

Supporting Information
For
Applicable β -Sulfonium Carbanions: Facile Construction of
Thiophene Derivatives

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1. General information

Tetrahydrofuran was dried with Na and distilled freshly before use. Et₃N was dried with NaH and distilled freshly before use. Other materials and solvents were purchased from commercial suppliers and used without additional purification. NMR spectra were measured in CDCl₃ and recorded on Bruker Avance spectrometers operating for ¹H NMR at 400 MHz, for ¹³C NMR at 100 MHz and for ³¹P at 160 MHz. Chemical shifts were calibrated using TMS for ¹H NMR and ¹³C NMR, and 85% H₃PO₄ for ³¹P NMR. Mass spectroscopy data of the products were collected with an HRMS-TOF instrument GCT Premier, which is produced by WATERS company, and the collision energy is 70eV. Infrared spectra were recorded with a Bruker ATRFTIR spectrometer.

2. General experimental procedures

Typical procedure for the synthesis of 3: To a 25mL Schlenk with Pd(PPh₃)₂Cl₂ (0.02 mmol) and CuI (0.03 mmol) was added acyl chloride (1.2 mmol) in tetrahydrofuran (10.0 mL) under N₂ atmosphere. The mixture was stirred at room temperature for 10 minutes. Then alkyne (1.0 mmol) was added at room temperature and the mixture was stirred for 10 minutes. Triethylamine (3.0 mmol) was added at room temperature and the reaction was monitored by TLC until completion. Then the reaction was quenched with water (30 mL), extracted with ethyl acetate (3 × 20 mL), dried with anhydrous Na₂SO₄. After evaporation, chromatography on silica gel of the reaction mixture afforded desired product.

The procedure for the synthesis of **3g**: To a 25mL Schlenk with 4-(2-(allylthio)phenyl)-4-methoxybut-2-yn-1-ol (1.0 mmol) was added DMP (1.2 mmol) in DCM (10.0 mL) under N₂ atmosphere at 0°C. The reaction was monitored by TLC until completion. Then the reaction was quenched with saturated Na₂S₂O₃ solution (30 mL), extracted with DCM (3 × 20 mL), dried with anhydrous Na₂SO₄. After evaporation, chromatography on silica gel of the reaction mixture afforded desired product.

The procedure for the synthesis of **3m**: To a 25mL Schlenk with allyl(2-(1-

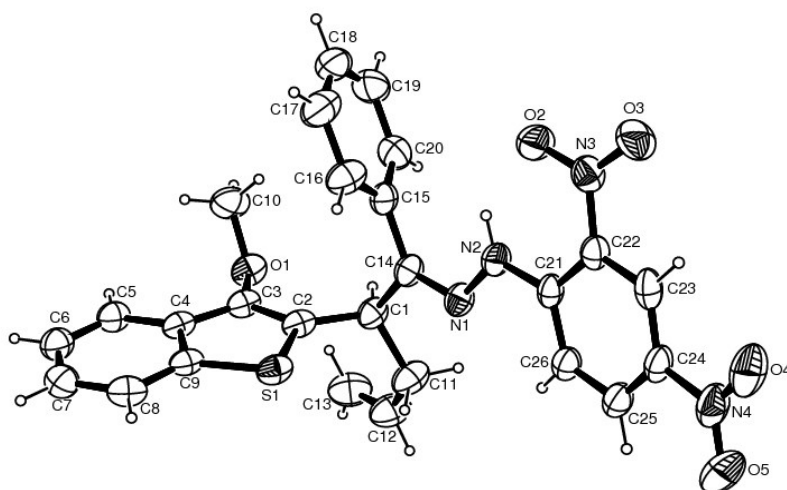
methoxyprop-2-ynyl)phenyl)sulfane (1.0 mmol) was added Methyl magnesium bromide (1.2 mmol) in THF (5.0 mL) under N₂ atmosphere at -78°C for 1h. Then the mixture was added to the solution of methyl chloroformate (1.3 mmol) in THF (5.0 mL) under N₂ atmosphere at -78°C for 3h. The reaction was monitored by TLC until completion and the reaction was quenched with saturated NH₄Cl solution (30 mL), extracted with ethyl acetate (3 × 20 mL), dried with anhydrous Na₂SO₄. After evaporation, chromatography on silica gel of the reaction mixture afforded desired product.

Typical procedure for the synthesis of 5: To a solution of alcohol (1.0 mmol) in tetrahydrofuran (10.0 mL) was added triethylamine (3.0 mmol) under N₂ atmosphere at -78°C. The resulting mixture was stirred at -78°C for 10 minutes. Then diphenylphosphinous chloride (1.2 mmol) was added at -78°C and the reaction was monitored by TLC until completion. Then the reaction was quenched with water (30 mL), extracted with ethyl acetate (3 × 20 mL), dried with anhydrous Na₂SO₄. After evaporation, chromatography on silica gel of the reaction mixture afforded desired product.

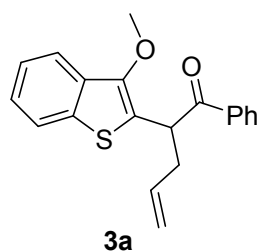
Typical procedure for the synthesis of 6: To a solution of **5a** (1.0 mmol) in tetrahydrofuran (10.0 mL) was added NaH (1.0 mmol) under N₂ atmosphere at 0°C. The resulting mixture was stirred at room temperature for 1 hour. Then aldehyde (1.0 mmol) was added and the reaction was monitored by TLC until completion, the reaction was quenched with water (30 mL), extracted with ethyl acetate (3 × 20 mL), dried with anhydrous Na₂SO₄. After evaporation, chromatography on silica gel of the reaction mixture afforded desired product.

