

Supplementary Information

Three-component tandem benzyl-C-(sp³)-H functionalization via thermally generated arynes with phenazine

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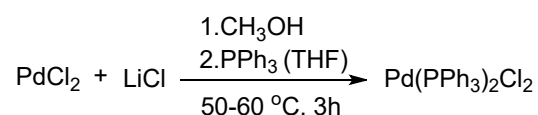
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1. General experimental procedures

The catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. All reactions without catalyst were carried out under air. The chemicals were purchased from Aladdin and TCI Chemicals. All solvents and materials were pre-dried, redistilled or recrystallized before use. ^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on a Bruker Avance 400 spectrometer with $\text{DMSO-}d_6$ as the solvent. Chemical shifts are reported in ppm by assigning TMS resonance in the ^1H NMR spectra as 0.00 ppm and $\text{DMSO-}d_6$ resonance in the ^{13}C spectra as 39.5 ppm. All coupling constants (J values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 300–400 mesh. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. The FT-IR spectra were recorded from KBr pellets or thin film from CHCl_3 on the NaCl window in the 4000–400 cm^{-1} ranges on a Nicolet 5DX spectrometer. High-resolution mass spectra were recorded on an Agilent 6210 ESI/TOF MS mass spectrometer. X-ray Crystallography diffraction data of **4a**, **4d**, **4j**, **4x**, **4A**, **4B**, **4F**, **4H** and **4I'** were collected at room temperature with a Bruker SMART Apex CCD diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite monochromator using the ω -scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

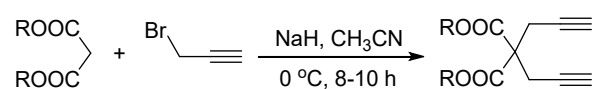
(1) General procedure for preparation of tetrayne 1:

Preparation of catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$:



3.54 g PdCl_2 and 4 g LiCl were mixed in a 500 mL three-necked flask with 150–200 mL methanol as solvent, magnetically stirred and heated in oil bath at 50–60 $^\circ\text{C}$. After the solid was dissolved, 25 mL of THF (removed water with sodium wire) containing 13.10 g PPh_3 were added in the above three-necked flask, and the color of the solution changed from brown to yellow, reflux reaction for 3 hours. After reaction solution cooled, filtered and washed with anhydrous ethanol, yellow solid $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ catalyst was obtained finally.

Preparation of diyne substrates:

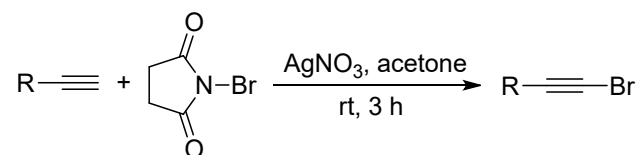


R = Me, Et, $i\text{Pr}$

10 g NaH (60%) and 200–300 mL acetonitrile were added in 500 mL three-necked flask with magnetic stirring. 100 mmol malonate and 30 g 3-bromopropyne (98%) were added in the above 500 mL three-

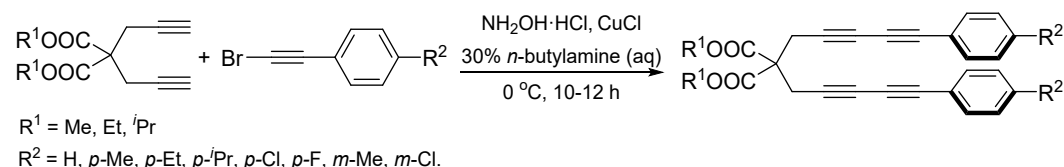
necked flask dropwise in turn by separatory funnel, magnetically stirred for 8-10 h under ice-water bath. The organic phase was extracted with ethyl acetate and dried with anhydrous MgSO_4 . The solvent was evaporated in vacuo and diyne substrates as yellow solid were obtained finally.

Preparation of brominated alkynes:



21.36 g 1-bromopyrrolidine-2, 5-dione (NBS), 0.85 g AgNO_3 , and 100 mmol phenylacetylene or substituted phenylacetylene or alkyl alkyne were added in 250 mL three-necked flask in turn, 150 mL acetone as a solvent, magnetically stirred at room temperature for 3 h. The organic phase was extracted with *n*-hexane and dried with anhydrous MgSO_4 . The solvent was evaporated in vacuo and brominated alkynes compound as brown solid were obtained finally.

Preparation of tetrayne substrates:



0.20 g $\text{NH}_2\text{OH}\cdot\text{HCl}$, 0.60 g CuCl and 40 mmol diyne substrate were added in 500 mL three-necked flask, protected with anhydrous anaerobic conditions under argon. After 0.5 h, 100ml of 30% *n*-butylamine aqueous solution (63.0 g H_2O +27.0 g *n*-butylamine) was used as solvent, and then 100 mmol brominated aryl alkyne were added subsequently, magnetically stirred for 10-12 h under ice-water bath. The organic phase was extracted with ethyl acetate and dried with anhydrous MgSO_4 . It was separated by column chromatography on silica gel to obtain tetrayne substrate as white solid finally.

(2) General procedure for preparation of the novel fused all-carbon annulenes 4a-4J:

Tetraynes (1.0 equiv.) and phenazine (**2a**) were added to 3.0 or 2.0 ml benzyl solvents (**3a-3e**), the mixture was stirred in Schlenk tube for 3 hours at 120 $^\circ\text{C}$ (oil bath temperature). Then the reaction mixture was cooled to room temperature, quenched with sat. NaCl aq. (30 mL) and extracted with ethyl acetate (3×10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 60/1) to afford the novel fused N,N'-disubstituted dihydrophenazine derivatives.

About the screening of the optimized conditions of this three-component tandem benzyl- $\text{C}(\text{sp}^3)\text{-H}$ functionalization via thermally generated arynes with phenazine, we listed the following table, which

explored from the reaction solvent, temperature and reaction time, respectively. The following tables are listed.

Table 5 Conditional optimization for the reaction ^{a,b}

Entry ^a	Temp. (°C)	Solvent	Time (h)	Yield (%) ^b
1	120	toulene	3	84
2	90-120	acetonitrile	3-12	0
3	90-120	acetonitrile + toulene	3-12	0
4	90-120	1,2-dichloroethane + toulene	3-12	0
5	90-120	1,2-dichloroethane	3-12	0
6	90	toulene	3	41
7	100	toulene	3	69
8	110	toulene	3	73
9	120	toulene	3	84
10	130	toulene	3	84
11	120	toulene	1	15
12	120	toulene	2	58
13	120	toulene	3	84
14	120	toulene	4	84
15	120	toulene	5	84

^aReaction conditions: tetraynes (1.0 mmol), Phenazine (1.0 equiv) and solvent (3 mL). ^bIsolated yield.

Table 6 Conditional optimization for the reaction ^{a,b}

Entry ^a	Temp. (°C)	Solvent	Time (h)	Yield (%) ^b
1	120	ethylbenzene	2	72

2	90-120	acetonitrile	3-12	0
3	90-120	acetonitrile + ethylbenzene	3-12	0
4	90-120	1,2-dichloroethane + ethylbenzene	3-12	0
5	90-120	1,2-dichloroethane	3-12	0
6	90	ethylbenzene	2	30
7	100	ethylbenzene	2	54
8	110	ethylbenzene	2	67
9	120	ethylbenzene	2	72
10	130	ethylbenzene	2	72
11	120	ethylbenzene	1	56
12	120	ethylbenzene	2	72
13	120	ethylbenzene	3	72
14	120	ethylbenzene	4	67
15	120	ethylbenzene	5	60

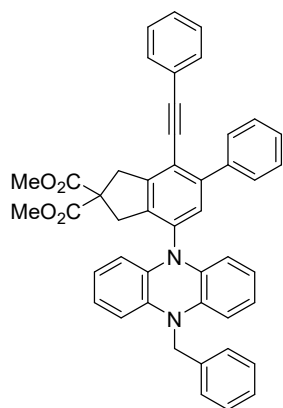
^aReaction conditions: tetraynes (1.0 mmol), Phenazine (1.0 equiv) and solvent (3 mL). ^bIsolated yield.

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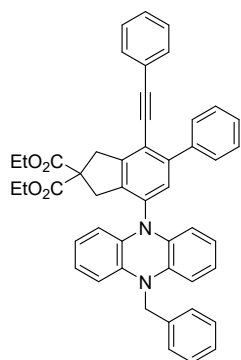
11. Lei, Y.; Zhu, W.; Zhang, Y.; Hu, Q.; Dong, J.; Hu, Y. Benzisoxazole core and benzoxazolopyrrolidine via HDDA-derived benzyne with PTIO/DMPO. *Chin. Chem. Lett.* **2023**, *34*, 107778.

2. Characterization Data for the New Compounds



Dimethyl 7-(10-benzylphenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (**4a**)

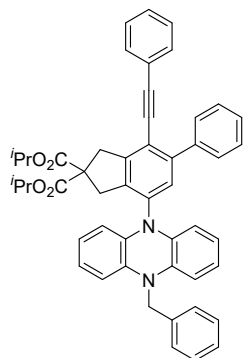
Yellow solid; 571 mg (84% yield); m. p. 184-186 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.77; ^1H NMR (400 MHz, DMSO- d_6) δ 7.72 (d, J = 5.2 Hz, 2H), 7.53-7.50 (m, 2H), 7.44-7.43 (m, 6H), 7.41-7.39 (m, 4H), 7.34 (d, J = 2.4 Hz, 1H), 7.30-7.29 (m, 1H), 6.46-6.44 (m, 2H), 6.40-6.37 (m, 2H), 6.16 (d, J = 2.4 Hz, 2H), 6.65 (d, J = 8.0 Hz, 2H), 4.80 (s, 2H), 3.82 (s, 2H), 3.70-3.69 (m, 6H), 3.47 (s, 2H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.4, 147.4, 145.8, 140.3, 139.1, 137.1, 136.1, 135.7, 135.3, 131.7, 130.6, 129.5, 129.4, 129.3, 128.7, 128.5, 127.3, 126.7, 122.6, 121.4, 117.5, 112.3, 111.8, 96.9, 86.9, 59.4, 53.7, 49.5, 26.5. FT-IR (KBr): ν = 3044, 1739, 1590, 1486, 1382, 1276, 1165, 1059, 958, 736, 690 cm^{-1} ; HRMS (ESI-TOF): m/z calcd for $\text{C}_{46}\text{H}_{36}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 703.2567, found 703.2564.



Diethyl 7-(10-benzylphenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (**4b**)

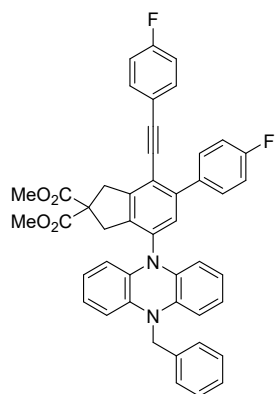
Yellow solid; 567 mg (80 % yield); m. p. 196-198 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.82; ^1H NMR (400 MHz, DMSO- d_6) δ 7.71 (d, J = 7.2 Hz, 2H), 7.53-7.50 (m, 2H), 7.50-7.46 (m, 1H), 7.44-7.43 (m, 5H), 7.41-7.39 (m, 4H), 7.35 (s, 1H), 7.30-7.27 (m, 1H), 6.46 (t, J = 7.4 Hz, 2H), 6.37 (t, J = 6.8 Hz, 2H), 6.17 (d, J = 7.6 Hz, 2H), 5.65 (d, J = 7.6 Hz, 2H), 4.80 (s, 2H), 4.16 (q, J = 7.6 Hz, 4H), 3.79 (s, 2H), 3.46 (s, 2H), 1.17-1.13 (m, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.9, 147.5, 145.8, 140.2, 139.1, 137.2, 136.1, 135.7, 135.4, 131.7, 130.5, 129.6, 129.5, 129.4, 129.2, 128.7, 128.5, 127.3, 126.7, 122.6, 122.2, 121.5, 117.5, 112.3, 111.8, 96.9, 86.7, 62.2, 59.7, 49.5, 14.3. FT-IR (KBr): ν = 2978, 1736, 1597,

1485, 1383, 1256, 1178, 1009, 736, 695 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{48}\text{H}_{40}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 731.2880, found 731.2891.



