

Supporting Information

Controllable One-step Synthesis of Spirocycles, Polycycles, Di- and Tetrahydronaphthalenes from Aryl-substituted Propargylic Alcohols

Wen Huang, Pengzhi Zheng, Zhengxing Zhang, Ruiting Liu, Zhenxia Chen, and Xigeng Zhou*

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, People's Republic of China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

E-mail: xgzhou@fudan.edu.cn; Tel: (+86) 21 6564-3769; Fax: (+86) 21 6564-1740

General Methods	S2
Experimental Procedures and characterization data for compounds 1-5	S2-S24
X-Ray Crystallographic analysis of 2a , 4a , 3b and 5d	S25-S26

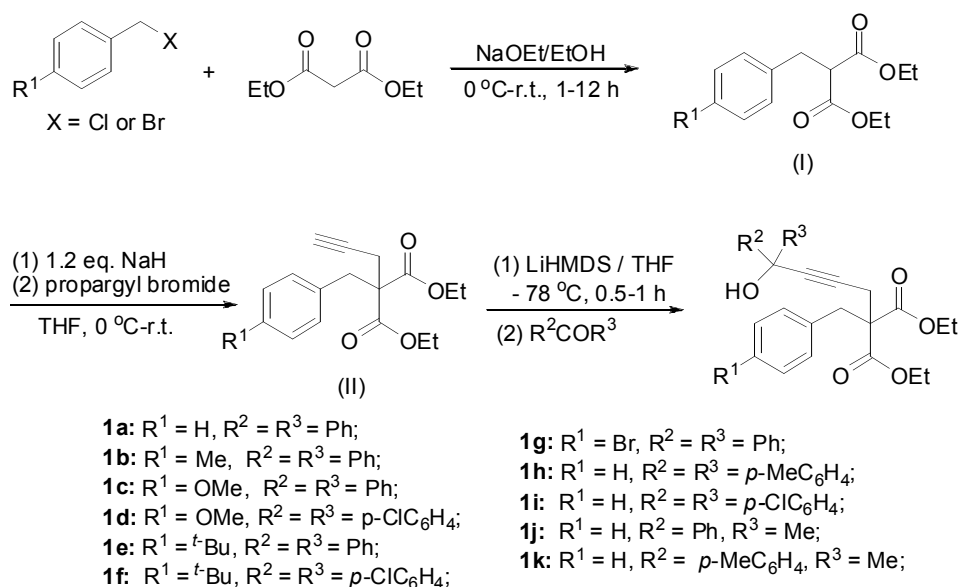
General Methods.

All reactions and manipulations were performed in air unless otherwise indicated. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz respectively using tetramethylsilane (TMS) as the internal standard. Mass spectra were recorded by EI, ESI and MALDI methods. High resolution mass spectra (HRMS) were recorded using ESI ionization sources. X-ray structural analysis was carried out using graphite-monochromated MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC or NMR experiment. Flash column chromatography was carried out using 300-400 mesh silica gel.

Experimental Procedures.

Starting Materials

General method for preparation of propargylic alcohols



The 2-benzyl malonic acid diethyl ester (**I**) and the 2-benzyl-2-propynyl propanedioic acid diethyl ester (**II**) were prepared by the literature methods reported by J. Zheng¹ and S. Murai.²

The propargylic alcohols based on diethylmalonate were synthesized according to a similar method reported by B. M. Trost and M. T. Rudd.³

Typical procedure for the synthesis of diethyl

2-(4-hydroxy-4,4-diphenylbut-2-ynyl)-2-(4-methylbenzyl)malonate (1b).

To a strongly stirred solution of EtONa (4.2 g of Na dissolved in 150 mL of EtOH), 34.6 g (0.216 mol) of diethyl malonate and 25 mL of EtOH solution containing 25.3 g (0.18 mol) of 4-methylbenzyl chloride were added dropwise. The resulting mixture was stirred at room temperature for 12 h; then the solvent was removed in *vacuo*. Then, 50 mL of ice-water was added to the residue. The crude mixture was extracted with ether (3 × 40 mL), the combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. The mixture was concentrated by rotary evaporation. Distilling the remained oil under reduced pressure gave diethyl 2-(4-methylbenzyl) malonate (**I**) as a colorless oil (21.83 g, 46% yield).

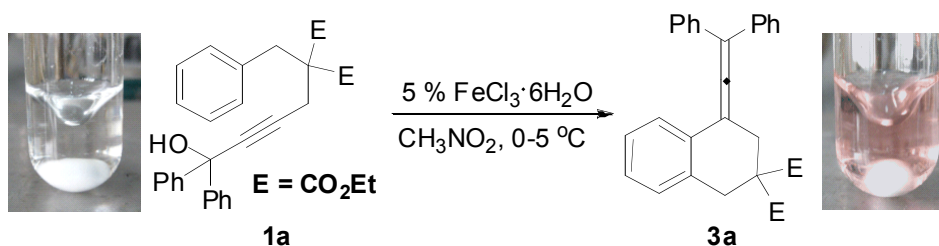
To a stirred suspension of NaH (0.96 g, 60 % in oil) in dry THF (30 mL) was added diethyl 2-(4-methylbenzyl) malonate (5.28 g, 0.02 mol) dropwise at 0 °C. The reaction mixture was warmed to room temperature until the evolution of dihydrogen gas subsided; then propargyl bromide (3.57 g, 24 mmol; 80% in toluene) was added dropwise at 0 °C. The mixture was slowly warmed to room temperature and continued to stir for 4 h. The reaction was then quenched with water and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic layer was washed with brine, dried (Na₂SO₄), and solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as the eluent to give the diethyl 2-(4-methylbenzyl)-2-(prop-2-ynyl)malonate (**II**) as a white solid (5.19 g, 86%).

To a solution of diethyl 2-(4-methylbenzyl)-2-(prop-2-ynyl)malonate (**II**) (0.91 g, 3 mmol) in dry THF (10 mL) was added LiHMDS (3.6 mL, 1 M in THF, 3.6 mmol) dropwise at -78 °C under N₂ atmosphere, and the reaction mixture was stirred for 0.5 h at that temperature, followed by the addition of benzophenone (0.60 g, 3.3 mmol).

The reaction was allowed to slowly warm to room temperature. The mixture was quenched with a saturated solution of NH_4Cl and the aqueous layer was extracted with ether (3 x 15 mL). The combined organic layer was washed with brine, dried (Na_2SO_4), and solvents were evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate as the eluent to give diethyl 2-(4-hydroxy-4,4-diphenylbut-2-ynyl)-2-(4-methylbenzyl)malonate as a white solid (1.09 g, 75%).

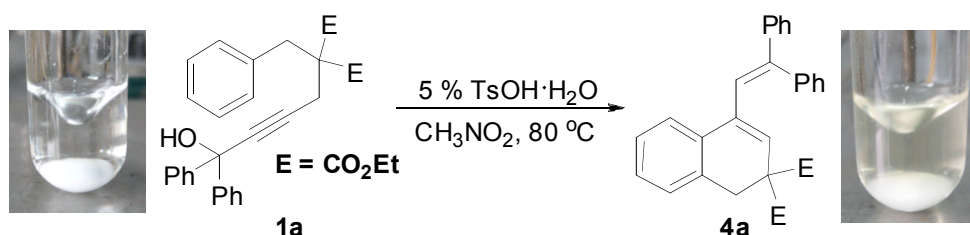
Other propargylic alcohols were prepared according to the similar procedure.

Typical procedure: Synthesis of tetrahydronaphthalenes 3a from propargylic alcohols 1a.



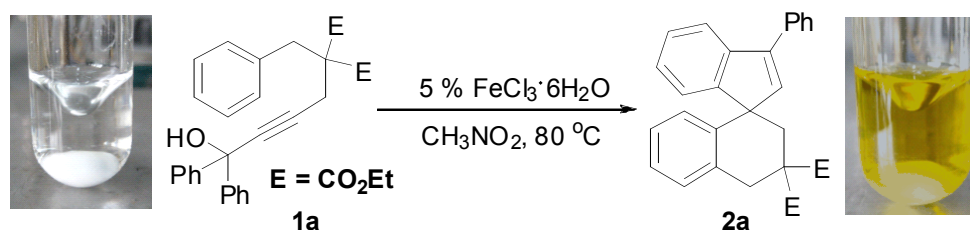
To a stirred solution of propargylic alcohol **1a** (0.2 mmol) in nitromethane (2 mL) in an ice-water bath was added 5 mol% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The color of the resulting mixture changed from colorless to pink quickly. TLC analysis showed that the reaction was complete in about 5-30 min. The crude mixture was directly purified by silica gel column chromatography to provide the desired product.

