Supplementary Material (ESI) for Chemical Communications

Gold(I)-Catalysed Arylation of 1,6-Enynes: Cyclopropyl Gold Carbenes as Bidentate Electrophiles

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General methods

All reactions were carried out under N_2 in solvents dried using a Solvent Purification System (SPS). Thin layer chromatography was carried out using TLC-aluminium sheets with 0.2 mm of silica gel (Merck GF_{234}). Chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm). NMR spectra were recorded at 23 ºC on a Bruker Avance 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Mass spectra were recorded on a Waters LCT Premier (ESI) and Waters GCT (EI, CI) spectrometers. Elemental analyses were performed on a LECO CHNS 932 micro-analyzer at the Universidad Complutense de Madrid. Melting points were determined using a Büchi melting point apparatus.

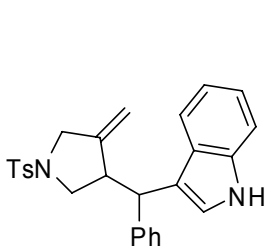
Compounds **5a**,[i] **5b**,[ii] **5c**,[iii] **5d-e**,[iv] **5f**[v] were synthesized according to literature procedures.

General procedure for the arylation 1,6-enynes (Table 1 and 2, Scheme 2 and 4)

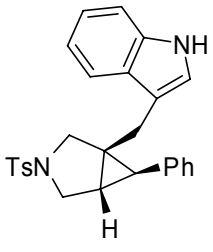
A solution of enyne **6** and the nucleophile in CH_2Cl_2 (3 mL) was added to a previously prepared mixture of the gold catalyst (5 mol% rel. to **5**) and $AgSbF_6$ (5 mol% rel. to **5**) in CH_2Cl_2 (1 mL). The reaction mixture was stirred at room temperature (unless stated

otherwise) for the time indicated in Table 1 and 2 and Scheme 2 and 4. The mixture was filtered trough silica gel with CH_2Cl_2 and the solvents evaporated. The residue was chromatographed to give the desired product.

3-((4-Methylene-1-tosylpyrrolidin-3-yl)(phenyl)methyl)-1*H*-indole (6a) and 3-(((1*R*,5*S*,6*R*)-6-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methyl)-1*H*-indole (7a)



6a

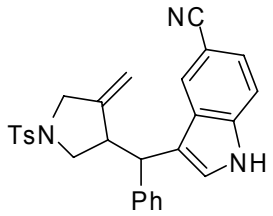


7a

Compounds **6a** and **7a** were synthesized following the general procedure (Table 1, entry 2) with catalyst **9**/$AgSbF_6$ starting from *N*-cinnamyl-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (125 mg, 0.38 mmol) and indole (0.50 mg, 0.42 mmol). The residue was purified by chromatography (5:1, hexane:EtOAc) to give a mixture of products **6a** and **7a** in a 10:1 ratio as an off-white solid (115 mg, 68%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (br s, 1H, **6a**), 7.89 (br s, 1H, **7a**), 7.61 (d, *J* = 8.1 Hz, 2H, **6a**), 7.60 (d, *J* = 8.1 Hz, 2H, **7a**), 7.35-7.09 (m, 20H), 7.04-6.97 (m, 3H), 6.59 (d, *J* = 1.9 Hz, 1H , **7a**), 4.75 (d, *J* = 1.5 Hz, 1H, **6a**), 4.25 (d, *J* = 1.6 Hz, 1H, **6a**), 3.96 (d, *J* = 10.2 Hz, 1H, **6a**), 3.90 (AB of triplet, *J* = 14.0, 2.0 Hz, 1H, **6a**), 3.85 (AB of triplet, *J* = 14.0, 2.0 Hz, 1H, **6a**), 3.70 (d, *J* = 9.3 Hz, 1H, **7a**), 3.64 (d, *J* = 9.5 Hz, 1H, **7a**), 3.49-3.32 (m, 3H, **6a**), 3.27 (dd, *J* = 9.3, 4.0 Hz, 1H, **7a**), 3.18 (d, *J* = 9.7 Hz, 1H, **7a**), 2.74 (AB, *J* = 16.0 Hz, 1H, **7a**), 2.72 (AB, *J* = 16.0 Hz, 1H, **7a**), 2.43 (s, 6H), 2.23 (d, *J* = 4.2 Hz, 1H), 1.95 (t, *J* = 4.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 145.2 (C, **6a**), 143.7 (C, **6a**), 143.6 (C, **7a**), 143.3 (C, **6a**), 137.3 (C, **7a**), 136.6 (C, **6a**), 136.1 (C, **7a**), 133.5 (C, **7a**), 133.0 (C, **6a**), 129.9 (CH, **6a**), 129.7 (CH, **7a**), 128.7 (CH, **7a**), 128.4 (CH, **6a**),

