Sequential Assembly Strategy for Tetrasubstituted Olefin Synthesis
Using Vinyl 2-Pyrimidyl Sulfide as a Platform

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General. ^1H and ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (^1H 300 MHz, ^{13}C 75 MHz), Varian MERCURYplus-400 (^1H 400 MHz, ^{13}C 100 MHz), and JEOL A-500 (^1H 500 MHz, ^{13}C 125 MHz) spectrometers in CDCl_3 . UV/Vis spectra were recorded on Shimadzu UV-2500 spectrophotometer. IR spectra were recorded on Shimadzu FTIR-8100 spectrophotometer. EI and CI mass spectra were recorded on JMS-SX102A spectrometer. FAB mass spectra were recorded on JMS-HX110A spectrometer. Gel permeation chromatography was carried out with Japan Analytical Industry LC-918. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ was purchased from Strem Chemicals, Inc. and used as received. 2-Pyrimidyl vinyl sulfide (**1**) was prepared by the procedure developed by Miyashita.¹

Aryl Groups Used in This Study. The following 13 aryl and heteroaryl groups were successfully installed into tri- and tetrasubstituted olefin structure. For simplicity, we assigned them alphabetically as follows and used them in compound assignment.

(1) (a) Miyashita, A.; Nagasaki, I.; Kawano, A.; Suzuki, Y.; Iwamoto, K.; Higashino, T. *Heterocycles* **1997**, 45, 745. (b) Nagasaki, I.; Matsumoto, M.; Yamashita, M.; Miyashita, A. *Heterocycles* **1999**, 51, 1015.

Typical Procedure for One-Pot Double Mizoroki–Heck Reaction of **1 with Aryl Iodides (procedure when two aryl groups are same).**

A mixture of 2-pyrimidinyl vinyl sulfide (**1**; 41.4 mg, 0.30 mmol), 2-iodotoluene (131.1 mg, 0.60 mmol), triethylamine (119 mg, 0.92 mmol), and $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (7.6 mg, 14.9 μmol) in dry toluene (1.5 mL) was stirred at $80\text{ }^\circ\text{C}$ for 14 h under argon. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The filtrate was evaporated, and the residue was chromatographed on silica gel (hexane/EtOAc = 10/1 ~ 5/1) to afford **2b** (85.4 mg, 90%) as pale yellow solid.

Typical Procedure for One-Pot Double Mizoroki–Heck Reaction of **1 with Aryl Iodides (procedure when two aryl groups are different).**

A mixture of 2-pyrimidinyl vinyl sulfide (**1**; 40.6 mg, 0.29 mmol), iodobenzene (60.6 mg, 0.30 mmol), triethylamine (116 mg, 0.90 mmol), and $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (7.4 mg, 14.5 μmol) in dry toluene (1.5 mL) was stirred at $60\text{ }^\circ\text{C}$ for 3 h under argon. To this mixture was added 2-iodotoluene (66.1 mg, 0.30 mmol) and the resultant mixture was further stirred at $90\text{ }^\circ\text{C}$ for 18 h. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The filtrate was evaporated, and the residue was chromatographed on silica gel (hexane/EtOAc = 5/1) to afford **2ab** (80.6 mg, 90%) as pale yellow solid.

2aa: 99% yield from **1** and iodobenzene. ^1H NMR (300 MHz, CDCl_3) δ 7.01 (t, $J = 4.8$ Hz, 1H), 7.22–7.50 (m, 10H), 7.79 (s, 1H), 8.56 (d, $J = 4.8$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 117.1, 119.1, 127.3, 127.4, 127.9, 128.2, 128.4, 129.6, 139.3, 140.8, 141.2, 157.4, 170.3. HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{S}$: 290.0878, found 290.0881.

2bb: 90% yield from **1** and 2-iodotoluene. ^1H NMR (300 MHz, CDCl_3) δ 2.16 (s, 3H), 2.35 (s, 3H), 7.00 (t, $J = 4.8$ Hz, 1H), 7.10–7.35 (m, 8H), 7.53 (s, 1H), 8.53 (d, $J = 4.8$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 20.0, 21.2, 117.0, 122.8, 125.64, 125.65, 127.1, 127.9, 129.7, 130.1, 130.6, 130.9, 135.7, 136.1, 139.4, 140.4, 140.9, 157.4, 170.6. HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}$: 318.1191, found 318.1190.

2cc: 81% yield from **1** and 3-iodotoluene. ^1H NMR (300 MHz, CDCl_3) δ 2.34 (s, 3H), 2.37 (s, 3H), 7.02 (t, $J = 4.8$ Hz, 1H), 7.07–7.35 (m, 8H), 7.73 (s, 1H), 8.57 (d, $J = 4.8$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.46, 21.47, 117.0, 118.7, 124.6, 126.7, 127.9, 128.1, 128.2, 128.3, 128.6, 130.2, 137.8, 138.0, 139.3, 141.2, 141.4, 157.4, 170.6. HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}$: 318.1191, found 318.1191.

2dd: 91% yield from **1** and 4-iodotoluene. ^1H NMR (300 MHz, CDCl_3) δ 2.35 (s, 3H), 2.40 (s, 3H), 7.00 (t, $J = 4.8$ Hz, 1H), 7.12 (d, $J = 7.8$ Hz, 2H), 7.18–7.30 (m, 6H), 7.67 (s, 1H), 8.55 (d, $J = 4.8$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.1, 21.2, 116.9, 117.6, 127.2, 128.9, 129.0, 129.5, 136.4, 137.1, 137.5, 138.7, 140.8, 157.3, 170.5. HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}$: 318.1191, found 318.1191.