Typical procedure: Synthesis of dihydronaphthalenes 4a from propargylic alcohols 1a.



To a stirred solution of propargylic alcohol **1a** (0.2 mmol) in nitromethane (2 mL) was added 5 mol % TsOH. The reaction mixture was heated to 80 °C until the reaction was complete (monitored by TLC or NMR). The crude mixture was purified by silica gel column chromatography to give the desired product.

Typical procedure: Synthesis of spirocyclic compounds **2a from propargylic alcohols **1a**.**

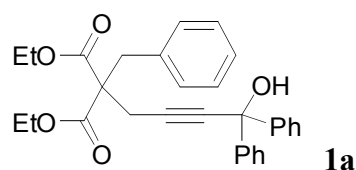


To a stirred solution of propargylic alcohol **1a** (0.2 mmol) in nitromethane (2 mL) was added 5 mol % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The reaction mixture was stirred at 80 °C until the completion of the reaction (monitored by TLC or NMR). The crude mixture was purified by silica gel column chromatography to provide the spirocyclic product.

References:

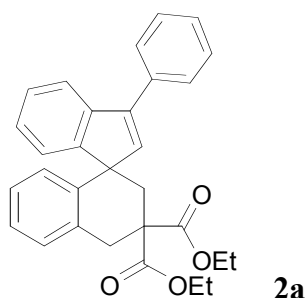
1. Wu, Z.-X.; Minhas, G. S.; Wen, D.; Jiang, H.-L.; Chen, K.-X.; Zimniak, P.; Zheng, J. *J. Med. Chem.* **2004**, *47*, 3282-3294.
2. Chatani, N.; Inoue, H.; Ikeda, T.; Murai, S. *J. Org. Chem.* **2000**, *65*, 4913-4918.
3. Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2005**, *127*, 4763-4776.

Characterizations of products:



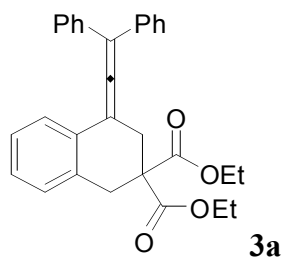
diethyl 2-benzyl-2-(4-hydroxy-4,4-diphenylbut-2-ynyl)malonate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.26 (t, J = 7.3 Hz, 6H), 2.92 (s, 2H), 3.53 (s, 2H), 3.91 (d, J = 3.2 Hz, 1H), 4.21-4.25 (m, 4H), 7.16-7.39 (m, 11H), 7.72 (d, J = 8.2 Hz, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 170.1, 145.6, 135.7, 130.2, 128.6, 128.3, 127.7, 127.3, 126.3, 87.4, 82.9, 74.6, 62.0, 58.6, 37.9, 22.9, 14.2; Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{O}_5$: C, 76.57; H, 6.43. Found: C, 76.51; H, 6.43. HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{30}\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 493.1991, Found: 493.1984.



diethyl 3-phenyl-2'*H*-spiro[indene-1,1'-naphthalene]-3',3'(4'*H*)-dicarboxylate

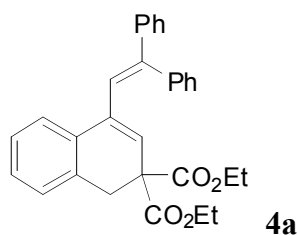
^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.14 (t, J = 7.3 Hz, 3H), 1.24 (t, J = 7.3 Hz, 3H), 2.58 (dd, J = 1.8, 14.2 Hz, 1H), 2.94 (d, J = 14.2 Hz, 1H), 3.29 (d, J = 16.5 Hz, 1H), 3.68 (d, J = 16.5 Hz, 1H), 4.10-4.24 (m, 4H), 6.46 (d, J = 8.2 Hz, 1H), 6.48 (s, 1H), 6.90 (t, J = 7.3 Hz, 1H), 7.10 (t, J = 7.3 Hz, 1H), 7.19-7.23 (m, 3H), 7.28-7.43 (m, 4H), 7.54-7.58 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 171.7, 171.5, 155.3, 142.8, 142.2, 141.5, 135.5, 135.4, 134.2, 129.2, 128.7, 127.9, 127.8, 127.2, 127.1, 127.0, 126.8, 126.4, 123.7, 120.9, 61.9, 61.3, 54.9, 53.4, 38.1, 35.4, 14.2, 14.0. Anal. Calcd for $\text{C}_{30}\text{H}_{28}\text{O}_4$: C, 79.62; H, 6.24. Found: C, 79.64; H, 6.15. HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{29}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 453.2066, Found: 453.2085.



diethyl

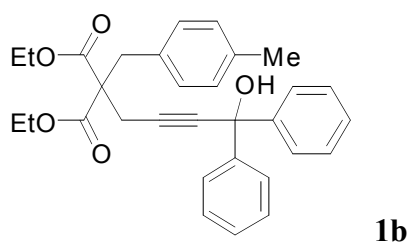
4-(2,2-diphenylvinylidene)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.11 (t, J = 6.8 Hz, 6H), 3.27 (s, 2H), 3.36 (s, 2H), 4.02-4.16 (m, 4H), 7.08-7.41 (m, 13H), 7.50-7.52 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 206.2, 170.6, 136.7, 133.4, 129.7, 129.5, 128.6, 128.5, 127.7, 127.6, 126.9, 126.5, 113.8, 101.9, 61.8, 53.8, 35.4, 33.8, 13.9; HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{29}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 453.2066, Found: 453.2048.



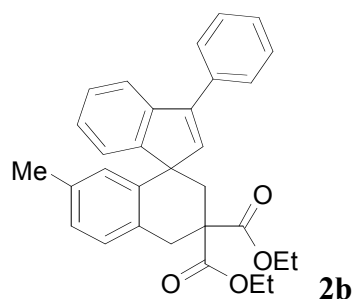
diethyl 4-(2,2-diphenylvinyl)naphthalene-2,2(1H)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.10 (t, J = 7.3 Hz, 6H), 3.29 (s, 2H), 3.83-3.95 (m, 2H), 4.04-4.13 (m, 2H), 5.77 (d, J = 1.4 Hz, 1H), 6.69 (d, J = 1.4 Hz, 1H), 7.08-7.20 (m, 8H), 7.27-7.38 (m, 6H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 169.9, 145.9, 143.0, 140.1, 137.2, 132.9, 132.8, 130.0, 128.3, 128.2, 127.9, 127.8, 127.0, 125.9, 124.8, 124.0, 61.7, 54.7, 34.2, 13.9; HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{28}\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 475.1885, Found: 475.1877.



diethyl 2-(4-hydroxy-4,4-diphenylbut-2-ynyl)-2-(4-methylbenzyl)malonate

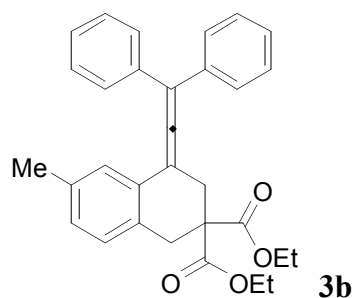
^1H NMR (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$): δ 1.19 (t, $J = 7.3$ Hz, 6H), 2.26 (s, 3H), 2.79 (s, 2H), 3.25 (s, 1H), 3.35 (s, 2H), 4.14-4.16 (m, 4H), 6.95-7.01 (m, 4H), 7.18-7.23 (m, 2H), 7.27-7.32 (m, 4H), 7.58-7.61 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$): δ 170.1, 145.3, 136.8, 132.5, 129.9, 129.2, 128.3, 127.7, 126.2, 87.1, 83.1, 74.6, 61.9, 58.5, 37.4, 22.8, 21.2, 14.2. Anal. Calcd for $\text{C}_{31}\text{H}_{32}\text{O}_5$: C, 76.84; H, 6.66. Found: C, 76.74; H, 6.56. HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{32}\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 507.2147, Found: 507.2170.