Diisopropyl 7-(10-benzylphenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4c)

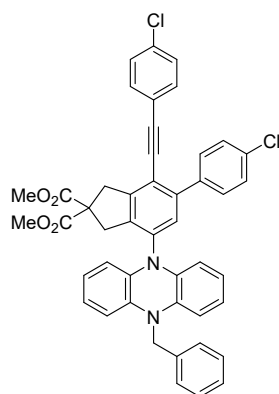
Yellow solid; 567 mg (77 % yield); m. p. 195-197 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.85; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.71 (d, J = 5.2 Hz, 2H), 7.53-7.50 (m, 2H), 7.46-7.44 (m, 6H), 7.41-7.39 (m, 4H), 7.35-7.34 (m, 1H), 7.30-7.29 (m, 1H), 6.46 (t, J = 7.8 Hz, 2H), 6.37 (t, J = 7.2 Hz, 2H), 6.18 (d, J = 7.2 Hz, 2H), 5.65 (d, J = 8.0 Hz, 2H), 4.96-4.93 (m, 2H), 4.80 (s, 2H), 3.75 (s, 2H), 3.43 (s, 2H), 1.21-1.19 (m, 6H), 1.14-1.12 (m, 6H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 170.4, 147.5, 145.8, 140.2, 139.1, 137.2, 136.1, 135.6, 131.6, 130.7, 129.6, 129.5, 129.4, 129.2, 128.7, 128.5, 127.3, 126.7, 122.6, 122.2, 121.5, 117.5, 112.3, 111.9, 96.8, 86.9, 69.7, 59.7, 49.5, 22.7. **FT-IR** (KBr): ν = 2923, 1730, 1601, 1490, 1382, 1259, 1191, 1104, 819, 732 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{50}\text{H}_{44}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 759.3193, found 759.3195.



Dimethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4d)

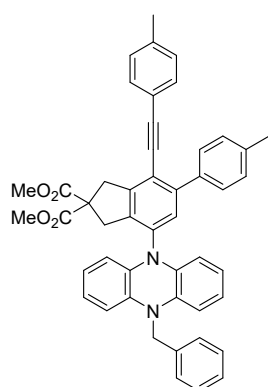
Yellow solid; 608 mg (85% yield); m. p. 195-197 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.74; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.77-7.73 (m, 2H), 7.53-7.50 (m, 2H), 7.43-7.39 (m, 3H), 7.36-7.32 (m, 3H), 7.30-7.24 (m, 2H), 7.19-7.13 (m, 2H), 6.46 (t, J = 7.6 Hz, 2H), 6.38 (t, J = 7.8 Hz, 2H), 6.16 (d, J = 8.0 Hz, 2H), 5.64 (d, J = 8.0 Hz, 2H), 4.79 (s, 2H), 3.81 (s, 2H), 3.69 (s, 6H), 3.46 (s, 2H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 171.4, 163.9 (d, $J_{\text{C-F}}$ = 266.6 Hz), 162.3 (d, $J_{\text{C-F}}$ = 267.7 Hz), 147.5, 144.7, 140.5, 137.1,

135.9 (d, J_{C-F} = 20.7 Hz), 135.4, 134.1 (d, J_{C-F} = 8.1 Hz), 131.7 (d, J_{C-F} = 9.1 Hz), 130.6, 129.3 (d, J_{C-F} = 14.1 Hz), 128.7, 127.3, 126.7, 125.8, 122.2, 121.5, 118.9, 117.4, 116.7 (d, J_{C-F} = 22.2 Hz), 115.6 (d, J_{C-F} = 22.2 Hz), 112.1 (d, J_{C-F} = 47.5 Hz), 59.6, 53.7, 49.5, 21.5; **^{19}F NMR** (376 MHz, DMSO- d_6): δ -109.7, -114.1; **FT-IR** (KBr): ν = 3055, 1733, 1598, 1486, 1385, 1279, 1232, 1160, 836, 741. cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{46}\text{H}_{34}\text{F}_2\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 739.2379, found 739.2381.



Dimethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4e)

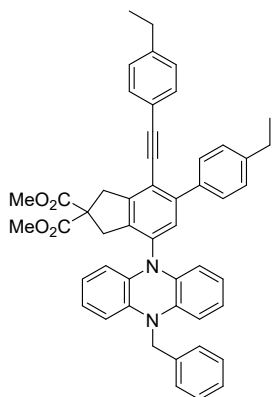
Yellow solid; 658 mg (88 % yield); m. p. 157-159 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.76; ^1H NMR (400 MHz, DMSO- d_6) δ 7.74 (d, J = 10.4 Hz, 2H), 7.58-7.56 (m, 2H), 7.54-7.48 (m, 4H), 7.41-7.36 (m, 5H), 7.30-7.29 (m, 1H), 6.46 (t, J = 7.6 Hz, 2H), 6.38 (t, J = 7.4 Hz, 2H), 6.16 (d, J = 6.8 Hz, 2H), 5.64 (d, J = 7.2 Hz, 2H), 4.80 (s, 2H), 3.81 (s, 2H), 3.69 (s, 6H), 3.46 (s, 2H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.4, 147.8, 144.3, 141.2, 140.9, 137.1, 136.0, 135.8, 135.7, 133.9, 133.3, 131.3, 131.1, 130.8, 130.7, 130.4, 129.8, 129.2, 128.4, 127.3, 126.3, 122.2, 121.5, 117.0, 112.3, 111.8, 95.7, 87.7, 59.6, 53.7, 49.5. **FT-IR** (KBr): ν = 3057, 1731, 1594, 1484, 1386, 1277, 1204, 1084, 828, 738 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{46}\text{H}_{34}\text{Cl}_2\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 771.1788, found 771.1795.



Dimethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(p-tolyl)-4-(p-tolylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4f)

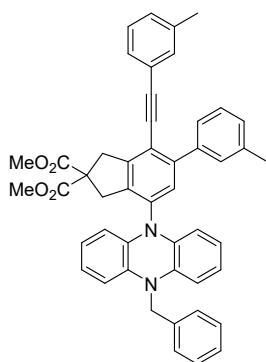
Yellow solid; 567 mg (80 % yield); m. p. 160-162 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.79; ^1H NMR (400 MHz, DMSO- d_6) δ 7.61 (d, J = 5.6 Hz, 2H), 7.40-7.36 (m, 5H), 7.33-7.29 (m, 5H), 7.26-7.25 (m, 2H), 6.45 (t, J = 8.0 Hz, 2H), 6.38 (t, J = 8.0 Hz, 2H), 6.15 (d, J = 8.0 Hz, 2H), 5.63 (d, J = 7.6 Hz,

2H), 4.79 (s, 2H), 3.80 (s, 2H), 3.69 (s, 6H), 3.45 (s, 2H), 2.35 (d, $J = 10.8$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.4, 147.4, 145.5, 139.9, 139.5, 137.9, 137.1, 136.2, 136.1, 135.7, 135.1, 131.6, 130.4, 129.9, 129.4, 129.3, 127.3, 126.7, 122.2, 121.5, 119.6, 117.6, 112.3, 111.8, 97.1, 86.4, 59.6, 53.6, 49.5, 26.8, 21.6, 21.3. **FT-IR** (KBr): $\nu = 2952, 1741, 1659, 1484, 1279, 1025, 1009, 823, 765, 738\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{48}\text{H}_{40}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 731.2880, found 731.2874.



Dimethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4g)

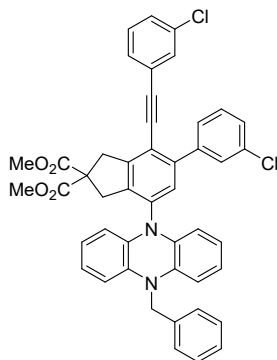
Yellow solid; 567 mg (77% yield); m. p. 154-156 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.78$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.63 (d, $J = 8.0$ Hz, 2H), 7.43-7.38 (m, 4H), 7.37-7.33 (m, 4H), 7.31-7.27 (m, 4H), 6.45 (t, $J = 7.8$ Hz, 2H), 6.38 (t, $J = 7.4$ Hz, 2H), 6.15 (d, $J = 7.6$ Hz, 2H), 5.63 (d, $J = 7.2$ Hz, 2H), 4.79 (s, 2H), 3.79 (s, 2H), 3.69 (s, 6H), 3.71-2.61 (m, 4H), 1.23 (t, $J = 7.6$ Hz, 3H), 1.18 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 172.1, 147.2, 145.7, 144.1, 137.1, 136.6, 136.2, 131.7, 129.5, 129.3, 128.8, 128.0, 127.3, 126.7, 122.2, 121.6, 119.9, 117.6, 112.2, 111.4, 97.2, 86.5, 59.6, 53.4, 28.6, 27.9, 16.0, 15.8. **FT-IR** (KBr): $\nu = 2959, 1737, 1599, 1486, 1382, 1279, 1253, 1063, 834, 735\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{50}\text{H}_{44}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 759.3193, found 759.3197.



Dimethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(m-tolyl)-4-(m-tolylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4h)

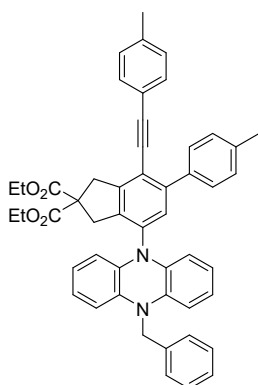
Yellow solid; 580 mg (82 % yield); m. p. 197-199 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.78$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.54-7.50 (m, 2H), 7.43-7.37 (m, 5H), 7.35-7.31 (m, 3H), 7.29-7.26 (m, 3H), 7.22-7.20 (m, 1H), 6.48-6.44 (m, 2H), 6.41-6.36 (m, 2H), 6.16 (d, $J = 6.4$ Hz, 2H), 5.65-5.62 (m, 2H),

4.80 (s, 2H), 3.80 (s, 2H), 3.69 (s, 6H), 3.46 (s, 2H), 2.40 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.4, 147.3, 145.8, 140.2, 139.0, 138.7, 137.8, 136.6, 136.1, 135.7, 135.2, 132.4, 130.6, 130.4, 130.2, 129.3, 129.1, 128.8, 128.6, 127.3, 126.7, 126.6, 122.5, 122.2, 121.5, 117.5, 112.3, 111.8, 97.1, 86.5, 59.3, 53.1, 48.6, 21.5, 19.7. **FT-IR** (KBr): ν = 3029, 1741, 1594, 1486, 1448, 1385, 1279, 1248, 784, 734 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{48}\text{H}_{40}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 731.2880, found 731.2887.



Ddimethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(3-chlorophenyl)-4-((3-chlorophenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4i)

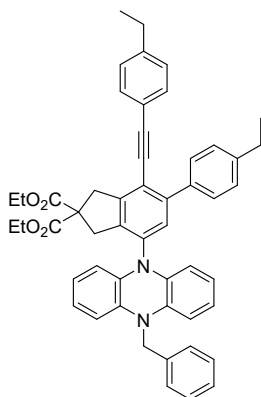
Yellow solid; 635 mg (85 % yield); m. p. 143-145 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.75; ^1H NMR (400 MHz, DMSO- d_6) δ 7.81-7.80 (m, 1H), 7.66-7.64 (m, 1H), 7.54-7.50 (m, 4H), 7.48-7.45 (m, 2H), 7.43-7.37 (m, 5H), 7.30-7.28 (m, 1H), 6.46 (t, J = 6.8 Hz, 2H), 6.38 (t, J = 7.0 Hz, 2H), 6.16 (d, J = 6.4 Hz, 2H), 5.64 (d, J = 6.4 Hz, 2H), 4.79 (s, 2H), 3.83 (s, 2H), 3.70 (s, 6H), 3.47 (s, 2H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.4, 147.8, 144.3, 141.2, 140.9, 137.1, 136.0, 135.8, 135.7, 133.9, 133.3, 131.3, 131.1, 130.8, 130.7, 130.4, 129.8, 129.2, 128.4, 127.3, 126.7, 124.3, 122.2, 121.5, 117.0, 112.2, 111.8, 95.7, 87.7, 59.6, 53.7, 49.5. **FT-IR** (KBr): ν = 3061, 1741, 1588, 1486, 1386, 1280, 1247, 1059, 785, 733 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{46}\text{H}_{34}\text{Cl}_2\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 771.1788, found 771.1793.



Diethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(p-tolyl)-4-(p-tolylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4j)

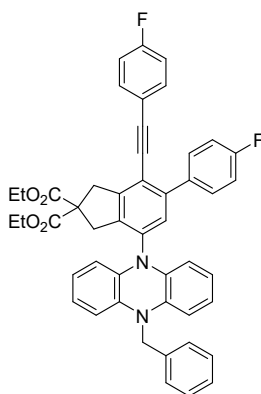
Yellow solid; 596 mg (81 % yield); m. p. 165-167 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.81; ^1H NMR (400 MHz, DMSO- d_6) δ 7.61 (d, J = 8.0 Hz, 2H), 7.42-7.37 (m, 4H), 7.35-7.30 (m, 5H), 7.30-7.24 (m, 3H), 6.47-6.43 (m, 2H), 6.38-6.34 (m, 2H), 6.16 (d, J = 8.0 Hz, 2H), 5.64-5.62 (m, 2H), 4.79 (s, 2H),

4.15 (q, $J = 6.8$ Hz, 4H), 3.77 (s, 2H), 3.44 (s, 2H), 2.36 (d, $J = 11.2$ Hz, 6H), 1.14 (d, $J = 7.2$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.9, 147.4, 145.5, 139.9, 139.5, 137.9, 137.2, 136.3, 136.1, 135.7, 135.2, 131.6, 130.5, 130.0, 129.4, 129.2, 127.3, 126.7, 122.2, 121.5, 119.6, 117.6, 112.3, 111.8, 97.1, 86.4, 62.2, 59.2, 49.5, 21.6, 21.3, 13.2. **FT-IR** (KBr): $\nu = 2980, 1734, 1597, 1484, 1382, 1250, 1179, 1062, 816, 735$ cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{50}\text{H}_{44}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 759.3193, found 759.3190.



Diethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4k)

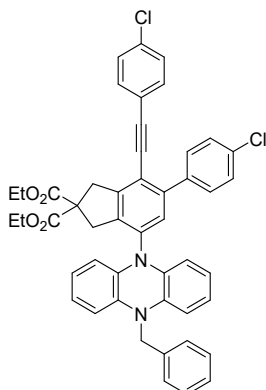
Yellow solid; 596 mg (78 % yield); m. p. 181-183 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.82$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.62 (d, $J = 7.6$ Hz, 2H), 7.42-7.38 (m, 4H), 7.36-7.32 (m, 4H), 7.29-7.26 (m, 4H), 6.45 (t, $J = 7.6$ Hz, 2H), 6.36 (t, $J = 7.6$ Hz, 2H), 6.16 (d, $J = 7.6$ Hz, 2H), 5.63 (d, $J = 7.6$ Hz, 2H), 4.79 (s, 2H), 4.15 (q, $J = 6.8$ Hz, 4H), 3.77 (s, 2H), 3.44 (s, 2H), 2.70-2.61 (m, 4H), 1.25-1.21 (m, 3H), 1.20-1.18 (m, 3H), 1.16-1.13 (m, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.9, 147.4, 145.6, 145.5, 144.1, 139.9, 137.2, 136.1, 135.7, 135.2, 131.7, 130.5, 129.5, 129.2, 128.8, 128.0, 127.3, 126.7, 122.2, 121.5, 119.9, 117.6, 112.3, 111.8, 97.1, 86.5, 62.2, 59.7, 28.6, 28.4, 17.2, 13.1. **FT-IR** (KBr): $\nu = 3055, 1729, 1488, 1383, 1250, 1185, 1098, 1057, 832, 733$ cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{52}\text{H}_{48}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 787.3506, found 787.3510.



Diethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4l)

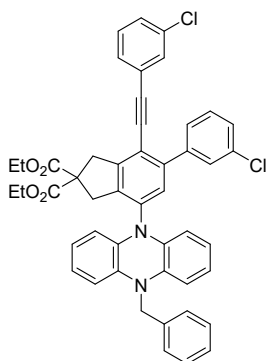
Yellow solid; 617 mg (83 % yield); m. p. 193-196 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.80$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.76-7.73 (m, 2H), 7.53-7.49 (m, 2H), 7.42-7.38 (m, 4H), 7.35-7.31 (m,

4H), 7.29-7.27 (m, 2H), 6.45 (t, $J = 7.0$ Hz, 2H), 6.36 (t, $J = 7.6$ Hz, 2H), 6.16 (d, $J = 6.4$ Hz, 2H), 5.64 (d, $J = 7.6$ Hz, 2H), 4.79 (s, 2H), 4.16 (q, $J = 4.2$ Hz, 4H), 3.79 (s, 2H), 3.46 (s, 2H), 1.15 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.9, 162.7 (d, $J_{\text{C-F}} = 249.5$ Hz), 162.3 (d, $J_{\text{C-F}} = 246.4$ Hz), 147.5, 144.7, 140.4, 137.2, 136.1, 135.6 (d, $J_{\text{C-F}} = 17.2$ Hz), 134.0 (d, $J_{\text{C-F}} = 9.1$ Hz), 131.6 (d, $J_{\text{C-F}} = 8.1$ Hz), 130.7, 129.23, 127.3, 126.7, 122.2, 121.5, 118.9 (d, $J_{\text{C-F}} = 3.0$ Hz), 117.4, 116.6 (d, $J_{\text{C-F}} = 28.3$ Hz), 115.5 (d, $J_{\text{C-F}} = 21.2$ Hz), 112.3, 111.9, 96.0, 86.4, 62.2, 59.7, 49.6, 26.8, 14.3; ^{19}F NMR (376 MHz, DMSO- d_6): δ -109.8, -114.1; FT-IR (KBr): $\nu = 3059, 1731, 1599, 1485, 1381, 1243, 1156, 1069, 838, 735\text{ cm}^{-1}$; HRMS (ESI-TOF): m/z calcd for $\text{C}_{48}\text{H}_{38}\text{F}_2\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 767.2692, found 767.2698.



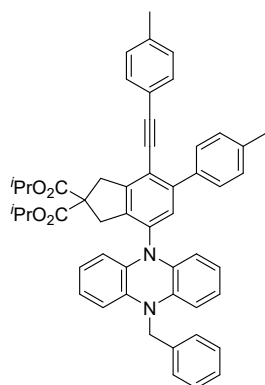
Diethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4m)

Yellow solid; 659 mg (85 % yield); m. p. 177-179 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.79$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.57-7.52 (m, 3H), 7.50-7.56 (m, 3H), 7.42-7.37 (m, 3H), 7.29-7.26 (m, 1H), 6.45 (t, $J = 7.6$ Hz, 2H), 6.36 (t, $J = 8.0$ Hz, 2H), 6.16 (d, $J = 6.4$ Hz, 2H), 5.64 (d, $J = 7.6$ Hz, 2H), 4.79 (s, 2H), 4.15 (q, $J = 6.8$ Hz, 4H), 3.79 (s, 2H), 3.46 (s, 2H), 1.14 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.8, 147.8, 144.4, 140.8, 137.8, 136.0, 135.7, 134.4, 133.4, 131.4, 130.7, 129.6, 129.2, 128.7, 127.3, 126.7, 122.2, 121.5, 121.3, 117.2, 112.3, 111.9, 96.0, 87.5, 62.2, 59.7, 49.6, 26.8, 14.3. FT-IR (KBr): $\nu = 3055, 1729, 1592, 1490, 1355, 1251, 1098, 995, 817, 743\text{ cm}^{-1}$; HRMS (ESI-TOF): m/z calcd for $\text{C}_{48}\text{H}_{38}\text{Cl}_2\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 799.2101, found 799.2105.



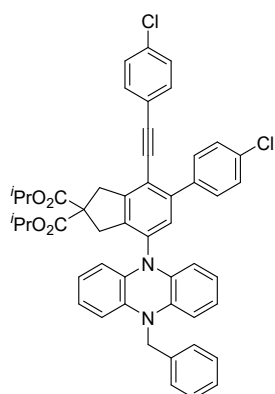
Diethyl 7-(10-benzylphenazin-5(10H)-yl)-5-(3-chlorophenyl)-4-((3-chlorophenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4n)

Yellow solid; 644 mg (83 % yield); m. p. 197-196 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.78; ^1H NMR (400 MHz, DMSO- d_6) δ 7.80 (s, 1H), 7.65 (d, J = 6.8 Hz, 1H), 7.56-7.50 (m, 4H), 7.48-7.42 (m, 3H), 7.40-7.39 (m, 4H), 7.30-7.27 (m, 1H), 6.46 (t, J = 7.6 Hz, 2H), 6.37 (t, J = 8.0 Hz, 2H), 6.17 (d, J = 6.4 Hz, 2H), 5.65 (d, J = 8.0 Hz, 2H), 4.79 (s, 2H), 4.16 (q, J = 7.2 Hz, 4H), 3.80 (s, 2H), 3.46 (s, 2H), 1.15 (t, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.4, 147.8, 144.3, 141.1, 141.0, 137.3, 136.0, 135.2, 133.9, 133.3, 131.3, 131.1, 130.7, 130.4, 129.8, 129.3, 129.2, 128.4, 127.3, 126.7, 124.3, 122.2, 121.5, 112.3, 111.9, 108.2, 95.5, 88.0, 81.5, 76.6, 62.2, 60.2, 15.5. **FT-IR** (KBr): ν = 2978, 1734, 1591, 1484, 1383, 1252, 1180, 1070, 882, 731 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{48}\text{H}_{38}\text{Cl}_2\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 799.2101, found 799.2096.