128.3 (CH, **6a**), 127.9 (CH, **6a**), 127.7 (CH, **7a**), 127.0 (C, **6a**), 126.5 (C, **6a**), 126.4 (CH, **7a**), 122.4 (CH, **6a**), 122.1 (CH, **7a**), 122.0 (CH, **7a**), 121.3 (CH, **6a**), 119.7 (CH, **6a**), 119.6 (CH, **6a**), 119.5 (CH, **7a**), 118.7 (CH, **7a**), 118.1 (C, **6a**), 113.3 (C, **7a**), 111.3 (CH, **6a**), 111.2 (CH, **7a**), 110.3 (CH_2, **6a**), 109.6 (C, **7a**), 54.6 (CH_2, **7a**), 53.2 (CH_2, **6a**), 52.5 (CH_2, **6a**), 51.0 (CH_2, **7a**), 48.0 (CH, **6a**), 45.9 (CH, **6a**), 35.9 (C, **7a**), 30.4 (CH, **7a**), 26.7 (CH, **7a**), 23.1 (CH_2, **7a**), 21.8 (CH_3, **6a**), 21.7 (CH_3, **7a**); HRMS-ESI *m/z* calcd for $C_{27}H_{26}N_2O_2SNa$: 465.1613; found: 465.1596 [M^++Na]

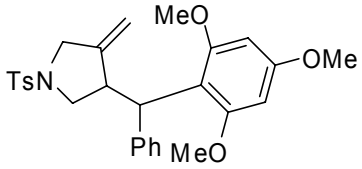
3-((4-Methylene-1-tosylpyrrolidin-3-yl)(phenyl)methyl)-1*H*-indole-5-carbonitrile (6b)



Compound **6b** was synthesized following the general procedure (Table 2, entry 1) starting from *N*-cinnamyl-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (100 mg, 0.31 mmol) and 5-cyanoindole (48 mg, 0.34 mmol). The residue was purified by chromatography (5:1, hexane:EtOAc) to give **6b** as a white solid (71 mg, 49%): mp 218-219°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (br s, 1H), 7.63 (d, J = 0.9 Hz, 1H), 7.60 (dt, J = 8.4, 1.8 Hz, 2H), 7.39 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 6.9 Hz, 2H), 7.21-7.19 (m, 1H), 7.17-7.14 (m, 1H), 7.13-7.11 (m, 2H), 4.78 (q, J = 1.5 Hz, 1H), 4.27 (q, J = 1.5 Hz, 1H), 3.93-3.84 (m, 3H), 3.44-3.30 (m, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 144.8 (C), 144.2 (C), 142.3 (C), 138.2 (C), 132.8 (C), 130.0 (CH), 128.7 (CH), 128.3 (CH), 127.9 (CH), 127.0 (CH), 126.9 (C), 125.5 (CH), 123.4 (CH), 120.8 (C), 119.1 (C), 112.4 (CH), 110.8 (CH_2), 102.9 (C), 53.1 (CH_2), 52.3

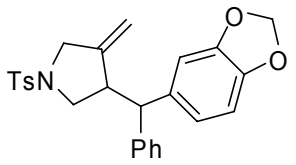
(CH_2), 47.8 (CH), 45.6 (CH), 21.8 (CH_3); HRMS-ESI *m/z* calcd for $C_{28}H_{25}N_3O_2SNa$: 490.1565; found: 490.1543 [M^++Na].