Typical procedure for the synthesis of 9: To a 25mL Schlenk with Pd(PPh₃)₂Cl₂ (0.02 mmol) and CuI (0.03 mmol) was added 1-iodo-4-methoxybenzene (1.2 mmol) in tetrahydrofuran (10.0 mL) under N₂ atmosphere. The mixture was stirred at room temperature for 10 minutes. Then allyl(2-(1-methoxyprop-2-ynyl)phenyl)sulfane (1.0 mmol) was added at room temperature and the mixture was stirred for 10 minutes. Triethylamine (3.0 mmol) was added at room temperature and the reaction was monitored by TLC until completion. Then the reaction was quenched with water (30

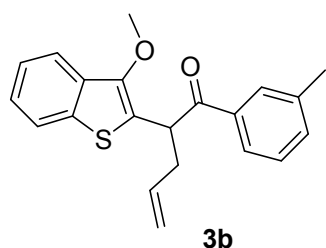
ORTEP Representation (2, 4-dinitrophenyl)hydrazone of 3a.



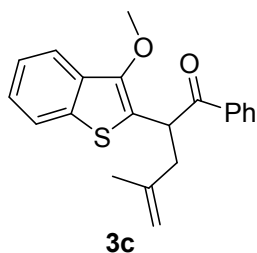
3. Characterization data



2-(3-methoxybenzo[b]thiophen-2-yl)-1-phenylpent-4-en-1-one (3a): Colorless oil; 274 mg, 85% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 2H), 7.34–7.25 (m, 2H), 5.85–5.73 (m, 1H), 5.24 (t, $J = 7.4$ Hz, 1H), 5.11 (d, $J = 16.0$ Hz, 1H), 5.01 (d, $J = 12.0$ Hz, 1H), 3.99 (s, 3H), 2.93 (dd, $J = 14.0, 6.0$ Hz, 1H), 2.73 (dd, $J = 12.0, 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.3, 147.9, 137.0, 136.0, 135.4, 133.4, 132.8, 128.7, 126.8, 124.6, 124.0, 123.2, 120.7, 117.5, 62.1, 44.8, 37.8; IR (neat) 2935, 1683, 736; MS (EI) m/z 322 (M^+), 217 (100%); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{S}$ 322.1028, found 322.1026.

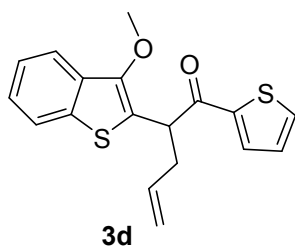


2-(3-methoxybenzo[b]thiophen-2-yl)-1-(m-tolyl)pent-4-en-1-one (3b): Colorless oil; 272 mg, 81% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.0$ Hz, 2H), 7.72–7.65 (m, 2H), 7.33–7.24 (m, 4H), 5.85–5.72 (m, 1H), 5.23 (t, $J = 7.4$ Hz, 1H), 5.11 (d, $J = 16.0$ Hz, 1H), 5.01 (d, $J = 12.0$ Hz, 1H), 3.98 (s, 3H), 2.93 (dd, $J = 12.0, 8.0$ Hz, 1H), 2.70 (dd, $J = 12.0, 8.0$ Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.5, 147.9, 138.4, 137.0, 136.1, 135.4, 134.2, 132.8, 129.2, 128.5, 126.9, 125.9, 124.5, 124.0, 123.2, 120.7, 117.4, 62.0, 44.8, 37.9, 21.4; IR (neat) 2934, 1681, 736; MS (EI) m/z 336 (M^+), 217 (100%); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{20}\text{O}_2\text{S}$ 336.1184, found 336.1180.



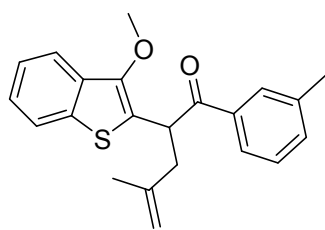
2-(3-methoxybenzo[b]thiophen-2-yl)-4-methyl-1-phenylpent-4-en-1-one (3c):

Colorless oil; 259 mg, 77% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.15–8.08 (m, 2H), 7.72–7.65 (m, 2H), 7.51 (t, $J = 7.3$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 2H), 7.33–7.23 (m, 2H), 5.42 (t, $J = 7.2$ Hz, 1H), 4.72 (d, $J = 16.0$ Hz, 2H), 3.98 (s, 3H), 2.99 (dd, $J = 14.0$, 8.0 Hz, 1H), 2.62 (dd, $J = 14.0$, 8.0 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.5, 147.8, 142.5, 137.0, 136.2, 133.3, 132.8, 128.7, 128.6, 127.1, 124.5, 124.0, 123.2, 120.7, 112.8, 62.0, 43.3, 41.7, 22.9; IR (neat) 2936, 1683, 733; MS (EI) m/z 336 (M^+), 173 (100%); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{20}\text{O}_2\text{S}$ 336.1184, found 336.1181.



2-(3-methoxybenzo[b]thiophen-2-yl)-1-(thiophen-2-yl)pent-4-en-1-one (3d):

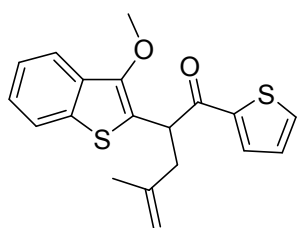
Colorless oil; 217 mg, 66% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.98 (dd, $J = 3.8$, 0.9 Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.61–7.56 (m, 1H), 7.35–7.22 (m, 2H), 7.10–7.04 (m, 1H), 5.86–5.73 (m, 1H), 5.17–4.98 (m, 3H), 4.00 (s, 3H), 2.92 (dd, $J = 14.0$, 8.0 Hz, 1H), 2.73 (dd, $J = 12.0$, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.0, 148.0, 143.4, 137.0, 135.1, 134.6, 132.9, 132.7, 128.3, 126.9, 124.7, 124.1, 123.3, 120.7, 117.6, 62.2, 46.2, 37.6; IR (neat) 2936, 1659, 728; MS (EI) m/z 328 (M^+), 217 (100%); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}_2$ 328.0592, found 328.0594.



