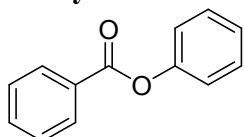


Typical reaction procedure for alkoxyacylation carbonylation reactions:

Pd(OAc)₂ (3 mol %) and Xantphos (3 mol %) were transferred into an oven-dried tube which was filled with nitrogen. Toluene (2.0 mL), aryl halides (1.0 mmol), phenols (2.0 mmol) were added to the reaction tube. Then a mixture of formic acid (2.0 mmol) and acetic anhydride (2.0 mmol), which was stirred for 1.5 h at 30 °C, added dropwise to the reaction tube. After that, was added Et₃N (5.0 mmol). The mixture was stirred for 12 h at 80 °C. After the reaction was complete, the reaction mixture was filtered and concentrated, column chromatography on silica gel (petroleum ether/ethyl acetate 50:1).

Phenyl benzoate

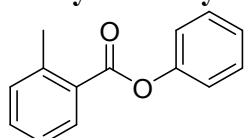


¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 165.10, 150.89, 133.51, 130.09, 129.50, 129.42, 128.50, 125.81, 121.65.

GC-MS (EI, 70 eV): *m/z*(%)=198.0 ([M]⁺, 6), 198.0 (11), 105.0 (100), 77.0 (42), 51.0 (10).

Phenyl 2-methylbenzoate

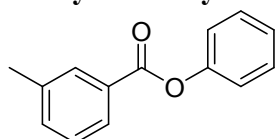


¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.36 – 7.27 (m, 3H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.70 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.74, 150.87, 141.22, 132.64, 131.89, 131.09, 129.41, 128.50, 125.85, 125.74, 121.76, 21.88.

GC-MS (EI, 70 eV): *m/z*(%)=212.0 ([M]⁺, 5), 119.0 (100), 91.0 (48), 65.0 (20).

Phenyl 3-methylbenzoate

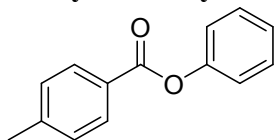


^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.1$ Hz, 2H), 7.31 (dd, $J = 15.4, 7.7$ Hz, 4H), 7.15 (dd, $J = 12.7, 5.3$ Hz, 1H), 7.11 (d, $J = 8.2$ Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.24, 150.94, 138.31, 134.26, 130.58, 129.42, 129.39, 128.38, 127.24, 125.75, 121.65, 21.19.

GC-MS (EI, 70 eV): $m/z(\%)=212.0$ ($[\text{M}]^+$, 7), 212.0 (11), 119.1 (100), 91.1 (43), 65.0 (15).

Phenyl 4-methylbenzoate

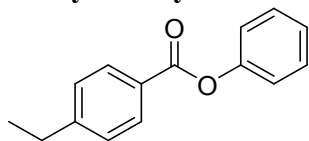


^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 7.9$ Hz, 2H), 7.29 (d, $J = 7.6$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.2$ Hz, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.12, 150.95, 144.29, 130.11, 129.35, 129.19, 126.74, 125.68, 121.68, 21.63.

GC-MS (EI, 70 eV): $m/z(\%)=212.0$ ($[\text{M}]^+$, 6), 212.0 (15), 119.1 (100), 91.1 (79), 65.0 (39).

Phenyl 4-ethylbenzoate

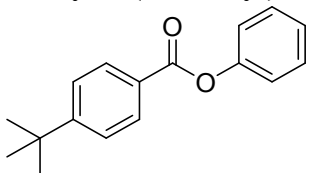


^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.1$ Hz, 2H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 7.4$ Hz, 1H), 7.22 (d, $J = 7.8$ Hz, 2H), 2.75 (q, $J = 7.6$ Hz, 2H), 1.29 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.17, 150.98, 150.52, 130.27, 129.39, 128.05, 126.96, 125.72, 121.71, 28.98, 15.19.

GC-MS (EI, 70 eV): $m/z(\%)=226.0$ ($[\text{M}]^+$, 7), 226.0 (11), 133.0 (100), 105.0 (34), 77.0 (30).

Phenyl 4-(*tert*-butyl)benzoate

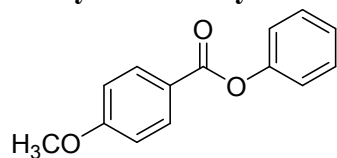


^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.1$ Hz, 2H), 7.40 (d, $J = 8.3$ Hz, 2H), 7.29 (t, $J = 7.7$ Hz, 2H), 7.14 (d, $J = 7.5$ Hz, 1H), 7.09 (d, $J = 8.4$ Hz, 2H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.04, 157.25, 150.96, 130.00, 129.35, 126.70, 125.67, 125.47, 121.69, 35.07, 31.02.