2ee: 92% yield from **1** and 4-iodoanisole. ^1H NMR (300 MHz, CDCl_3) δ 3.82 (s, 3H), 3.86 (s, 3H), 6.85 (d, $J = 9.0$ Hz, 2H), 6.94 (d, $J = 8.7$ Hz, 2H), 7.01 (t, $J = 4.8$ Hz, 1H), 7.25–7.32 (m, 4H), 7.55 (s, 1H), 8.56 (d, $J = 4.8$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 55.1, 55.2, 113.5, 113.6, 116.2, 116.9, 128.5, 130.9, 131.7, 134.3, 140.4, 157.3, 159.0, 159.1, 170.7. HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$: 350.1089, found 350.1089.

2ff: 95% yield from **1** and 1-iodonaphthalene. ^1H NMR (300 MHz, CDCl_3) δ 6.99 (t, J = 4.8 Hz, 1H), 7.30–7.60 (m, 8H), 7.75–7.80 (m, 1H), 7.82–7.90 (m, 3H), 7.93 (s, 1H), 8.03 (d, J = 8.1 Hz, 1H), 8.52 (d, J = 4.8 Hz, 2H), 8.63–8.70 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 117.0, 125.1, 125.3, 125.6, 125.7, 125.80, 125.83 (two carbons), 126.36, 126.41, 126.6, 127.7, 127.8, 128.50 (two carbons), 128.55, 130.7, 131.3, 134.0, 134.3, 137.6, 138.1, 140.0, 157.3, 170.4. HRMS (EI) m/z calcd for $\text{C}_{26}\text{H}_{18}\text{N}_2\text{S}$: 390.1191, found 390.1191.

2ab: 90% yield from **1**, iodobenzene, and 2-iodotoluene. Stereochemistry was determined to be 97% *E*. ^1H NMR (300 MHz, CDCl_3) δ 2.09 (s, 3H), 7.02 (t, J = 4.8 Hz, 1H), 7.15–7.40 (m, 9H), 7.43 (s, 1H), 8.55 (d, J = 4.8 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 20.5, 117.1, 120.1, 125.7, 127.5, 127.6, 128.2, 128.8, 130.32, 130.34, 136.4, 139.4, 140.8, 142.4, 157.4, 170.2. HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{S}$: 304.1034, found 304.1034.

2ad: 88% yield from **1**, iodobenzene, and 4-iodotoluene. Stereochemistry was determined to be 96% *E*. ^1H NMR (300 MHz, CDCl_3) δ 2.41 (s, 3H), 7.02 (t, J = 4.8 Hz, 1H), 7.22–7.40 (m, 9H), 7.74 (s, 1H), 8.57 (d, J = 4.8 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.1, 117.0, 118.1, 127.2, 127.9, 128.4, 129.0, 129.6, 137.3, 138.5, 139.5, 140.9, 157.4, 170.6. HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{S}$: 304.1034, found 304.1034.

2ae: 88% yield from **1**, iodobenzene, and 4-iodoanisole. Stereochemistry was determined to be 95% *E*. ^1H NMR (300 MHz, CDCl_3) δ 3.81 (s, 3H), 6.85 (d, J = 8.7 Hz, 2H), 7.01 (t, J = 4.8 Hz, 1H), 7.28 (d, J = 8.7 Hz, 2H), 7.30–7.43 (m, 5H), 7.64 (s, 1H), 8.56 (d, J = 4.8 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 55.3, 113.6, 116.96, 117.02, 127.9, 128.4, 128.6, 129.7, 134.1, 139.5, 140.8, 157.4, 159.2, 170.8. HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{OS}$: 320.0983, found 320.0984.

2da: 94% yield from **1**, 4-iodotoluene, and iodobenzene. Stereochemistry was determined to be 97% *Z*. ^1H NMR (300 MHz, CDCl_3) δ 2.41 (s, 3H), 7.02 (t, J = 4.8 Hz, 1H), 7.22–7.40 (m, 9H), 7.74 (s, 1H), 8.57 (d, J = 4.8 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.3, 117.1, 118.7, 127.3, 127.4, 128.2, 129.1, 129.5, 136.3, 137.7, 140.9, 141.5, 157.4, 170.5. HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{S}$: 304.1034, found 304.1034.

2de: 89% yield from **1**, 4-iodotoluene, and 4-iodoanisole. Stereochemistry was determined to be 97% *E*. ^1H NMR (300 MHz, CDCl_3) δ 2.40 (s, 3H), 3.81 (s, 3H), 6.85 (d, J = 9.0 Hz, 2H), 7.00 (t, J = 4.8 Hz, 1H), 7.20–7.30 (m, 6H), 7.59 (s, 1H), 8.55 (d, J = 4.8 Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.3, 55.2, 113.5, 116.5, 116.9, 128.5, 129.1, 129.5, 134.2, 136.5, 137.6, 140.7, 157.3, 159.1, 170.7. HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{OS}$: 334.1140, found 334.1142.

2ea: 86% yield from **1**, 4-iodoanisole, and iodobenzene. Stereochemistry was determined to be 96% *Z*. ^1H NMR (300 MHz, CDCl_3) δ 3.86 (s, 3H), 6.95 (d, J = 8.7 Hz, 2H), 7.02 (t, J = 4.8 Hz, 1H), 7.20–7.40 (m, 7H), 7.70 (s, 1H), 8.57 (d, J = 4.8 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 55.1, 113.7, 117.0, 118.4, 127.26, 127.29, 128.1, 130.8, 131.5, 140.4, 141.5, 157.3, 159.0, 170.3. HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{OS}$: 320.0983, found 320.0983.

2ed: 86% yield from **1**, 4-iodoanisole, and 4-iodotoluene. Stereochemistry was determined to be 97% *Z*. ^1H NMR (300 MHz, CDCl_3) δ 2.35 (s, 3H), 3.85 (s, 3H), 6.94 (d, J = 9.0 Hz, 2H), 7.01 (t, J = 4.8 Hz, 1H), 7.12 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 9.0 Hz, 2H), 7.64 (s, 1H), 8.56 (d, J = 4.8 Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.1, 55.2, 113.7, 116.9, 117.4, 127.3, 128.9, 130.9, 131.7, 137.2, 138.8, 140.6, 157.3, 159.1, 170.6. HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{OS}$: 334.1140, found 334.1140.

