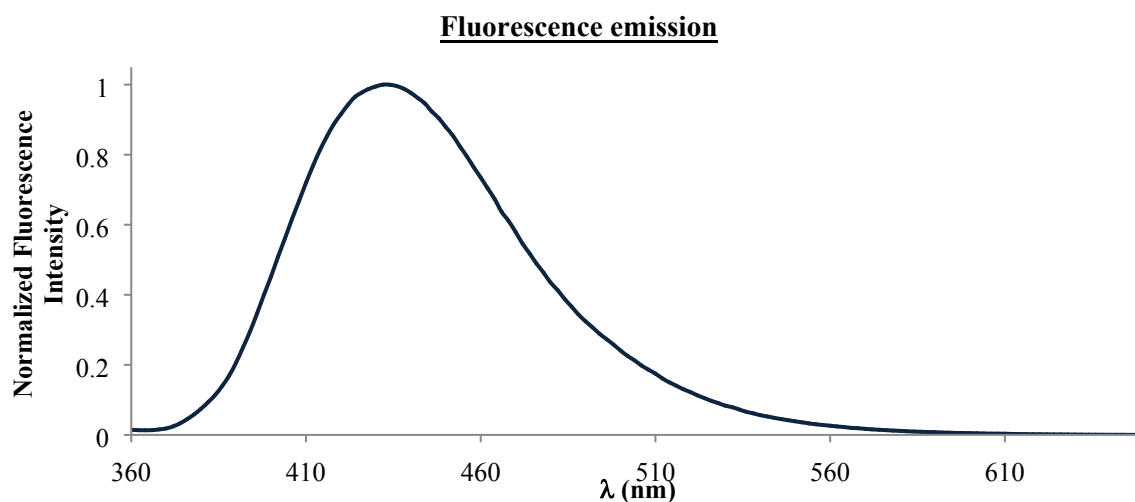
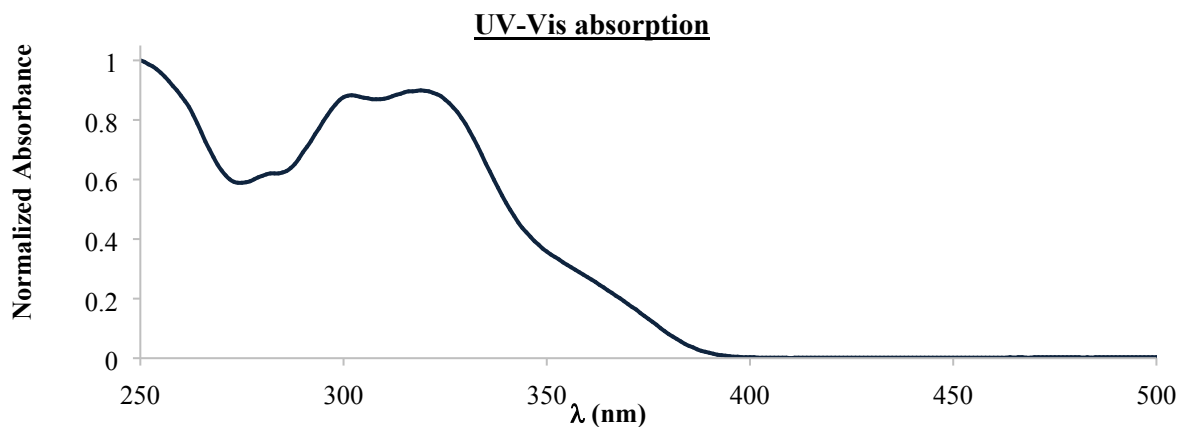
15-Methyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (Compound (±)-1b)



Absorbance max: 301 nm and 319 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 435 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 340$ nm, $\epsilon_{340\text{nm}} = 3370$ $\text{cm}^{-1} \cdot \text{M}^{-1}$ at 10 °C). A $1 \cdot 10^{-4}$ M solution of (±)-**1b** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 110 min at 20 °C ($\lambda_{\text{ex}} = 340$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 435$ nm) were measured at 5-minute time intervals. QY in DCE at 20 °C = 0.01.¹

¹ Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 0.27). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

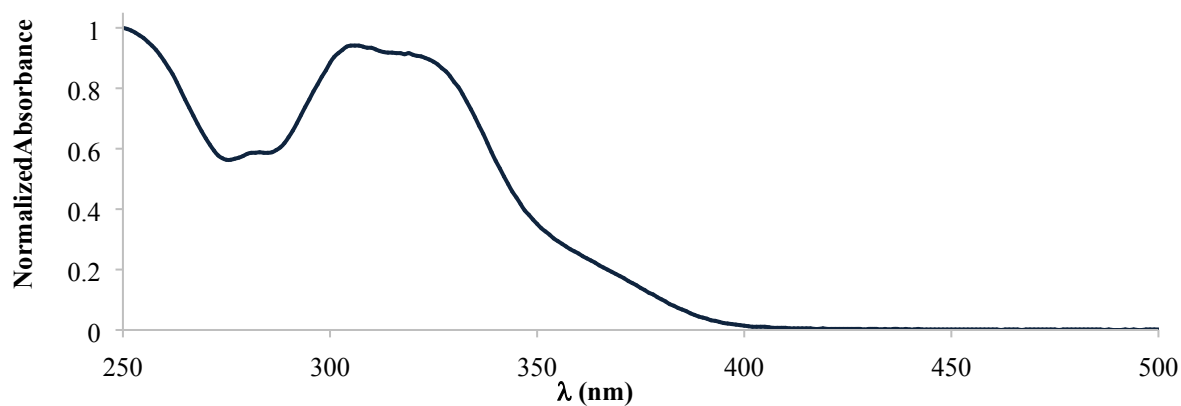
15-(Propan-2-yl)-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (**Compound** (\pm)-**1c**)



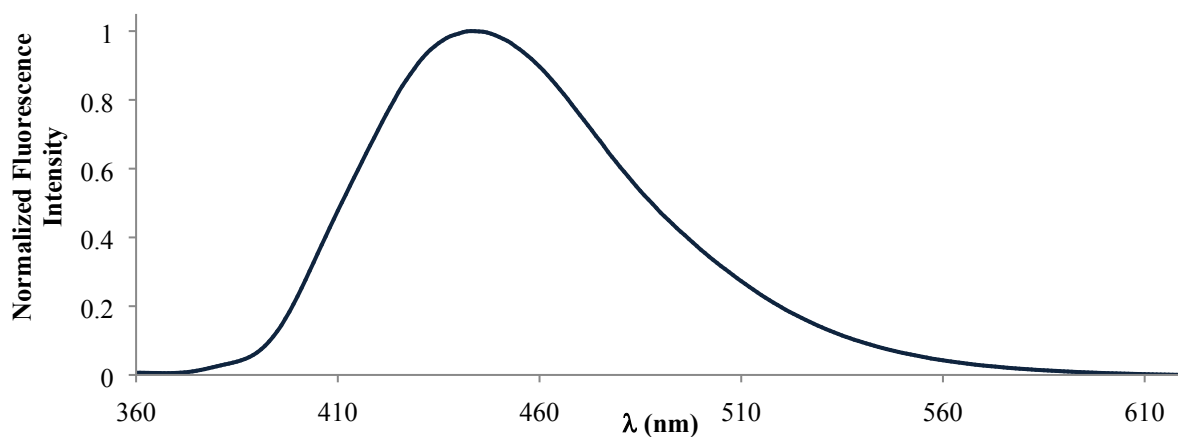
Absorbance max: 300 nm and 320 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 432 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 340$ nm, $\epsilon_{340\text{nm}} = 3150$ cm²·mol⁻¹ at 10 °C). A $1 \cdot 10^{-4}$ M solution of (\pm)-**1c** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 110 min at 20 °C ($\lambda_{\text{ex}} = 340$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 432$ nm) were measured at 5-minute time intervals. QY n.d. (<0.1%).

12-Oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one
(Compound (±)-**1d**)

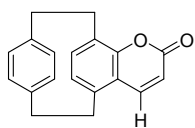
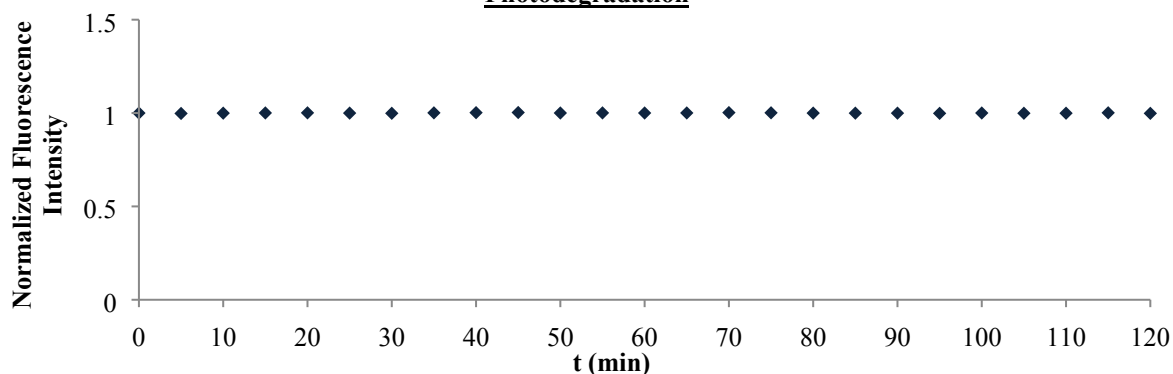
UV-Vis absorption



Fluorescence emission



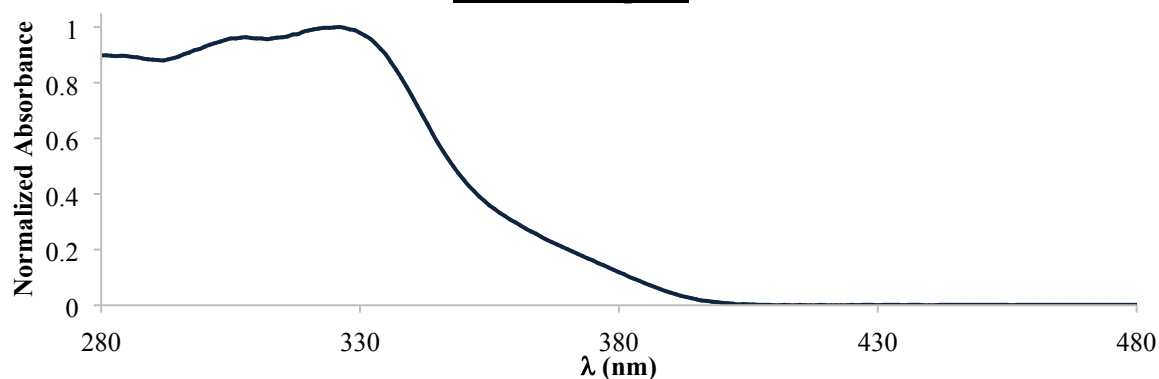
Photodegradation



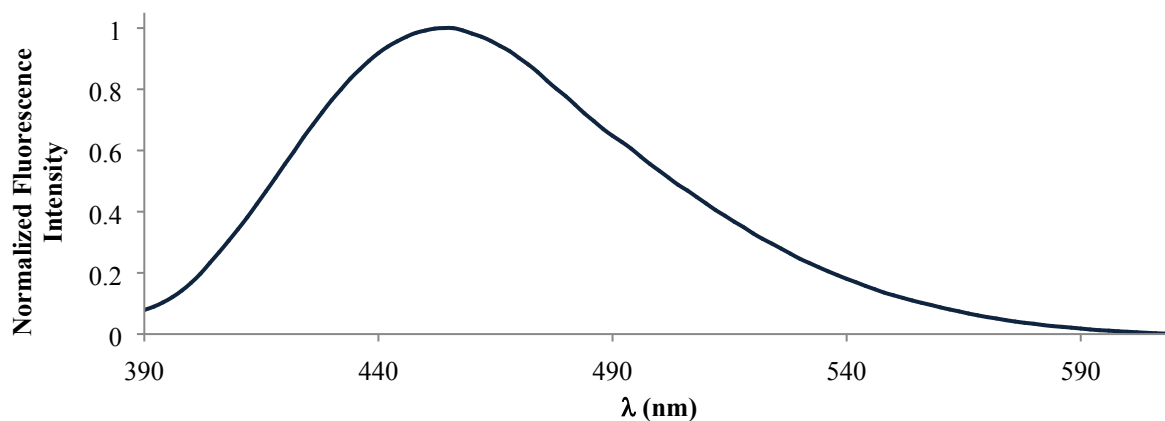
Absorbance max: 304 nm and 320 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 445 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 340$ nm, $\epsilon_{340\text{nm}} = 3160$ cm²·mol⁻¹ at 10 °C). A $1 \cdot 10^{-4}$ M solution of (±)-**1d** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 120 min at 20 °C ($\lambda_{\text{ex}} = 340$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 445$ nm) were measured at 5-minute time intervals. QY n.d. (<0.1%).

5-Bromo-15-phenyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (**Compound (±)-1e**)

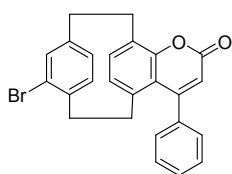
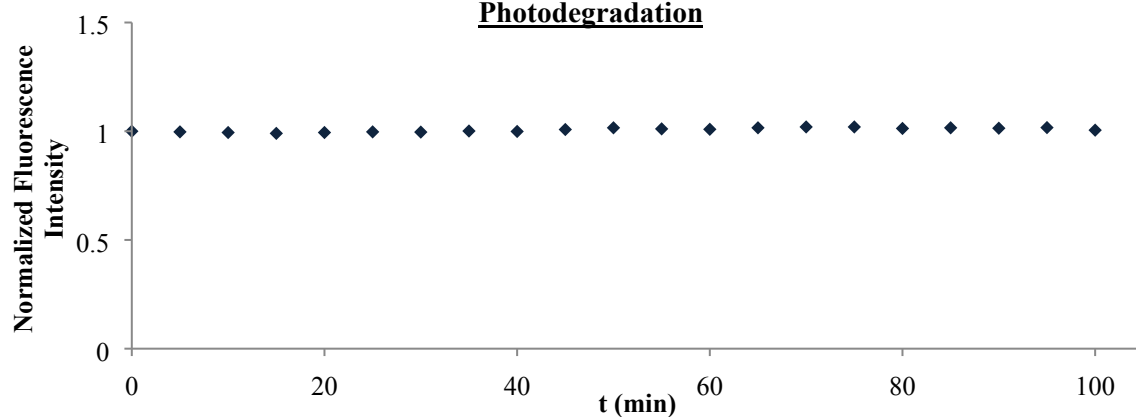
UV-Vis absorption



Fluorescence emission

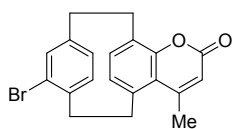
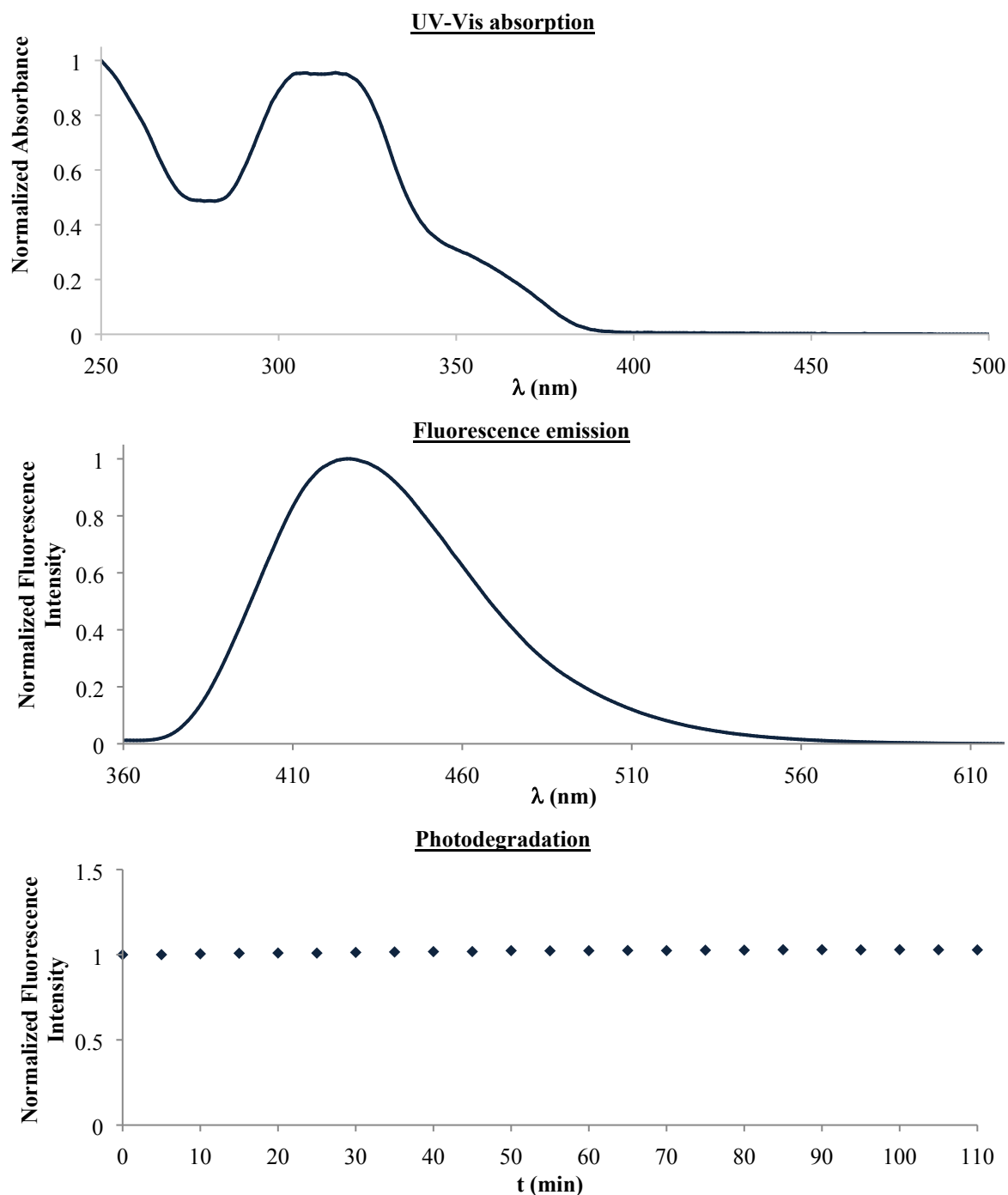


Photodegradation



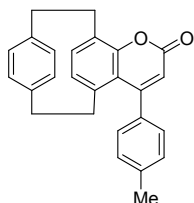
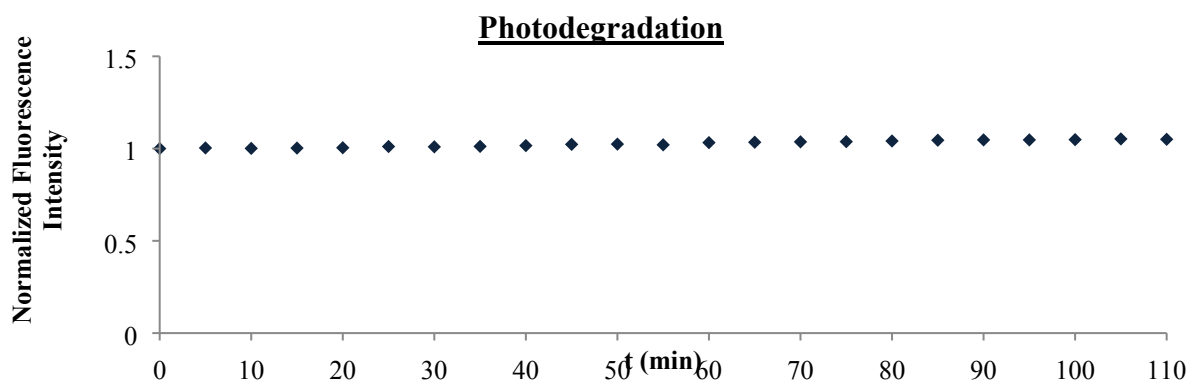
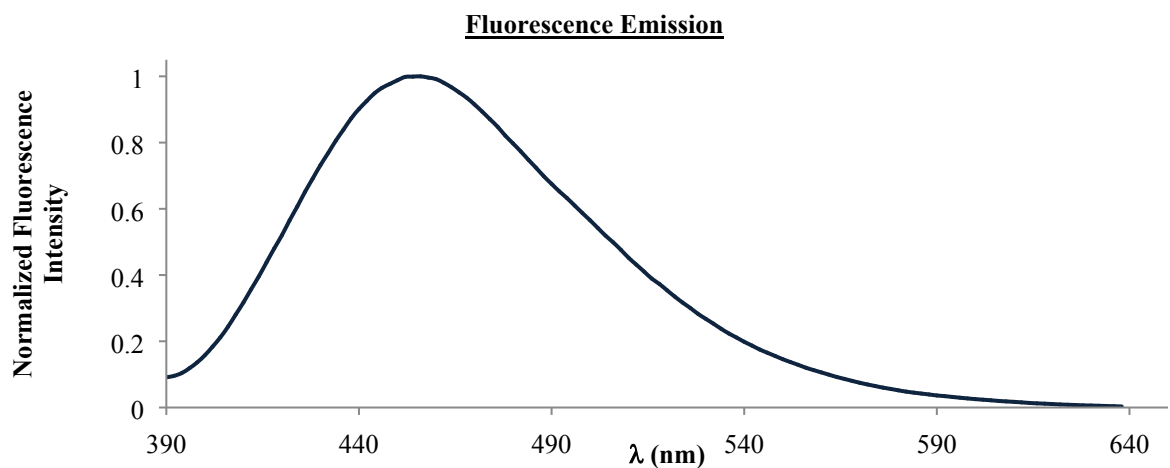
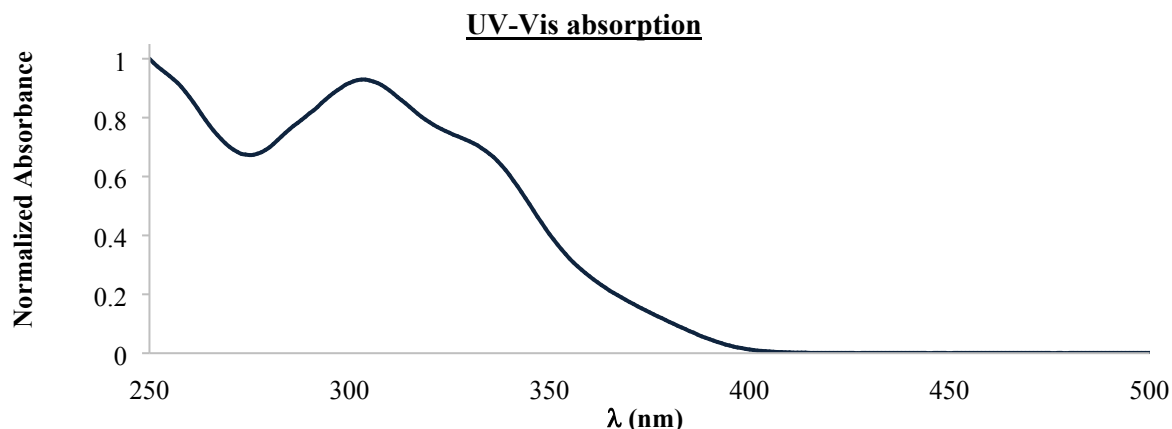
Absorbance max: 307 nm and 325 nm ($1 \cdot 10^{-4}$ M solution in DCE);
 Emission max: 450 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 320$ nm, $\epsilon_{320\text{nm}} = 6900 \text{ cm}^{-1} \cdot \text{M}^{-1}$ at 10°C). A $1 \cdot 10^{-4}$ M solution of (\pm)-**1e** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 105 min at 20°C ($\lambda_{\text{ex}} = 320$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 450$ nm) were measured at 5-minute time intervals. QY n.d. ($<0.1\%$).

5-Bromo-15-methyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (**Compound (±)-1f**)



Absorbance max: 306 nm and 320 nm ($1 \cdot 10^{-4}$ M solution in DCE);
 Emission max: 425 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 340$ nm, $\epsilon_{340\text{nm}} = 3230 \text{ cm}^{-1} \cdot \text{M}^{-1}$ at 10°C). A $1 \cdot 10^{-4}$ M solution of (±)-**1f** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 110 min at 20°C ($\lambda_{\text{ex}} = 340$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 425$ nm) were measured at 5-minute time intervals. QY n.d. ($<0.1\%$).

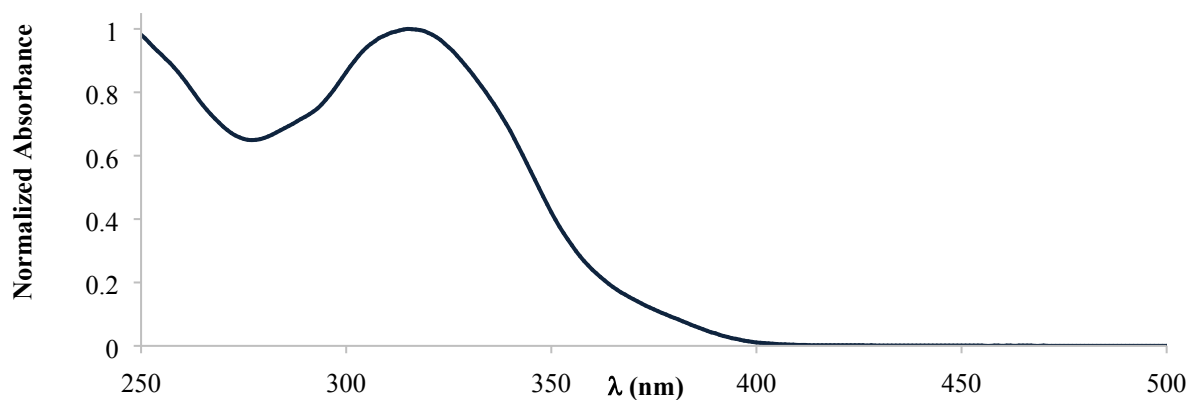
15-(4-Methylphenyl)-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (**Compound (±)-1g**)



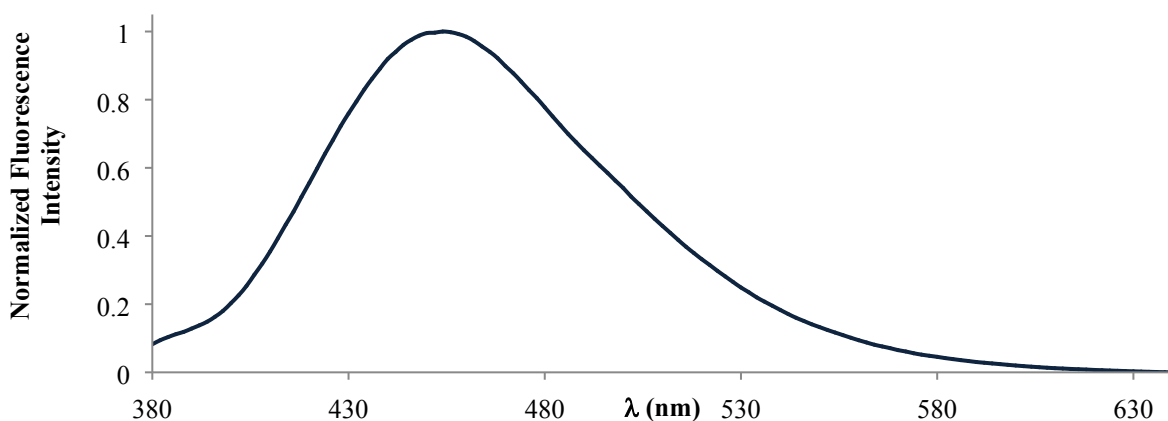
Absorbance max: 300 nm, 330 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 455 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 340$ nm, $\epsilon_{340\text{nm}} = 6220$ cm²·mol⁻¹ at 10 °C). A $1 \cdot 10^{-4}$ M solution of (±)-**1g** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 110 min at 20 °C ($\lambda_{\text{ex}} = 340$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 455$ nm) were measured at 5-minute time intervals. QY n.d. (<0.1%).