3e

2-(3-methoxybenzo[b]thiophen-2-yl)-4-methyl-1-(m-tolyl)pent-4-en-1-one (3e):

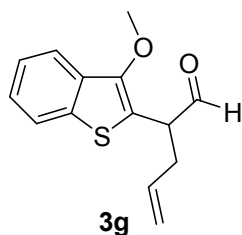
Colorless oil; 284 mg, 81% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.98–7.86 (m, 2H), 7.68 (dd, $J = 7.7, 3.3$ Hz, 2H), 7.34–7.24 (m, 4H), 5.41 (t, $J = 7.2$ Hz, 1H), 4.72 (d, $J = 12.0$ Hz, 2H), 3.98 (s, 3H), 2.99 (dd, $J = 12.0, 8.0$ Hz, 1H), 2.60 (dd, $J = 12.0, 4.0$ Hz, 1H), 2.37 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.6, 147.7, 142.6, 138.5, 137.0, 136.2, 134.1, 132.8, 129.2, 128.5, 127.2, 125.8, 124.5, 123.9, 123.2, 120.7, 112.7, 61.9, 43.3, 41.7, 22.9, 21.4; IR (neat) 2935, 1682, 734; MS (EI) m/z 350 (M^+), 231 (100%); HRMS (EI) calcd for $\text{C}_{22}\text{H}_{22}\text{O}_2\text{S}$ 350.1341, found 350.1344.



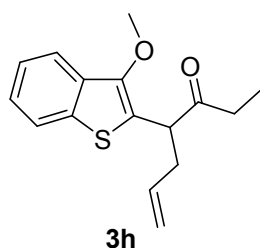
3f

2-(3-methoxybenzo[b]thiophen-2-yl)-4-methyl-1-(thiophen-2-yl)pent-4-en-1-one

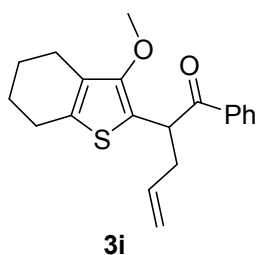
(3f): Colorless oil; 229 mg, 67 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 4.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.36–7.27 (m, 2H), 7.17–7.07 (m, 1H), 5.23 (t, $J = 7.3$ Hz, 1H), 4.75 (d, $J = 4.0$ Hz, 2H), 4.01 (s, 3H), 2.98 (dd, $J = 16.0, 8.0$ Hz, 1H), 2.61 (dd, $J = 14.0, 8.0$ Hz, 1H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 161.3, 147.9, 143.5, 142.3, 137.0, 134.5, 132.7, 128.3, 127.2, 124.6, 124.0, 123.2, 120.7, 112.9, 62.0, 44.8, 41.4, 22.8; IR (neat) 2932, 1662, 733; MS (EI) m/z 342 (M^+), 231 (100%); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2\text{S}_2$ 342.0748, found 342.0745.



2-(3-methoxybenzo[b]thiophen-2-yl)pent-4-enal (3g): Colorless oil; 202 mg, 82 % yield; ^1H NMR (400 MHz, CDCl_3) δ 9.72 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.42–7.30 (m, 2H), 5.84–5.70 (m, 1H), 5.14 (d, J = 16.0 Hz, 1H), 5.05 (d, J = 8.0 Hz, 1H), 4.14 (m, 1H), 3.95 (s, 3H), 2.95–2.83 (m, 1H), 2.62–2.49 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.2, 149.6, 136.9, 134.3, 133.0, 124.9, 124.3, 123.2, 120.8, 117.8, 62.2, 50.6, 34.0; IR (neat) 2935, 1725, 737; MS (EI) m/z 246 (M^+), 217 (100%); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$ 246.0715, found 246.0715.

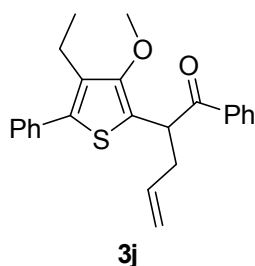


4-(3-methoxybenzo[b]thiophen-2-yl)hept-6-en-3-one (3h): Colorless oil; 206 mg, 75 % yield; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 8.0 Hz, 2H), 7.40–7.28 (m, 2H), 5.81–5.69 (m, 1H), 5.09 (d, J = 16.0 Hz, 1H), 5.00 (d, J = 12.0 Hz, 1H), 4.05–3.90 (m, 3H), 3.97 (s, 3H), 2.83 (dd, J = 16.0, 8.0 Hz, 1H), 2.60–2.37 (m, 3H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.0, 148.6, 136.7, 135.2, 132.9, 126.5, 124.7, 124.2, 123.2, 120.7, 117.3, 61.9, 49.8, 36.3, 34.9, 7.8; IR (neat) 2936, 1717, 736; MS (EI) m/z 274 (M^+), 217 (100%); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}$ 274.1028, found 274.1032.



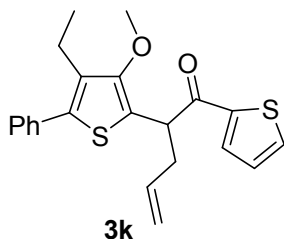
2-(3-methoxy-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)-1-phenylpent-4-en-1-one

(3i): Colorless oil; 238 mg, 73 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.0$ Hz, 2H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.43 (t, $J = 7.4$ Hz, 2H), 5.85–5.71 (m, 1H), 5.14–4.97 (m, 3H), 3.75 (s, 3H), 2.87 (dd, $J = 16.0, 8.0$ Hz, 1H), 2.65–2.55 (m, 3H), 2.47 (s, 2H), 1.77 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 151.8, 136.3, 135.9, 134.3, 133.1, 128.7, 128.6, 121.4, 116.9, 61.2, 44.2, 38.2, 25.5, 23.6, 23.3, 22.3; IR (neat) 2934, 1683, 737; MS (EI) m/z 326 (M^+), 221 (100%); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2\text{S}$ 326.1341, found 326.1341.



