Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis and photophysical studies of through-space conjugated [2.2]paracyclophane-based naphthalene fluorophores

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Supporting Information

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General Remarks

All reactions were carried out under inert atmosphere, in oven-dried glassware, using dry solvents unless otherwise specified. All commercially available compounds were purchased from Aldrich Chemical Co., Acros Organics, Alfa Aesar or Carbosynth and used as received. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck $60F_{254}$) visualized either with a UV lamp (254 nm) or by using solutions of *p*-anisaldehyde/sulfuric acid/acetic acid (AcOH) in ethanol (EtOH) or $KMnO_4/K_2CO_3$/AcOH in water followed by heating. Flash chromatography was performed on silica gel (60-230 mesh) unless otherwise specified. Organic extracts were dried over anhydrous $MgSO_4$. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avancell 500 spectrometer, at 500 MHz (H value) or 125 MHz (C value) in $CDCl_3$ unless otherwise specified. Spectra were referenced to residual chloroform (7.26 ppm, ^1H; 77.0 ppm, ^{13}C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet or overlap of nonequivalent resonances), dd (doublet of doublet), td (triplet of doublet), and br (broad signal). Coupling constants, *J*, are reported in hertz (Hz). All NMR spectra were obtained at 300K unless otherwise specified. All microwave-mediated reactions were carried out using a Biotage Initiator™ Exp or CEM discover microwave synthesizer. The microwave reactions were carried out in 2 - 5 mL microwave vials. Absorption and fluorescence spectra were recorded on UV-2700 spectrophotometer (Shimadzu) and F-7000 fluorescence spectrometer (Hitachi), respectively. The photophysical measurements were performed on air-equilibrated solutions, using quarts cuvettes with 1 cm optical path length. The fluorescence quantum yields (error ± 10%) were determined with anthracene (QY = 0.27 in ethanoml) and 9,10-diphenyl anthracene (QY = 0.90 in cyclohexane) as references and corrected for refractive index differences between ethanol or cyclohexane and dichloromethane. IR spectra were obtained using a spectrum one FT-IR spectrometer (Perkin Elmer). High Resolution mass spectra were recorded on a ThermoFischer Exactive Orbitrap spectrometer.

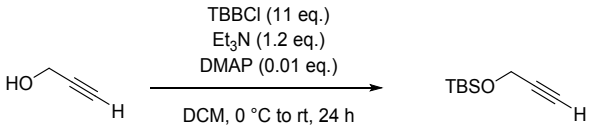
Abbreviation list

Cy	Cyclohexane
Dbu	1,8-Diazabicycloundec-7-ene
DCC	Dicyclohexylcarbodiimide
DCM	Dichloromethane
DIBAL-H	Diisobutylaluminum hydride
DMAP	4-(Dimethylamino)pyridine
DMSO	Dimethyl sulfoxide
EDC	*N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide
EtOAc	Ethyl acetate
HPLC	High pressure liquid chromatography
MeCN	Acetonitrile
$PhNO_2$	Nitrobenzene
PTSA	*p*-Toluenesulfonic acid monohydrate
QY	Quantum yield
rt	Room temperature
TBAF	Tetrabutylammonium fluoride
TBSCl	*tert*-Butyldimethylsilyl chloride
Tf_2O	Trifluoromethanesulfonic anhydride
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMSA	Trimethylsilylacetylene

Experimental and analytical data

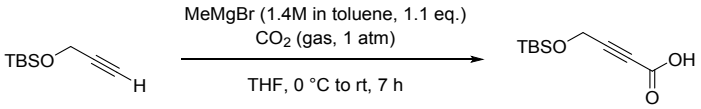
Synthesis of 3-arylpropiolic acids

*Synthesis of tert-butyldimethyl(prop-2-yn-1-yloxy)silane (**S1**)*



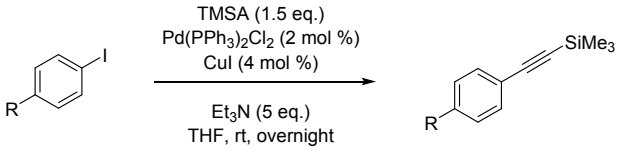
To an ice cold solution of TBSCl (8.87 g, 10.2 mL, 58.9 mmol, 1.1 eq.), Et_3N (6.5 g, 8.93 mL, 64.2 mmol, 1.2 eq.) and DMAP (0.0654 g, 0.535 mmol, 0.01 eq.) in dry DCM (20 mL) was added dropwise 2-propyn-1-ol (3 g, 3.16 mL, 53.5 mmol1 eq.) in dry DCM (5 mL). After stirring at rt for 24 h, the reaction solution was washed with brine (3 x 40 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Compound **S1** (8.19 g, 48.1 mmol, 90 % yield) was isolated as a yellow oil and was used in the following synthetic step without any further purification. **^{1}H NMR** (250 MHz, $CDCl_3$): δ 4.31 (d, J = 2.4 Hz, 2H), 2.39 (t, J = 2.4 Hz, 1H), 0.91 (s, 9H), 0.13 (s, 6H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 82.4 (C), 72.8 (CH), 51.4 (CH_2), 25.7($3CH_3$), 18.2 (C), -5.3 ($2CH_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[1]

*Synthesis of 4-[(tert-butyldimethylsilyl)oxy]but-2-ynoic acid (**S2**)*



A solution of compound **S1** (1 g, 5.87 mmol, 1 eq.) in dry THF (15 mL) was added dropwise into MeMgBr (1.4 M toluene/THF, 1.4 M, 4.61 mL, 6.46 mmol, 1.1 eq.) at 0 °C. After stirring at 0 °C for 2 h and then at rt for 3 h, a stream of dry CO_2 was passed through the pale yellow solution for 2 h. The solution was then diluted with saturated aqueous NH_4Cl solution (50 mL) and extracted with DCM (3 x 30 mL). The aqueous phased was then acidified with 1 M HCl to pH 5.0 and extracted with EtOAc (3 x 40 mL). The combined organic layers (EtOAc) were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give compound **S2** (0.415 g, 1.94 mmol, 33 % yield) as an amorphous pale yellow solid. **^{1}H NMR** (250 MHz, DMSO-d_6): δ 13.6 (br s, 1H), 4.48 (s, 2H), 0.88 (s, 9H), 0.11 (s, 6H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6): δ 154.1 (C), 86.7 (C), 77.0 (C), 48.6 (CH_2), 25.8 ($3CH_3$), 17.8 (C), -3.2 ($2CH_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[2]

General procedure A: Sonogashira couplings

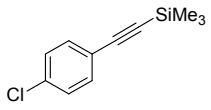


[1] Karjalainen, O. K.; Passiniemi, M.; Koskinen, A. M. P. *Org. Lett.* **2010**, *12*, 1145.

[2] Tsou, H.-R.; Mamuya, N.; Johnson, B. D.; Reich, M. F.; Gruber, B. C.; Ye, F.; Nilakantan, R.; Shen, R.; Discafani, C.; DeBlanc, R.; Davis, R.; Koehn, F. E.; Greenberger, L. M.; Wamg, Y.-F.; Wissner, A. *J. Med. Chem*. **2001**, *44*, 2719.

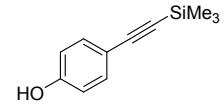
To a solution of the desired 4-iodobenzene (1 eq.), CuI (0.04 eq.) and $Pd(PPh_3)_2Cl_2$ (0.02 eq.) in dry THF was added Et_3N (5 eq.) under an argon atmosphere. TMSA (1.5 eq.) was then added dropwise via syringe. The resulting solution was stirred at room temperature overnight. The reaction mixture was then concentrated under reduced pressure and the crude residue was purified by silica gel column chromatography to afford the pure product.

- [2-(4-Chlorophenyl)ethynyl]trimethylsilane (**S3**)



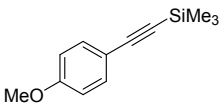
Substrate **S3** was synthesized following the general procedure A (pag. 5): 1-chloro-4-iodobenzene (2 g, 8.39 mmol, 1 eq.), CuI (64 mg, 0.34 mmol, 0.04 eq.) and $Pd(PPh_3)_2Cl_2$ (0.118 g, 0.17 mmol, 0.02 eq.), Et_3N (5.83 mL, 41.90 mmol, 5 eq.), TMSA (1.24 g, 1.79 mL, 12.6 mmol, 1.5 eq.), and THF (40 mL). The title compound was isolated (eluent: cyclohexane) as an amorphous yellow solid (1.63 g, 7.82 mmol, 93 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.42 – 7.39 (m, 2H), 7.30 – 7.28 (m, 2H), 0.27 (s, 9H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 134.5 (C), 133.2 (2CH), 128.5 (2CH), 121.6 (C), 103.8 (C), 95.3 (C), -0.1 ($3CH_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[3]

- 4-[2-(Trimethylsilyl)ethynyl]phenol (**S4**)



Substrate **S4** was synthesized following the general procedure A (pag. 5): 4-iodophenol (3 g, 13.6 mmol, 1 eq.), CuI (0.104 g, 0.545 mmol, 0.04 eq.) and $Pd(PPh_3)_2Cl_2$ (0.316 g, 0.45 mmol, 0.033 eq.), Et_3N (3.45 g, 4.74 mL, 34.1 mmol, 2.5 eq.), TMSA (1.1 eq., 1.47 g, 2.14 mL, 15 mmol), and THF (70 mL). The title compound was isolated (eluent: EtOAc/pentane 1:9) as an amorphous brown solid (2.6 g, 13.6 mmol, quantitative yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.40 – 7.32 (m, 2H), 6.80 – 6.70 (m, 2H), 0.23 (s, 9H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 156.5 (C), 133.8 (2CH), 115.6 (C), 114.9 (2CH), 105.5 (C), 92.4 (C), 0.1 ($3CH_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[4]

- [2-(4-Methoxyphenyl)ethynyl]trimethylsilane (**S5**)

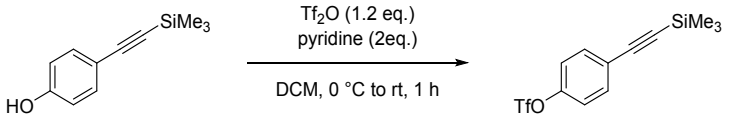


Substrate **S4** was synthesized following the general procedure A (pag. 5): 4-iodoanisole (0.988 g, 4.22 mmol, 1 eq.), CuI (0.0322 g, 0.169 mmol, 0.04 eq.) and $Pd(PPh_3)_2Cl_2$ (0.0978 g, 0.139 mmol, 0.033 eq.), Et_3N (1.07 g, 1.47 mL, 10.6 mmol, 2.5 eq.), TMSA (0.456 g, 0.661 mL, 4.64 mmol, 1.1 eq.), and THF (25 mL). The title compound was isolated (eluent: EtOAc/pentane 1:9) as a brown oil (0.82 g, 4.01 mmol, 95 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.40 (d, J =17.6 Hz, 2H), 6.81 (d, J =17.6 Hz, 2H), 3.80 (s, 3H), 0.24 (s, 9H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.7 (C), 133.5 (2CH), 155.3 (C), 133.8 (2CH), 105.2 (C), 92.4 (C), 55.3 (CH_3), -0.1 ($3CH_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[4]

[3] Araki, Y.; Kobayashi, K.; Yonemoto, M.; Kondo, Y. *Org. Biomol. Chem*. **2011**, *9*, 78.

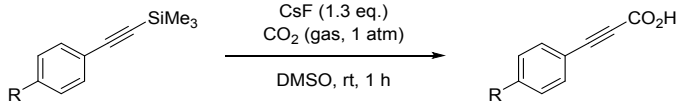
[4] Pirali, T.; Gatti, S.; Di Brisco, R.; Tacchi, S.; Zaninetti, R.; Brunelli, E.; Massarotti, A.; Sorba, G.; Canonico, P.; Moro, L.; Genazzani, Armando A.; Tron, G.; Billington, Richard A. *ChemMedChem* , **2007**, *2*, 437.

*Synthesis of 4-[2-(trimethylsilyl)ethynyl]phenyl trifluoromethanesulfonate (**S6**)*



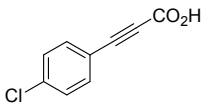
A 100 mL round-bottomed flask was charged with 4-[2-(trimethylsilyl)ethynyl]phenol (2.59 g, 13.6 mmol, 1 eq.) and dry DCM (15 mL). The resulting solution was cooled to 0 °C, and pyridine (2.15 g, 2.2 mL, 27.2 mmol 2 eq.) was added dropwise via syringe. A solution of trifluoromethanesulfonic anhydride (4.61 g, 2.71 mL, 16.3 mmol, 1.2 eq.) in dry DCM (4 mL) was finally added dropwise via syringe, and the flask was allowed to warm to rt. After stirring at rt for 1 h, TLC analysis indicated complete consumption of the starting material. The reaction was diluted with EtOAc (40 mL), washed with a 1M HCl solution (3 x 30 mL), saturated aqueous $NaHCO_3$ (3 x 30 mL), water (3 x 30 mL), and brine (2 x 30 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product purified via silica gel column chromatography, eluting with 10:0 to 9:1 Cy:EtOAc. Compound **S6** (3.15 g, 9.77 mmol, 72 % yield) was isolated as a colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 – 7.46 (m, 2H), 7.25 – 7.16 (m, 2H), 0.25 (s, 9H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.1 (C), 133.8 (2CH), 123.9 (C), 121.3 (2CH), 118.7 (q, J = 318 Hz, CF_3), 102.8 (C), 96.7 (C), -0.2 ($3CH_3$) ppm. Spectroscopic data were consistent with the literature data for this compound.[5]

General procedure B: Alkyne Carboxylation



A flame dried round-bottomed flask was charged with DMSO. CO_2 gas (balloon) was allowed to bubble through the DMSO for 5 min. CsF (1.3 eq.) was then added followed by the desired alkyne (1 eq.). The reaction was stirred at room temperature for 1 h then quenched with water. The aqueous phase was extracted with DCM then acidified with a 2 M HCl solution and extracted with ethyl acetate. The combined organic phases (EtOAc) were washed with brine dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the product.

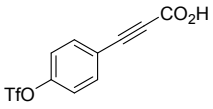
- 3-(4-Chlorophenyl)propiolic acid (**S7**)



Substrate **S7** was synthesized following the general procedure B (pag. 7): **S3** (1 g, 4.79 mmol, 1 eq.), CsF (0.946 g, 6.23 mmol, 1.3 eq.), and DMSO (10 mL). The title compound was isolated as an amorphous yellow solid (0.81 g, 4.49 mmol, 94 % yield). **^{1}H NMR** (500 MHz, DMSO-d_6): δ 13.87 (br s, 1H), 7.66 – 7.64 (m, 2H), 755 – 7.53 (m, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6): δ 154.1 (C), 135.8 (C), 134.3 (2CH), 129.2 (2CH), 117.8 (C), 83.1 (C), 82.5 (C) ppm. Spectroscopic data were consistent with the literature data for this compound.[6]

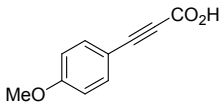
[5] Kim, S.; Rojas-Martina, J.; Toste F. D. *Chem. Sci.* **2016**, 7, 85.
[6] Yonemoto-Kobayashi, M.; Inamoto, K.; Tanaka, Y.; Kondo, Y. *Org. Biomol. Chem*. **2013**, *11*, 3773.

- 3-{4-[(trifluoromethyl)sulfonyloxy]phenyl}propiolic acid (**S8**)



Substrate **S8** was synthesized following the general procedure B (pag. 7): **S6** (0.987 g, 3.06 mmol, 1 eq.), CsF (0.605 g, 3.98 mmol, 1.3 eq.), and DMSO (10 mL). The title compound was isolated as an amorphous yellow solid (0.77 g, 2.62 mmol, 85 %). **^{1}H NMR** (500 MHz, DMSO-d_6): δ 13.91 (br s , 1H), 7.84 (d, J = 9.0 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6): δ 153.9 (C), 150.1 (C), 135.1 (2CH), 122.4 (2CH), 119.9 (C), 118.4 (q, J = 1276 Hz, CF_3), 82.9 (C), 82.1 (C) ppm. **HRMS** (ESI): m/z [M-H]$^-$ calcd for $C_{10}H_4O_5F_3S$: 292.9737; found: 292.9746.

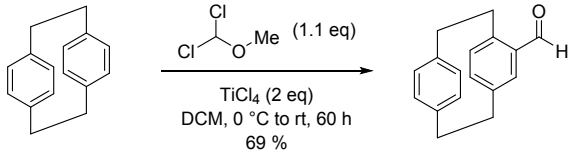
- 3-(4-methoxyphenyl)propiolic acid (**S9**)



Substrate **S9** was synthesized following the general procedure B (pag. 7): **S5** (0.6 g, 2.94 mmol, 1 eq.), CsF (0.58 g, 3.82 mmol, 1.3 eq.), and DMSO (5 mL). The title compound was isolated as an amorphous yellow solid (0.325 g, 1.84 mmol, 63 %). **^{1}H NMR** (500 MHz, DMSO-d_6): δ 13.4 (br s, 1H), 7.41 – 7.38 (m, 2H), 6.86 – 6.82 (m, 2H), 3.63 (s, 3H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6): δ 161.2 (C), 154.5 (C), 134.6 (2CH), 114.7 (2CH), 110.5 (C), 85.3 (C), 81.0 (C), 55.4 (CH_3) ppm. Spectroscopic data were consistent with the literature data for this compound.[3]

Synthesis of 4-formyl[2.2]paracyclophanes 1a-c

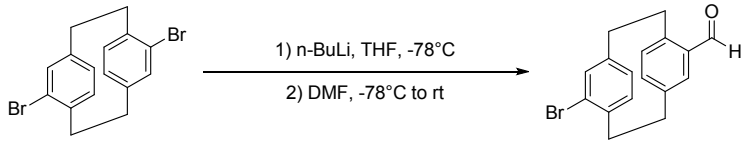
*Synthesis of 4-formyl-[2,2]paracyclophane (**1a**)*



Compound **1a** was synthesized *via* a modification of the procedure originally reported by Rieche and co-workers.[7] To a 0 °C cooled solution of [2.2]paracyclophane (3 g, 14.4 mmol, 1 eq.) in dry DCM (100 mL), $TiCl_4$ (1 M in DCM, 58 mL, 28.8 mmol, 2 eq.) and 1,1-dichlorodimethyl ether (1.82 g, 1.43 mL, 15.8 mmol, 1.1 eq.) were added sequentially. The resulting mixture was allowed to warm to rt. After stirring at rt for 60 h, the black solution was poured onto ice and stirred for 3 h until it became dark yellow. The organic phase was separated and the aqueous phase extracted with DCM (2 x 50 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified *via* silica gel column chromatography (eluent: DCM/Cy 1:2). Compound **1a** (2.35 g, 9.94 mmol, 69 % yield) was isolated as an amorphous white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.01 (d, J = 1.9 Hz, 1H), 6.73 (dd, J = 7.8, 1.9 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 6.56 (dd, J = 7.8, 1.8 Hz, 1H), 6.50 (dd, J = 7.8, 1.8 Hz, 1H), 6.43 (dd, J = 7.8, 1.8 Hz, 1H), 6.37 (dd, J = 7.8, 1.9 Hz, 1H), 4.12-4.08 (m, 1H), 3.29-2.96 (m, 7H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.0 (CH), 143.4 (C), 140.8 (C), 139.7 (C), 139.6 (C), 138.2 (CH), 136.8 (C), 136.5 (CH), 136.3 (CH), 133.4 (CH), 133.1 (CH), 132.5 (CH), 132.3 (CH), 35.4 (CH_2), 35.3 (CH_2), 35.1 (CH_2) 33.8 (CH_2) ppm. Spectroscopic data were consistent with the literature data for this compound.[8]

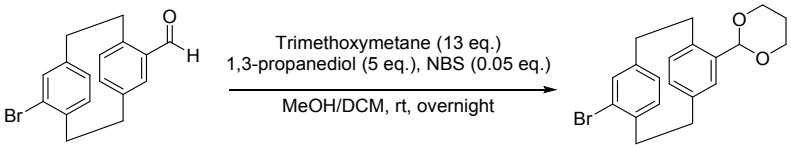
*Synthesis of 4-formyl-16-bromo[2.2]paracyclophane (**1b**)*

[7] A. Rieche, H. Gross, E. Hoft, *Chem. Ber.* **1960**, *93*, 88-94.
[8] Friedmann, C. J.; Ay, S.; Brase, S. *J. Org. Chem.* **2010**, *75*, 4612.



To a flame-dried 100 mL round-bottomed flask was added 4,16-dibromo[2.2]paracyclophane (800 mg, 2.185 mmol, 1 eq.) and dry THF (90 mL). The solution was cooled to -78 °C in a dry ice/acetone bath and *n*-BuLi (1 M in THF, 1.3 mL, 3.278 mmol, 1.5 eq.) was added dropwise via syringe turning the mixture yellow. The reaction was stirred for 30 min, and then anhydrous DMF (1.3 mL, 17.48 mmol, 8 eq.) was added dropwise via syringe turning the mixture colourless. The solution was allowed to warm to rt and stirred for 2.5 h. The mixture was then quenched with a saturated aqueous NH_4Cl solution (50 mL), and THF was removed under vacuum. The resulting solution was taken up with DCM and washed three times with distilled water. The organic layer was collected, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified *via* silica gel column chromatography (eluent: EtOAc/Cy 1:29 to 1:14) to give compound **1b** (354 g, 1.123 mmol, 51 % yield) as an amorphous white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.41 (dd, *J* = 7.6, 2 Hz, 1H), 6.96 (d, *J* = 1.9 Hz, 1H), 6.57-6.55 (m, 2H), 6.44-6.38 (m, 2H), 4.12 (qd, *J* = 10, 2 Hz, 1H), 3.50 (qd, *J* = 10.4, 2.8 Hz, 1H), 3.28-3.23 (m, 1H), 3.15-2.87 (m, 5H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.2 (CH), 142.8 (C), 141.6 (C), 140.3 (C), 139.1 (C), 137.3 (CH), 137.2 (CH), 136.7 (C), 135.3 (CH), 134.2 (CH), 133.9 (CH), 130.8 (CH), 127.4 (C), 35.3(CH_2), 34.3 (CH_2), 33.3 (CH_2), 33.1 (CH_2) ppm. Spectroscopic data were consistent with the literature data for this compound.[9]

*Synthesis of 2-{14-bromotricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl}-1,3-dioxane (**S10**)*

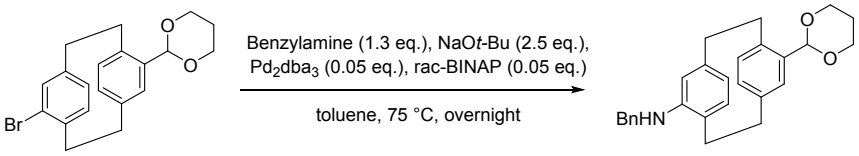


To a flame-dried 25 mL round-bottomed flask were added compound **1b** (300 mg, 0.952 mmol, 1 eq.) in dry DCM (8 mL) under an argon atmosphere. To the resulting solution 1,3-propanediol (0.344 mL, 4.76 mmol, 5 eq.), anhydrous MeOH (0.193 mL, 4.76 mmol, 5 eq.), trimethoxymethane (0.135 mL, 1.24 mmol, 1.3 eq.) and NBS (9 mg, 0.046 mmol, 0.05 eq.) were added successively to obtain an colourless mixture. The reaction was stirred at 20°C overnight, then quenched with a saturated $NaHCO_3$ solution (20 mL). The aqueous phase was extracted with DCM (3 x 15 mL), the combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via silica gel column chromatography (eluent : EtOAc/Cy 1:14) to afford compound **S10** (301 mg, 0.806 mmol, 85 %) as an amorphous white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.68 (d, *J* = 1.8 Hz, 1H), 6.64 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.56 (d, *J* = 1.8 Hz, 1H), 6.39 (dd, *J* = 12.0, 7.7 Hz, 2H), 5.44 (s, 1H), 4.37-4.34 (m, 1H), 4.25-4.21 (m, *J*1H), 4.06 – 3.97 (m, 2H), 3.53 – 3.42 (m, 2H), 3.20 (ddd, *J* = 13.1, 10.5, 5.0 Hz, 1H), 3.08 – 2.83 (m, 5H), 2.25 – 2.16 (m, 1H), 1.47 – 1.44 (m, 1H) ppm.**^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.2 (C), 139.2 (C), 138.8 (C), 136.9 (C), 136.8 (CH), 136.7 (C), 134.6 (CH), 134.3 (CH), 130.5 (CH), 130.3 (CH), 129.2 (CH), 126.6 (C), 101.0 (CH), 67.6 (CH_2), 67.5 (CH_2), 35.1 (CH_2), 34.2 (CH_2), 33.2 (CH_2), 32.7 (CH_2), 25.8 (CH_2)

[9] Wielopolski, M.; Molina-Ontoria, A.; Schubert, C.; Margraf, J. T.; Krokos, E.; Kirschner, J.; Gouloumis, A.; Clark, T.; Guldi, D. M.; Martin, N. *J. Am. Chem. Soc.* **2013**, *135*, 10372.

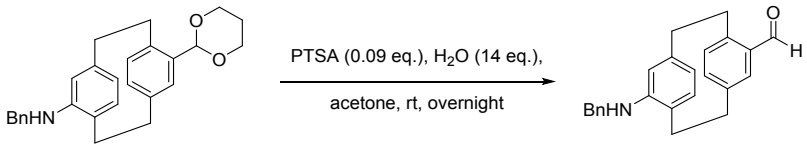
ppm. **IR** (neat): 3347, 2932, 2854, 2211, 1688, 1603, 1587, 1509, 1391, 1282, 1160, 1147, 1108, 1088, 1062, 1032, 908, 834, 732 cm^{-1}. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{20}H_{21}O_2BrNa$: 395.0617; found: 395.0615.

*Synthesis of N-benzyl-11-(1,3-dioxan-2-yl)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4(16),5,7(15),10,13-hexaen-5-amine (**S11**)*



To a flame-dried 100 mL round-bottomed flask were added successively compound **S10** (852 mg, 2.28 mmol, 1 eq.), $Pd_2(dba)_3$ (124 mg, 0.135 mmol, 0.05 eq.) , rac-BINAP (70 mg, 0.112 mmol, 0.05 eq.) and sodium tert-butoxide (566 mg, 5.89 mmol, 2.5 eq.) under an argon atmosphere. Toluene (50 mL) and benzylamine (333 mg, 0.34 mL, 3.11 mmol, 1.3 eq.) were finally added. The solution was heated to 75°C and stirred under an argon atmosphere overnight. The reaction was then quenched with a saturated Na_2CO_3 solution (40 mL) and the aqueous phase was extracted with Et_2O (3 x 45 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via silica gel chromatography (eluent: EtOAc/Cy 1:9) to afford compound **S11** (856 mg, 2.14 mmol, 94 %) as an amorphous white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) : *δ* 7.47-7-46 (m, 2H), 7.42-7.39 (m, 2H), 7.35-7.32 (m, 1H), 6.98 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.61 (d, *J* = 1.6 Hz, 1H), 6.33 (d, *J* = 7.7 Hz, 1H), 6.24 (d, *J* = 7.6 Hz, 1H), 6.17 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.50 (s, 1H), 5.45 (d, *J* = 0.9 Hz, 1H), 4.39-4.36 (m, 1H), 4.26-4.20 (m, 2H), 4.11-4.00 (m, 3H), 3.83 (s br, 1H), 3.49-3.44 (m, 1H), 3.12-2.95 (m, 5H), 2.87-2.81 (m, 1H), 2.74-2.67 (m, 1H), 2.22-2.13 (m, 1H), 1.46-1.43 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 146.6 (C), 140.7 (C), 139.5 (C), 138.7 (C), 137.1 (C), 136.4 (C), 134.4 (CH), 133.0 (CH), 130.2 (CH), 128.7 (2CH), 128.0 (2CH), 127.9 (CH), 127.4 (CH), 123.9 (C), 120.3 (CH), 116.2 (CH), 101.1 (CH), 67.6 (CH_2), 67.5 (CH_2), 48.3 (CH_2), 34.4 (CH_2), 32.8 (CH_2), 32.4 (CH_2), 31.9 (CH_2), 25.8 (CH_2) ppm. **IR** (neat): 3422, 2924, 2850, 1594, 1570, 1509, 1425, 1275, 1236, 1146, 1122, 1110, 1089, 1007, 908, 874, 792, 698, 670 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{27}H_{30}O_2N$: 400.2271; found: 400.2266.

*Synthesis of 14-(benzylamino)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaene-5-carbaldehyde (**1c**)*

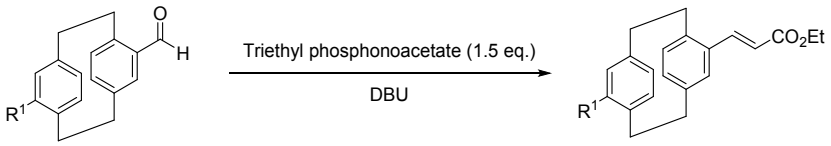


To a 25 mL round-bottomed flask were added successively compound **S11** (730 mg, 1.83 mmol, 1 eq.), p-toluenesulfonic acid monohydrate (33 mg, 0.173 mmol, 0.09 eq.), H_2O (500 mg, 0.5 mL, 27.8 mmol, 14 eq.) and acetone (10 mL). The resulting colourless solution was stirred overnight at rt. The consumption of the starting material was followed by TLC using EtOAc/Cy 2:8 as the eluent. At the end of the reaction, the solvent was removed under vacuum. The residue was taken up with DCM (20 mL) then washed with a saturated $NaHCO_3$ solution (3x10 mL), and brine (2x10 mL). The organic layer was collected, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product

was purified by filtration through a short plug of silica gel with DCM washings. Compound **1c** (604 mg, 1.77 mmol, 97 %) was isolated as an amorphous green solid. **^{1}H NMR** (500 MHz, $CDCl_3$) : *δ* 9.95 (s, 1H), 7.46-7.40 (m, 4H), 7.36-7.34 (m, 1H), 7.26-7.24 (m, 1H), 6.85 (br s, 1H), 6.40 (d, *J* = 7.6 Hz, 1H), 6.25 (d, *J* = 7.6 Hz, 1H), 6.03 (d, *J* = 7.2 Hz, 1H), 5.39 (br s, 1H), 4.20 (d, *J* = 13.0 Hz, 1H), 4.09-4.05 (m, 2H), 3.88 (br s, 1H), 3.16-3.10 (m, 4H), 2.96-2.72 (m, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 192.3 (CH), 146.7 (C), 142.9 (C), 141.2 (C), 139.5 (C), 139.3 (C), 137.3 (CH), 136.2 (C), 133.9 (CH), 133.8 (CH), 132.0 (CH), 129.0 (2CH), 128.2 (2CH), 127.8 (CH), 124.5 (C), 121.4 (CH), 116.3 (CH), 48.4 (CH_2), 34.8 (CH_2), 33.3 (CH_2), 32.4 (CH_2), 32.1 (CH_2) ppm. **IR** (neat): 3419, 2927, 2852, 1682, 1593, 1569, 1509, 1424, 1229, 1143, 1123, 908, 827, 729, 698, 665 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{24}ON$: 342.1852; found: 342.1845.

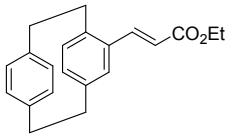
Synthesis of [2.2]paracyclophanes-based ethyl cinnamates 2a-c

General procedure C: Horner–Wadsworth–Emmons reaction



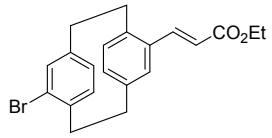
The desired 4-formyl[2.2]paracyclophane (1 eq.) and triethyl phosphonoacetate (1.5 eq.) were placed in round-bottomed flask under an argon atmosphere. Dbu was added and the reaction was stirred at rt for 3 h. Water was then added and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography to afford the pure product.

- 3-([2.2]Paracyclophen-4-yl)acrylate (**2a**)



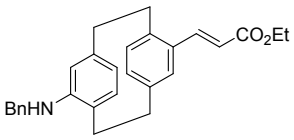
Substrate **2a** was synthesized following the general procedure C (pag. 11): **1a** (1 g, 4.23 mmol, 1 eq.), triethyl phosphonoacetate (1.26 mL, 6.35 mmol, 1.5 eq.), and DBU (5 mL). The title compound was isolated (eluent: EtOAc/Cy 1:9, 1.28 g) as an amorphous white solid (4.18 mmol, quantitative yield). **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.81 (d, *J* = 15.8 Hz, 1H), 6.69 (d, *J* = 1.6 Hz, 1H), 6.61 – 6.55 (m, 2H), 6.54 (s, 2H), 6.50 (d, *J* = 7.9 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 6.26 (d, *J* = 15.8 Hz, 1H), 4.32 (qd, *J* = 7.2, 1.3 Hz, 2H), 3.60 (ddd, *J* = 13.6, 9.9, 1.9 Hz, 1H), 3.24 – 3.09 (m, 3H), 3.09 – 2.83 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$); δ 167.3 (C), 142.4 (CH), 140.6 (C), 140.2 (C), 139.3 (C), 139.2 (C), 135.1 (CH), 134.6 (C), 134.4 (CH), 133.0 (CH), 132.9 (CH), 131.8 (CH), 131.1 (CH), 130.5 (CH), 118.1 (CH), 60.4 (CH_2), 35.4 (CH_2), 35.1 (CH_2), 35.0 (CH_2), 33.7 (CH_2), 14.3 (CH_3) ppm. **IR** (neat): 2929, 1707, 1627, 1590, 1499, 1482, 1310, 1263, 1221, 1115, 1036, 980, 860, 798, 716 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{23}O_2$: 307.1693; found: 307.1689.

- (2*E*)-3-[14-(Benzylamino)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl]prop-2-enoate (**2b**)



Substrate **2b** was synthesized following the general procedure C (pag. 11): **1b** (300 mg, 0.952 mmol, 1 eq.), triethyl phosphonoacetate (0.38 mL, 1.904 mmol, 1.5 eq.), and DBU (2 mL). The title compound was isolated (eluent: DCM) as an amorphous white solid (347 mg, 1.133 mmol, 89%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 15.8 Hz, 1H), 7.21 (dd, *J* = 1.8 Hz, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 2.9 Hz, 1H), 6.58-6.55 (m, 2H), 6.48 (d, *J* = 7.9 Hz , 1H), 6.37 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 4.33-4.28 (m, 2H), 3.62-3.56 (m, 1H), 3.53-3.47 (m, 1H), 3.22-3.17 (m, 1H), 3.07-2.83 (m, 5H), 1.38 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 167.3 (C), 142.3 (CH), 141.1 (C), 140.1 (C), 139.8 (C), 138.9 (C), 137.2 (CH), 134.7 (C), 134.3 (CH), 133.6 (CH), 131.4 (CH), 10.8 (CH), 129.6 (CH), 126.9 (C), 118.4 (CH), 60.5 (CH_2), 35.3 (CH_2), 34.2 (CH_2), 33.1 ($2CH_2$), 14.4 (CH_3) ppm. **IR** (neat): 2933, 2855, 1708, 1629, 1588, 1479, 1365, 1311, 1264, 1222, 1172, 1033, 980, 861, 707 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{22}O_2Br$: 385.0798; found: 385.0807.