2ef: 90% yield from **1**, 4-iodoanisole, and 1-iodonaphthalene. Stereochemistry was determined to be 97% *E*. ¹H NMR (300 MHz, CDCl₃) δ 3.80 (s, 3H), 6.86 (d, *J* = 9.0 Hz, 2H), 7.01 (t, *J* = 4.8 Hz, 1H), 7.33–7.47 (m, 4H), 7.49–7.53 (m, 3H), 7.83–7.86 (m, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 8.54 (d, *J* = 4.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 55.2, 113.6, 117.1, 119.8, 125.3, 125.6, 125.9, 126.3, 127.7, 128.0, 128.1, 130.1, 131.9, 132.5, 133.8, 139.1, 140.7, 157.4, 158.9, 170.3. HRMS (EI) *m/z* calcd for C₂₃H₁₈N₂OS₂: 370.1140, found 370.1141.

2gd: 89% yield from **1**, 3-iodothiophene, and 4-iodotoluene. Stereochemistry was determined to be 95% *Z*. ¹H NMR (300 MHz, CDCl₃) δ 2.36 (s, 3H), 7.03 (t, *J* = 4.5 Hz, 1H), 7.09 (d, *J* = 4.8 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.35 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.40 (d, *J* = 3.0 Hz, 1H), 7.64 (s, 1H), 8.57 (d, *J* = 4.5 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 21.0, 117.0, 118.3, 125.1, 125.4, 127.2, 128.6, 128.8, 135.4, 137.2, 138.5, 139.5, 157.3, 170.1. HRMS (EI) *m/z* calcd for C₁₇H₁₄N₂S₂: 310.0598, found 310.0600.

2ge: 94% yield from **1**, 3-iodothiophene, and 4-iodoanisole. Stereochemistry was determined to be 97% *Z*. ¹H NMR (300 MHz, CDCl₃) δ 3.83 (s, 3H), 6.87 (d, *J* = 9.0 Hz, 2H), 7.03 (t, *J* = 4.8 Hz, 1H), 7.09 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.32 (d, *J* = 9.0 Hz, 2H), 7.37 (dd, *J* = 4.8, 3.3 Hz, 1H), 7.40 (dd, *J* = 3.3, 1.5 Hz, 1H), 7.56 (s, 1H), 8.57 (d, *J* = 4.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 55.2, 113.5, 117.0, 117.3, 125.2, 125.5, 128.6, 128.7, 134.1, 135.4, 139.6, 157.4, 159.1, 170.4. HRMS (EI) *m/z* calcd for C₁₇H₁₄N₂OS₂: 326.0548, found 326.0543.

2gf: 92% yield from **1**, 3-iodothiophene, and 1-iodonaphthalene. Stereochemistry cannot be determined (virtually single isomer). ¹H NMR (300 MHz, CDCl₃) δ 7.03 (t, *J* = 4.8 Hz, 1H), 7.14 (dd, *J* = 5.4, 1.5 Hz, 1H), 7.26 (dd, *J* = 5.4, 3.0 Hz, 1H), 7.30–7.60 (m, 6H), 7.84–7.90 (m, 3H), 8.55 (d, *J* = 4.8 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 117.3, 120.0, 125.0, 125.1, 125.4, 125.7, 126.0, 126.2, 127.2, 128.10, 128.11, 128.2, 132.0, 133.7, 133.9, 140.5, 140.7, 157.5, 169.8. HRMS (EI) *m/z* calcd for C₂₀H₁₄N₂S₂: 346.0598, found 346.0601.

Typical Procedure for α -Lithiation/Cross-coupling of **2** (Table 2).

To a solution of **2ed** (100.4 mg, 0.30 mmol) in THF (1.0 mL) was added dropwise a solution of *t*-BuLi solution (0.66 mmol, 1.27 M, 0.5 mL) in pentane at -78 °C for 30 min under argon. The reaction mixture was gradually warmed to 0 °C and stirred for 2 h at 0 °C. To this mixture was added a solution of CuI (27.6 mg, 0.14 mmol), Pd(PPh₃)₄ (17.7 mg, 0.015 mmol), and iodobenzene (92 mg, 0.45 mmol) in THF (0.5 mL) and the resultant mixture was further stirred at 50 °C for 3 h. The reaction mixture was quenched with acetic acid (20 μ L, 0.33 mmol), and treated with a solution of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ; 74.3 mg, 0.32 mmol) in THF (1.0 mL). The mixture was stirred at room temperature for 30 min and then treated with an aqueous solution of sodium hydroxide (0.25 M, 2 mL, 0.5 mmol). Extractive work-up and subsequent silica gel chromatography (hexane/EtOAc = 5/1) afforded **3eda** (97.4 mg, 70%) as white solid.

3aae: 82% yield from **2aa** and 4-iodoanisole. ¹H NMR (400 MHz, CDCl₃) δ 1.24 (s, 9H), 3.69 (s, 3H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 5.2 Hz, 1H), 7.00–7.02 (m, 2H), 7.07–7.12 (m, 3H), 7.21–7.25 (m, 3H), 7.34–7.37 (m, 4H), 8.27 (d, *J* = 5.2 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 29.3, 37.8, 55.1, 112.0, 112.6, 126.6, 127.1, 127.5, 127.7, 129.2, 129.8, 130.7, 132.1, 133.2, 142.5, 144.1, 148.7, 156.9, 158.1, 170.9, 177.8. HRMS (EI) *m/z* calcd for C₂₉H₂₈N₂OS₂: 452.1922, found 452.1923.