2-(4-ethyl-3-methoxy-5-phenylthiophen-2-yl)-1-phenylpent-4-en-1-one (3j):

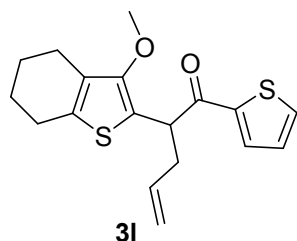
Colorless oil; 278 mg, 74 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 8.0$ Hz, 2H), 7.54 (t, $J = 7.3$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.41–7.32 (m, 4H), 7.32–7.27 (m, 1H), 5.90–5.75 (m, 1H), 5.16 – 5.07 (m, 2H), 5.02 (d, $J = 8.0$ Hz, 1H), 3.85 (s, 3H), 2.95 (dd, $J = 16.0, 8.0$ Hz, 1H), 2.71–2.54 (m, 3H), 1.10 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.7, 153.4, 136.3, 136.0, 135.7, 135.1, 133.3, 133.2, 128.7, 128.6, 128.5, 127.4, 125.1, 117.2, 100.0, 62.4, 44.6, 38.6, 19.8, 14.5; IR (neat) 2971, 1684, 700; MS (EI) m/z 376 (M^+), 271 (100%); HRMS (EI) calcd for $\text{C}_{24}\text{H}_{24}\text{O}_2\text{S}$ 376.1497, found 376.1495.



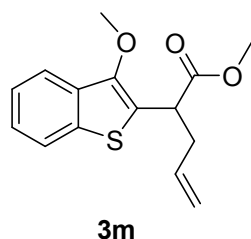
2-(4-ethyl-3-methoxy-5-phenylthiophen-2-yl)-1-(thiophen-2-yl)pent-4-en-1-one

(3k): Colorless oil; 252 mg, 66 % yield; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 4.0$ Hz, 1H), 7.64 (d, $J = 4.0$ Hz, 1H), 7.42–7.34 (m, 4H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.18–7.07 (m, 1H), 5.88 – 5.78 (m, 1H), 5.13 (d, $J = 16.0$ Hz, 1H), 5.03 (d, $J = 8.0$ Hz,

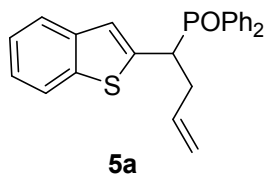
1H), 4.92 (t, $J = 7.5$ Hz, 1H), 3.86 (s, 3H), 2.92 (dd, $J = 14.0, 8.0$ Hz, 1H), 2.72–2.56 (m, 3H), 1.11 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.5, 135.6, 143.7, 135.4, 135.0, 134.4, 133.3, 132.7, 128.8, 128.5, 128.3, 127.4, 125.1, 117.4, 100.0, 62.4, 46.1, 38.3, 19.8, 14.5; IR (neat) 2970, 1663, 731; MS (EI) m/z 382 (M^+), 271 (100%); HRMS (EI) calcd for $\text{C}_{22}\text{H}_{22}\text{O}_2\text{S}_2$ 382.1061, found 382.1063.



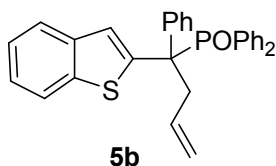
2-(3-methoxy-4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)-1-(thiophen-2-yl)pent-4-en-1-one (3l): Colorless oil; 213 mg, 64 % yield; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 4.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.10 (s, 1H), 5.83–5.72 (m, 1H), 5.10 (d, $J = 16.0$ Hz, 1H), 5.01 (d, $J = 12.0$ Hz, 1H), 4.85 (t, $J = 7.5$ Hz, 1H), 3.76 (s, 3H), 2.94–2.79 (m, 1H), 2.65–2.54 (m, 3H), 2.48 (s, 2H), 1.79 (d, $J = 4.0$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.7, 135.6, 134.4, 134.2, 132.7, 128.8, 128.2, 121.5, 117.1, 61.3, 45.7, 37.9, 25.5, 23.6, 23.3, 22.3; IR (neat) 2931, 1663, 732; MS (EI) m/z 332 (M^+), 221 (100%); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}_2$ 332.0905, found 332.0906.



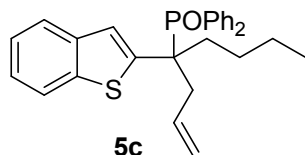
methyl 2-(3-methoxybenzo[b]thiophen-2-yl)pent-4-enoate (3m): Colorless oil; 198mg, 72% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.77–7.67 (m, 2H), 7.33 (m, 2H), 5.76 (m, 1H), 5.13 (dd, $J = 17.0, 1.6$ Hz, 1H), 5.08–4.99 (m, 1H), 4.31 (t, $J = 7.8$ Hz, 1H), 3.96 (s, 3H), 3.71 (s, 3H), 2.84 (m, 1H), 2.65–2.55 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 148.5, 136.6, 134.5, 132.8, 126.1, 124.7, 124.1, 123.1, 120.7, 117.7, 62.0, 52.3, 43.2, 37.8; IR (neat) 2930, 1668, 736; MS (EI) m/z 276 (M^+), 217 (100%); HRMS (EI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3\text{S}$ 276.0820, found 276.0822.