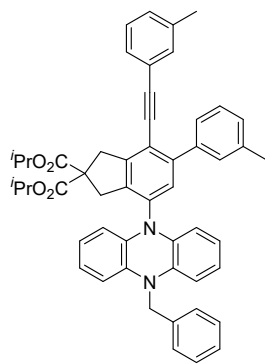
Diisopropyl 7-(10-benzylphenazin-5(10H)-yl)-5-(p-tolyl)-4-(p-tolyne)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4o)

Yellow solid; 611 mg (80 % yield); m. p. 220-222 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.86; ^1H NMR (400 MHz, DMSO- d_6) δ 7.60 (d, J = 6.0 Hz, 2H), 7.39-7.38 (m, 4H), 7.34-7.29 (m, 6H), 7.26-7.24 (m, 2H), 6.44 (t, J = 7.8 Hz, 2H), 6.35 (t, J = 8.0 Hz, 2H), 6.16 (d, J = 8.0 Hz, 2H), 5.63 (d, J = 7.6 Hz, 2H), 4.97-4.91 (m, 2H), 4.78 (s, 2H), 3.72 (s, 2H), 3.42 (s, 2H), 2.35 (d, J = 11.2 Hz, 6H), 1.18 (d, J = 6.4 Hz, 6H), 1.12 (d, J = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.4, 147.5, 145.5, 139.8, 139.5, 137.8, 137.2, 136.3, 135.6, 135.4, 131.6, 130.5, 130.0, 129.4, 129.2, 127.3, 126.7, 122.1, 121.5, 119.6, 117.6, 112.3, 111.8, 97.0, 86.4, 69.7, 59.7, 49.5, 31.4, 26.8, 21.6, 14.4. **FT-IR** (KBr): ν = 2979, 1728, 1594, 1489, 1382, 1260, 1098, 1010, 829, 736 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{52}\text{H}_{48}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 787.3506, found 787.3505.



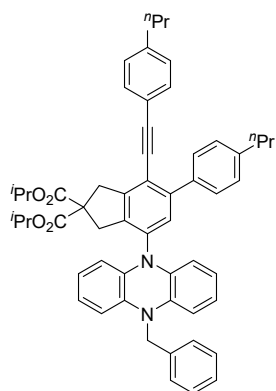
Diisopropyl 7-(10-benzylphenazin-5(10H)-yl)-5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4p)

Yellow solid; 683 mg (85 % yield); m. p. 193-195 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.83; ^1H NMR (400 MHz, DMSO- d_6) δ 7.75-7.73 (m, 2H), 7.56-7.54 (m, 3H), 7.53-7.47 (m, 3H), 7.40-7.39 (m, 5H), 7.30-7.28 (m, 1H), 6.45 (t, J = 7.8 Hz, 2H), 6.36 (t, J = 7.6 Hz, 2H), 6.18 (d, J = 8.0 Hz, 2H), 5.63 (d, J = 8.0 Hz, 2H), 4.97-4.91 (m, 2H), 4.80 (s, 2H), 3.74 (s, 2H), 3.43 (s, 2H), 1.19 (d, J = 6.0 Hz, 6H), 1.12 (d, J = 6.0 Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.3, 147.3, 146.4, 145.6, 144.4, 142.5, 141.0, 137.8, 137.5, 137.4, 137.2, 137.0, 136.8, 136.1, 135.7, 133.4, 131.4, 129.6, 129.2, 128.7, 126.7, 125.9, 125.2, 124.9, 122.2, 111.9, 95.8, 87.3, 79.3, 77.7, 76.9, 69.8, 59.7, 21.6. **FT-IR** (KBr): ν = 2922, 1730, 1598, 1488, 1383, 1271, 1104, 1066, 788, 734 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{50}\text{H}_{42}\text{Cl}_2\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 827.2414, found 827.2411.



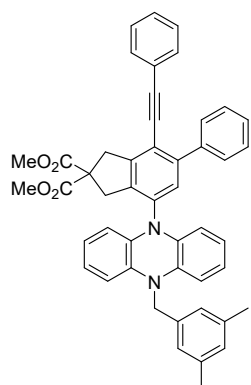
Diisopropyl 7-(10-benzylphenazin-5(10H)-yl)-5-(m-tolyl)-4-(m-tolylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4q)

Yellow solid; 573 mg (75 % yield); m. p. 189-191 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.85; ^1H NMR (400 MHz, DMSO- d_6) δ 7.73-7.49 (m, 2H), 7.42-7.37 (m, 5H), 7.34-7.28 (m, 3H), 7.26-7.24 (m, 3H), 7.22-7.20 (m, 1H), 6.45 (t, J = 7.6 Hz, 2H), 6.36 (t, J = 7.6 Hz, 2H), 6.17 (d, J = 8.0 Hz, 2H), 5.63 (d, J = 7.6 Hz, 2H), 4.98-4.92 (m, 2H), 4.79 (s, 2H), 3.74 (s, 2H), 3.43 (s, 2H), 2.39 (s, 3H), 2.32 (s, 3H), 1.20 (d, J = 6.4 Hz, 6H), 1.13 (d, J = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.4, 147.5, 145.8, 140.1, 139.1, 138.7, 137.8, 137.2, 136.1, 135.7, 131.9, 130.6, 130.4, 130.1, 129.2, 129.1, 128.7, 128.5, 127.3, 126.7, 122.5, 122.2, 122.2, 121.5, 117.5, 117.5, 112.3, 111.9, 97.1, 86.7, 69.7, 59.7, 47.7, 34.7, 29.0, 26.8, 25.3, 21.7, 21.2. **FT-IR** (KBr): ν = 2922, 1729, 1600, 1489, 1383, 1268, 1104, 1067, 787, 733 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{52}\text{H}_{48}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 787.3506, found 787.3510.



Diisopropyl 7-(10-benzylphenazin-5(10H)-yl)-5-(4-propylphenyl)-4-((4-propylphenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4r)

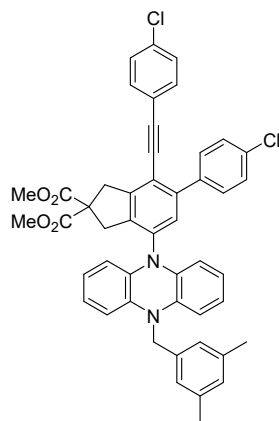
Yellow solid; 582 mg (71 % yield); m. p. 178-180 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.87; ^1H NMR (400 MHz, DMSO- d_6) δ 7.61 (d, J = 8.0 Hz, 2H), 7.40-7.38 (m, 4H), 7.34-7.30 (m, 5H), 7.28-7.23 (m, 3H), 6.44 (t, J = 7.6 Hz, 2H), 6.35 (t, J = 7.6 Hz, 2H), 6.17 (d, J = 8.0 Hz, 2H), 5.63 (d, J = 8.0 Hz, 2H), 4.97-4.91 (m, 2H), 4.79 (s, 2H), 3.72 (s, 2H), 3.42 (s, 2H), 2.64-2.56 (m, 4H), 1.67-1.56 (m, 4H), 1.19 (d, J = 6.4 Hz, 6H), 1.12 (d, J = 6.0 Hz, 6H), 0.94-0.90 (m, 3H), 0.89-0.85 (m, 3H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.4, 147.4, 145.6, 144.0, 142.5, 139.8, 137.2, 136.6, 136.2, 135.6, 135.4, 131.6, 130.5, 129.4, 129.2, 128.6, 127.3, 126.7, 122.1, 121.5, 117.6, 111.9, 97.1, 86.5, 69.7, 59.7, 49.5, 37.6, 37.4, 34.0, 24.5, 24.3, 22.2, 21.6. **FT-IR** (KBr): ν = 2929, 1728, 1600, 1488, 1383, 1256, 1187, 1102, 814, 731 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{56}\text{H}_{56}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 843.4132, found 843.4135.



Dimethyl 7-(10-(3,5-dimethylbenzyl)phenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4s)

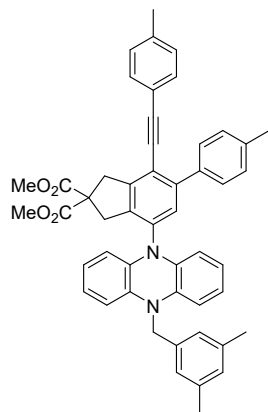
Yellow solid; 496 mg (70 % yield); m. p. 200-202 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.79; ^1H NMR (400 MHz, DMSO- d_6) δ 7.71 (d, J = 6.8 Hz, 2H), 7.53-7.49 (m, 2H), 7.46-7.43 (m, 6H), 7.35 (s, 1H), 6.97 (s, 2H), 6.91 (s, 1H), 6.46 (t, J = 8.0 Hz, 2H), 6.38 (t, J = 7.6 Hz, 2H), 6.15 (d, J = 8.0 Hz, 2H), 5.65 (d, J = 7.6 Hz, 2H), 4.70 (s, 2H), 3.82 (s, 2H), 3.48 (s, 2H), 2.27 (s, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.4, 147.4, 145.7, 140.2, 139.1, 138.3, 137.5, 136.1, 135.9, 135.4, 131.7, 130.7, 129.6, 129.5, 129.3, 128.9, 128.5, 124.2, 122.6, 122.2, 121.5, 117.5, 112.3, 111.8, 96.9, 86.9, 59.6, 53.6, 50.3, 21.6. **FT-IR**

(KBr): ν = 2912, 1729, 1602, 1486, 1385, 1258, 1163, 1001, 741, 680 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{48}\text{H}_{40}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 731.2880, found 731.2877.



Dimethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-7-(10-(3,5-dimethylbenzyl)phenazin-5(10H)-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4t)

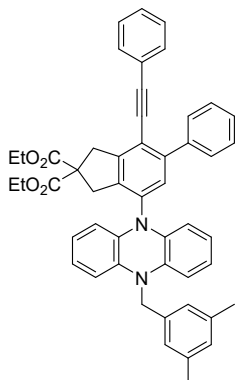
Yellow solid; 575 mg (74 % yield); m. p. 191-193 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.78; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.57-7.53 (m, 3H), 7.51-7.47 (m, 3H), 7.38 (s, 1H), 6.96 (s, 2H), 6.91 (s, 1H), 6.46 (t, J = 8.0 Hz, 2H), 6.37 (t, J = 7.6 Hz, 2H), 6.15 (d, J = 8.0 Hz, 2H), 5.64 (d, J = 8.0 Hz, 2H), 4.70 (s, 2H), 3.81 (s, 2H), 3.48 (s, 2H), 2.27 (s, 6H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 171.4, 147.7, 144.4, 140.8, 138.3, 137.8, 137.5, 136.1, 135.9, 135.7, 134.4, 133.5, 133.4, 131.4, 130.8, 129.6, 128.9, 128.7, 124.2, 122.3, 121.5, 121.3, 117.1, 112.4, 111.8, 96.0, 87.5, 59.6, 53.6, 50.3, 21.6. **FT-IR** (KBr): ν = 2950, 1739, 1600, 1487, 1383, 1253, 1087, 1011, 827, 735 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{48}\text{H}_{38}\text{Cl}_2\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 799.2101, found 799.2107.



Dimethyl 7-(10-(3,5-dimethylbenzyl)phenazin-5(10H)-yl)-5-(p-tolyl)-4-(p-tolylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4u)

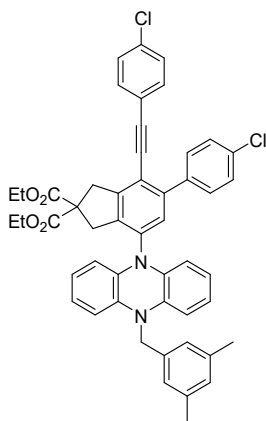
Yellow solid; 530 mg (72 % yield); m. p. 187-189 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.80; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.35-7.33 (m, 2H), 7.32-7.30 (m, 3H), 7.26-7.24 (m, 2H), 6.96 (s, 2H), 6.91 (s, 1H), 6.46 (t, J = 6.8 Hz, 2H), 6.37 (t, J = 7.2 Hz, 2H), 6.14 (d, J = 7.6 Hz, 2H), 5.63 (d, J = 6.4 Hz, 2H), 4.69 (s, 2H), 3.79 (s, 2H), 3.69 (s, 6H), 3.46 (s, 2H), 2.36 (d, J = 11.2 Hz, 6H), 2.27 (s, 6H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 171.4, 147.3, 145.4, 139.9, 139.5, 138.3, 137.9, 137.5,

136.2, 135.9, 135.2, 131.6, 130.5, 130.0, 129.4, 129.3, 128.9, 124.1, 122.2, 121.5, 119.6, 117.5, 112.3, 111.8, 97.1, 86.4, 59.6, 53.6, 50.2, 21.6, 21.3. **FT-IR** (KBr): ν = 2916, 1742, 1599, 1486, 1383, 1253, 1164, 1053, 814, 736 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{50}\text{H}_{44}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 759.3193, found 759.3189.