3aed: 78% yield from **2ae** and 4-iodotoluene. ¹H NMR (400 MHz, CDCl₃) δ 1.23 (s, 9H), 2.20 (s, 3H), 3.72 (s, 3H), 6.60–6.63 (m, 2H), 6.84–6.86 (m, 2H), 6.90–6.92 (m, 3H), 7.21–7.25 (m, 3H), 7.33–7.35 (m, 4H), 8.26 (d, *J* = 5.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 21.7, 29.7, 38.2, 55.5, 112.4, 113.4, 127.6, 128.1, 128.4, 129.1, 129.6, 131.2, 132.4, 135.2, 136.5, 138.7, 144.7, 149.4, 157.3, 158.6, 171.6, 178.2. HRMS (EI) *m/z* calcd for C₃₀H₃₀N₂OS₂: 466.2079, found 466.2079.

3dea: 82% yield from **2de** and iodobenzene. ^1H NMR (400 MHz, CDCl_3) δ 1.24 (s, 9H), 2.34 (s, 3H), 3.73 (s, 3H), 6.61 (d, $J = 8.4$ Hz, 2H), 6.86–6.87 (m, 1H), 6.93 (d, $J = 8.4$ Hz, 2H), 7.01–7.07 (m, 5H), 7.26–7.28 (m, 2H), 7.46–7.48 (m, 2H), 8.28 (d, $J = 4.4$ Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 21.2, 29.0, 37.5, 54.8, 112.0, 112.9, 126.4, 127.2, 128.1, 128.5, 129.5, 130.9, 132.1, 134.7, 137.0, 141.36, 141.38, 149.7, 157.0, 158.3, 171.2, 177.9. HRMS (EI) m/z calcd for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{OS}_2$: 466.2079, found 466.2079.

3eda: 70% yield from **2ed** and iodobenzene. ^1H NMR (400 MHz, CDCl_3) δ 1.30 (s, 9H), 2.25 (s, 3H), 3.79 (s, 3H), 6.77–6.79 (m, 5H), 6.87–6.89 (m, 5H), 7.30 (dd, $J = 1.6$ Hz, 6.8 Hz, 2H), 7.42–7.47 (m, 2H), 8.29 (d, $J = 5.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.7, 29.6, 38.2, 55.5, 112.4, 113.5, 126.7, 127.5, 128.5, 128.8, 131.0, 131.1, 131.3, 136.9, 137.0, 140.0, 141.7, 150.1, 157.3, 159.1, 171.5, 178.2. HRMS (EI) m/z calcd for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{OS}_2$: 466.2079, found 466.2079.

3edf: 65% yield from **2ed** and 1-iodonaphthalene. ^1H NMR (400 MHz, CDCl_3) δ 1.27 (s, 9H), 2.11 (s, 3H), 3.80 (s, 3H), 6.70 (d, $J = 5.8$ Hz, 2H), 6.79–6.86 (m, 5H), 7.18–7.23 (m, 1H), 7.38–7.44 (m, 1H), 7.44–7.48 (m, 3H), 7.60–7.65 (m, 2H), 7.72 (d, $J = 8.0$ Hz, 1H), 8.24 (d, $J = 5.2$ Hz, 1H), 8.48 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 20.9, 29.1, 37.5, 55.0, 112.2, 113.0, 124.7, 125.2, 125.6, 126.1, 126.6, 127.5, 128.0 (2C), 129.1, 129.4, 130.9, 131.8, 133.3, 135.7, 136.5, 138.7, 139.5, 152.6, 157.0, 158.9, 171.5, 177.9. HRMS (EI) m/z calcd for $\text{C}_{34}\text{H}_{32}\text{N}_2\text{OS}_2$: 516.2235, found 516.2236.

3ffd: 55% yield from **2ff** and 4-iodotoluene. It was found that two isomeric forms (nearly 1:1 ratio) are distinguishable at room temperature for this compound (CDCl_3 solution). Considering the severe steric demand of two naphthyl groups, we assume these to be the rotamers as depicted below.

^1H NMR (400 MHz, CDCl_3) δ 1.198 (s, 9H), 1.200 (s, 9H), 2.01 (s, 3H), 2.09 (s, 3H), 6.64 (d, $J = 8.0$ Hz, 2H), 6.69 (d, $J = 8.0$ Hz, 2H), 6.81 (d, $J = 4.8$ Hz, 1H), 6.84 (d, $J = 4.8$ Hz, 1H), 7.20–7.47 (m, 20H), 7.63–7.74 (m, 6H), 7.82 (t, $J = 7.2$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 1H), 8.21–8.24 (m, 2H), 8.31 (d, $J = 8.0$ Hz, 1H), 8.80 (d, $J = 8.4$ Hz, 1H), 8.87 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 20.88, 20.94, 37.6, 112.07, 112.11, 125.0, 125.2, 125.32, 125.35, 125.4, 125.6, 125.76, 125.89, 125.99, 126.08, 126.13, 126.5, 127.28, 127.34, 127.5, 127.6, 127.7, 127.88, 127.92, 128.3, 128.6, 129.5, 129.7, 129.9, 130.5, 130.9, 132.3, 133.7, 133.9, 136.1, 136.5, 136.6, 136.7, 137.1, 137.8, 140.5, 140.8, 140.9, 141.3, 142.0, 144.3, 156.9, 157.0, 170.5, 171.1, 177.9. HRMS (EI) m/z calcd for $\text{C}_{37}\text{H}_{32}\text{N}_2\text{S}$: 536.2286, found: 536.2281.

Typical Procedure for the Synthesis of Tetrasubstituted Olefins 4 (Table 3, Runs 1–9).

To a solution of 4-fluorophenylmagnesium bromide (0.3 mmol, 1.0 M, 0.30 mL) were added **3eda** (34.5 mg, 0.074 mmol), Pd₂(dba)₃ (2.3 mg, 0.025 mmol), and dry toluene (1.5 mL) at room temperature under argon, and the mixture was stirred at 90 °C for 20 h. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short gel pad (EtOAc). The filtrate was evaporated, and the residue was chromatographed (hexane/EtOAc = 50/1), and purified by gel permeation chromatography to afford **4edai** (42%).

4aaea:² 72% yield from **3aae** and phenylmagnesium bromide. ¹H NMR (400 MHz, CDCl₃) δ 3.73 (s, 3H), 6.62 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.00–7.10 (m, 15H).