GC-MS (EI, 70 eV): $m/z(\%)=254.0$ ($[\text{M}]^+$, 5), 161.1 (100), 146.0 (33), 118.0 (30), 91.0 (28).

Phenyl 4-methoxybenzoate

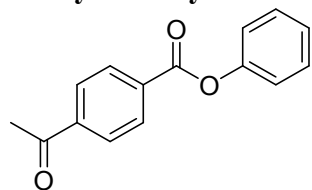


^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.7$ Hz, 2H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.24 (dd, $J = 12.5, 5.4$ Hz, 1H), 7.19 (d, $J = 8.1$ Hz, 2H), 6.96 (d, $J = 8.8$ Hz, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 164.82, 163.82, 151.01, 132.20, 129.35, 125.63, 121.80, 121.73, 113.76, 55.41.

GC-MS (EI, 70 eV): $m/z(\%)=228.0$ ($[\text{M}]^+$, 8), 135.0 (100), 107.0 (20), 92.0 (32), 77.0 (36).

Phenyl 4-acetylbenzoate

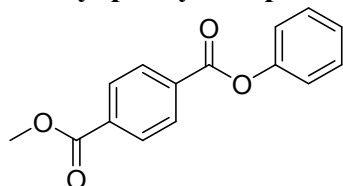


^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 8.2$ Hz, 2H), 8.05 (d, $J = 8.2$ Hz, 2H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.26 (dd, $J = 13.6, 6.1$ Hz, 1H), 7.21 (d, $J = 8.1$ Hz, 2H), 2.65 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 197.43, 164.29, 150.69, 140.66, 133.29, 130.38, 129.55, 128.32, 126.12, 121.53, 26.90.

GC-MS (EI, 70 eV): $m/z(\%)=240.0$ ($[\text{M}]^+$, 9), 240.0 (11), 147.0 (100), 119.0 (12), 91.0 (12).

Methyl phenyl terephthalate

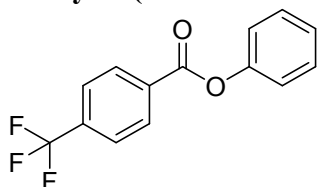


^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 8.3$ Hz, 2H), 8.17 (d, $J = 8.3$ Hz, 2H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.31 – 7.21 (m, 3H), 3.96 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.11, 164.32, 150.71, 134.42, 133.30, 130.07, 129.66, 129.52, 126.07, 121.52, 52.46.

GC-MS (EI, 70 eV): $m/z(\%)=256.0$ ($[\text{M}]^+$, 9), 256.0 (10), 163.0 (100), 135.0 (11).

Phenyl 4-(trifluoromethyl)benzoate

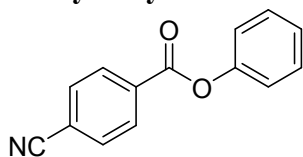


^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, $J = 8.2$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.29 (s, 1H), 7.22 (d, $J = 7.9$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 164.01, 150.74, 135.03 (q, $J = 32.33$ Hz), 132.89, 130.58, 129.63, 126.25, 125.63 (q, $J = 3.68$ Hz), 123.62 (q, $J = 273.60$ Hz), 121.57.

GC-MS (EI, 70 eV): $m/z(\%)=266.0$ ($[\text{M}]^+$, 9), 266.0 (29), 247.0 (10), 174.0 (21), 173.0 (100), 145.0 (83).

Phenyl 4-cyanobenzoate

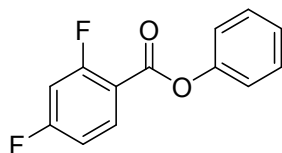


^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 8.2$ Hz, 2H), 7.81 (d, $J = 8.2$ Hz, 2H), 7.45 (t, $J = 7.8$ Hz, 2H), 7.30 (t, $J = 7.4$ Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.55, 150.51, 133.40, 132.36, 130.60, 129.63, 126.33, 121.40, 117.82, 116.97.

GC-MS (EI, 70 eV): $m/z(\%)=223.0$ ($[\text{M}]^+$, 6), 233.0 (33), 130.0 (100), 102.0 (51).