15-(4-Methoxyphenyl)-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17-,19-heptaen-13-one (**Compound (±)-1h**)

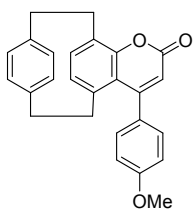
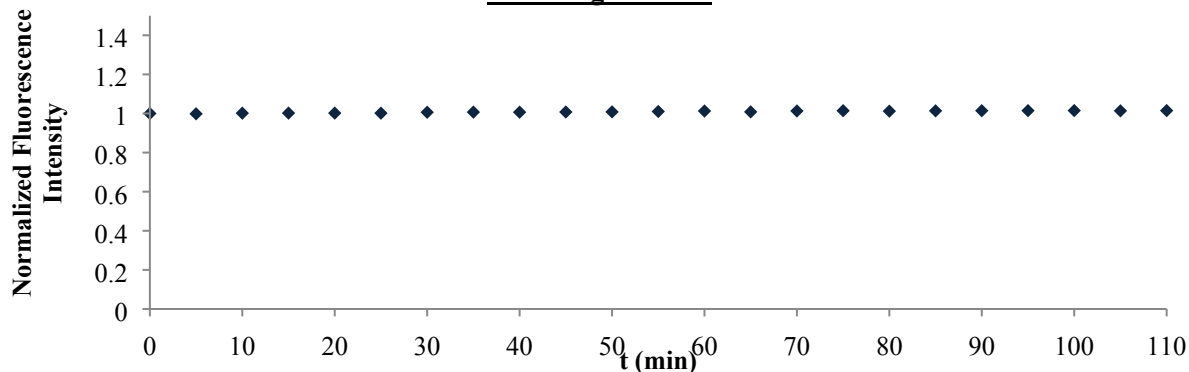
UV-Vis absorption



Fluorescence emission

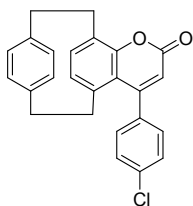
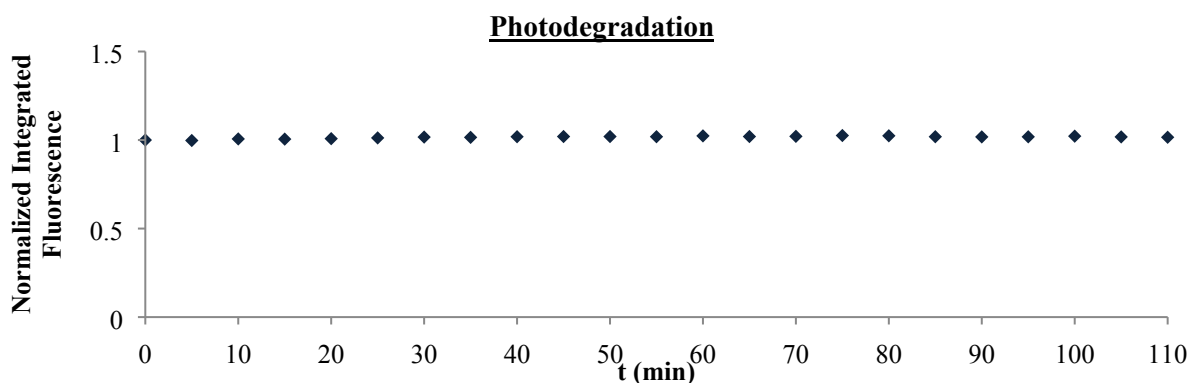
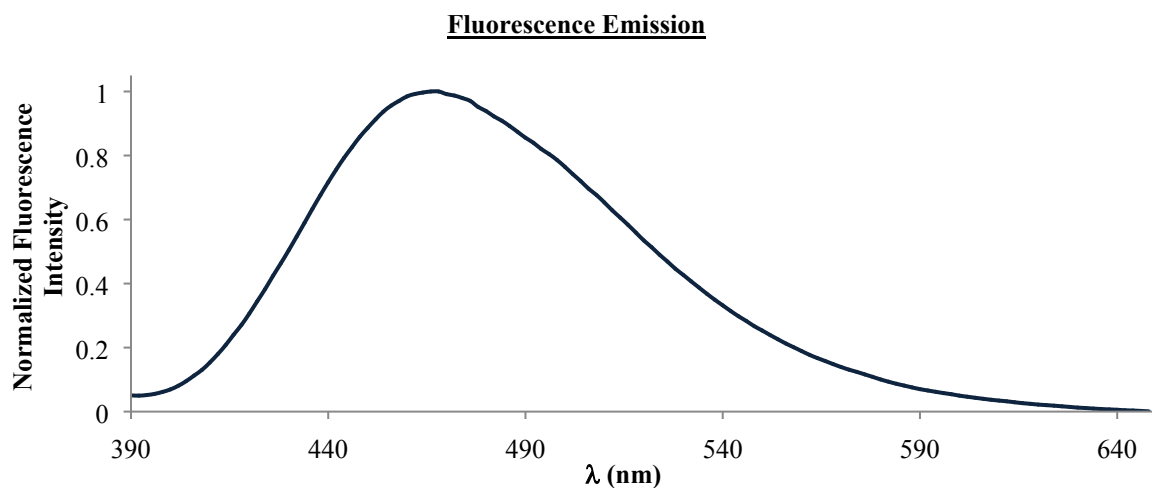
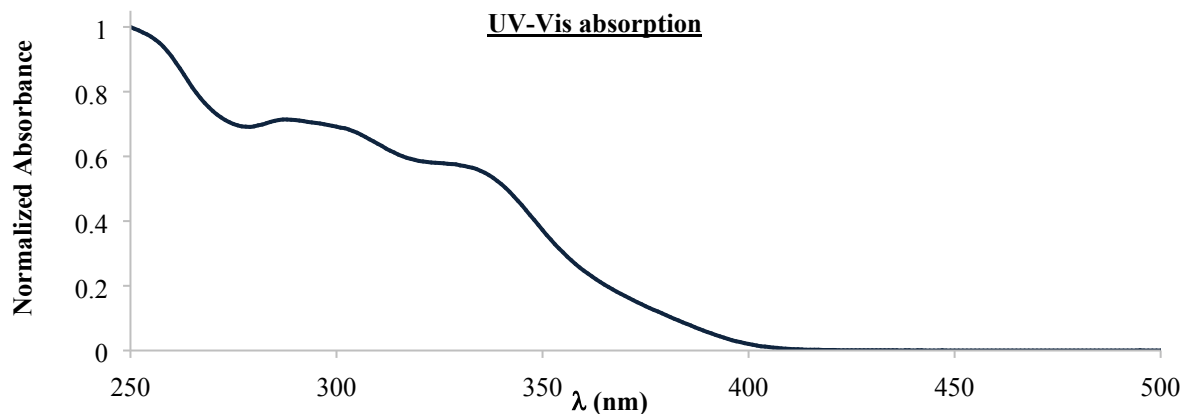


Photodegradation



Absorbance max: 315 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 455 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 330$ nm, $\epsilon_{330\text{nm}} = 7400$ cm⁻¹·M⁻¹ at 10 °C). A $1 \cdot 10^{-4}$ M solution of (±)-**1h** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 110 min at 20 °C ($\lambda_{\text{ex}} = 330$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 455$ nm) were measured at 5-minute time intervals. QY n.d. (<0.1%).

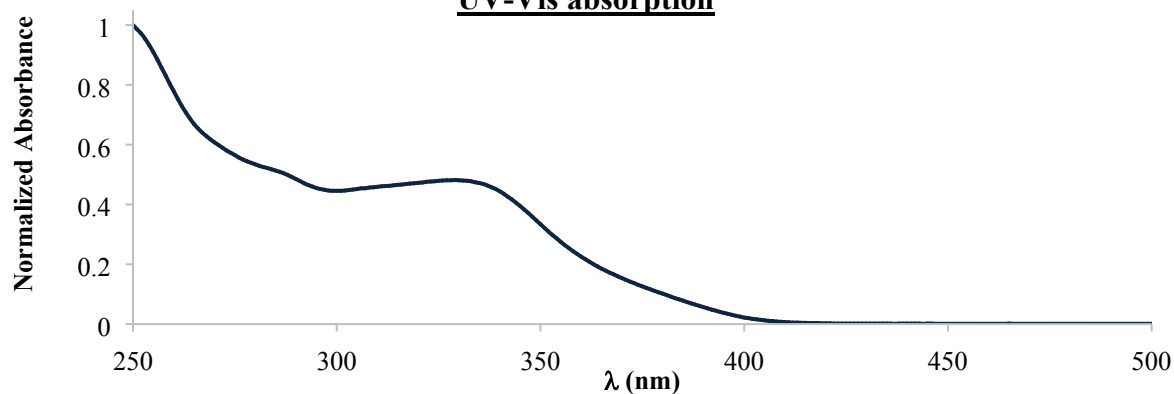
15-(4-Chlorophenyl)-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (Compound (±)-1i)



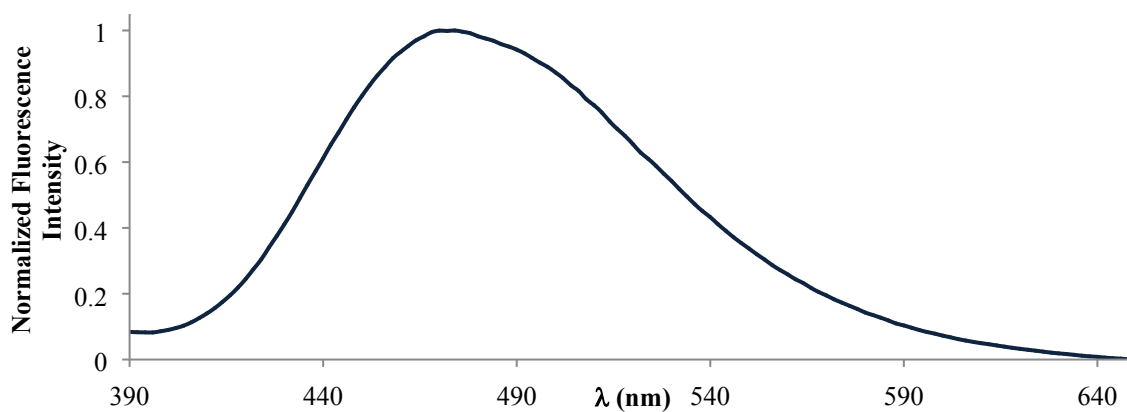
Absorbance max: 288 nm, 310 nm, 335 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 465 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 340$ nm, $\epsilon_{340\text{nm}} = 6310$ $\text{cm}^{-1} \cdot \text{M}^{-1}$ at 10°C). A $1 \cdot 10^{-4}$ M solution of (±)-**1i** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 110 min at 20°C ($\lambda_{\text{ex}} = 340$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 465$ nm) were measured at 5-minute time intervals. QY n.d. ($<0.1\%$).

4-{13-Oxo-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-15-yl}phenyl trifluoromethanesulfonate (**Compound** (\pm)-**1j**)

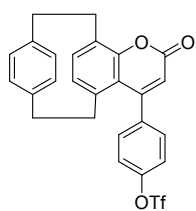
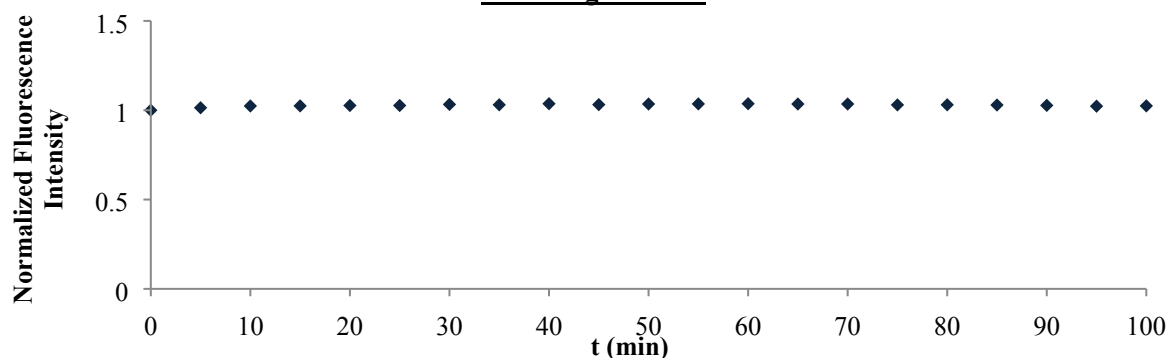
UV-Vis absorption



Fluorescence emission



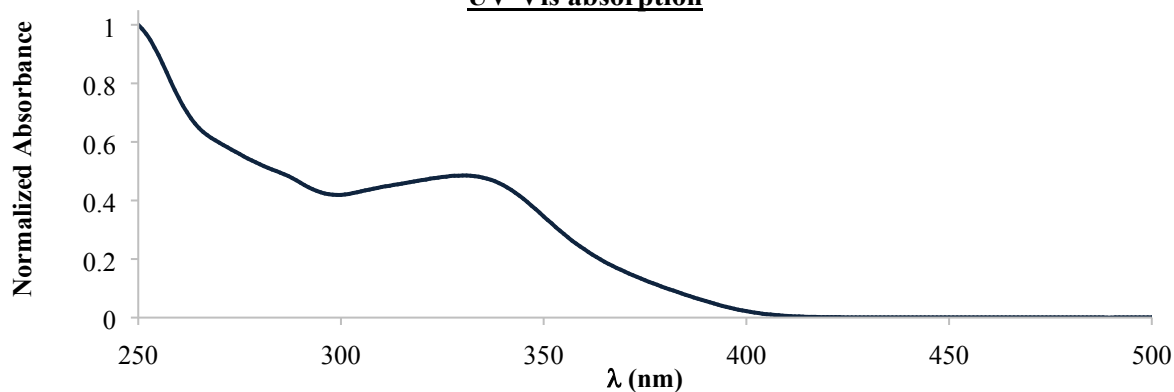
Photodegradation



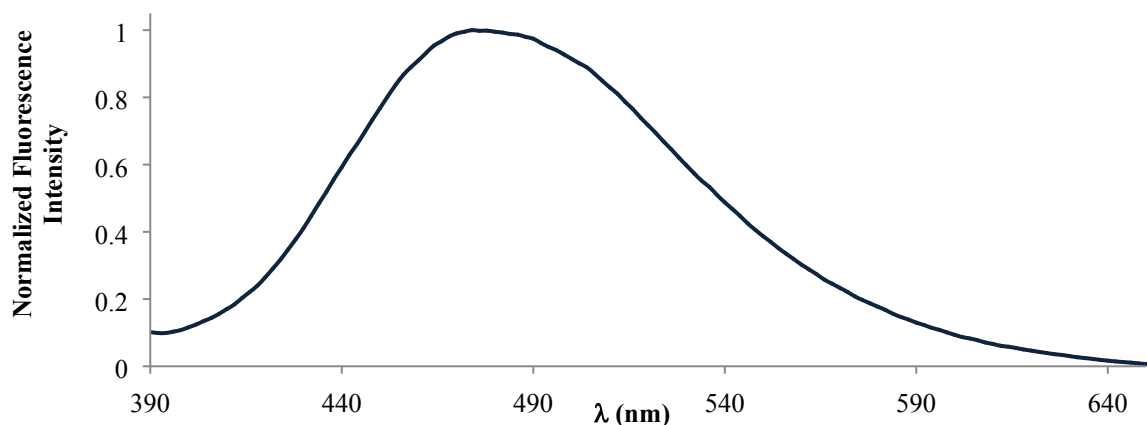
Absorbance max: 280 nm and 330 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 470 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 340$ nm, $\epsilon_{340\text{nm}} = 5460 \text{ cm}^{-1} \cdot \text{M}^{-1}$ at 10°C). A $1 \cdot 10^{-4}$ M solution of (\pm)-**1j** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 100 min at 20°C ($\lambda_{\text{ex}} = 340$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 470$ nm) were measured at 5-minute time intervals. QY n.d. ($<0.1\%$).

15-[4-(Trifluoromethyl)phenyl]-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (**Compound (±)-1k**)

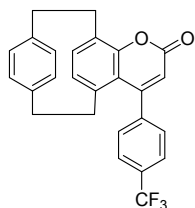
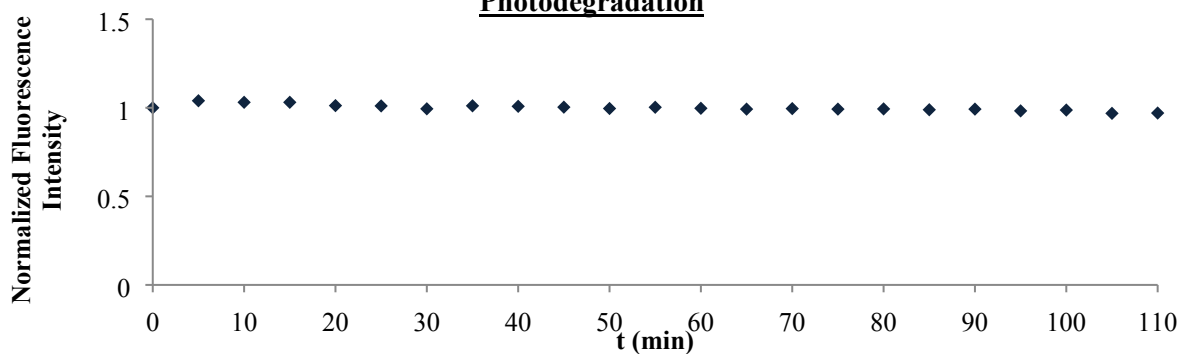
UV-Vis absorption



Fluorescence emission



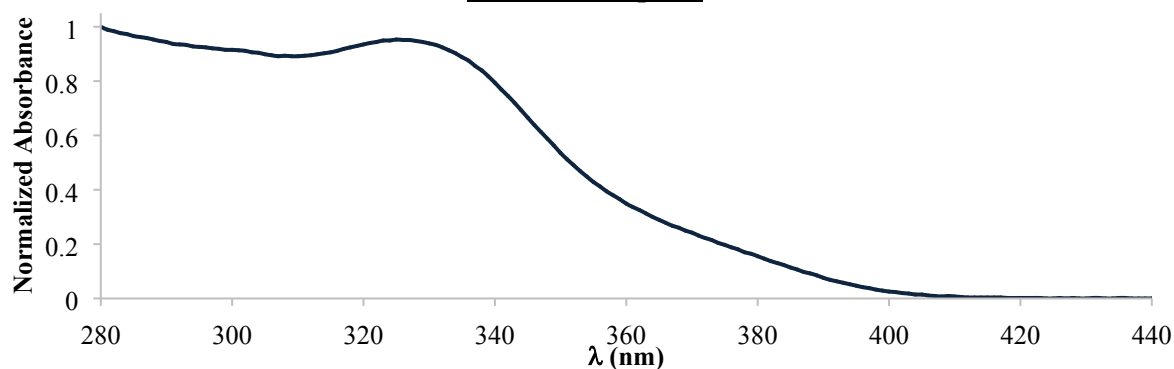
Photodegradation



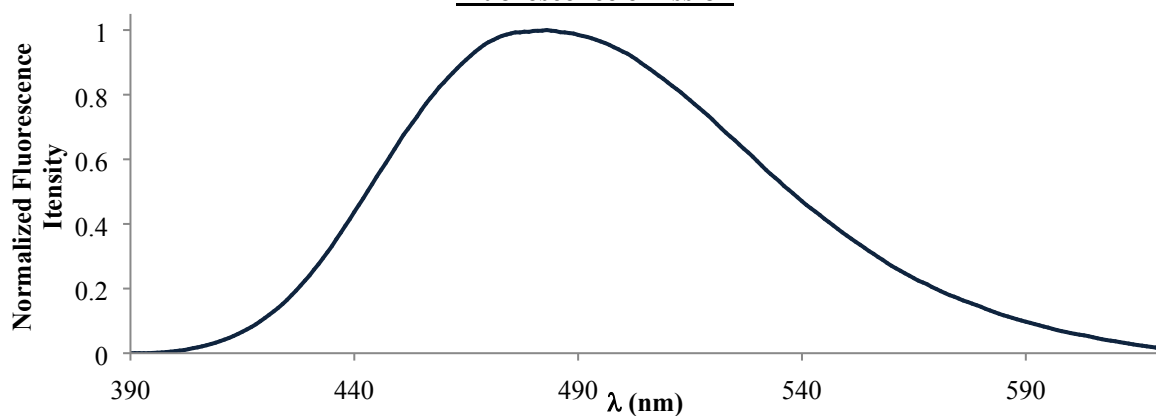
Absorbance max: 270 nm and 335 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 475 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 340$ nm, $\epsilon_{340\text{nm}} = 5500$ cm²·mol⁻¹ at 10 °C). A $1 \cdot 10^{-4}$ M solution of (±)-**1k** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 110 min at 20 °C ($\lambda_{\text{ex}} = 340$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 475$ nm) were measured at 5-minute time intervals. QY n.d. (<0.1%).

2,2-Dimethyl-N-{13-oxo-15-phenyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa1(16), 4(20),5,7(19),10,14,17-heptaen-5-yl}propanamide (**Compound (±)-11**)

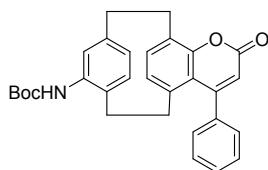
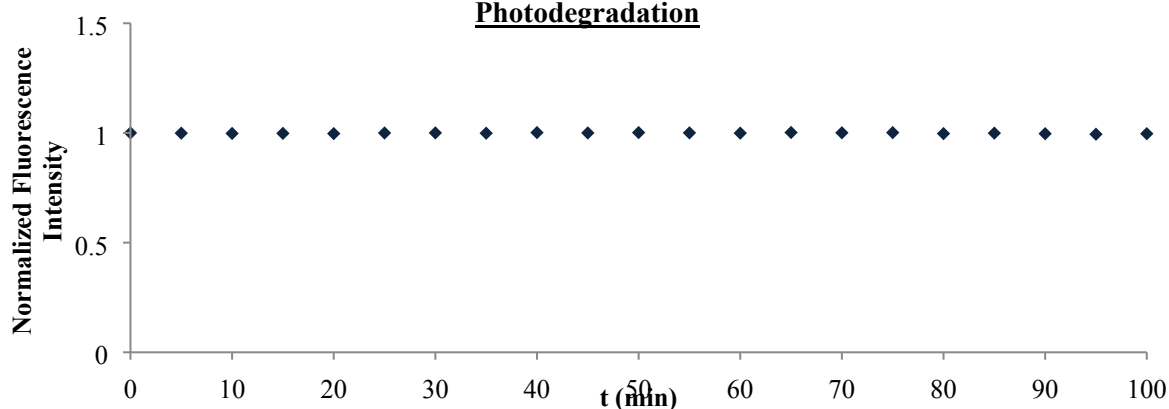
UV-Vis absorption



Fluorescence emission



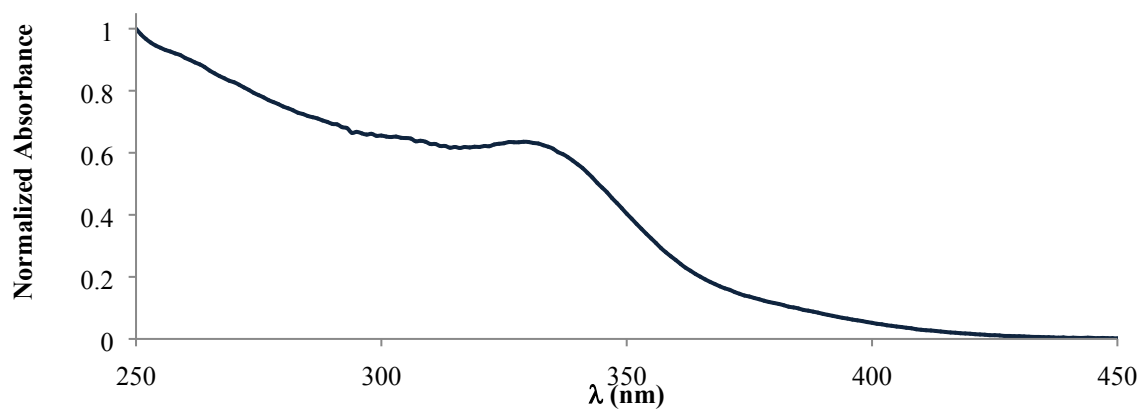
Photodegradation



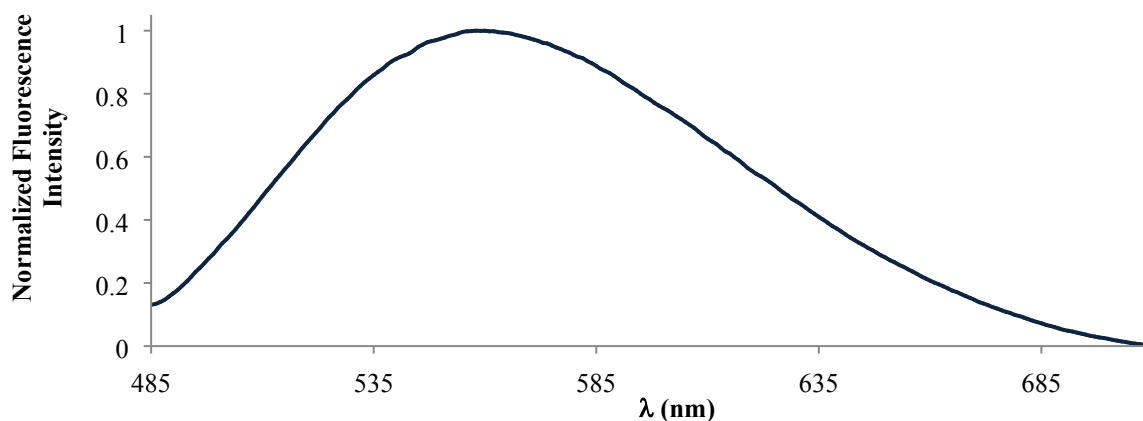
Absorbance max: 327 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 483 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 330$ nm, $\epsilon_{330\text{nm}} = 5800$ cm⁻¹·M⁻¹ at 10 °C). A $1 \cdot 10^{-5}$ M solution of (±)-**11** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 100 min at 20 °C ($\lambda_{\text{ex}} = 330$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 483$ nm) were measured at 5-minute time intervals. QY n.d. (<0.1%).