3-Methylene-4-(phenyl(2,4,6-trimethoxyphenyl)methyl)-1-tosylpyrrolidine (6c)



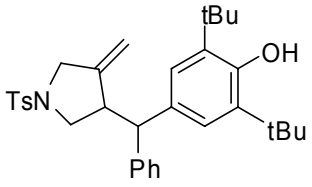
Compound **6c** was synthesized following the general procedure (Table 2, entry 2) starting from *N*-cinnamyl-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (100 mg, 0.31 mmol) and 1,3,5-trimethoxybenzene (57 mg, 0.34 mmol). The residue was purified by chromatography (20:1, hexane:EtOAc) to give **6c** as a white solid (114 mg, 75%): mp 190-191°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.34-7.30 (m, 4H), 7.18-7.15 (m, 2H), 7.07 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.07 (s, 2H), 4.71 (q, *J* = 1.9 Hz, 1H), 4.48 (d, *J* = 11.1 Hz, 1H), 4.36 (q, *J* = 2.0 Hz, 1H), 4.03-3.98 (m, 1H), 3.95 (dt, *J* = 13.8, 1.6 Hz, 1H), 3.82 (dq, *J* = 13.8, 1.6 Hz, 1H), 3.78 (s, 3H), 3.74 (br s, 6H), 3.32 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.78 (dd, *J* = 9.6, 8.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 160.0 (2C), 147.6 (C), 143.6 (C), 143.5 (C), 133.6 (C), 129.7 (CH), 128.7 (CH), 128.0 (CH), 127.9 (CH), 125.8 (CH), 112.6 (C), 108.7 (CH_2), 91.3 (CH), 55.8 (CH_3), 55.4 (CH_3), 53.4 (CH_2), 53.2 (CH_2), 43.6 (CH), 42.1 (CH), 21.7 (CH_3); HRMS-ESI *m/z* calcd for $C_{28}H_{31}NO_5SNa$: 516.1821; found: 516.1829 [M^++Na]; Anal. Calcd for $(C_{28}H_{31}NO_5)_3(H_2O)$: C, 67.31; H, 6.39; N, 6.42; found: C, 67.40; H, 6.20; N, 2.93; S, 6.24.

3-(Benzo[*d*][1,3]dioxol-5-yl(phenyl)methyl)-4-methylene-1-tosylpyrrolidine (6d)



Compound **6d** was synthesized following the general procedure (Table 2, entry 3) starting from *N*-cinnamyl-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (100 mg, 0.31 mmol) and 1,3-benzodioxole (0.043 mL, 0.38 mmol). The residue was purified by chromatography (30:1, hexane:EtOAc) to give **6d** as a white solid (102 mg, 74%): mp 145-146°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.26-7.22 (m, 2H), 7.17-7.13 (m, 3H), 6.71-6.68 (m, 1H), 6.63-6.61 (m, 2H), 5.92 (q, J = 1.3 Hz, 2H), 4.72 (q, J = 1.8 Hz, 1H), 4.27 (q, J = 1.8 Hz, 1H), 3.89-3.81 (m, 2H), 3.66 (d, J = 11.3 Hz, 1H), 3.41-3.36 (m, 1H), 3.26 (dd, J = 10.0, 6.7 Hz, 1H), 3.03 (dd, J = 10.0, 5.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 148.1 (C), 145.3 (2C), 143.8 (C), 143.0 (C), 137.0 (C), 133.1 (C), 129.9 (CH), 128.7 (CH), 128.1 (CH), 128.0 (CH), 126.8 (CH), 121.1 (CH), 110.2 (CH_2), 108.6 (CH), 108.2 (CH), 101.2 (CH_2), 53.8 (CH), 53.0 (CH_2), 52.6 (CH_2), 47.0 (CH), 21.7 (CH_3); HRMS-ESI *m/z* calcd for $C_{26}H_{25}NO_4SNa$: 470.1402; found: 470.1400 [M^++Na].

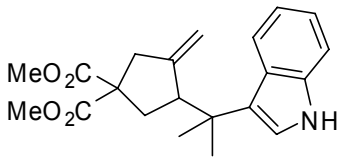
2,6-Di-tert-butyl-4-((4-methylene-1-tosylpyrrolidin-3-yl)(phenyl)methyl)phenol (6e)