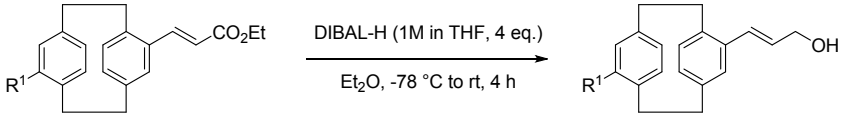
- (2*E*)-3-[14-(Benzylamino)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl]prop-2-enoate (**2c**)



Substrate **2c** was synthesized following the general procedure C (pag. 11): **1c** (503 mg, 1.47 mmol, 1 eq.), triethyl phosphonoacetate (495 mg, 0.438 mL, 2.21 mmol, 1.5 eq.), and DBU (2 mL). The title compound was isolated (eluent: DCM) as an amorphous green solid (514 mg, 1.25 mmol, 85 %). **^{1}H NMR** (500 MHz, $CDCl_3$) : δ 7.83 (d, *J* = 15.8 Hz, 1H), 7.47 – 7.7.45 (m, 2H), 7.43 – 7.40 (m, 2H), 7.36 – 7.33 (m, 1H), 7.05 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.59 (br s, 1H), 6.35 (d, *J* = 7.8 Hz, 1H), 6.22 – 6.18 (m, 2H), 6.13 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.44 (br s, 1H), 4.31 (q, *J* = 7.0 Hz, 2H), 4.22 (d, *J* = 13.1 Hz, 1H), 4.08 (d, *J* = 13.1 Hz, 1H), 3.86 (s br, 1H), 3.59 – 3.54 (m, 1H), 3.16 – 3.01 (m, 4H), 2.95 – 2.88 (m, 1H), 2.86 – 2.79 (m, 1H), 2.74 – 2.67 (m, 1H), 1.38 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 167.6 (C), 146.6 (C), 143.2 (CH), 140.8 (C), 140.2 (C), 139.5 (C), 139.3 (C), 134.5 (C), 133.7 (CH), 133.1 (CH), 131.9 (CH), 129.7 (CH), 128.9 (2CH), 128.2 (2CH), 127.6 (CH), 124.3 (C), 121.0 (CH), 117.9 (CH), 116.4 (CH), 60.5 (CH_2), 48.5 (CH_2), 34.8 (CH_2), 33.3 (CH_2), 32.6 (CH_2), 32.2 (CH_2), 14.5 (CH_3) ppm. **IR** (neat): 3424, 2927, 2851, 1704, 1627, 1594, 1570, 1509, 1425, 1311, 1173, 1036, 980, 867, 742, 699 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{28}H_{30}O_2N$: 412.2271; found: 412.2264.

Synthesis of [2.2]paracyclophanes-based cinnamic alcohols 3a-c

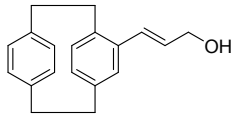
General procedure D: Reduction of esters to alcohols



To a flame-dried round-bottomed flask was added the desired [2.2]paracyclophanes-derived cinnamic esters (1 eq.) and dry Et_2O. The solution was cooled to −78 °C in a dry ice/acetone bath and DIBAL-H (1 M in THF, 4 eq.) was added dropwise *via* syringe turning the mixture yellow. The reaction was allowed to warm to rt and stirred for 4 h, becoming colourless. EtOAc was then added and the resulting solution was washed with Rochelle's salt and brine. The organic layer was

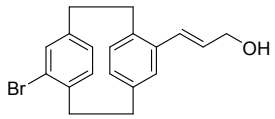
dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified *via* silica gel column chromatography to give the pure product.

- 3-([2.2]Paracyclopheny-4-yl)prop-2-en-1-ol (**3a**)



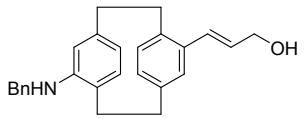
Substrate **3a** was synthesized following the general procedure D (pag. 12): **2a** (1.1 g, 3.59 mmol, 1 eq.), DIBAL-H (1 M in THF, 14.4 mL, 14.4 mmol, 4 eq.), and Et_2O (40 mL). The title compound was isolated (eluent: EtOAc/Cy 2:8) as an amorphous white solid (0.71 g, 2.69 mmol, 75 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.67 – 6.59 (m, 2H), 6.52 – 6.28 (m, 6H), 6.09 (dt, *J* = 15.7, 5.8 Hz, 1H), 4.33 (dd, *J* = 5.8, 1.4 Hz, 2H), 3.42 (ddd, *J* = 13.5, 10.0, 1.9 Hz, 1H), 3.14 – 2.83 (m, 6H), 2.79 – 2.73 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.9 (C), 139.3 (2C), 137.9 (C), 136.8 (C), 134.8 (CH), 133.0 (2CH), 131.9 (CH), 131.8 (CH), 130.7 (CH), 129.6 (CH), 129.6 (CH), 129.2 (CH), 64.1 (CH_2), 35.4 (CH_2), 35.2 (CH_2), 34.7 (CH_2), 33.6 (CH_2) ppm. **IR** (neat): 2925, 2851, 1591, 1499, 1482, 1454, 1435, 1412, 1358, 1265, 1100, 1054, 966, 900, 872 cm^{-1}. **HRMS** (APCI): *m/z* $[M–H]^-$ calcd for $C_{19}H_{19}O$: 263.1441; found: 263.1440.

- (2*E*)-3-{14-Bromotricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl}prop-2-en-1-ol (**3b**)



Substrate **3b** was synthesized following the general procedure D (pag. 12): **2b** (200 mg, 0.519 mmol, 1 eq.), DIBAL-H (1 M in THF, 2.1 mL, 2.076 mmol, 4 eq.), and Et_2O (30 mL). The title compound was isolated (eluent: EtOAc/Cy 1:14 to 8:2) as an amorphous white solid (133 g, 0.388 mmol, 75 %). **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.09 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.70 (d, *J* = 15.8 Hz, 1H), 6.66 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.54-6.51 (m, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 6.26 (d, *J* = 7.8 Hz, 1H), 6.34 (d, *J* = 7.8 Hz, 1H), 6.14 (dt, *J* = 15.7, 5.8 Hz, 1H), 4.39 (br s, 2H), 3.51-3.45 (m, 1H), 3.20-3.15 (m, 1H), 3.02-2.81 (m, 6H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 141.3 (C), 139.6 (C), 139.0 (C), 137.6 (C), 137.3 (CH), 137.0 (C), 134.1 (CH), 133.9 (CH), 131.0 (CH), 129.6 (CH), 129.5 (CH), 129.1 (CH), 128.7 (CH), 126.9 (C), 64.2 (CH_2), 35.5 (CH_2), 34.1 (CH_2), 33.4 (CH_2), 33.2 (CH_2) ppm. **IR** (neat): 2925, 2851, 1591, 1499, 1482, 1454, 1435, 1412, 1358, 1265, 1100, 1054, 966, 900, 872 cm^{-1}. **HRMS** (APCI): *m/z* $[M–H]^-$ calcd for $C_{19}H_{18}OBr$: 341.0547; found: 341.0541.

- (2*E)*-3-[14-(Benzylamino)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl]prop-2-en-1-ol (**3c**)

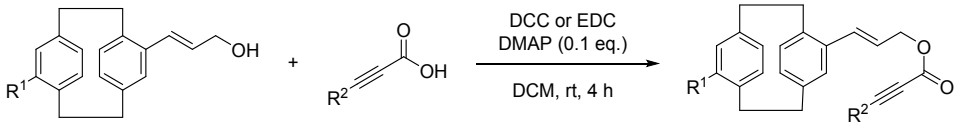


Substrate **3c** was synthesized following the general procedure D (pag. 12): **2c** (300 mg, 0.729 mmol, 1 eq.), DIBAL-H (1 M in THF, 2.9 mL, 2.916 mmol, 4 eq.), and Et_2O (20 mL). The title compound was isolated (eluent: EtOAc/Cy 1:15 to 8:2) as an amorphous white solid (236 g, 0.366 mmol, 88 %). **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.47 – 7.46 (m, 2H), 7.42 – 7.39 (m, 2H), 7.35 – 7.32 (m, 1H), 6.93 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.72 (d, *J* = 15.7 Hz, 1H), 6.45 (br d, *J* = 1.4 Hz, 1H), 6.31 (d, *J* = 7.7 Hz, 1H), 6.22 – 6.18 (m, 2H), 6.09 (dt, *J* = 15.7 , 5.9 Hz, 1H), 5.46 (br s, 1H), 4.38 (d, *J* = 5.9 Hz, 2H), 4.24 (d, *J* = 13.1 Hz, 1H), 4.09 (d, *J* = 13.1 Hz, 1H), 3.83 (br s, 1H), 3.48 – 343 (m, 1H), 3.16 – 2.96 (m, 4H), 2.91 – 2.85 (m, 1H), 2.80 – 2.68 (m, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 146.6 (C), 140.8 (C), 139.6 (C), 139.0 (C), 137.5 (C), 136.7 (C), 133.8 (CH), 132.8 (CH), 131.3 (CH), 130.3 (CH), 128.9 (3CH), 128.2 (2CH), 127.7 (CH), 127.6

(CH), 124.2 (C), 120.6 (CH), 116.4 (CH), 64.4 (CH_2), 48.5 (CH_2), 34.5 (CH_2), 33.2 (CH_2), 32.7 (CH_2), 32.2 (CH_2) ppm. **IR** (neat): 3416, 3028, 2926, 2851, 2218, 1704, 1594, 1570, 1508, 1424, 1281, 1185, 1170, 965, 910, 869, 729, 698 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{26}H_{28}ON$: 370.2165; found: 370.2151.

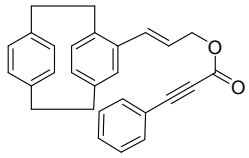
Synthesis of [2.2]paracyclophanes-based styrenes 4a-h

General procedure E: Acylation reactions



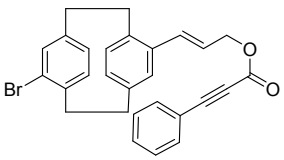
The selected [2.2]paracyclophanes-based cinnamic alcohol (1 eq.), DMAP (0.01 eq.) and the desired propiolic acid (1.05 eq.) were dissolved in dry DCM (4 mL) under an argon atmosphere. DCC or EDC hydrochloride (1.5 eq.) were added turning the reaction yellow and cloudy. The mixture was stirred at rt for 4 h, followed by filtration through a short plug of silica gel with DCM washings. The filtrate was concentrated under reduced pressure and the crude residue was purified by silica gel column chromatography to afford the pure product.

- 3-([2.2]Paracyclophen-4-yl)allyl 3-phenylpropiolate (**4a**)



Substrate **4a** was synthesized following the general procedure E (pag. 14): **3a** (150 mg, 0.567 mmol, 1 eq.), DMAP (6.93 mg, 0.0567 mmol, 0.01 eq.), phenylpropiolic acid (87 mg, 0.596 mmol, 1.05 eq.), DCC (1 M in DCM, 0.851 mL, 0.851 mmol, 1.5 eq.), and DCM (4 mL). The title compound was isolated (eluent: DCM/Cy 1:1) as an amorphous white solid (170 mg, 0.433 mmol, 76%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.60 – 7.49 (m, 2H), 7.43 – 7.35 (m, 1H), 7.35 – 7.24 (m, 2H), 6.80 – 6.65 (m, 1H), 6.59 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.54 – 6.38 (m, 4H), 6.39 – 6.27 (m, 2H), 6.04 (dt, *J* = 15.6, 6.7 Hz, 1H), 4.88 (qdd, *J* = 12.5, 6.7, 1.3 Hz, 2H), 3.40 (ddd, *J* = 13.7, 10.0, 1.9 Hz, 1H), 3.17 – 2.93 (m, 4H), 2.93 – 2.80 (m, 2H), 2.75 (ddd, *J* = 13.7, 10.3, 6.7 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.9 (C), 139.9 (C), 139.3 (C), 139.2 (C), 138.4 (C), 136.1 (C), 134.9 (CH), 133.8 (CH), 133.0 (4CH), 132.4 (CH), 131.8 (CH), 130.7 (CH), 130.6 (CH), 129.7 (CH), 128.6 (2 CH), 122.6 (CH), 119.6 (C), 86.6 (C), 80.5 (C), 67.0 (CH_2), 35.4 (CH_2), 35.2 (CH_2), 34.7 (CH_2), 33.7 (CH_2) ppm. **IR** (neat): 2933, 2856, 2358, 2218, 2116, 1704, 1650, 1489, 1444, 1276, 1178, 1165, 953, 913 cm^{-1}. **HRMS** (APCI): *m/z* $[M-H]^-$ calcd for $C_{28}H_{23}O_2$: 391.1704; found: 391.1695.

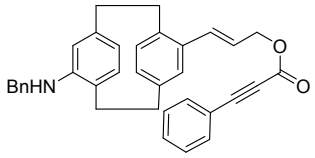
- (2*E*)-3-{14-Bromotricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl}prop-2-en-1-yl 3-phenylprop-2-ynoate (**4b**)



Substrate **4b** was synthesized following the general procedure E (pag. 14): **3b** (100 mg, 0.291 mmol, 1 eq.), DMAP (3.56 mg, 0.026 mmol, 0.01 eq.), phenylpropiolic acid (45 mg, 0.306 mmol, 1.05 eq.), DCC (1 M in DCM, 0.437 mL, 0.437 mmol, 1.5 eq.), and DCM (4 mL). The title compound was isolated (eluent: AcOEt/Cy 1:14 to 8:2) as an amorphous white solid (106 mg, 0.224 mmol, 77%). **^{1}H**

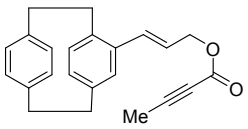
NMR (500 MHz, $CDCl_3$): *δ* 7.62-7.60 (m, 2H), 7.48-7.44 (m, 1H), 7.40-7.37 (m, 2H), 7.12 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.81 (d, *J* = 15.7 Hz, 1H), 6.66 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.54-6.53 (m, 2H), 6.42 (d, *J* = 7.8 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 6.12 (dt, *J* = 15.7, 6.7 Hz, 1H), 5.00-4.91 (m, 2H), 3.51-3.46 (m, 2H), 3.21-3.15 (m, 1H), 3.04-2.91 (m, 3H), 2.88-2.82 (m, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 154.1 (C), 141.3 (C), 139.6 (C), 139.0 (C), 138.0 (C), 137.3 (CH), 136.3 (C), 134.2 (CH), 133.9 (CH), 133.8 (CH), 133.2 (2CH), 131.0 (CH), 130.9 (CH), 129.2 (2CH), 128.7 (2CH), 127.0 (C), 123.0 (CH), 119.7 (C), 86.9 (C), 80.7 (C), 67.1 (CH_2), 35.5 (CH_2), 34.1 (CH_2), 33.4 (CH_2), 33.3 (CH_2) ppm. **IR** (neat): 2933, 2856, 2358, 2218, 2116, 1704, 1650, 1489, 1444, 1276, 1178, 1165, 953, 913 cm^{-1}. **HRMS** (APCI): *m/z* $[M-H]^-$ calcd for $C_{28}H_{22}O_2Br$: 471.0954; found: 471.0966.

- (2*E*)-3-[14-(Benzylamino)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl]prop-2-en-1-yl 3-phenylprop-2-ynoate (**4c**)



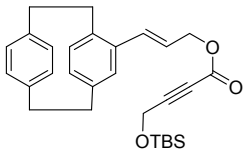
Substrate **4c** was synthesized following the general procedure E (pag. 14): **3c** (150 mg, 0.406 mmol, 1 eq.), DMAP (4.96 mg, 0.0406 mmol, 0.1 eq.), phenylpropiolic acid (62 mg, 0.426 mmol, 1.05 eq.), DCC (1 M in DCM, 0.447 mL, 0.447 mmol, 1.1 eq.), and DCM (10 mL). The title compound was isolated (eluent DCM/Cy 1:2) as an amorphous yellow solid (75 mg, 0.15 mmol, 37 %). **^{1}H NMR** (500 MHz, $CDCl_3$) : *δ* 7.62 – 7.61 (m, 2H), 7.47 – 7.32 (m, 8H), 6.97 (dd, *J* = 7.7 Hz, *J* = 1.7 Hz, 1H), 6.83 (d, *J* = 15.6 Hz, 1H), 6.47 (d br, *J* = 1.2 Hz, 1H), 6.32 (d, *J* = 7.8 Hz, 1H), 6.32 – 6.19 (m, 2H), 6.07 (dt, *J* = 15.6 Hz, *J* = 6.8 Hz, 1H), 5.45 (s br, 1H), 4.95 (qd, *J* = 6.8 Hz, *J* = 1 Hz, 2H), 4.23 – 4.21 (m, 1H), 4.09 (d br, *J* = 12 Hz, 1H), 3.83 (s br, 1H), 3.49 – 3.44 (m, 1H), 3.16 – 2.98 (m, 4H), 2.92 – 2.86 (m, 1H), 2.81 – 2.68 (m, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 154.1 (C), 146.5 (C), 140.7 (C), 139.6 (C), 139.1 (C), 137.9 (C), 136.0 (C), 134.6 (CH), 133.7 (CH), 133.1 (2CH), 132.8 (CH), 131.3 (CH), 130.8 (CH), 128.9 (2CH), 128.7 (2CH), 128.2 (2CH), 128.1 (CH), 127.6 (CH), 124.2 (C), 122.3 (CH), 120.6 (CH), 119.7 (C), 116.3 (CH), 86.6 (C), 80.7 (C), 67.2 (CH2), 48.4 (CH2), 34.4 (CH_2), 33.2 (CH_2), 32.6 (CH_2), 32.1 (CH_2) ppm. **IR** (neat): 3423, 3029, 2927, 2852, 2218, 2116, 1705, 1594, 1570, 1509, 1490, 1452, 1443, 1425, 1280, 1184, 1168, 963, 757, 698, 689 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{35}H_{32}O_2N$: 498.2428; found: 498.2412.

- 3-([2.2]Paracyclophen-5-yl)prop-2-en-1-yl but-2-ynoate (**4d**)



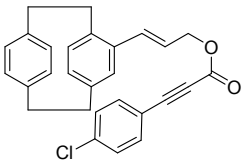
Substrate **4d** was synthesized following the general procedure E (pag. 14): **3a** (100 mg, 0.378 mmol, 1 eq.), DMAP (4.62 mg, 0.0378 mmol, 0.01 eq.), 2-butynoic acid (33.4 mg, 0.397 mmol, 1.05 eq.), DCC (1 M in DCM, 0.567 mL, 0.567 mmol, 1.5 eq.), and DCM (5 mL). The title compound was isolated (eluent: DCM/Cy 4:6) as an amorphous white solid (104 mg, 0.315 mmol, 83 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.75 (d, *J* = 15.6 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.53 – 6.48 (m, 4H), 6.43 (d, *J* = 7.7 Hz, 1H), 6.39 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.07 (dt, *J* = 15.7, 6.7 Hz, 1H), 4.87 (qdd, *J* = 12.6, 6.6, 1.3 Hz, 2H), 3.46 (ddd, *J* = 13.7, 9.9, 1.9 Hz, 1H), 3.22 – 3.06 (m, 3H), 3.07 – 2.89 (m, 3H), 2.82 (ddd, *J* = 13.7, 10.4, 6.7 Hz, 1H) 2.02 (s, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.6 (C), 139.9 (C), 139.3 (C), 139.2 (C), 138.4 (C), 136.1 (C), 134.9 (CH), 133.7 (CH), 133.0 (2CH), 132.4 (CH), 131.8 (CH), 130.6 (CH), 129.6 (CH), 122.7 (CH), 85.9 (C), 72.4 (C), 66.7 (CH_2), 35.4 (CH_2), 35.2 (CH_2), 34.7 (CH_2), 33.7 (CH_2), 3.8 (CH_3) ppm. **IR** (neat): 3662, 2927, 2239, 2117, 1707, 1393, 1249, 1065, 967, 899, 799, 752, 719 cm^{-1}. **HRMS** (APCI): *m/z* $[M-H]^-$ calcd for $C_{23}H_{21}O_2$: 329.1547; found: 329.1542.

- 3-([2.2]Paracyclophen-5-yl)-prop-2-en-1-yl 4-[(tert-butyldimethylsilyl)oxy]but-2-ynoate (**4e**)



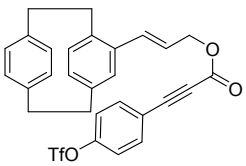
Substrate **4e** was synthesized following the general procedure E (pag. 14): **3a** (0.348 g, 1.32 mmol, 1 eq.), DMAP (0.0161 g, 0.132 mmol, 0.01 eq.), propiolic acid **S2** (0.311 g, 1.45 mmol, 1.1 eq.), EDC hydrochloride (0.442 g, 2.3 mmol, 1.75 eq.), and DCM (25 mL). The title compound was isolated (eluent: 5 to 20% EtOAc in pentane) as a colourless oil (151 mg, 0.328 mmol, 25 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.75 (dd, *J* = 15.6, 1.4 Hz, 1H), 6.64 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.56 – 6.47 (m, 4H), 6.44 (d, *J* = 7.7 Hz, 1H), 6.39 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.06 (dt, *J* = 15.7, 6.7 Hz, 1H), 4.99 – 4.80 (m, 2H), 4.46 (s, 2H), 3.46 (ddd, *J* = 13.7, 9.9, 1.9 Hz, 1H), 3.20 – 3.06 (m, 3H), 3.06 – 2.89 (m, 3H), 2.82 (ddd, *J* = 13.7, 10.3, 6.7 Hz, 1H), 0.92 (s, 9H), 0.15 (s, 6H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.2 (C), 140.0 (C), 139.3 (C), 139.2 (C), 138.4 (C), 136.1 (C), 134.9 (CH), 133.7 (CH), 133.0 (2 CH), 132.4 (CH), 131.7 (CH), 130.6 (CH), 129.6 (CH), 122.5 (CH), 86.3 (C), 76.5 (C), 66.9 (CH_2), 51.4 (CH_2), 35.4 (CH_2), 35.2 (CH_2), 34.7 (CH_2), 33.7 (CH_2), 25.7 ($3CH_3$), 18.2 (C), -5.2 ($2CH_3$) ppm. **IR** (neat): 2226, 1709, 1595, 1498, 1426, 1285, 1249, 1213, 1184, 1140, 1016, 964, 883, 844, 798, 748, 720, 700, 644, 608 cm^{-1}. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{29}H_{36}O_3NaSi$: 483.2326; found: 483.2327.

- 3-([2.2]Paracyclophen-5-yl)prop-2-en-1-yl 3-(4-chlorophenyl)prop-2-ynoate (**4f**)



Substrate **4f** was synthesized following the general procedure E (pag. 14): **3a** (100 mg, 0.378 mmol, 1 eq.), DMAP (4.62 mg, 0.0378 mmol, 0.01 eq.), 3-(4-chlorophenyl)prop-2-ynoic acid (72 mg, 0.397 mmol, 1.05 eq.), DCC (1 M in DCM, 0.567 mL, 0.567 mmol, 1.5 eq.), and DCM (5 mL). The title compound was isolated (eluent: DCM/Cy 3:7) as an amorphous white solid (67 mg, 0.157 mmol, 41 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 – 7.49 (m, 2H), 7.42 – 7.32 (m, 2H), 6.86 – 6.74 (m, 1H), 6.66 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.54 – 6.49 (m, 4H), 6.44 (d, *J* = 7.8 Hz, 1H), 6.41 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.11 (dt, *J* = 15.7, 6.7 Hz, 1H), 4.95 (qdd, *J* = 12.5, 6.7, 1.3 Hz, 2H), 3.47 (ddd, *J* = 13.7, 9.9, 1.9 Hz, 1H), 3.21 – 3.07 (m, 3H), 3.08 – 2.89 (m, 3H), 2.83 (ddd, *J* = 13.6, 10.4, 6.8 Hz, 1H) ppm.**^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.75 (C), 140.0 (C), 139.3 (C), 139.2 (C), 138.4 (C), 137.1 (C), 136.1 (C), 134.9 (CH), 134.2 (2CH), 134.0 (CH), 133.1 (CH), 133.0 (CH), 132.5 (CH), 131.8 (CH), 130.7 (CH), 129.7 (CH), 129.1 (2CH), 122.5 (CH), 118.1 (C), 85.3 (C), 81.3 (C), 67.2 (CH_2), 35.4 (CH_2), 35.2 (CH_2), 34.7 (CH_2), 33.7 (CH_2) ppm. **IR** (neat): 2927, 2221, 1707, 1489, 1284, 1183, 1169, 1089, 830 cm^{-1}. **HRMS** (APCI): *m/z* $[M+H]^+$ calcd for $C_{28}H_{24}O_2Cl$: 427.1465; found: 427.1450.

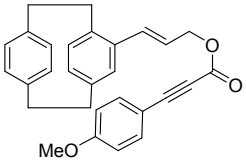
- 3-([2.2]Paracyclophen-5-yl)-prop-2-en-1-yl 3-{4-[(trifluoromethyl)-sulfonyloxy]phenyl} prop-2-ynoate (**4g**)



Substrate **4g** was synthesized following the general procedure E (pag. 14): **3a** (0.659 g, 2.49 mmol, 1 eq.), DMAP (0.031 g, 0.249 mmol, 0.01 eq.), propiolic acid **S8** (72 mg, 0.397 mmol, 1.05 eq.), EDC hydrochloride (0.836 g, 4.36 mmol, 1.75 eq.), and DCM (50 mL). The title compound was isolated (eluent: 5 to 20% EtOAc in pentane) as an amorphous white solid (0.47 g, 0.869 mmol, 35 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.75 – 7.67 (m, 2H), 7.36 – 7.30 (m, 2H), 6.86 – 6.76 (m, 1H), 6.66 (dd, *J* = 7.8, 1.8 Hz,

1H), 6.54 – 6.50 (m, 4H), 6.45 (d, *J* = 7.8 Hz, 1H), 6.41 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.11 (dt, *J* = 15.6, 6.7 Hz, 1H), 4.97 (qdd, *J* = 12.4, 6.7, 1.3 Hz, 2H), 3.48 (ddd, *J* = 13.6, 9.9, 1.9 Hz, 1H), 3.21 – 3.07 (m, 3H), 3.07 – 2.90 (m, 3H), 2.84 (ddd, *J* = 13.6, 10.3, 6.7 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.5 (C), 150.5 (C), 140.0 (C), 139.4 (C), 139.2 (C), 138.4 (C), 136.0 (C), 135.0 (2CH), 134.9 (CH), 134.2 (CH), 133.1 (CH), 133.0 (CH), 132.5 (CH), 131.8 (CH), 130.6 (CH), 129.6 (CH), 122.3 (CH), 121.9 (2CH), 120.3 (C), 118.7 (q, *J* = 319 Hz, CF_3) 83.8 (C), 81.9 (C), 67.3 (CH_2), 35.4 (CH_2), 35.2 (CH_2), 34.7 (CH_2), 33.7 (CH_2) ppm. **IR** (neat): 2952, 2222, 1713, 1591, 1427, 1364, 1248, 1183, 1141, 1104, 1047, 966, 883, 837, 780 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{29}H_{24}O_5F_3S$: 541.1291; found: 541.1292.

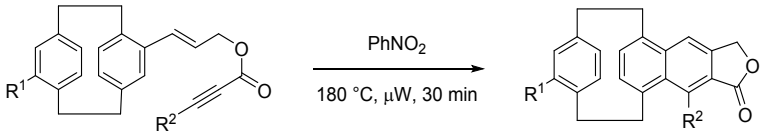
- 3-([2.2]Paracyclophen-5-yl)prop-2-en-1-yl 3-(4-methoxyphenyl)prop-2-ynoate (**4h**)



Substrate **4h** was synthesized following the general procedure E (pag. 14): **3a** (216 mg, 0.817 mmol 1 eq.), DMAP (19 mg, 0.156 mmol, 0.02 eq.), propiolic acid **S9** (150 mg, 0.851 mmol, 1.05 eq.), DCC (1 M in DCM 0.9 mL, 0.9 mmol, 1.1 eq.), and DCM (20 mL). The title compound was isolated (eluent: DCM/Cy 1:1 to 2:1) as an amorphous white solid (208 mg, 0.492 mmol, 60 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 6.92 – 6.87 (m, 2H), 6.79 (d, *J* = 15.8 Hz, 1H), 6.68 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.59 – 6.48 (m, 4H), 6.47 – 6.38 (m, 2H), 6.14 – 6.09 (m, 1H), 4.95 (qdd, *J* = 12.6, 6.8, 1.2 Hz, 2H), 3.84 (s, 3H), 3.48 (ddd, *J* = 13.4, 9.9, 1.7 Hz, 1H), 3.21 – 3.01 (m, 4H), 3.00 – 2.91 (m, 2H), 2.83 (ddd, *J* = 13.7, 10.4, 6.8 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.6 (C), 154.2 (C), 139.9 (C), 139.3 (C), 139.2 (C), 138.3 (C), 136.1 (C), 135.0 (2CH), 134.8 (CH), 133.7 (CH), 133.0 (2 CH), 132.2 (CH), 131.8 (CH), 130.6 (CH), 129.7 (CH), 122.8 (CH), 114.3 (2CH), 111.3 (C), 87.5 (C), 80.0 (C), 66.9 (CH_2), 55.3 (CH_3), 35.4 (CH_2), 35.15 (CH_2), 34.7 (CH_2), 33.9 (CH_2) ppm. **IR** (neat): 2928, 2853, 2211, 1702, 1603, 1509, 1283, 1253, 1188, 1160, 1029, 963, 834 cm^{-1}. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{29}H_{26}NaO_3$: 445.1774; found: 445.1761.

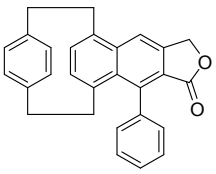
Synthesis of [2.2]paracyclophanes-based naphthalenes 5a-h

General procedure F: Intramolecular dehydrogenative Diels–Alder reaction



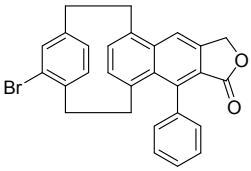
To a microwave irradiation vial was added the selected [2.2]paracyclophanes-based styrenes (1 eq.) and nitrobenzene. The solution was irradiated at 180 °C for 30 min turning the reaction brown or black. The mixture was concentrated under high vacuum and the crude residue purified by silica gel column chromatography to afford the pure product.

- 1^{9}-Phenyl-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^{1}-one (**5a**)



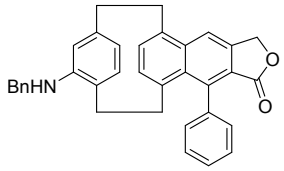
Substrate **5a** was synthesized following the general procedure F (pag. 17): **4a** (74 mg, 0.189 mmol, 1 eq.), and nitrobenzene (6 mL). The title compound was isolated (eluent: EtOAc/pentane 1:9) as an amorphous white solid (41 mg, 0.105 mmol, 56 %). **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.79 (s, 1H), 7.64 – 7.57 (m, 1H), 7.51 (t, *J* = 7.5, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.1 Hz, 1H), 6.77 (d, *J* = 7.2 Hz, 1H), 6.53 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.45 (dd, *J* = 8.0, 1.9 Hz, 1H), 5.76 (dd, *J* = 7.7, 1.9 Hz, 1H), 5.68 – 5.51 (m, 2H), 5.32 (dd, *J* = 14.5, 1.2 Hz, 1H), 3.87 – 3.76 (m, 1H), 3.30 – 3.10 (m, 2H), 3.05 – 3.00 (m, 1H), 2.83 – 2.72 (m, 1H), 2.58 – 2.51 (m, 1H), 2.37 – 2.31 (m, 1H), 2.23 – 2.18 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.8 (C), 141.3 (C), 140.2 (C), 140.0 (2C), 138.8 (C), 137.7 (C), 137.0 (C), 136.9 (C), 135.1 (C), 134.8 (CH), 133.5 (CH), 132.0 (CH), 131.6 (CH), 130.1 (C), 129.8 (C), 129.4 (CH), 128.8 (CH), 128.3 (CH), 128.1 (C), 127.3 (C), 119.2 (C), 117.1 (CH), 67.8 (CH_2), 37.0 (CH_2), 35.1 (CH_2), 34.3 (CH_2), 33.1 (CH_2) ppm. **IR** (neat): 2937, 1760, 1616, 1493, 1444, 1402, 1354, 1333, 1207, 1124, 1078, 1068, 1030, 909, 870, 838 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{28}H_{23}O_2$: 425.1303; found: 425.1291.

- 4^3-Bromo-1^9-phenyl-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**5b**)



Substrate **5b** was synthesized following the general procedure F (pag. 17): **4b** (158 mg, 0.335 mmol, 1 eq.), and nitrobenzene (10 mL). The title compound was isolated (eluent: EtOAc/pentane 2:8) as an amorphous yellow solid (54 mg, 0.115 mmol, 34%). Semi-preparative HPLC purification (column: Uptisphere Strategy Si 100Å 5μm, flow: 30 mL/min, eluent: EtOAc/heptane 25:75, λ = 260 nm and 310 nm, T = 25 °C) was performed prior to spectroscopic characterization. **^{1}H NMR** (500 MHz, $CDCl_3$); *δ* 7.83 – 7.82 (m br, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.85 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 1.4 Hz, 1H), 5.72 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.57 – 5.53 (m, 2H), 5.32 (d, *J* = 14.5 Hz, 1H), 3.87 – 3.82 (m, 1H), 3.19 – 3.11 (m, 2H), 2.98 – 2.85 (m, 3H), 2.22 – 2.16 (m, 1H), 2.04 – 1.99 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 169.7 (C), 141.4 (C), 139.9 (2C), 139.2 (C), 138.3 (C), 136.6 (C), 137.7 (C), 136.4 (C), 135.9 (CH), 135.4 (C), 133.4 (CH), 131.4 (CH), 130.2 (CH), 130.0 (CH), 129.5 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 127.4 (CH), 125.7 (C), 119.4 (C), 117.4 (CH), 67.8 (CH_2), 35.6 (CH_2), 33.9 (CH_2), 33.4 (CH_2), 32.9 (CH_2) ppm. **IR** (neat): 2931, 1757, 1617, 1444, 1353, 1334, 1207, 1124, 1079, 1069, 1033, 908, 729 cm^{-1}. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $C_{28}H_{21}BrO_2Na$: 491.0617; found: 491.0628.

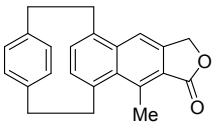
- 1^9-Phenyl-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**5c**)



Substrate **5c** was synthesized following the general procedure F (pag. 17): **4c** (54 mg, 0.108 mmol, 1 eq.), and nitrobenzene (3 mL). The title compound was isolated (eluent: EtOAc/pentane 2:8) as an amorphous yellow solid (27 mg, 0.1054 mmol, 50 %). Semi-preparative HPLC purification (column: Uptisphere Strategy Si 100Å 5μm, flow: 30 mL/min, eluent: EtOAc/heptane 2:8, λ = 260 nm and 310 nm, T = 25 °C) was performed prior to spectroscopic characterization. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 – 7.38 (m, 2H), 7.59 – 7.53 (m, 1H), 7.47 (tt, *J* = 8.8, 1.9 Hz, 1H), 7.41 (d, *J* = 6.9 Hz, 2H), 7.36 – 7.33 (m, 3H), 7.31 – 7.29 (m, 1H), 7.15 (d, *J* = 7.1 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.63 (d, *J* = 7.1 Hz, 1H), 5.60 (d, *J* = 0.9 Hz, 1H), 5.53 (dd, *J* = 14.3, 0.9 Hz,

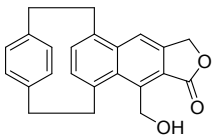
1H), 5.36 (d, *J* = 7.6 Hz, 1H), 5.30 (dd, *J* = 14.5, 1.1 Hz, 1H), 5.23 (dd, *J* = 7.4, 1.6 Hz, 1H), 4.24 (d, *J* = 13.2 Hz, 1H), 4.09 (d, *J* = 13.2 Hz, 1H), 3.86 – 3.76 (m, 1H), 3.14 – 3.03 (m, 2H), 2.96 – 2.89 (m, 1H), 2.84 (dt, *J* = 13.7, 9.0 Hz, 1H), 2.61 (dd, *J* = 14.1, 8.9 Hz, 1H),2.34 (s, br, 1H), 2.15 – 2.08 (m, 1H), 2.00 (dd, *J* = 13.6, 9.3 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6) δ 169.5 (C), 148.9 (C), 146.5 (C), 140.6 (C), 140.0 (C), 139.54 (C), 139.20 (C), 138.71 (C), 138.27 (C), 137.20 (C), 136.63 (C), 134.57 (C), 132.7 (CH), 130.6 (CH), 130.0 (CH), 129.8 (CH), 128.8 (CH), 128.5 (CH), 128.1 (2CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 127.0 (CH), 126.5 (CH), 122.2 (C), 119.6 (CH), 118.3 (CH), 114.1 (CH), 67.8 (CH_2), 46.4 (CH_2), 33.5 (CH_2), 33.1 (CH_2), 32.2 (CH_2), 31.9 (CH_2) ppm. **IR** (neat): 2987, 1760, 1616, 1594, 1572, 1515, 1443, 1359, 1332, 1275, 1067, 1028, 913, 748 cm^{-1}. **HRMS** (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{35}H_{30}O_2N$: 496.2271; found: 496.2264.