diethyl

7'-methyl-3-phenyl-2'*H*-spiro[indene-1,1'-naphthalene]-3',3'(4'*H*)-dicarboxylate

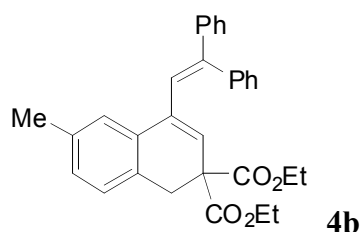
^1H NMR (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$): δ 1.14 (t, $J = 7.3$ Hz, 3H), 1.24 (t, $J = 7.3$ Hz, 3H), 2.05 (s, 3H), 2.53 (dd, $J = 1.8, 14.2$ Hz, 1H), 2.91 (d, $J = 14.2$ Hz, 1H), 3.25 (d, $J = 16.0$ Hz, 1H), 3.63 (d, $J = 16.0$ Hz, 1H), 3.98-4.23 (m, 4H), 6.26 (s, 1H), 6.48 (s, 1H), 6.92 (d, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 7.8$ Hz, 1H), 7.20-7.43 (m, 6H), 7.55-7.60 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$): δ 171.8, 171.5, 155.4, 142.8, 142.3, 141.4, 136.2, 135.5, 135.2, 131.2, 129.1, 128.7, 128.1, 127.9, 127.8, 127.3, 127.1, 126.4, 123.8, 120.9, 61.8, 61.6, 54.9, 53.5, 38.4, 35.1, 21.1, 14.2, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{30}\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 489.2042, Found: 489.2044.



diethyl

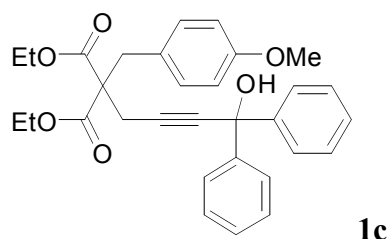
4-(2,2-diphenylvinylidene)-6-methyl-3,4-dihydronaphthalene-2,2(1*H*)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.11 (t, $J = 7.3$ Hz, 6H), 2.23 (s, 3H), 3.26 (s, 2H), 3.31 (s, 2H), 4.03-4.15 (m, 4H), 6.96 (dd, $J = 1.8, 7.8$ Hz, 1H), 7.08 (d, $J = 7.8$ Hz, 1H), 7.25-7.34 (m, 7H), 7.39-7.42 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 206.3, 170.7, 136.8, 136.4, 130.5, 129.4, 129.0, 128.7, 128.6, 127.6, 126.8, 113.7, 102.0, 61.8, 53.9, 35.2, 33.9, 21.3, 14.0. Anal. Calcd for $\text{C}_{31}\text{H}_{30}\text{O}_4$: C, 79.80; H, 6.48. Found: C, 79.85; H, 6.74. HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{31}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 467.2222, Found: 467.2231.



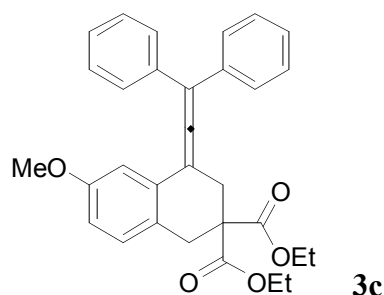
diethyl 4-(2,2-diphenylvinyl)-6-methylnaphthalene-2,2(1*H*)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.10 (t, $J = 7.3$ Hz, 6H), 2.26 (s, 3H), 3.25 (s, 2H), 3.84-3.92 (m, 2H), 4.02-4.12 (m, 2H), 5.76 (d, $J = 1.5$ Hz, 1H), 6.69 (d, $J = 1.5$ Hz, 1H), 6.98-7.20 (m, 8H), 7.29-7.36 (m, 5H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 170.0, 145.7, 143.1, 140.2, 137.3, 136.5, 132.7, 130.1, 129.7, 129.0, 128.3, 128.2, 128.0, 127.8, 127.7, 127.0, 126.1, 125.6, 124.1, 61.6, 54.8, 33.9, 21.3, 13.9; HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{30}\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 489.2042, Found: 489.2066.



diethyl 2-(4-hydroxy-4,4-diphenylbut-2-ynyl)-2-(4-methoxybenzyl)malonate

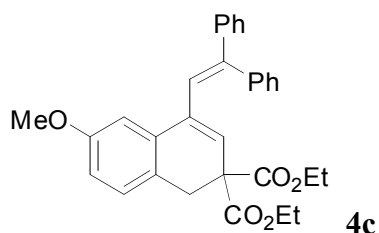
^1H NMR (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$): δ 1.21 (t, J = 7.3 Hz, 6H), 2.79 (s, 2H), 3.14 (s, 1H), 3.34 (s, 2H), 3.73 (s, 3H), 4.15-4.18 (m, 4H), 6.72 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 7.21-7.26 (m, 2H), 7.29-7.35 (m, 4H), 7.57-7.62 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$): δ 170.0, 158.8, 145.2, 131.0, 128.3, 127.7, 127.5, 126.1, 113.9, 87.0, 83.1, 74.6, 61.9, 58.5, 55.3, 36.9, 22.7, 14.1. Anal. Calcd for $\text{C}_{31}\text{H}_{32}\text{O}_6$: C, 74.38; H, 6.44. Found: C, 74.15; H, 6.58. HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{32}\text{O}_6\text{Na}$ ($[\text{M}+\text{Na}]^+$): 523.2097, Found: 523.2109.



diethyl

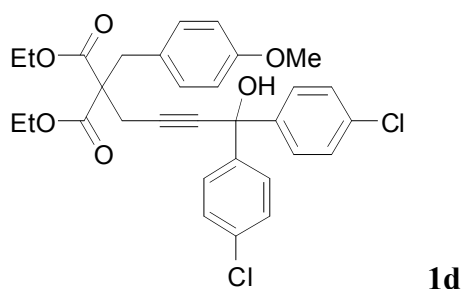
4-(2,2-diphenylvinylidene)-6-methoxy-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$): δ 1.12 (t, J = 6.9 Hz, 6H), 3.25 (s, 2H), 3.90 (s, 2H), 3.70 (s, 3H), 4.05-4.15 (m, 4H), 6.75 (dd, J = 2.7, 8.3 Hz, 1H), 7.03 (d, J = 2.7 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 7.23-7.35 (m, 6H), 7.37-7.40 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$): δ 206.2, 170.7, 158.3, 136.7, 130.7, 130.4, 128.6, 128.5, 127.7, 125.8, 114.4, 114.0, 110.6, 102.0, 61.8, 55.3, 54.0, 34.7, 33.7, 14.0; HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{30}\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 505.1991, Found: 505.1998



diethyl 4-(2,2-diphenylvinyl)-6-methoxynaphthalene-2,2(1*H*)-dicarboxylate

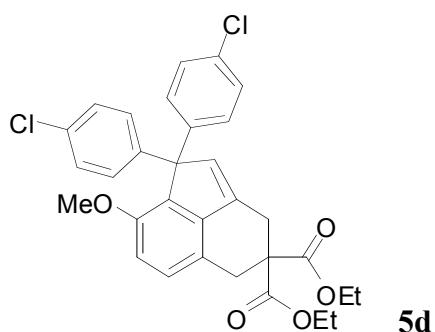
^1H NMR (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$): δ 1.10 (t, $J = 7.3$ Hz, 6H), 3.22 (s, 2H), 3.74 (s, 3H), 3.87-3.92 (m, 2H), 4.07-4.12 (m, 2H), 5.80 (d, $J = 1.3$ Hz, 1H), 6.67 (d, $J = 1.3$ Hz, 1H), 6.72 (dd, $J = 2.3, 8.2$ Hz, 1H), 6.90 (d, $J = 2.3$ Hz, 1H), 7.09-7.35 (m, 11H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$): δ 169.9, 158.7, 146.0, 143.0, 140.1, 137.2, 134.0, 130.0, 128.6, 128.3, 128.2, 128.0, 127.9, 127.1, 125.7, 124.8, 124.7, 112.9, 111.3, 61.6, 55.5, 54.9, 33.5, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{30}\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 505.1991, Found: 505.2003.