Compound **6e** was synthesized following the general procedure (Table 2, entry 4) starting from *N*-cinnamyl-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (100 mg, 0.31 mmol) and 2,6-di-*tert*-butylphenol (70 mg, 0.34 mmol). The residue was purified by

chromatography (20:1, hexane:EtOAc) to give **6e** as a white solid (125 mg, 76%): mp 204-206°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.24-7.20 (m, 4H), 7.14 (tt, J = 6.8, 1.8 Hz, 1H), 6.96 (s, 2H), 5.06 (s, 1H), 4.70 (d, J = 1.9 Hz, 1H), 4.28 (d, J = 1.9 Hz, 1H), 3.85 (AB, J = 14.0 Hz, 1H), 3.82 (AB, J = 14.0 Hz, 1H), 3.70 (d, J = 11.0 Hz, 1H), 3.42-3.36 (m, 1H), 3.16 (dd, J = 9.9, 7.0 Hz, 1H), 3.00 (dd, J = 9.9, 5.8 Hz, 1H), 2.45 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 152.6 (C), 145.8 (C), 143.8 (C), 143.7 (C), 136.1 (C), 133.5 (C), 133.0 (C), 129.8 (CH), 128.6 (CH), 128.3 (CH), 128.0 (CH), 126.5 (CH), 124.5 (CH), 109.8 (CH_2), 54.3 (CH), 53.2 (CH_2), 52.8 (CH_2), 47.4 (CH), 34.5 (C), 30.5 (CH_3), 21.7 (CH_3); HRMS-ESI *m/z* calcd for $C_{33}H_{41}NO_3SNa$: 554.2705; found: 554.2717 [M^++Na].

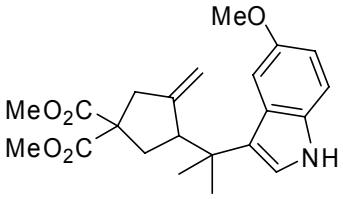
Dimethyl 3-(2-(1*H*-indol-3-yl)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (6f)



Compound **6f** was synthesized following the general procedure (Table 2, entry 5) starting from dimethyl 2-(3-methylbut-2-enyl)-2-(prop-2-ynyl)malonate (100 mg, 0.42 mmol) and indole (52 mg, 0.44 mmol). The residue was purified by chromatography (20:1, hexane:EtOAc) to give **6f** as a colourless oil (117 mg, 78%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (br s, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.17 (dt, J = 7.0, 1.0 Hz, 1H), 7.09 (dt, J = 7.0, 1.1 Hz, 1H), 6.93 (d, J = 2.5 Hz, 1H), 4.93 (br s, 1H), 4.46 (br s, 1H), 3.68 (s, 6H), 3.45 (dt, J = 7.3, 1.6 Hz, 1H), 2.87-2.78 (m, 2H), 2.42 (ddd, J = 13.6, 8.6, 1.3 Hz, 1H), 1.88 (dd, J = 13.7, 9.2 Hz, 1H), 1.45 (s, 3H), 1.37 (s,

3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 172.4 (C), 172.2 (C), 149.1 (C), 137.3 (C), 125.8 (C), 124.8 (C), 121.8 (CH), 121.4 (CH), 121.1 (CH), 119.2 (CH), 111.5 (CH), 110.7 (CH_2), 58.8 (C), 52.8 (CH_3), 52.7 (CH_3), 49.7 (CH), 44.3 (CH_2), 38.1 (C), 36.7 (CH_2), 25.7 (CH_3), 24.8 (CH_3); HRMS-ESI *m/z* calcd for $C_{21}H_{25}NO_4Na$: 378.1681; found: 378.1664 [M^++Na]; Anal. Calcd for $(C_{21}H_{25}NO_4)_3(H_2O)$: C, 69.78; H, 7.16; N, 3.88; found: C, 70.12; H, 6.93; N, 3.96.

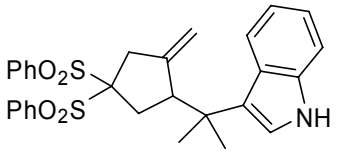
Dimethyl 3-(2-(5-methoxy-1*H*-indol-3-yl)propan-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (6g)