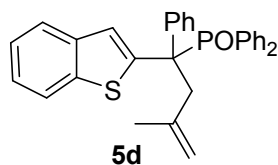
(1-(benzo[b]thiophen-2-yl)but-3-en-1-yl)diphenylphosphine oxide (5a): White solid; 322 mg, 83% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.96–7.87 (m, 2H), 7.69 (d, $J = 4.0$ Hz, 1H), 7.65–7.49 (m, 6H), 7.34–7.32 (m, 1H), 7.31–7.22 (m, 4H), 7.18 (d, $J = 4.0$ Hz, 1H), 5.74–5.60 (m, 1H), 4.96 (dd, $J = 17.0, 1.4$ Hz, 1H), 4.91 (d, $J = 10.0$ Hz, 1H), 3.92–3.82 (m, 1H), 2.92–2.80 (m, 1H), 2.74–2.66 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.7, 138.7 (d, $J = 6.0$ Hz), 134.8 (d, $J = 14.0$ Hz), 132.6, 132.0 (d, $J = 2.0$ Hz), 131.7 (d, $J = 2.0$ Hz), 131.4 (d, $J = 9.0$ Hz), 131.1 (d, $J = 9.0$ Hz), 129.0, 128.9 (d, $J = 12.0$ Hz), 128.3 (d, $J = 12.0$ Hz), 124.2, 124.1, 123.8, 123.2, 122.0, 117.4, 43.1 (d, $J = 67.0$ Hz), 34.8; ^{31}P NMR (160 MHz, CDCl_3) δ 31.6; IR (neat) 3057, 1186, 697; MS (EI) m/z 388 (M^+), 201 (100%); HRMS (EI) calcd for $\text{C}_{24}\text{H}_{21}\text{OPS}$ 388.1051, found 388.1050.



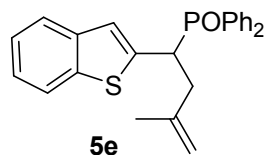
(1-(benzo[b]thiophen-2-yl)-1-phenylbut-3-en-1-yl)diphenylphosphine oxide (5b): White solid; 362 mg, 78% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.0$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 9.0$ Hz, 3H), 7.44–7.38 (m, 2H), 7.37–7.27 (m, 7H), 7.27–7.18 (m, 6H), 5.58–5.42 (m, 1H), 5.00 (d, $J = 16.0$ Hz, 1H), 4.85 (d, $J = 12.0$ Hz, 1H), 3.52–3.43 (m, 1H), 3.20–3.04 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6 (d, $J = 3.0$ Hz), 144.0, 139.0, 136.5, 133.5 (d, $J = 8.0$ Hz), 133.2 (d, $J = 8.0$ Hz), 132.5 (d, $J = 11.0$ Hz), 132.0 (d, $J = 2.0$ Hz), 131.9 (d, $J = 2.0$ Hz), 131.1 (d, $J = 5.0$ Hz), 128.1, 127.9 (d, $J = 6.0$ Hz), 127.8, 127.7, 126.4 (d, $J = 6.0$ Hz), 124.2, 124.1, 123.5, 121.9, 118.6, 55.5 (d, $J = 63.0$ Hz), 39.8; ^{31}P NMR (160 MHz, CDCl_3) δ 36.0; IR (neat) 3056, 1175, 696; MS (EI) m/z 464 (M^+), 263 (100%); HRMS (EI) calcd for $\text{C}_{30}\text{H}_{25}\text{OPS}$ 464.1364, found 464.1366.



(4-(benzo[b]thiophen-2-yl)oct-1-en-4-yl)diphenylphosphine oxide (5c): White solid; 298 mg, 67% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.79–7.65 (m, 5H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.54–7.47 (m, 2H), 7.42–7.26 (m, 6H), 6.64 (d, $J = 4.0$ Hz, 1H), 6.02–5.87 (m, 1H), 5.11 (d, $J = 16.0$ Hz, 1H), 5.05 (d, $J = 10.0$ Hz, 1H), 3.24–3.13 (m, 1H), 2.95–2.76 (m, 1H), 2.43–2.31 (m, 1H), 2.08–1.89 (m, 1H), 1.66–1.48 (m, 1H), 1.31–1.17 (m, 3H), 0.80 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.8, 139.2 (d, $J = 4.0$ Hz), 133.2 (d, $J = 7.0$ Hz), 132.9 (d, $J = 7.0$ Hz), 131.8, 130.8, 129.9, 128.2, 128.0, 124.5, 124.3, 124.2 (d, $J = 15.0$ Hz), 123.3, 121.9, 118.4, 48.9 (d, $J = 65.0$ Hz), 38.5, 34.0, 25.3 (d, $J = 6.0$ Hz), 23.2, 13.9; ^{31}P NMR (160 MHz, CDCl_3) δ 35.1; IR (neat) 3058, 1182, 699; MS (EI) m/z 444 (M^+), 243 (100%); HRMS (EI) calcd for $\text{C}_{28}\text{H}_{29}\text{OPS}$ 444.1677, found 444.1669.