4aaeh: 46% yield from **3aae** and 2-naphthylmagnesium bromide. ¹H NMR (400 MHz, CDCl₃) δ 3.75 (s, 3H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.04–7.17 (m, 11H), 7.34–7.41 (m, 2H), 7.49–7.59 (m, 3H), 7.70–7.72 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 55.1, 113.0, 125.6 (two carbons), 126.27, 126.32, 126.8, 127.4, 127.7 (two carbons), 127.9, 129.6, 130.5, 131.37, 131.41, 132.0, 132.7, 133.1, 136.2, 140.3, 140.6, 141.6, 143.8, 144.1, 158.1. HRMS (EI) *m/z* calcd for C₃₁H₂₄O: 412.1827, found 412.1828.

4aedd: 40% yield from **3aed** and *p*-tolylmagnesium bromide. ¹H NMR (400 MHz, CDCl₃) δ 2.24 (s, 3H), 2.26 (s, 3H), 3.73 (s, 3H), 6.62 (d, *J* = 8.4 Hz, 2H), 6.87–6.92 (m, 10H), 7.00–7.02 (m, 3H), 7.06–7.08 (m, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 21.16, 21.17, 55.1, 113.0, 126.1, 127.5, 128.3, 128.4, 131.21, 131.24, 131.4, 132.5, 135.7, 136.5, 139.5, 139.9, 141.1, 141.2, 144.4, 157.9. HRMS (EI) *m/z* calcd for C₂₉H₂₆O: 390.1984, found 390.1984.

4dea: 52% yield from **3dea** and 4-fluorophenylmagnesium bromide. ^1H NMR (400 MHz, CDCl_3) δ 2.26 (s, 3H), 3.72 (s, 3H), 6.61 (d, $J = 8.0$ Hz, 2H), 6.77 (dd, $J = 8.4, 8.0$ Hz, 2H), 6.87–7.01 (m, 9H), 7.02–7.10 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.2, 55.5, 113.0, 114.5 (d, $J_{\text{C-F}} = 21.4$ Hz), 126.2, 127.7, 128.4, 131.2, 131.3, 132.5, 132.8 (d, $J_{\text{C-F}} = 7.1$ Hz), 136.1 (d, $J_{\text{C-F}} = 3.1$ Hz), 138.4, 140.07, 140.10, 140.64, 140.79, 144.0, 158.0, 161.2 (d, $J_{\text{C-F}} = 244.1$ Hz). HRMS (EI) m/z calcd for $\text{C}_{28}\text{H}_{23}\text{FO}$: 394.1733, found 394.1732.

4eda: 42% yield from **3eda** and 4-fluorophenylmagnesium bromide. ^1H NMR (400 MHz, CDCl_3) δ 2.24 (s, 3H), 3.74 (s, 3H), 6.62–6.64 (m, 2H), 6.76–6.80 (m, 2H), 6.88–6.91 (m, 6H), 6.95–7.00 (m, 4H), 7.07–7.09 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.2, 55.5, 113.1, 114.6 (d, $J_{\text{C-F}} = 21.3$ Hz), 126.2, 127.7, 128.3, 131.2, 131.3, 132.5, 132.9 (d, $J_{\text{C-F}} = 7.9$ Hz), 136.06, 136.11, 138.4, 140.1 (d, $J_{\text{C-F}} = 3.1$ Hz), 140.65, 140.75, 158.1, 161.2 (d, $J_{\text{C-F}} = 244.1$ Hz). HRMS (EI) m/z calcd for $\text{C}_{28}\text{H}_{23}\text{FO}$: 394.1733, found 394.1733.

4edfa: 22% yield from **3edf** and phenylmagnesium bromide. ^1H NMR (400 MHz, CDCl_3) δ 2.10 (s, 3H), 3.76 (s, 3H), 6.67–6.71 (m, 4H), 6.81 (d, $J = 8.0$ Hz, 2H), 6.99–7.06 (m, 7H), 7.23–7.36 (m, 4H), 7.63–7.65 (m, 1H), 7.72–7.74 (m, 1H), 7.99–8.02 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 21.0, 55.1, 113.1, 125.27, 125.29, 125.8, 126.0, 126.4, 127.0, 127.7, 128.0, 128.2, 129.3, 129.9, 130.4, 132.4, 132.6, 133.7, 135.8, 135.9, 137.9, 141.0, 141.6, 142.5, 143.4, 158.2. HRMS (EI) m/z calcd for $\text{C}_{32}\text{H}_{26}\text{O}$: 426.1984, found 426.1984.

4edfh: 14% yield from **3edf** and 2-naphthylmagnesium bromide. ^1H NMR (400 MHz, CDCl_3) δ 2.13 (s, 3H), 3.75 (s, 3H), 6.66–6.73 (m, 4H), 6.45 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H), 7.24–7.36 (m, 7H), 7.43 (s, 1H), 7.47–7.51 (m, 2H), 7.65–7.70 (m, 2H), 7.76 (d, $J = 8.0$ Hz, 1H), 8.02 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 21.0, 55.1, 113.2, 125.29, 125.33, 125.5, 125.8, 126.4, 126.9, 127.1, 127.4, 128.00, 128.04, 128.2, 129.0, 129.2, 129.5, 130.0, 131.3, 131.9, 132.5, 132.8, 133.2, 133.7, 135.7, 136.0, 137.7, 141.1, 141.2, 141.7, 143.1, 158.3. HRMS (EI) m/z calcd for $\text{C}_{36}\text{H}_{28}\text{O}$: 476.2140, found 476.2141.