Compound **6g** was synthesized following the general procedure (Table 2, entry 6) starting from dimethyl 2-(3-methylbut-2-enyl)-2-(prop-2-ynyl)malonate (100 mg, 0.42 mmol) and 5-methoxyindole (0.68 mg, 0.46 mmol). The residue was purified by chromatography (20:1, hexane:EtOAc) to give **6g** as a yellow oil (103 mg, 63%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (br s, 1H), 7.29 (d, *J* = 2.1 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 6.91 (d, *J* = 2.4, Hz, 1H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.95 (br s, 1H), 4.50 (br s, 1H), 3.87 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.40 (t, *J* = 8.7 Hz, 1H), 2.81 (br s, 2H), 2.43 (dd, *J* = 13.7, 8.6 Hz, 1H), 1.88 (dd, *J* = 13.7, 9.1 Hz, 1H), 1.43 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 172.3 (C), 172.1 (C), 153.5 (C), 149.2 (C), 132.6 (C), 126.2 (C), 124.3 (C), 122.1 (CH), 112.0 (CH), 111.5 (CH), 110.7 (CH_2), 104.1 (CH), 58.8 (C), 56.3 (CH_3), 52.8 (2 CH_3), 49.5 (CH), 44.3 (CH_2), 38.0 (C), 36.7 (CH_2), 25.8 (CH_3), 24.8 (CH_3); HRMS-ESI *m/z* calcd for $C_{22}H_{27}NO_5Na$: 408.1787;

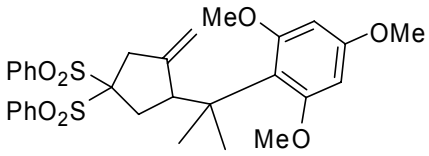
found: 408.1771 [M^++Na]; Anal. Calcd for $C_{22}H_{27}NO_5$: C, 68.55; H, 7.06; N, 3.63; found: C, 67.99; H, 7.01; N, 3.54.

3-(2-(2-Methylene-4,4-bis(phenylsulfonyl)cyclopentyl)propan-2-yl)-1*H*-indole (6h)



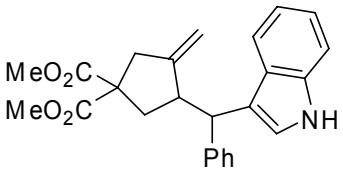
Compound **6h** was synthesized following the general procedure (Table 2, entry 7) starting from 4,4-bis(phenylsulfonyl)-7-methyl-6-octen-1-yne (100 mg, 0.25 mmol) and indole (32 mg, 0.27 mmol). The residue was purified by chromatography (3:1, hexane:EtOAc) to give **6h** as a white solid (100 mg, 78%): mp 116-118ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (overlapped br s, 1H), 7.97 (overlapped d, J = 7.6 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.68-7.63 (m, 2H), 7.53 (t, J = 8.0 Hz, 2H), 7.47 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.69 (d, J = 1.8 Hz, 1H), 4.92 (s, 1H), 4.66 (s, 1H), 3.52-3.43 (m, 2H), 2.81 (d, J = 17.1 Hz, 1H), 2.55 (dd, J = 15.4, 8.5 Hz, 1H), 2.29 (dd, J = 15.4, 9.2 Hz, 1H), 1.48 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 147.08 (C), 137.39 (C), 137.23 (C), 136.03 (C), 134.53 (CH), 134.38 (CH), 131.07 (CH, 2C), 130.96 (CH, 2C), 128.56 (CH, 4C), 125.38 (C), 123.93 (C), 121.90 (CH), 121.00 (CH), 120.89 (CH), 119.22 (CH), 111.50 (CH), 111.12 (CH_2), 91.86 (C), 50.73 (CH), 41.21 (CH_2), 38.44 (C), 34.14 (CH_2), 26.41 (CH_3), 23.59 (CH_3); HRMS-ESI *m/z* calcd for $C_{29}H_{29}NO_4NaS_2$: 542.1436; found: 524.1415 [M^++Na].

1,3,5-Trimethoxy-2-(2-(2-methylene-4,4-bis(phenylsulfonyl)cyclopentyl)propan-2-yl)benzene (6i)