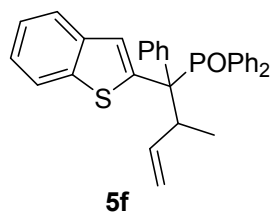


(1-(benzo[b]thiophen-2-yl)-3-methyl-1-phenylbut-3-en-1-yl)diphenylphosphine oxide (5d): White solid; 349 mg, 73% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 8.0$ Hz, 1H), 7.68 (d, $J = 4.0$ Hz, 1H), 7.48 (t, $J = 6.0$ Hz, 2H), 7.44–7.35 (m, 4H), 7.35–7.26 (m, 7H), 7.24–7.16 (m, 3H), 7.12–7.06 (m, 2H), 4.60 (s, 1H), 4.36 (s, 1H), 3.55 (dd, $J = 16.0, 8.0$ Hz, 1H), 3.07 (dd, $J = 16.0, 8.0$ Hz, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 139.7, 139.4, 139.2, 139.0, 136.0, 133.6 (d, $J = 8.0$ Hz), 133.2 (d, $J = 9.0$ Hz), 131.9, 131.3, 131.1, 128.0, 127.9 (d, $J = 6.0$ Hz), 127.7, 127.5, 126.6, 124.2, 124.1, 123.5, 121.8, 115.4, 55.7 (d, $J = 59.0$ Hz), 41.0, 25.2; ^{31}P NMR (160 MHz, CDCl_3) δ 36.0; IR (neat) 3057, 1179, 699; MS (EI) m/z 478 (M^+), 277 (100%); HRMS (EI) calcd for $\text{C}_{31}\text{H}_{27}\text{OPS}$ 478.1520, found 478.1516.



(1-(benzo[b]thiophen-2-yl)-3-methyl-1-phenylbut-3-en-1-yl)diphenylphosphine

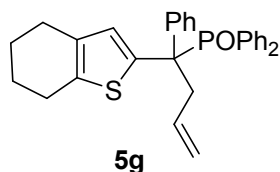
oxide (5e): White solid; 314 mg, 78% yield; ^1H NMR (400 MHz, CDCl_3) δ 8.00–7.88 (m, 2H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.64–7.49 (m, 6H), 7.39–7.33 (m, 1H), 7.29–7.18 (m, 4H), 7.13 (d, $J = 4.0$ Hz, 1H), 4.63 (d, $J = 12.0$ Hz, 2H), 4.02 (dd, $J = 16.0, 6.0$ Hz, 1H), 2.90–2.76 (m, 1H), 2.74–2.60 (m, 1H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.5, 141.3, 139.6, 138.8, 132.0 (d, $J = 8.0$ Hz), 131.8, 131.7, 131.4 (d, $J = 8.0$ Hz), 131.1 (d, $J = 9.0$ Hz), 130.9, 128.9 (d, $J = 11.0$ Hz), 128.2 (d, $J = 11.0$ Hz), 124.1 (d, $J = 7.0$ Hz), 124.0, 123.7, 123.2, 122.0, 113.4, 41.7 (d, $J = 67.0$ Hz), 38.3, 22.1; ^{31}P NMR (160 MHz, CDCl_3) δ 32.1; IR (neat) 3058, 1185, 697; MS (EI) m/z 402 (M^+), 201 (100%); HRMS (EI) calcd for $\text{C}_{25}\text{H}_{23}\text{OPS}$ 402.1207, found 402.1209.



5f

(1-(benzo[b]thiophen-2-yl)-2-methylbut-3-en-1-yl)diphenylphosphine oxide (5f):

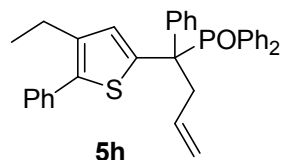
White solid; 220 mg, 46% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.75 (t, $J = 7.0$ Hz, 2H), 7.52 (m, 3H), 7.48–7.39 (m, 2H), 7.40–7.26 (m, 8H), 7.22–7.14 (m, 4H), 6.47–6.30 (m, 1H), 5.01 (d, $J = 12.0$ Hz, 1H), 4.74 (d, $J = 16.0$ Hz, 1H), 3.39 (dd, $J = 14.0, 8.0$ Hz, 1H), 1.02 (d, $J = 4.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.9, 140.1 (d, $J = 4.0$ Hz), 139.7, 138.7, 136.8, 134.0 (d, $J = 8.0$ Hz), 133.5, 133.3, 132.8, 132.4, 131.8, 131.5 (d, $J = 3.0$ Hz), 128.3 (d, $J = 6.0$ Hz), 128.1, 127.7 (d, $J = 5.0$ Hz), 127.6 (d, $J = 4.0$ Hz), 127.0 (d, $J = 2.0$ Hz), 124.2, 124.0, 123.6, 121.6, 114.6, 59.2 (d, $J = 61.0$ Hz), 42.6, 18.5 (d, $J = 8.0$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 35.2; IR (neat) 3057, 1179, 698; MS (EI) m/z 478 (M^+), 277 (100%); HRMS (EI) calcd for $\text{C}_{31}\text{H}_{27}\text{OPS}$ 478.1520, found 478.1524.



5g

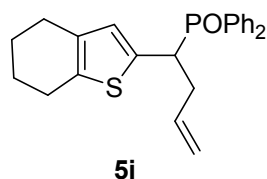
diphenyl(1-phenyl-1-(4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)but-3-en-1-

yl)phosphine oxide (5g): White solid; 309 mg, 66% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 8.0$ Hz, 2H), 7.49–7.34 (m, 4H), 7.34–7.28 (m, 3H), 7.28–7.18 (m, 6H), 6.55 (d, $J = 2.0$ Hz, 1H), 5.54–5.39 (m, 1H), 4.99 (d, $J = 16.0$ Hz, 1H), 4.90 (d, $J = 8.0$ Hz, 1H), 3.26 (dd, $J = 12.0, 8.0$ Hz, 1H), 3.17 (dd, $J = 14.0, 6.0$ Hz, 1H), 2.70 (s, 2H), 2.48 (s, 2H), 1.88–1.73 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.9, 137.6, 135.6 (d, $J = 3.0$ Hz), 134.5 (d, $J = 3.0$ Hz), 133.5, 133.4 (d, $J = 8.0$ Hz), 133.3, 133.1, 131.6, 130.8, 130.7, 130.5 (d, $J = 5.0$ Hz), 129.7, 129.5, 127.8, 127.7, 127.5 (d, $J = 2.0$ Hz), 118.2, 54.4 (d, $J = 65.0$ Hz), 40.0, 25.4, 24.8, 23.7, 23.0; ^{31}P NMR (160 MHz, CDCl_3) δ 36.7; IR (neat) 3059, 1177, 699; MS (EI) m/z 468 (M^+), 267 (100%); HRMS (EI) calcd for $\text{C}_{30}\text{H}_{29}\text{OPS}$ 468.1677, found 468.1678.