4edfj: 21% yield from **3edf** and 2-thienylmagnesium bromide. ^1H NMR (400 MHz, CDCl_3) δ 2.10 (s, 3H), 3.85 (s, 3H), 6.38–6.41 (m, 1H), 6.65–6.68 (m, 3H), 6.77–6.82 (m, 3H), 6.87–6.89 (m, 2H), 6.99–7.04 (m, 1H), 7.35–7.42 (m, 6H), 7.69–7.71 (m, 1H), 7.78–7.79 (m, 1H), 7.98–8.00 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 21.0, 55.2, 112.7, 113.9, 123.4, 125.7, 126.0, 126.2, 127.5, 128.0, 128.3, 129.2, 130.8, 131.5, 132.1, 132.8, 133.6, 135.5, 135.9, 140.3, 140.8, 141.9, 146.4, 159.0. HRMS (EI) m/z calcd for $\text{C}_{30}\text{H}_{24}\text{OS}$: 432.1548, found 432.1544.

4ffda: 31% yield from **3ffd** and phenylmagnesium bromide. It was found that two isomeric forms (nearly 3:2 ratio) are distinguishable at room temperature for this compound (CDCl_3 solution). Considering the severe steric demand of two naphthyl groups, we assume these to be the rotamers as depicted below.

^1H NMR (400 MHz, CDCl_3) δ 2.11 (s, 3H for minor isomer), 2.14 (s, 3H for major isomer), 6.70–6.76 (m, 2H for both isomers), 6.85–6.95 (m, 4H for both isomers), 6.96–7.05 (m, 2H for both isomers), 7.06–7.45 (m, 9H for both isomers), 7.59–7.75 (m, 4H for both isomers), 8.16 (dd, $J = 7.6, 4.0$ Hz, 2H for major isomer), 8.40 (t, $J = 6.8$ Hz, 2H for minor isomer). ^{13}C NMR (150 MHz, CDCl_3) δ 21.0, 125.08, 125.15, 125.20, 125.28, 125.30, 125.6, 125.7, 125.8, 126.0, 126.1, 126.2, 126.5, 127.0, 127.15, 127.27, 127.33, 127.38, 128.01, 128.05, 128.1, 126.26, 128.27, 128.30, 128.4, 129.2, 130.3, 130.4, 130.6, 131.4, 131.6, 133.67, 133.68, 133.74, 134.2, 136.1, 136.2, 137.0, 140.0, 140.6, 141.4, 141.5, 141.9, 143.2, 143.4, 143.8, 145.0, 145.3. HRMS (EI) m/z calcd for $\text{C}_{35}\text{H}_{26}$: 446.2034, found: 446.2034.

Typical Procedure for the Synthesis of Trisubstituted Olefins 5 (Table 3, Runs 10–23).

To a solution of *p*-tolylmagnesium bromide (1.50 mmol, 1.5 M, 1.0 mL) in toluene (prepared by removal of THF under reduced pressure from a commercially available THF solution and subsequent addition of dry toluene) were added **2ae** (160.2 mg, 0.50 mmol), Pd[P(*t*-Bu)₃]₂ (12.8 mg, 0.025 mmol), and dry toluene (1.0 mL) at room temperature under argon, and the mixture was stirred at 60 °C for 15 h. After cooling the reaction mixture to room temperature, water (ca. 5 mL) was added to the mixture. Extractive work-up and subsequent silica gel chromatography (hexane/EtOAc = 50/1) afforded **5aed** (105.2 mg, 69%) as white solid.

5abe: 58% yield from **2ab** and 4-methoxyphenylmagnesium bromide. ¹H NMR (300 MHz, CDCl₃) δ 2.11 (s, 3H), 3.77 (s, 3H), 6.55 (s, 1H), 6.69 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 7.14–7.29 (m, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 20.5, 55.1, 113.4, 125.6, 127.2, 128.2, 128.3, 129.6, 129.87, 129.89, 130.2, 130.4, 130.6, 136.3, 140.5, 141.2, 158.4. HRMS (EI) *m/z* calcd for C₂₂H₂₀O: 300.1514, found 300.1515.

5ddb: 62% yield from **2dd** and *o*-tolylmagnesium bromide. ¹H NMR (300 MHz, CDCl₃) δ 2.31 (s, 6H), 2.37 (s, 3H), 6.52–6.88 (m, 3H), 6.95–7.06 (m, 4H), 7.11–7.15 (m, 3H), 7.23–7.26 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 20.2, 21.1, 21.2, 125.2, 126.1, 126.5, 128.0, 128.7, 128.8, 129.7, 130.6, 136.7, 136.9, 137.3, 141.0, 143.1. HRMS (EI) *m/z* calcd for C₂₃H₂₂: 298.1721, found 298.1720.

5cch: 66% yield from **2cc** and 2-naphthylmagnesium bromide. ¹H NMR (300 MHz, CDCl₃) δ 2.30 (s, 3H), 2.36 (s, 3H), 7.00–7.25 (m, 10H), 7.35–7.42 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.56–7.74 (m, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 21.4, 21.5, 124.9, 125.7, 125.8, 127.0, 127.1, 127.4, 127.6, 127.92, 127.94, 128.1, 128.21, 128.26, 128.31, 128.5, 129.1, 130.9, 132.2, 133.3, 135.2, 137.7, 138.2, 140.3, 143.1, 143.5. HRMS (EI) *m/z* calcd for C₂₆H₂₂: 334.1721, found 334.1721.

5eei: 85% yield from **2ee** and 4-fluorophenylmagnesium bromide. ^1H NMR (300 MHz, CDCl_3) δ 3.82 (s, 3H), 3.84 (s, 3H), 6.78–6.87 (m, 7H), 6.97–7.02 (m, 2H), 7.08–7.11 (m, 2H), 7.23–7.26 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 55.2, 55.3, 113.5, 114.0, 114.8 (d, $J_{\text{C-F}} = 21.1$ Hz), 124.9, 128.8, 130.9 (d, $J_{\text{C-F}} = 7.5$ Hz), 131.5, 132.4, 133.9 (d, $J_{\text{C-F}} = 3.6$ Hz), 136.2, 141.5, 158.9, 159.2, 161.1 (d, $J_{\text{C-F}} = 246.4$ Hz). HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{19}\text{FO}_2$: 334.1369, found 334.1368.