Compound **6i** was synthesized following the general procedure (Table 2, entry 8) starting from 4,4-bis(phenylsulfonyl)-7-methyl-6-octen-1-yne (100 mg, 0.25 mmol) and 1,3,5-trimethoxybenzene (46 mg, 0.27 mmol). The residue was purified by chromatography (3:1, hexane:EtOAc) to give **6i** as a white solid (85 mg, 60%): mp 123-125ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.3 Hz, 4H), 7.69-7.63 (m, 2H), 7.55-7.49 (m, 4H), 6.12 (s, 2H), 4.92 (s, 1H), 4.82 (s, 1H), 3.80-3.78 (m, 10H), 3.60 (d, J = 17.2 Hz, 1H), 2.70 (d, J = 17.1 Hz, 1H), 2.59 (dd, J = 15.3, 8.2 Hz, 1H), 2.25 (dd, J = 15.6, 8.7 Hz, 1H), 1.50 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 160.52 (C, 2C), 159.11 (C), 148.21 (C), 137.47 (C), 136.08 (C), 134.41 (CH), 134.19 (CH), 131.14 (CH, 4C), 128.45 (CH, 2C), 128.37 (CH, 2C), 116.39 (C), 110.12 (CH_2), 92.60 (CH, 2C), 92.11 (C), 55.88 (CH_3, 2C), 55.16 (CH_3), 49.54 (CH), 43.00 (C), 41.15 (CH_2), 35.01 (CH_2), 27.95 (CH_3), 25.48 (CH_3); HRMS-ESI *m/z* calcd for $C_{30}H_{34}O_7NaS_2$: 593.1644; found: 593.1621 [M^++Na]. The spectroscopic data are consistent with the published data.[vi]

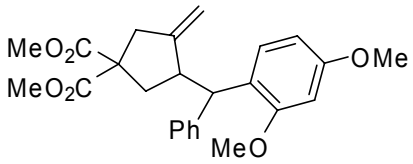
Dimethyl 3-((1*H*-indol-3-yl)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (6j)



Compound **6j** was synthesized following the general procedure (Table 2, entry 9) starting from dimethyl 2-cinnamyl-2-(prop-2-ynyl)malonate (100 mg, 0.35 mmol) and indole (40 mg, 0.34 mmol). The residue was purified by chromatography (10:1,

hexane:EtOAc) to give **6j** as a colourless oil (100 mg, 71%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (br s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.33-7.30 (m, 3H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.15-7.13 (m, 2H), 7.11 (td, *J* = 7.7, 1.2 Hz, 1H), 7.04 (t, *J* = 0.8 Hz, 1H), 4.78 (s, 1H), 4.15 (d, *J* = 10.4 Hz, 1H), 4.12 (s, 1H), 3.72 (s, 3H), 3.63 (s, 3H), 3.52 (dq, *J* = 8.3, 1.9 Hz, 1H), 3.11 (AB of q, *J* = 15.9, 2.2 Hz, 1H), 2.88 (AB of d, *J* = 15.9, 1.4 Hz, 1H), 2.74 (ddd, *J* = 13.7, 7.9, 1.4 Hz, 1H), 1.97 (dd, *J* = 13.7, 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 172.5 (C), 172.3 (C), 149.1 (C), 144.5 (C), 136.3 (C), 128.7 (CH), 128.3 (CH), 127.4 (C), 126.3 (CH), 122.2 (CH), 121.5 (CH), 119.6 (CH), 119.5 (CH), 118.9 (C), 111.2 (CH), 110.2 (CH_2), 58.6 (C), 53.0 (CH_3), 52.9 (CH_3), 48.2 (CH), 47.0 (CH), 42.0 (CH_2), 40.0 (CH_2); HRMS-ESI *m/z* calcd for $C_{25}H_{25}NO_4Na$: 426.1681; found: 426.1672 [M^++Na]; Anal. Calcd for $(C_{25}H_{25}NO_4)_3(H_2O)_4$: C, 70.24; H, 6.52; N, 3.28; found: C, 70.67; H, 6.10; N, 3.27. The spectroscopic data are consistent with the published data.[vi]

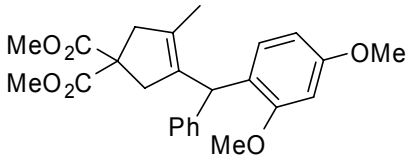
Dimethyl 3-((2,4-dimethoxyphenyl)(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (6k)



Compound **6k** was synthesized following the general procedure (Table 2, entry 10) starting from dimethyl 2-cinnamyl-2-(prop-2-ynyl)malonate (100 mg, 0.35 mmol) and 1,3-dimethoxybenzene (0.044 mL, 0.34 mmol). A sample for ^{1}H NMR was taken after 3h at -40 ºC, which showed complete conversion to **6k**. After passing the reaction mixture over silica with CH_2Cl_2 and purification by chromatography (20:1, hexane:EtOAc), only the isomerised compound **11** was obtained (102 mg, 72%). ^{1}H