(1-(4-ethyl-5-phenylthiophen-2-yl)-1-phenylbut-3-en-1-yl)diphenylphosphine

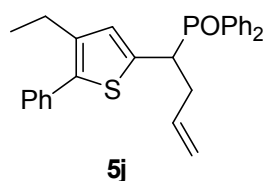
oxide (5h): White solid; 352 mg, 68% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.72–7.63 (m, 2H), 7.60–7.53 (m, 2H), 7.49–7.43 (m, 1H), 7.41–7.35 (m, 4H), 7.30 (d, $J = 8.0$ Hz, 6H), 7.23–7.11 (m, 2H), 7.04 (d, $J = 2.0$ Hz, 2H), 6.94 (d, $J = 2.0$ Hz, 2H), 5.88–5.78 (m, 1H), 5.20 (d, $J = 12.0$ Hz, 2H), 3.07 (dd, $J = 14.0, 8.0$ Hz, 1H), 2.90 (dd, $J = 14.0, 8.0$ Hz, 1H), 1.95 (dd, $J = 18.0, 8.0$ Hz, 1H), 1.78 (dd, $J = 16.0, 8.0$ Hz, 1H), 0.97 (t, $J = 7.0$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.5, 142.3, 133.1, 132.1 (d, $J = 4.0$ Hz), 132.0 (d, $J = 3.0$ Hz), 131.4, 131.2, 130.1 (d, $J = 5.0$ Hz), 128.5, 128.3, 128.2, 128.0, 127.9, 127.3, 127.2, 126.7, 125.6 (d, $J = 6.0$ Hz), 118.6, 69.5, 40.1, 21.9, 12.0; ^{31}P NMR (160 MHz, CDCl_3) δ 27.4; IR (neat) 3056, 1185, 697; MS (EI) m/z 518 (M^+), 317 (100%); HRMS (EI) calcd for $\text{C}_{34}\text{H}_{31}\text{OPS}$ 518.1833, found 518.1829.



diphenyl(1-(4,5,6,7-tetrahydrobenzo[b]thiophen-2-yl)but-3-en-1-yl)phosphine

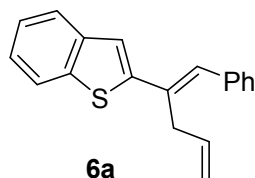
oxide (5i): White solid; 251 mg, 64% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.92–7.81

(m, 2H), 7.79–7.68 (m, 1H), 7.61–7.49 (m, 4H), 7.45–7.38 (m, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 6.47 (s, 1H), 5.79–5.61 (m, 1H), 5.07–4.84 (m, 2H), 3.80–3.67 (m, 1H), 2.72–2.56 (m, 4H), 2.48–2.39 (m, 2H), 1.80–1.62 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.3, 140.1, 135.5, 135.0, 134.9, 134.7, 132.7, 131.8, 131.4 (d, $J = 9.0$ Hz), 131.3, 128.7 (d, $J = 9.0$ Hz), 128.1, 128.0, 117.0, 42.4 (d, $J = 67.0$ Hz), 34.6, 25.1, 24.8, 23.6, 22.8; ^{31}P NMR (160 MHz, CDCl_3) δ 31.9; IR (neat) 3056, 1183, 699; MS (EI) m/z 392 (M^+), 201 (100%); HRMS (EI) calcd for $\text{C}_{24}\text{H}_{25}\text{OPS}$ 392.1364, found 392.1359.



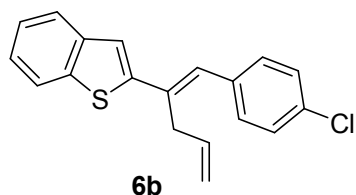
(1-(4-ethyl-5-phenylthiophen-2-yl)but-3-en-1-yl)diphenylphosphine oxide (5j):

White solid; 314 mg, 71% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.97–7.84 (m, 2H), 7.62–7.52 (m, 5H), 7.45–7.39 (m, 1H), 7.38–7.27 (m, 7H), 6.69 (s, 1H), 5.79–5.70 (m, 1H), 4.99 (t, $J = 15.0$ Hz, 2H), 3.76 (t, $J = 8.0$ Hz, 1H), 2.82–2.64 (m, 2H), 2.54 (dd, $J = 16.0, 8.0$ Hz, 2H), 1.06 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.4, 139.7, 135.5, 135.3, 134.6, 132.0, 131.5 (d, $J = 9.0$ Hz), 129.6 (d, $J = 5.0$ Hz), 129.1, 128.8 (d, $J = 11.0$ Hz), 128.4, 128.2, 128.0, 127.1, 117.2, 100.0, 42.9 (d, $J = 69.0$ Hz), 34.5, 22.0, 15.4; ^{31}P NMR (160 MHz, CDCl_3) δ 31.9; IR (neat) 3056, 1183, 699; MS (EI) m/z 442 (M^+), 241 (100%); HRMS (EI) calcd for $\text{C}_{28}\text{H}_{27}\text{OPS}$ 442.1520, found 442.1525.