20-Amino-15-phenyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (**Compound (±)-1m**)

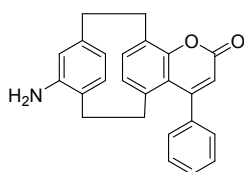
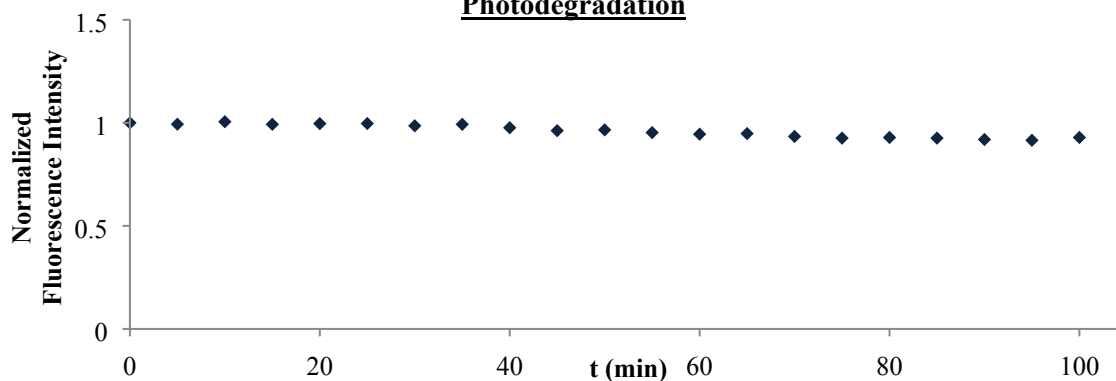
UV-Vis absorption



Fluorescence emission



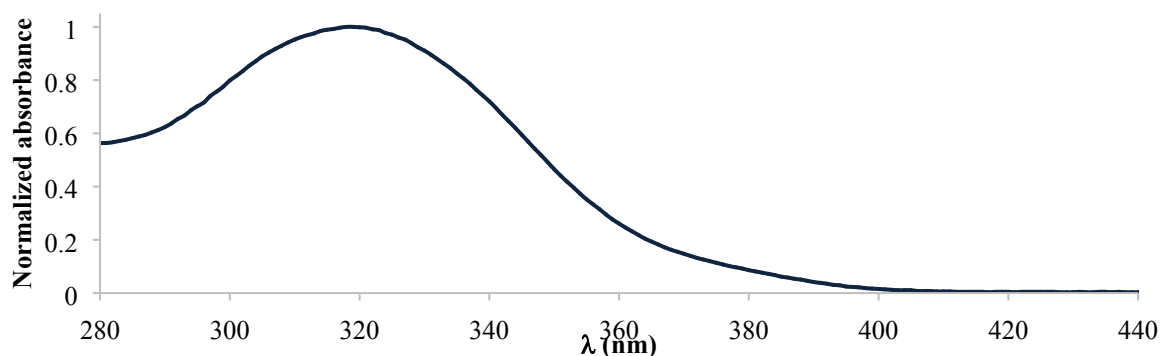
Photodegradation



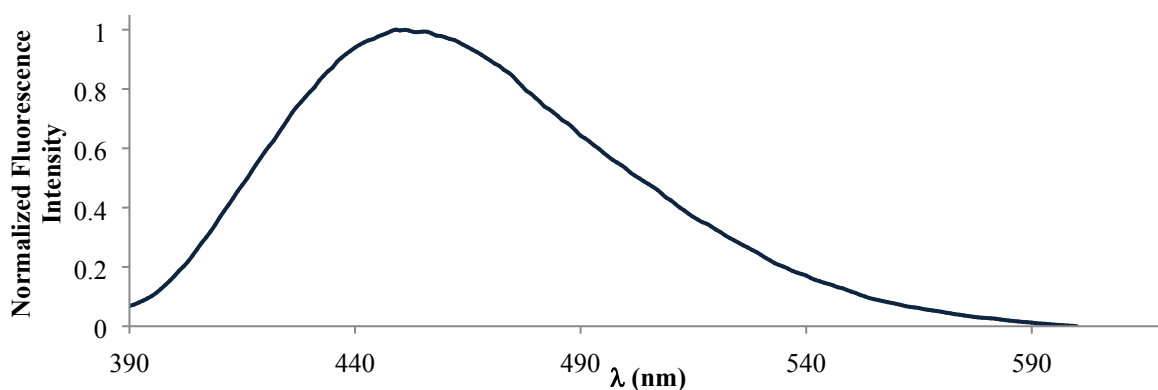
Absorbance max: 330 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 575 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 365$ nm, $\epsilon_{365\text{nm}} = 2900 \text{ cm}^{-1} \cdot \text{M}^{-1}$ at 10°C). A $1 \cdot 10^{-5}$ M solution of (\pm)-**1m** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 110 min at 20°C ($\lambda_{\text{ex}} = 365$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 575$ nm) were measured at 5-minute time intervals. QY n.d. ($<0.1\%$).

tert-Butyl *N*-(4-{13-oxo-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(17),4,6,10(18),11(16),14,19-heptaen-15-yl}phenyl)carbamate (**Compound** (±)-**1n**)

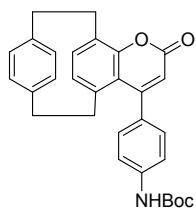
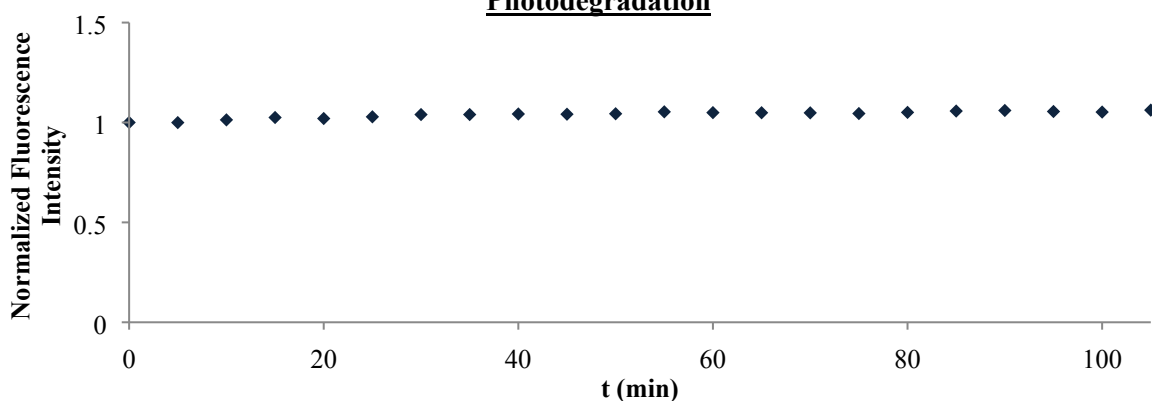
UV-Vis absorption



Fluorescence emission

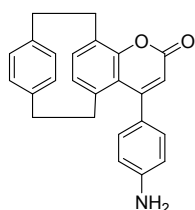
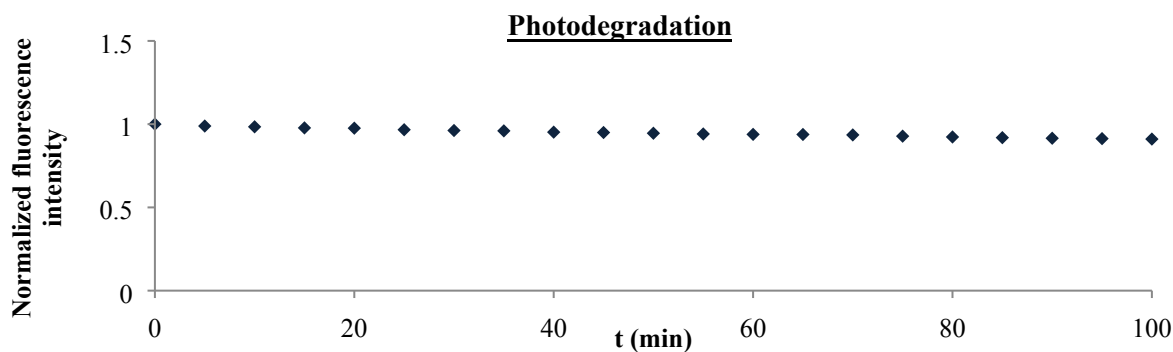
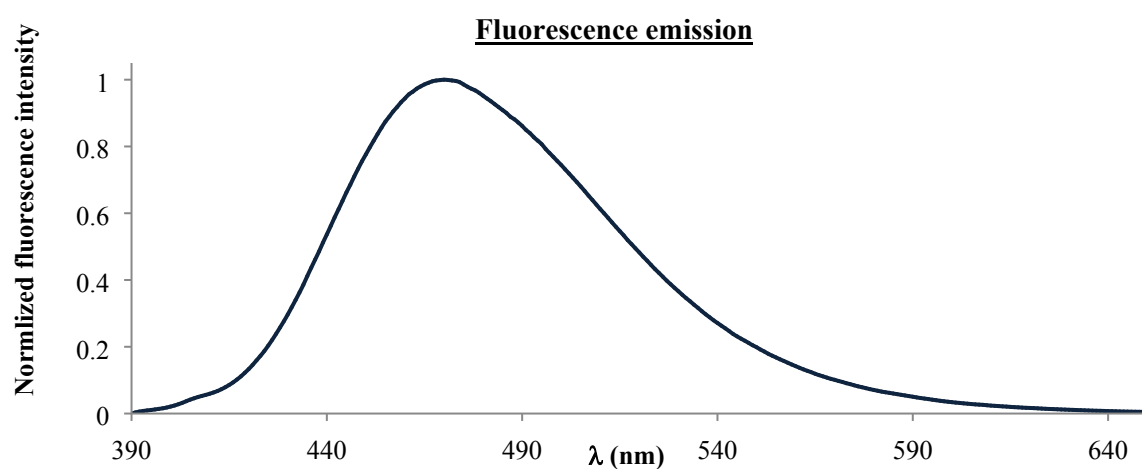
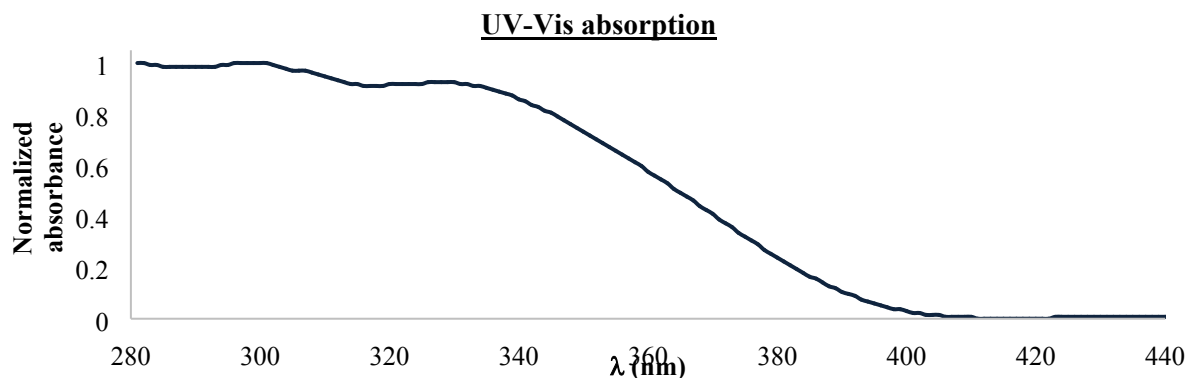


Photodegradation



Absorbance max: 317 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 450 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 310$ nm, $\epsilon_{310\text{nm}} = 7800 \text{ cm}^{-1} \cdot \text{M}^{-1}$ at 10°C). A $1 \cdot 10^{-5}$ M solution of (±)-**1n** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 105 min at 20°C ($\lambda_{\text{ex}} = 315$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 450$ nm) were measured at 5-minute time intervals. QY n.d. ($<0.1\%$).

15-(4-Aminophenyl)-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(17),4,6,10(18),11(16),14,19-heptaen-13-one (**Compound (±)-1o**)

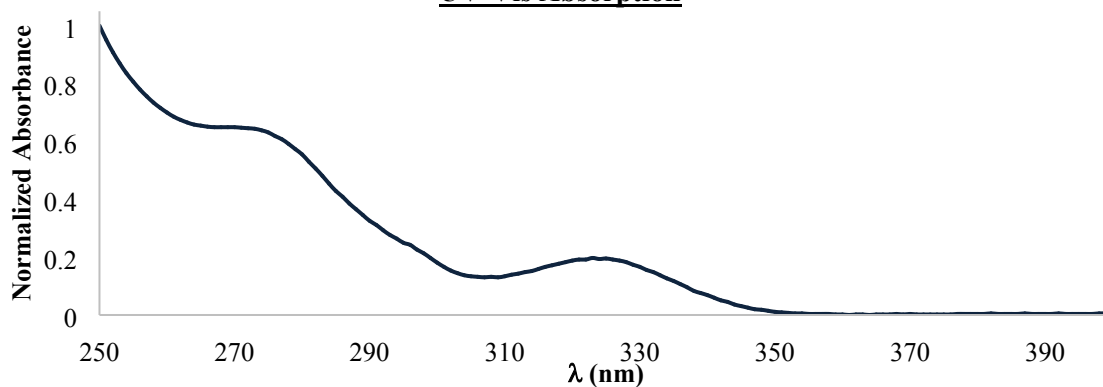


Absorbance max: 300 nm and 330 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 470 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 360$ nm, $\epsilon_{360\text{nm}} = 9500 \text{ cm}^{-1} \cdot \text{M}^{-1}$ at 10°C). A $1 \cdot 10^{-5}$ M solution of (\pm)-**1o** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 100 min at 20°C ($\lambda_{\text{ex}} = 360$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 470$ nm) were measured at 5-minute time intervals. QY in DCM at $20^\circ \text{C} = 0.05$.²

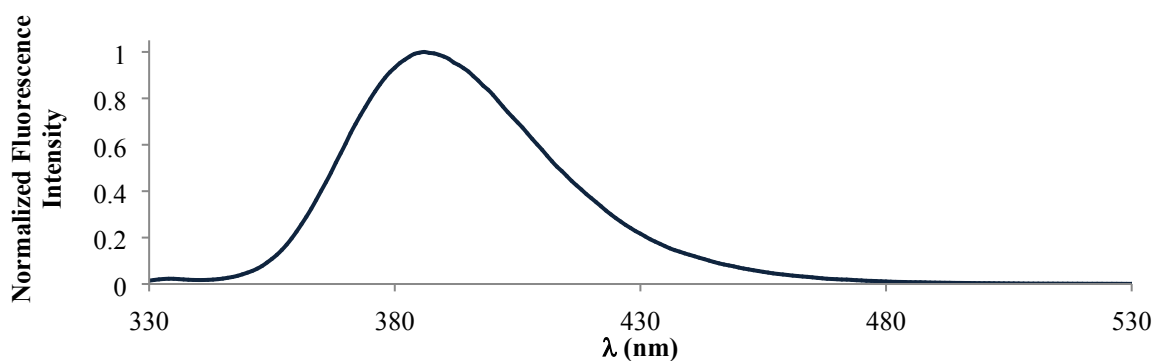
² Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 0.27). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

4-Amino[2.2]paracyclophane (Compound (±)-6)

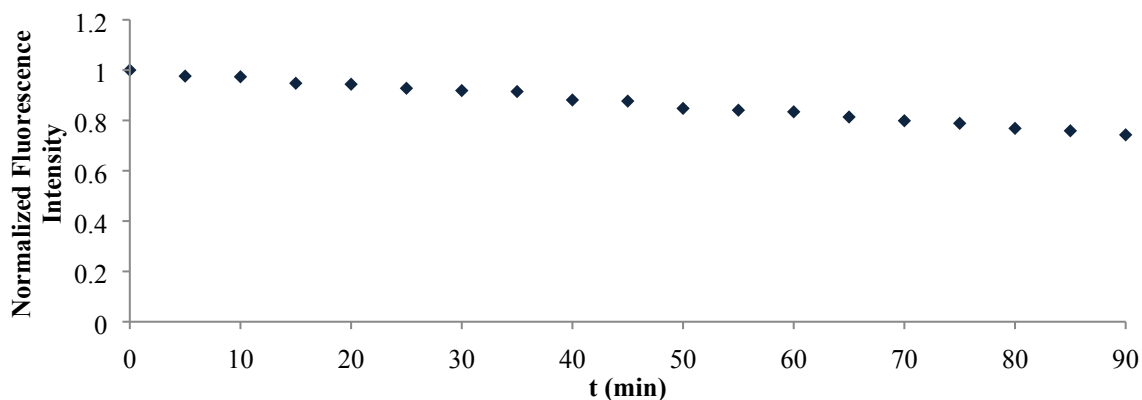
UV-Vis Absorption



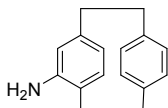
Fluorescence emission



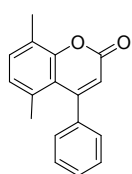
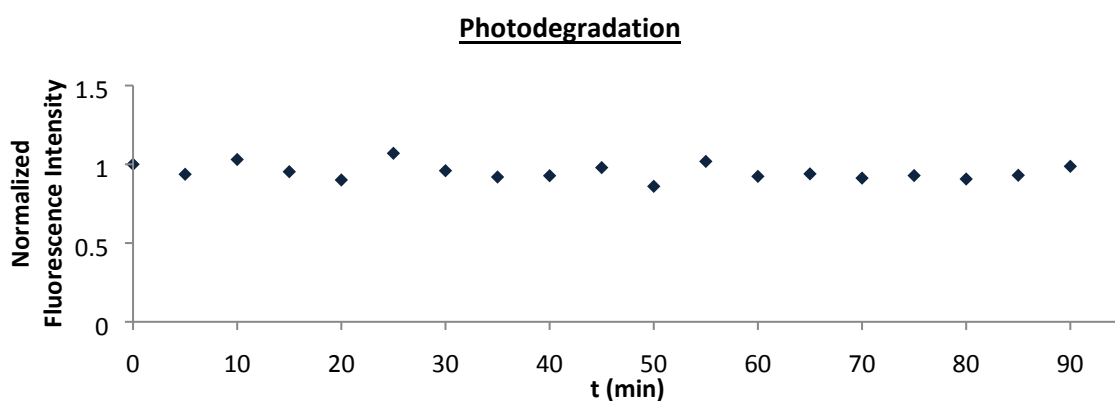
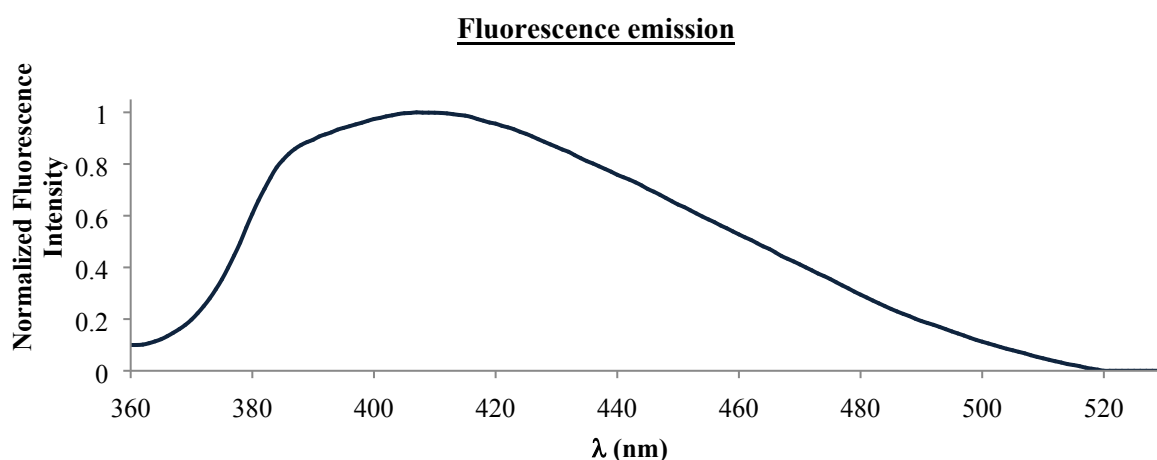
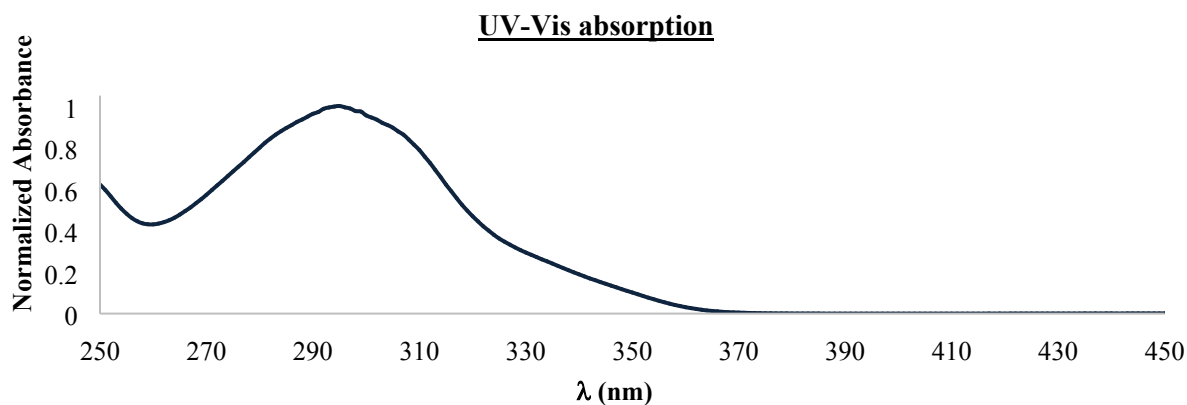
Photodegradation



Absorbance max: 274, 324 nm ($1 \cdot 10^{-4}$ M solution in DCM); Emission max: 386 nm ($1 \cdot 10^{-4}$ M solution in DCM, $\lambda_{\text{ex}} = 300$ nm). A $1 \cdot 10^{-4}$ M solution of (±)-**6** in DCM was used to perform the photodegradation study. The sample was continuously irradiated for 90 min at 20 °C ($\lambda_{\text{ex}} = 300$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 386$ nm) were measured at 5-minute time intervals. QY n.d. (<0.1%).

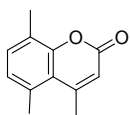
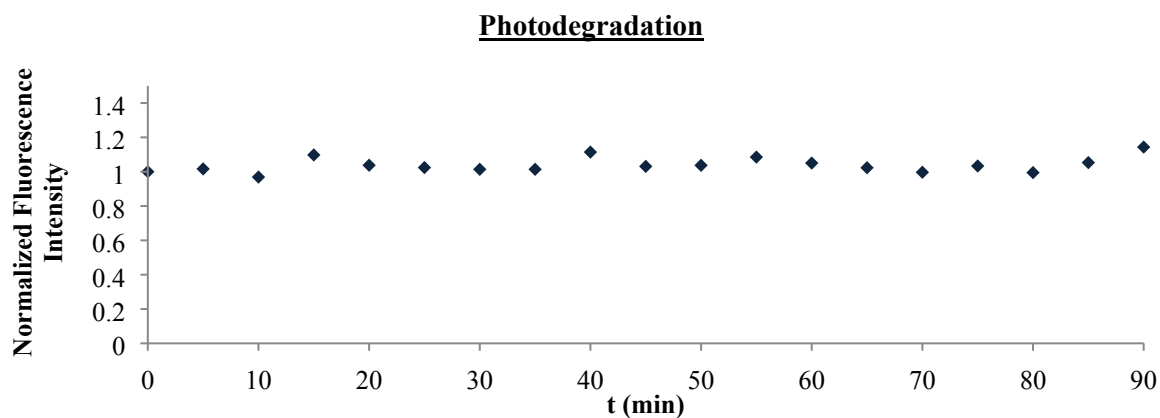
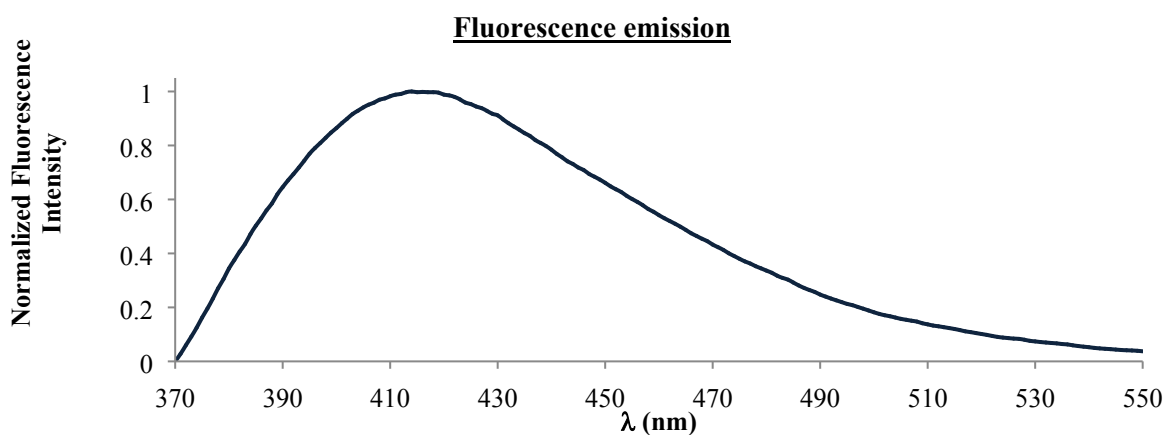
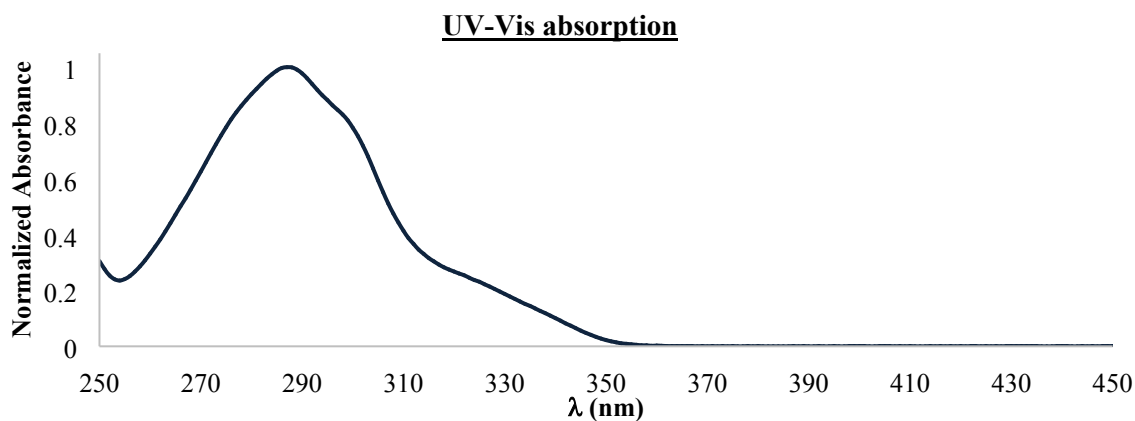


5,8-Dimethyl-4-phenyl-2H-chromen-2-one (Compound 7a)



Absorbance max: 294, 310, 330, 350 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 418 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 340$ nm). A $1 \cdot 10^{-4}$ M solution of **7a** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 95 min at 20 °C ($\lambda_{\text{ex}} = 340$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 415$ nm) were measured at 5-minute time intervals. QY n.d. (<0.1%).