diethyl

2-(4,4-bis(4-chlorophenyl)-4-hydroxybut-2-ynyl)-2-(4-methoxybenzyl)malonate

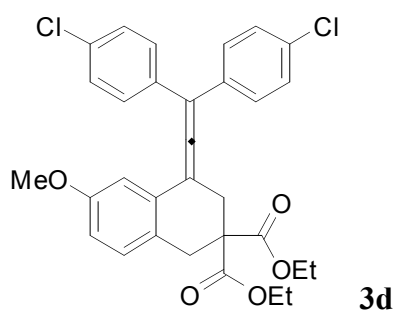
^1H NMR (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$): δ 1.21 (t, $J = 7.3$ Hz, 6H), 2.77 (s, 2H), 3.30 (s, 2H), 3.57 (s, 1H), 3.73 (s, 3H), 4.13-4.17 (m, 4H), 6.73 (d, $J = 8.2$ Hz, 2H), 6.96 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.7$ Hz, 4H), 7.48 (d, $J = 8.7$ Hz, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$): δ 169.9, 158.8, 143.5, 133.8, 130.9, 128.5, 127.6, 127.2, 113.9, 86.1, 83.8, 73.6, 61.9, 58.4, 55.3, 37.0, 22.7, 14.1. HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{30}\text{Cl}_2\text{O}_6\text{Na}$ ($[\text{M}+\text{Na}]^+$): 591.1317, Found: 591.1313.



diethyl

1,1-bis(4-chlorophenyl)-8-methoxy-3,5-dihydroacenaphthylene-4,4(1*H*)-dicarboxylate

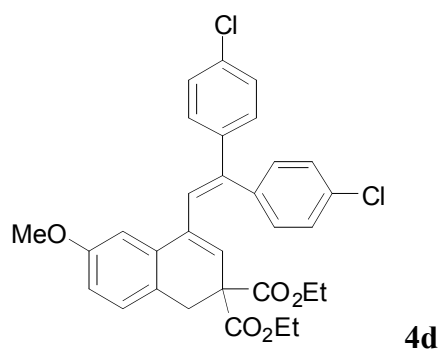
^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.15 (t, $J = 7.3$ Hz, 6H), 3.17 (d, $J = 1.3$ Hz, 2H), 3.32 (s, 2H), 3.60 (s, 3H), 3.98-4.16 (m, 4H), 6.23 (s, 1H), 6.65 (d, $J = 8.2$ Hz, 1H), 7.08-7.17 (m, 9H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 170.8, 154.1, 141.2, 140.1, 137.4, 135.5, 133.8, 132.4, 129.8, 128.4, 128.0, 122.2, 110.7, 66.7, 61.8, 56.0, 55.4, 33.1, 31.2, 14.1. HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{28}\text{Cl}_2\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 573.1211, Found: 573.1192.



diethyl

4-(2,2-bis(4-chlorophenyl)vinylidene)-6-methoxy-3,4-dihydronaphthalene-2,2(1*H*)-dicarboxylate

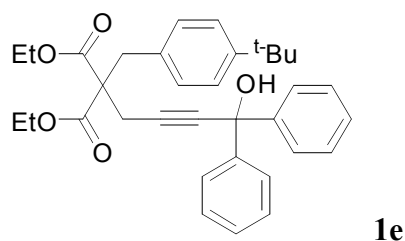
^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.13 (t, $J = 7.3$ Hz, 6H), 3.23 (s, 2H), 3.30 (s, 2H), 3.70 (s, 3H), 4.04-4.16 (m, 4H), 6.76 (dd, $J = 2.7, 8.7$ Hz, 1H), 6.95 (d, $J = 2.7$ Hz, 1H), 7.10 (d, $J = 8.2$ Hz, 1H), 7.24-7.32 (m, 8H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 206.1, 170.5, 158.3, 134.8, 133.7, 130.6, 130.0, 129.8, 128.8, 125.9, 114.5, 112.2, 110.8, 102.9, 61.8, 55.3, 53.9, 34.6, 33.5, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{29}\text{Cl}_2\text{O}_5$ ($[\text{M}+\text{H}]^+$): 551.1392, Found: 551.1378.



diethyl

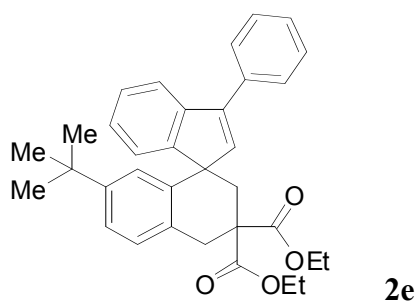
4-(2,2-bis(4-chlorophenyl)vinyl)-6-methoxynaphthalene-2,2(1*H*)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.13 (t, $J = 7.3$ Hz, 6H), 3.23 (s, 2H), 3.75 (s, 3H), 3.89-3.96 (m, 2H), 3.98-4.16 (m, 2H), 5.78 (d, $J = 1.2$ Hz, 1H), 6.64 (d, $J = 1.2$ Hz, 1H), 6.75 (dd, $J = 2.6, 8.0$ Hz, 1H), 6.86 (d, $J = 2.2$ Hz, 1H), 7.05-7.08 (m, 2H), 7.12-7.30 (m, 7H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 169.8, 158.8, 143.9, 140.8, 138.1, 136.9, 134.0, 133.6, 133.2, 131.4, 129.4, 128.7, 128.6, 128.4, 126.8, 125.2, 124.8, 112.8, 111.5, 61.8, 55.5, 54.8, 33.3, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{31}\text{H}_{28}\text{Cl}_2\text{NaO}_5$ ($[\text{M}+\text{Na}]^+$): 573.1211, Found: 573.1229.



diethyl 2-(4-*tert*-butylbenzyl)-2-(4-hydroxy-4,4-diphenylbut-2-ynyl)malonate

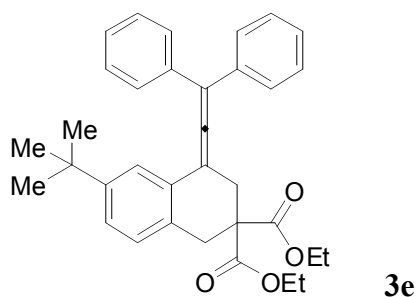
^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.21 (t, $J = 7.3$ Hz, 6H), 1.27 (s, 9H), 2.80 (s, 2H), 2.97 (s, 1H), 3.37 (s, 2H), 4.12-4.18 (m, 4H), 7.02 (d, $J = 8.2$ Hz, 2H), 7.21-7.26 (m, 4H), 7.30-7.34 (m, 4H), 7.62 (d, $J = 7.3$ Hz, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 170.0, 150.0, 145.2, 132.5, 129.7, 128.3, 127.7, 126.1, 125.4, 86.9, 83.2, 74.6, 61.8, 58.5, 37.3, 34.5, 31.4, 22.8, 14.1. HRMS-ESI-TOF: calcd for $\text{C}_{34}\text{H}_{38}\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 549.2617, Found: 549.2638.



diethyl

7'-tert-butyl-3-phenyl-2'H-spiro[indene-1,1'-naphthalene]-3',3'(4'H)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.04 (s, 9H), 1.14 (t, $J = 7.3$ Hz, 3H), 1.24 (t, $J = 7.3$ Hz, 3H), 2.55 (dd, $J = 1.8, 14.2$ Hz, 1H), 2.94 (d, $J = 14.2$ Hz, 1H), 3.25 (d, $J = 16.0$ Hz, 1H), 3.67 (dd, $J = 1.8, 16.0$ Hz, 1H), 3.98-4.22 (m, 4H), 6.43 (s, 1H), 6.46 (s, 1H), 7.14-7.36 (m, 6H), 7.42 (t, $J = 7.3$ Hz, 2H), 7.53-7.57 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 171.9, 171.7, 155.2, 149.3, 142.9, 142.2, 141.4, 135.7, 135.0, 131.2, 128.7, 128.6, 127.8, 127.7, 127.1, 126.3, 124.2, 123.7, 123.6, 120.8, 61.8, 61.6, 55.1, 53.5, 38.1, 34.9, 34.3, 31.4, 14.2, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{34}\text{H}_{36}\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 531.2511, Found: 531.2506.