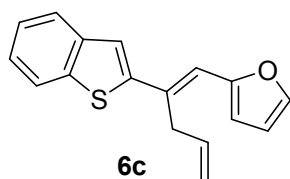


(E)-2-(1-phenylpenta-1,4-dien-2-yl)benzo[b]thiophene (6a): Colorless oil; 185 mg, 67% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.45–7.34 (m, 4H), 7.34–7.25 (m, 4H), 7.19 (s, 1H), 6.16–6.05 (m, 1H), 5.28–5.16 (m, 2H), 3.52 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 140.5, 138.7, 136.9, 135.7, 133.0, 130.2, 128.8, 128.4, 127.3, 124.6, 124.4, 123.5,

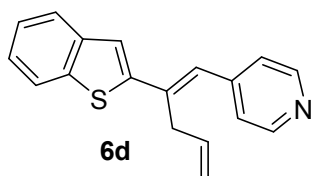
122.0, 120.9, 116.7, 34.5; IR (neat) 3059, 1600, 747; MS (EI) m/z 276 (M^+), 199 (100%); HRMS (EI) calcd for $C_{19}H_{16}S$ 276.0973, found 276.0974.



(E)-2-(1-(4-chlorophenyl)penta-1,4-dien-2-yl)benzo[b]thiophene (6b): Colorless oil; 229 mg, 74% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.0, 4.0 Hz, 1H), 7.69 (dd, J = 6.0, 2.0 Hz, 1H), 7.40–7.27 (m, 7H), 7.11 (s, 1H), 6.14–6.02 (m, 1H), 5.27–5.15 (m, 2H), 3.54–3.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 140.4, 138.8, 135.4, 135.3, 133.6, 133.1, 130.1, 128.9, 128.6, 124.7, 124.5, 123.6, 122.0, 121.2, 116.9, 34.4; IR (neat) 3061, 1488, 744; MS (EI) m/z 310 (M^+), 199 (100%); HRMS (EI) calcd for $C_{19}H_{15}ClS$ 310.0583, found 310.0587.

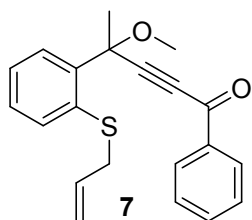


(E)-2-(2-(benzo[b]thiophen-2-yl)penta-1,4-dien-1-yl)furan (6c): Colorless oil; 202 mg, 76% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.79–7.71 (m, 1H), 7.68 (dd, J = 6.5, 2.1 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.34–7.24 (m, 3H), 6.89 (s, 1H), 6.50–6.44 (m, 2H), 6.08–5.97 (m, 1H), 5.23 (dd, J = 18.0, 2.0 Hz, 1H), 5.11 (dd, J = 12.0, 2.0 Hz, 1H), 3.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 146.3, 142.5, 140.6, 138.8, 135.0, 130.9, 124.6, 124.4, 123.5, 122.0, 120.9, 117.3, 116.2, 111.8, 111.2, 35.2; IR (neat) 3061, 1440, 738; MS (EI) m/z 266 (M^+), 199 (100%); HRMS (EI) calcd for $C_{17}H_{14}OS$ 266.0765, found 266.0768.

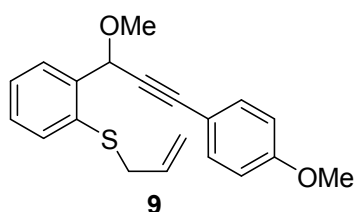


(E)-4-(2-(benzo[b]thiophen-2-yl)penta-1,4-dien-1-yl)pyridine (6d): Colorless oil; 177 mg, 64% yield; 1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.34–7.30 (m, 3H), 7.26 (s, 1H), 7.08 (s, 3H), 6.50 (s, 1H), 5.98–5.87

(m, 1H), 5.26–5.12 (m, 2H), 3.32 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.8, 141.4, 140.1, 139.6, 138.5, 134.5, 127.5, 124.6, 124.4, 123.9, 123.7, 123.4, 122.2, 117.9, 115.9, 44.6; IR (neat) 3062, 1594, 748; MS (EI) m/z 277 (M^+), 199 (100%); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{15}\text{NS}$ 277.0925, found 277.0928.



4-(2-(allylthio)phenyl)-4-methoxy-1-p-tolylpent-2-yn-1-one (7): Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (m, 1H), 7.62–7.56 (m, 2H), 7.39 (dd, $J = 11.4, 4.5$ Hz, 2H), 7.34 (dd, $J = 4.9, 3.6$ Hz, 1H), 7.29 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.23–7.18 (m, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 5.89 (m, 1H), 5.26 (dd, $J = 17.0, 1.4$ Hz, 1H), 5.11 (dd, $J = 10.1, 1.1$ Hz, 1H), 3.58 (dd, $J = 6.7, 1.1$ Hz, 2H), 3.26 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.4, 140.5, 138.9, 135.4, 133.2, 128.6, 128.4, 128.3, 128.1, 127.7, 126.7, 124.7, 118.1, 91.2, 87.3, 78.2, 52.5, 36.2, 27.9; MS (EI) m/z 336 (M^+), 231 (100%); IR (neat) 3058, 1186, 696; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{20}\text{O}_2\text{S}$ 336.1184, found 336.1182.



allyl(2-(1-methoxy-3-(4-methoxyphenyl)prop-2-ynyl)phenyl)sulfane (9): Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.78 (m, 1H), 7.42 (m, 3H), 7.31 – 7.27 (m, 2H), 6.85 – 6.82 (m, 2H), 5.93 – 5.82 (m, 1H), 5.80 (s, 1H), 5.12 – 5.03 (m, 2H), 3.80 (s, 3H), 3.56 (dd, $J = 7.0, 1.0$ Hz, 2H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.7, 139.7, 134.8, 133.4, 133.3, 131.6, 128.7, 128.1, 127.1, 117.9, 114.7, 113.9, 87.6, 85.3, 71.0, 56.3, 55.3, 38.2; IR (neat) 3067, 1196, 786; MS (EI) m/z 324 (M^+), 217 (100%); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2\text{S}$ 324.1184, found 324.1183.

4. The ^1H and ^{13}C NMR spectra of compounds