- 1^9-Methyl-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**5d**)



Substrate **5d** was synthesized following the general procedure F (pag. 17): **4d** (40 mg, 0.121 mmol, 1 eq.), and nitrobenzene (5 mL). The title compound was isolated (eluent: EtOAc/pentane 1:9) as an amorphous white solid (21 mg, 0.0639 mmol, 53 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.53 (s, 1H), 6.81 (d, *J* = 7.1 Hz, 1H), 6.74 (d, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 1.2 Hz, 2H), 5.61 (dt, *J* = 8.0, 1.2 Hz, 1H), 5.43 (dd, *J* = 14.5, 1.1 Hz, 1H), 5.42 – 5.34 (m, 1H), 5.23 (dd, *J* = 14.5, 1.2 Hz, 1H), 4.03 – 3.88 (m, 1H), 3.72 – 3.67 (m, 1H), 3.21 – 2.99 (m, 7H), 2.93 – 2.87 (m, 1H), 2.76 – 2.58 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.9 (C), 140.1 (C), 139.5 (C), 138.6 (C), 138.5 (C), 138.4 (C), 137.9 (C), 137.6 (C), 135.7 (C), 134.7 (CH), 133.0 (CH), 131.9 (CH), 131.5 (CH), 129.4 (CH), 128.9 (CH), 120.2 (C), 115.4 (CH), 68.2 (CH_2), 38.6 (CH_2), 35.2 (CH_2), 34.2 (CH_2), 33.3 (CH_2), 16.7 (CH_3) ppm. **IR** (neat): 2971, 1748, 1622, 1529, 1453, 1404, 1378, 1352, 1232, 1189, 1156, 1040, 910, 878, 801, 732 cm^{-1}. **HRMS** (APCI): *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{21}O_2$: 329.1536; found: 329.1529.

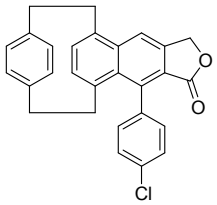
- 1^9-(Hydroxymethyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**5e**)



Substrate **5e** was synthesized *via* the Diels-Alder reaction, and a subsequent deprotection of the hydroxyl group. To a Biotage® microwave irradiation vial was added compound **4e** (151 mg, 0.328 mmol, 1 eq.) and nitrobenzene (6.5 mL). The solution was irradiated at 180 °C for 30 min turning the reaction golden. The mixture was then concentrated under high vacuum. The crude material (149 mg, 0.325 mmol, 1 eq.) was dissolved in THF (10 mL) and TBAF (127 mg, 0.487 mmol, 1.5 eq.) was added. The resulting solution was stirred at rt for 2 h under an argon atmosphere. The reaction was then quenched with a saturated NH_4Cl solution (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: EtOAc/pentane 4:6) to afford compound **5e** (21 mg, 0.061 mmol, 19 % yield) as an amorphous yellow solid.**^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (s, 1H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.51 (s, 2H), 5.87 (d, *J* = 15.4 Hz, 1H), 5.72 – 5.64 (m, 2H), 5.55 (d, *J* = 8.0 Hz, 1H), 5.08 (s, 2H), 3.93 – 3.79 (m, 1H), 3.52 – 3.37 (m, 1H), 3.30 – 3.14 (m, 3H), 3.03 – 2.97 (m, 2H), 2.83 – 2.78 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.1 (C), 146.5 (C), 138.9 (C), 138.7 (C), 138.6 (C), 137.6 (C), 135.9 (C), 135.6 (C), 134.2 (2CH), 133.0 (C), 132.5 (CH), 132.1 (CH), 129.4 (CH), 129.0 (CH), 125.2 (CH), 120.7 (C), 71.6 (CH_2), 63.2 (CH_2), 35.1

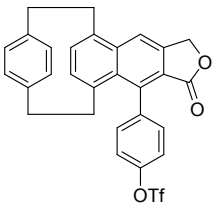
(CH_2), 34.9 (CH_2), 34.5 (CH_2), 33.6 (CH_2) ppm. **IR** (neat): 3364, 2926, 1745, 1728, 1500, 1452, 1349, 1264, 1206, 1083, 1044, 1016, 879, 813, 735, 720 cm-1. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{21}O_3$: 345.1485; found: 345.1489.

- 1^9-(4-Chlorophenyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**5f**)



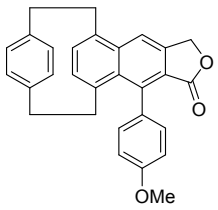
Substrate **5f** was synthesized following the general procedure F (pag. 17): **4f** (36 mg, 0.0843 mmol, 1 eq.), and nitrobenzene (3 mL). The title compound was isolated (eluent: EtOAc/pentane 1:9) as an amorphous yellow solid (28 mg, 0.0659 mmol, 78 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.82 – 7.80 (m, 2H), 7.57 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.37 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.95 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.86 (d, *J* = 7.1 Hz, 1H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.54 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.45 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.74 (dd, *J* = 7.8, 1.9 Hz, 1H), 5.57 (dd, *J* = 14.5, 1.1 Hz, 1H), 5.52 (dd, *J* = 7.7, 1.9 Hz, 1H), 5.33 (dd, *J* = 14.5, 1.1 Hz, 1H), 3.89 – 3.75 (m, 1H), 3.27 – 3.14 (m, 2H), 3.05 – 2.99 (m, 1H), 2.81 – 2.77 (m, 1H), 2.69 – 2.54 (m, 1H), 2.38 – 2.23 (m, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.8 (C), 140.3 (C), 140.1 (C), 139.8 (C), 139.5 (C), 138.6 (C), 137.7 (C), 137.2 (C), 135.2 (C), 135.0 (CH), 134.9 (C), 134.4 (C), 133.6 (C), 132.0 (CH), 131.6 (2CH), 131.1 (CH), 129.4 (CH), 128.7 (CH), 128.4 (CH), 127.7 (CH), 119.3 (CH), 117.4 (CH), 67.9 (CH_2), 37.2 (CH_2), 35.1 (CH_2), 34.3 (CH_2), 33.1 (CH_2) ppm. **IR** (neat): 2971, 1759, 1616, 1490, 1456, 1408, 1354, 1334, 1206, 1087, 1073, 1032, 1016, 909, 873, 831, 800, 731 cm^{-1}. **HRMS** (APCI): *m/z* $[M+H]^+$ calcd for $C_{28}H_{22}O_2Cl$: 425.1303; found: 425.1291.

- 4-(1^3-Oxo-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphane-1^4-yl)phenyl trifluoromethanesulfonate (**5g**)



Substrate **5g** was synthesized following the general procedure F (pag. 17): **4g** (156 mg, 0.289 mmol, 1 eq.), and nitrobenzene (6.5 mL). The title compound was isolated (eluent: EtOAc/pentane 2:8) as an amorphous yellow solid (118 mg, 0.219 mmol, 76 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.84 (s, 1H), 7.51 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 7.2 Hz, 1H), 6.55 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.46 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.74 (dd, *J* = 7.7, 1.8 Hz, 1H), 5.58 (dd, *J* = 14.6, 0.9 Hz, 1H), 5.53 (dd, *J* = 7.7, 1.8 Hz, 1H), 5.34 (dd, *J* = 14.6, 0.9 Hz, 1H), 3.91 – 3.75 (m, 1H), 3.30 – 3.12 (m, 2H), 3.05 – 3.00 (m, 1H), 2.86 – 2.76 (m, 1H), 2.66 – 2.58 (m, 1H), 2.35 – 2.24 (m, 1H), 2.15 – 2.10 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.7 (C), 149.5 (C), 140.2 (C), 140.1 (C), 139.2 (C), 138.7 (C), 138.5 (C), 137.8 (C), 137.3 (2 C), 135.3 (CH), 134.9 (C), 133.8 (CH), 132.1 (CH), 132.0 (CH), 131.7 (2CH), 129.5 (CH), 128.8 (CH), 121.0 (CH), 120.3 (CH), 119.4 (C), 118.9 (q, *J* = 341 Hz, CF_3), 117.8 (CH), 70.0 (CH_2), 37.0 (CH_2), 35.1 (CH_2), 34.3 (CH_2), 33.1 (CH_2) ppm. **IR** (neat): 2933, 1760, 1617, 1499, 1421, 134, 1248, 1211, 1132, 1074, 1018, 970, 887, 803, 731, 606 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{29}H_{22}O_5F_3S$: 539.1135; found: 539.1134.

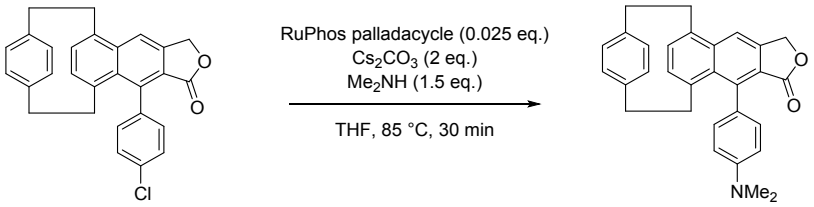
- 1^9-(4-methoxyphenyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**5h**)



Substrate **5h** was synthesized following the general procedure F (pag. 17): **4h** (81 mg, 0.192 mmol, 1 eq.), and nitrobenzene (5 mL). The title compound was isolated (eluent: EtOAc/Cy 2:8) as an amorphous yellow solid (36 mg, 0.086 mmol, 44%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.75 (s, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.93 (br s, 2H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 7.2 Hz, 1H), 6.52 (dd, *J* = 7.9 Hz, *J* = 1.6 Hz, 1H), 6.44 (dd, *J* = 7.9 Hz, *J* = 1.4 Hz, 1H), 5.75 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 1H), 5.55 (d, *J* = 14.5 Hz, 1H), 5. 53 (dd, *J* = 7.7 Hz, *J* = 1.6 Hz, 1H), 5.31 (d, *J* = 14.5 Hz, 1H), 3.92(s, 3H), 3.83 – 3.78 (m, 1H), 3.25 – 3.20 (m, 1H), 3.18 – 3.12 (m, 1H), 3.05 – 2.99 (m, 1H), 2.79 – 275 (m, 1H), 2.58 – 2.54 (m, 1H), 2.33 – 2.26 (m, 2H) ppm.**^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.1 (C), 159.6 (C), 141.2 (C), 140.1 (C), 140.0 (C), 138.8 (C), 137.6 (C), 136.9 (C), 135.4 (C), 134.6 (CH), 133.5 (CH), 132.0 (CH), 131.4 (2CH), 131.0 (C), 129.2 (CH), 128.9 (C), 128.6 (CH), 119.2 (C), 116.8 (2CH), 113.7 (CH), 112.7 (CH), 67.8 (CH_2), 55.2 (CH_3), 37.2 (CH_2), 35.1 (CH_2), 34.2 (CH_2), 33.1 (CH_2) ppm. **IR** (neat): 2934, 2856, 1758, 1611, 1514, 1246, 1072, 1031, 909, 802, 730 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{29}H_{24}NaO_3$: 443.1618; found: 443.1613.

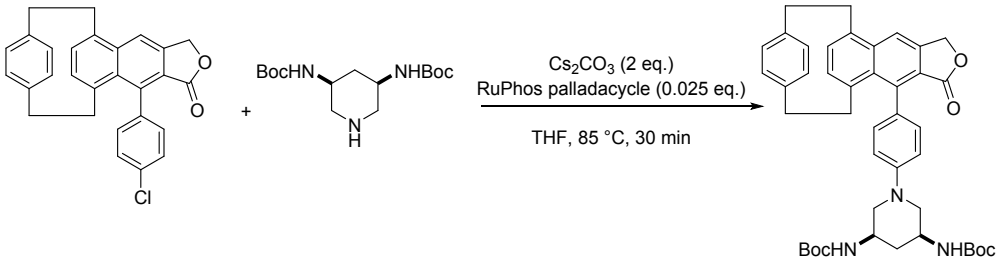
Post-functionalization of the pCp-based fluorophores

*Synthesis of 1^9-(4-(dimethylamino)phenyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**6**)*



A Biotage® microwave vial (2 – 5 mL) was equipped with a stir bar and charged with RuPhos palladacycle (2.5 mg, 0.003 mmol, 0.025 eq.) and Cs_2CO_3 (76.7 mg, 0.235 mmol, 2 eq.). The tube was sealed with a septum, then evacuated and refilled with argon three times through a needle. Compound **5f** in dry THF (3 mL) was added via syringe followed by Me_2NH (2 M in THF, 0.088 mL, 0.177 mmol, 1.5 eq.). The resulting solution was heated at 85 °C in an oil bath and stirred for 30 min. The mixture was then cooled to rt, diluted with 1 M HCl solution (30 mL), and extracted with DCM (2 x 10 mL). The aqueous phase was basified with 3 M aq NaOH and extracted with EtOAc (3 x 15 mL). The combined organic layers (EtOAc) were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: EtOAc/pentane 4:6) to afford the compound **6** (21 mg, 0.048 mmol, 41 % yield) as an amorphous yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.74 – 7.71 (br m, 2H), 6.97 – 6.92 (br m, 2H), 6.83 (d, *J* = 7.3 Hz, 2H), 6.76 (d, *J* = 7.1 Hz, 1H), 6.51 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.44 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.76 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.61 – 5.48 (m, 2H), 5.31 (dd, *J* = 14.4, 0.9 Hz, 1H), 3.88 – 3.76 (m, 1H), 3.27 – 3.18 (m, 1H), 3.20 – 2.95 (m, 8H), 2.85 – 2.70 (m, 1H), 2.67 – 2.54 (m, 1H), 2.45 – 2.36 (m, 1H), 2.35 – 2.26 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.2 (C), 150.3 (C), 142.5 (C), 140.6 (C), 140.5 (C), 140.1 (C), 140.0 (C), 137.6 (C), 136.8 (C), 135.7 (C), 134.3 (CH), 133.4 (CH), 131.9 (2CH), 131.4 (2CH), 129.1 (CH), 128.5 (2CH), 124.3 (C), 119.0 (C), 116.3 (2CH), 67.7 (CH_2), 40.4 ($2CH_3$), 37.4 (CH_2), 35.1 (CH_2), 34.3 (CH_2), 33.1 (CH_2) ppm. **IR** (neat): 2926, 2855, 1760, 1720, 1612, 1524, 1443, 1354, 1195, 1070, 1031, 946, 872, 800 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{30}H_{28}O_2N$: 434.2115; found: 434.2101.

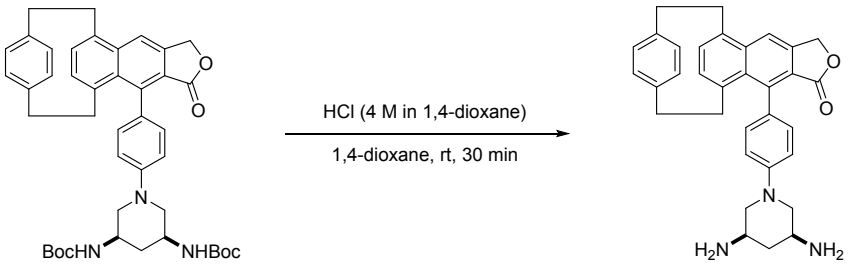
*Synthesis of di-tert-butyl 1-((4-(1^3-oxo-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphane-1^4-yl)phenyl)piperidine-3,5-diyl)dicarbamate (**S12**)*



A Biotage® microwave vial (2 – 5 mL) was equipped with a stir bar and charged with RuPhos palladacycle (1.52 mg, 0.00177 mmol 0.025 eq.), *tert*-butyl *N*-[(5-{[(*tert*-butoxy)carbonyl]amino}piperidin-3-yl]carbamate[10] (33.4 mg, 0.106 mmol, 1.5 eq.) and Cs_2CO_3 (46 mg, 0.141 mmol, 2 eq.). The tube was sealed with a septum, then evacuated and refilled with argon three times through a needle. Compound **5f** (30 mg, 0.0706 mmol, 1 eq.) in dry THF (3 mL) was added via syringe. The resulting solution was heated at 85 °C in an oil bath and stirred for 3 h. The mixture was then cooled to rt, diluted with a saturated NH_4Cl solution (30 mL), and extracted with extracted with EtOAc (3 x 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: EtOAc/pentane 4:6) to afford the title compound (47 mg, 0.067 mmol, 95%) as amorphous yellow solid. **^{1}H NMR** (500 MHz, CD_3OD): δ 7.89 (s, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.78 (t, *J* = 6.0 Hz, 2H), 6.51 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.42 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.78 (dd, *J* = 7.7, 1.6 Hz, 1H), 5.57 (d, *J* = 14.9 Hz, 1H), 5.49 (dd, *J* = 7.5, 1.4 Hz, 1H), 5.31 (d, *J* = 14.9 Hz, 1H), 3.98 (d, *J* = 17.7 Hz, 2H), 3.89 – 3.79 (m, 1H), 3.74 (s, 2H), 3.27 – 3.09 (m, 2H), 3.09 – 3.00 (m, 1H), 2.76 – 2.68 (m, 1H), 2.62 – 2.48 (m, 3H), 2.40 – 2.17 (m, 4H), 1.47 (s, 18H) ppm. **^{13}C NMR** (125 MHz, CD_3OD): δ 172.6 (C), 157.6 (C), 151.7 (C), 142.7 (C), 142.3 (C), 141.7 (C), 141.3 (C), 139.9 (C), 139.1 (C), 138.7 (C), 136.6 (C), 135.9 (CH), 134.8 (CH), 133.2 (CH), 132.6 (CH), 132.5 (CH), 132.3 (CH), 132.2 (CH), 130.3 (CH), 129.9 (CH), 129.5 (CH), 119.9 (C), 118.6 (CH), 116.8 (CH), 115.9 (CH), 80.3 (2C), 69.6 (CH_2), 55.2 (CH_2), 47.5 (2CH), 38.2 (CH_2), 38.1 (CH_2), 36.0 (CH_2), 35.1 (CH_2), 33.9 (CH_2), 30.7 (CH_2), 28.8 ($6CH_3$) ppm. **IR** (neat): 2965, 2930, 2857, 2492, 1760, 1704, 1610, 1518, 1401, 1366, 1239, 1157, 1121, 1072, 1004, 976, 909, 865, 801, 636 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{43}H_{50}O_6N_3$: 704.3694; found: 704.3710.

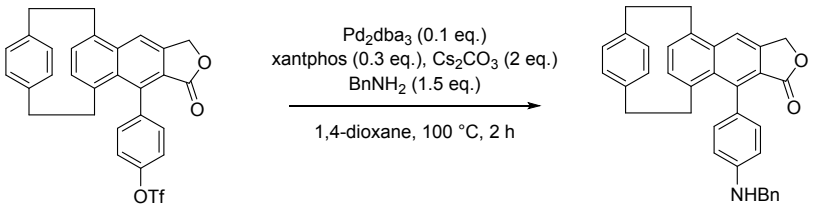
*Synthesis of 1^9-(4-(3,5-diaminopiperidin-1-yl)phenyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**7**)*

[10] The synthesis of this compound was previously reported by our laboratory, see: Blond, A.; Dockerty, P.; Alvarez, R.; Turcaud, S.; Lecourt, T.; Micouin, L. *J. Org. Chem.* **2013**, *78*, 12236.



Compound **S12** (47 mg, 0.0668 mmol, 1 eq.) was dissolved in 1,4-dioxane (0.6 mL). Aqueous HCl (4 M, 0.6 mL) was added and the resulting solution was stirred at rt under an argon atmosphere for 30 min. The reaction was then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography [eluent: DCM/(MeOH:NH_4OH 30%$_{aq}$ 9:1) 8:2] to afford compound **7** (25 mg, 0.0496 mmol, 74 % yield) as amorphous yellow solid. **^{1}H NMR** (500 MHz, CD_3OD): δ 7.90 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.1 Hz, 1H), 6.78 (t, *J* = 9.0 Hz, 2H), 6.51 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.41 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.78 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.58 (d, *J* = 14.8 Hz, 1H), 5.48 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.32 (d, *J* = 14.8 Hz, 1H), 3.84 (t, *J* = 11.3 Hz, 3H), 3.25 – 2.98 (m, 6H), 2.83 – 2.60 (m, 3H), 2.58 – 2.50 (m, 1H), 2.39 – 2.13 (m, 3H) ppm. **^{13}C NMR** (125 MHz, CD_3OD): δ 171.2 (C), 150.5 (C), 141.1 (C), 140.5 (C), 140.3 (2C), 139.7 (C), 138.3 (C), 137.7 (C), 137.3 (C), 135.1 (C), 134.5 (CH), 133.3 (CH), 131.8 (CH), 131.1 (2CH), 130.8 (CH), 128.9 (CH), 128.1 (CH), 118.4 (C), 117.2 (CH), 115.4 (CH), 114.7 (CH), 68.1 (CH_2), 55.6 (CH_2), 55.5 (CH_2), 46.5 (2CH), 39.8 (CH_2), 36.7 (CH_2), 34.5 (CH_2), 33.6 (CH_2), 32.4 (CH_2) ppm. **IR** (neat): 3344, 292, 1758, 1608, 1513, 1457, 1395, 1356, 1331, 1205, 1124, 1068, 1029 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{33}H_{34}O_2N_3$: 504.2646; found: 504.2648.

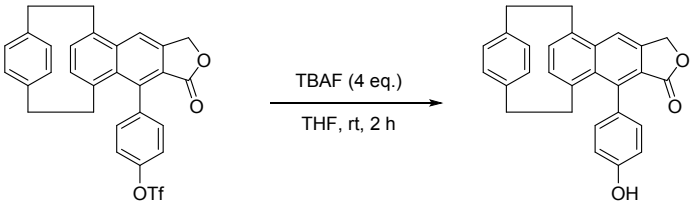
*Synthesis of 1^9-(4-(benzylamino)phenyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**8**)*



A biotage microwave vial was charged with compound **5g** (40 mg, 0.0743 mmol, 1 eq.), Pd_2dba_3 (6.8 mg, 0.00743 mmol, 0.1 eq.), xantphos (12.9 mg, 0.0223 mmol, 0.3 eq.), and Cs_2CO_3 (48.4 mg, 0.149 mmol, 2 eq.). The vial was sealed and evacuated/backfilled with argon three times. 1,4-Dioxane (5 mL) was added, followed by benzylamine (11.9 mg, 0.0122 mL, 0.111 mmol, 1.5 eq.) and the reaction was stirred at 100 °C for 2 h. The reaction was then cooled to rt, filtered through Celite, and concentrated under reduced pressure. The crude residue was purified by silica gel flash chromatography (eluent: EtOAc/Cy 1:9 to 2:8) to provide compound **8** (10 mg, 0.0202 mmol, 27 % yield) as an amorphous yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.71 (s, 1H), 7.45 (br d, *J* = 7.3 Hz, 1H), 7.46 – 7.43 (m, 2H),), 7.41 – 7.35 (m, 2H), 7.33 – 7.29 (m, 1H), 6.87 (br d, *J* = 7.7 Hz, 1H), 6.83 – 6.80 (br m, 2H), 6.76 (d, *J* = 7.3 Hz, 1H), 6.65 (br d, *J* = 7.9 Hz, 1H), 6.51 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.45 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.76 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.59 – 5.46 (m, 2H), 5.36 – 5.27 (m, 1H), 4.42 (s, 2H), 4.18 (br s, 1H), 3.87 – 3.72 (m, 1H), 3.28 – 3.18 (m, 1H), 3.19 – 3.10 (m, 1H), 3.08 – 2.94 (m, 1H), 2.84 – 2.70 (m, 1H), 2.68 – 2.52 (m, 1H), 2.49 – 2.41 (m, 1H), 2.41 – 2.27 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 170.2 (C), 148.3 (C), 142.2 (C), 140.5 (C), 140.4 (C), 140.1 (C), 139.2 (C), 138.9 (C),

137.6 (C), 136.8 (C), 135.6 (C), 134.4 (CH), 133.4 (CH), 132.0 (CH), 131.5 (C and CH), 130.9 (CH), 129.2 (CH), 128.7 (2CH), 128.6 (CH), 127.7 (2CH), 127.4 (CH), 125.6 (C), 119.0 (C), 116.4 (CH), 112.2 (CH), 111.7 (CH), 67.7 (CH_2), 48.5 (CH_2), 37.4 (CH_2), 35.1 (CH_2), 34.3 (CH_2), 33.1 (CH_2) ppm. **IR** (neat): 2926, 2854, 1759, 1612, 1523, 1455, 1263, 1124, 1072, 1030, 805, 739 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{35}H_{30}O_2N$: 496.2271; found: 496.2267.

*Synthesis of 1^9-(4-hydroxyphenyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**9**)*



A Biotage® microwave vial was charged with compound **5g** (50 mg, 0.0928 mmol, 1 eq.). THF (5 mL) and TBAF (97.1 mg, 0.371 mmol, 4 eq.) were added, the tube was sealed and the solution was stirred at rt for 2 h under an argon atmosphere. The reaction was then quenched with a saturated NH_4Cl solution (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: EtOAc/pentane 4:6) to afford compound **9** (37 mg, 0.091 mmol, 98 % yield) as an amorphous yellow solid. Semi-preparative HPLC purification (column: Uptisphere Strategy Si 100Å 5µm, flow: 30 mL/min, eluent: EtOAc/heptane 2:8, λ = 260 nm and 310 nm, T = 25 °C) was performed prior to spectroscopic characterization. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 9.59 (s, 1H), 7.95 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 6.8 Hz, 1H), 6.89 (d, *J* = 7.1 Hz, 1H), 6.84 – 6.76 (m, 2H), 6.70 (d, *J* = 7.7 Hz, 1H), 6.50 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.41 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.77 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.61 (d, *J* = 14.9 Hz, 1H), 5.50 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.36 (d, *J* = 15.1 Hz, 1H), 3.86 – 3.76 (m, 1H), 3.21 – 3.08 (m, 2H), 3.03 – 2.95 (m, 1H), 2.79 – 2.66 (m, 1H), 2.62 – 2.53 (m, 1H), 2.21 – 2.11 (m, 2H) ppm. **^{13}C NMR** (125 MHz, DMSO-d_6): δ 169.6 (C), 157.3 (C), 140.9 (C), 140.5 (C), 139.7 (C), 139.3 (C), 138.0 (C), 137.6 (C), 137.2 (C), 134.7 (C), 134.4 (CH), 133.1 (CH), 132.1 (CH), 131.2 (2CH), 128.9 (CH), 128.2 (CH), 127.5 (CH), 118.7 (C), 117.9 (CH), 117.6 (C), 114.6 (CH), 114.1 (CH), 67.8 (CH_2), 36.6 (CH_2), 34.4 (CH_2), 33.5 (CH_2), 32.4 (CH_2) ppm. **IR** (neat): 3362, 2926, 1735, 1612, 1515, 1439, 1357, 1266, 1210, 1124, 1074, 1032, 816, 764, 749 cm^{-1}. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{28}H_{23}O_3$: 407.1642; found: 407.1641.

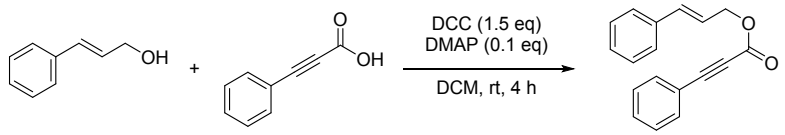
Synthesis of the paracyclophane-deprived naphthalene 10

The preparation of model substrates followed the procedures reported by Brummond and co-workers.[11,12]

*Synthesis of cinnamyl 3-phenylpropiolate (**S13**)*

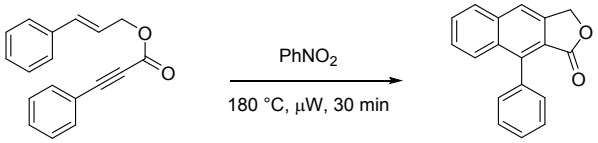
[11] (a) Kocsis, L. S.; Brummond, K. M. *Org. Lett.* **2014**, *16*, 4158; (b) Kocsis, L. S.; Benederrt, E.; Brummond, K. M. *Org. Lett.* **2012**, *14*, 4430.

[12] Benedetti, E.; Kocsis, L. S.; Brummond, K. M. *J. Am. Chem. Soc.* **2012**, *134*, 12418.



Cinnamyl alcohol (312 mg, 1.03 mmol, 1 eq.), DMAP (18 mg, 0.15 mmol, 0.1 eq.) and 3-phenylpropiolic acid (150 mg, 1.03 mmol, 1 eq.) were dissolved in dry DCM (5 mL) under an argon atmosphere. DCC (1 M in DCM, 1.6 mL, 1.6 mmol, 1.5 eq.) was added and the reaction was stirred at rt for 4 h. The mixture was then filtered over a short pad of silica with DCM washings. The resulting solution was then concentrated under reduced pressure and the crud product was purified by silica gel column chromatography (eluent: DCM) to give the title compound (230 mg, 86 % yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.61 – 7.58 (m, 2H), 7.48 – 7.26 (m, 8H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.90 (dd, *J* = 6.6, 1.2 Hz, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.8 (C), 135.9 (C), 135.3 (CH), 133.0 (2CH), 130.7 (CH) 128.6 (2CH), 128.6 (2CH), 128.2 (CH), 126.7 (2CH), 122.0 (CH), 119.5 (C), 86.6 (C), 80.4 (C), 66.5 (CH_2) ppm. Spectroscopic data were consistent with the literature data for this compound.[11a]

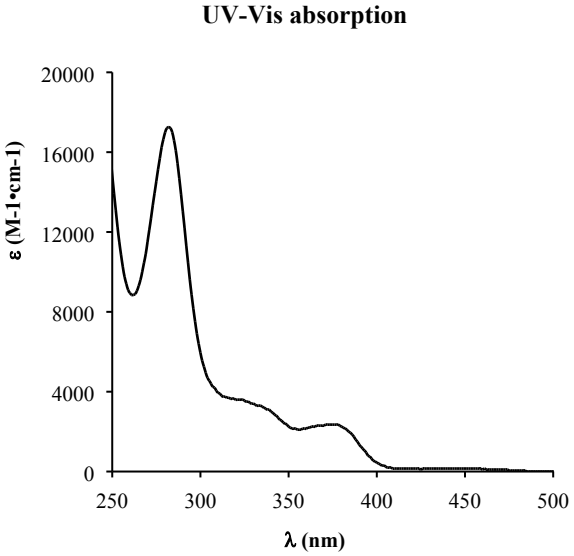
*Synthesis of 9-phenylnaphtho[2,3-c]furan-1(3H)-one (**10**)*

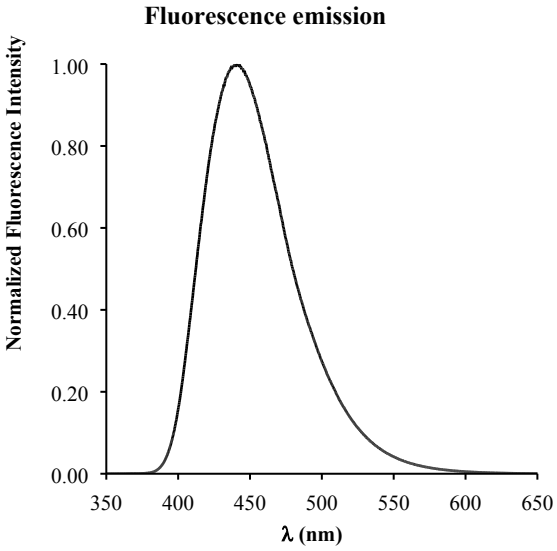


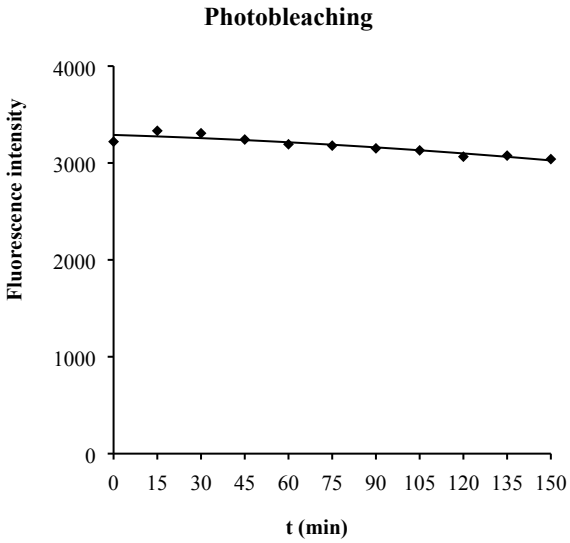
To a microwave irradiation vial was added compound **S8** (60 mg, 0.229 mmol, 1 eq.) and nitrobenzene (4 mL). The solution was irradiated at 180 °C for 30 min turning the reaction orange. The mixture was concentrated under high vacuum and purified by silica gel column chromatography (eluent: EtOAc/pentane 1:9) to afford compound **S10** (34 mg, 0.129 mmol, 56 % yield) as an amorphous brown solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.92 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 8.2 Hz, 1H), 7.57 – 7.52 (m, 3H), 7.49 (t, *J* = 8.2 Hz, 1H), 7.40 – 7.38 (m, 2H), 5.46 (d, *J* = 0.8 Hz, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.8 (C), 142.4 (C), 140.3 (C), 136.4 (C), 134.6 (C), 132.9 (C), 130.2 (2CH), 128.8 (CH), 128.4 (CH), 128.3 (CH), 128.2 (3CH), 126.9 (CH), 120.5 (CH), 120.1 (C), 68.3 (CH_2) ppm. Spectroscopic data were consistent with the literature data for this compound. [11a]

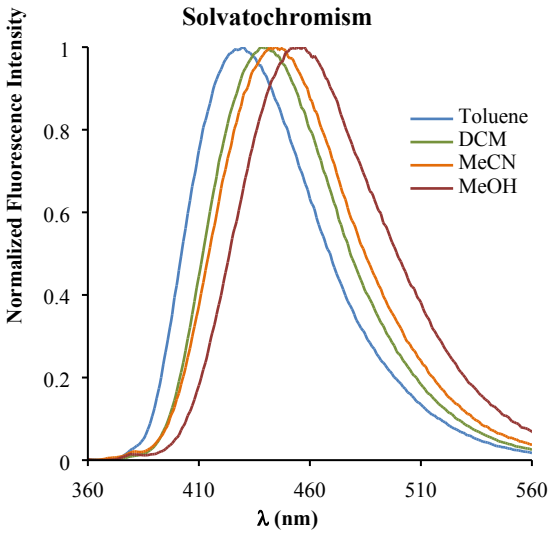
UV-Vis and Fluorescence spectroscopy

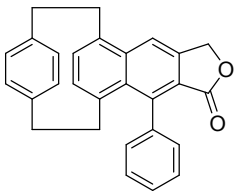
*1^9-Phenyl-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**5a**)*







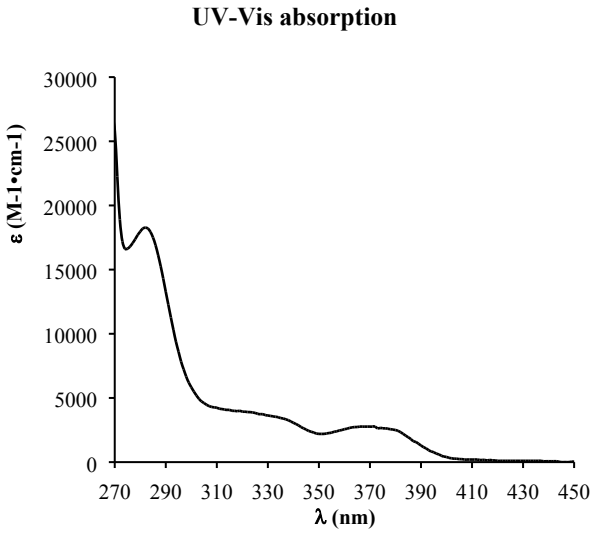


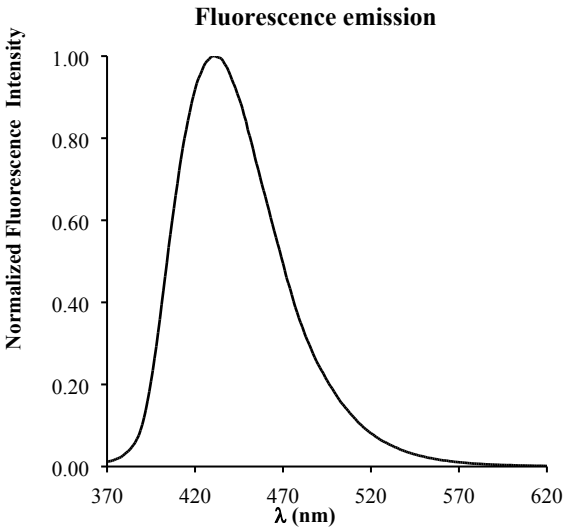


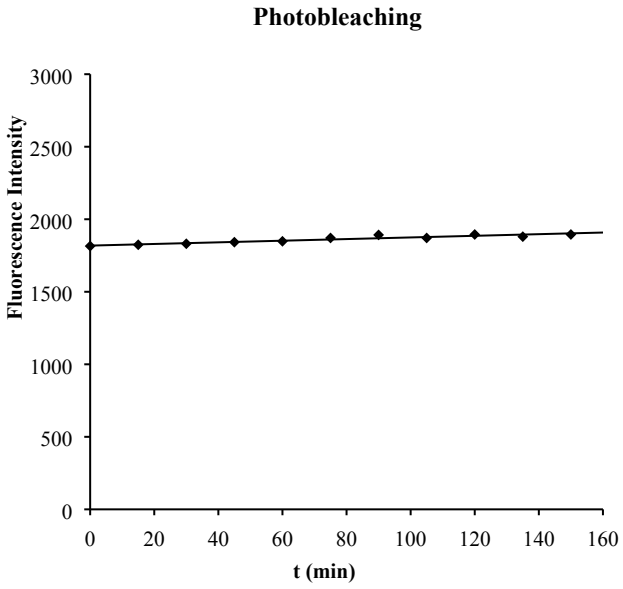
Absorbance max: 282, 329, 376 nm ($1 \bullet 10^{-5}$ M solution in DCM); Emission max: 440 nm ($1 \bullet 10^{-5}$ M solution in DCM, λ_{ex} = 330 nm). QY in DCM = 62%[13] A $1 \bullet 10^{-5}$ M solution of **5a** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 375 nm) and maximum emission intensity changes (λ_{max} = 440 nm) were measured at 15-minute time intervals.