Diethyl 7-(10-(3,5-dimethylbenzyl)phenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4v)

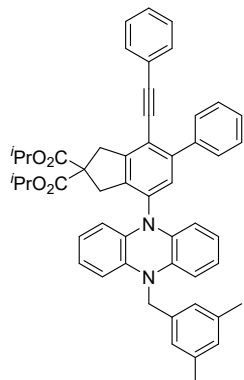
Yellow solid; 538 mg (73 % yield); m. p. 207-209 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.83; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.72-7.70 (m, 2H), 7.53-7.49 (m, 2H), 7.46-7.43 (m, 6H), 7.35 (s, 1H), 6.97 (s, 2H), 6.91 (s, 1H), 6.48-6.44 (m, 2H), 6.36 (t, J = 7.6 Hz, 2H), 6.16 (d, J = 6.4 Hz, 2H), 5.65 (d, J = 7.6 Hz, 2H), 4.70 (s, 2H), 4.12 (q, J = 6.8 Hz, 4H), 3.79 (s, 2H), 3.47 (s, 2H), 2.27 (s, 6H), 1.14 (t, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 170.9, 147.5, 145.7, 140.1, 139.1, 138.3, 137.4, 136.1, 135.8, 135.6, 131.7, 130.8, 129.6, 129.4, 128.9, 128.7, 128.5, 124.2, 122.6, 122.2, 121.5, 117.5, 112.3, 111.9, 96.8, 86.9, 62.2, 59.7, 50.1, 21.6. **FT-IR** (KBr): ν = 2990, 1732, 1591, 1485, 1384, 1356, 1253, 1154, 895, 741 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{50}\text{H}_{44}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 759.3193, found 759.3198.



Diethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-7-(10-(3,5-dimethylbenzyl)phenazin-5(10H)-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4w)

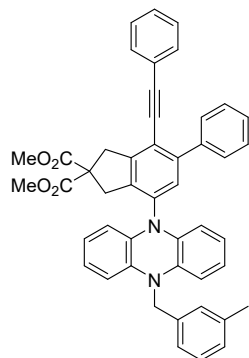
Yellow solid; 611 mg (76 % yield); m. p. 183-185 $^{\circ}\text{C}$; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.82; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.57-7.55 (m, 2H), 7.53-7.52 (m, 2H), 7.48-7.46 (m, 2H), 7.38 (s, 1H), 6.97 (s, 2H), 6.91 (s, 1H), 6.46 (t, J = 6.0 Hz, 2H), 6.36 (t, J = 6.4 Hz, 2H), 6.16 (d, J = 6.4 Hz, 2H), 5.64 (d, J = 8.0 Hz, 2H), 4.70 (s, 2H), 4.15 (q, J = 6.8 Hz, 4H), 3.78 (s, 2H), 3.47 (s, 2H),

2.26 (s, 6H), 1.14 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.8, 147.8, 144.3, 143.4, 140.7, 138.2, 137.8, 137.4, 136.0, 135.9, 135.8, 134.4, 131.5, 131.4, 130.9, 129.8, 129.6, 128.7, 124.2, 122.3, 121.5, 121.3, 117.1, 112.3, 111.9, 95.9, 87.5, 62.2, 59.7, 50.1, 21.5. **FT-IR** (KBr): $\nu = 3056, 1734, 1592, 1484, 1354, 1272, 1144, 1103, 817, 744\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{50}\text{H}_{42}\text{Cl}_2\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 827.2414, found 827.2409.



Diisopropyl 7-(10-(3,5-dimethylbenzyl)phenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4x)

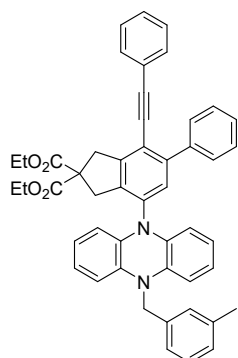
Yellow solid; 543 mg (71 % yield); m. p. 201-203 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.86$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.71 (d, $J = 7.2$ Hz, 2H), 7.53-7.49 (m, 2H), 7.45-7.46 (m, 6H), 7.34 (s, 1H), 6.97 (s, 2H), 6.91 (s, 1H), 6.45 (t, $J = 7.6$ Hz, 2H), 6.35 (t, $J = 7.6$ Hz, 2H), 6.16 (d, $J = 6.4$ Hz, 2H), 5.65 (d, $J = 6.4$ Hz, 2H), 4.97-4.91 (m, 2H), 4.70 (s, 2H), 3.74 (s, 2H), 3.45 (s, 2H), 2.27 (s, 6H), 1.19 (d, $J = 6.4$ Hz, 6H), 1.11 (d, $J = 6.4$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.4, 147.6, 145.7, 140.1, 139.2, 138.2, 137.4, 136.1, 135.8, 131.6, 130.3, 129.5, 129.4, 128.9, 128.7, 128.5, 124.2, 122.6, 122.2, 121.5, 117.5, 112.3, 111.9, 96.8, 86.9, 69.7, 59.7, 49.9, 30.6, 26.8, 21.6. **FT-IR** (KBr): $\nu = 2978, 1727, 1599, 1488, 1380, 1283, 1251, 1162, 737, 696\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{52}\text{H}_{48}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 787.3506, found 787.3505.



Dimethyl 7-(10-(3-methylbenzyl)phenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4y)

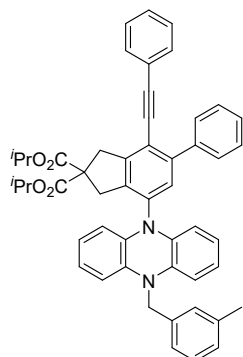
Yellow solid; 535 mg (77 % yield); m. p. 183-185 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.79$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.71(d, $J = 7.2$ Hz, 2H), 7.53-7.49 (m, 2H), 7.46-7.43 (m, 6H), 7.34 (s, 1H),

7.30-7.26 (m, 1H), 7.19 (s, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 6.46 (t, $J = 7.6$ Hz, 2H), 6.38 (t, $J = 7.6$ Hz, 2H), 6.15 (d, $J = 7.6$ Hz, 2H), 5.65 (d, $J = 8.0$ Hz, 2H), 4.74 (s, 2H), 3.82 (s, 2H), 3.69 (s, 6H), 3.47 (s, 2H), 3.23 (s, 3H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.4, 147.4, 145.8, 140.3, 139.1, 138.4, 137.2, 136.1, 135.8, 135.4, 131.7, 130.6, 129.6, 129.5, 129.4, 129.1, 128.7, 128.5, 128.0, 127.2, 123.7, 122.5, 122.2, 121.5, 117.5, 112.3, 111.8, 96.9, 86.9, 59.6, 49.8, 21.7. **FT-IR** (KBr): $\nu = 2950, 1739, 1593, 1489, 1385, 1264, 1161, 1061, 742, 696\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{47}\text{H}_{38}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 717.2724, found 717.2721.



Diethyl 7-(10-(3-methylbenzyl)phenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4z)

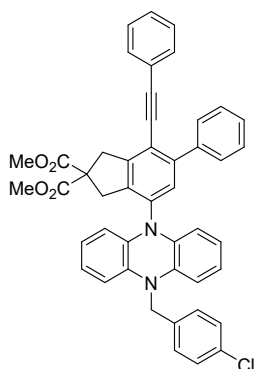
Yellow solid; 535 mg (74 % yield); m. p. 206-208 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.81$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.70 (d, $J = 6.8$ Hz, 2H), 7.52-7.49 (m, 2H), 7.45-7.43 (m, 6H), 7.34 (s, 1H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.19 (s, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 6.45 (t, $J = 7.8$ Hz, 2H), 6.36 (d, $J = 7.8$ Hz, 2H), 6.16 (d, $J = 8.0$ Hz, 2H), 5.65 (d, $J = 6.4$ Hz, 2H), 4.74 (s, 2H), 4.15 (q, $J = 6.8$ Hz, 4H), 3.79 (s, 2H), 3.46 (s, 2H), 1.14 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.9, 147.5, 145.7, 143.4, 140.2, 139.1, 138.4, 137.2, 136.1, 135.7, 135.5, 131.6, 131.5, 130.7, 129.8, 129.6, 129.5, 129.3, 129.1, 128.7, 128.5, 128.0, 127.2, 123.7, 122.6, 122.2, 121.5, 117.5, 112.3, 111.8, 96.9, 86.9, 62.2, 59.7, 49.8, 21.6. **FT-IR** (KBr): $\nu = 2986, 1733, 1596, 1486, 1384, 1254, 1155, 1068, 743, 693\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{49}\text{H}_{42}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 745.3037, found 745.3042.



Diisopropyl 7-(10-(3-methylbenzyl)phenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4A)

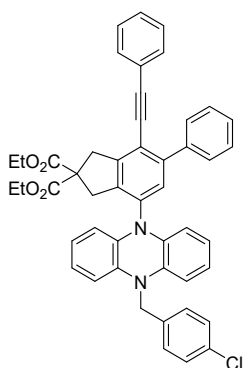
Yellow solid; 563 mg (75 % yield); m. p. 188-190 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.84$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.71 (d, $J = 6.8$ Hz, 2H), 7.53-7.49 (m, 2H), 7.45-7.43 (m, 6H), 7.34 (s, 1H),

7.27 (t, $J = 7.6$ Hz, 1H), 7.20-7.15 (m, 2H), 7.19 (d, $J = 7.2$ Hz, 1H), 6.45 (t, $J = 7.6$ Hz, 2H), 6.36 (d, $J = 7.6$ Hz, 2H), 6.17 (d, $J = 7.6$ Hz, 2H), 5.64 (d, $J = 8.8$ Hz, 2H), 4.97-4.91 (m, 2H), 4.75 (s, 2H), 3.74 (s, 2H), 3.44 (s, 2H), 2.32 (s, 3H), 1.19 (d, $J = 6.4$ Hz, 6H), 1.11 (d, $J = 6.4$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.4, 147.6, 145.7, 140.1, 139.1, 138.4, 137.3, 136.1, 135.7, 131.6, 130.8, 129.5, 129.4, 129.1, 128.7, 128.5, 128.0, 127.2, 123.7, 122.6, 122.2, 121.5, 117.5, 112.3, 111.9, 96.8, 86.9, 69.7, 56.7, 49.7, 21.6. **FT-IR** (KBr): $\nu = 3027, 1917, 1753, 1720, 1597, 1258, 1106, 970, 754, 700\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{51}\text{H}_{46}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 773.3350, found 773.3354.