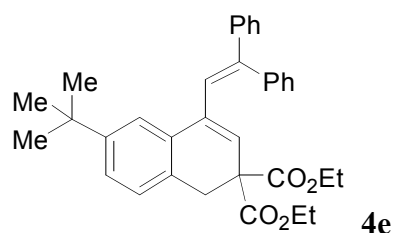


diethyl

6-tert-butyl-4-(2,2-diphenylvinylidene)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate

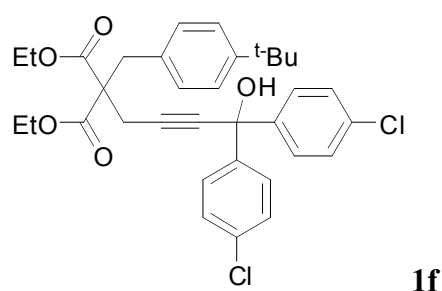
^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.12 (t, $J = 7.3$ Hz, 6H), 1.23 (s, 9H), 3.27 (s, 2H), 3.33 (s, 2H), 4.05-4.15 (m, 4H), 7.12 (d, $J = 8.2$ Hz, 1H), 7.20 (dd, $J = 1.8, 8.2$ Hz, 1H), 7.23-7.42 (m, 10H), 7.54 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 206.1, 170.7, 149.5, 137.0, 130.5, 129.1, 129.0, 128.6, 128.5, 127.6, 125.4,

123.0, 113.9, 102.2, 61.8, 53.9, 35.0, 34.5, 33.9, 31.4, 14.1. HRMS-ESI-TOF: calcd for $C_{34}H_{37}O_4$ ($[M+H]^+$): 509.2692, Found: 509.2694.



diethyl 6-*tert*-butyl-4-(2,2-diphenylvinyl)naphthalene-2,2(1H)-dicarboxylate

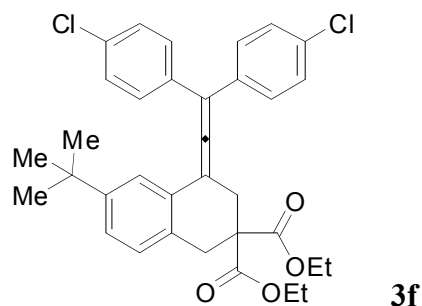
1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.10 (t, J = 7.3 Hz, 6H), 1.25 (s, 9H), 3.26 (s, 2H), 3.89-3.95 (m, 2H), 4.06-4.12 (m, 2H), 5.81 (d, J = 1.5 Hz, 1H), 6.73 (d, J = 1.5 Hz, 1H), 7.09-7.20 (m, 7H), 7.30-7.36 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 170.1, 149.7, 145.8, 143.2, 140.3, 137.8, 132.3, 130.1, 129.7, 128.4, 128.3, 127.9, 127.8, 127.4, 127.1, 126.0, 125.2, 124.2, 121.8, 61.7, 54.8, 34.6, 33.9, 31.5, 14.0. HRMS-ESI-TOF: calcd for $C_{34}H_{36}O_4Na$ ($[M+Na]^+$): 531.2511, Found: 531.2492.



diethyl

2-(4,4-bis(4-chlorophenyl)-4-hydroxybut-2-ynyl)-2-(4-*tert*-butylbenzyl)malonate

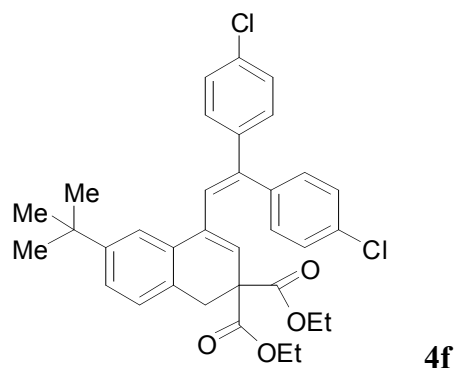
1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.22 (t, J = 7.3 Hz, 6H), 1.27 (s, 9H), 2.78 (s, 2H), 3.22 (s, 1H), 3.32 (s, 2H), 4.16-4.19 (m, 4H), 6.97 (d, J = 8.2 Hz, 2H), 7.22-7.30 (m, 6H), 7.48-7.52 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 169.9, 150.1, 143.5, 133.8, 132.2, 129.6, 128.5, 127.5, 125.5, 86.0, 84.0, 73.7, 61.9, 58.3, 37.3, 34.5, 31.4, 22.8, 14.1. HRMS-ESI-TOF: calcd for $C_{34}H_{36}Cl_2O_5Na$ ($[M+Na]^+$): 617.1837, Found: 617.1857.



diethyl

4-(2,2-bis(4-chlorophenyl)vinylidene)-6-tert-butyl-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate

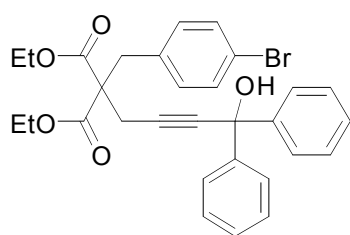
^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.14 (t, J = 6.9 Hz, 6H), 1.22 (s, 9H), 3.23 (s, 2H), 3.33 (s, 2H), 4.03-4.17 (m, 4H), 7.13 (d, J = 8.2 Hz, 1H), 7.20-7.34 (m, 9H), 7.43 (d, J = 2.3 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 206.1, 170.6, 149.6, 135.1, 133.6, 130.6, 129.7, 129.2, 128.8, 128.3, 125.7, 122.8, 112.1, 103.1, 61.8, 53.8, 34.8, 34.5, 33.6, 31.3, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{34}\text{H}_{35}\text{Cl}_2\text{O}_4$ ($[\text{M}+\text{H}]^+$): 577.1912, Found: 577.1923.



diethyl

4-(2,2-bis(4-chlorophenyl)vinyl)-6-tert-butyl-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate

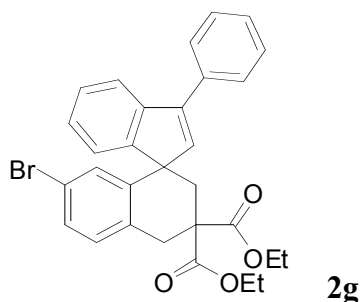
^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.13 (t, J = 7.3 Hz, 6H), 1.25 (s, 9H), 3.26 (s, 2H), 3.91-3.96 (m, 2H), 4.10-4.15 (m, 2H), 5.78 (d, J = 1.3 Hz, 1H), 6.69 (d, J = 1.3 Hz, 1H), 7.04-7.06 (m, 2H), 7.12-7.18 (m, 3H), 7.21-7.27 (m, 4H), 7.30-7.33 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 169.9, 149.9, 143.6, 141.0, 138.3, 137.4, 134.0, 133.2, 131.9, 131.4, 129.7, 129.6, 128.6, 128.4, 127.6, 127.1, 125.6, 124.5, 121.6, 61.8, 54.7, 34.6, 33.7, 31.4, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{34}\text{H}_{34}\text{Cl}_2\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 599.1732, Found: 599.1742.



1g

diethyl 2-(4-bromobenzyl)-2-(4-hydroxy-4,4-diphenylbut-2-ynyl)malonate

^1H NMR (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$): δ 1.20 (t, J = 7.3 Hz, 6H), 2.77 (s, 2H), 3.27 (s, 1H), 3.32 (s, 2H), 4.14-4.18 (m, 4H), 6.92 (d, J = 8.2 Hz, 2H), 7.21-7.32 (m, 8H), 7.56 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$): δ 169.7, 145.2, 134.6, 131.7, 131.6, 128.3, 127.8, 126.2, 121.3, 87.4, 82.7, 74.6, 62.0, 58.2, 37.1, 22.8, 14.1. Anal. Calcd for $\text{C}_{30}\text{H}_{29}\text{BrO}_5$: C, 65.58; H, 5.32. Found: C, 65.61; H, 5.38. HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{29}\text{BrO}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 571.1096, Found: 571.1122.