4,5,8-Trimethyl-2H-chromen-2-one (Compound 7b)



Absorbance max: 286, 299, 330 nm ($1 \cdot 10^{-4}$ M solution in DCE); Emission max: 413 nm ($1 \cdot 10^{-4}$ M solution in DCE, $\lambda_{\text{ex}} = 310$ nm). A $1 \cdot 10^{-4}$ M solution of **7b** in DCE was used to perform the photodegradation study. The sample was continuously irradiated for 90 min at 20 °C ($\lambda_{\text{ex}} = 310$ nm) and maximum emission intensity changes ($\lambda_{\text{max}} = 400$ nm) were measured at 5-minute time intervals. QY n.d. ($<0.1\%$).

Circular dichroism and circularly polarized luminescence

The circular dichroism measurements for compounds (*S_p*)- and (*R_p*)-**1b** were performed in dichloromethane. The concentration of all the samples was $\sim 10^{-5}$ M. Absorption dissymmetry factors were obtained using the following formula:

$$g_{\text{abs}} = \left| 2 [\epsilon_{\text{L}}(\lambda) - \epsilon_{\text{R}}(\lambda)] / [\epsilon_{\text{L}}(\lambda) + \epsilon_{\text{R}}(\lambda)] \right|$$

where ϵ_{L} and ϵ_{R} denote the molar extinction coefficients for left and right circularly polarized light, respectively.

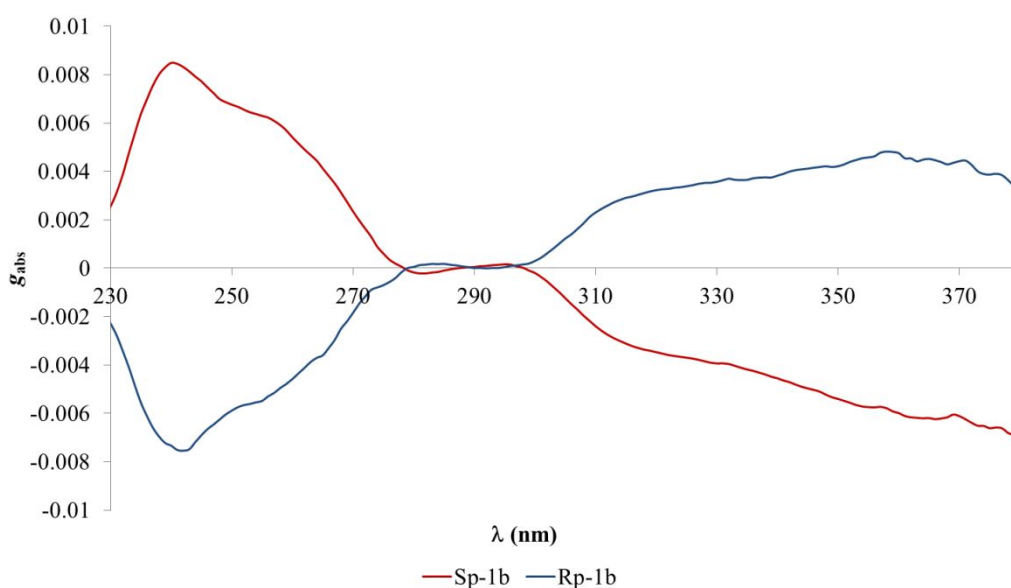


Figure S1. Absorption dissymmetry factors of compounds (*S_p*)-**1b** and (*R_p*)-**1b**

The circularly polarized luminescence (CPL) measurements for compounds (*S_p*)- and (*R_p*)-**1b** were performed using a home-built CPL spectrofluoropolarimeter. The samples were excited using a 90° geometry with a Xenon ozone-free lamp 150 W LS. The following parameters were used: emission slit width ≈ 2 mm, integration time = 4 sec, scan speed = 50 nm/min, accumulations = 5. The concentration of all the samples was $\sim 10^{-5}$ M in DCM. Excitation of the samples were performed at 330 nm.

Luminescence dissymmetry factors were obtained using the following formula:

$$g_{\text{lum}} = \left| 2 [I_{\text{L}}(\lambda) - I_{\text{R}}(\lambda)] / [I_{\text{L}}(\lambda) + I_{\text{R}}(\lambda)] \right|$$

where I_{L} and I_{R} are the photoluminescence intensities of left and right circularly polarized luminescence.

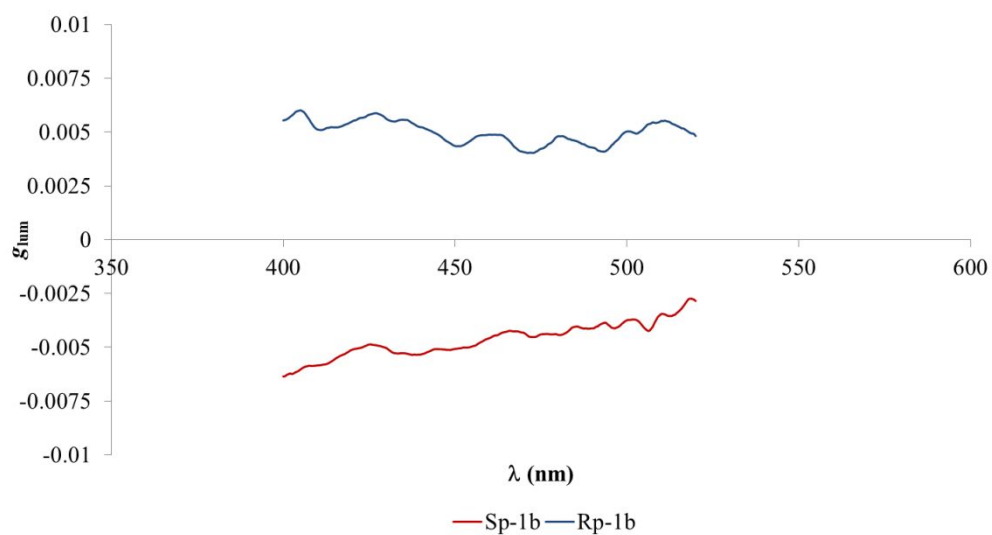
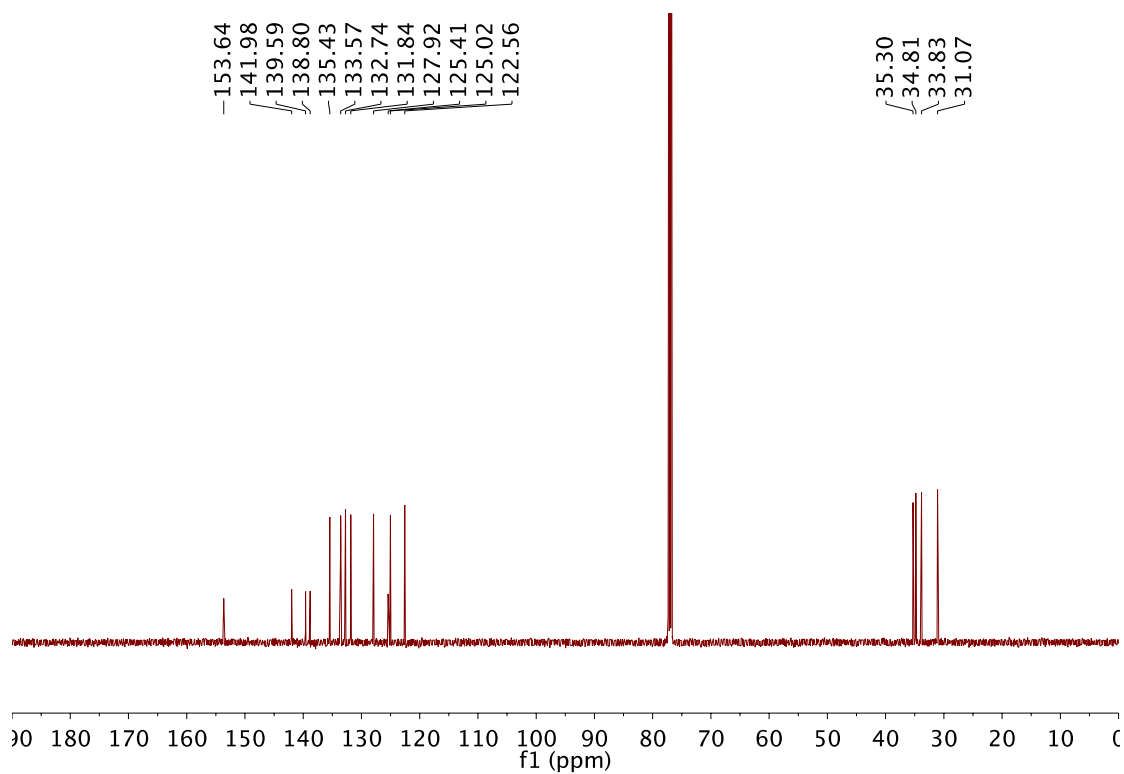
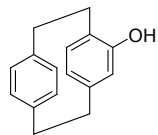
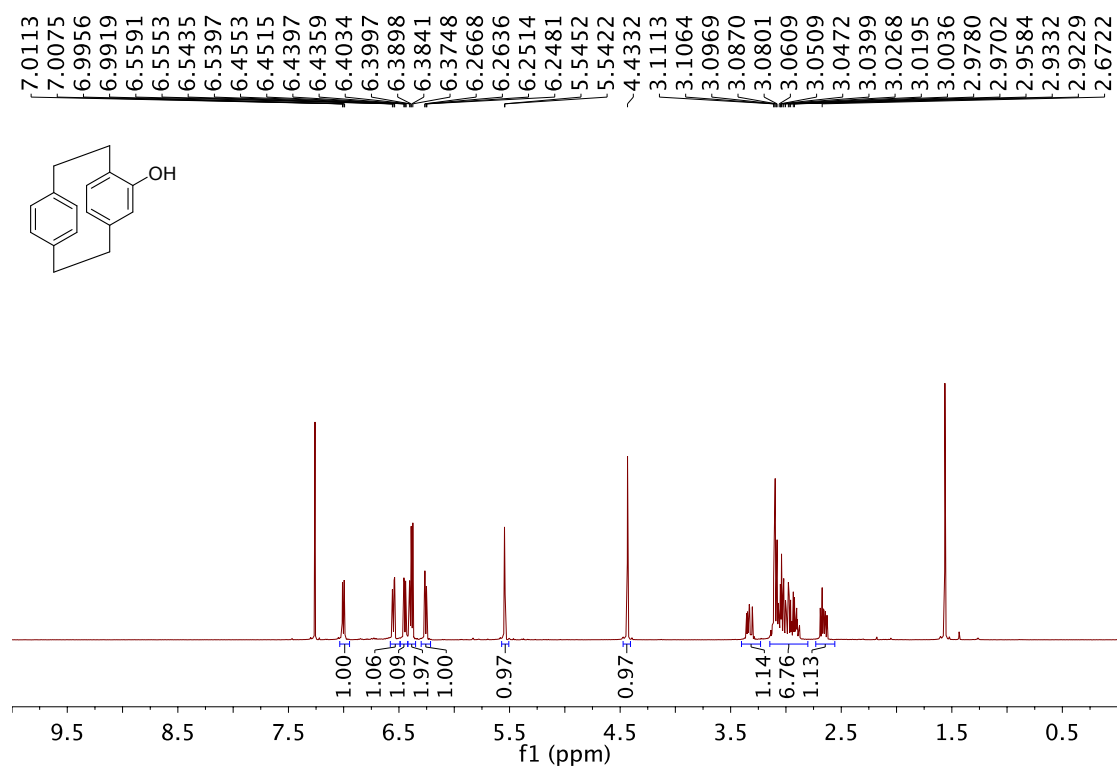


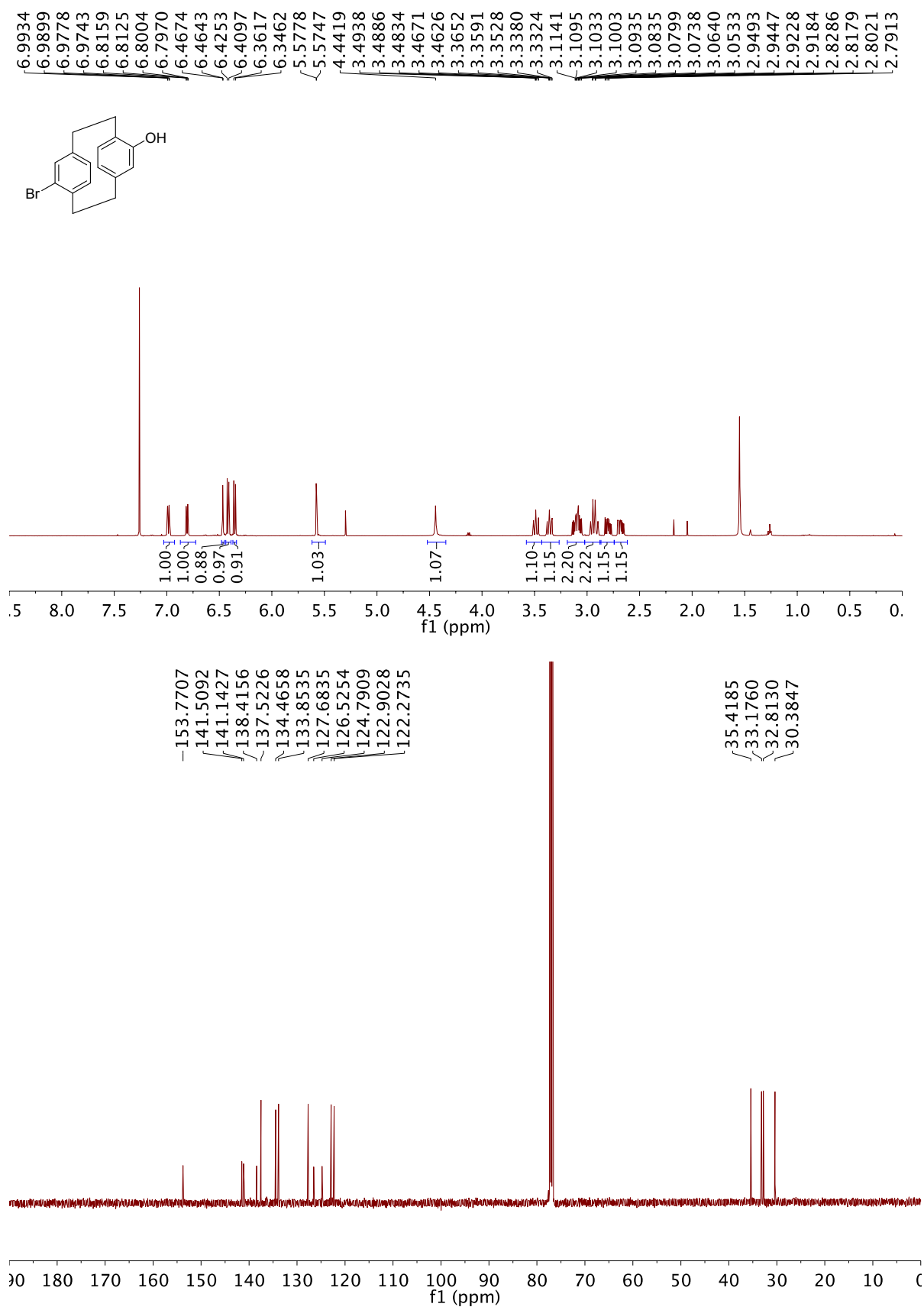
Figure S2. Luminescence dissymmetry factors of compounds (S_p) -1b and (R_p) -1b

¹H NMR and ¹³C NMR spectra

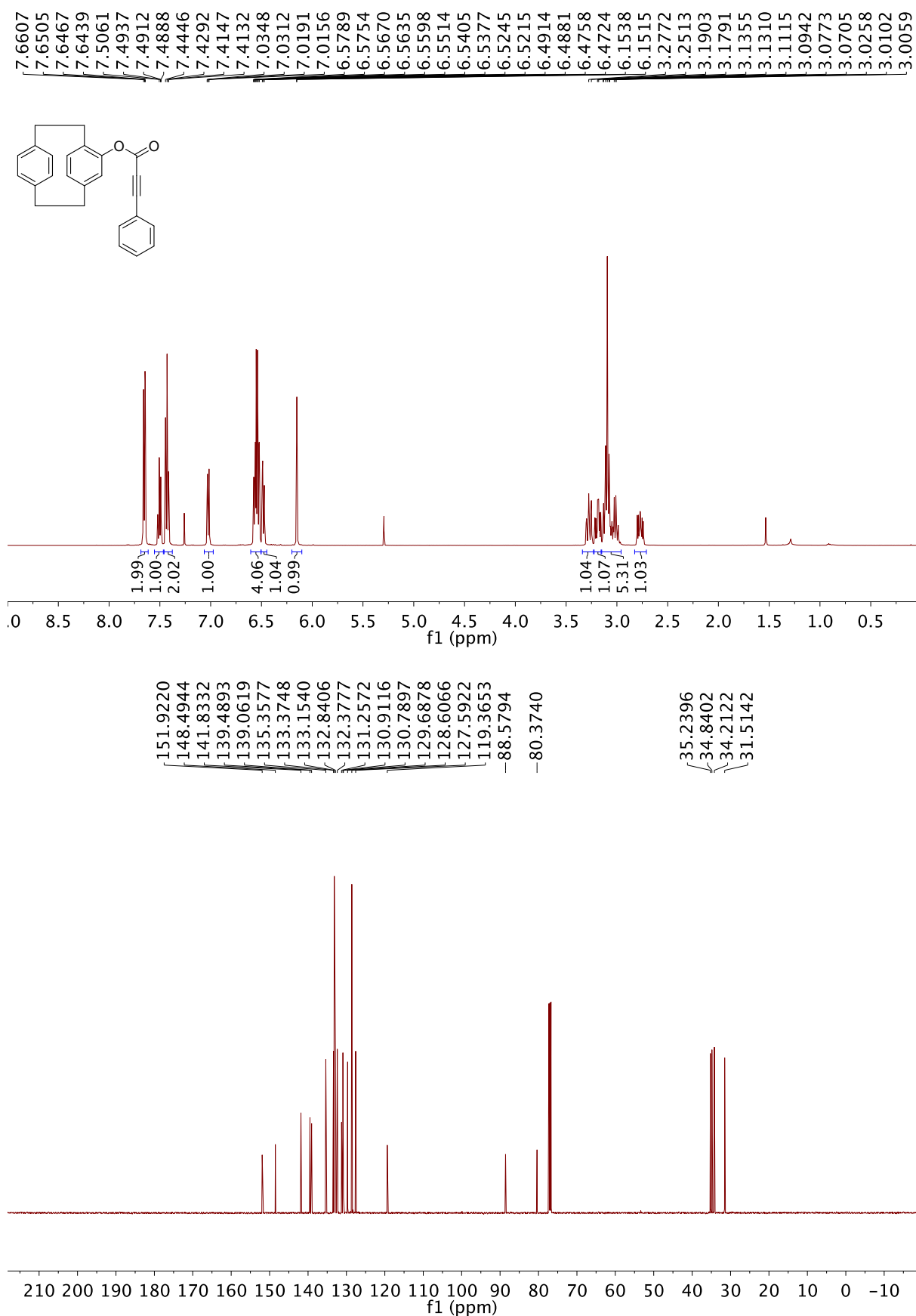
4-hydroxy[2.2]paracyclophane (**Compound (±)-3a**)



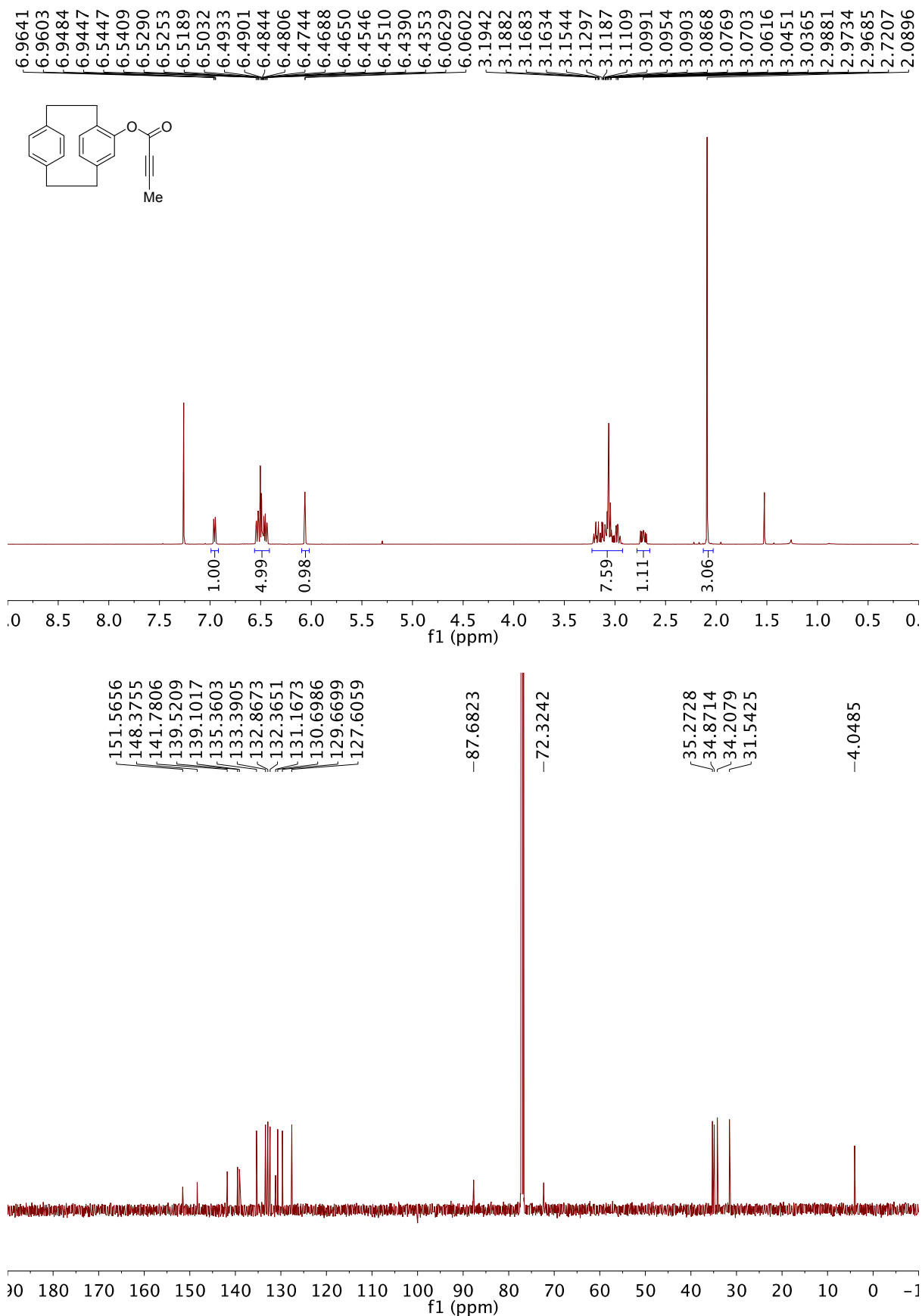
4-hydroxy-16-bromo-[2.2]paracyclophane (**Compound (±)-3b**)



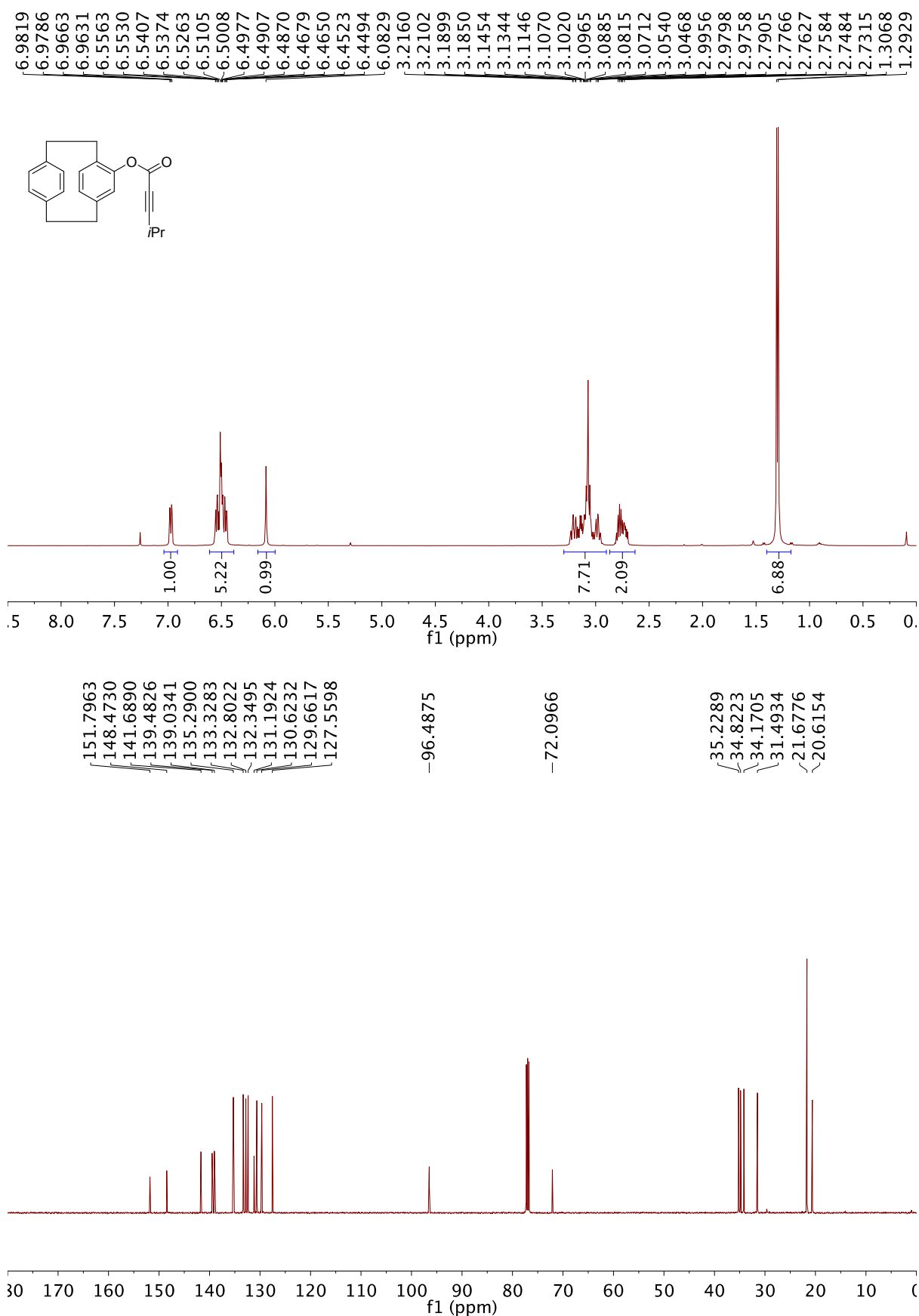
Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl 3-phenylprop-2-ynoate
(Compound (±)-2a)