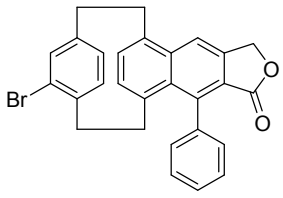
[13] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

*4^3-Bromo-1^9-phenyl-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**5b**)*







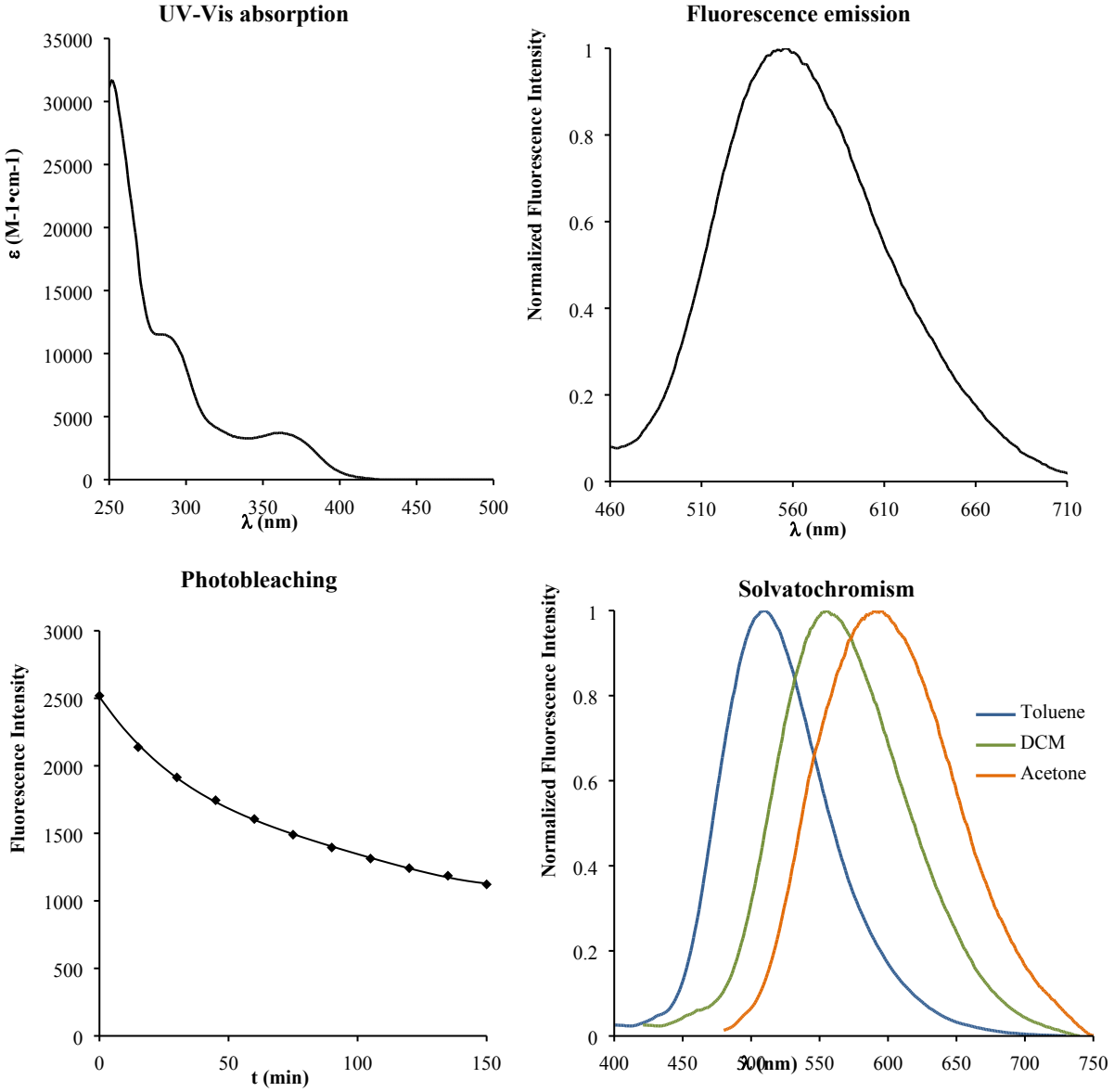


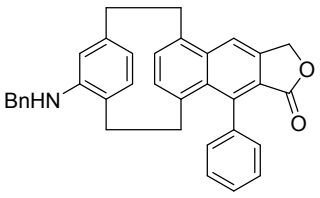
Absorbance max: 282, 329, 371 nm (1•10^{-5} M solution in DCM); Emission max: 430 nm (1•10^{-5} M solution in DCM, λ_{ex} = 340 nm). QY in DCM = 17%[14]

A 1•10^{-5} M solution of **5a** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 370 nm) and maximum emission intensity changes (λ_{max} = 430 nm) were measured at 15-minute time intervals.

[14] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

*1^9-phenyl-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**5c**)*



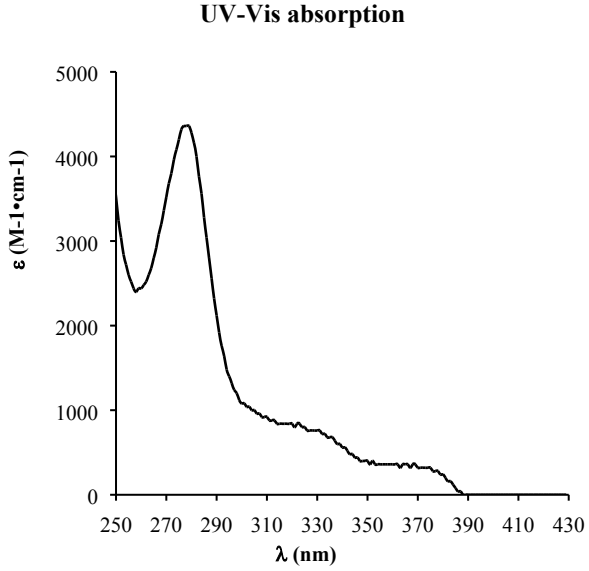


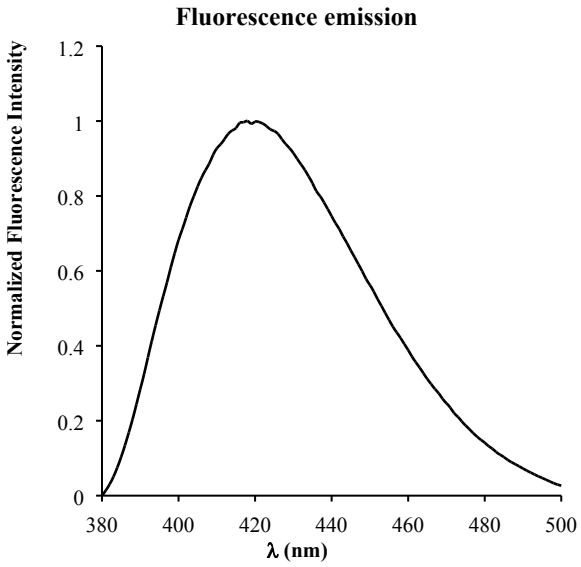
Absorbance max: 252, 286, 365 nm ($2 \bullet 10^{-5}$ M solution in DCM); Emission max: 555 nm ($1 \bullet 10^{-4}$ M solution in DCM, λ_{ex} = 380 nm). QY in DCM = 6%[15]

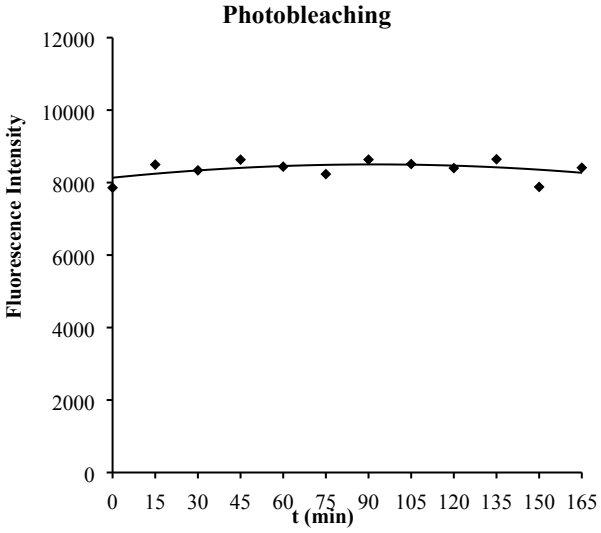
A $1 \bullet 10^{-5}$ M solution of **5c** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 380 nm) and maximum emission intensity changes (λ_{max} = 555 nm) were measured at 15-minute time intervals.

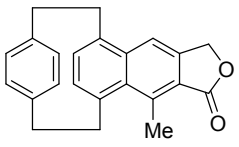
[15] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

*1^9-Methyl-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**5d**)*





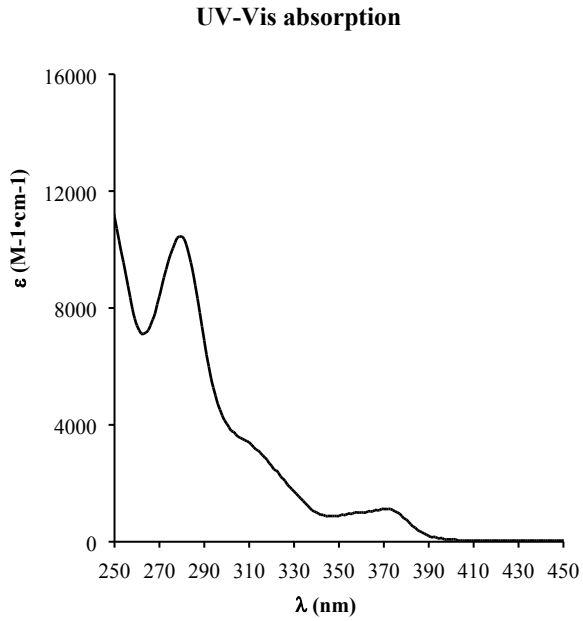


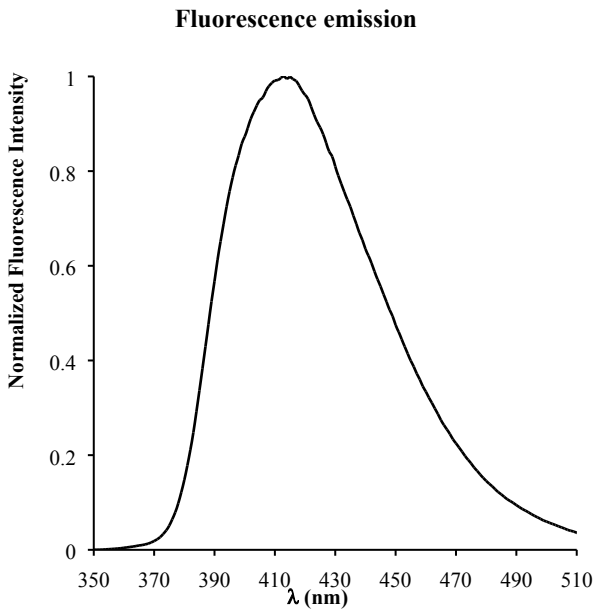


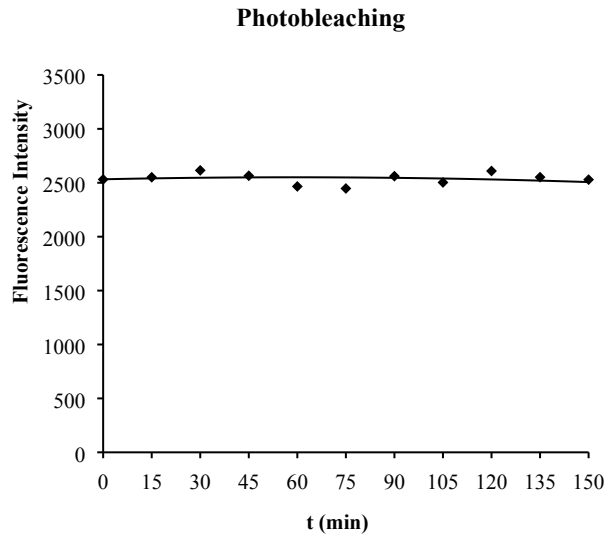
Absorbance max: 278, 324, 373 nm ($1•10^{-5}$ M solution in DCM); Emission max: 420 nm ($1•10^{-5}$ M solution in DCM, λ_{ex} = 290 nm). QY in DCM = 39%[16]
A $1•10^{-5}$ M solution of **5d** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 370 nm) and maximum emission intensity changes (λ_{max} = 420 nm) were measured at 15-minute time intervals.

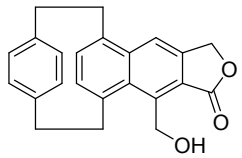
[16] Relative quantum yield (QY) was calculated using 9,10-diphenylanthracene in cyclohexane as fluorescence standard (QY = 90%). The excitation wavelength was fixed at 275 nm for both the sample and the standard.

*1^9-(Hydroxymethyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclo-hexaphan-1^1-one (**5e**)*







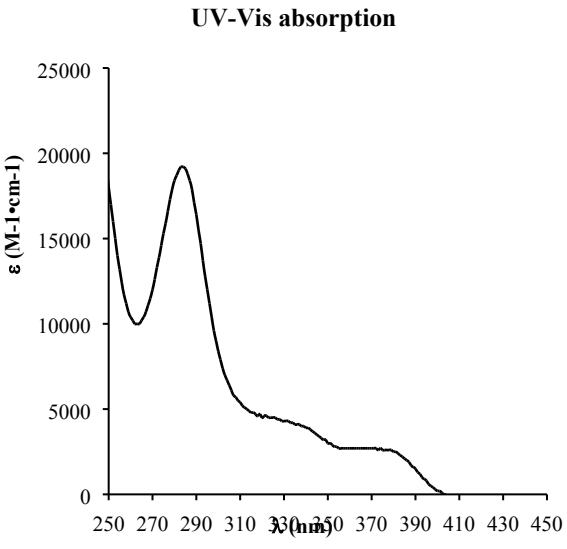


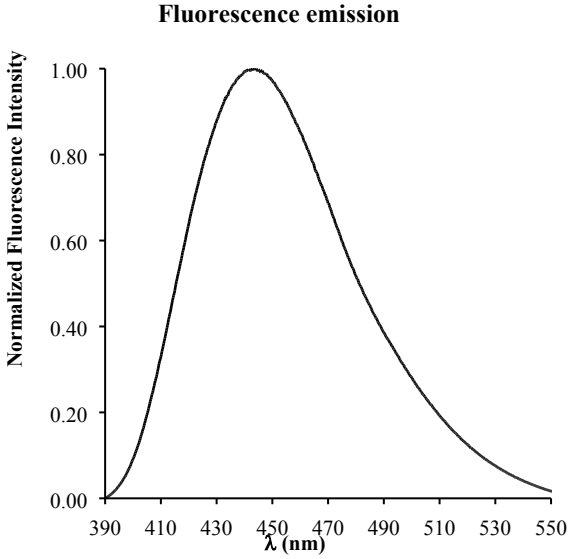
Absorbance max: 280, 312, 373 nm ($1 \bullet 10^{-5}$ M solution in DCM); Emission max: 415 nm ($1 \bullet 10^{-5}$ M solution in DCM, λ_{ex} = 275 nm). QY in DCM = 16%[17]

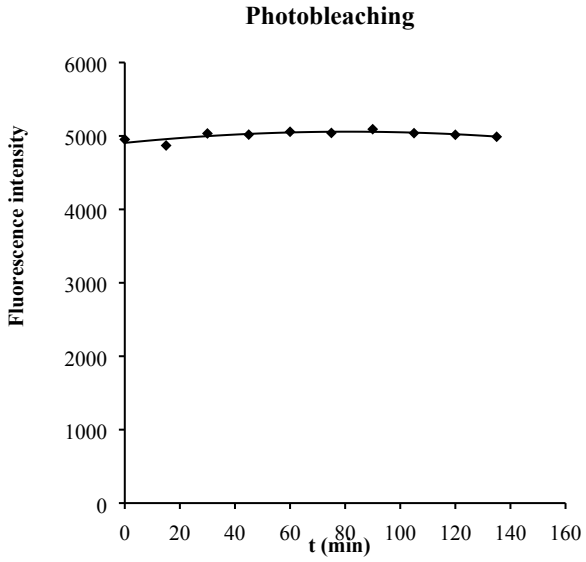
A $1 \bullet 10^{-5}$ M solution of **5e** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 310 nm) and maximum emission intensity changes (λ_{max} = 415 nm) were measured at 15-minute time intervals.

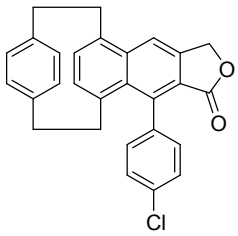
[17] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

*1^9-(4-Chlorophenyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)benzenacyclo-hexaphan-1^1-one (**5f**)*





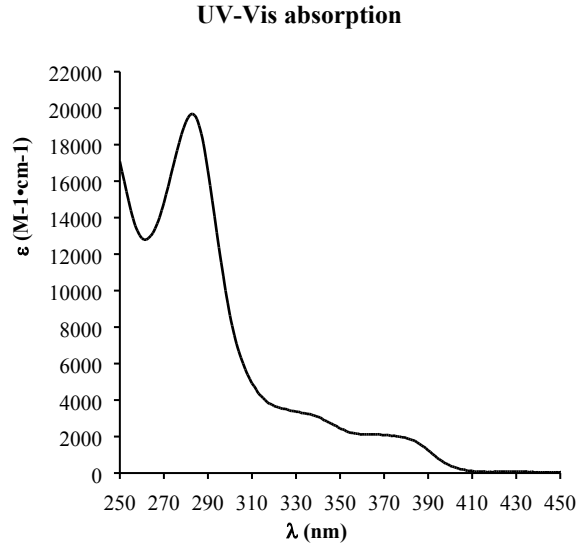


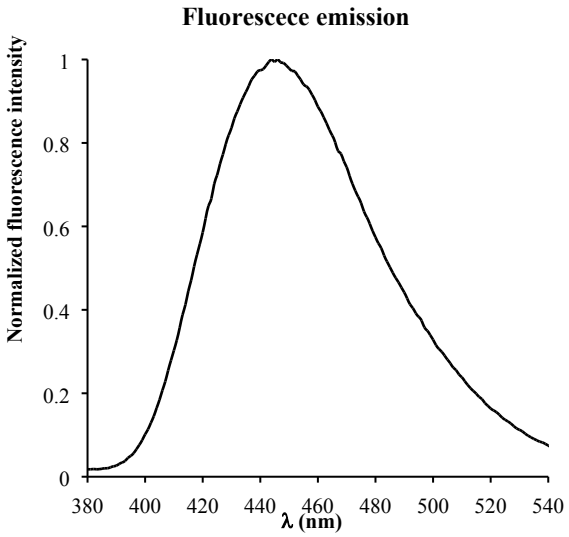


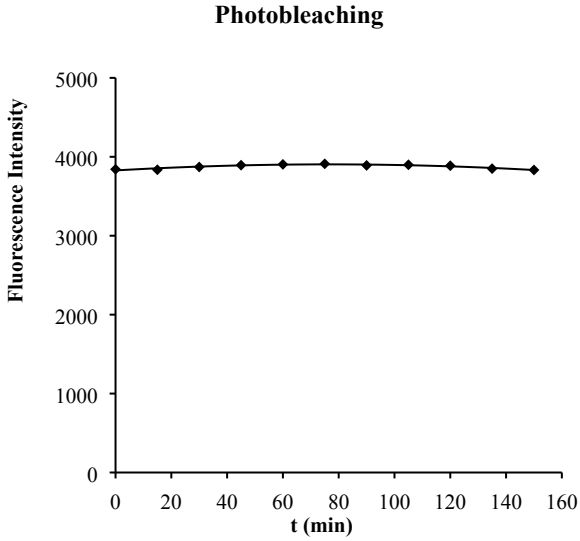
Absorbance max: 283, 330, 375 nm ($1•10^{-5}$ M solution in DCM); Emission max: 440 nm ($1•10^{-5}$ M solution in DCM, λ_{ex} = 290 nm). QY in DCM = 41%[18] A $1•10^{-5}$ M solution of **5f** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 380 nm) and maximum emission intensity changes (λ_{max} = 440 nm) were measured at 15-minute time intervals.

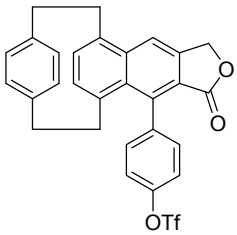
[18] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

*4-(1³-Oxo-1¹,1³-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphane-1⁴-yl)phenyl trifluoromethanesulfonate (**5g**)*





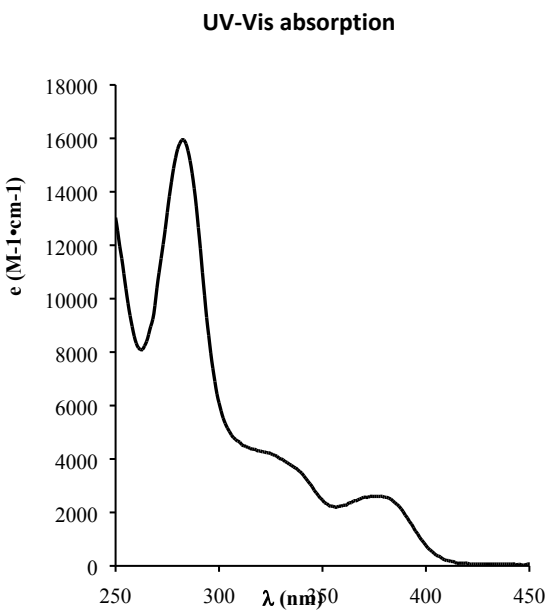


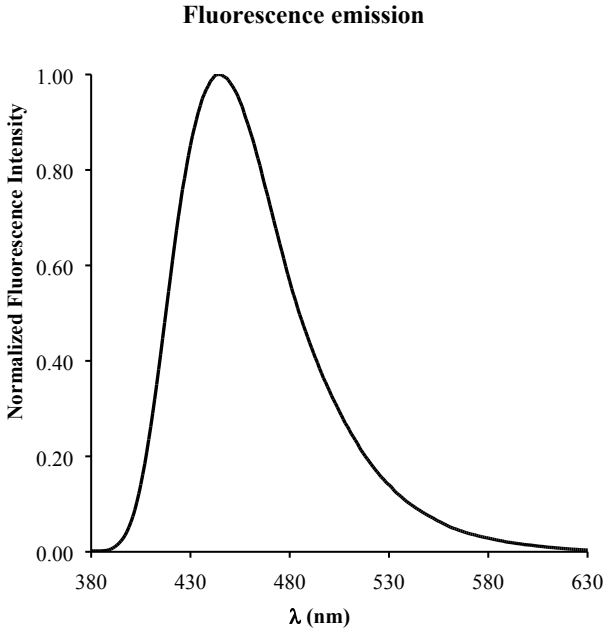


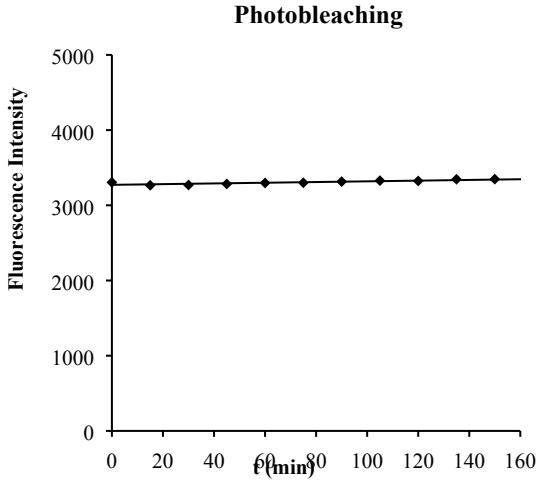
Absorbance max: 280, 333, 378 nm (1•10^{-5} M solution in DCM); Emission max: 445 nm (1•10^{-5} M solution in DCM, λ_{ex} = 340 nm). QY in DCM = 43%[19]
A 1•10^{-5} M solution of **5g** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 380 nm) and maximum emission intensity changes (λ_{max} = 445 nm) were measured at 15-minute time intervals.

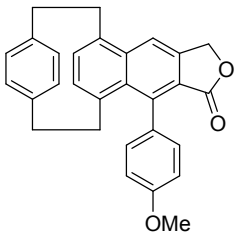
[19] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

1^{9}-(4-methoxyphenyl)-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^{1}-one (**5h**)







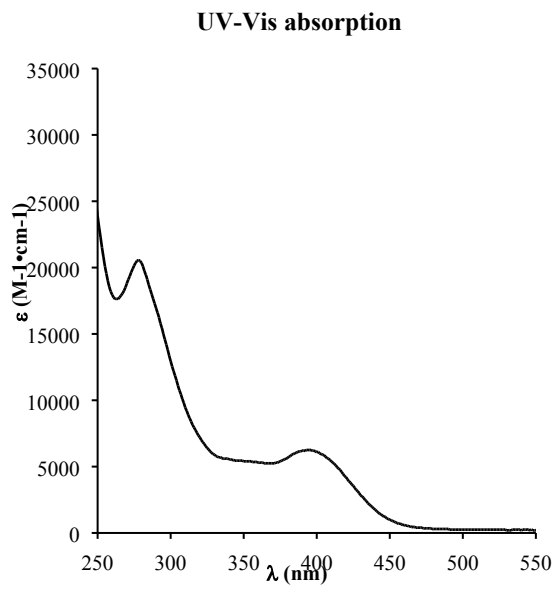


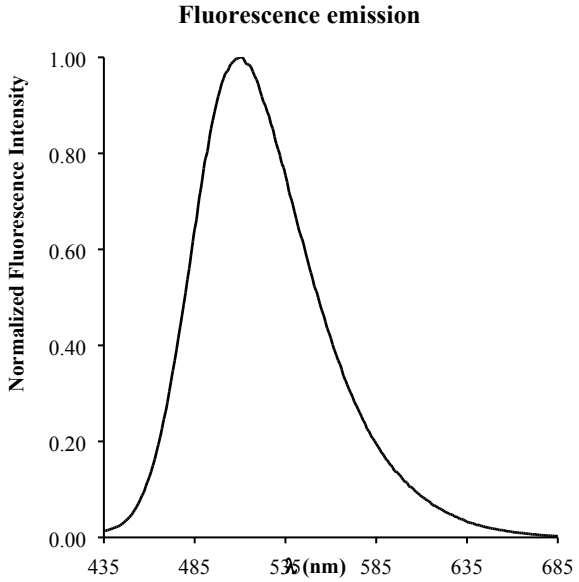
Absorbance max: 282, 325, 378 nm ($1\bullet10^{-5}$ M solution in DCM); Emission max: 443 nm ($1\bullet10^{-5}$ M solution in DCM, λ_{ex} = 340 nm). QY in DCM = 41%[20]

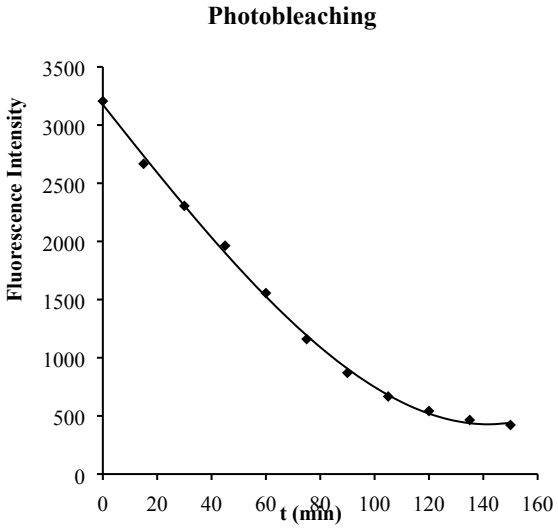
A $1\bullet10^{-5}$ M solution of **5h** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 378 nm) and maximum emission intensity changes (λ_{max} = 443 nm) were measured at 15-minute time intervals.

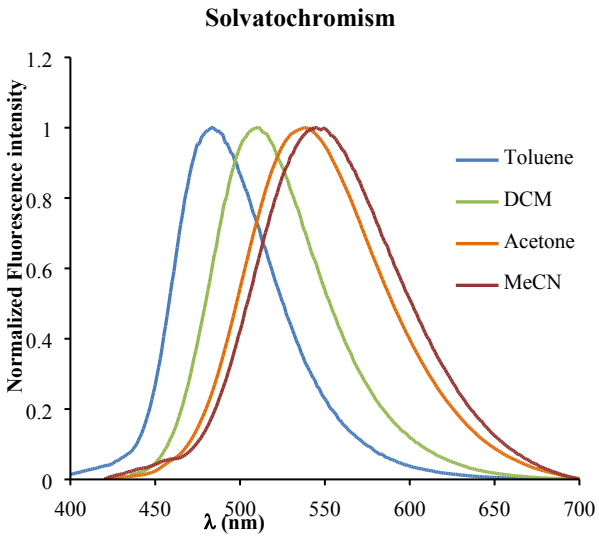
[20] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

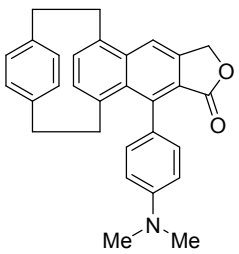
*1^9-(4-(Dimethylamino)phenyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclo hexaphan-1^1-one (**6**)*









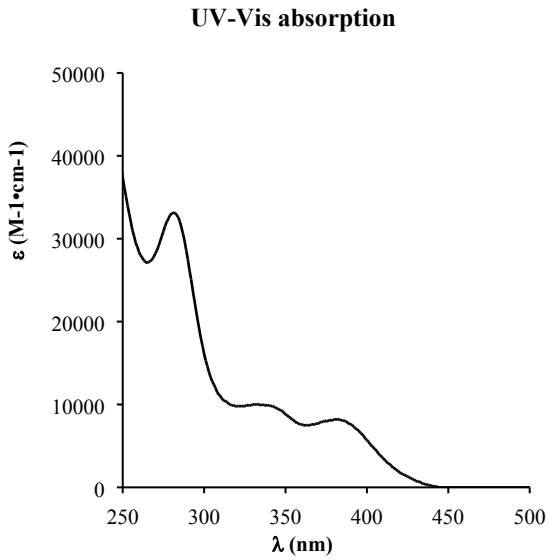


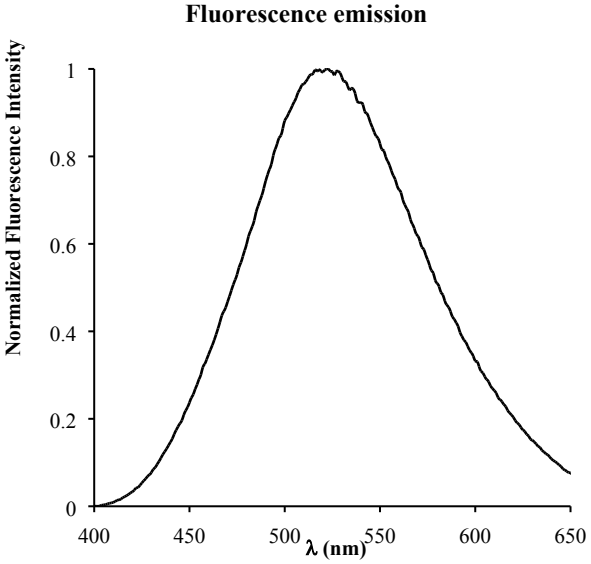
Absorbance max: 278, 400 nm ($1 \bullet 10^{-5}$ M solution in DCM); Emission max: 510 nm ($1 \bullet 10^{-5}$ M solution in DCM, λ_{ex} = 400 nm). QY in DCM = 23%[21]

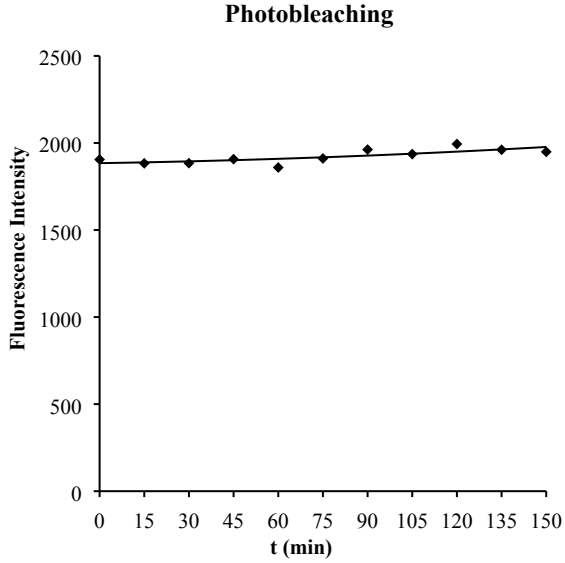
A $1 \bullet 10^{-5}$ M solution of **6** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 400 nm) and maximum emission intensity changes (λ_{max} = 510 nm) were measured at 15-minute time intervals.