5ffd: 67% yield from **2ff** and *p*-tolylmagnesium bromide. The reaction was performed at 90 °C. ^1H NMR (300 MHz, CDCl_3) δ 2.20 (s, 3H), 6.83 (s, 3H), 7.08 (s, 1H), 7.24–7.33 (m, 3H), 7.36–7.52 (m, 6H), 7.72–7.75 (m, 1H), 7.81–8.01 (m, 3H), 8.02 (d, $J = 8.4$ Hz, 1H), 8.60–8.70 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.1, 125.1, 125.6, 125.77, 125.80, 125.9, 126.0, 126.1, 126.2, 126.3, 127.5, 127.8, 127.9, 128.3, 128.6, 128.7, 129.0, 131.4, 131.5, 134.1, 134.4, 134.85, 134.87, 136.8, 137.3, 139.5, 142.1. HRMS (EI) m/z calcd for $\text{C}_{29}\text{H}_{22}$: 370.1721, found 370.1724.

5gdk: 63% yield from **2gd** and 9-phenanthrylmagnesium bromide. Stereochemistry was determined to be 94% *Z* (starting from 95% *Z* of **2gd**). ^1H NMR (300 MHz, CDCl_3) δ 2.43 (s, 3H), 6.75 (dd, $J = 4.8, 1.2$ Hz, 1H), 6.97 (dd, $J = 3.0, 1.2$ Hz, 1H), 7.03 (dd, $J = 4.8, 3.0$ Hz, 1H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.30 (s, 1H), 7.40–7.70 (m, 8H), 8.19 (dd, $J = 8.1, 1.2$ Hz, 1H), 8.66 (d, $J = 8.1$ Hz, 1H), 8.73 (d, $J = 8.1$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.2, 122.4, 122.9, 124.5, 125.3, 125.5, 125.9, 126.37, 126.45, 126.52, 126.57, 127.7, 128.0, 128.6, 129.5, 129.7, 130.3, 131.4, 131.6, 134.1, 134.1, 137.7, 139.5, 140.35, 140.39. HRMS (EI) m/z calcd for $\text{C}_{27}\text{H}_{20}\text{S}$: 376.1286, found 376.1287.

5gel: 52% yield from **2ge** and 3,4-(methylenedioxy)phenylmagnesium bromide. Stereochemistry was determined to be 93% *Z* (starting from 97% *Z* of **2ge**). ^1H NMR (300 MHz, CDCl_3) δ 3.82 (s, 3H), 5.90 (s, 2H), 6.45 (s, 1H), 6.66 (s, 2H), 6.77–6.90 (m, 4H), 7.06–7.07 (m, 1H), 7.25–7.28 (m, 2H), 7.31–7.34 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 55.3, 100.8, 107.9, 108.7, 113.5, 123.7, 124.6, 125.6, 126.8, 128.4, 129.4, 131.9, 135.3, 135.7, 140.5, 146.2, 147.2, 159.2. HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{O}_3\text{S}$: 336.0820, found 336.0820.

5gfm: 58% yield from **2gf** and 3-methoxyphenylmagnesium bromide. Stereochemistry was determined to be 95% *Z*. ^1H NMR (300 MHz, CDCl_3) δ 3.70 (s, 3H), 6.73 (s, 1H), 6.80 (dm, $J = 8.4$ Hz, 1H), 6.85 (s, 1H), 6.89–6.95 (m, 2H), 7.15–7.24 (m, 2H), 7.30–7.50 (m, 5H), 7.80–7.90 (m, 2H), 7.97 (dm, $J = 8.7$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 55.0, 113.4, 113.8, 121.9, 124.8, 125.0, 125.3, 125.6, 125.9, 126.0, 126.9, 127.9, 128.2, 128.7, 129.2, 131.0, 131.8, 133.9, 136.4, 138.8, 141.3, 141.8, 159.3. HRMS (EI) m/z calcd for $\text{C}_{23}\text{H}_{18}\text{OS}$: 342.1078, found 342.1078.

5ade: 76% yield from **2ad** and 4-methoxyphenylmagnesium bromide. Stereochemistry was determined to be 94% *E* (starting from 96% *E* of **2ad**). ^1H NMR (300 MHz, CDCl_3) δ 2.35 (s, 3H), 3.75 (s, 3H), 6.67 (d, $J = 8.7$ Hz, 2H), 6.89 (s, 1H), 6.94 (d, $J = 8.7$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 7.15–7.25 (m, 5H), 7.30–7.40 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.1, 55.1, 113.3, 126.8, 127.2, 127.3, 128.6, 128.9, 130.1, 130.4, 130.7, 137.0, 140.4, 140.74, 140.75, 158.2. HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}$: 300.1514, found 300.1514.

5aed: 69% yield from **2ae** and *p*-tolylmagnesium bromide. Stereochemistry was determined to be 93% *E* (starting from 95% *E* of **2ae**). ^1H NMR (300 MHz, CDCl_3) δ 2.26 (s, 3H), 3.81 (s, 3H), 6.80–7.00 (m, 7H), 7.20–7.40 (m, 7H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.1, 55.2, 113.5, 126.4, 127.2, 128.57, 128.61, 128.63, 129.3, 130.3, 134.7, 136.1, 136.2, 140.7, 141.1, 159.0. HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}$: 300.1514, found 300.1514.

5dae: 62% yield from **2da** and 4-methoxyphenylmagnesium bromide. Stereochemistry was determined to be 96% *Z* (starting from 97% *Z* of **2da**). ^1H NMR (300 MHz, CDCl_3) δ 2.39 (s, 3H), 3.76 (s, 3H), 6.68 (d, $J = 8.4$ Hz, 2H), 6.88 (s, 1H), 6.98 (d, $J = 9.0$ Hz, 2H), 7.05–7.20 (m, 4H), 7.20–7.35 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.3, 55.1, 113.3, 127.1, 127.40, 127.41, 128.1, 129.4, 130.19, 130.23, 130.7, 136.9, 137.5, 140.5, 143.8, 158.2. HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}$: 300.1514, found 300.1513.