Dimethyl 7-(10-(4-chlorobenzyl)phenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4B)

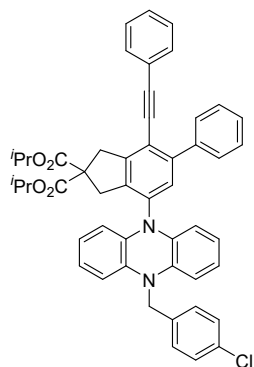
Yellow solid; 607 mg (85 % yield); m. p. 190-192 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.76$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.71 (d, $J = 6.8$ Hz, 2H), 7.53-7.48 (m, 3H), 7.46 (s, 2H), 7.44 (s, 5H), 7.41-7.49 (m, 2H), 7.35 (s, 1H), 6.47 (t, $J = 7.6$ Hz, 2H), 6.39 (t, $J = 7.6$ Hz, 2H), 6.15 (d, $J = 6.4$ Hz, 2H), 5.65 (d, $J = 8.0$ Hz, 2H), 4.79 (s, 2H), 3.81 (s, 2H), 3.70 (s, 6H), 3.45 (s, 2H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.4, 147.4, 145.8, 140.3, 139.1, 136.3, 136.1, 135.5, 135.3, 131.8, 131.7, 130.6, 129.6, 129.5, 129.4, 129.2, 128.8, 128.7, 128.5, 122.5, 122.2, 121.7, 117.5, 112.2, 111.9, 96.9, 86.9, 59.6, 53.7, 48.9. **FT-IR** (KBr): $\nu = 2978, 1726, 1600, 1488, 1379, 1282, 1102, 1026, 734, 694\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{46}\text{H}_{35}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 737.2178, found 737.2181.



Diethyl 7-(10-(4-chlorobenzyl)phenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4C)

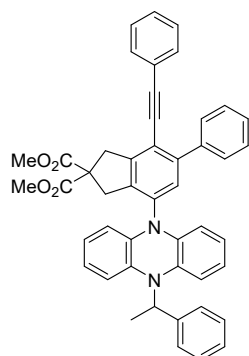
Yellow solid; 601 mg (81 % yield); m. p. 185-187 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.78$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.70 (d, $J = 6.8$ Hz, 2H), 7.52-7.47 (m, 3H), 7.45 (s, 2H), 7.43 (s, 5H), 7.41-

7.48 (m, 2H), 7.34 (s, 1H), 6.46 (t, $J = 7.8$ Hz, 2H), 6.38 (t, $J = 7.8$ Hz, 2H), 6.15 (d, $J = 8.0$ Hz, 2H), 5.66 (d, $J = 7.6$ Hz, 2H), 4.78 (s, 2H), 4.16 (q, $J = 6.8$ Hz, 4H), 3.80 (s, 2H), 3.45 (s, 2H), 1.14 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.9, 147.5, 143.4, 140.3, 139.1, 136.3, 136.1, 135.5, 135.4, 131.8, 131.7, 131.5, 129.8, 129.6, 129.3, 129.2, 128.8, 128.7, 128.5, 122.6, 122.2, 121.7, 117.5, 112.3, 111.9, 96.9, 86.9, 62.2, 59.7, 48.9, 14.3. **FT-IR** (KBr): $\nu = 3052, 1749, 1592, 1487, 1436, 1282, 1198, 1066, 742, 696\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{48}\text{H}_{39}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 765.2491, found 765.2487.



Diisopropyl 7-(10-(4-chlorobenzyl)phenazin-5(10H)-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4D)

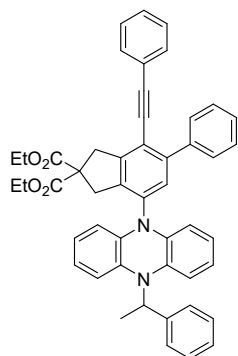
Yellow solid; 616 mg (80 % yield); m. p. 173-175 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.83$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.67 (d, $J = 7.2$ Hz, 2H), 7.47 (t, $J = 7.2$ Hz, 2H), 7.43-7.41 (m, 3H), 7.39-7.38 (m, 6H), 7.38-7.36 (m, 1H), 7.30 (s, 1H), 6.42 (t, $J = 7.6$ Hz, 2H), 6.33 (t, $J = 8.0$ Hz, 2H), 6.13 (d, $J = 8.0$ Hz, 2H), 5.61 (d, $J = 6.4$ Hz, 2H), 4.94-4.87 (m, 2H), 4.75 (s, 2H), 3.70 (s, 2H), 3.39 (s, 2H), 1.15 (t, $J = 6.4$ Hz, 6H), 1.08 (t, $J = 6.4$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 175.1, 152.3, 150.5, 144.9, 143.9, 141.1, 140.9, 140.3, 140.2, 136.6, 136.4, 135.4, 134.4, 134.3, 134.1, 134.0, 133.5, 133.4, 133.3, 127.3, 127.0, 126.4, 122.3, 117.0, 116.7, 101.6, 91.6, 74.5, 64.4, 53.6, 39.4, 36.2, 26.4, 19.2. **FT-IR** (KBr): $\nu = 3056, 1730, 1578, 1490, 1356, 1243, 1102, 1065, 815, 744\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{50}\text{H}_{43}\text{ClN}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 793.2804, found 793.2807.



Dimethyl 5-phenyl-7-(10-(1-phenylethyl)phenazin-5(10H)-yl)-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4E)

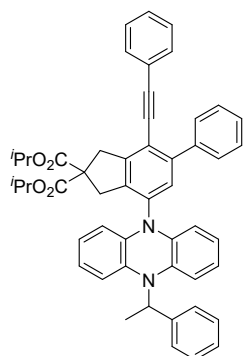
Yellow solid; 474 mg (72 % yield); m. p. 194-196 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.78$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.72 (d, $J = 7.6$ Hz, 2H), 7.52 (t, $J = 7.2$ Hz, 2H), 7.46-7.43 (m, 6H), 7.41-

7.38 (m, 4H), 7.30-7.27 (m, 2H), 6.56-6.49 (m, 4H), 6.31 (d, $J = 6.0$ Hz, 2H), 5.78 (d, $J = 6.0$ Hz, 2H), 5.22-5.17 (m, 1H), 3.81 (s, 2H), 3.68 (s, 6H), 3.37 (s, 2H), 1.85 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.4, 147.3, 145.6, 141.8, 140.2, 139.1, 138.6, 135.5, 135.4, 131.7, 130.6, 129.6, 129.4, 129.1, 128.7, 128.5, 127.3, 126.8, 122.6, 122.0, 121.9, 117.5, 116.1, 112.3, 96.9, 86.9, 59.6, 58.4, 53.7, 18.0. **FT-IR** (KBr): $\nu = 2978, 1729, 1572, 1463, 1370, 1249, 1103, 1056, 756, 694\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{47}\text{H}_{38}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 717.2724, found 717.2418.



Diethyl 5-phenyl-7-(10-(1-phenylethyl)phenazin-5(10H)-yl)-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4F)

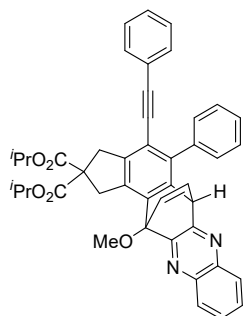
Yellow solid; 542 mg (75 % yield); m. p. 185-187 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.83$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.67 (d, $J = 7.2$ Hz, 2H), 7.47 (t, $J = 7.4$ Hz, 2H), 7.41 (s, 1H), 7.39-7.38 (m, 6H), 7.36-7.33 (m, 3H), 7.24-7.22 (m, 2H), 6.51-6.42 (m, 4H), 6.27 (d, $J = 7.6$ Hz, 2H), 5.74 (d, $J = 7.6$ Hz, 2H), 5.17-5.11 (m, 1H), 4.10 (q, $J = 6.8$ Hz, 4H), 3.74 (s, 2H), 1.80 (d, $J = 7.2$ Hz, 3H), 1.11-1.06 (m, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 175.6, 152.1, 150.3, 146.6, 144.9, 143.9, 143.4, 140.3, 136.4, 135.4, 134.4, 134.3, 134.1, 133.8, 133.4, 133.3, 132.0, 131.5, 127.3, 126.8, 126.6, 122.3, 120.8, 117.1, 101.6, 91.6, 67.0, 64.4, 63.2, 22.7, 19.0. **FT-IR** (KBr): $\nu = 2979, 1724, 1447, 1327, 1255, 1189, 1106, 1026, 758, 694\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{49}\text{H}_{42}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 745.3037, found 745.3035.



Diisopropyl 5-phenyl-7-(10-(1-phenylethyl)phenazin-5(10H)-yl)-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4G)

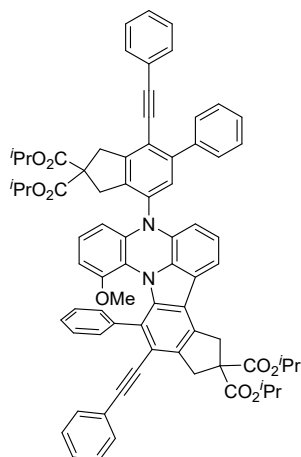
Yellow solid; 533 mg (71 % yield); m. p. 203-205 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.86$; ^1H NMR (400 MHz, DMSO- d_6) δ 7.68 (d, $J = 7.2$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.43-7.39 (m, 6H), 7.38-7.34 (m, 4H), 7.27-7.23 (m, 2H), 6.53-6.43 (m, 4H), 6.29 (d, $J = 8.0$ Hz, 2H), 5.76 (d, $J = 8.0$ Hz, 2H),

5.17-5.12 (m, 1H), 4.93-4.87 (m, 2H), 3.70 (s, 2H), 3.31 (s, 2H), 1.81 (d, $J = 6.8$ Hz, 3H), 1.15 (d, $J = 6.4$ Hz, 6H), 1.08-1.05 (m, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 175.1, 152.1, 150.3, 148.1, 146.6, 144.8, 143.9, 143.4, 140.4, 136.4, 136.3, 135.5, 134.6, 134.3, 134.1, 133.8, 133.4, 133.3, 132.0, 131.5, 127.3, 126.8, 126.6, 122.2, 120.9, 117.1, 101.5, 91.6, 74.5, 64.4, 63.4, 31.6, 26.4, 26.3, 22.6. **FT-IR** (KBr): $\nu = 2949, 1734, 1595, 1483, 1393, 1251, 1165, 1055, 740, 794\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{51}\text{H}_{46}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 773.3350, found 773.3348.



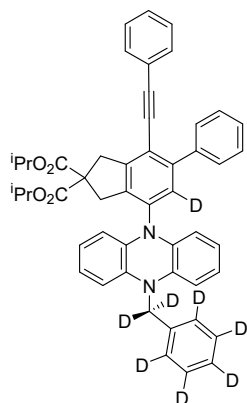
Diisopropyl (6S,13R)-13-methoxy-5-phenyl-4-(phenylethynyl)-1,3,6,13-tetrahydro-2H-6,13-ethenoindeno[4,5-b]phenazine-2,2-dicarboxylate (4H)

Yellow solid; 485 mg (72 % yield); m. p. 199-201 °C; TLC (petroleum ether/EtOAc = 8:1): $R_f = 0.38$; ^1H NMR (400 MHz, DMSO- d_6) δ 8.01 (d, $J = 7.6$ Hz, 1H), 7.92 (d, $J = 6.8$ Hz, 1H), 7.76-7.75 (m, 2H), 7.56-7.54 (m, 2H), 7.46 (d, $J = 7.6$ Hz, 1H), 7.33-7.32 (m, 4H), 7.28-7.25 (m, 1H), 7.16-7.15 (m, 2H), 5.13 (d, $J = 6.0$ Hz, 1H), 5.03-4.97 (m, 1H), 4.94-4.88 (m, 1H), 4.08 (s, 3H), 3.95 (q, $J = 18.0$ Hz, 2H), 3.526 (q, $J = 17.2$ Hz, 2H), 1.24 (t, $J = 6.4$ Hz, 6H), 1.16 (t, $J = 6.0$ Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.0, 170.9, 156.7, 155.7, 142.7, 139.7, 139.1, 138.8, 138.4, 138.3, 137.5, 137.1, 134.7, 131.4, 130.6, 130.2, 130.1, 129.3, 129.2, 129.0, 128.8, 128.7, 128.4, 122.6, 116.3, 96.3, 87.6, 87.2, 69.5, 59.4, 55.3, 48.4, 21.6. **FT-IR** (KBr): $\nu = 2982, 1732, 1596, 1483, 1335, 1246, 1185, 1058, 742, 696\text{ cm}^{-1}$; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{44}\text{H}_{38}\text{N}_2\text{O}_5$ $[\text{M}+\text{Na}]^+$ 697.2673, found 697.2679.