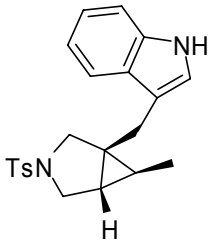
NMR (400 MHz, $CDCl_3$) of **6k**: δ = 7.30-7.08 (m, 6H), 6.46 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 4.72 (br s, 1H), 4.18 (d, *J* = 11.5 Hz, 1H), 4.03 (s, 1H), 3.76 (s, 6H), 3.72 (s, 3H), 3.67 (s, 3H), 3.58-3.52 (m, 1H), 3.12 (dq, *J* = 16.2, 2.4 Hz, 1H), 2.90 (dd, *J* = 16.2, 1.6 Hz, 1H), 2.55 (ddd, *J* = 13.4, 7.5, 1.6 Hz, 1H), 1.71 (dd, *J* = 13.4, 9.4 Hz, 1H). The spectroscopic data are consistent with the published data.[vi]

Dimethyl 3-((2,4-dimethoxyphenyl)(phenyl)methyl)-4-methylcyclopent-3-ene-1,1-dicarboxylate (11)



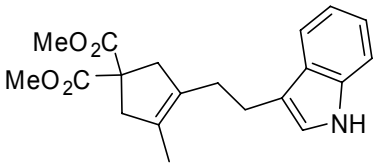
Compound **11** was synthesized following the general procedure (Table 2, entry 11) starting from dimethyl 2-cinnamyl-2-(prop-2-ynyl)malonate (100 mg, 0.35 mmol) and 1,3-dimethoxybenzene (0.044 mL, 0.34 mmol). The residue was purified by chromatography (20:1, hexane:EtOAc) to give **11** as a colourless oil (107 mg, 75%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 7.4 Hz, 2H), 7.18-7.14 (m, 1H), 7.09 (d, *J* = 7.4 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.45 (d, *J* = 1.9 Hz, 1H), 6.41 (dd, *J* = 8.3, 1.9 Hz, 1H), 5.38 (s, 1H), 3.79 (s, 3H), 3.71 (s, 6H), 3.68 (s, 3H), 3.04 (AB, *J* = 16.8 Hz, 1H), 2.99 (AB, *J* = 16.8 Hz, 1H), 2.84 (AB, *J* = 16.7 Hz, 1H), 2.77 (AB, *J* = 16.7 Hz, 1H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 173.1 (C), 172.9 (C), 159.5 (C), 158.4 (C), 143.4 (C), 133.2 (C), 131.5 (C), 130.3 (CH), 128.6 (CH), 128.2 (CH), 125.9 (CH), 123.9 (C), 104.1 (CH), 98.7 (CH), 57.5 (C), 55.7 (CH_3), 55.5 (CH_3), 52.9 (CH_3), 52.8 (CH_3), 46.1 (CH_2), 43.1 (CH_2), 41.9 (CH), 13.8 (CH_3); HRMS-ESI *m/z* calcd for $C_{25}H_{28}O_6Na$: 447.1784; found: 447.1776 [M^++Na]; Anal. Calcd for $(C_{25}H_{28}O_6)_3(H_2O)$: C, 69.75; H, 6.71; found: C, 70.08; H, 6.59.

3-(((1*R*,5*S*,6*S*)-6-Methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methyl)-1*H*-indole (7b)