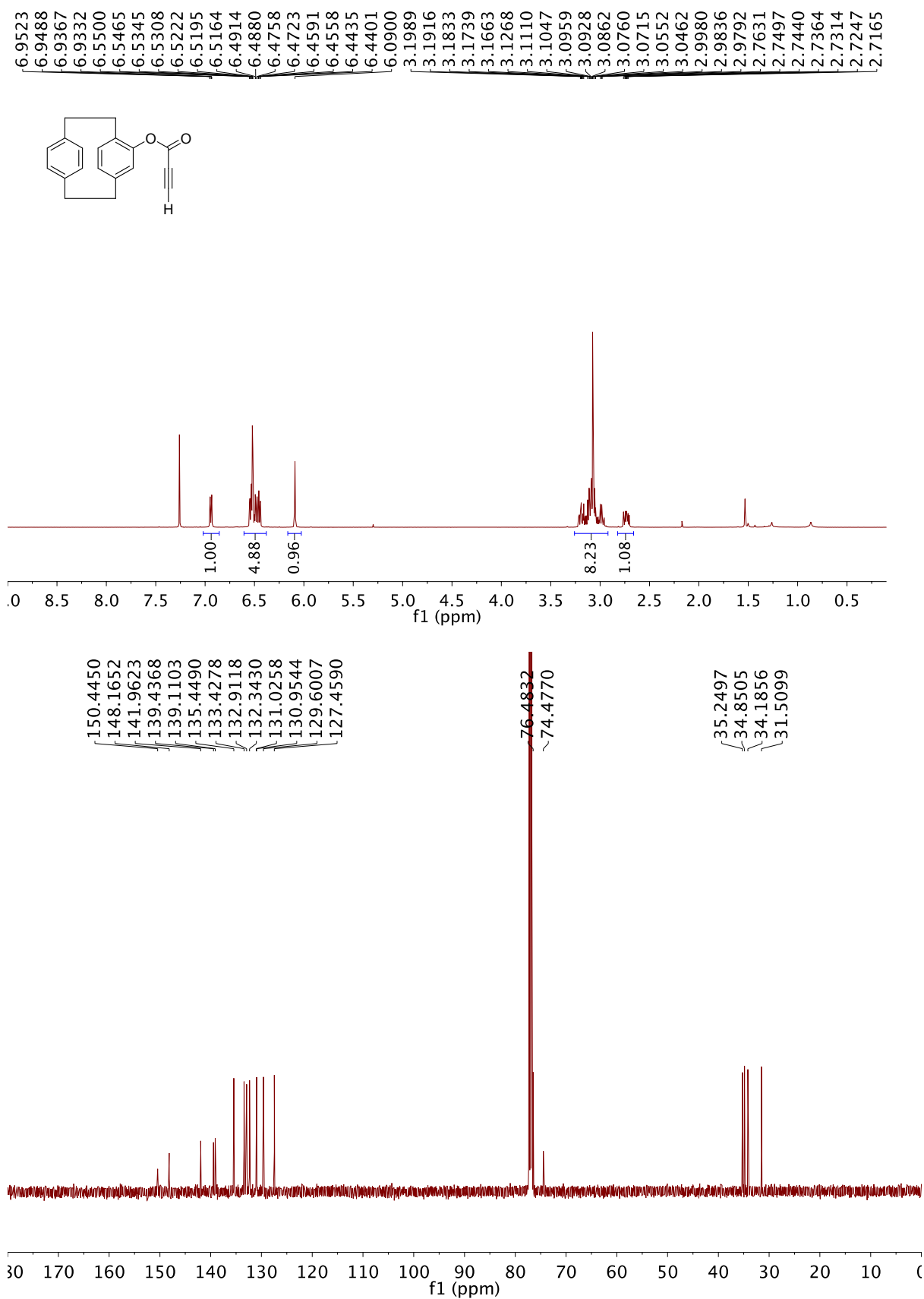
Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4(16),5,7(15),10,13-hexaen-5-yl but-2-ynoate
(Compound (±)-2b)



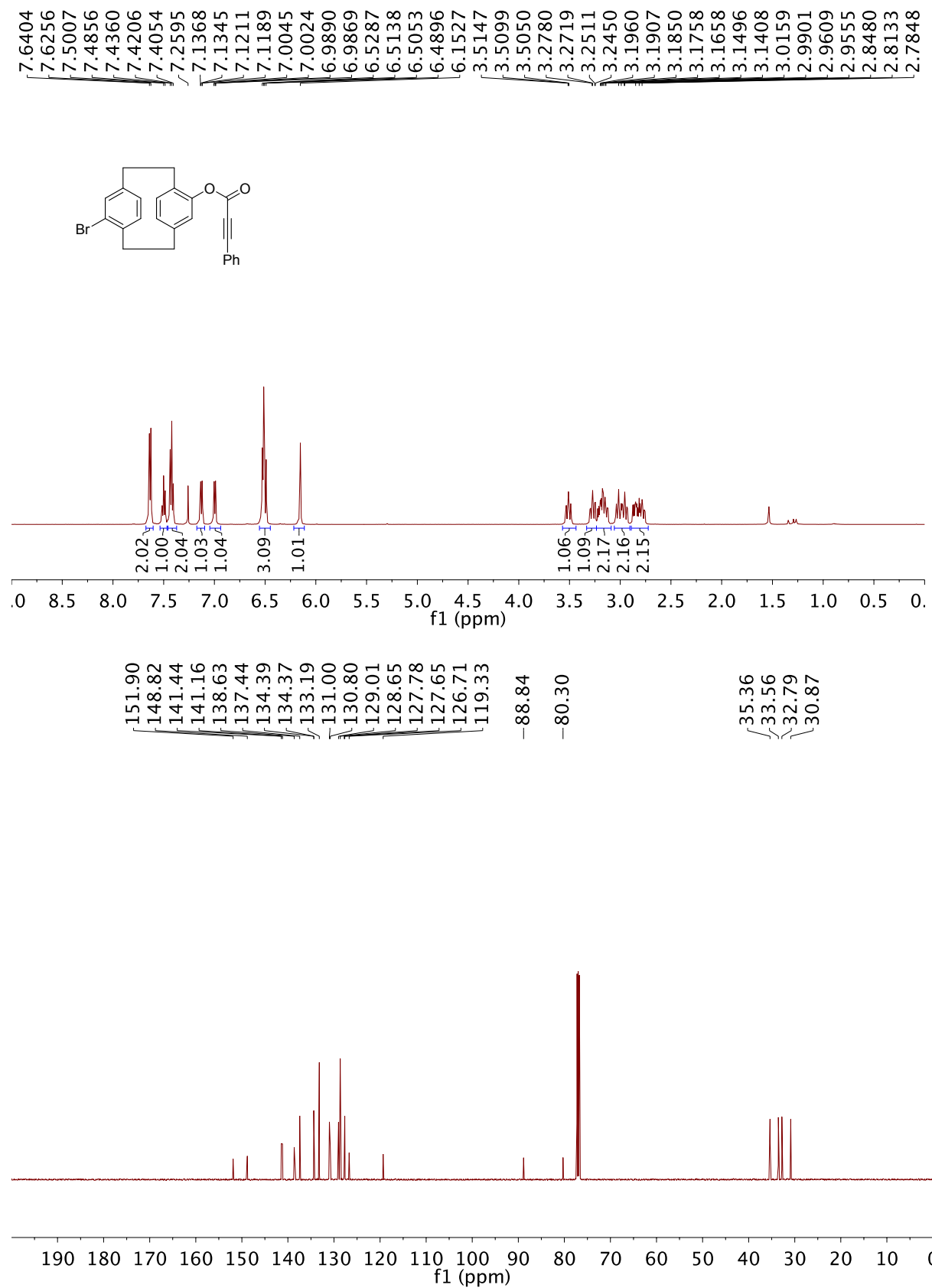
Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl 4-methylpent-2-ynoate
(Compound (±)-2c)



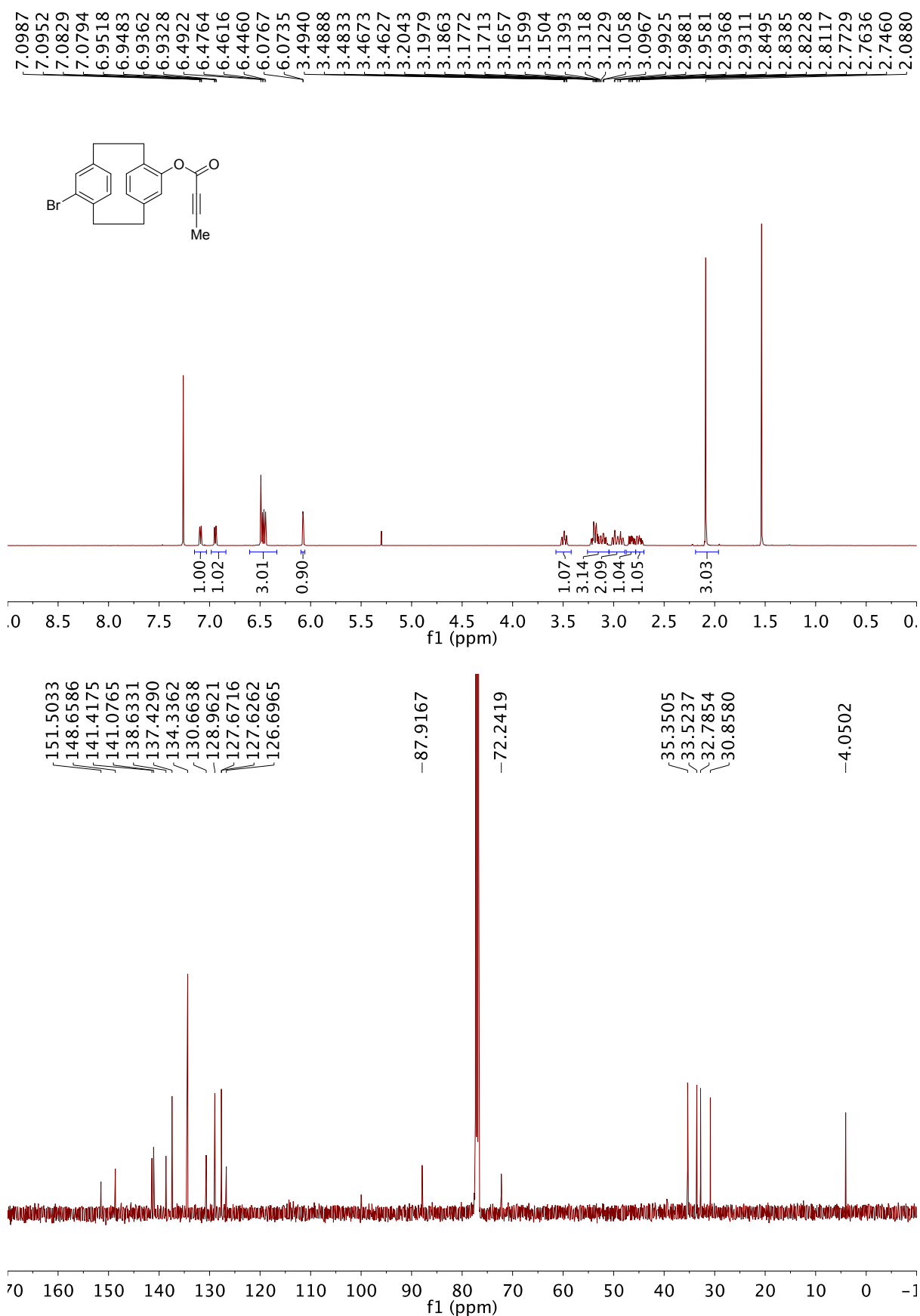
Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4(16),5,7(15),10,13-hexaen-5-yl prop-2-ynoate
(Compound (±)-2d)



14-Bromotricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl 3-phenylprop-2-ynoate (Compound (±)-2e)



14-Bromotricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl but-2-ynoate
(Compound (±)-2f)



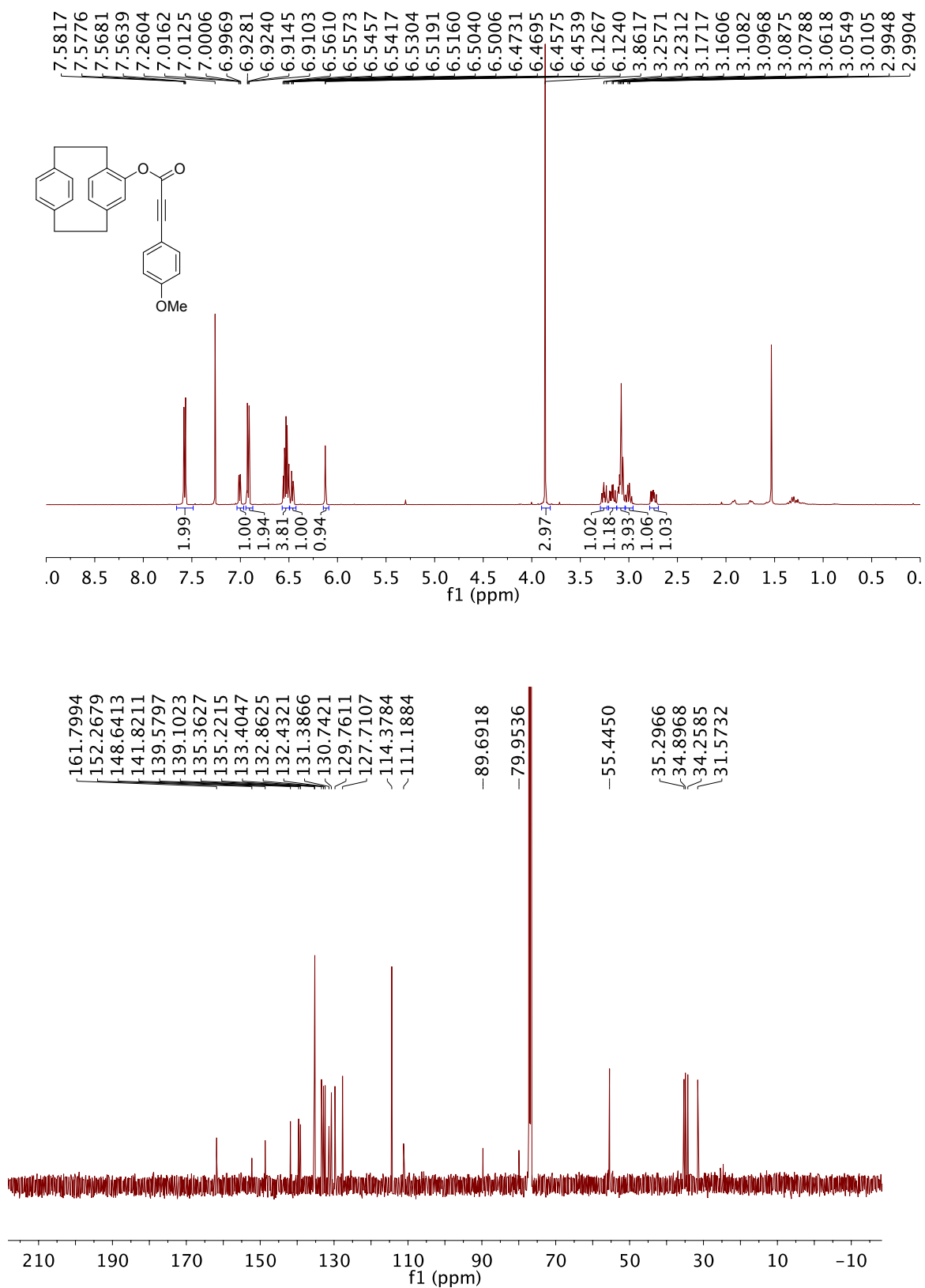
Chemical structure of compound 10: CC1=CC=C(C#CC(=O)Oc2ccc3ccccc3c2)C=C1

¹H NMR (400 MHz, CDCl₃) peaks (ppm): 7.5358, 7.5196, 7.2600, 7.2301, 7.2291, 7.2144, 7.2133, 7.0148, 7.0110, 6.9992, 6.9955, 6.5619, 6.5581, 6.5473, 6.5425, 6.5323, 6.5209, 6.5176, 6.5053, 6.5019, 6.4743, 6.4708, 6.4587, 6.4553, 6.1307, 3.2632, 3.2576, 3.2367, 3.2314, 3.1725, 3.1613, 3.1162, 3.1109, 3.1048, 3.0976, 3.0805, 3.0635, 3.0564, 3.0124, 2.9963, 2.9924, 2.7581, 2.7520, 2.7471, 2.4124.

¹H NMR integrations: 1.95, 1.99, 1.00, 3.98, 1.04, 0.96, 1.07, 1.09, 4.15, 1.10, 1.04, 3.07.

¹³C NMR (100 MHz, CDCl₃) peaks (ppm): 152.1201, 148.5849, 141.8380, 141.6868, 139.5689, 139.1053, 135.3809, 133.4080, 133.2240, 132.8679, 132.4296, 131.3386, 130.7771, 129.7524, 129.4362, 127.6735, 116.3137, -89.2299, -80.1237, 35.2947, 34.8963, 34.2577, 31.5717, 21.7722.

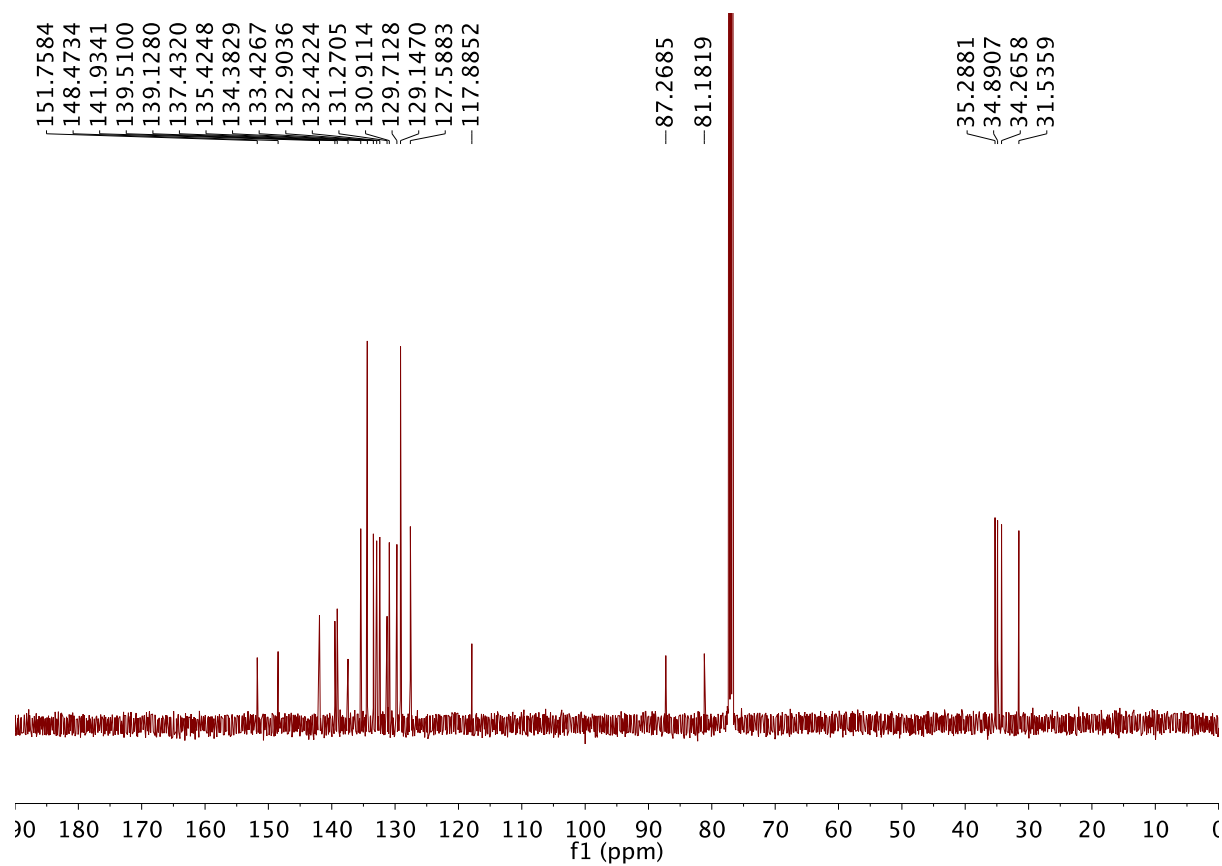
Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl 3-(4-methoxyphenyl)prop-2-ynoate (Compound (±)-2h)



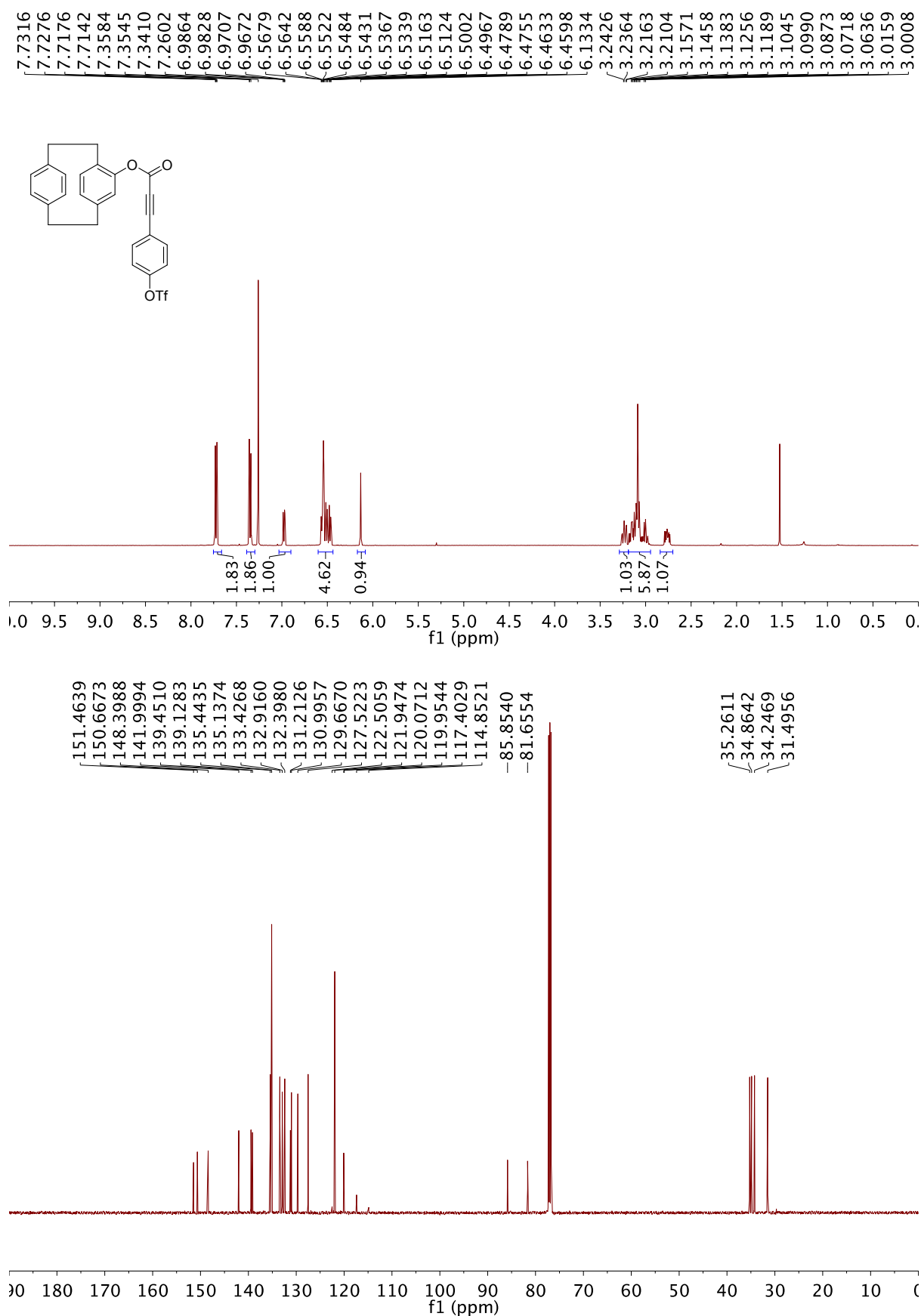
Chemical structure: CCOC(=O)c1c[nH]c1C#CCc2ccc(Cl)cc2

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 8 ppm. The x-axis is labeled f1 (ppm). The spectrum displays aromatic signals (6.5-7.6 ppm), an alkyne proton (~3.3 ppm), and aliphatic signals (1.0-1.5 ppm). Integration values are shown below the peaks.