5dea: 73% yield from **2de** and phenylmagnesium bromide. Stereochemistry was determined to be 95% *E* (starting from 97% *E* of **2de**). ¹H NMR (300 MHz, CDCl₃) δ 2.38 (s, 3H), 3.82 (s, 3H), 6.80–6.90 (m, 3H), 7.00–7.20 (m, 7H), 7.25–7.30 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 21.3, 55.2, 113.5, 126.25, 126.32, 127.9, 128.8, 129.3, 129.4, 130.2, 136.3, 137.0, 137.4, 137.7, 142.1, 159.1. HRMS (EI) *m/z* calcd for C₂₂H₂₀O: 300.1514, found 300.1515.

5ead: 76% yield from **2ea** and *p*-tolylmagnesium bromide. Stereochemistry was determined to be 94% *Z* (starting from 96% *Z* of **2ea**). ¹H NMR (300 MHz, CDCl₃) δ 2.27 (s, 3H), 3.84 (s, 3H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.88 (s, 1H), 6.96 (s, 4H), 7.13 (d, *J* = 8.7 Hz, 2H), 7.25–7.35 (m, 5H). ¹³C NMR (125 MHz, CDCl₃) δ 21.2, 55.2, 114.0, 127.3, 127.6, 127.8, 128.1, 128.7, 129.4, 131.6, 132.7, 134.7, 136.4, 141.3, 143.9, 158.8. HRMS (EI) *m/z* calcd for C₂₂H₂₀O: 300.1514, found 300.1512.

5eda: 81% yield from **2ed** and phenylmagnesium bromide. Stereochemistry was determined to be 96% *Z* (starting from 97% *Z* of **2ed**). ¹H NMR (300 MHz, CDCl₃) δ 2.36 (s, 3H), 3.83 (s, 3H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.87 (s, 1H), 7.00–7.20 (m, 8H), 7.20–7.30 (m, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 21.1, 55.1, 113.9, 126.4, 127.0, 127.6, 127.9, 128.8, 129.4, 131.6, 132.6, 137.3, 137.7, 141.0, 142.1, 158.8. HRMS (EI) *m/z* calcd for C₂₂H₂₀O: 300.1514, found 300.1518.

X-ray Crystal Structure Analysis of 5gel. A colorless platelet crystal of **5gel** (C₂₀H₁₆O₃S) having approximate dimensions of 0.10 × 0.10 × 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-K α radiation. Indexing was performed from 2 stills which were exposed for 3 seconds. The crystal-to-detector distance was 127.40 mm. Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions: $a = 9.8578(2)$ Å, $b = 8.8632(2)$ Å, $c = 19.536(2)$ Å, $\beta = 90.691(3)^\circ$, $V = 1706.8(1)$ Å³. For $Z = 4$ and $F.W. = 336.40$, the calculated density is 1.31 g/cm³. The systematic absences of $[h0l: h \pm 2n, 0k0: k \pm 2n]$ uniquely determine the space group to be P21/a (No. 14).

The data were collected at a temperature of 23 ± 1 °C to a maximum 2θ value of 55.0° . A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at $\chi = 45.0^\circ$ and $\phi = 0.0^\circ$. The exposure rate was 2.0 [sec./°]. The detector at the zero swing position. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at $\chi = 45.0^\circ$ and $\phi = 180.0^\circ$. The exposure rate was 2.0 [sec./°]. The detector at the zero swing position. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. Of the 10494 reflections which were collected, 3674 were unique ($R_{int} = 0.129$); equivalent reflections were merged. The linear absorption coefficient, μ , for Mo-K α radiation is 2.0 cm⁻¹, was applied which resulted in transmission factors ranging from 0.83 to 1.21. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 198.110001).

The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement on F was based on 1025 observed reflections ($I > 3.00\sigma(I)$) and 234 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.115$ ($R_w = 0.131$). All calculations were performed using the CrystalStructure crystallographic software package. The ORTEP drawing of **5gel** is shown below. Thermal ellipsoids are drawn at 50% probability level and hydrogen atoms are omitted for clarity.

^{13}C -NMR (75 MHz, CDCl_3)

^{13}C -NMR (125 MHz, CDCl_3)

^{13}C -NMR (125 MHz, CDCl_3)

^{13}C -NMR (75 MHz, CDCl_3)

^{13}C -NMR (75 MHz, CDCl_3)

^{13}C -NMR (125 MHz, CDCl_3)

^{13}C -NMR (125 MHz, CDCl_3)

^{13}C -NMR (125 MHz, CDCl_3)

^{13}C -NMR (75 MHz, CDCl_3)

^{13}C -NMR (75 MHz, CDCl_3)

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3)

^{13}C -NMR (75 MHz, CDCl_3)

^{13}C -NMR (75 MHz, CDCl_3)

^{13}C -NMR (125 MHz, CDCl_3)

¹³C NMR (125 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

¹³C NMR (150 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

13C NMR (150 MHz, CDCl3)

¹³C NMR (150 MHz, CDCl₃)

¹³C NMR (150 MHz, CDCl₃)

13C NMR (150 MHz, CDCl3)

¹³C NMR (125 MHz, CDCl₃)

¹³C NMR (125 MHz, CDCl₃)

13c-mms0-77.4
single pulse decoupled gated NOE

¹³C NMR (150 MHz, CDCl₃)

^{13}C NMR (150 MHz, CDCl_3)

¹³C NMR (150 MHz, CDCl₃)

¹³C NMR (125 MHz, CDCl₃)

¹³C NMR (75 MHz, CDCl₃)

5cch

^{13}C -NMR (125 MHz, CDCl_3)

^{13}C -NMR (125 MHz, CDCl_3)

^{13}C -NMR (125 MHz, CDCl_3)

^{13}C -NMR (75 MHz, CDCl_3)

^{13}C -NMR (125 MHz, CDCl_3)

^{13}C -NMR (125 MHz, CDCl_3)