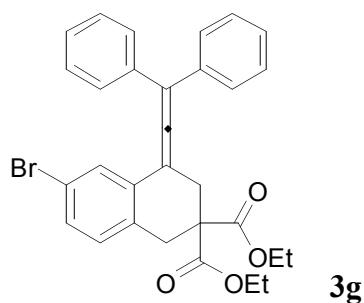


2g

diethyl

7'-bromo-3-phenyl-2'H-spiro[indene-1,1'-naphthalene]-3',3'(4'H)-dicarboxylate

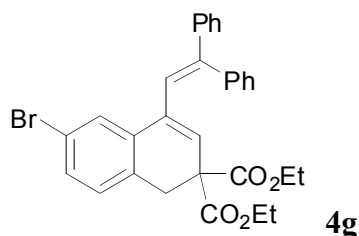
^1H NMR (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$): δ 1.16 (t, J = 6.9 Hz, 3H), 1.25 (t, J = 6.9 Hz, 3H), 2.53 (dd, J = 1.8, 14.2 Hz, 1H), 2.88 (d, J = 14.2 Hz, 1H), 3.20 (d, J = 16.5 Hz, 1H), 3.61 (dd, J = 1.4, 16.0 Hz, 1H), 4.0-4.25 (m, 4H), 6.44 (s, 1H), 6.57 (d, J = 1.8 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 7.20-7.27 (m, 3H), 7.31-7.46 (m, 4H), 7.56-7.59 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$): δ 171.4, 171.3, 154.5, 142.6, 142.1, 141.3, 138.1, 135.1, 133.3, 130.8, 130.1, 129.8, 128.7, 128.1, 127.8, 127.5, 126.7, 123.6, 121.2, 120.4, 61.9, 61.7, 54.7, 53.2, 38.0, 34.9, 14.2, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{27}\text{BrO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 553.0990, Found: 553.0979.



diethyl

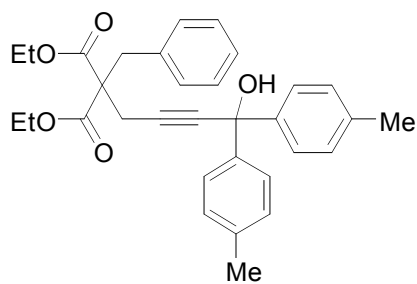
6-bromo-4-(2,2-diphenylvinylidene)-3,4-dihydronaphthalene-2,2(1*H*)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.11 (t, $J = 7.3$ Hz, 6H), 3.24 (s, 2H), 3.28 (s, 2H), 4.03-4.15 (m, 4H), 7.06 (d, $J = 8.2$ Hz, 1H), 7.23-7.40 (m, 11H), 7.60 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 206.1, 170.4, 136.3, 132.3, 132.1, 131.0, 130.7, 129.0, 128.7, 128.6, 127.9, 120.7, 114.4, 101.1, 61.9, 53.6, 35.0, 33.6, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{27}\text{BrO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 553.0990, Found: 553.0989.



diethyl 6-bromo-4-(2,2-diphenylvinyl)naphthalene-2,2(1*H*)-dicarboxylate

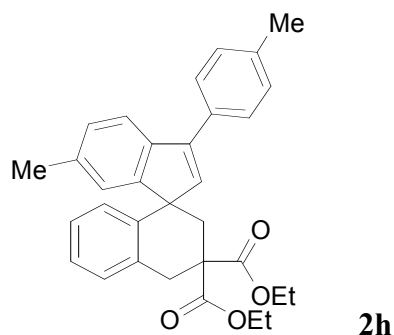
^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.12 (t, $J = 7.3$ Hz, 6H), 3.22 (s, 2H), 3.87-3.96 (m, 2H), 4.06-4.15 (m, 2H), 5.85 (d, $J = 1.4$ Hz, 1H), 6.64 (d, $J = 1.4$ Hz, 1H), 7.04 (d, $J = 8.0$ Hz, 1H), 7.11-7.13 (m, 2H), 7.18-7.35 (m, 9H), 7.42 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 169.6, 146.6, 142.6, 139.9, 136.4, 134.8, 131.7, 131.0, 130.0, 129.3, 128.7, 128.4, 128.2, 128.1, 127.8, 127.3, 125.6, 124.9, 120.7, 61.8, 54.6, 33.7, 13.9. HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{27}\text{BrO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 553.0990, Found: 553.1007.



1h

diethyl 2-benzyl-2-(4-hydroxy-4,4-dip-tolylbut-2-ynyl)malonate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.19 (t, $J = 7.3$ Hz, 6H), 2.28 (s, 6H), 2.78 (s, 2H), 3.19 (d, $J = 1.8$ Hz, 1H), 3.39 (s, 2H), 4.12-4.18 (m, 4H), 7.03-7.19 (m, 9H), 7.47 (d, $J = 7.8$ Hz, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 170.0, 142.7, 137.3, 135.7, 130.1, 129.0, 128.5, 127.3, 126.2, 87.5, 82.6, 74.4, 61.9, 58.5, 37.8, 22.9, 21.2, 14.2. Anal. Calcd for $\text{C}_{32}\text{H}_{34}\text{O}_5$: C, 77.08; H, 6.87. Found: C, 77.15; H, 6.88; HRMS-ESI-TOF: calcd for $\text{C}_{32}\text{H}_{34}\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 521.2304, Found: 521.2288.

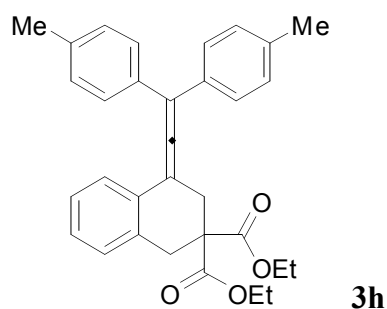


2h

diethyl

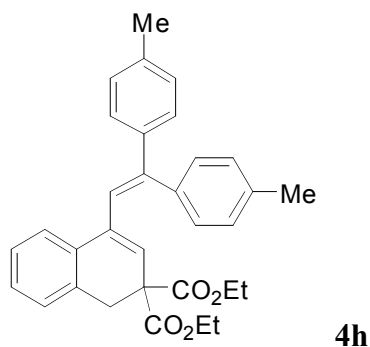
6-methyl-3-*p*-tolyl-2'*H*-spiro[indene-1,1'-naphthalene]-3',3'(4'*H*)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.15 (t, $J = 7.3$ Hz, 3H), 1.25 (t, $J = 7.3$ Hz, 3H), 2.33 (s, 3H), 2.38 (s, 3H), 2.54 (dd, $J = 1.8, 14.2$ Hz, 1H), 2.91 (d, $J = 14.2$ Hz, 1H), 3.27 (d, $J = 16.5$ Hz, 1H), 3.67 (dd, $J = 1.8, 16.5$ Hz, 1H), 3.98-4.28 (m, 4H), 6.38 (s, 1H), 6.47 (d, $J = 8.2$ Hz, 1H), 6.90 (t, $J = 8.2$ Hz, 1H), 7.04-7.22 (m, 6H), 7.42 (d, $J = 7.7$ Hz, 1H), 7.46 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 171.8, 171.5, 155.6, 141.2, 140.7, 140.3, 137.5, 136.1, 135.9, 134.2, 132.7, 129.3, 129.1, 127.8, 127.6, 127.3, 126.8, 126.7, 124.5, 120.6, 61.8, 61.6, 54.6, 53.4, 38.3, 35.4, 21.6, 21.4, 14.2, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{32}\text{H}_{33}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 481.2379, Found: 481.2373.