Diisopropyl 7-(2,2-bis(isopropoxycarbonyl)-6-phenyl-7-(phenylethynyl)-2,3-dihydro-1H-inden-4-yl)-11-methoxy-13-phenyl-14-(phenylethynyl)-1,3-dihydrocyclopenta[4,5]indolo[3,2,1-de]phenazine-2,2(7H)-dicarboxylate (4I')

Yellow solid; 125 mg (11 % yield); m. p. 257-259 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.33; ^1H NMR (400 MHz, DMSO- d_6) δ 7.71 (d, J = 7.2 Hz, 2H), 7.64-7.60 (m, 2H), 7.58-7.55 (m, 3H), 7.50 (t, J = 7.2 Hz, 2H), 7.44-7.43 (m, 2H), 7.43-7.41 (m, 5H), 7.38-7.34 (m, 4H), 7.24-7.21 (m, 2H), 6.94 (t, J = 8.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.57 (t, J = 8.0 Hz, 1H), 5.98 (d, J = 8.0 Hz, 1H), 5.88-5.70 (m, 2H), 5.12-5.06 (m, 1H), 4.97-4.85 (m, 4H), 3.98-3.90 (m, 2H), 3.76 (s, 4H), 3.71 (s, 3H), 3.59 (d, J = 16.4 Hz, 1H), 1.30-1.29 (m, 3H), 1.30-1.29 (m, 3H), 1.28-1.27 (m, 3H), 1.20-1.18 (m, 3H), 1.17-1.14 (m, 6H), 1.14-1.13 (m, 3H), 1.11-1.10 (m, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 171.0, 170.2, 159.4, 158.2, 154.5, 152.8, 149.6, 146.5, 140.6, 139.9, 138.7, 138.5, 136.9, 133.4, 131.6, 131.3, 130.6, 130.0, 129.7, 129.6, 129.4, 129.2, 128.8, 128.7, 127.0, 126.2, 125.7, 124.6, 124.0, 123.3, 123.3, 122.5, 118.4, 118.1, 116.6, 112.9, 111.5, 107.7, 105.8, 96.4, 94.8, 88.1, 86.8, 69.7, 69.6, 60.1, 59.8, 56.1, 21.8, 21.7, 21.6. **FT-IR** (KBr): ν = 2983, 1732, 1594, 1483, 1355, 1246, 1184, 1016, 741, 696 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{75}\text{H}_{66}\text{N}_2\text{O}_9$ $[\text{M}+\text{Na}]^+$ 1161.4661, found 1161.4670.

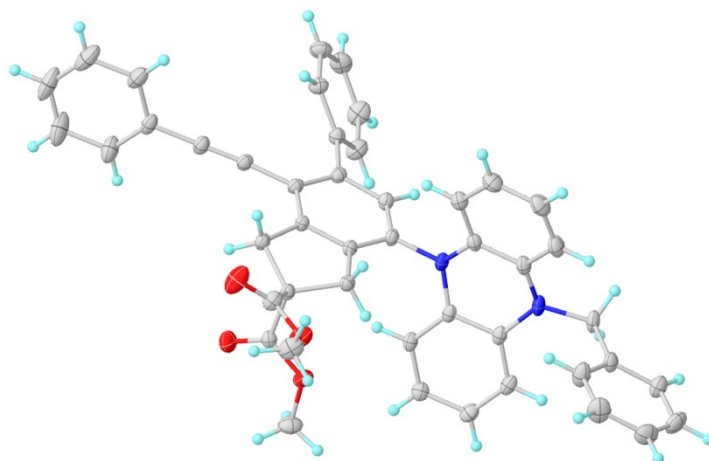


Diisopropyl 5-phenyl-7-(10-((phenyl-D5)methyl-D2)phenazin-5(10H)-yl)-4-(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate-6-D (4J)

Yellow solid; 558 mg (75 % yield); m. p. 149-151 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.79; ^1H NMR (400 MHz, DMSO- d_6) δ 7.71 (d, J = 6.8 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.45 (s, 1H), 7.45-7.43 (m, 5H), 7.45 (t, J = 7.2 Hz, 2H), 6.36 (t, J = 7.2 Hz, 2H), 6.17 (d, J = 6.8 Hz, 2H), 5.63 (d, J = 7.6 Hz, 2H), 3.74 (s, 2H), 3.43 (s, 2H), 1.19 (d, J = 6.0 Hz, 6H), 1.12 (d, J = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 170.4, 167.2, 147.4, 145.7, 141.2, 140.4, 138.8, 136.9, 136.1, 135.6, 131.6, 131.5, 129.5, 129.4, 128.7, 122.5, 122.2, 121.5, 117.5, 116.4, 116.2, 115.2, 114.4, 112.2, 111.9, 111.4, 110.5, 110.1, 109.5, 109.2, 96.8, 90.3, 86.8, 69.8, 59.7, 21.7, 21.6. **FT-IR** (KBr): ν = 2980, 1729, 1597, 1487, 1340, 1276, 1187, 1106, 741, 694 cm^{-1} ; **HRMS** (ESI-TOF): m/z calcd for $\text{C}_{50}\text{H}_{36}\text{D}_8\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 767.3695, found 767.3694.

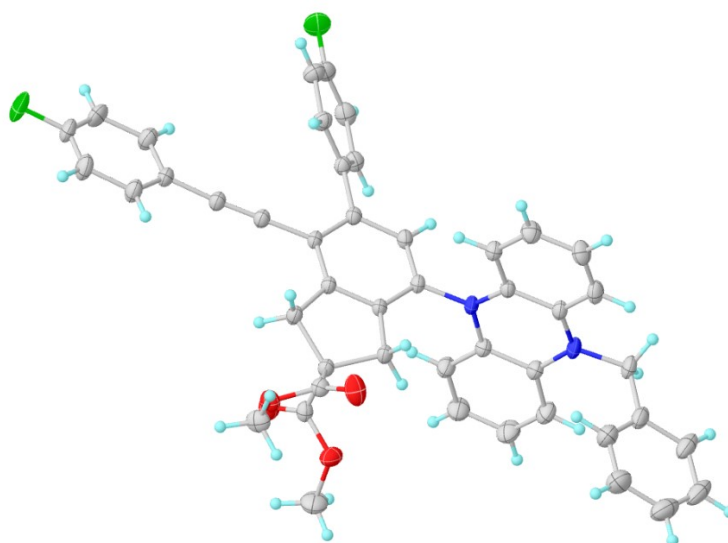
3. X-Ray Crystallographic Studies

Single-Crystal Growth Method. Suitable single crystals for Single Crystal X-Ray Diffraction (SC-XRD) experiment were growth by means of solvent diffusion method in a sealed vial. The general vapor diffusion method for single crystals growth used in this paper is described as follows: 10 mg sample was dissolved in 4 mL DMSO- d_6 (or a mixture of ethyl acetate and DMSO- d_6 which ratio is about 1/2) was filtered into the 25 mL vial, and cover with lid to make the system as a sealed vial, which was stand for several days.



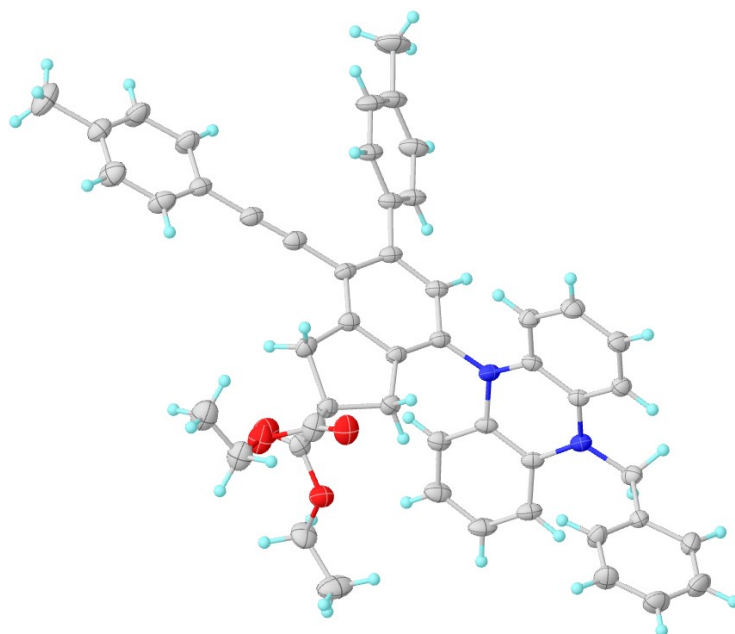
4a

Representative diagram for the complex **4a** with thermal ellipsoids set at 20% probability level.



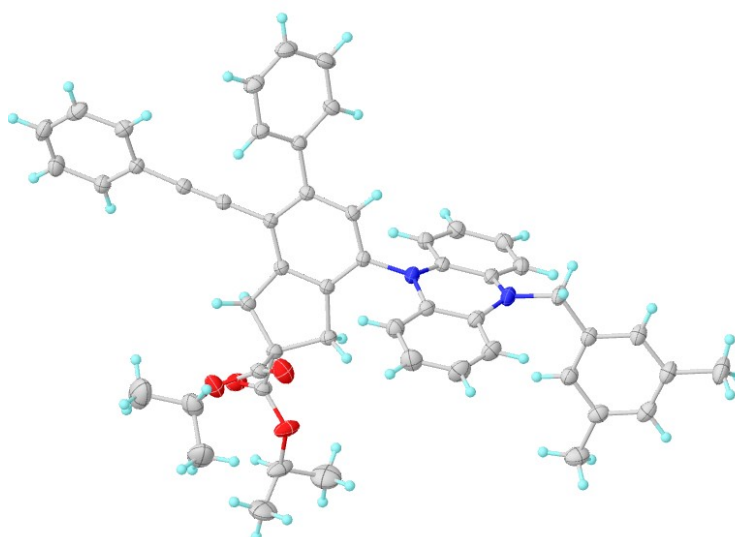
4d

Representative diagram for the complex **4d** with thermal ellipsoids set at 20% probability level.



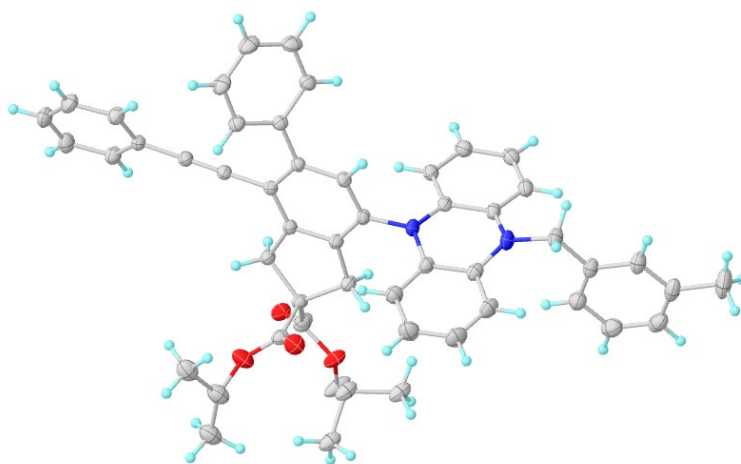
4j

Representative diagram for the complex **4j** with thermal ellipsoids set at 20% probability level.