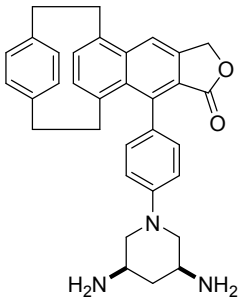
[21] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

*1^{9}-(4-(3,5-Diaminopiperidin-1-yl)phenyl)-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzena cyclohexaphan-1^{1}-one (**7**)*







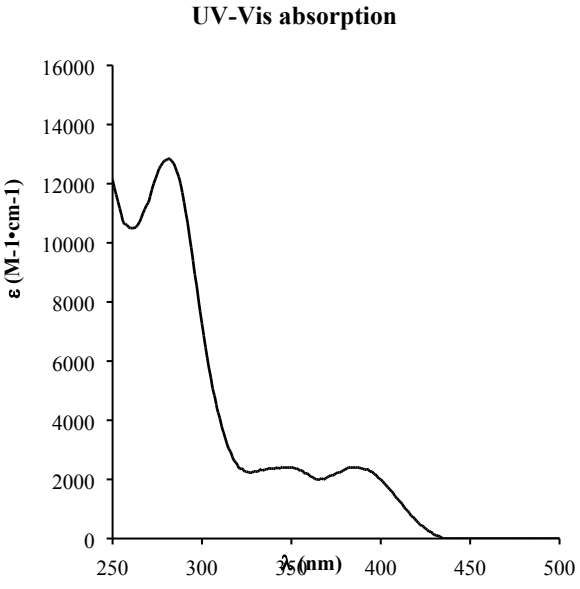


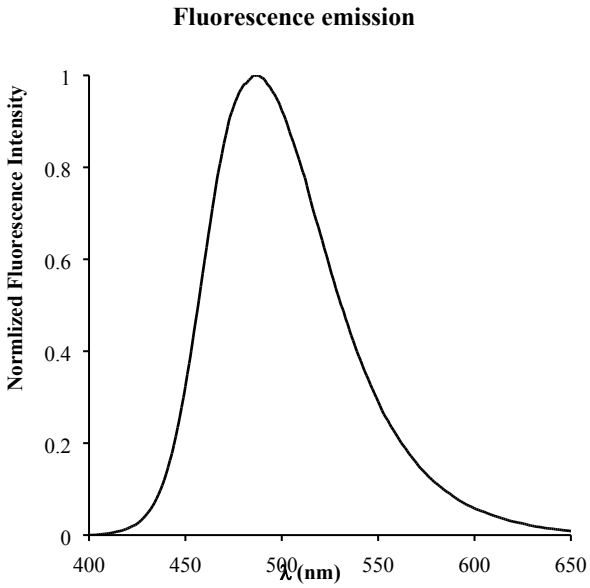
Absorbance max: 275, 333 and 384 nm ($1•10^{-5}$ M solution in MeOH); Emission max: 520 nm ($1•10^{-5}$ M solution in DMSO, λ_{ex} = 340 nm). QY in DMSO = 10%; QY in MeOH = 2%.[22]

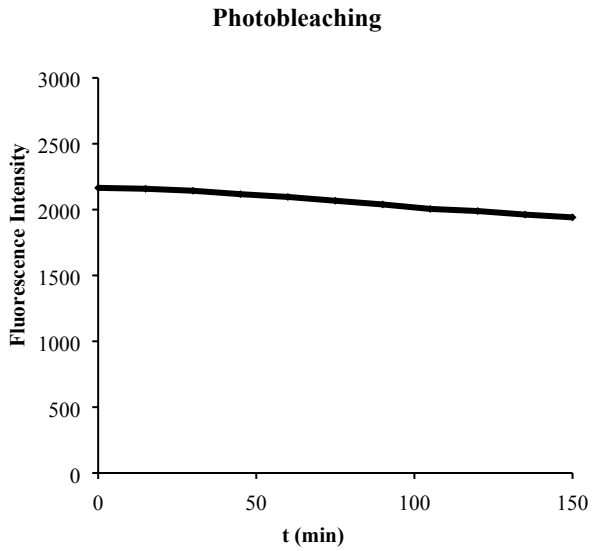
A $1•10^{-5}$ M solution of **7** in DMSO was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 390 nm) and maximum emission intensity changes (λ_{max} = 520 nm) were measured at 15-minute time intervals.

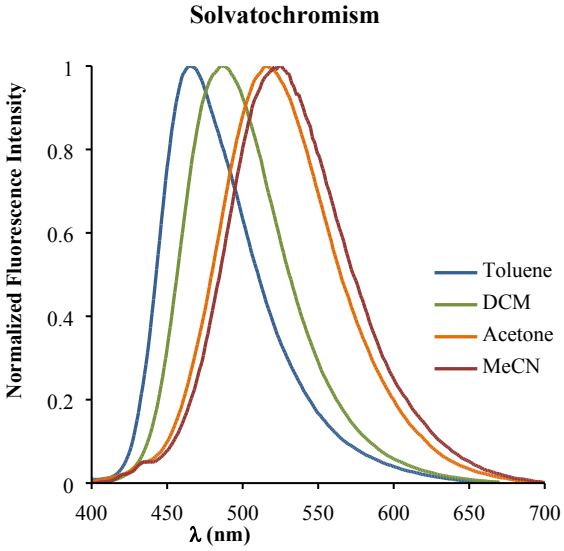
[22] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

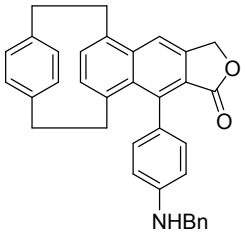
*1^9-(4-(Benzylamino)phenyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^1-one (**8**)*









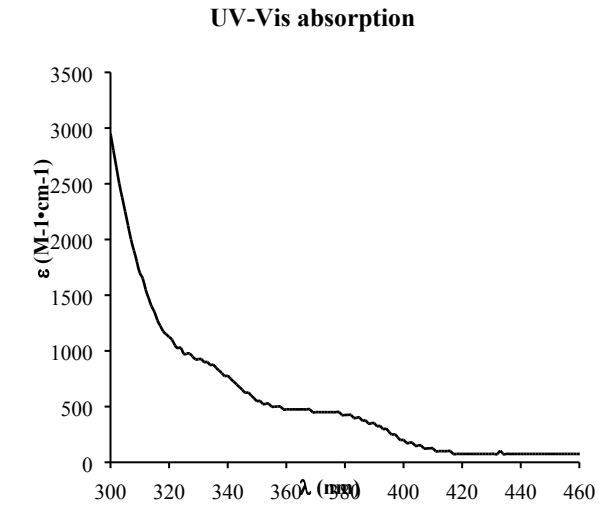


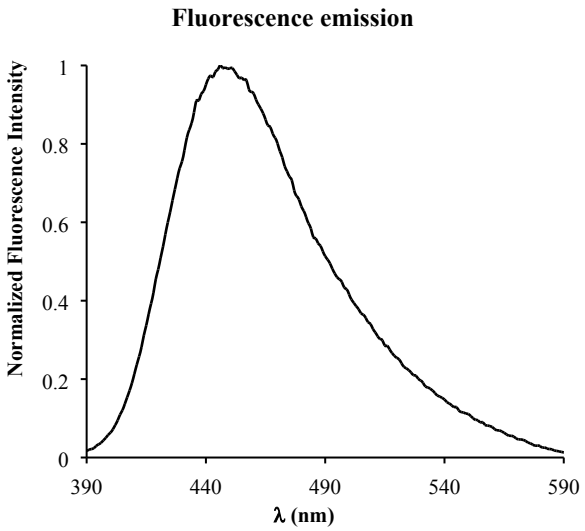
Absorbance max: 280, 350, 385 nm ($1 \bullet 10^{-5}$ M solution in DCM); Emission max: 485 nm ($1 \bullet 10^{-5}$ M solution in DCM, λ_{ex} = 380 nm). QY in DCM = 30%[23]

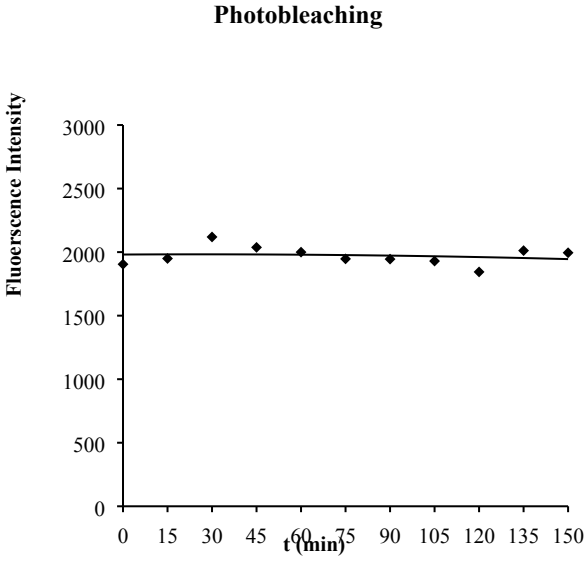
A $1 \bullet 10^{-5}$ M solution of **8** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 380 nm) and maximum emission intensity changes (λ_{max} = 485 nm) were measured at 15-minute time intervals.

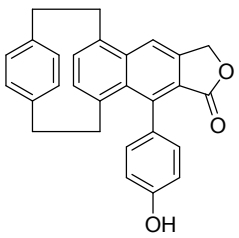
[23] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

*1^9-(4-Hydroxyphenyl)-1^1,1^3-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclo-hexaphan-1^1-one (**9**)*







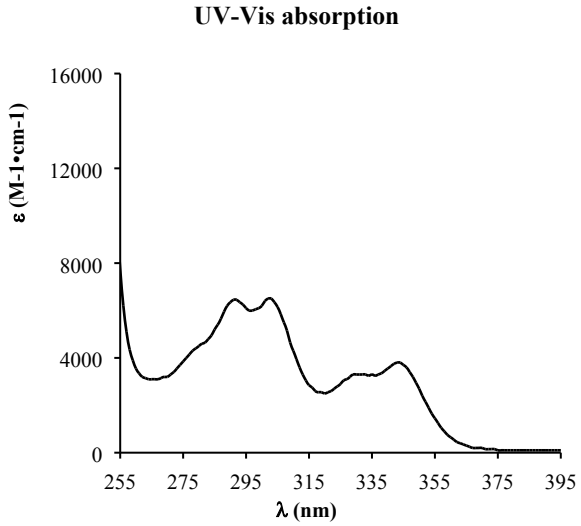


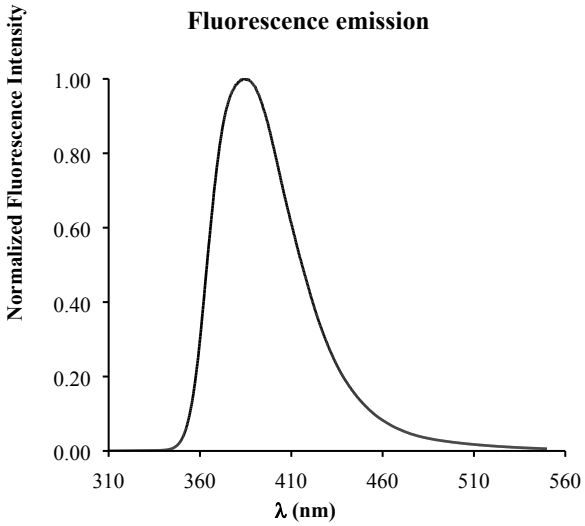
Absorbance max: 330, 374 nm ($4 \bullet 10^{-5}$ M solution in DMSO); Emission max: 454 nm ($4 \bullet 10^{-5}$ M solution in DMSO, λ_{ex} = 340 nm). QY in DMSO = 16%[24]

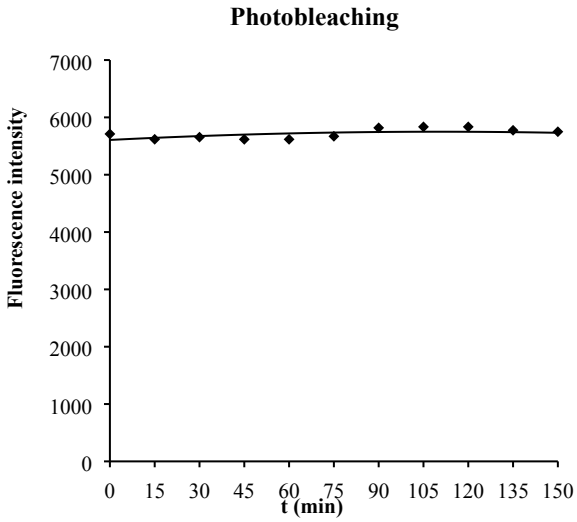
A $1 \bullet 10^{-5}$ M solution of **9** in DMSO was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 380 nm) and maximum emission intensity changes (λ_{max} = 454 nm) were measured at 15-minute time intervals.

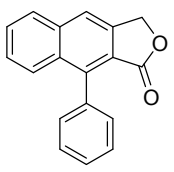
[24] Relative quantum yield (QY) was calculated using anthracene in ethanol as fluorescence standard (QY = 27%). The excitation wavelength was fixed at 340 nm for both the sample and the standard.

*9-Phenylnaphtho[2,3-c]furan-1(3H)-one (**10**)*









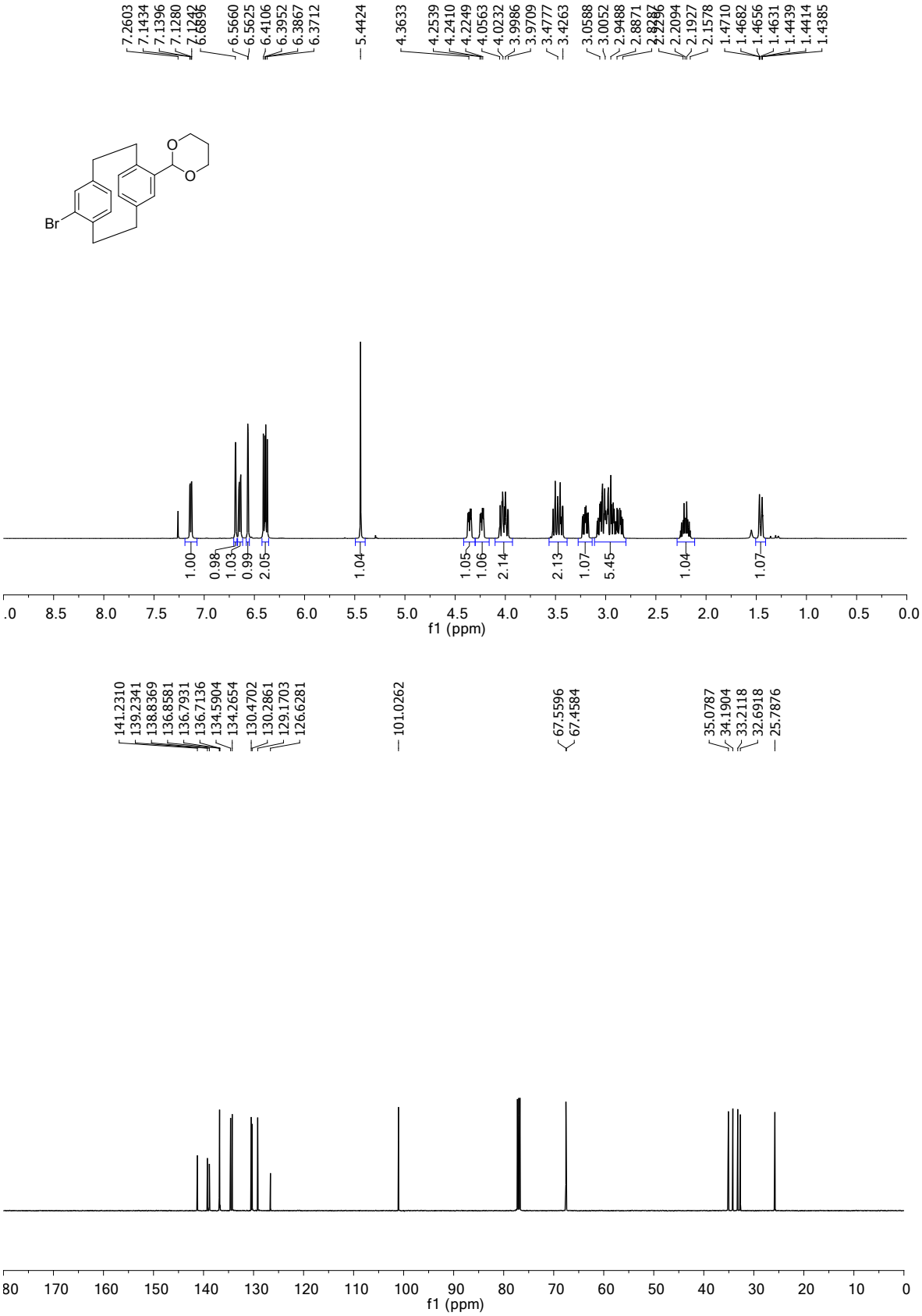
Absorbance max: 290, 304, 329, 345 nm ($1 \bullet 10^{-5}$ M solution in DCM); Emission max: 380 nm ($1 \bullet 10^{-5}$ M solution in DCM, λ_{ex} = 290 nm). QY in DCM = 22%.[25]

A $1 \bullet 10^{-5}$ M solution of **10** in DCM was used to perform the photobleaching study. The sample was continuously irradiated for 150 min at 20 °C (λ_{ex} = 340 nm) and maximum emission intensity changes (λ_{max} = 380 nm) were measured at 15-minute time intervals.

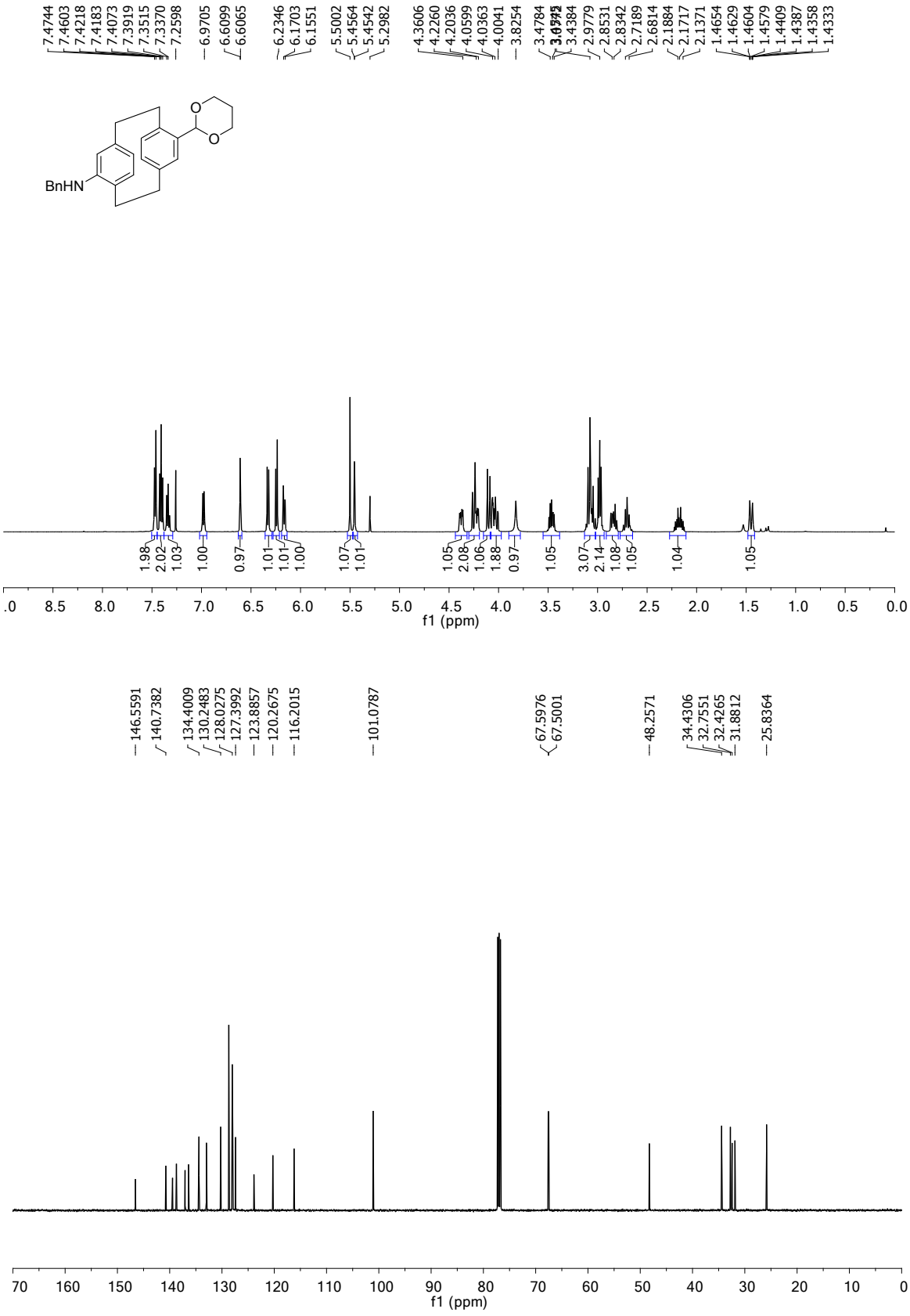
[25] Relative quantum yield (QY) was calculated using 9,10-diphenylanthracene in cyclohexane as fluorescence standard (QY = 90%). The excitation wavelength was fixed at 275 nm for both the sample and the standard.

^{1}H NMR and ^{13}C NMR spectra

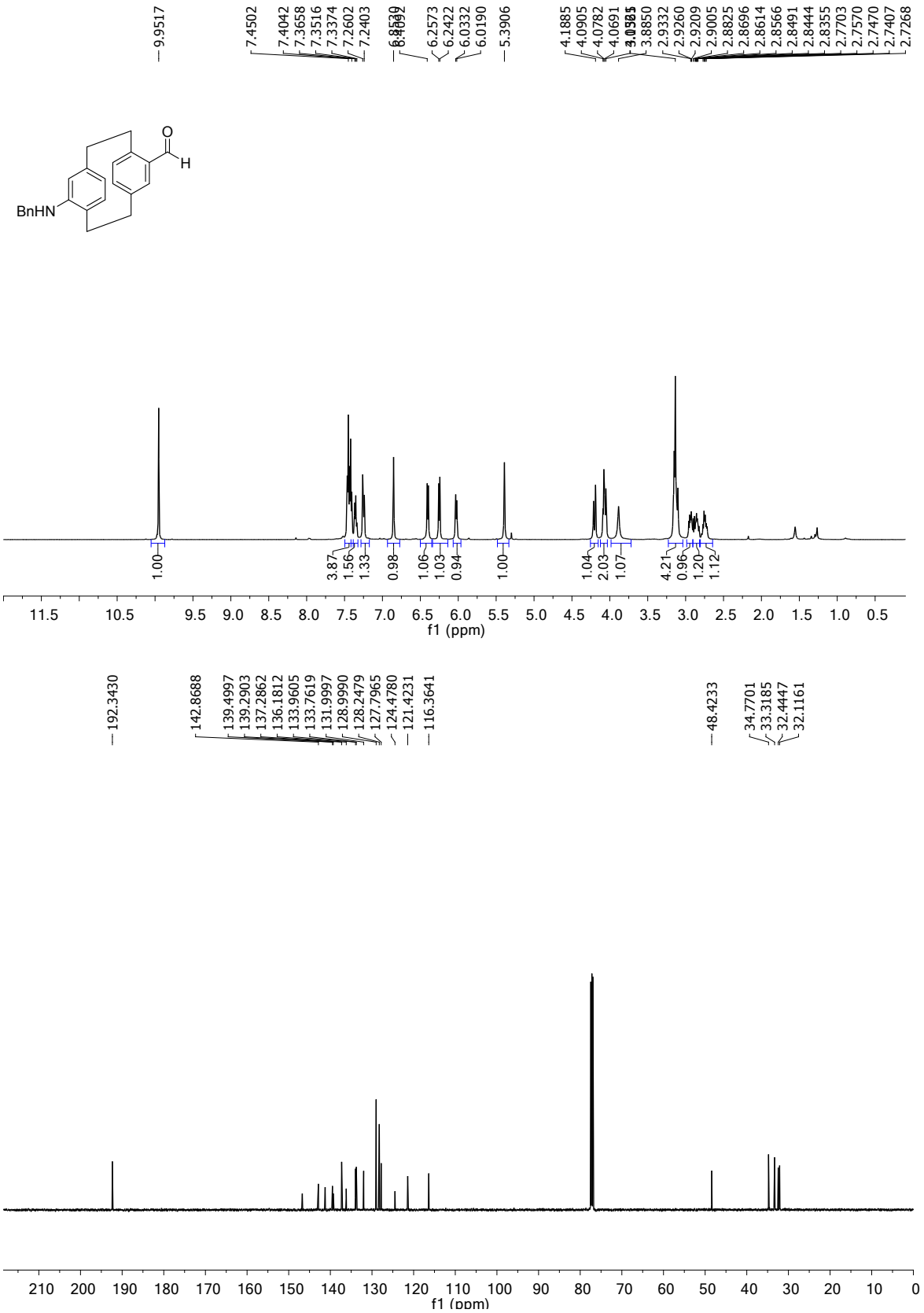
*2-{14-Bromotricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl}-1,3-dioxane (**S10**)*



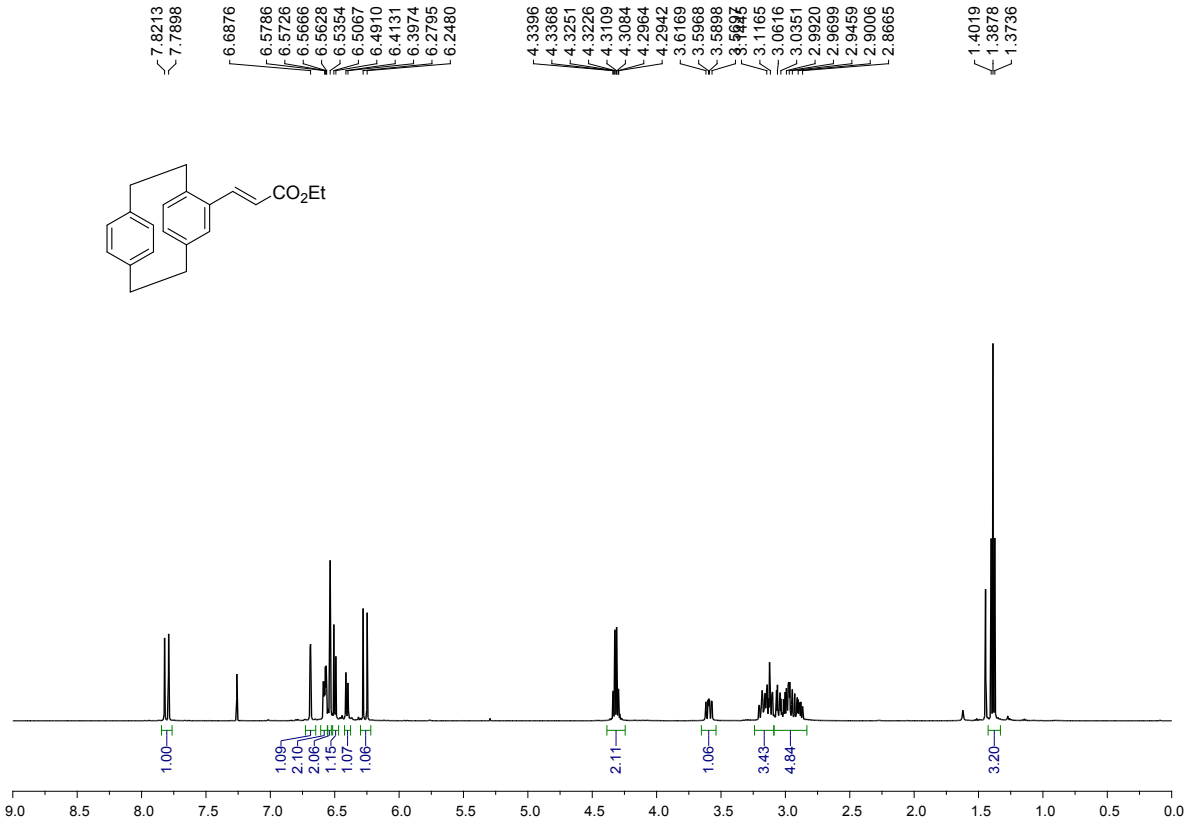
*N-benzyl-11-(1,3-dioxan-2-yl)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4(16),5,7(15),10,13-hexaen-5-amine (**S11**)*

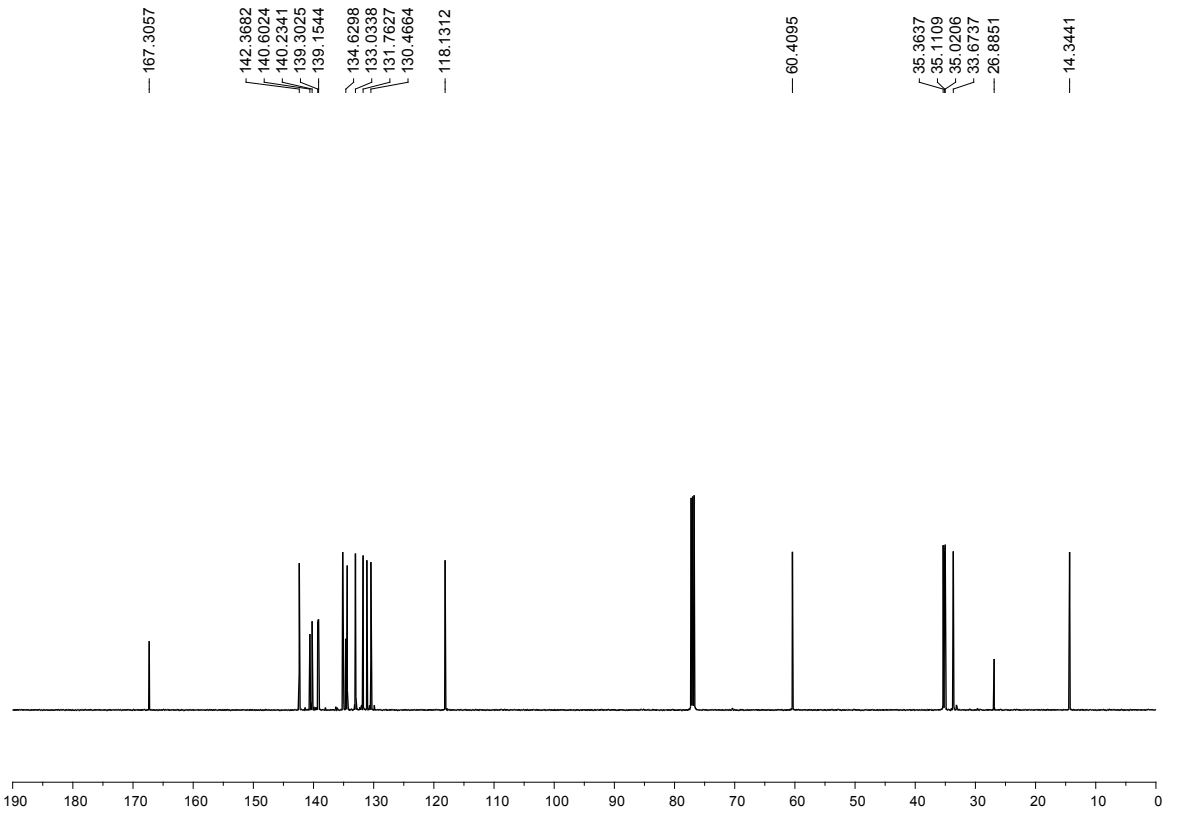


*14-(Benzylamino)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaene-5-carbaldehyde (**1c**)*

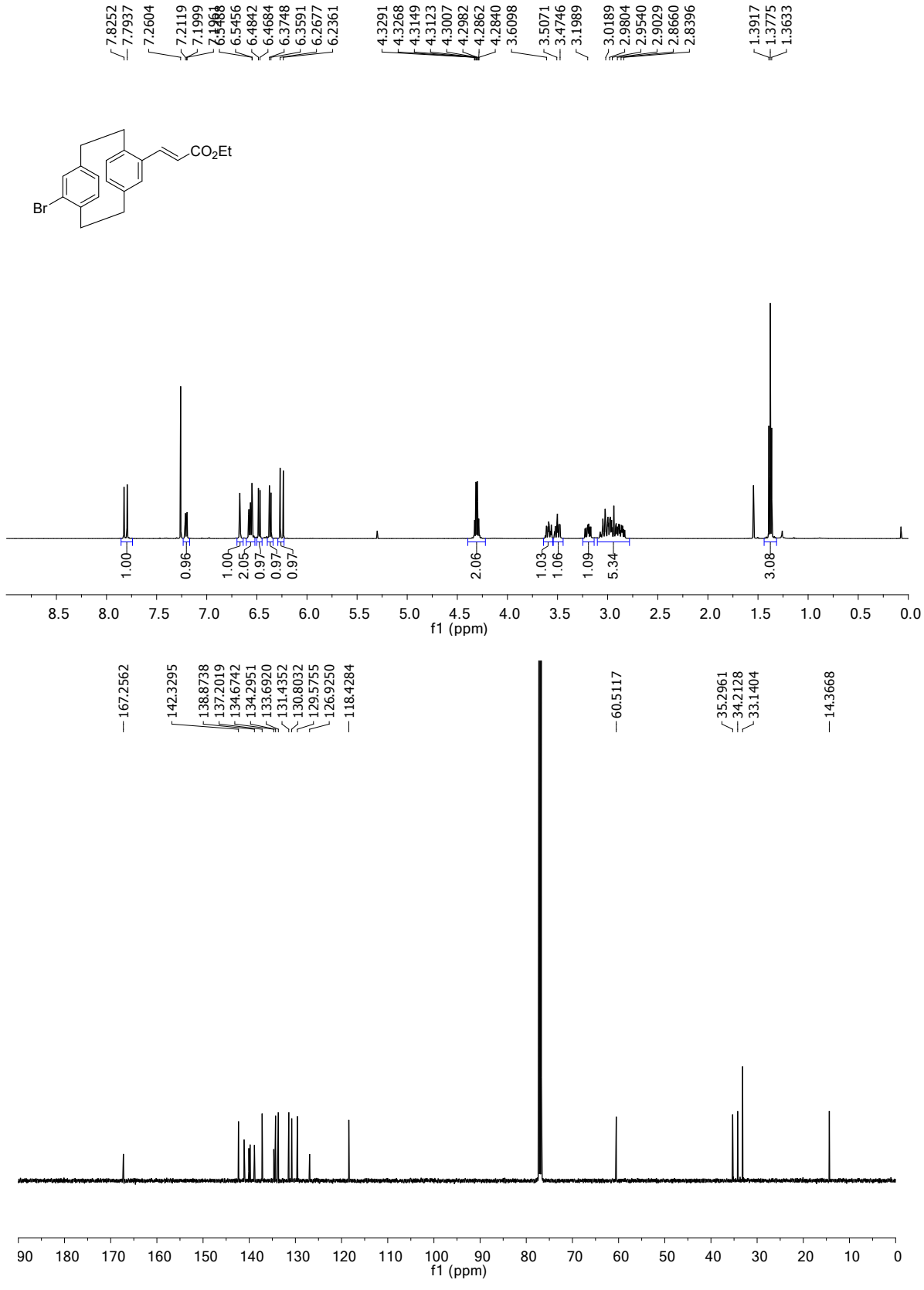


*3-([2.2]Paracyclophen-4-yl)acrylate (**2a**)*

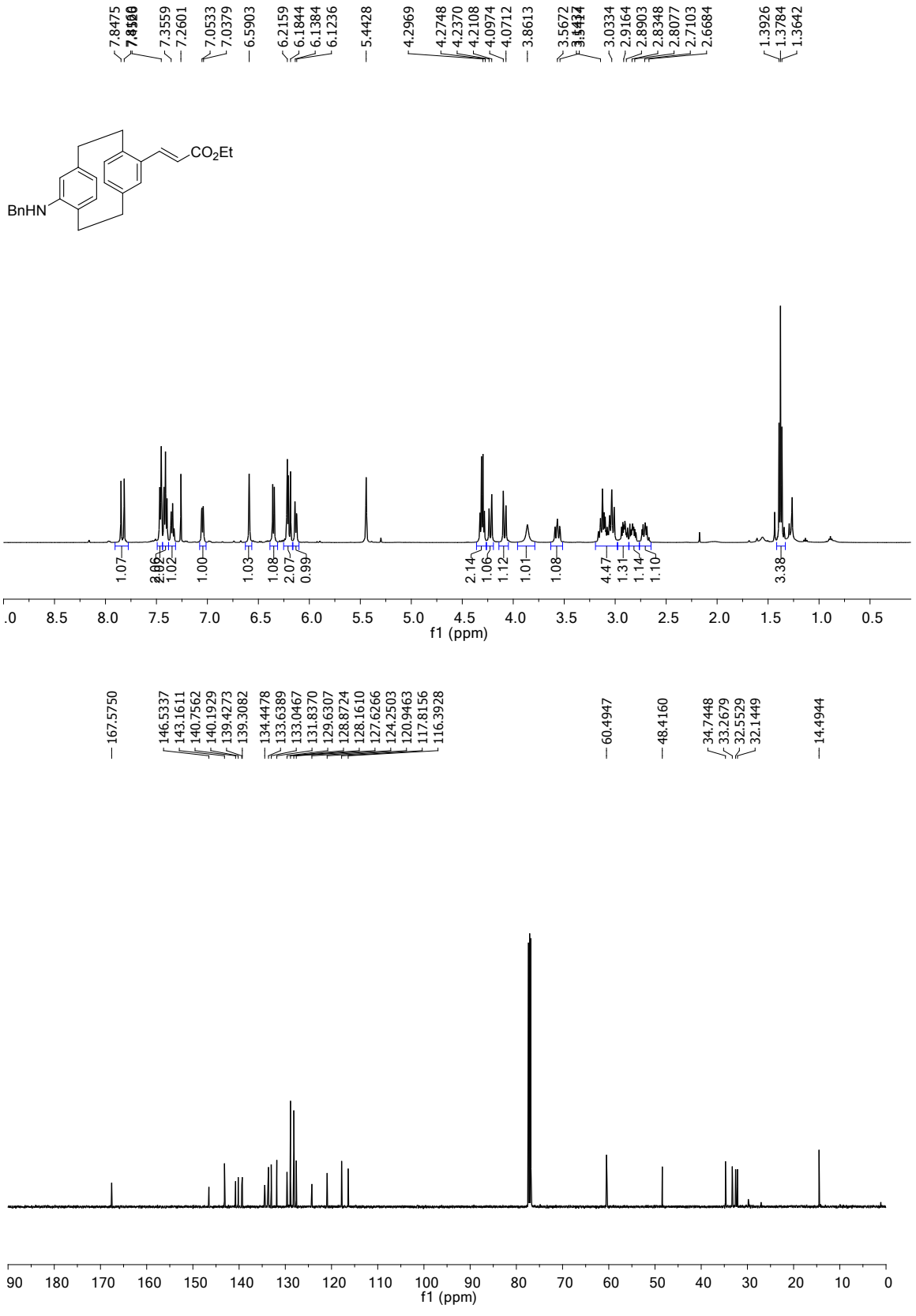




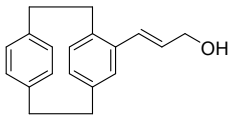
*(2E)-3-[14-(Benzylamino)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl]prop-2-enoate (**2b**)*