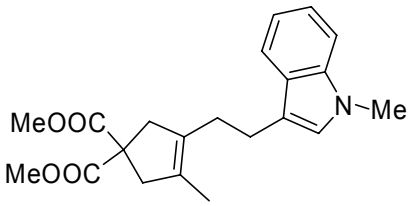
Compounds **7b** was synthesized following the general procedure (Scheme 2) starting from (*E*)-*N*-(but-2-enyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (100 mg, 0.38 mmol) and indole (0.47 mg, 0.40 mmol). The residue was purified by chromatography (10:1, hexane:EtOAc) to give **7b** as a white solid (72 mg, 50%): mp 66-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (br, s, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.19 (dt, *J* = 7.2, 0.9 Hz, 1H), 7.07 (dt, *J* = 7.1, 0.9 Hz, 1H), 6.95 (d, *J* = 1.9 Hz, 1H), 3.57 (d, *J* = 9.2, Hz, 1H), 3.54 (dt, *J* = 9.2 Hz, 1H), 3.08 (dd, *J* = 9.1, 3.9 Hz, 1H), 2.97 (AB, *J* = 16.0 Hz, 1H), 2.96 (d, *J* = 9.1 Hz, 1H), 2.84 (AB, *J* = 16.0 Hz, 1H), 2.42 (s, 3H), 1.16 (d, *J* = 6.3 Hz, 2H), 1.10-1.07 (m, 1H), 1.02 (t, *J* = 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 143.4 (C), 136.3 (C), 135.5 (C), 129.6 (CH), 127.7 (CH), 127. (C), 127.6 (C), 122.2 (CH), 122.0 (CH), 119.5 (CH), 118.8 (CH), 114.2 (C), 111.3 (CH), 54.7 (CH_2), 50.7 (CH_2), 31.6 (C), 29.0 (CH), 24.2 (CH_2), 21.7 (CH_3), 19.5 (CH), 12.7 (CH_3); HRMS-ESI *m/z* calcd for $C_{22}H_{24}N_2O_2SNa$: 403.1456; found: 403.1438 [M^++Na]; Anal. Calcd for $C_{22}H_{24}N_2O_2S$: C, 69.44; H, 6.36; N, 7.36; S, 8.43; found: C, 69.26; H, 6.47; N, 7.20; S, 7.74.

Dimethyl 3-(2-(1*H*-indol-3-yl)ethyl)-4-methylcyclopent-3-ene-1,1-dicarboxylate (14a)



Compound **14a** was synthesized following the general procedure (Scheme 4) starting from dimethyl 2-(2-methylallyl)-2-(prop-2-ynyl)malonate (100 mg, 0.45 mmol) and indole (58 mg, 0.49 mmol). The residue was purified by chromatography (30:1, hexane:EtOAc) to give **14a** colourless oil (85 mg, 56%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (br s), 7.60 (d, J = 7.9 Hz, H), 7.34 (d, J = 8.2 Hz, H), 7.18 (t, J = 7.9 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 6.95 (d, J = 2.0 Hz, 1H), 3.73 (s, 6H), 3.05 (br s, 2H), 2.95 (br s, 2H), 2.82 (t, J = 7.7 Hz, 2H), 2.43 (t, J = 7.7 Hz, 2H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 173.2 (2C), 136.4 (C), 132.3 (C), 129.1 (C), 127.6 (C), 122.0 (CH), 121.3 (CH), 119.3 (CH), 119.0 (CH), 116.5 (C), 111.2 (CH), 57.5 (C), 52.9 (2 CH_3), 46.1 (CH_2), 43.8 (CH_2), 28.8 (CH_2), 23.6 (CH_2), 13.4 (CH_3); HRMS-ESI *m/z* calcd for $C_{20}H_{23}NO_4Na$: 364.1525; found: 364.1530 [M^++Na].

Dimethyl 3-methyl-4-(2-(1-methyl-1*H*-indol-3-yl)ethyl)cyclopent-3-ene-1,1-dicarboxylate (14b)



Compound **14b** was synthesized following the general procedure (Scheme 4) starting from dimethyl 2-(2-methylallyl)-2-(prop-2-ynyl)malonate (50 mg, 0.22 mmol) and 1-methyl-1*H*-indole (32 mg, 0.24 mmol). The residue was purified by chromatography

(10:1, hexane:EtOAc) to give **14b** as a colourless oil (35 mg, 45%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 7.1 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.1 Hz, 1H), 6.80 (s, 1H), 3.74 (s, 3H), 3.73 (s, 6H), 3.05 (br s, 2H), 2.96 (br s, 2H), 2.80 (t, *J* = 8.2 Hz, 2H), 2.42 (t, *J* = 8.1 Hz, 2H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 173.01 (C, 2C), 136.99 (C), 132.27 (C), 128.81 (C), 127.83 (C), 126.05 (CH), 121.39 (CH), 118.89 (CH), 118.53 (CH), 114.84 (C), 109.08 (CH), 57.29 (C), 52.74 (CH_3, 2C), 45.93 (CH_2), 43.70 (CH_2), 32.55 (CH_3), 28.99 (CH_2), 23.45 (CH_2), 13.27 (CH_3); HRMS-ESI *m/z* calcd for $C_{21}H_{25}NO_4Na$: 378.1681; found: 378.1665 [M^++Na].

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