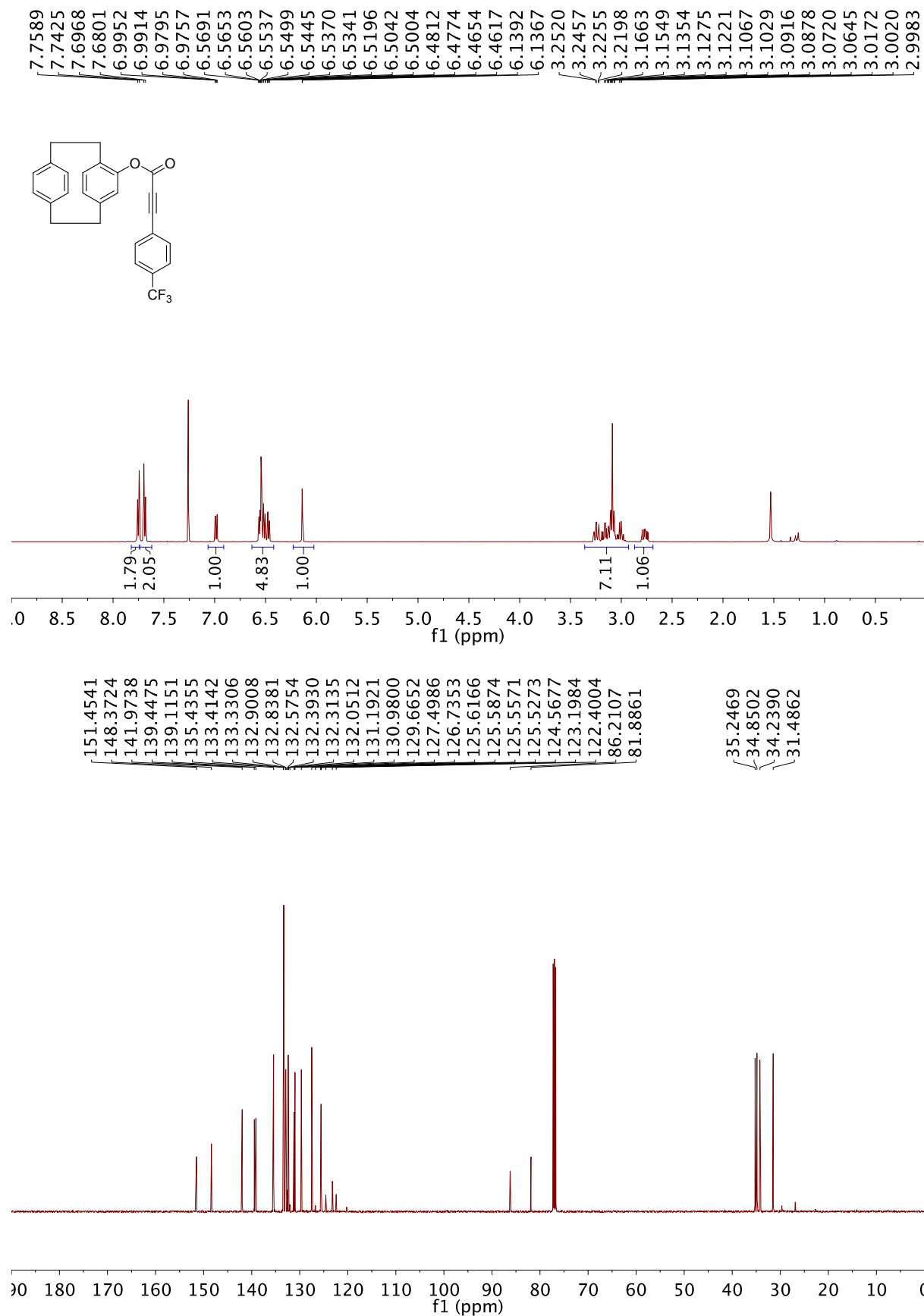
Chemical Shift (ppm)	Integration
7.5741	1.90
7.5704	1.92
7.5609	1.90
7.5570	1.92
7.4131	0.98
7.4092	3.75
7.3997	0.96
7.3960	0.97
7.2603	0.98
6.9971	3.75
6.9934	0.96
6.9815	0.97
6.9778	3.75
6.6550	0.96
6.5613	0.97
6.5523	3.75
6.5495	0.96
6.5457	0.97
6.5369	3.75
6.5285	0.96
6.5254	0.97
6.5164	3.75
6.5127	0.96
6.5008	0.97
6.4971	3.75
6.4766	0.96
6.4730	0.97
6.4610	3.75
6.4574	0.96
6.1288	0.97
6.1263	3.75
3.2431	0.96
3.2228	0.97
3.2172	3.75
3.1634	0.96
3.1522	0.97
3.1203	3.75
3.1000	0.96
3.0945	0.97
3.0868	3.75
3.0833	0.96
3.0673	0.97
3.0594	3.75
3.0129	0.96
2.9976	0.97



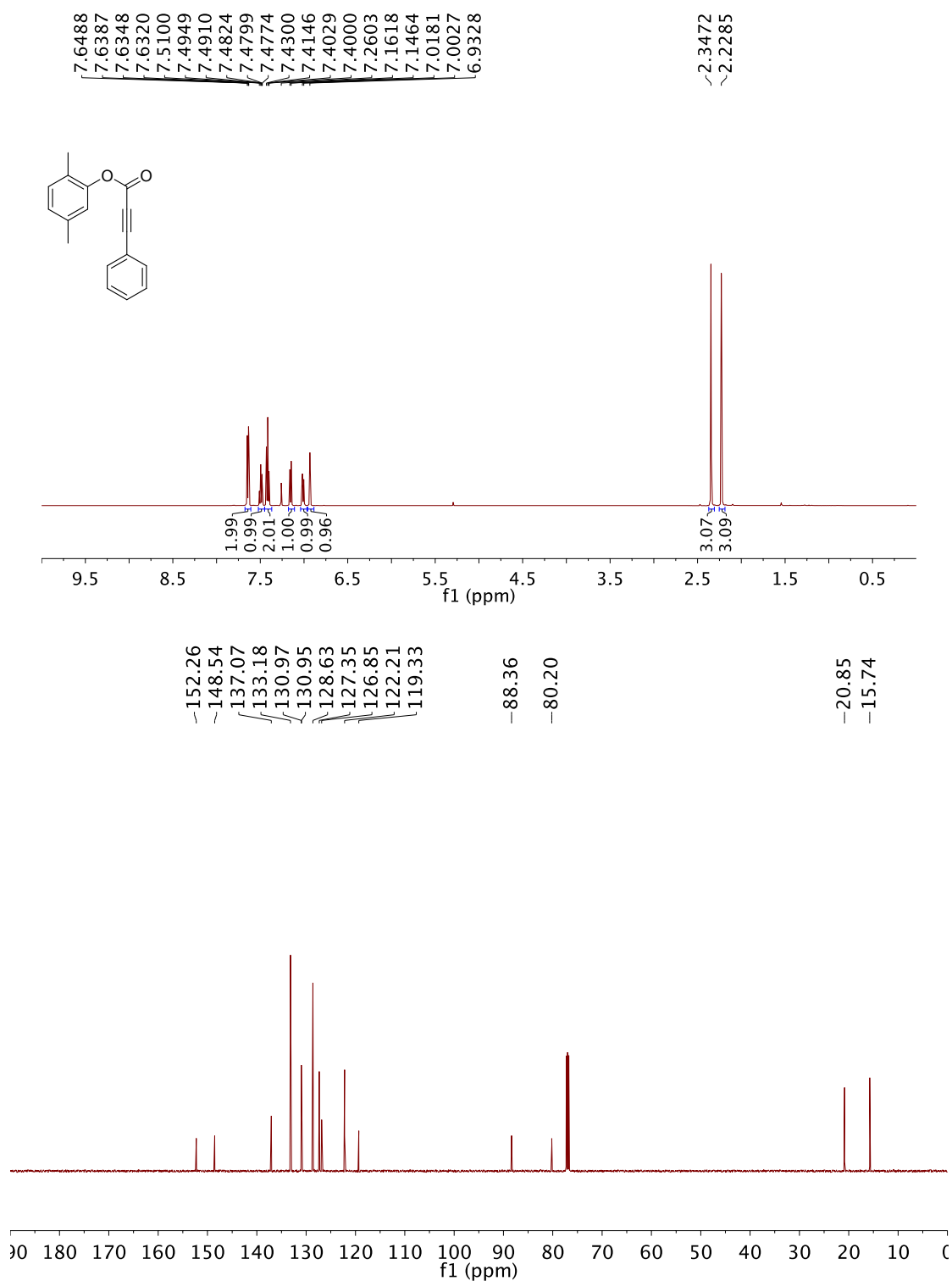
Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4(16),5,7(15),10,13-hexaen-5-yl 3-{4-[(trifluoromethyl)sulfonyloxy]phenyl}prop-2-ynoate (Compound (±)-2l)



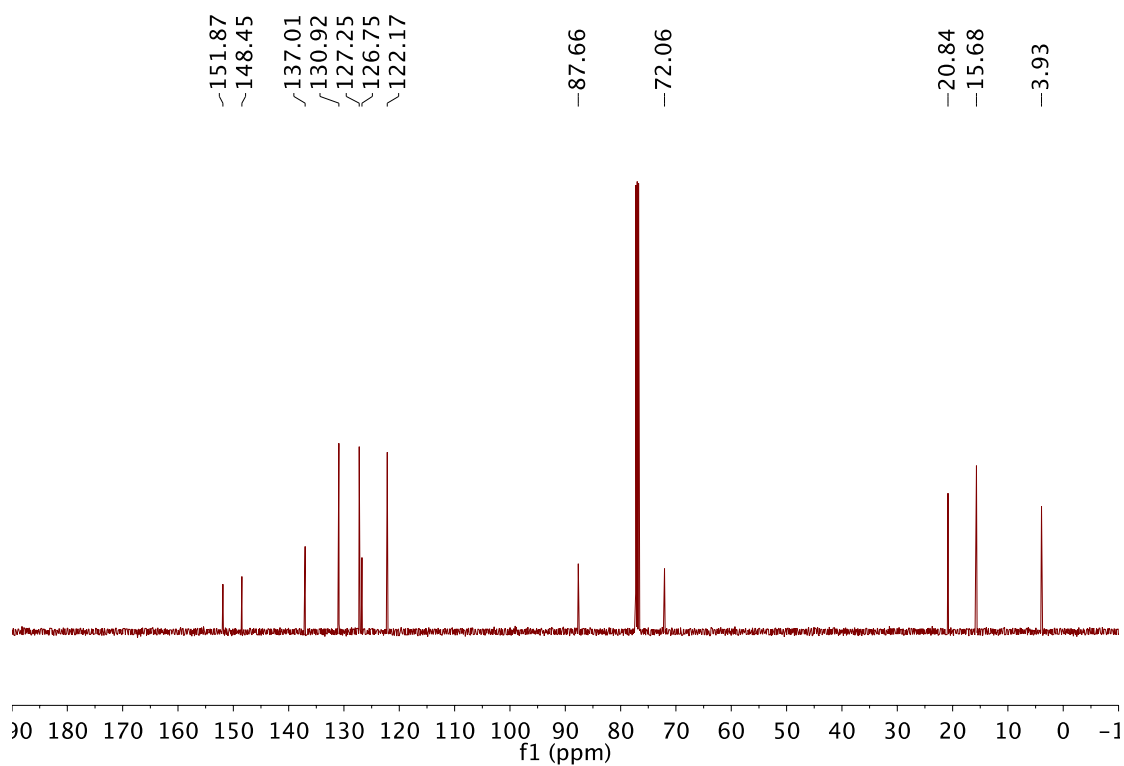
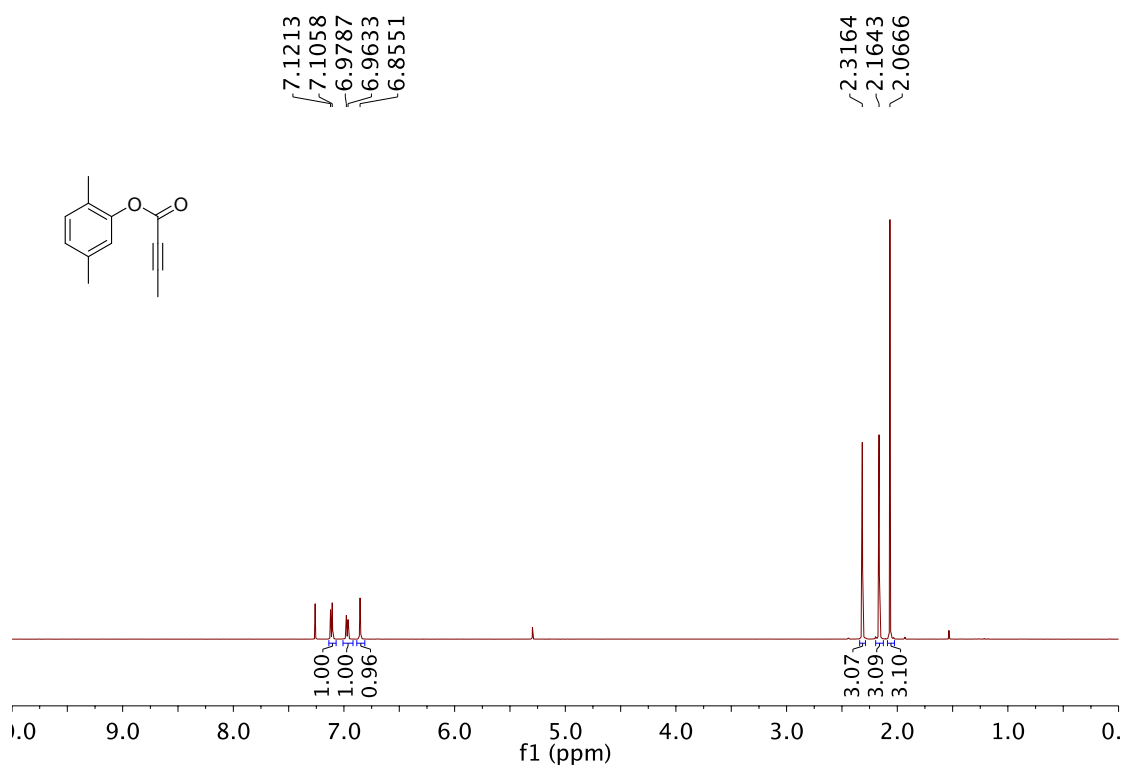
Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl 3-[4-(trifluoromethyl)-phenyl]prop-2-ynoate (Compound (±)-2k)



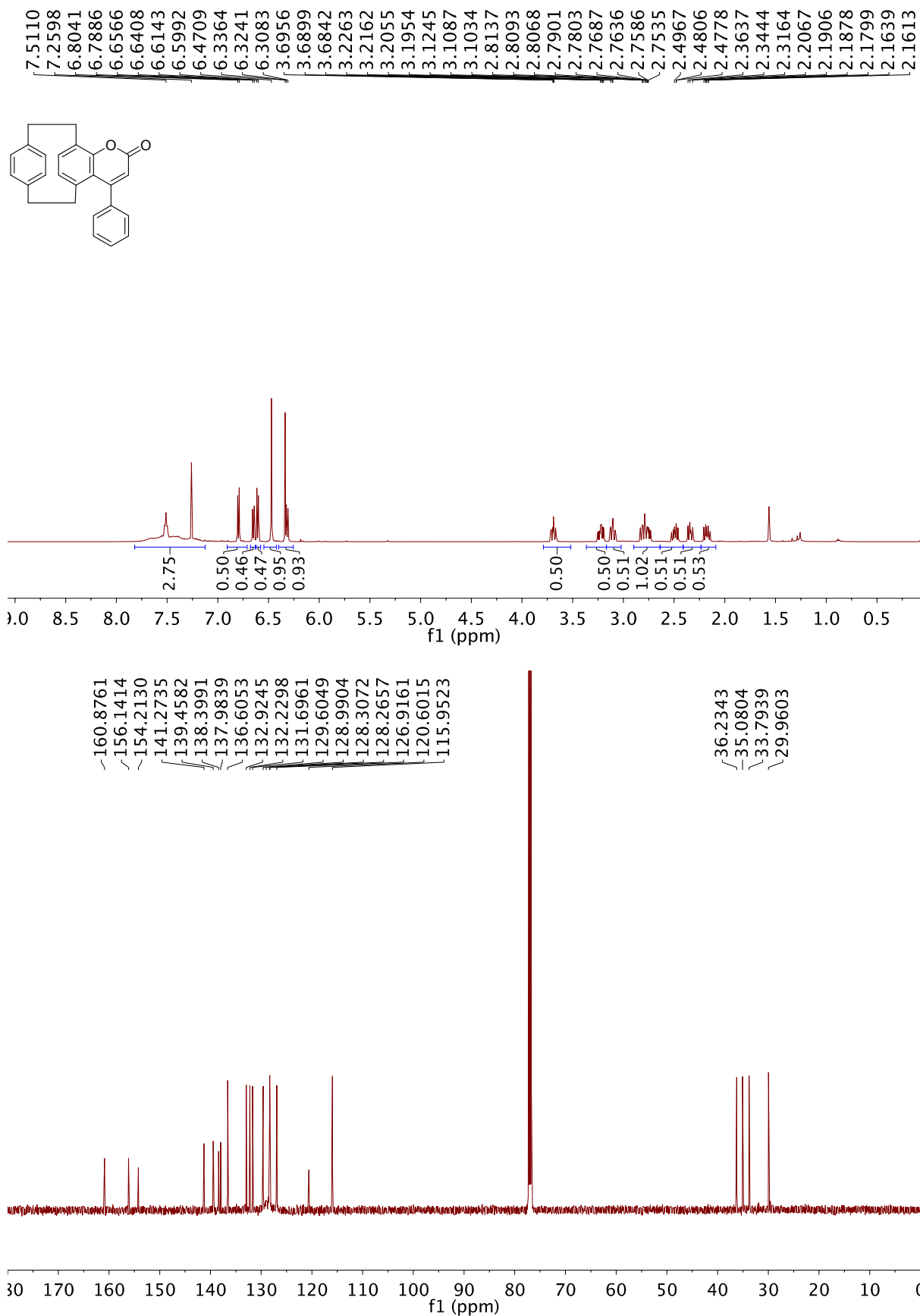
2,5-Dimethylphenyl 3-phenylpropiolate (**Compound S1**)



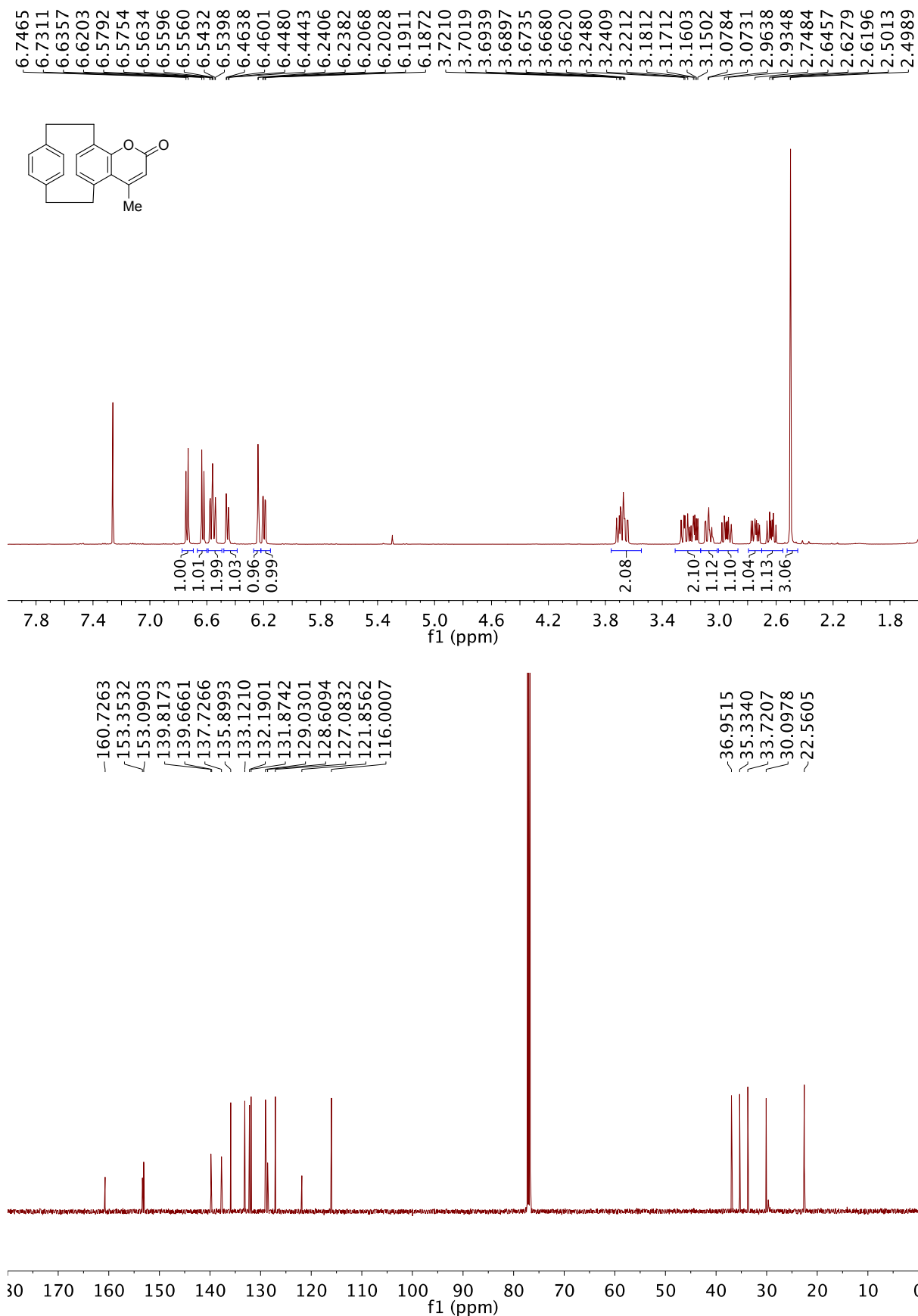
2,5-Dimethylphenyl but-2-ynoate (**Compound S2**)



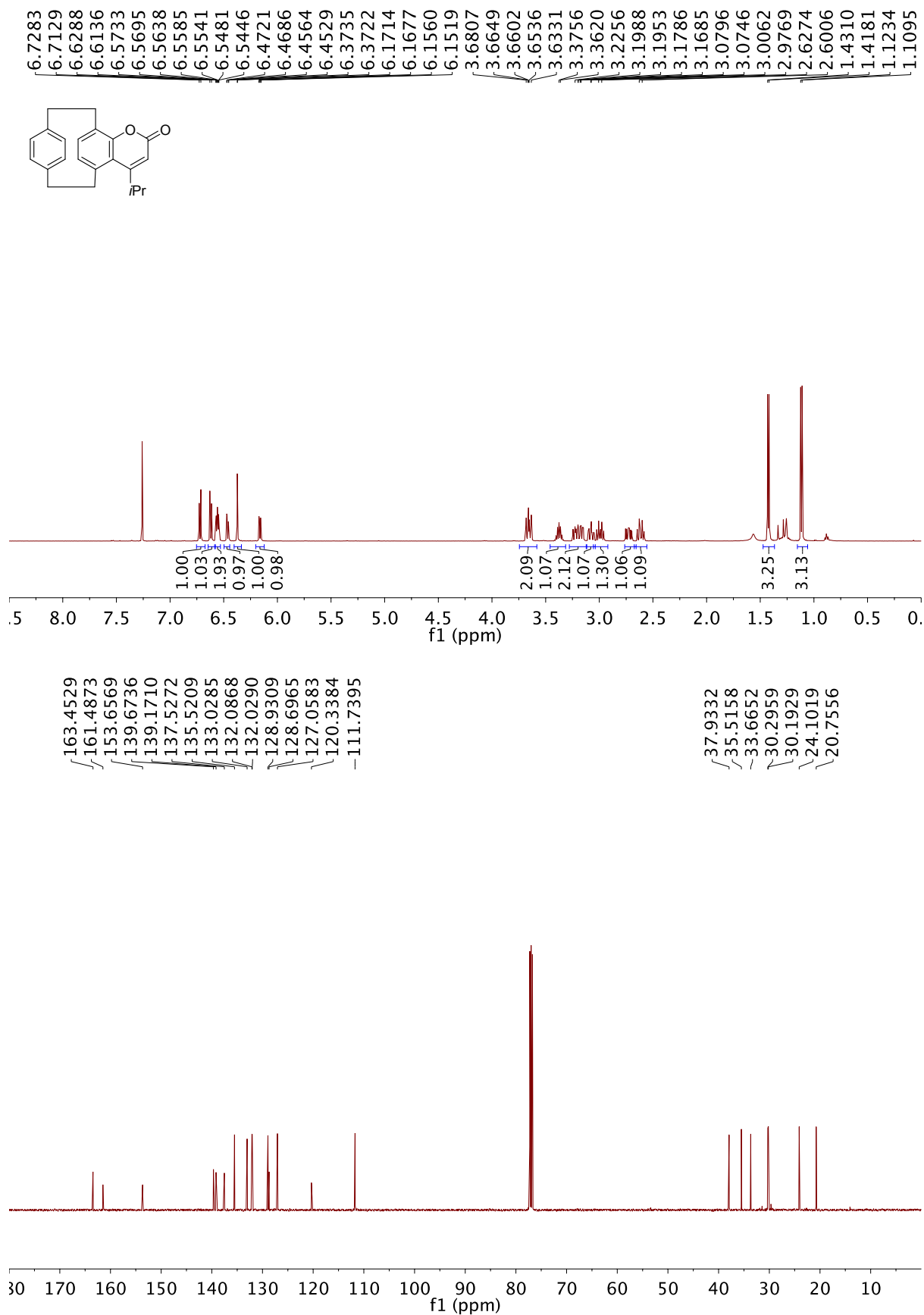
15-Phenyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (Compound (±)-1a)



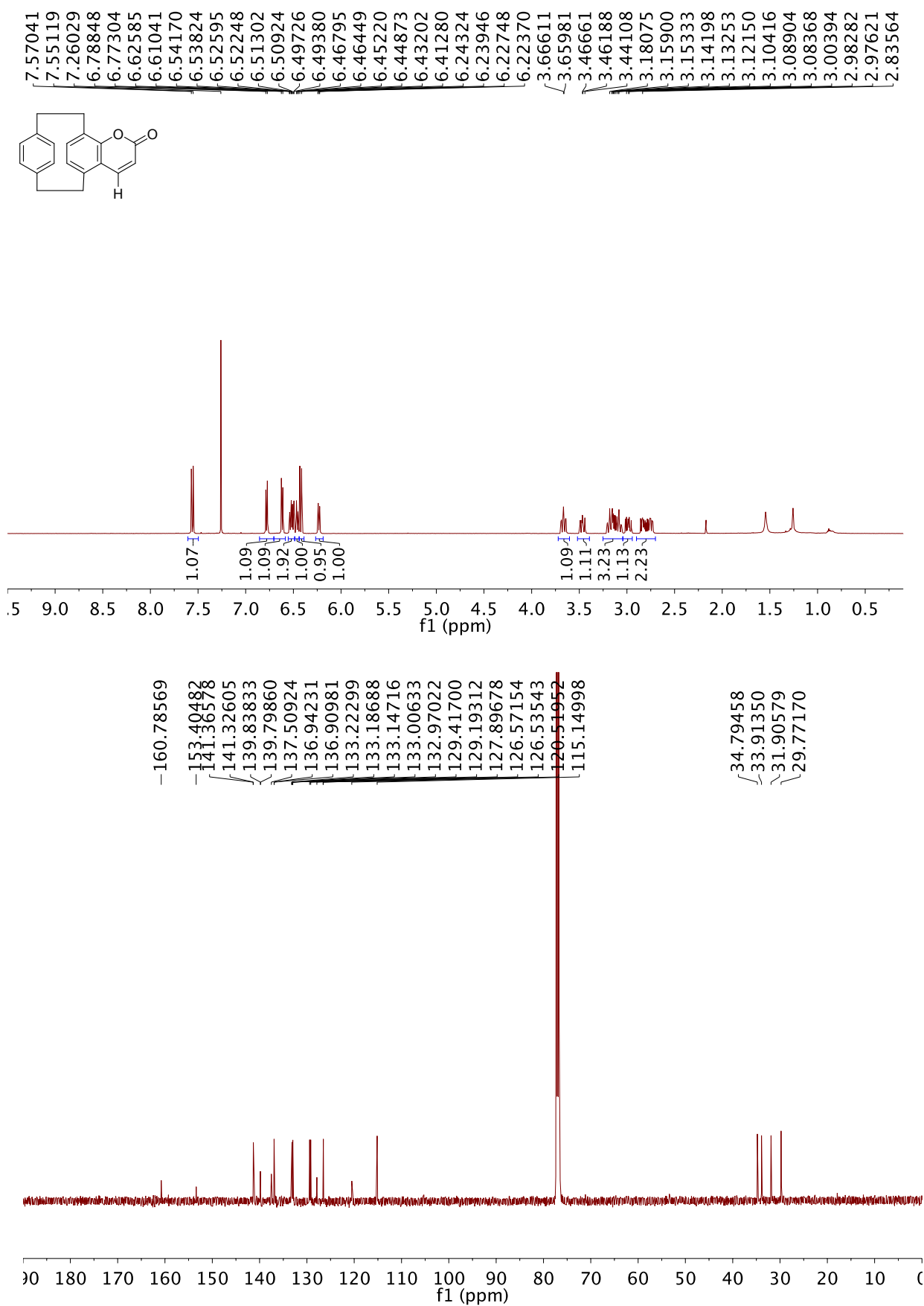
15-Methyl-12-oxatetracyclo[8.6.2.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (Compound (±)-1b)