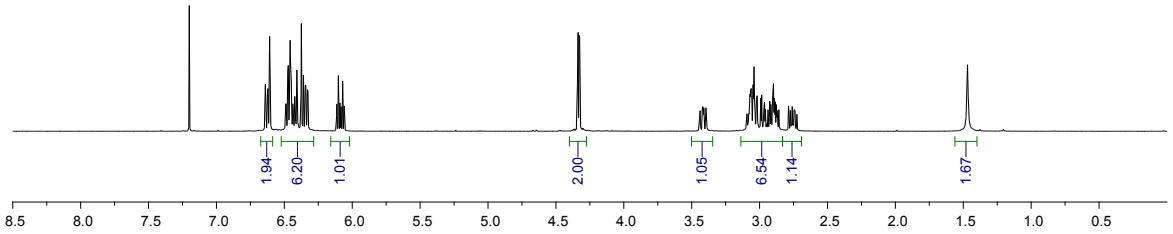


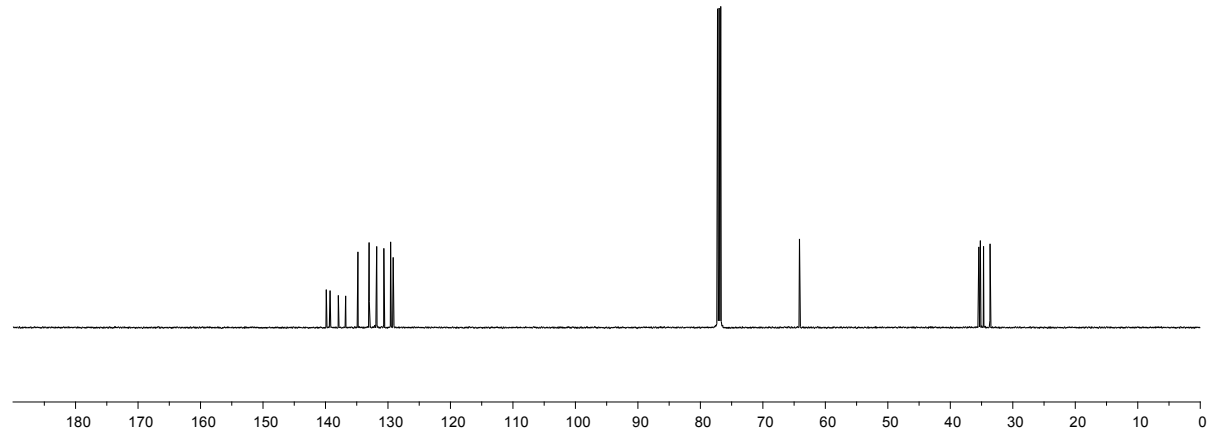
*Ethyl (2E)-3-[14-(benzylamino)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl]prop-2-enoate (**2c**)*



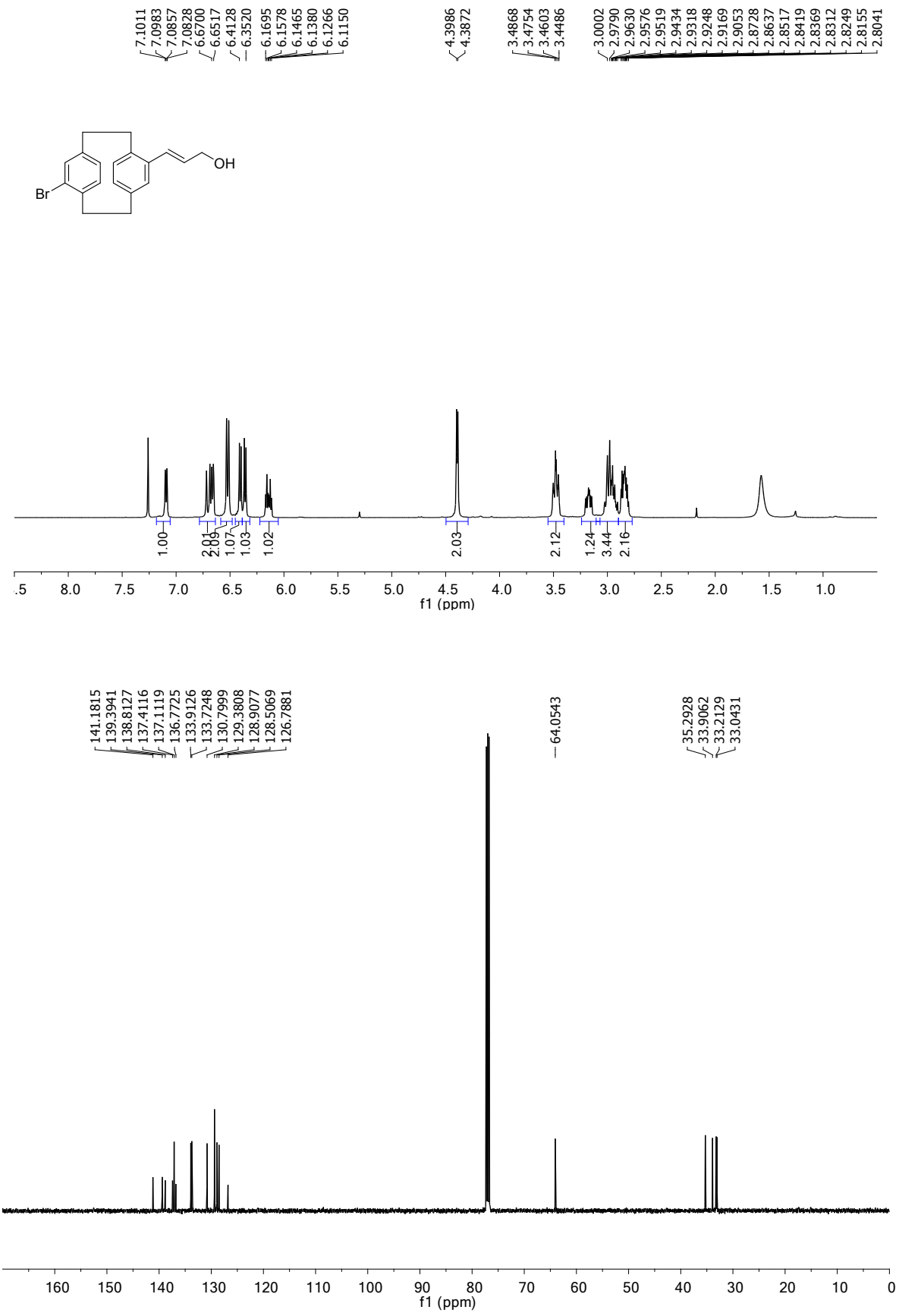
*3-([2.2]Paracyclopheny-4-yl)prop-2-en-1-ol (**3a**)*



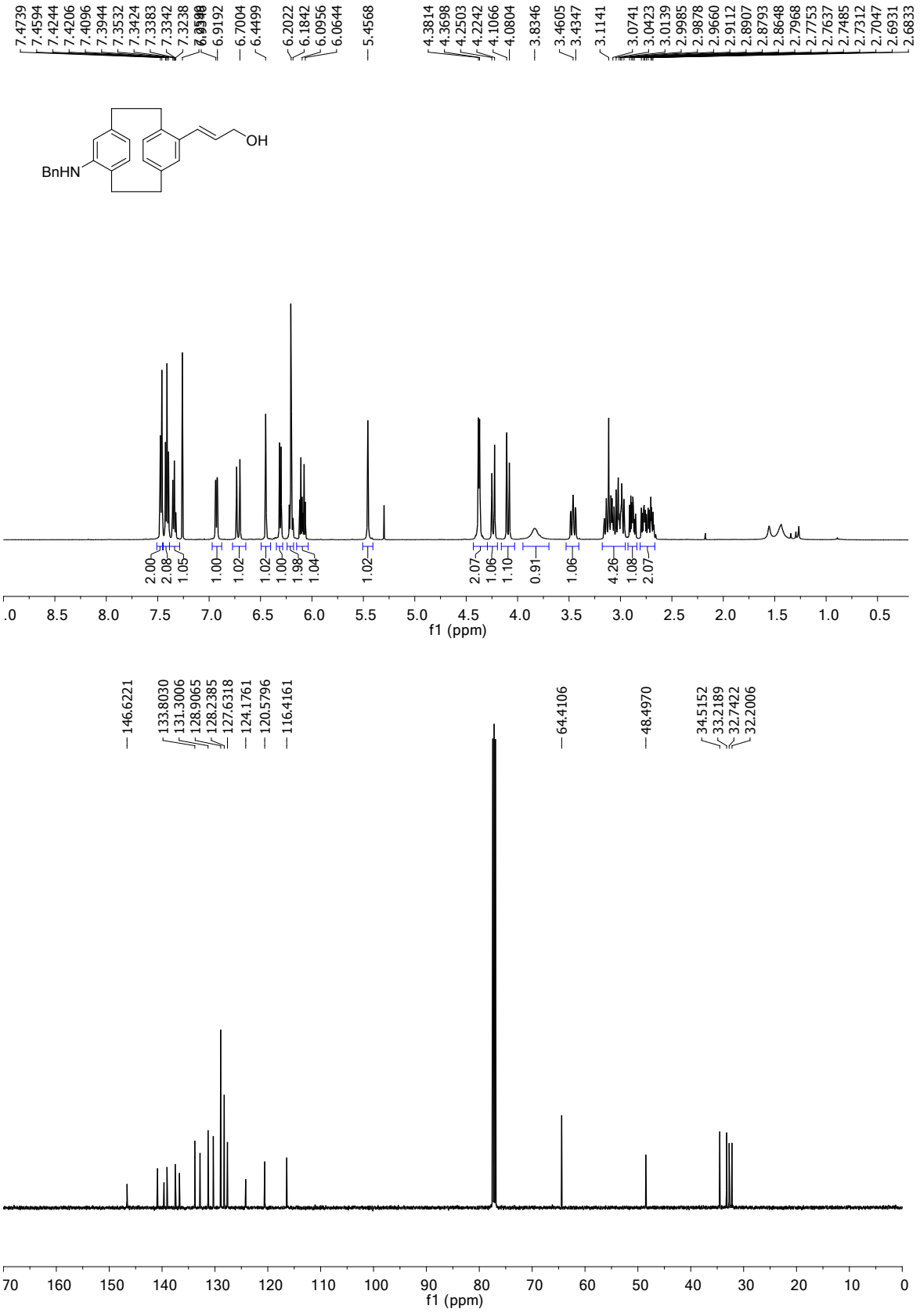




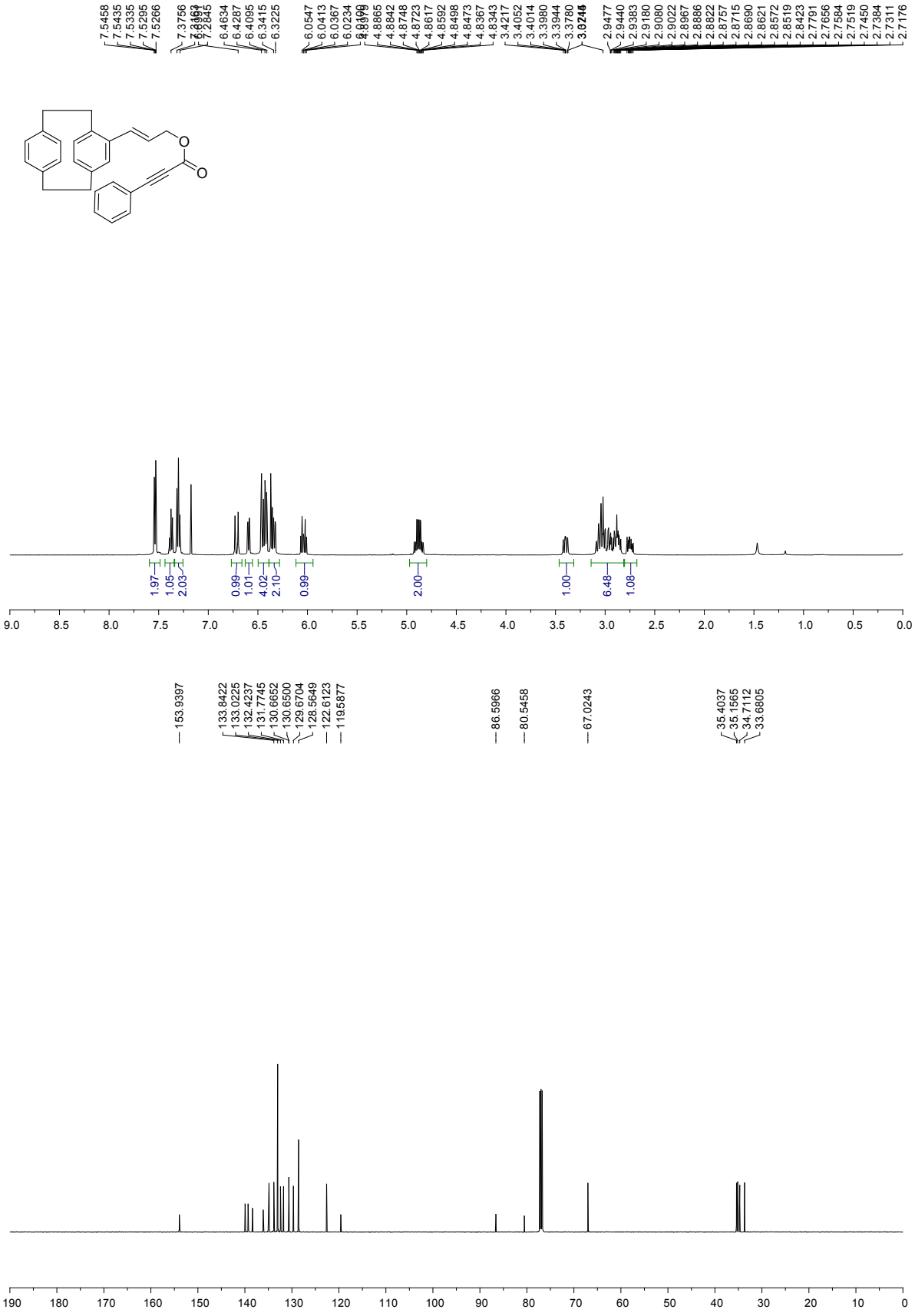
*(2E)-3-{14-Bromotricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl}prop-2-en-1-ol (**3b**)*



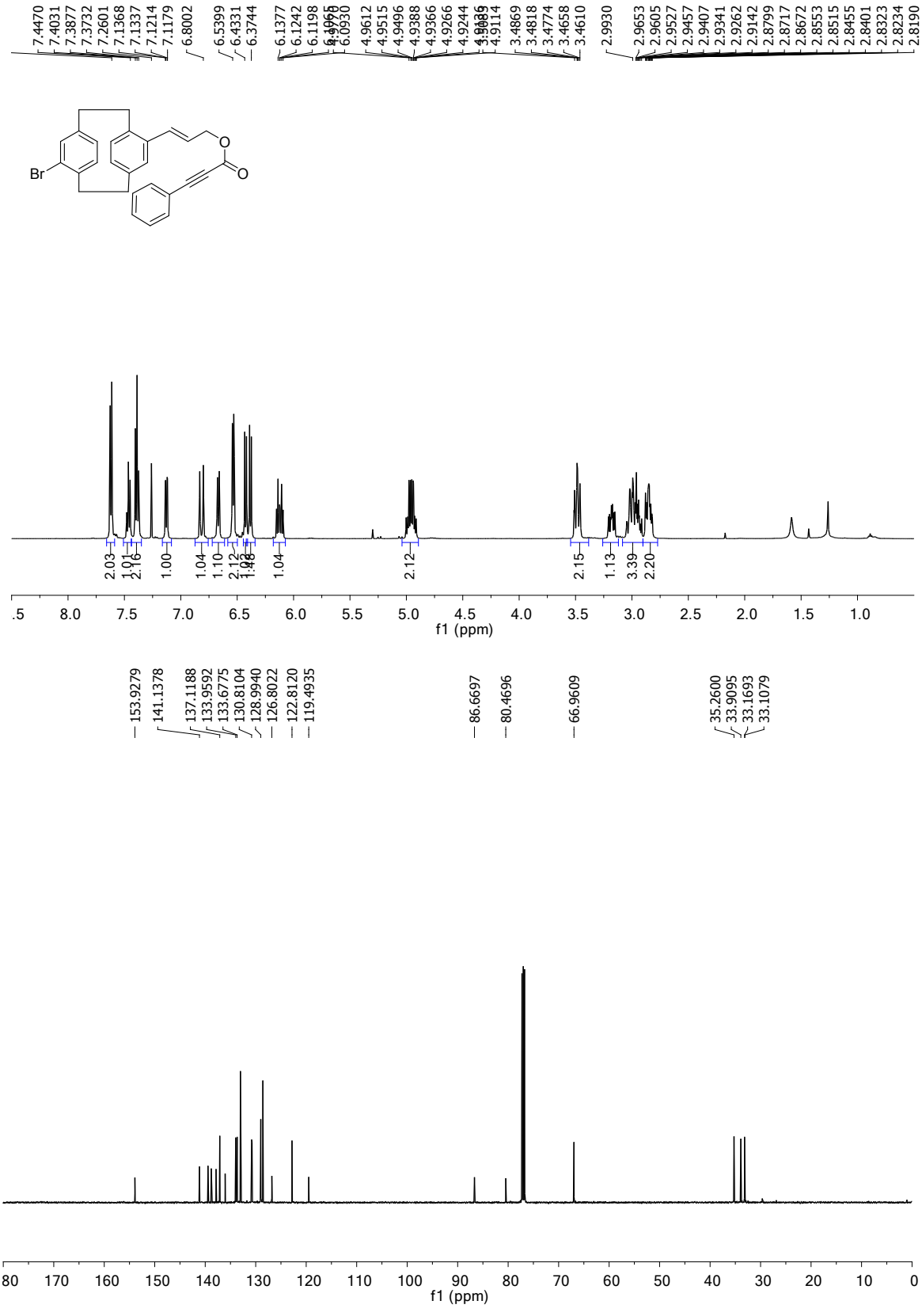
*(2E)-3-[14-(benzylamino)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl]prop-2-en-1-ol (**3c**)*



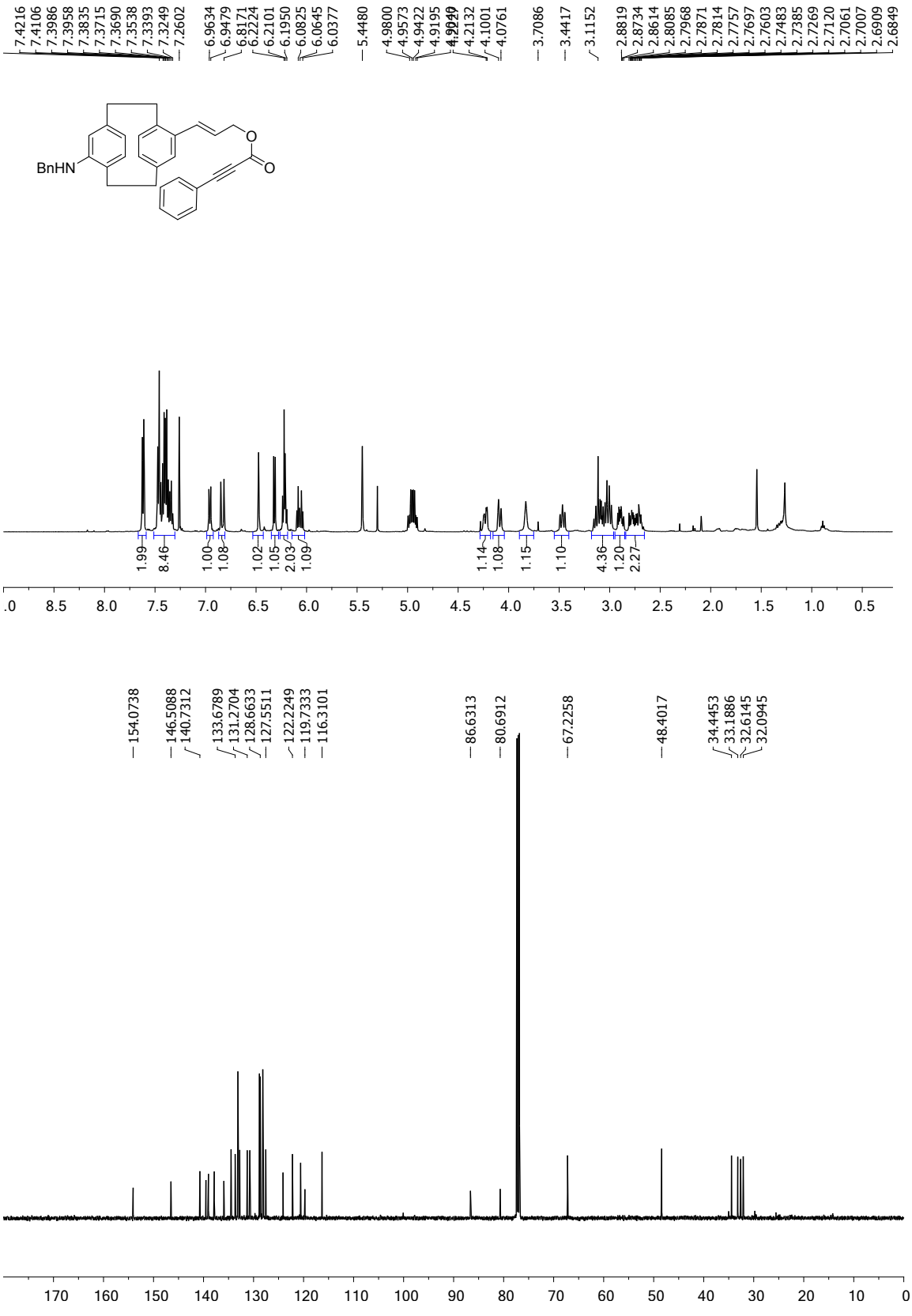
*3-([2.2]Paracyclophen-4-yl)allyl 3-phenylpropiolate (**4a**)*



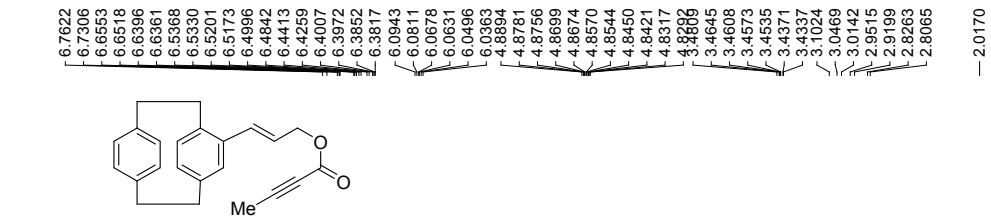
*(2E)-3-{14-Bromotricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl}prop-2-en-1-yl-3-phenylprop-2-ynoate (**4b**)*

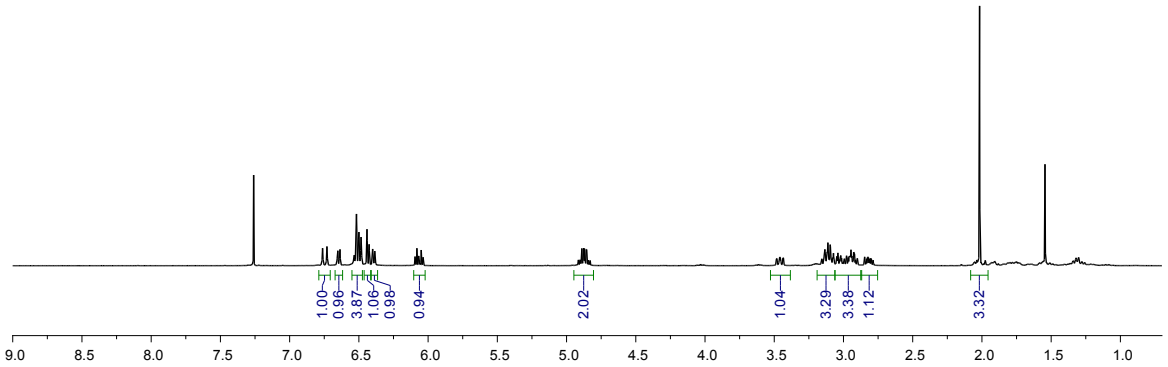


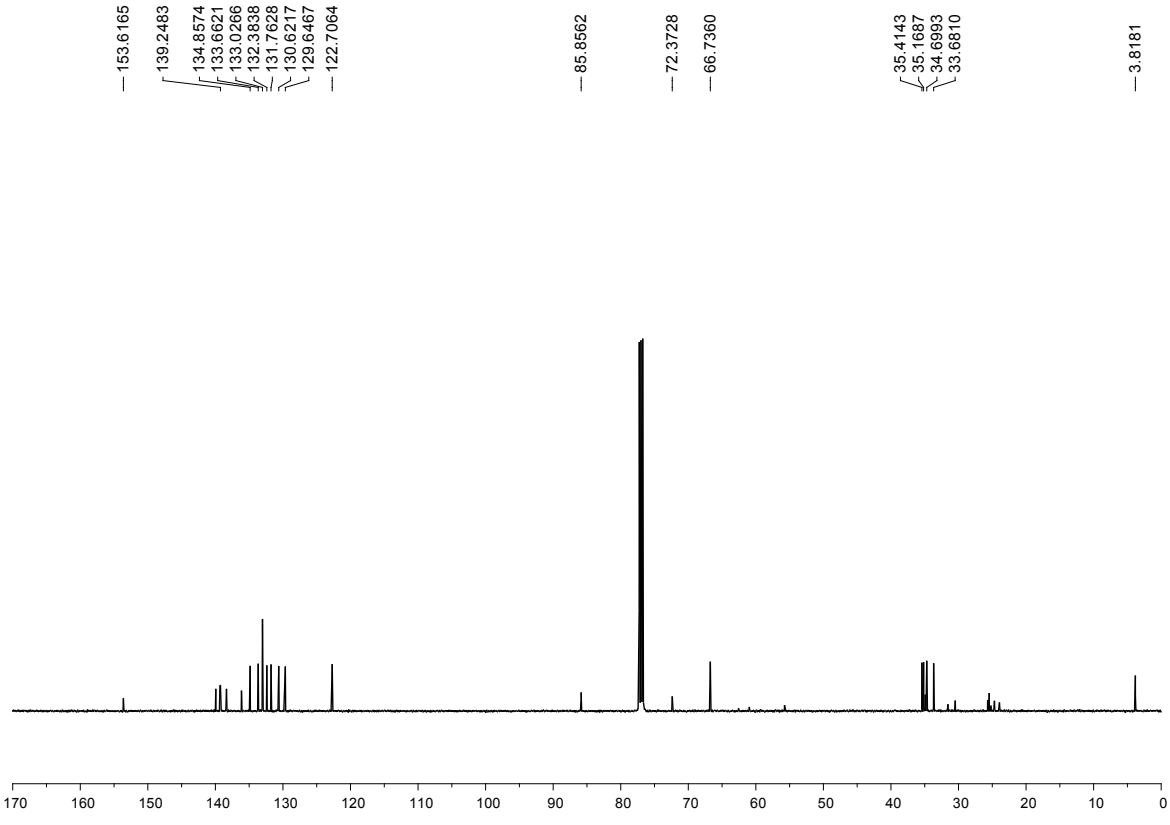
*(2E)-3-[14-(benzylamino)tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl]prop-2-en-1-yl 3-phenylprop-2-ynoate (**4c**)*



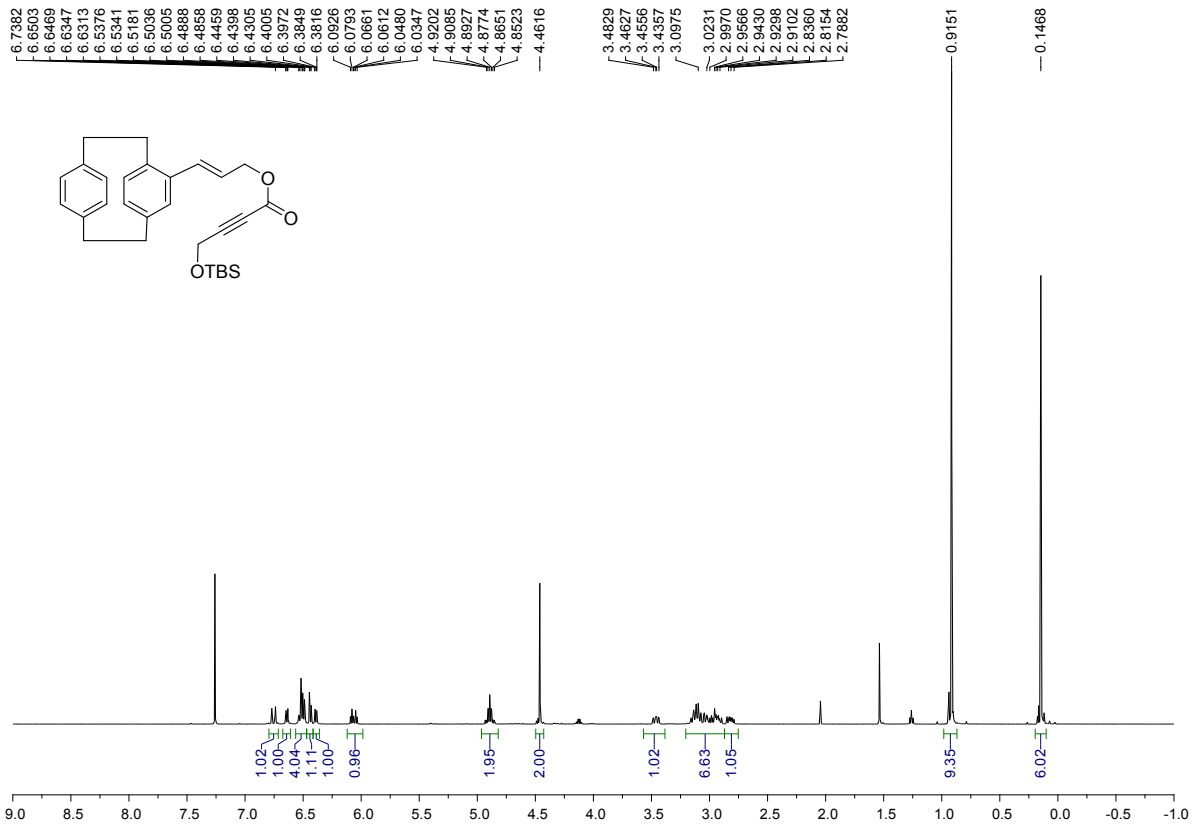
*3-([2.2]Paracyclophen-5-yl)prop-2-en-1-yl but-2-ynoate (**4d**)*