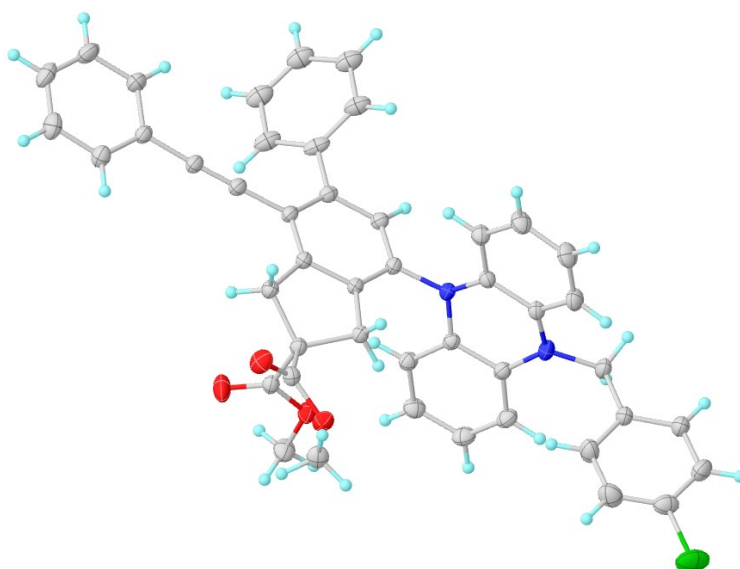
4x

Representative diagram for the complex **4x** with thermal ellipsoids set at 20% probability level.



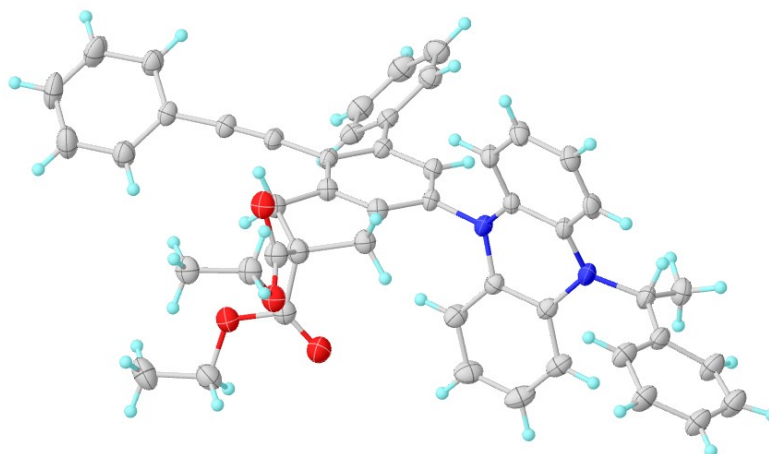
4A

Representative diagram for the complex **4A** with thermal ellipsoids set at 20% probability level.



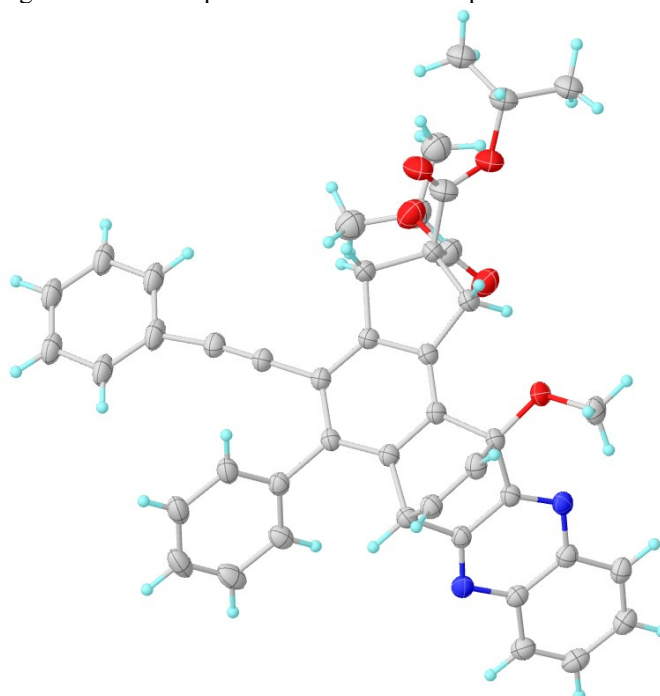
4B

Representative diagram for the complex **4B** with thermal ellipsoids set at 20% probability level.



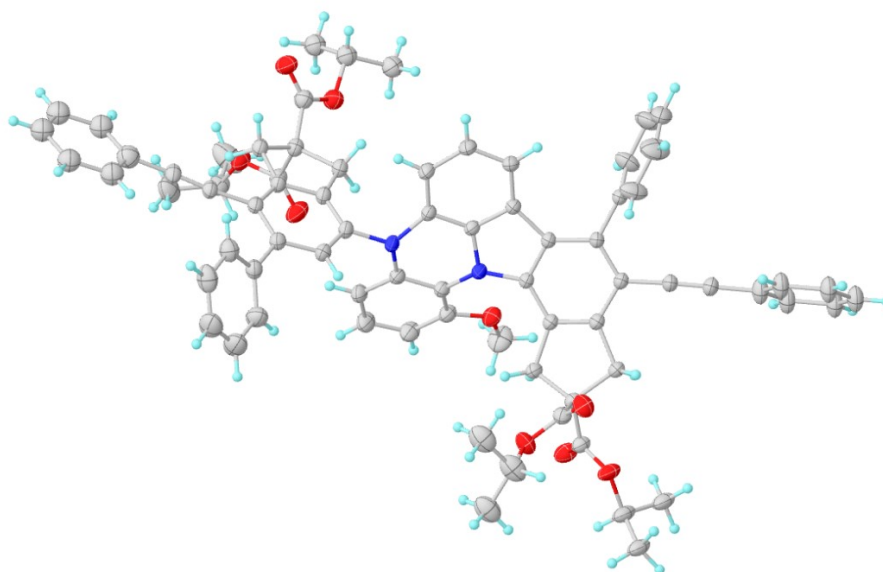
4F

Representative diagram for the complex **4F** with thermal ellipsoids set at 20% probability level.



4H

Representative diagram for the complex **4H** with thermal ellipsoids set at 20% probability level.



4I'

Representative diagram for the complex **4I'** with thermal ellipsoids set at 20% probability level.

Crystal data and structure refinement for complexes **4a**, **4b**, **4i**, **4x**

	4a	4d	4j	4x
Formula	C ₄₆ H ₃₆ N ₂ O ₄	C ₄₆ H ₃₄ F ₂ N ₂ O ₄	C ₅₀ H ₄₄ N ₂ O ₄	C ₅₂ H ₄₈ N ₂ O ₄
FW	680.77	716.25	736.33	764.36
T (K)	273.15	273.15	273.15	273.15
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic

Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.4985(4)	11.8312(3)	12.7014(9)	12.4510(3)
<i>b</i> (Å)	12.1145(4)	13.2147(3)	12.8424(8)	13.0800(3)
<i>c</i> (Å)	13.9075(5)	15.2145(4)	14.1011(10)	27.5697(6)
α (deg)	70.901(2)	76.822(2)	106.295(2)	84.7720(10)
β (deg)	73.620(2)	73.368(2)	108.766(2)	88.0100(10)
γ (deg)	87.248(2)	73.606(2)	92.511(2)	73.9620(10)
<i>V</i> (Å ³)	1765.02(11)	2158.32(10)	2067.5(2)	4297.06(17)
<i>Z</i>	2	2	2	2
F (000)	716.0	874.0	780.0	1624.0
ρ_{calc} (g·cm ⁻³)	1.281	1.283	1.184	1.182
μ (mm ⁻¹)	0.648	0.698	0.075	0.583
θ range (°)	3.484 to 68.462	3.071 to 68.395	2.563 to 25	1.609 to 68.314
Reflections collected	32646	37186	61438	76448
Independent reflections	6490	7961	7251	15733
<i>R</i> _{int}	0.0592	0.0723	0.0860	0.0845
Data/restraints/parameters	6490/66/471	7916/48/489	7251/24/509	15733/79/1077

Goodness-of-fit on F_2	1.100	1.006	1.012	1.065
R_I , wR_2 [$I > 2\sigma(I)$]	0.0606, 0.1753	0.0592, 0.1736	0.0696, 0.1884	0.0555, 0.1529
R_I , wR_2 (all data)	0.0704, 0.1861	0.0897, 0.2001	0.1195, 0.2374	0.0798, 0.1683
Largest diff. peak and hole e.Å ⁻³	0.75/-0.47	0.19/-0.23	0.66/-0.71	0.29/-0.39

Crystal data and structure refinement for complexes **4A**, **4B**, **4F**, **4H**, **4I**

	4A	4B	4F	4H	4I'
Formula	C ₅₁ H ₄₆ N ₂ O ₄	C ₄₆ H ₃₅ ClN ₂ O ₄	C ₄₉ H ₄₂ N ₂ O ₄	C ₄₄ H ₃₈ N ₂ O ₅	C ₇₅ H ₆₆ N ₂ O ₉
FW	750.35	714.23	722.32	674.28	1138.48
T (K)	273.15	273.15	273.15	273.15	273.15
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	11.4985(4)	10.3480(2)	12.6572(16)	8.6001(7)	15.3348(9)
b (Å)	12.1145(4)	13.4185(3)	20.628(2)	10.2098(10)	15.7859(9)
c (Å)	13.9075(5)	15.4355(3)	29.589(4)	21.2354(16)	16.1062(9)
α (deg)	70.901(2)	112.6600(10)	90	97.638(6)	61.643(2)
β (deg)	73.620(2)	105.0610(10)	90	98.178(6)	82.789(3)
γ (deg)	87.248(2)	98.3290(10)	90	92.956(6)	74.741(4)
V (Å ³)	1765.02(11)	1836.32(7)	7725.5(16)	1824.5(3)	3310.1(3)
Z	2	2	8	2	2
F (000)	716.0	748.0	3048.0	712.0	1204.0
ρ_{calc} (g·cm ⁻³)	1.281	1.293	1.241	1.228	1.143
μ (mm ⁻¹)	0.648	1.303	0.621	0.641	0.596
θ range (°)	6.968 to 136.924	3.306 to 68.434	2.987 to 68.629	4.25 to 68.536	2.987 to 68.381
Reflections collected	32646	28852	99883	21008	53948
Independent reflections	6490	6725	7118	6654	12134
R_{int}	0.0592	0.0533	0.0781	0.1341	0.0833
Data/restraints/parameters	6490/66/471	6725/36/480	7188/827/611	6654/350/487	12134/933/903
Goodness-of-fit on F_2	1.100	1.114	1.100	1.190	1.102
R_I , wR_2 [$I > 2\sigma(I)$]	0.0606, 0.1753	0.0628, 0.1789	0.0956, 0.2651	0.1427, 0.3905	0.1002, 0.2940
R_I , wR_2 (all data)	0.0704, 0.1861	0.0745, 0.1908	0.1064, 0.2765	0.2303, 0.4700	0.1429, 0.3417
Largest diff. peak and hole e.Å ⁻³	0.75/-0.47	0.60/-0.41	0.67/-0.66	0.52/-0.54	0.63/-0.60

X-Ray Data Collection and Structure Refinement Details: Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 273(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program. 1. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations based on F_2 using the SHELXTL program package; 2. The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvent were squeezed by using PLATON; 3. All crystal structural pictures drawn by IUCr web.

References

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4. ^1H NMR & ^{13}C NMR Spectra for New Compounds