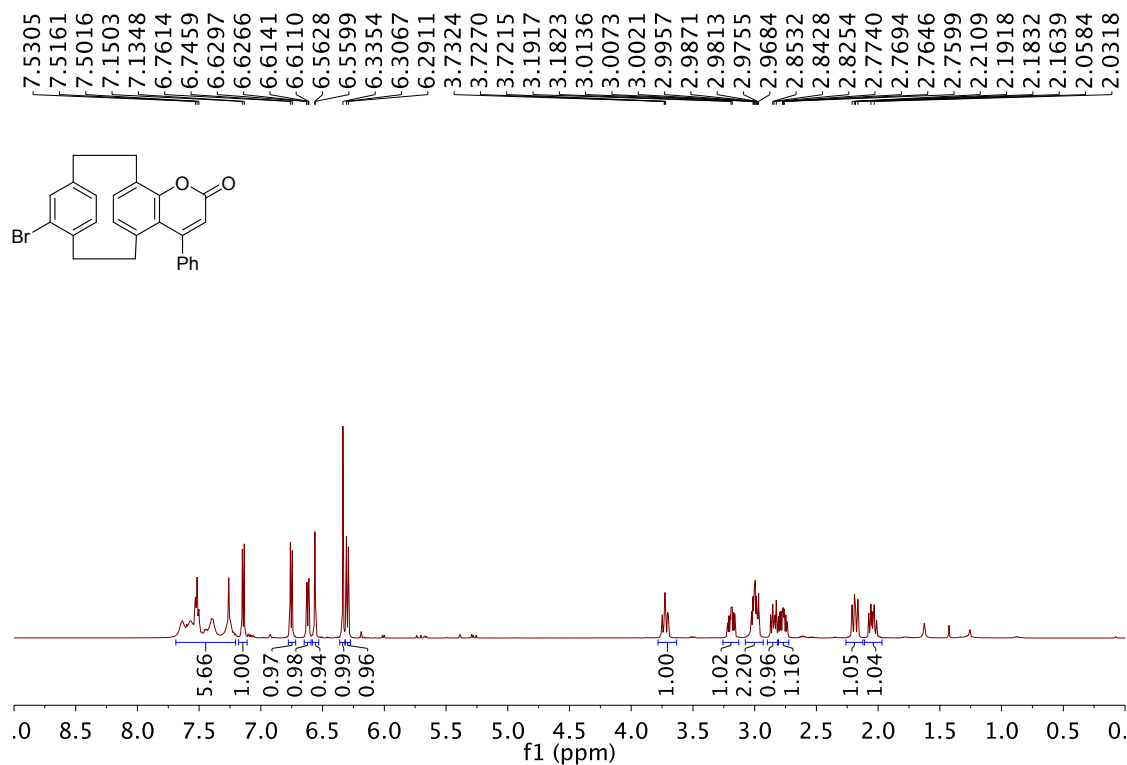
15-(Propan-2-yl)-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (Compound (±)-1c)



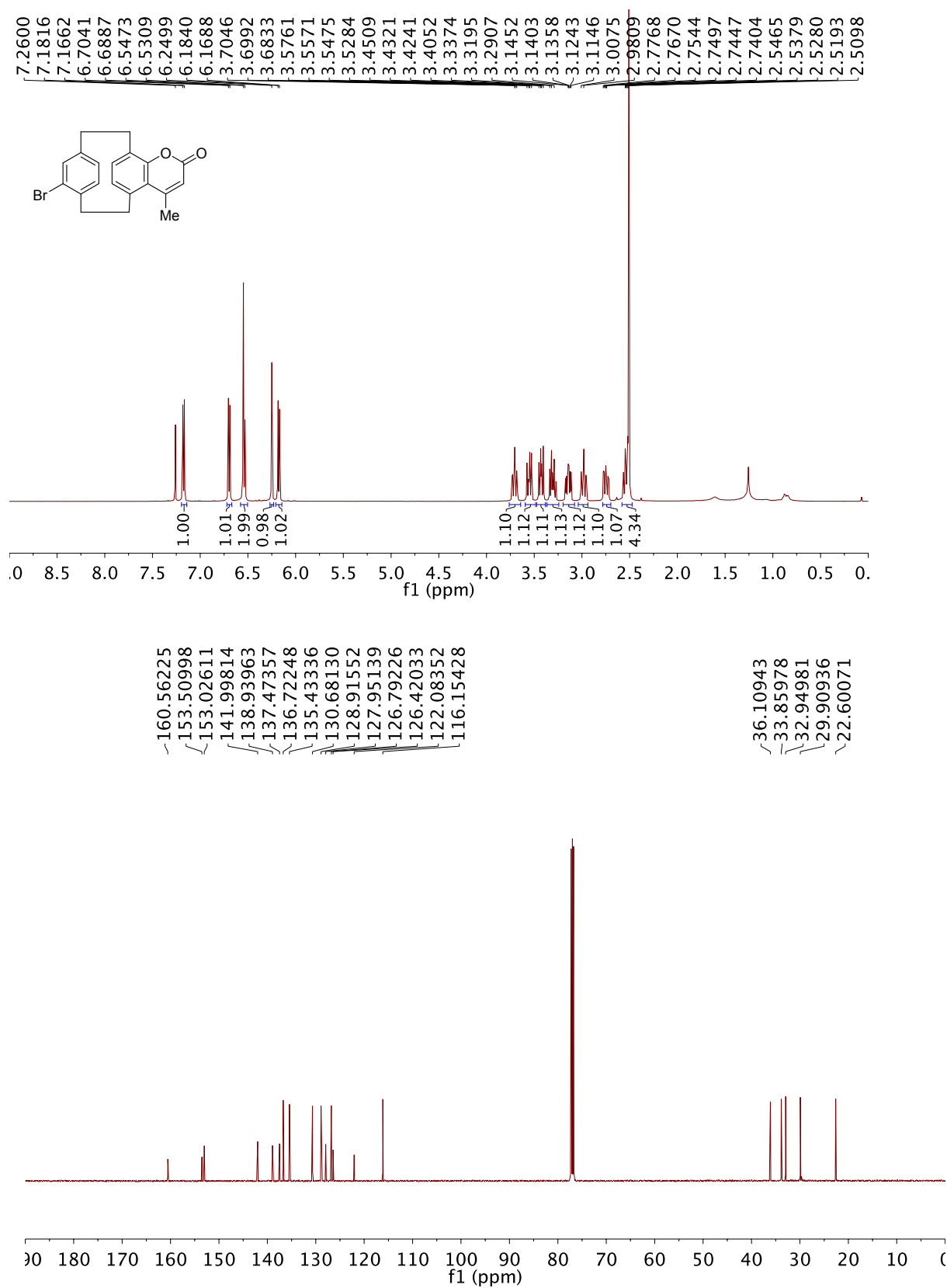
12-Oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one
(Compound (±)-1d)



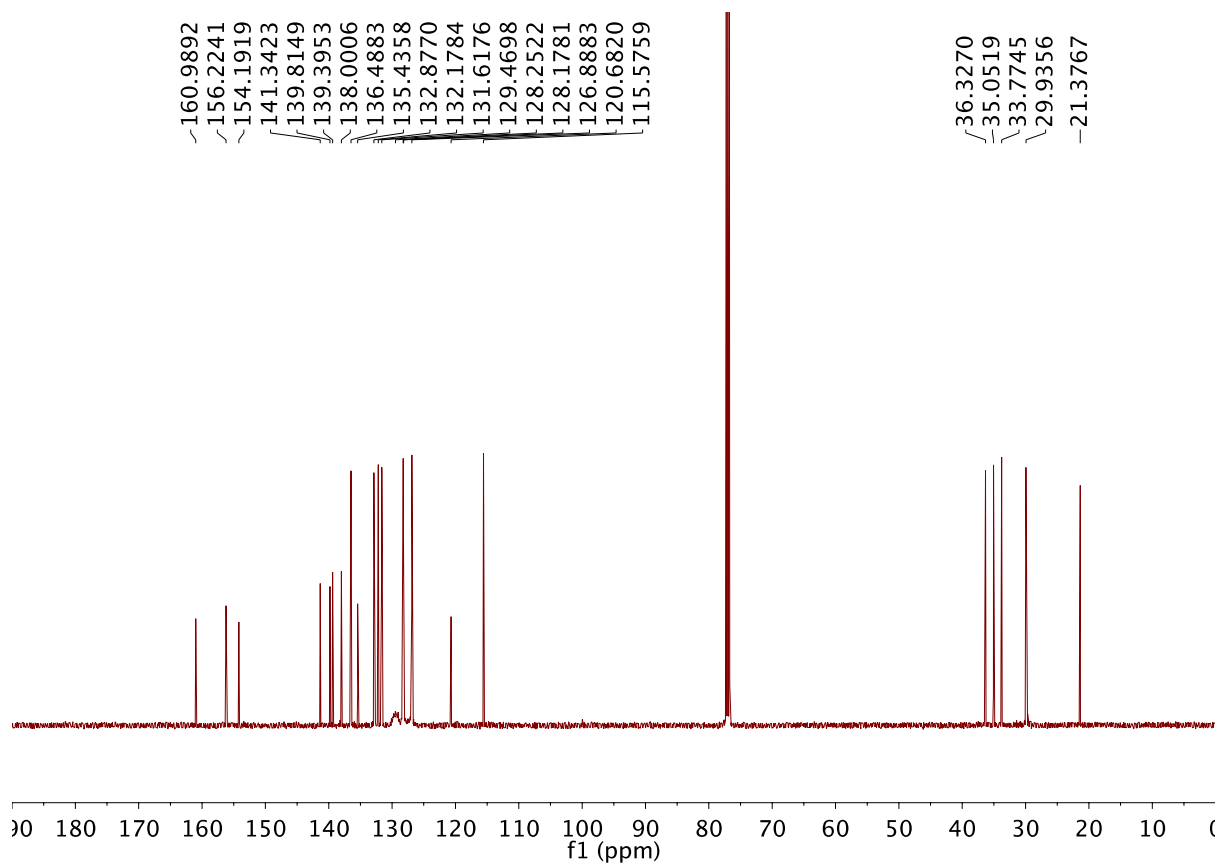
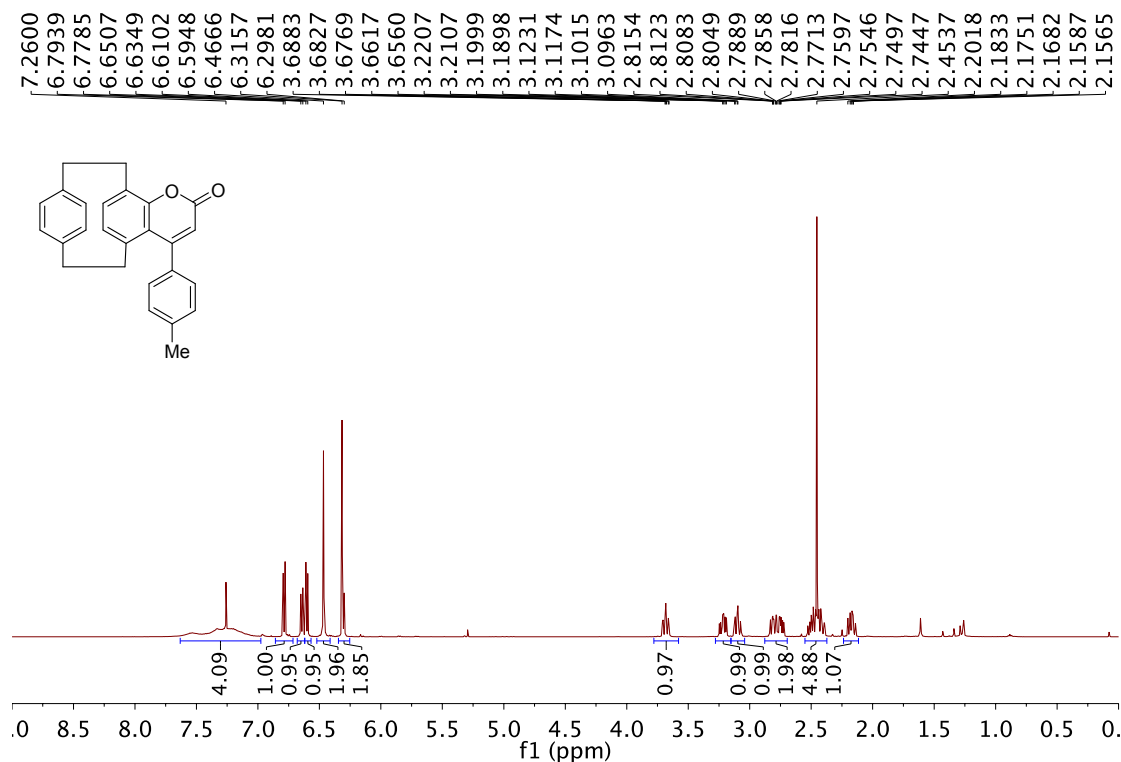
5-Bromo-15-phenyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (Compound (±)-1e)



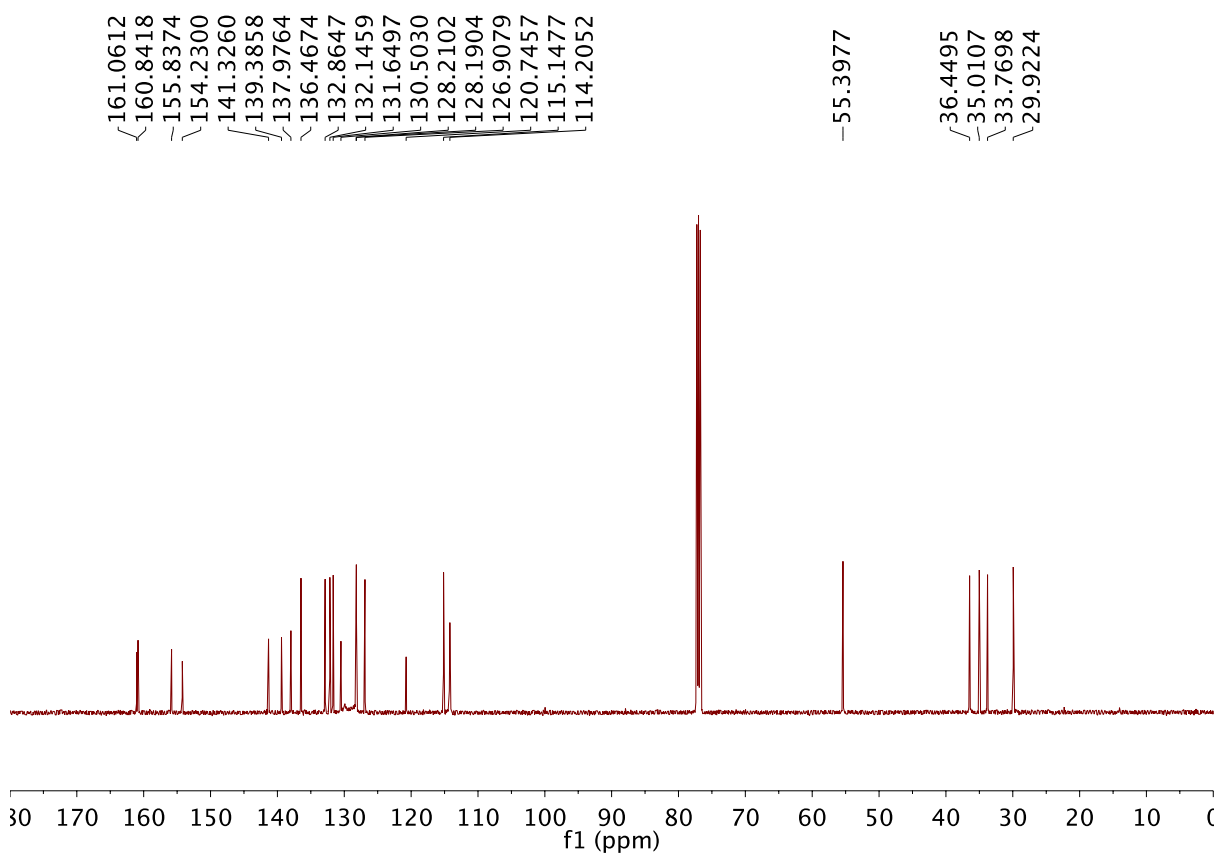
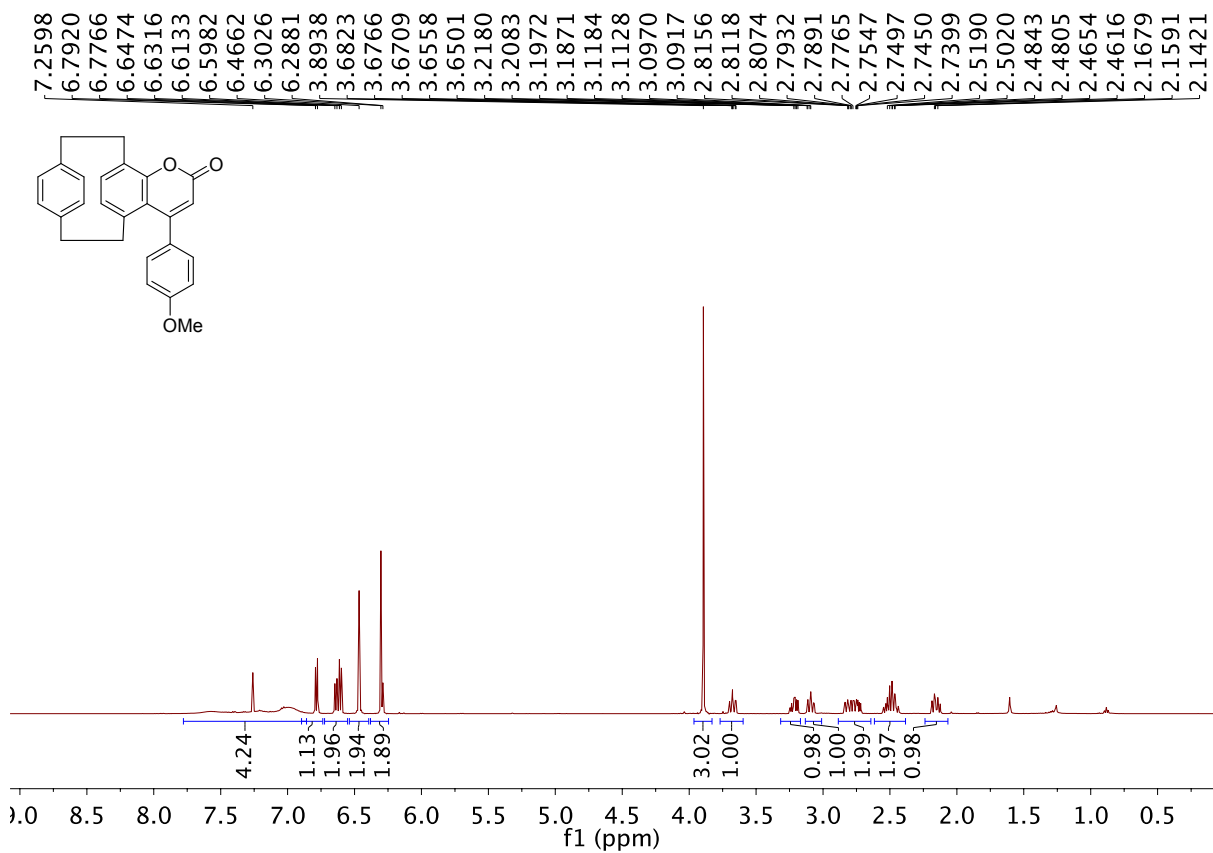
5-Bromo-15-methyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (Compound (±)-1f)



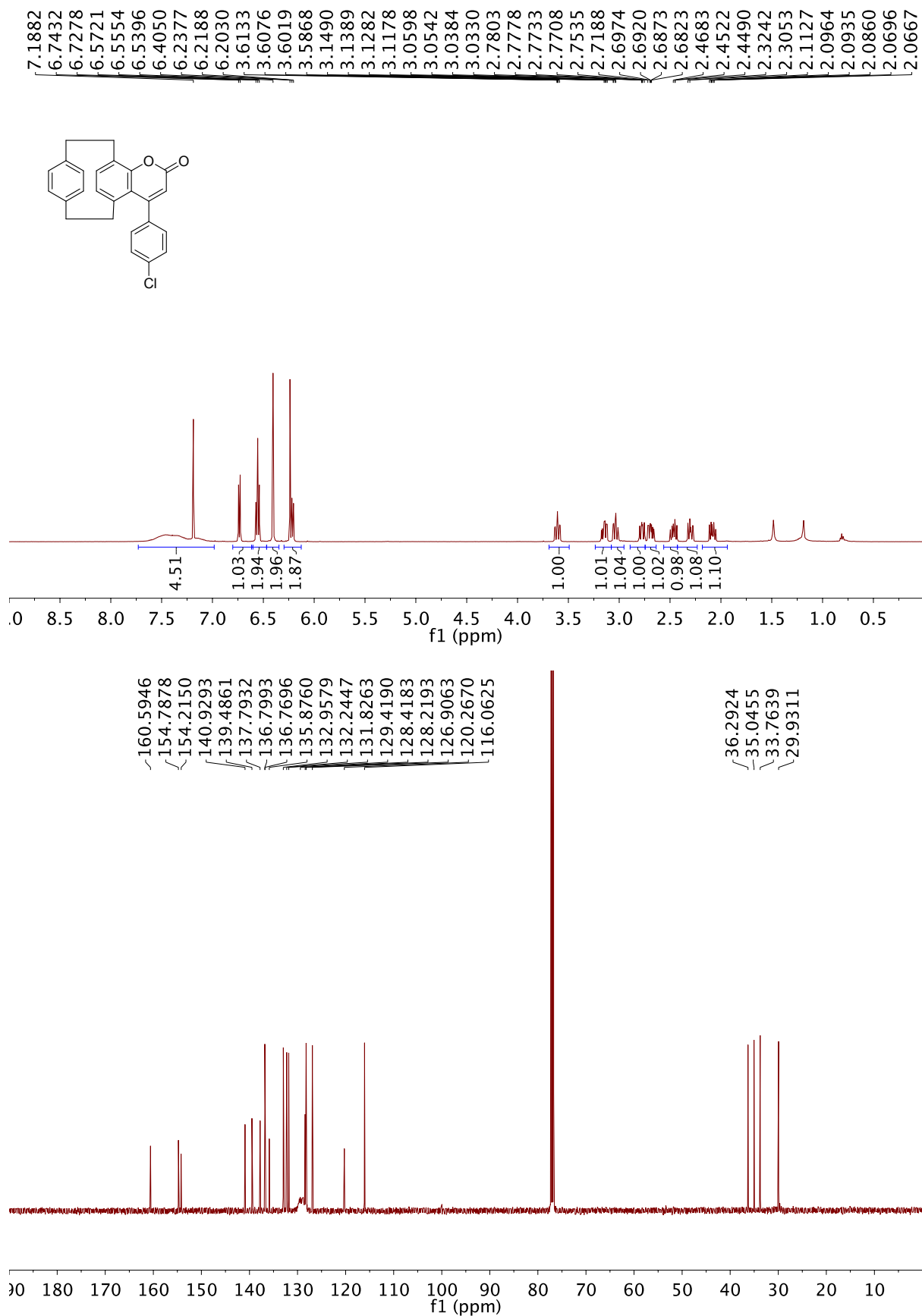
15-(4-Methylphenyl)-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (Compound (±)-1g)



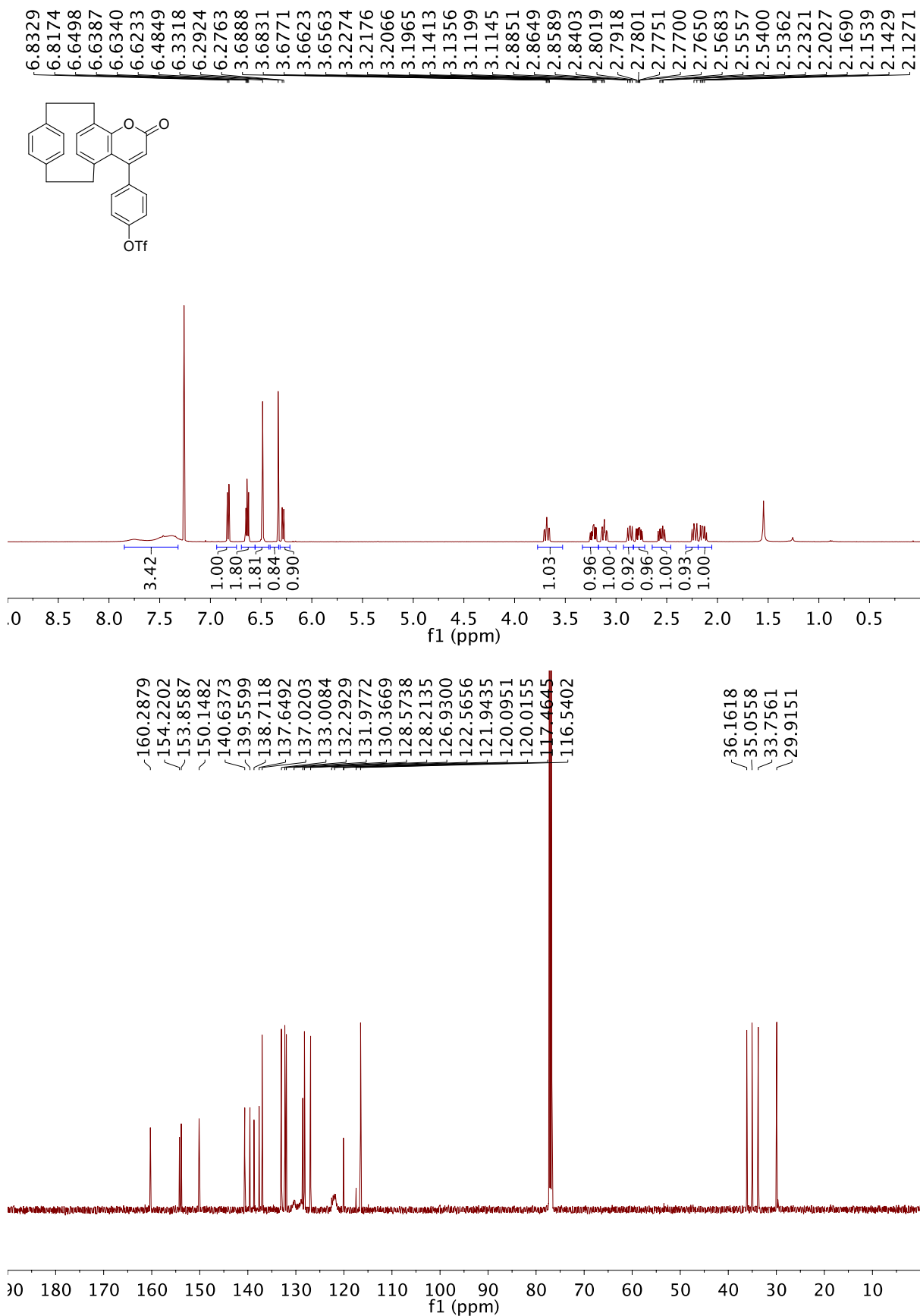
15-(4-Methoxyphenyl)-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (Compound (±)-1h)