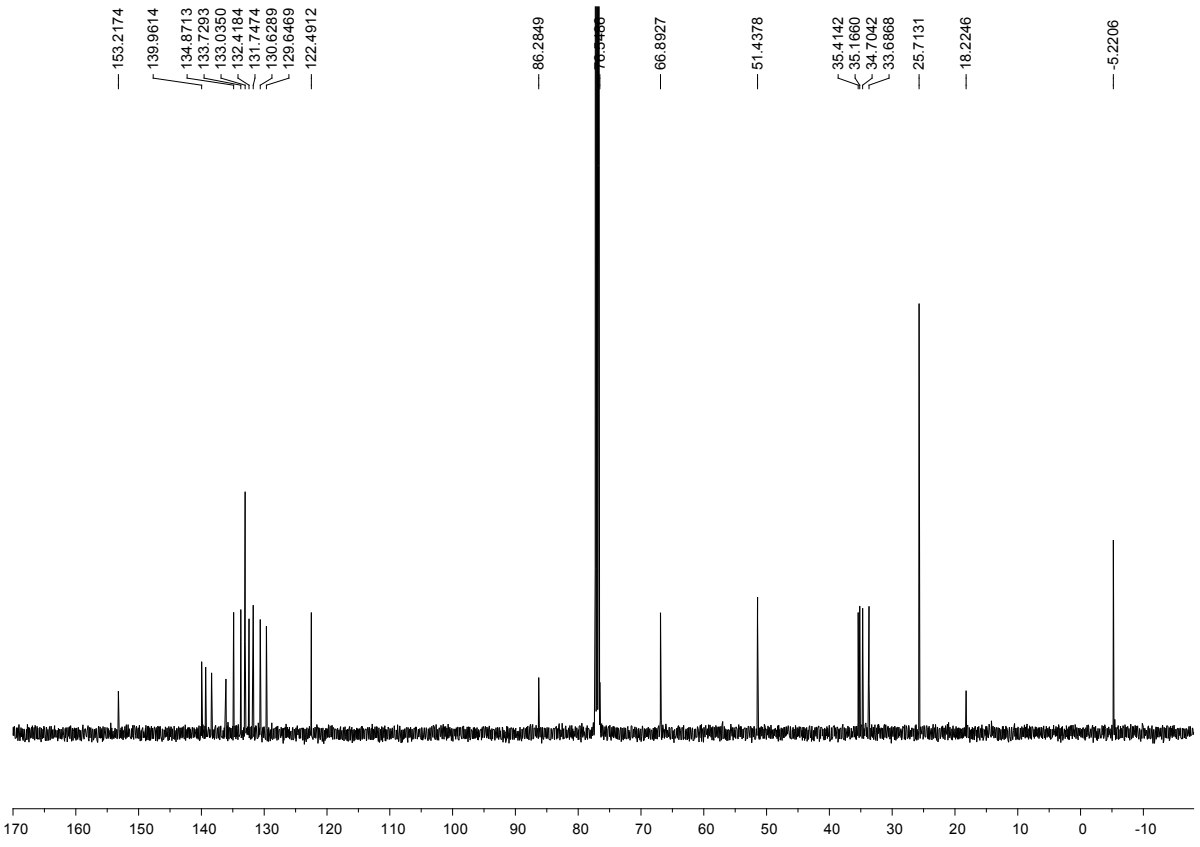




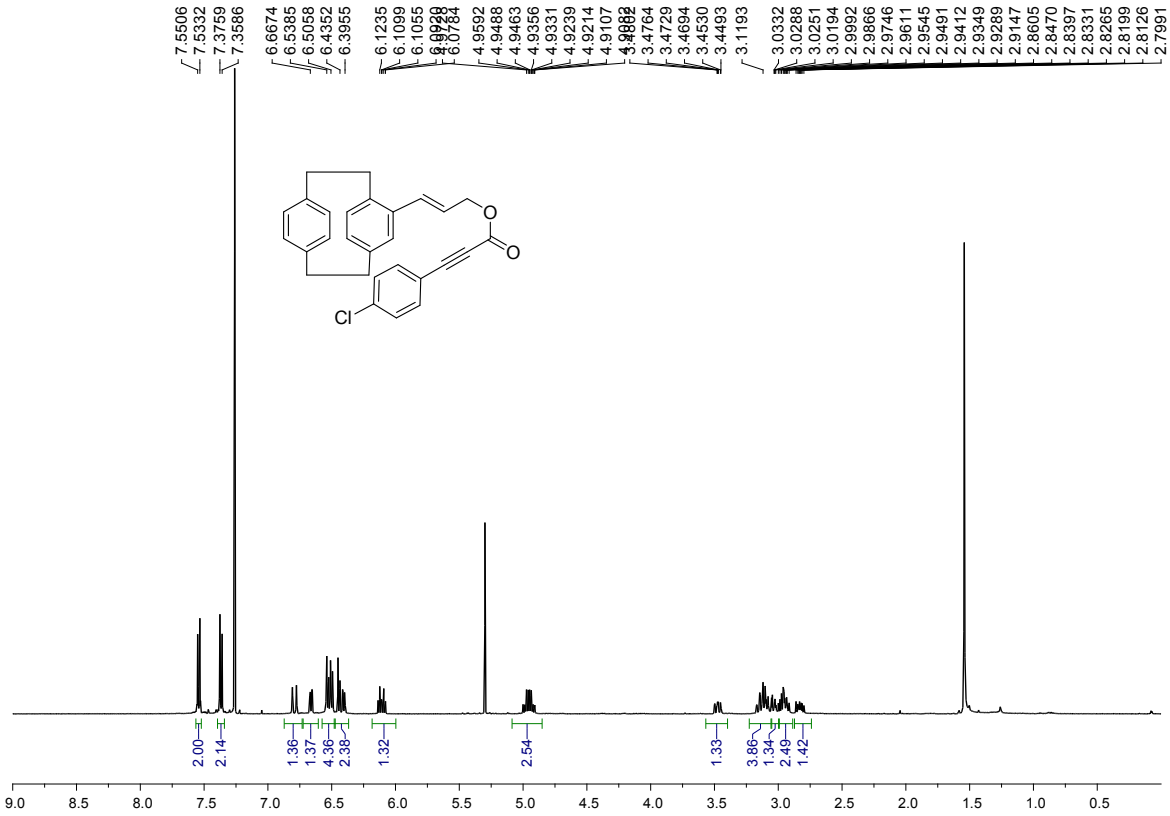


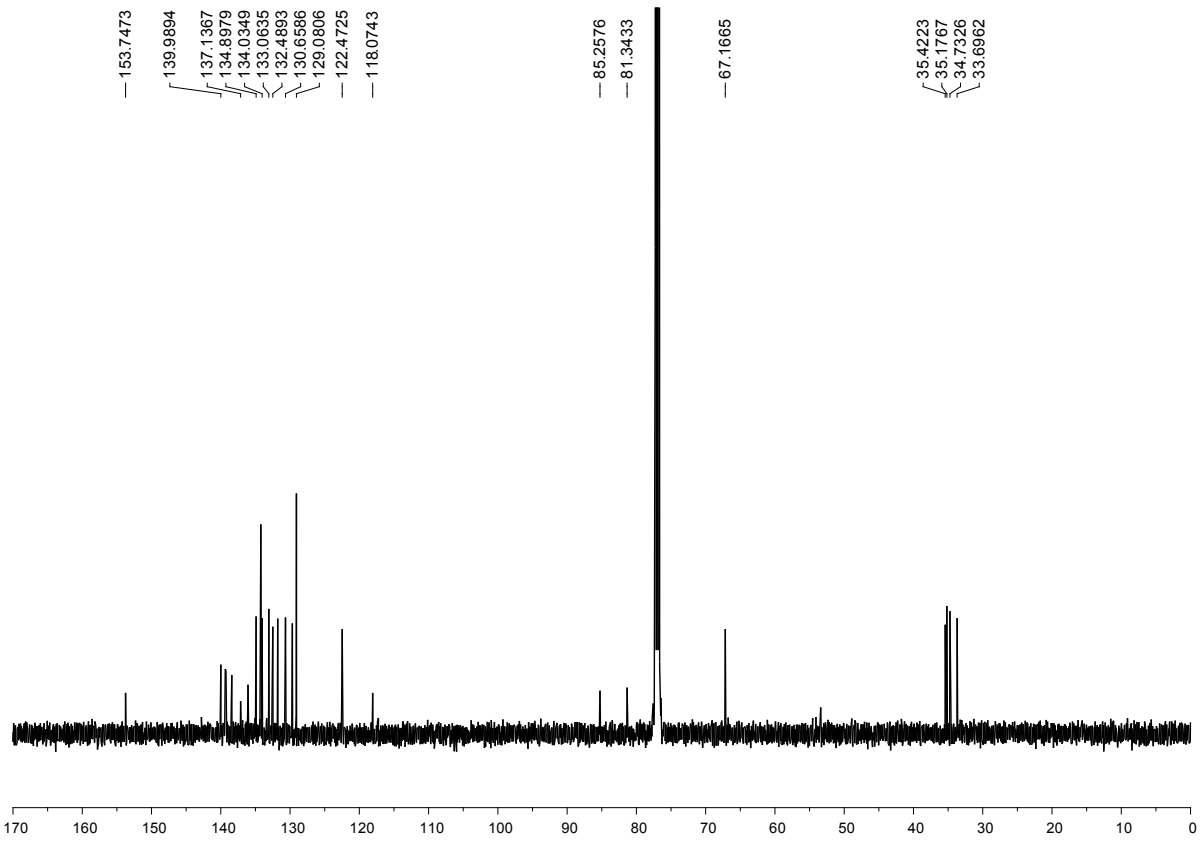
*3-([2.2]Paracyclophen-5-yl)-prop-2-en-1-yl 4-[(tert-butyldimethylsilyl)oxy]but-2-ynoate (**4e**)*



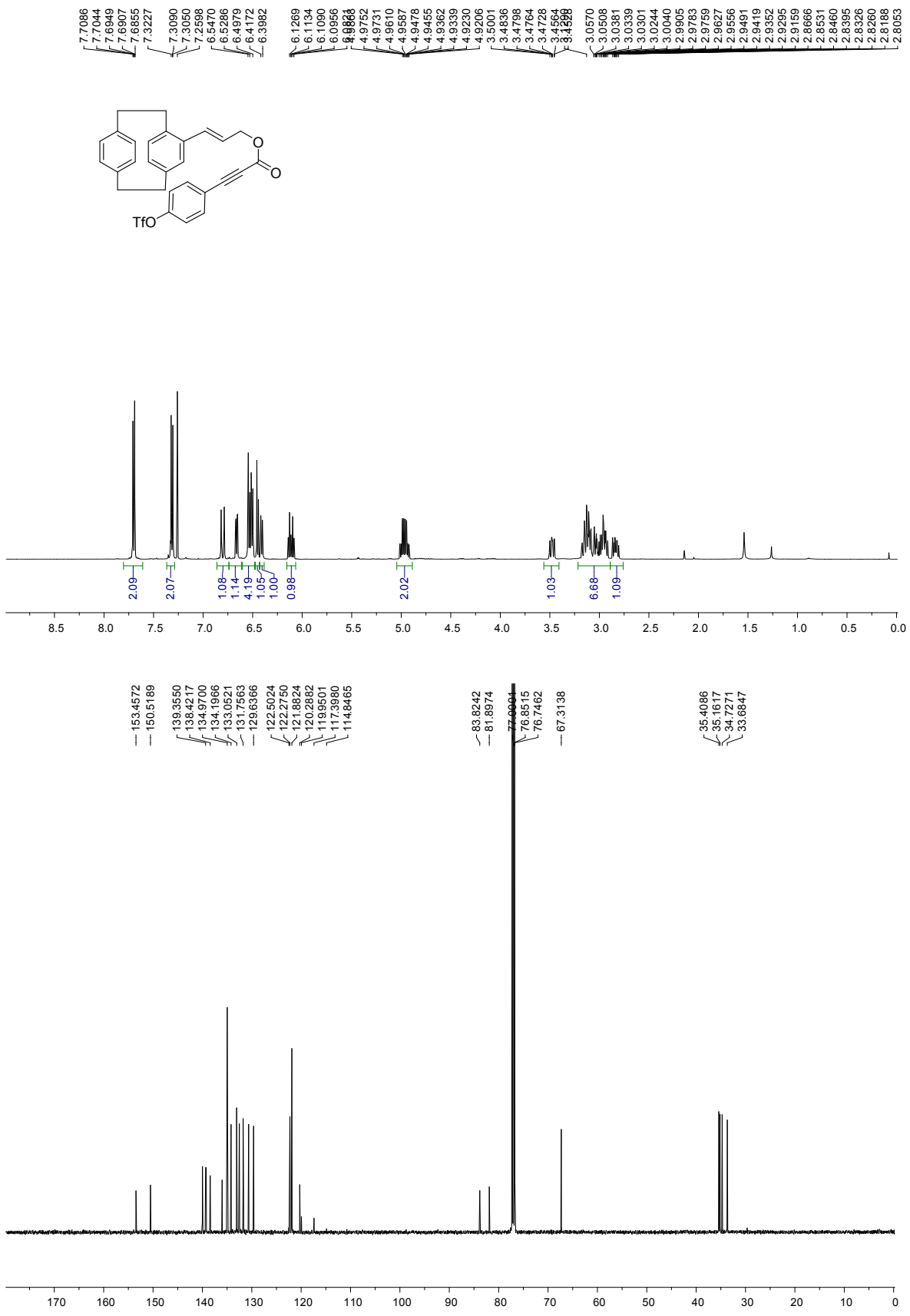


*3-([2.2]Paracyclophen-5-yl)prop-2-en-1-yl 3-(4-chlorophenyl)prop-2-ynoate (**4f**)*

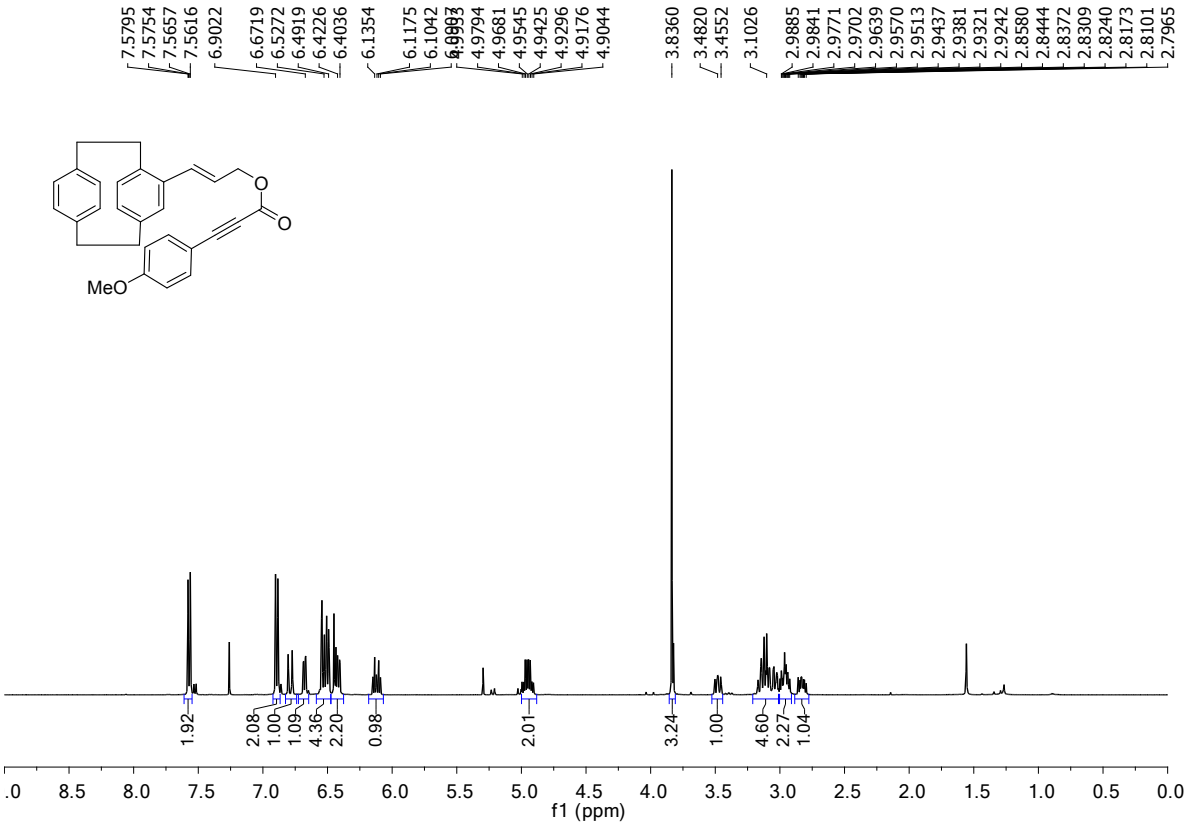


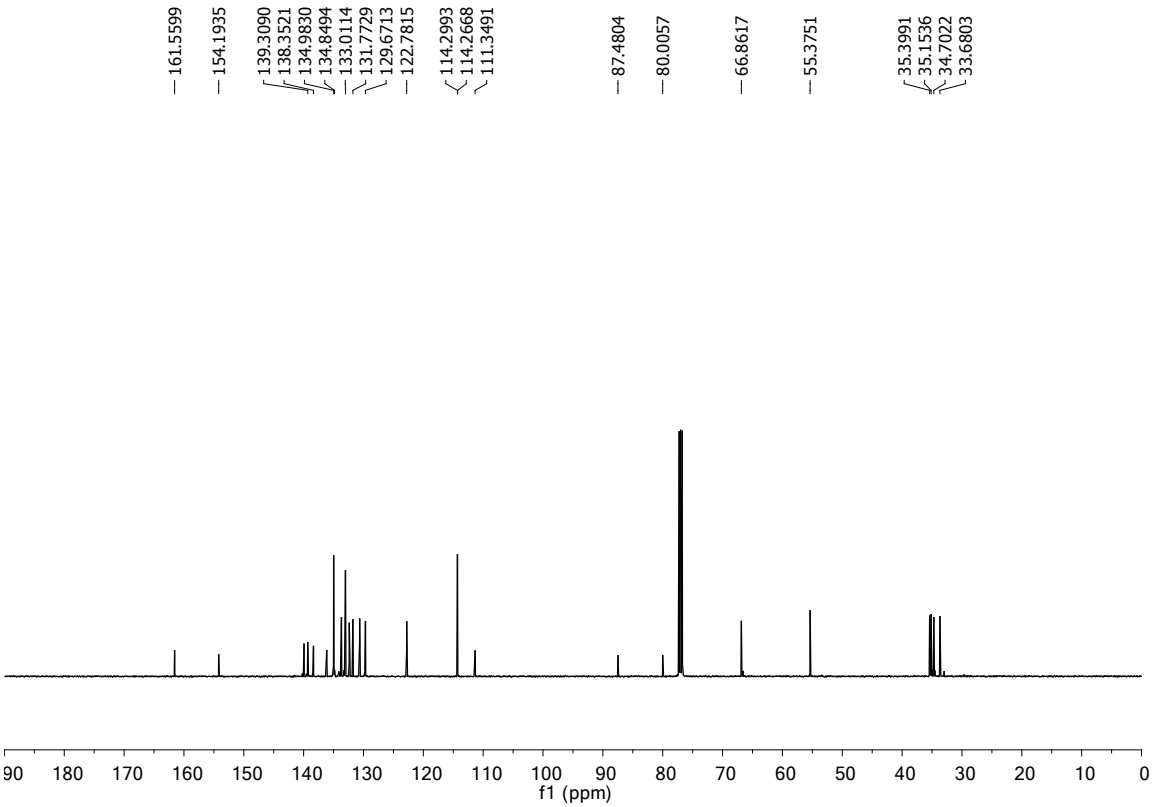


*3-([2.2]Paracyclophen-5-yl)-prop-2-en-1-yl 3-{4-[(trifluoromethyl)sulfonyloxy]phenyl}prop-2-ynoate (**4g**)*

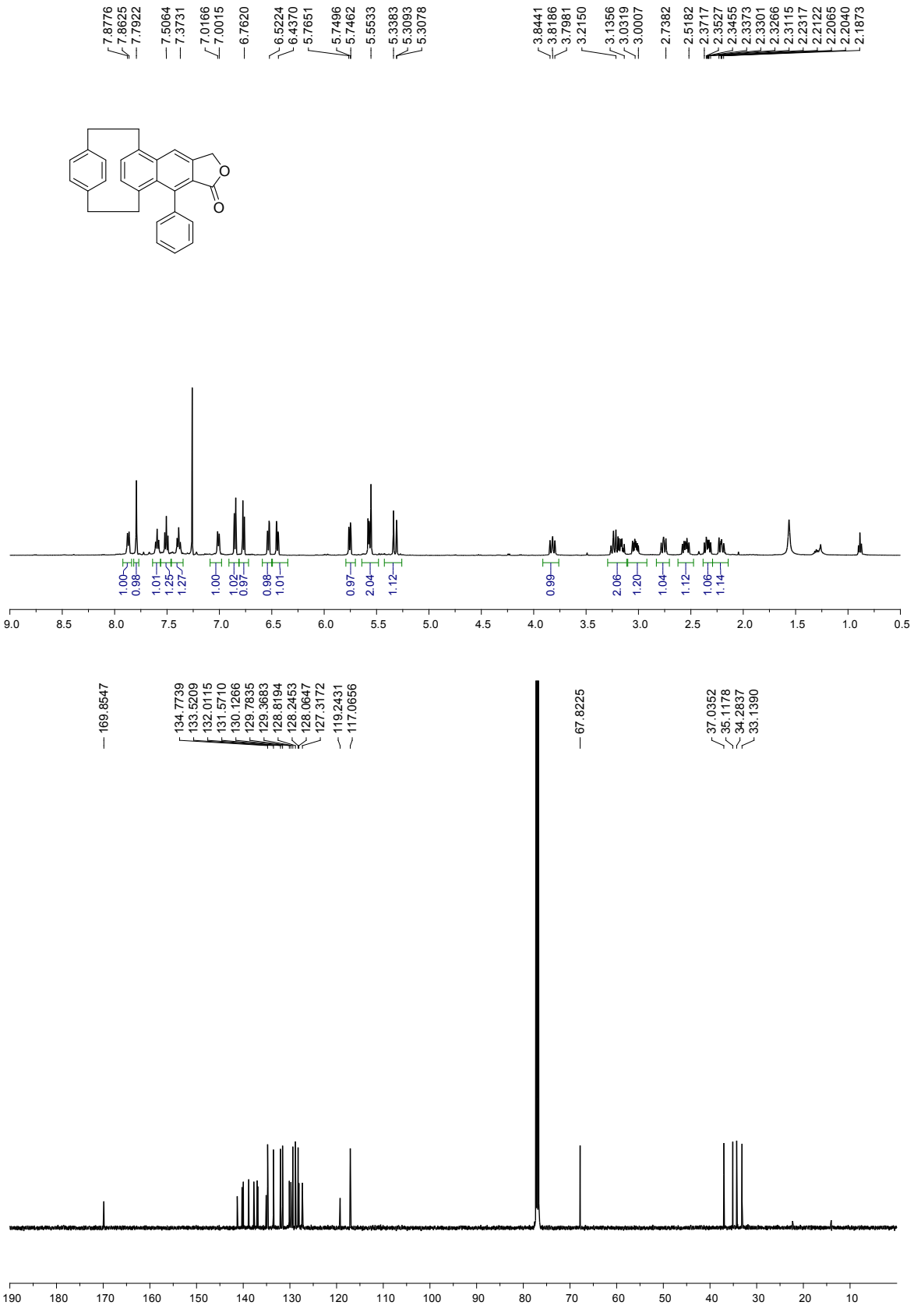


*3-([2.2]Paracyclophen-5-yl)prop-2-en-1-yl 3-(4-methoxyphenyl)prop-2-ynoate (**4h**)*

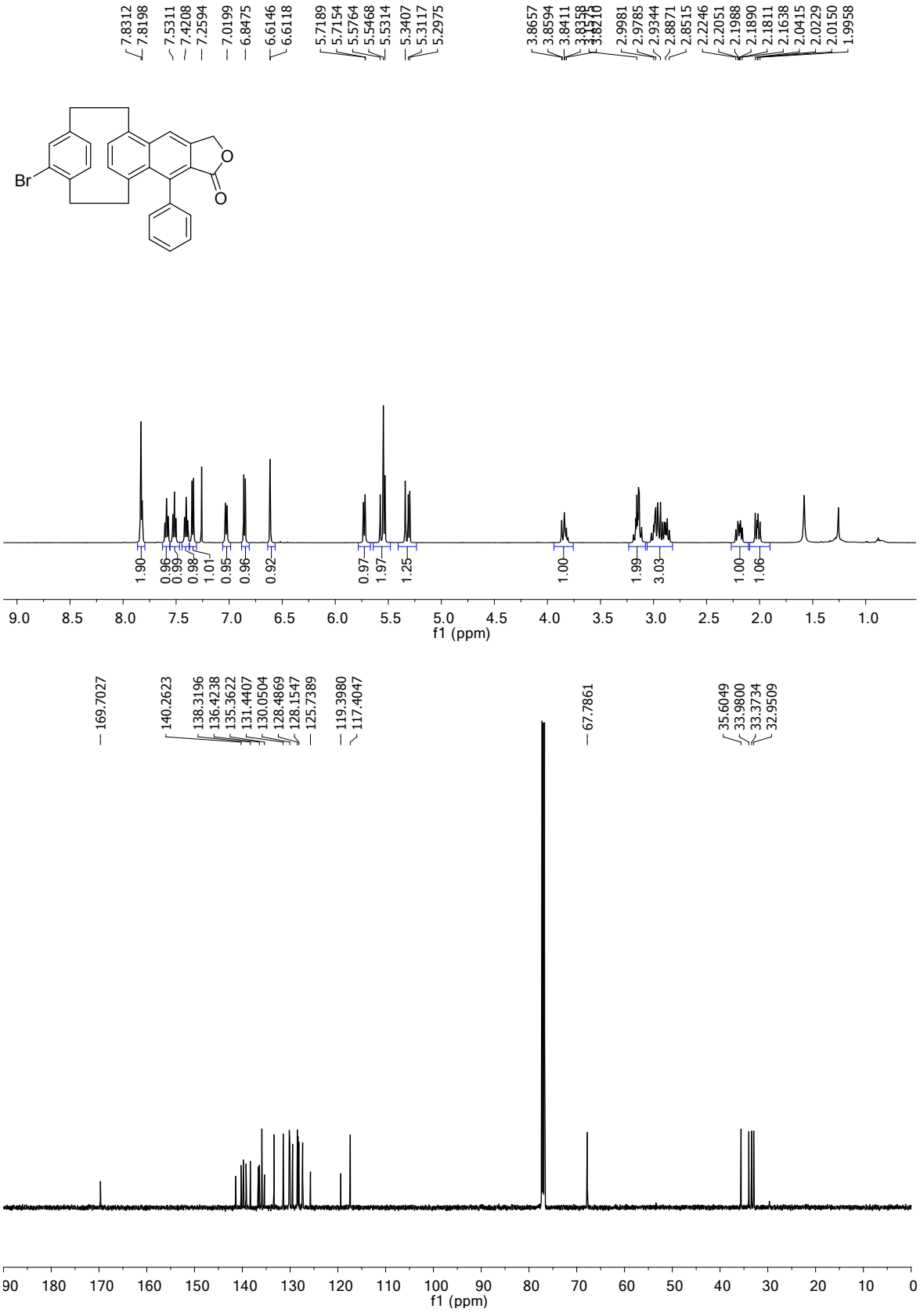




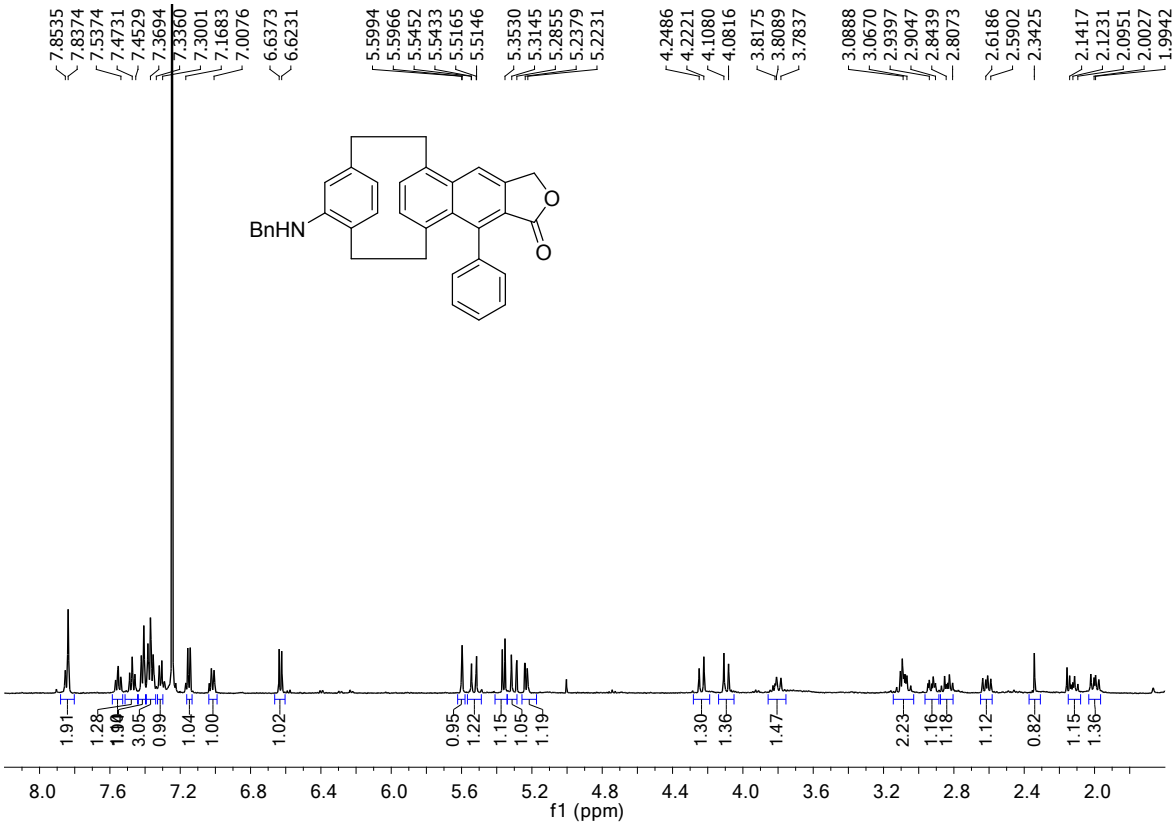
*1^{9}-Phenyl-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^{1}-one (**5a**)*

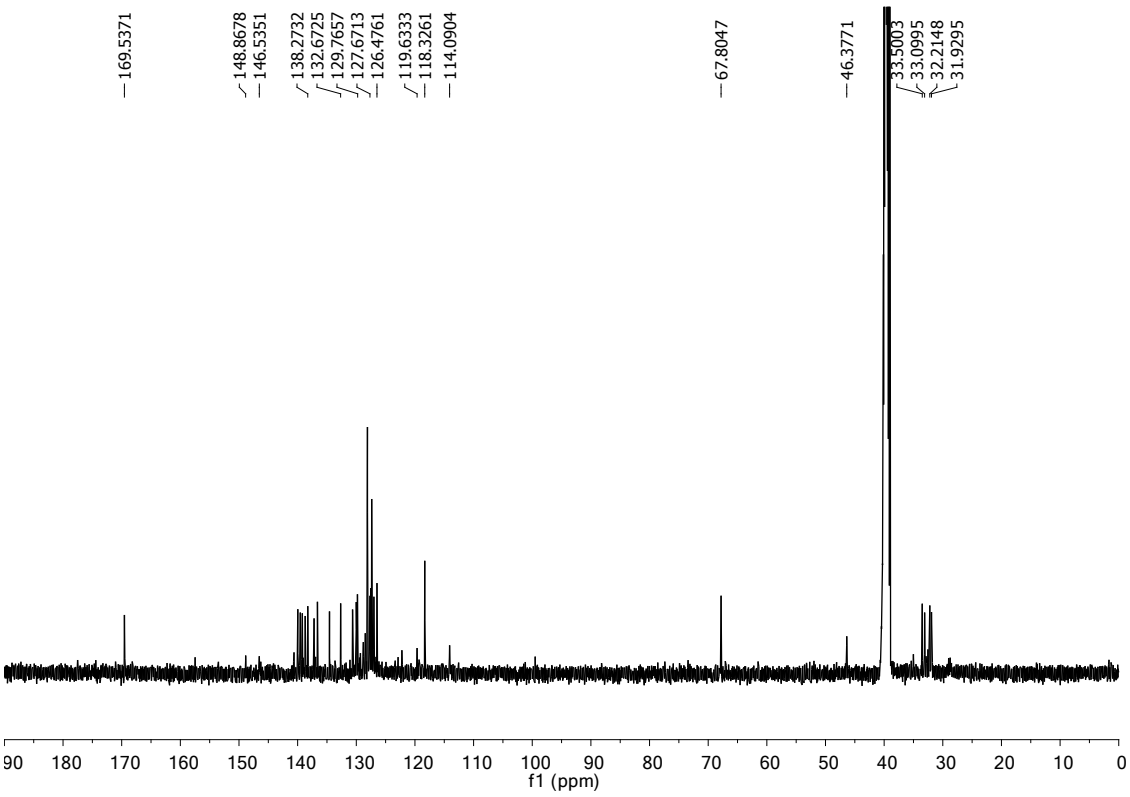


4³-Bromo-1⁹-phenyl-1¹,1³-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1¹-one ***(5b)***

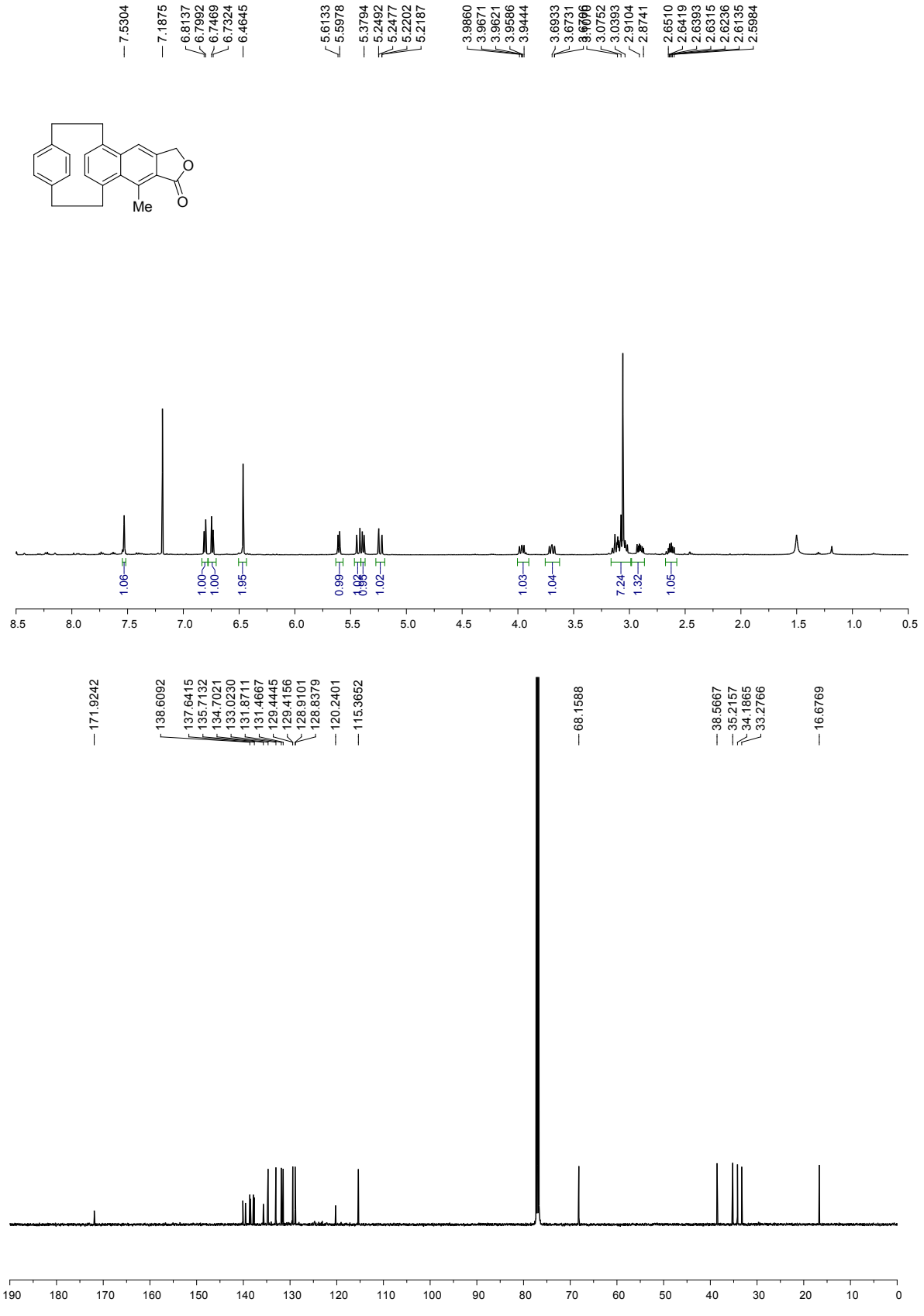


*1^{9}-Phenyl-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^{1}-one (**5c**)*