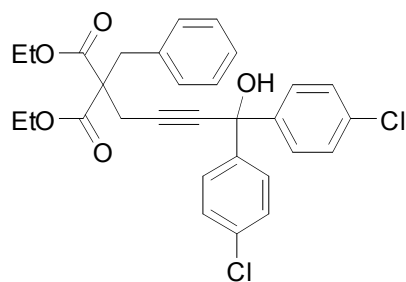
diethyl 4-(2,2-dip-tolylvinylidene)-3,4-dihydronaphthalene-2,2(1*H*)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.11 (t, $J = 7.3$ Hz, 6H), 2.33 (s, 6H), 3.26 (s, 2H), 3.35 (s, 2H), 4.05-4.15 (m, 4H), 7.09-7.16 (m, 7H), 7.28 (d, $J = 7.8$ Hz, 4H), 7.50 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 205.9, 170.7, 137.4, 133.8, 133.3, 130.0, 129.4, 129.2, 128.5, 127.6, 126.8, 126.6, 113.5, 101.6, 61.8, 53.9, 35.5, 33.8, 21.3, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{32}\text{H}_{33}\text{O}_4$ ($[\text{M}+\text{H}]^+$): 481.2379, Found: 481.2379.



diethyl 4-(2,2-dip-tolylvinyl)naphthalene-2,2(1*H*)-dicarboxylate

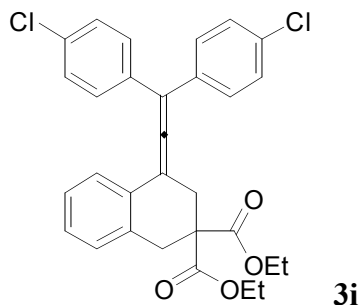
^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.10 (t, $J = 7.3$ Hz, 6H), 2.28 (s, 3H), 2.36 (s, 3H), 3.30 (s, 2H), 3.86-3.92 (m, 2H), 4.05-4.12 (m, 2H), 5.78 (d, $J = 1.4$ Hz, 1H), 6.60 (d, $J = 1.4$ Hz, 1H), 6.98-7.08 (m, 4H), 7.12-7.36 (m, 8H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 170.0, 145.8, 140.5, 137.6, 137.4, 137.3, 136.4, 133.0, 132.8, 129.9, 129.3, 129.0, 128.7, 128.3, 128.2, 127.8, 127.0, 124.9, 123.7, 61.6, 54.7, 34.2, 21.3, 21.2, 13.9. HRMS-ESI-TOF: calcd for $\text{C}_{32}\text{H}_{32}\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 503.2198, Found: 503.2175.



1i

diethyl 2-benzyl-2-(4,4-bis(4-chlorophenyl)-4-hydroxybut-2-ynyl)malonate

^1H NMR (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$): δ 1.21 (t, J = 7.3 Hz, 6H), 2.78 (s, 2H), 3.35 (s, 2H), 3.48 (s, 1H), 4.14-4.18 (m, 4H), 7.04-7.06 (m, 2H), 7.19-7.29 (m, 7H), 7.47-7.49 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$): δ 169.9, 143.5, 135.4, 133.8, 129.9, 128.6, 128.5, 127.6, 127.3, 86.2, 83.8, 73.6, 62.0, 58.3, 37.8, 22.8, 14.1. Anal. Calcd for $\text{C}_{30}\text{H}_{28}\text{Cl}_2\text{O}_5$: C, 66.79; H, 5.23. Found: C, 66.57; H, 5.31. HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{28}\text{Cl}_2\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 561.1211, Found: 561.1227.

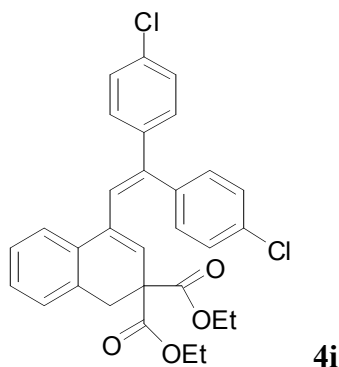


3i

diethyl

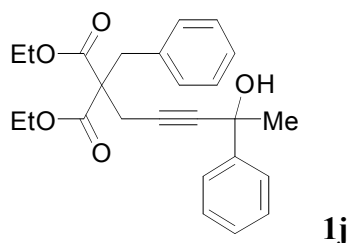
4-(2,2-bis(4-chlorophenyl)vinylidene)-3,4-dihydronaphthalene-2,2(1H)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$): δ 1.13 (t, J = 7.3 Hz, 6H), 3.25 (s, 2H), 3.36 (s, 2H), 4.06-4.15 (m, 4H), 7.12-7.32 (m, 11 H), 7.42 (d, J = 7.3 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$): δ 206.2, 170.4, 134.8, 133.6, 133.5, 129.8, 129.6, 129.1, 128.8, 128.1, 127.0, 126.4, 112.1, 102.8, 61.9, 53.7, 35.3, 33.6, 14.0. HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{26}\text{Cl}_2\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 543.1106, Found: 543.1092.



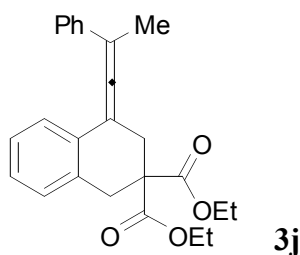
diethyl 4-(2,2-bis(4-chlorophenyl)vinyl)naphthalene-2,2(1*H*)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.13 (t, $J = 7.3$ Hz, 6H), 3.30 (s, 2H), 3.89-3.97 (m, 2H), 4.08-4.17 (m, 2H), 5.76 (d, $J = 1.3$ Hz, 1H), 6.66 (d, $J = 1.3$ Hz, 1H), 7.04 (d, $J = 8.2$ Hz, 2H), 7.17-7.31 (m, 10H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 169.8, 143.8, 140.9, 138.2, 136.9, 134.0, 133.2, 132.8, 132.5, 131.3, 129.4, 128.7, 128.6, 128.4, 128.0, 127.2, 127.0, 124.7, 124.4, 61.8, 54.6, 34.1, 14.0; Anal. Calcd for $\text{C}_{30}\text{H}_{26}\text{Cl}_2\text{O}_4$: C, 69.10; H, 5.03. Found: C, 69.00; H, 5.20; HRMS-ESI-TOF: calcd for $\text{C}_{30}\text{H}_{26}\text{Cl}_2\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 543.1106, Found: 543.1098.



diethyl 2-benzyl-2-(4-hydroxy-4-phenylpent-2-ynyl)malonate

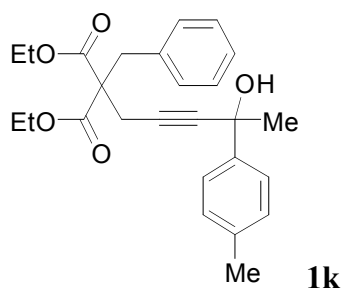
^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.21 (t, $J = 7.3$ Hz, 6H), 1.78 (s, 3H), 2.74 (s, 2H), 3.25 (s, 1H), 3.39 (s, 2H), 4.14-4.18 (m, 4H), 7.13-7.15 (m, 2H), 7.19-7.35 (m, 6H), 7.65 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 169.9, 146.0, 135.7, 130.0, 128.5, 128.3, 127.6, 127.3, 125.1, 88.0, 80.2, 69.9, 61.9, 58.5, 37.7, 33.6, 22.6, 14.2; HRMS-ESI-TOF: calcd for $\text{C}_{25}\text{H}_{28}\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 431.1834, Found: 431.1860.



diethyl

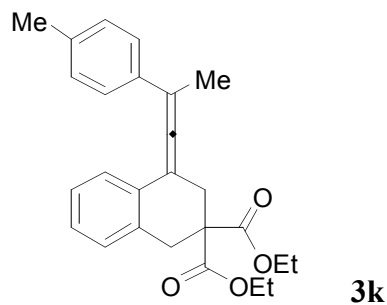
4-(2-phenylprop-1-enylidene)-3,4-dihydronaphthalene-2,2(1*H*)-dicarboxylate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.15 (t, J = 6.9 Hz, 3H), 1.23 (t, J = 6.9 Hz, 3H), 2.20 (s, 3H), 3.13 (d, J = 14.6 Hz, 1H), 3.19 (d, J = 14.6 Hz, 1H), 3.32 (d, J = 16.5 Hz, 1H), 3.38 (d, J = 16.5 Hz, 1H), 4.10-4.22 (m, 4H), 7.05-7.22 (m, 4H), 7.28-7.30 (m, 2H), 7.38-7.43 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 204.4, 170.8, 170.7, 136.9, 133.2, 130.3, 129.3, 128.5, 127.4, 127.1, 126.7, 126.6, 126.0, 104.6, 100.6, 61.8, 53.8, 35.5, 33.7, 17.0, 14.2, 14.1; HRMS-ESI-TOF: calcd for $\text{C}_{25}\text{H}_{26}\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 413.1729, Found: 413.1750.