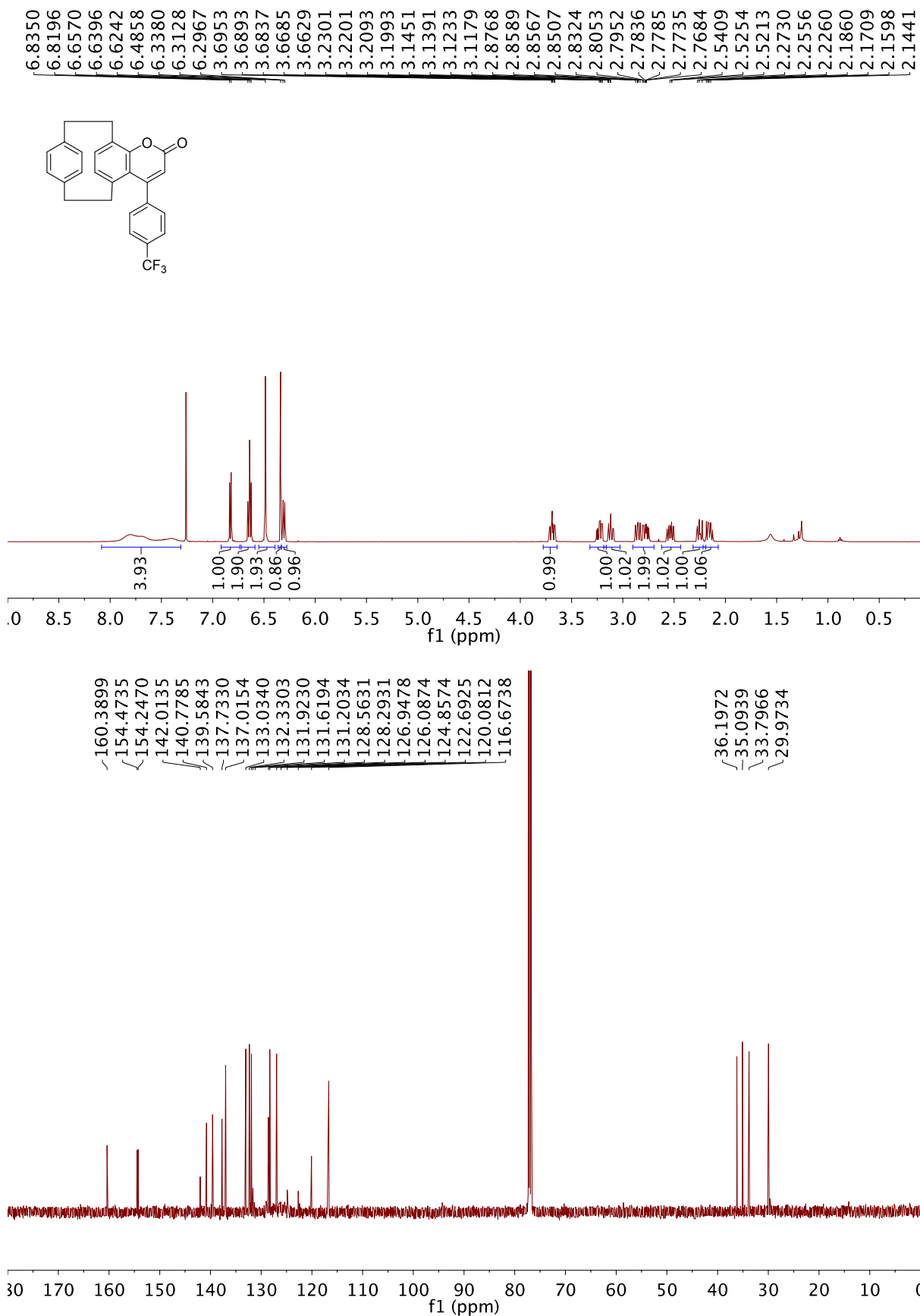
15-(4-Chlorophenyl)-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one (Compound (±)-1i)



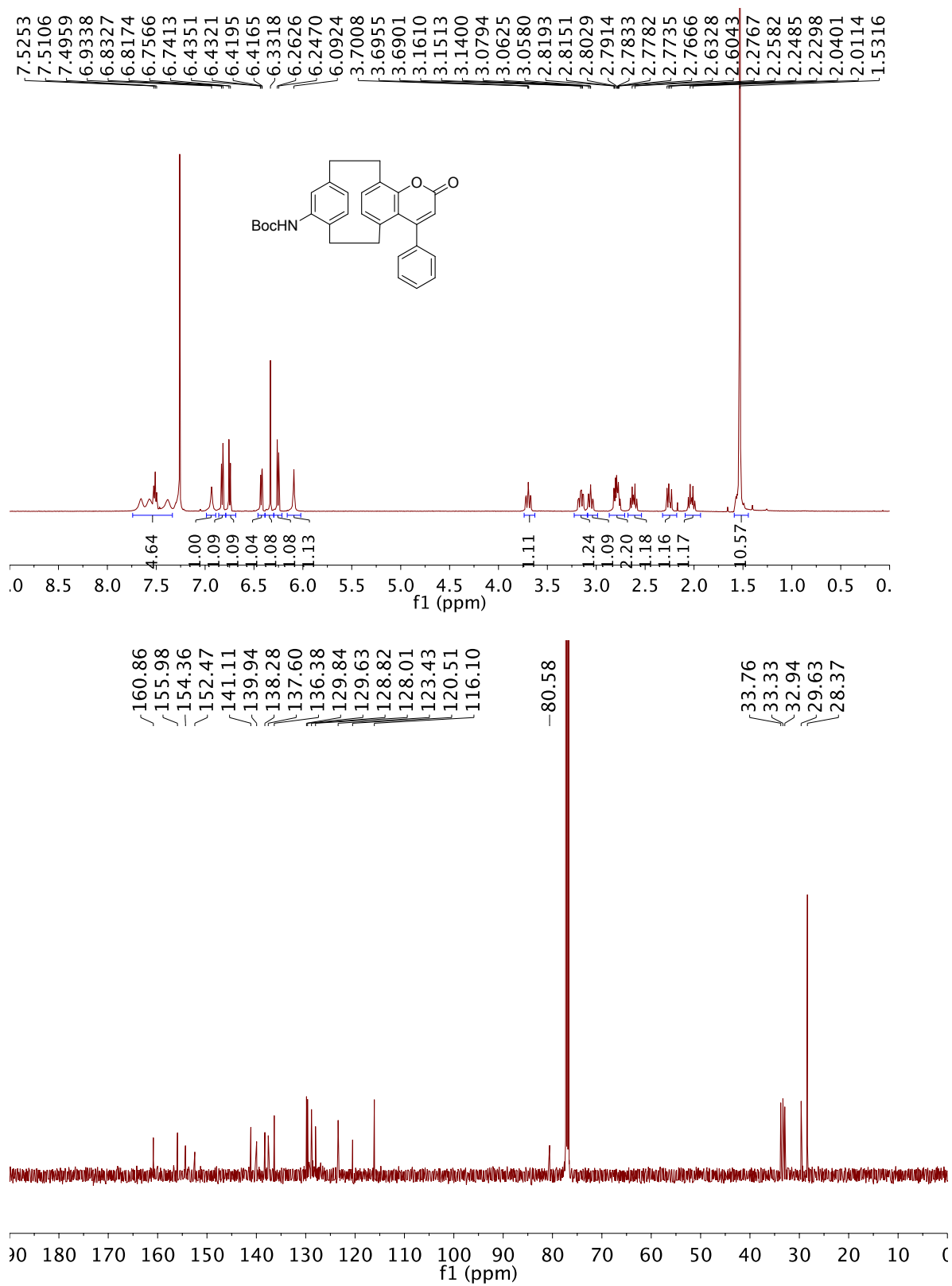
4-{13-Oxo-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]}icosa-1(16),4,6,10,14,17,19-heptaen-15-yl}phenyl trifluoromethanesulfonate (**Compound (±)-1j**)



15-[4-(Trifluoromethyl)phenyl]-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-
1(16),4,6,10,14,17,19-heptaen-13-one (**Compound (±)-1k**)



2,2-Dimethyl-N-{13-oxo-15-phenyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]}icosa-1(16),4(20),5,7(19),10,14,17-heptaen-5-yl}propanamide (Compound (±)-11)



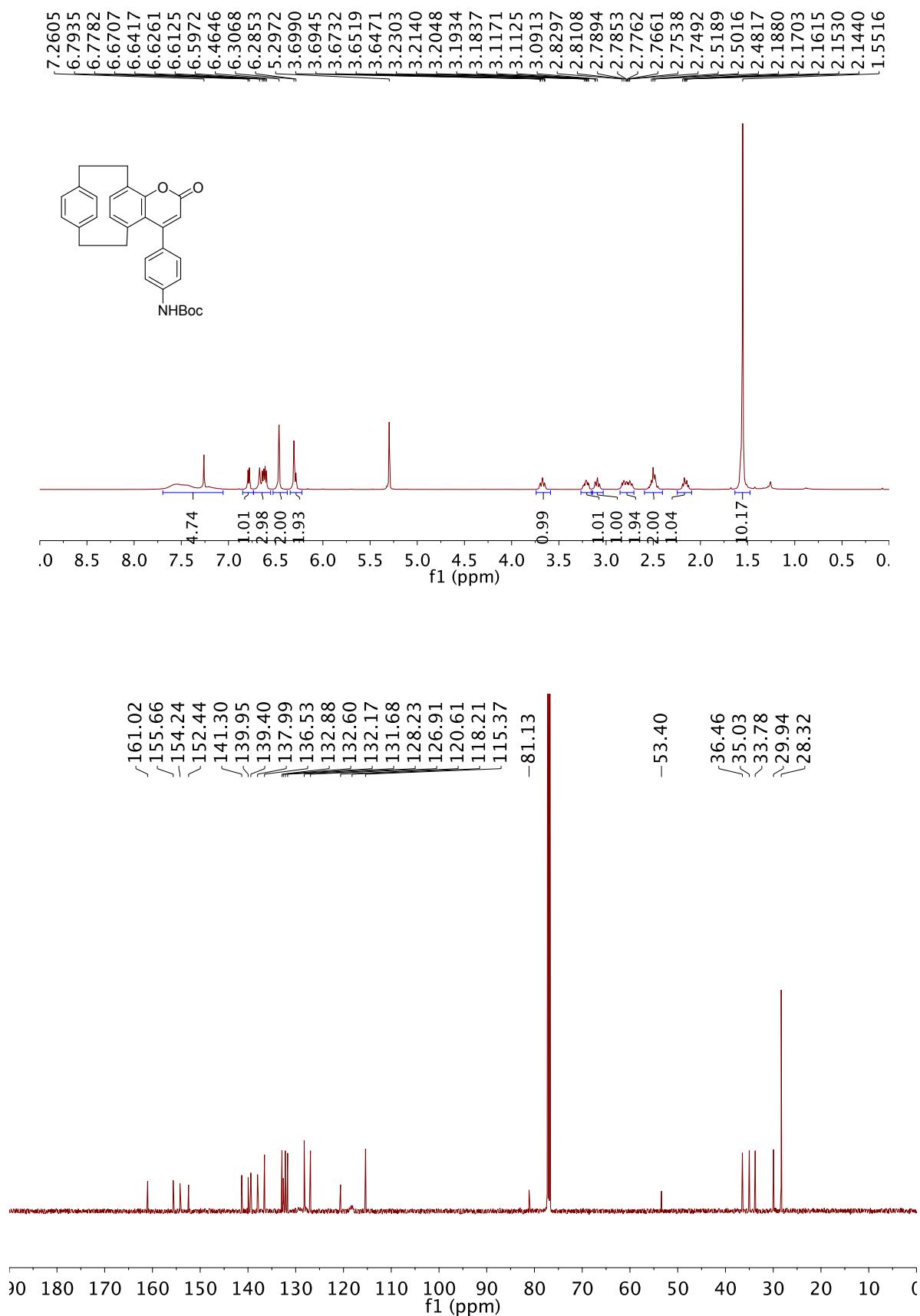
Chemical structure of 2-(4-aminophenyl)-2-phenyl-6,7-bis(4-aminophenyl)quinoline is shown above the spectrum.

¹H NMR spectrum (ppm) with chemical shifts and integrations:

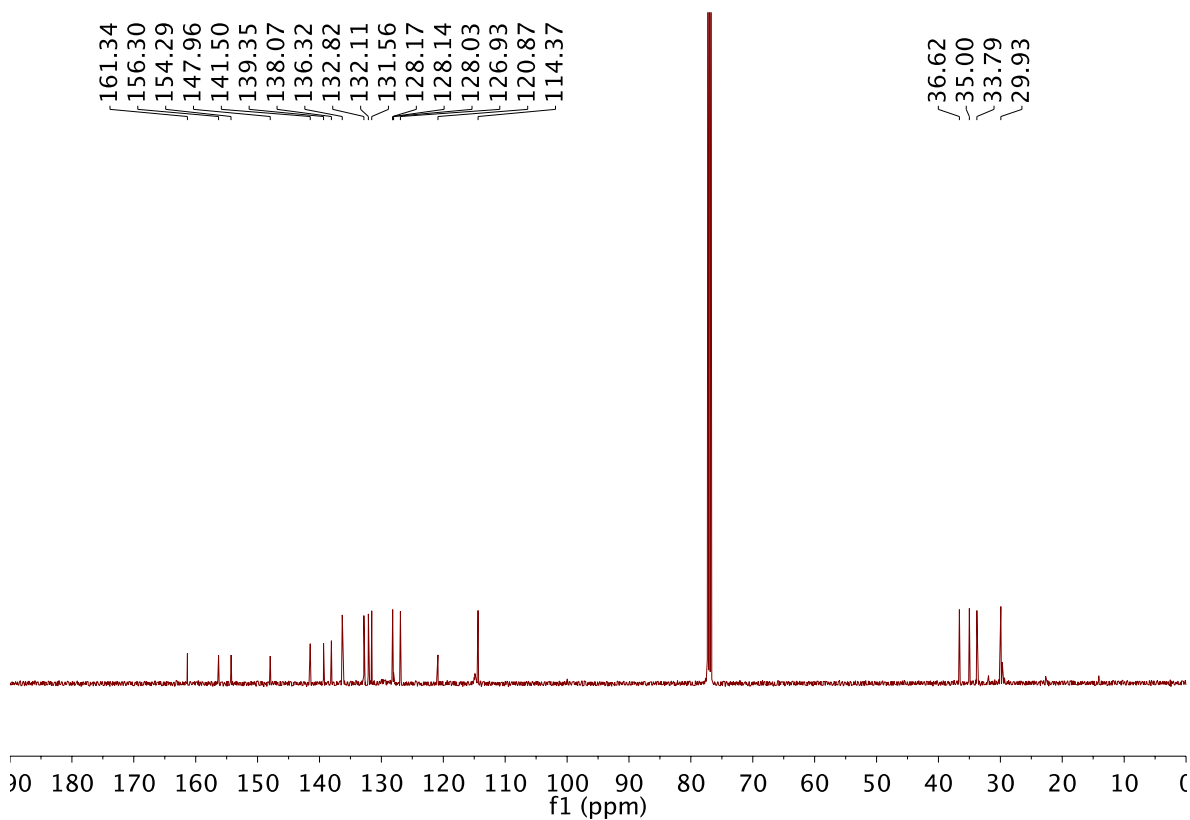
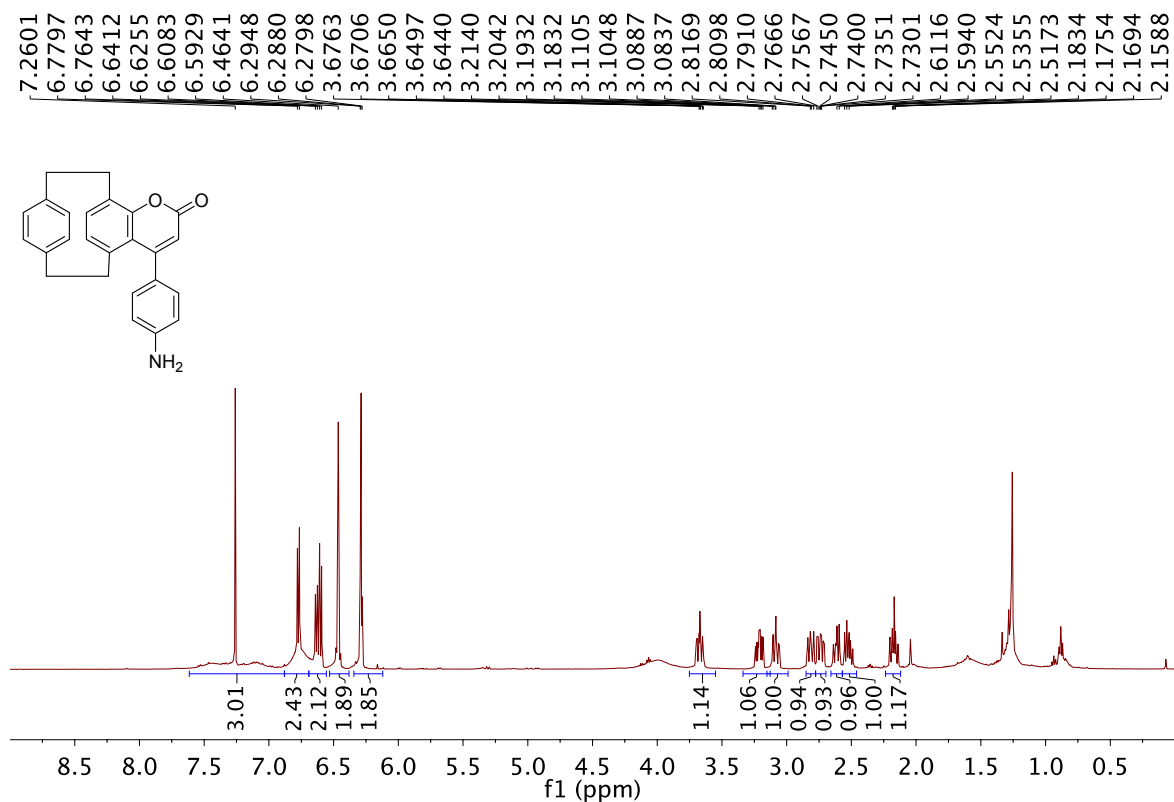
Chemical Shift (ppm)	Integration
7.5177	0.86
7.5031	0.96
7.4884	1.16
7.2600	1.04
7.1455	1.37
7.1301	0.98
6.6808	1.98
6.6654	1.98
6.1570	1.00
6.1547	1.00
6.1414	1.00
6.1392	1.00
6.1270	1.00
6.1116	1.00
5.5207	1.00
3.7185	1.10
3.7132	1.46
3.7079	1.09
3.1099	1.08
3.1009	3.18
2.9103	1.71
2.9056	1.19
2.8046	1.71
2.7768	1.19
2.7589	1.71
2.7444	1.19
2.7353	1.71
2.7224	1.19
2.7180	1.71
2.7134	1.19
2.7089	1.71
2.7000	1.19
2.6864	1.71
2.6825	1.19
2.6723	1.71
2.6545	1.19
2.1853	1.71
2.1681	1.19
2.1575	1.71
2.1386	1.19
1.9557	1.71
1.9279	1.19



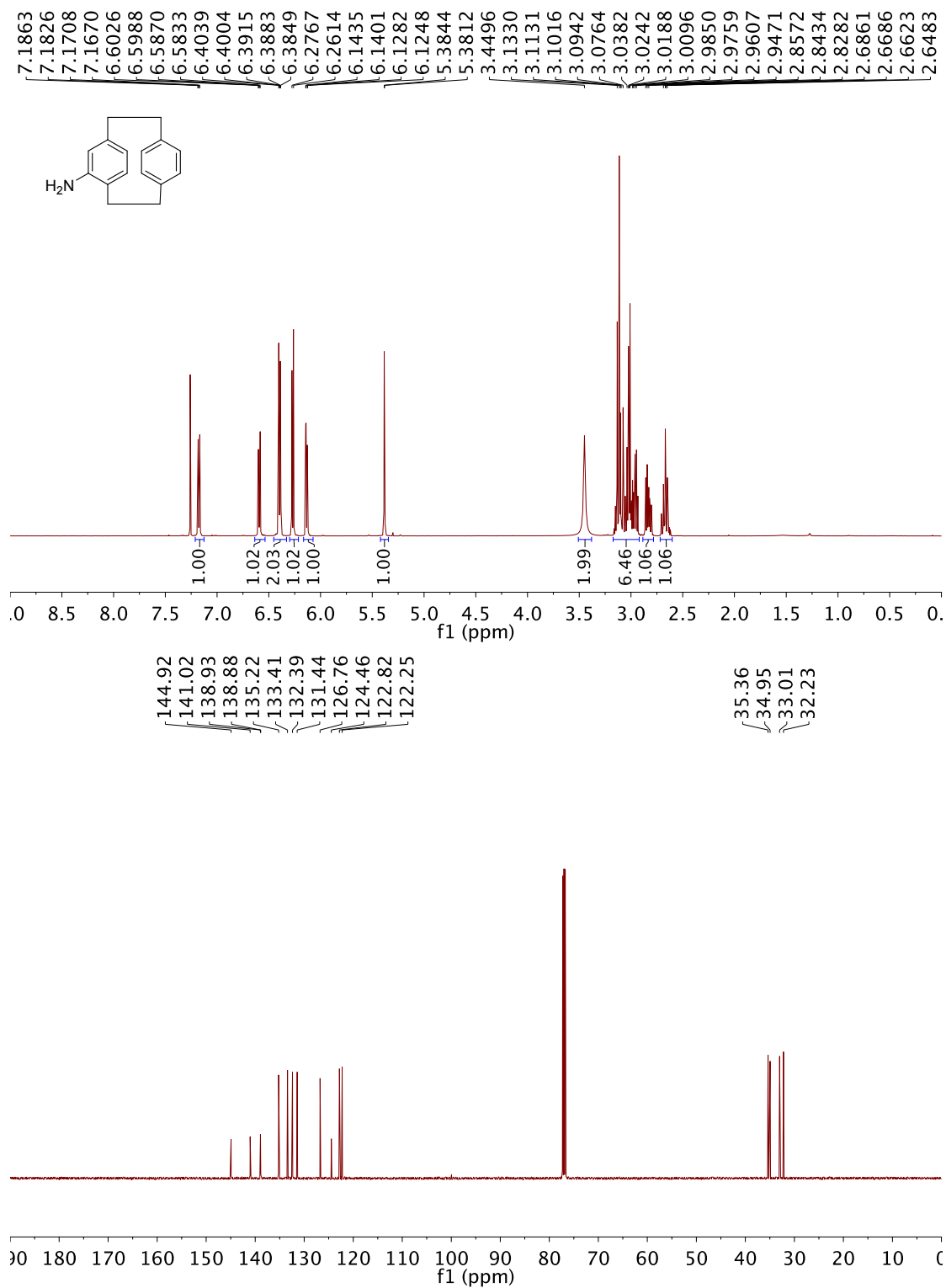
tert-Butyl *N*-(4-{13-oxo-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa1(17),4,6,10(18),11(16),14,19-heptaen-15-yl}phenyl)carbamate (**Compound (±)-1n**)



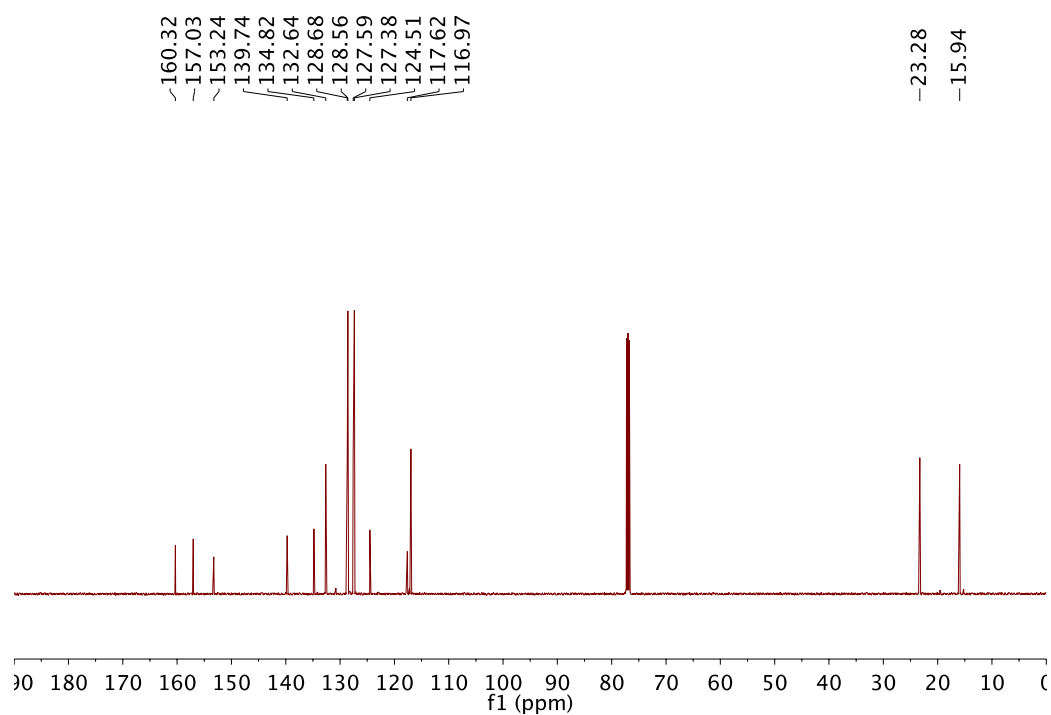
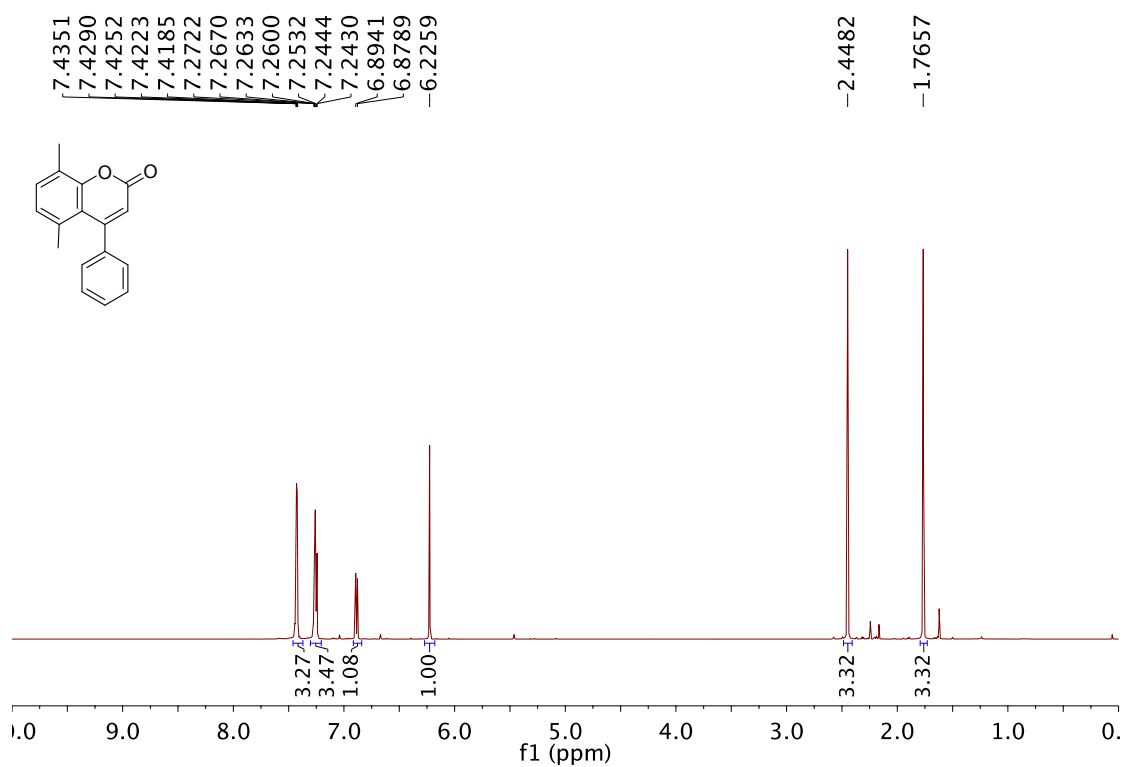
15-(4-Aminophenyl)-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosan-1(17),4,6,10(18),11(16),14,19-heptaen-13-one (**Compound (±)-1o**)



4-Amino[2.2]paracyclophane (**Compound (±)-6**)



5,8-Dimethyl-4-phenyl-2H-chromen-2-one (Compound 7a)



4,5,8-Trimethyl-2H-chromen-2-one (Compound 7b)