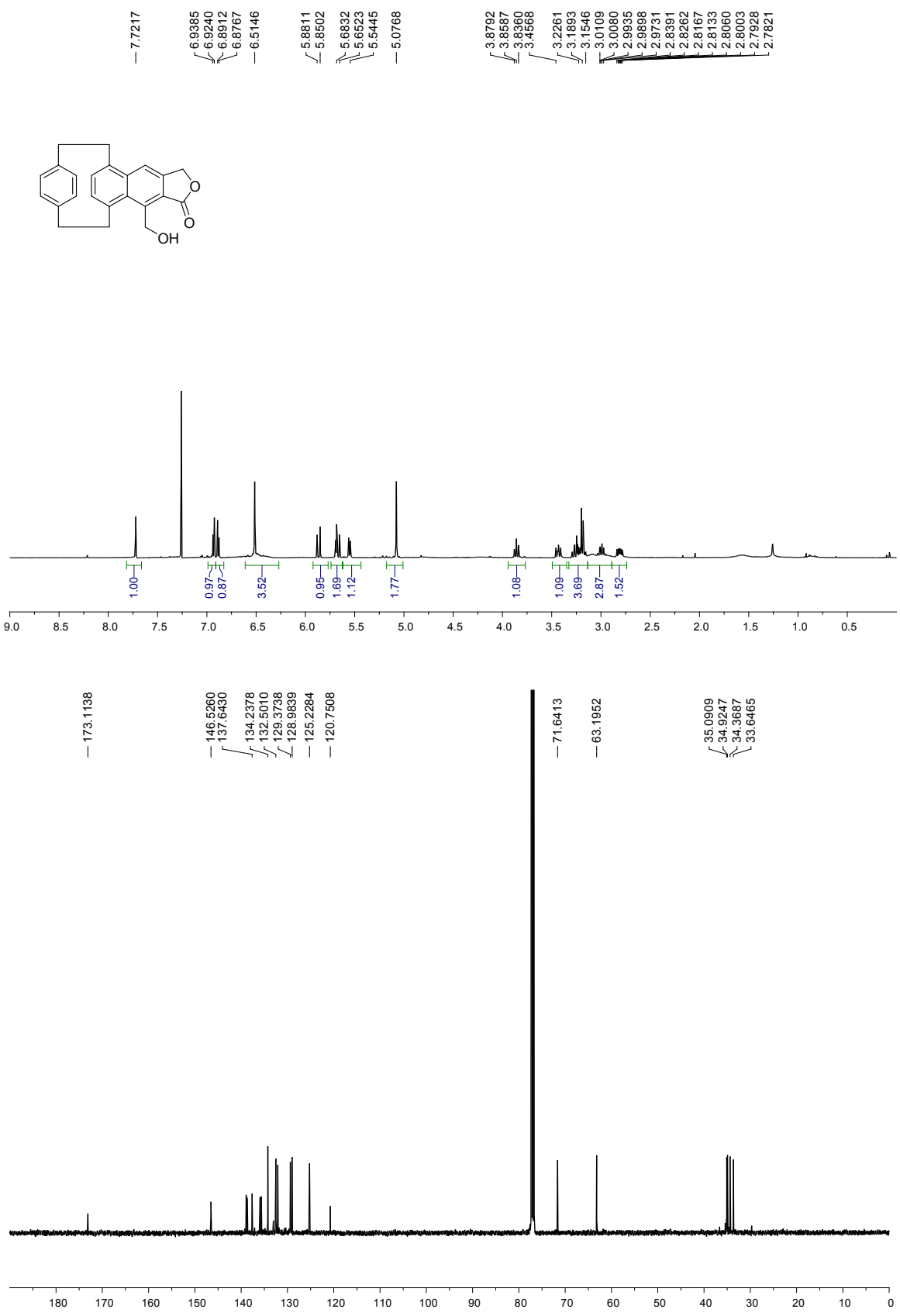




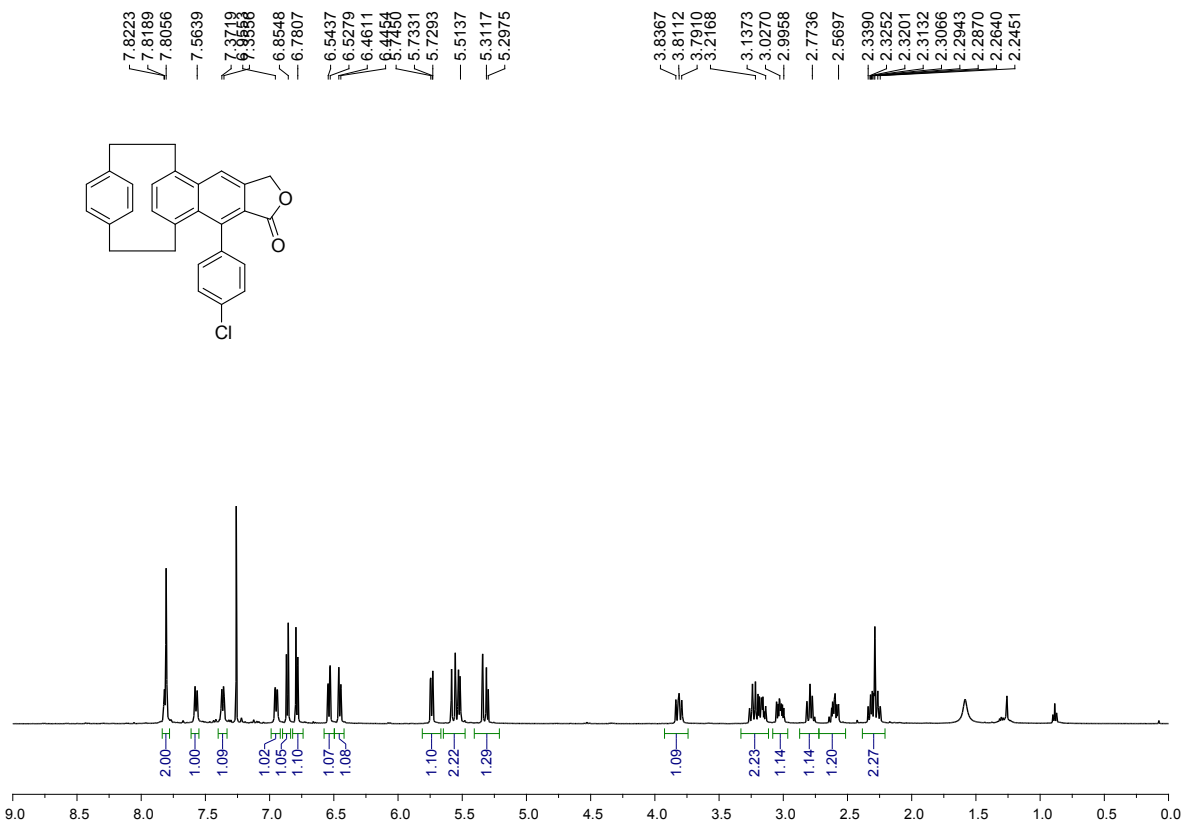
*1^{9}-Methyl-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^{1}-one (**5d**)*

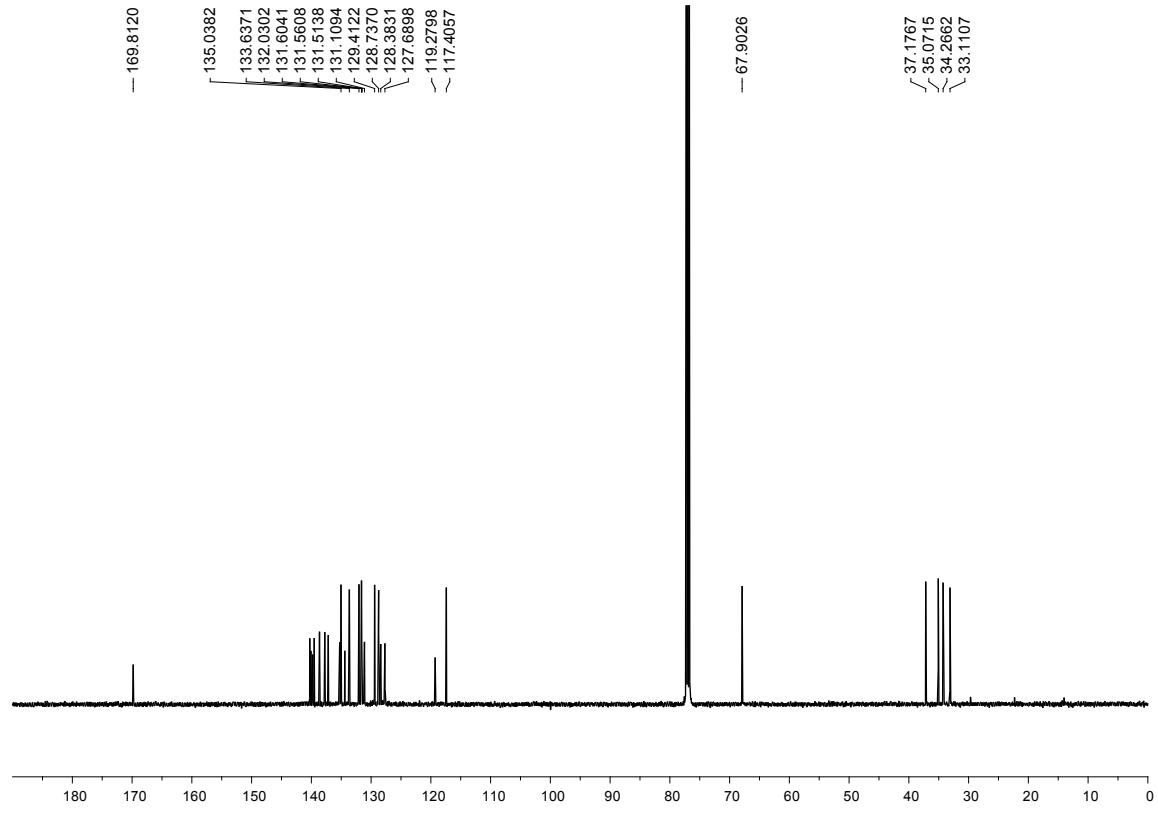


1^{9}-(hydroxymethyl)-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclo-hexaphan-1^{1}-one ***(5e)***

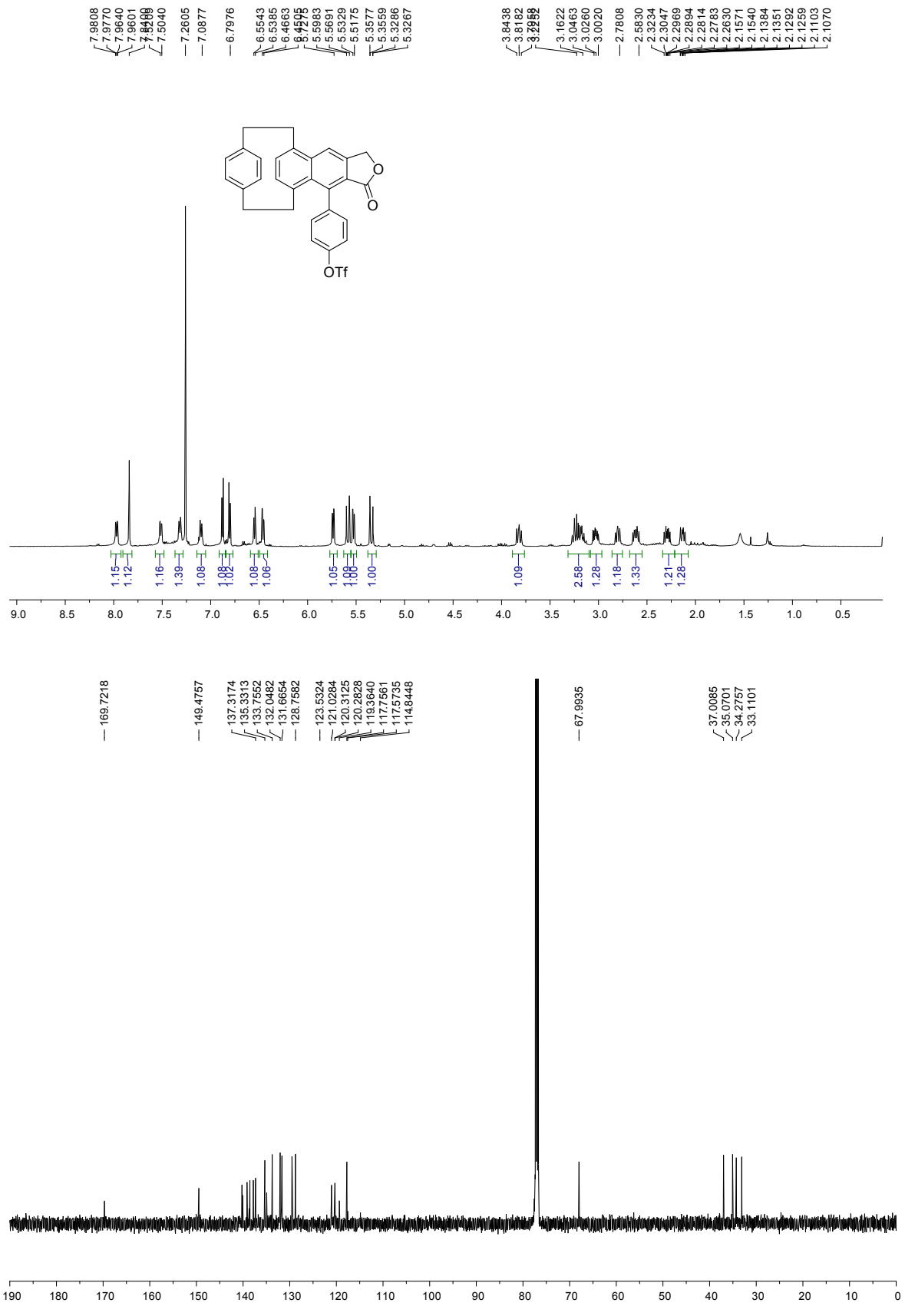


1^{9}-(4-Chlorophenyl)-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclo-hexaphan-1^{1}-one ***(5f)***

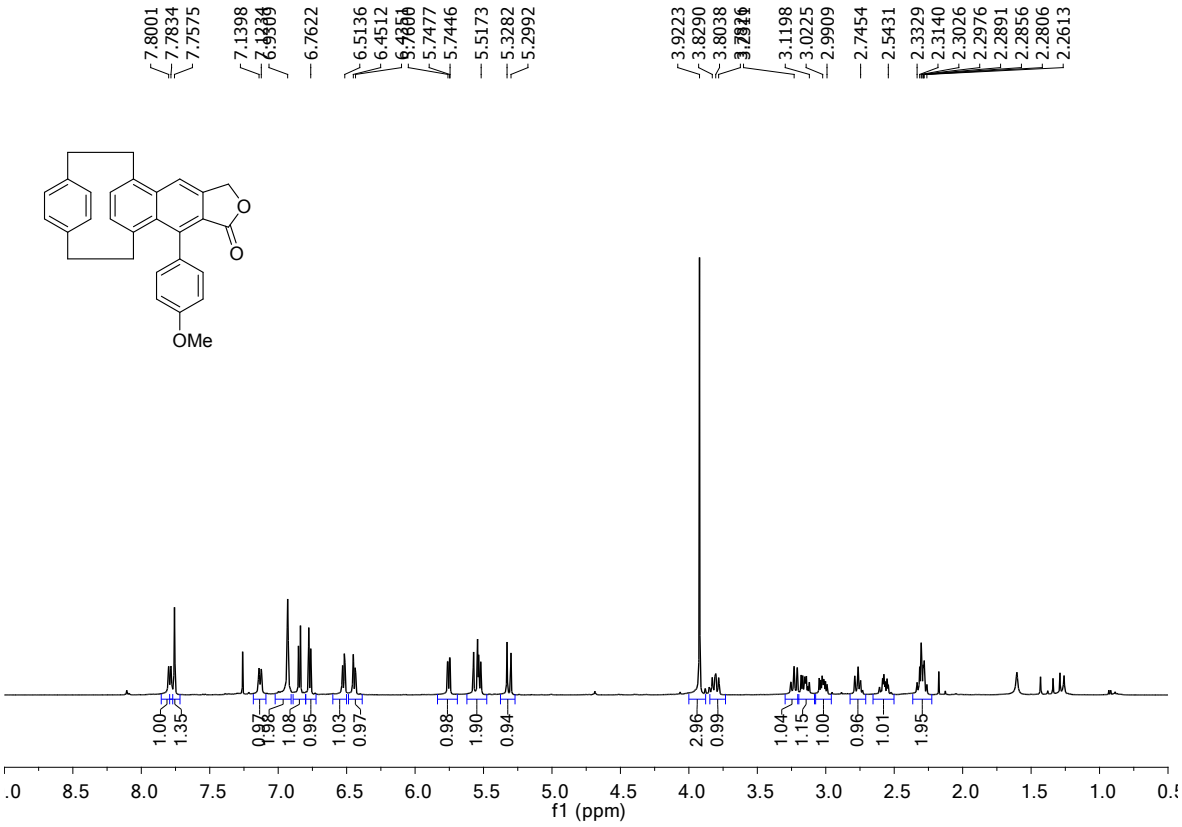


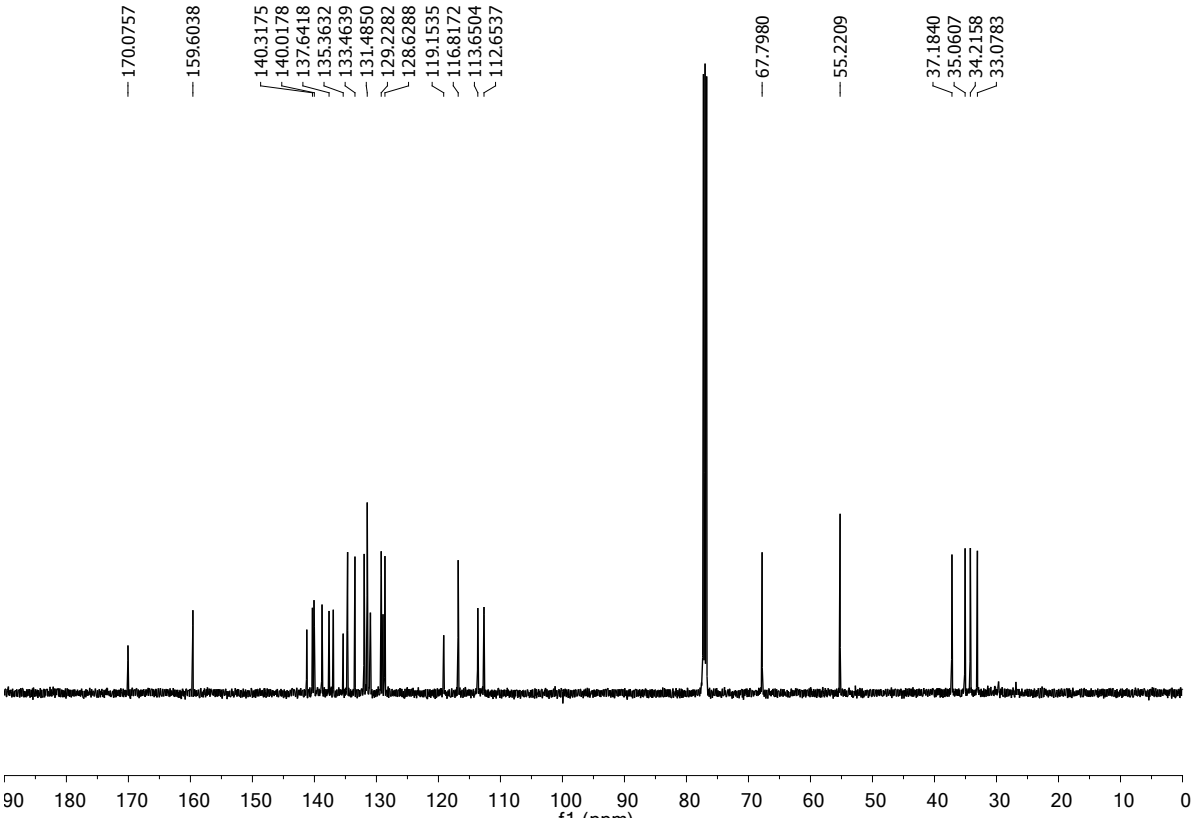


*4-(1³-Oxo-1¹,1³-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphane-1⁴-yl)phenyl trifluoromethanesulfonate (**5g**)*

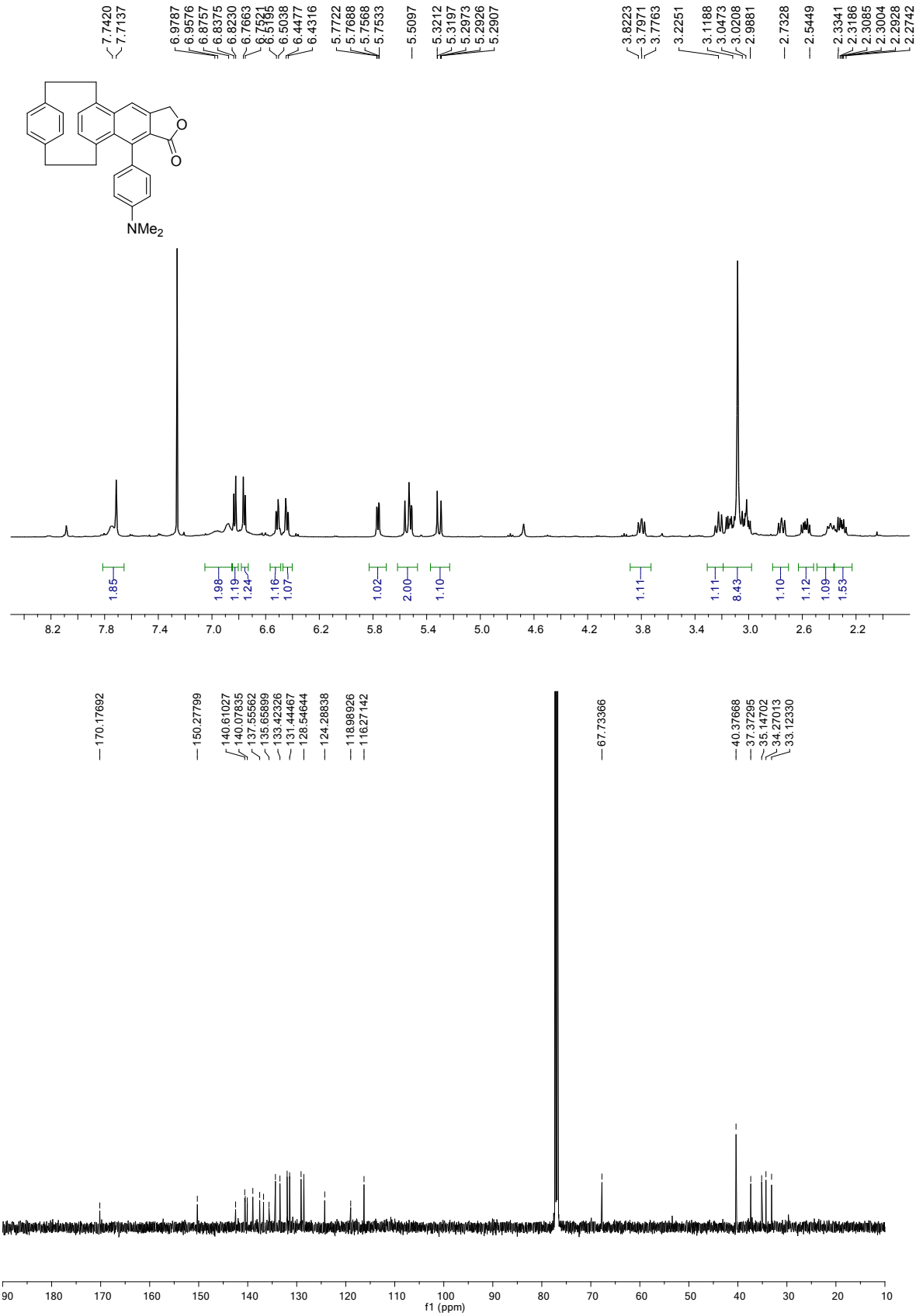


*1^{9}-(4-methoxyphenyl)-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^{1}-one (**5h**)*

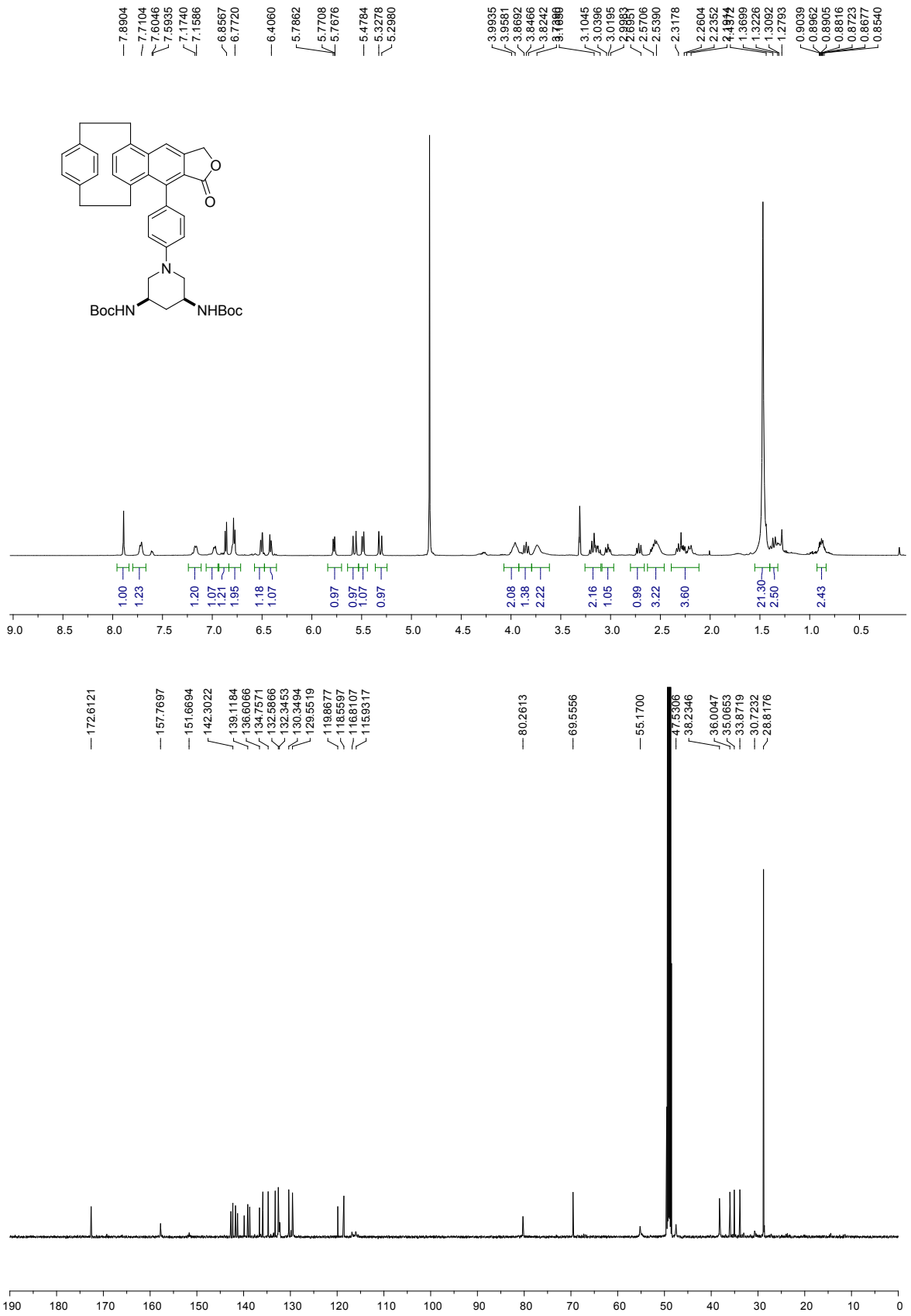




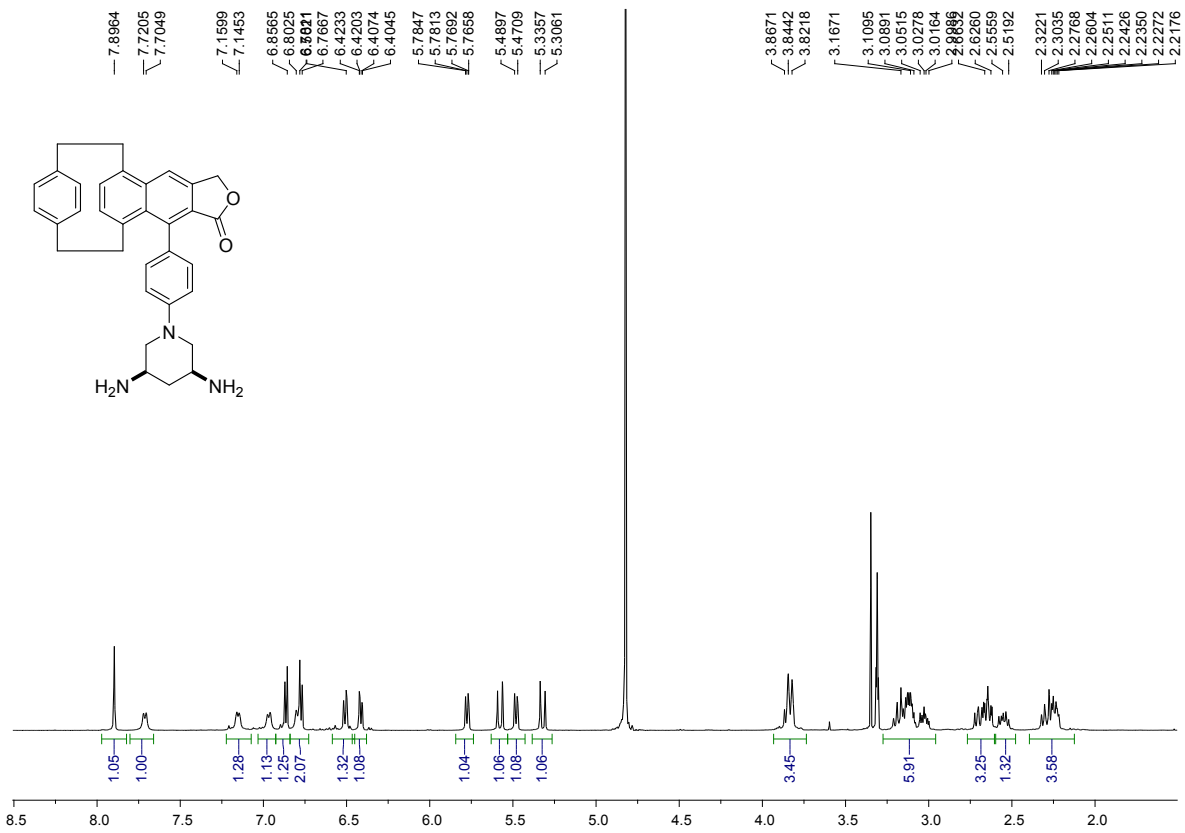
*1^{9}-(4-(Dimethylamino)phenyl)-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzena-cyclohexaphan-1^{1}-one (**6**)*

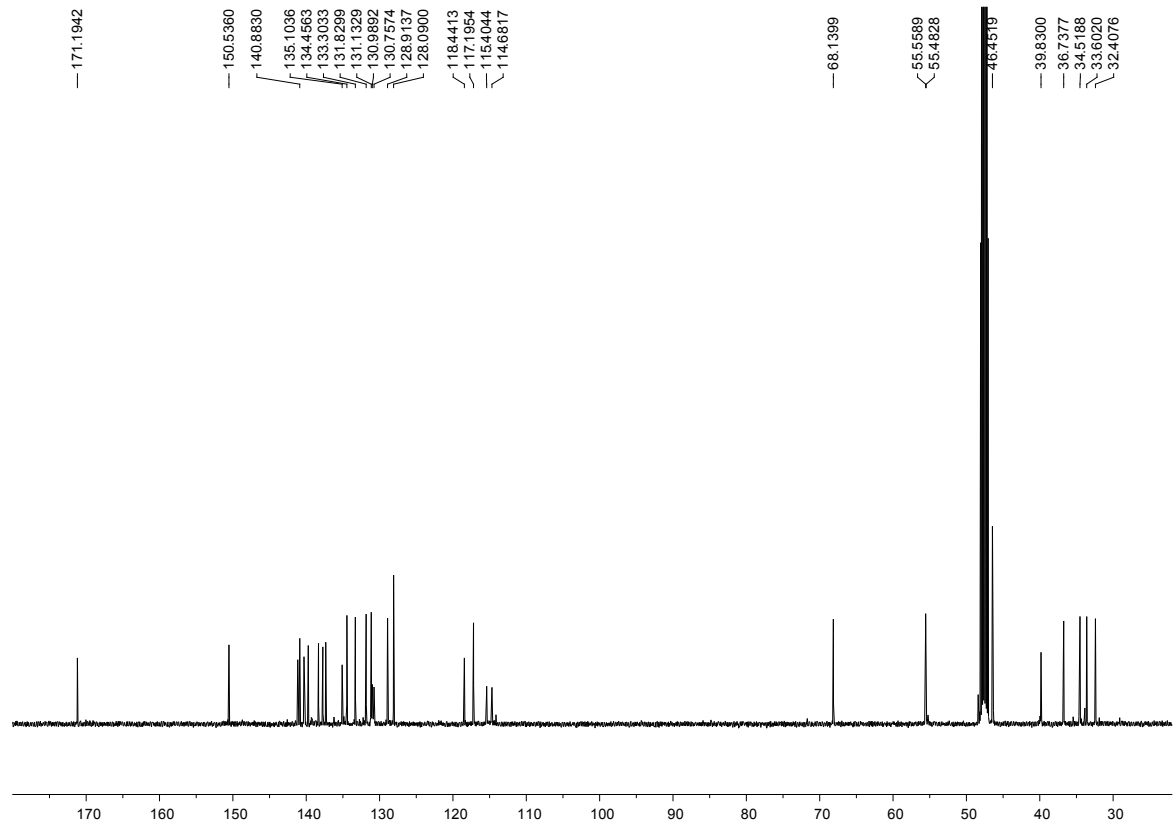


*di-tert-Butyl-1-((4-(1³-oxo-1¹,1³-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzena-cyclohexaphane-1⁴-yl)phenyl)piperidine-3,5-diyl)dicarbamate (**S12**)*

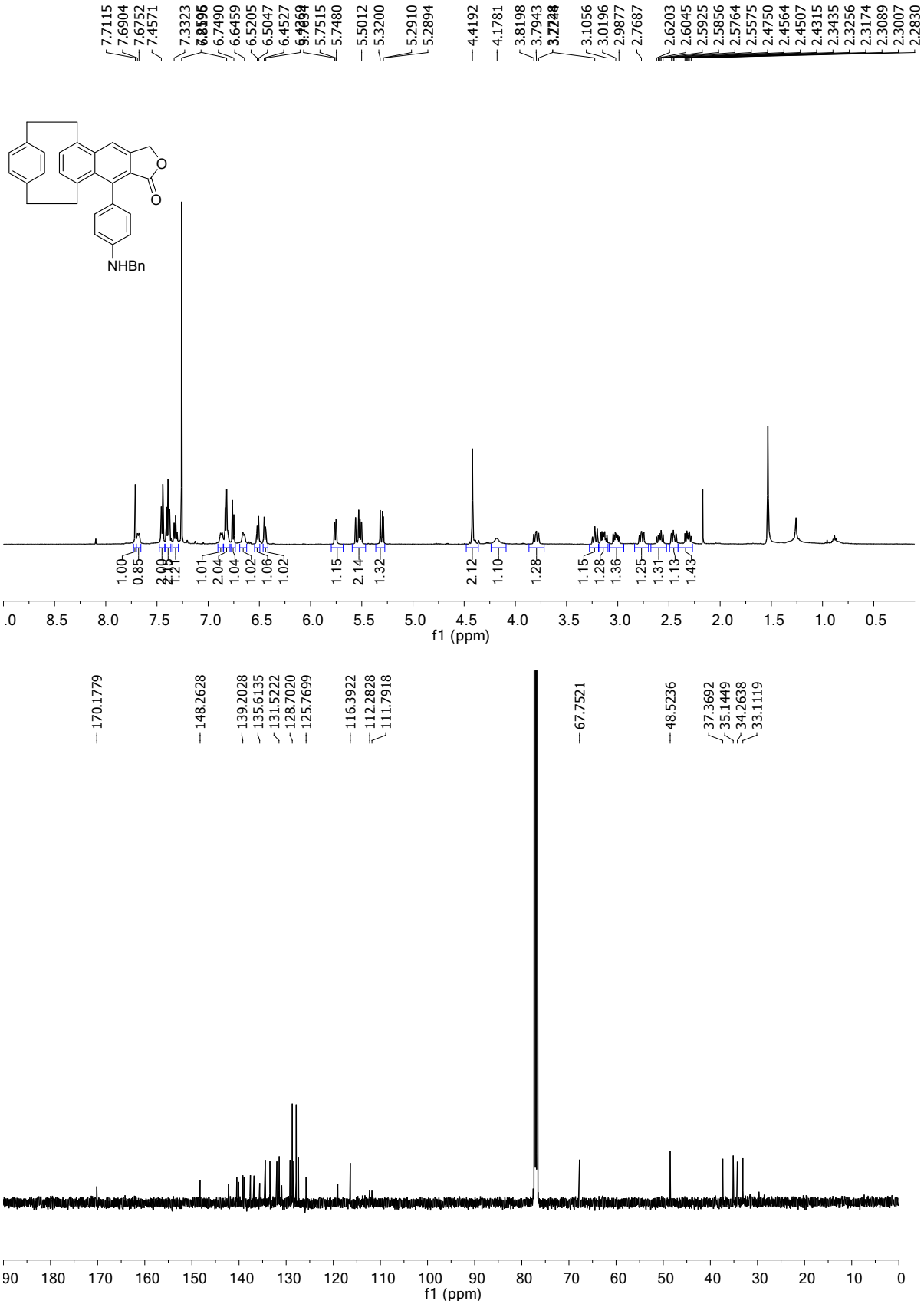


*1^{9}-(4-(3,5-Diaminopiperidin-1-yl)phenyl)-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzena-cyclohexaphan-1^{1}-one (**7**)*





*1^{9}-(4-(benzylamino)phenyl)-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclohexaphan-1^{1}-one (**8**)*



*1^{9}-(4-Hydroxyphenyl)-1^{1},1^{3}-dihydro-1(5,8)-naphtho[2,3-c]furana-4(1,4)-benzenacyclo-hexaphan-1^{1}-one (**9**)*