diethyl 2-benzyl-2-(4-hydroxy-4-p-tolylpent-2-ynyl)malonate

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ 1.24 (dt, J = 0.9, 7.3 Hz, 6H), 1.77 (s, 3H), 2.34 (s, 3H), 2.66-2.67 (m, 1H), 2.75 (s, 2H), 3.39 (s, 2H), 4.17-4.21 (m, 4H), 7.12-7.25 (m, 7H), 7.53 (d, J = 8.2 Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ 169.9, 142.9, 137.4, 135.7, 130.0, 129.0, 128.5, 127.2, 125.0, 88.0, 80.2, 69.9, 61.8, 58.4, 37.6, 33.5, 22.6, 21.1, 14.2; HRMS-ESI-TOF: calcd for $\text{C}_{26}\text{H}_{30}\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 445.1991, Found: 445.1975.



diethyl

4-(2-p-tolylprop-1-enylidene)-3,4-dihydronaphthalene-2,2(1*H*)-dicarboxylate

¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 1.16 (t, *J* = 6.9 Hz, 3H), 1.23 (t, *J* = 6.9 Hz, 3H), 2.18 (s, 3H), 2.32 (s, 3H), 3.12 (d, *J* = 14.6 Hz, 1H), 3.18 (d, *J* = 14.6 Hz, 1H), 3.32 (d, *J* = 16.5 Hz, 1H), 3.37 (d, *J* = 16.5 Hz, 1H), 4.08-4.22 (m, 4H), 7.06-7.18 (m, 5H), 7.29-7.32 (m, 2H), 7.35-7.38 (dd, *J* = 1.4, 7.7 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz, 25 °C): δ 204.2, 170.8, 170.7, 136.8, 133.8, 133.1, 130.5, 129.3, 129.2, 127.3, 126.7, 126.6, 125.9, 104.5, 100.5, 61.8, 61.7, 53.8, 35.5, 33.7, 21.2, 17.0, 14.2, 14.1; HRMS-ESI-TOF: calcd for C₂₆H₂₈O₄Na ([M+Na]⁺): 427.1885, Found: 427.1907.

Figure 1 ORTEP diagram of the single-crystal X-ray structure of **2a** (CCDC 684335).

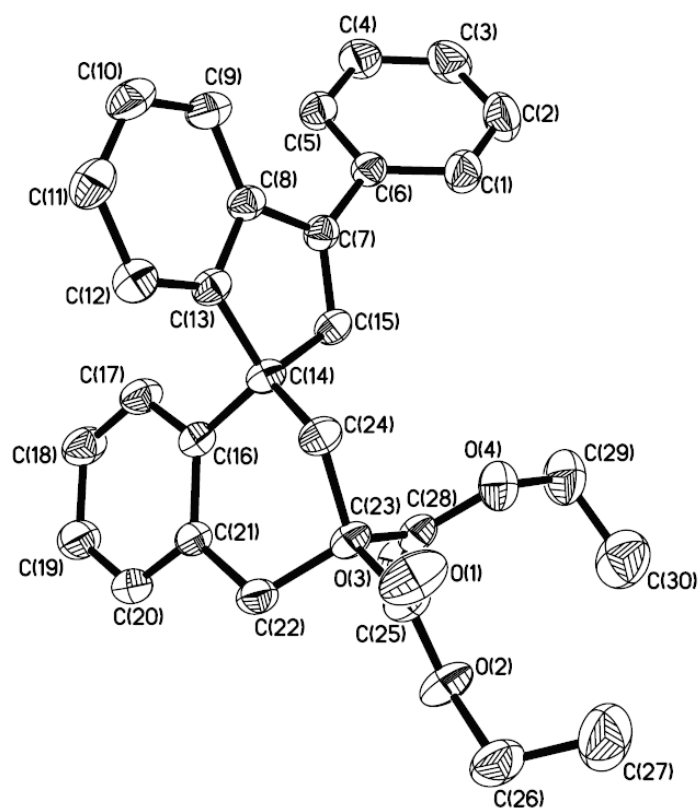


Figure 2 ORTEP diagram of the single-crystal X-ray structure of **4a** (CCDC 684332).

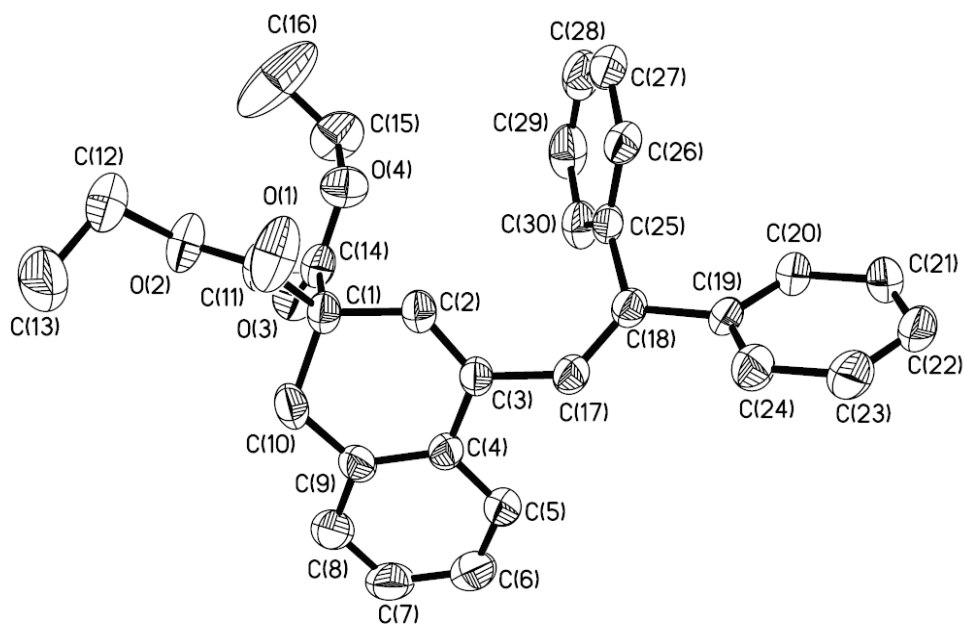


Figure 3 ORTEP diagram of the single-crystal X-ray structure of **3b** (CCDC 684333).

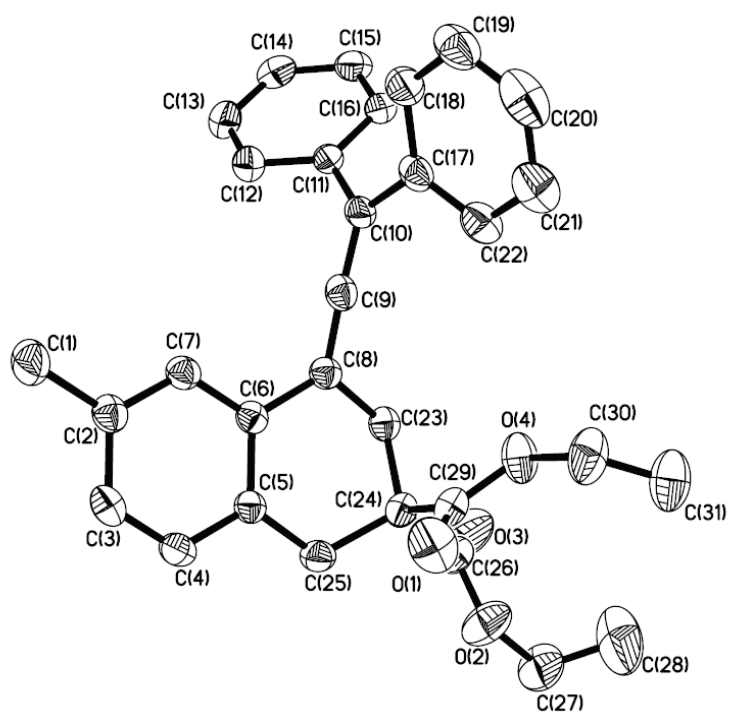


Figure 4 ORTEP diagram of the single-crystal X-ray structure of **5d** (CCDC 684334).