Phenyl 2,4-difluorobenzoate

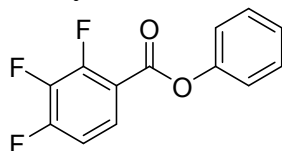


^1H NMR (400 MHz, CDCl_3) δ 8.12 (dd, $J = 15.4, 8.1$ Hz, 1H), 7.41 (t, $J = 7.8$ Hz, 2H), 7.26 (t, $J = 7.4$ Hz, 1H), 7.21 (d, $J = 7.9$ Hz, 2H), 7.03 – 6.88 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.49 (d, $J = 12.60$ Hz), 164.76 (dd, $J = 12.44, 33.01$ Hz), 162.00 (bdd), 150.55, 134.44 (dd, $J = 1.84, 10.66$ Hz), 129.56, 126.16, 121.67, 114.64 (dd, $J = 3.65, 9.53$ Hz), 111.87 (dd, $J = 4.05, 21.63$ Hz), 105.52 (t, $J = 25.71$).

GC-MS (EI, 70 eV): $m/z(\%)=234.0$ ($[M]^+$, 5), 234.0 (44), 141.1 (100), 113.0 (68), 63.0 (30).

Phenyl 2,3,4-trifluorobenzoate

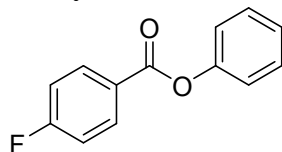


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 – 7.84 (m, 1H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.22 (t, $J = 6.6$ Hz, 2H), 7.09 (q, $J = 7.4$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.28 (bs), 155.80 (m), 153.37 (m), 150.77 (m), 150.38, 129.61, 126.79 (m), 126.33, 121.49, 115.85 (m), 112.347 (dd, $J = 4.05, 18.01$ Hz).

GC-MS (EI, 70 eV): $m/z(\%)=252.0$ ($[M]^+$, 7), 252.0 (26), 159.0 (100), 131.0 (41), 81.0 (20).

Phenyl 4-fluorobenzoate

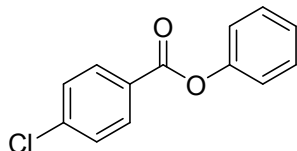


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.12 (dd, $J = 8.5, 5.7$ Hz, 2H), 7.32 (t, $J = 7.8$ Hz, 2H), 7.16 (dd, $J = 13.7, 6.3$ Hz, 1H), 7.14 – 7.08 (m, 3H), 7.06 (d, $J = 8.5$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.21 (d, $J = 255.78$ Hz), 164.80, 164.12, 150.77, 132.83 (d, $J = 9.56$ Hz), 129.45, 125.91, 121.59, 115.82 (d, $J = 22.11$ Hz).

GC-MS (EI, 70 eV): $m/z(\%)=216.0$ ($[M]^+$, 8), 216.0 (46), 123.0 (100), 95.0 (79), 75.0 (34).

Phenyl 4-chlorobenzoate

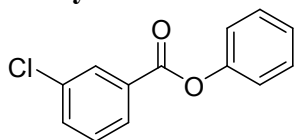


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.18 – 8.10 (m, 2H), 7.48 (t, $J = 7.1$ Hz, 2H), 7.46 – 7.39 (m, 2H), 7.33 – 7.27 (m, 1H), 7.24 – 7.17 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.33, 150.75, 140.11, 131.53, 129.53, 128.93, 128.01, 126.03, 121.59.

GC-MS (EI, 70 eV): $m/z(\%)=232.0$ ($[M]^+$, 7), 232.0 (14), 141.0 (65), 139.0 (100), 111.0 (50), 75.0 (15).

Phenyl 3-chlorobenzoate

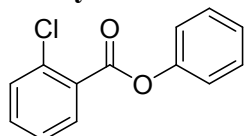


^1H NMR (400 MHz, CDCl_3) δ 8.10 – 8.05 (m, 1H), 8.00 – 7.94 (m, 1H), 7.48 (ddd, $J = 8.0, 2.0, 1.0$ Hz, 1H), 7.33 (dt, $J = 8.5, 6.5$ Hz, 3H), 7.21 – 7.14 (m, 1H), 7.13 – 7.08 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.85, 150.63, 134.64, 133.49, 131.23, 130.06, 129.81, 129.47, 128.18, 126.01, 121.48.

GC-MS (EI, 70 eV): $m/z(\%)=232.0$ ($[\text{M}]^+$, 6), 232.0 (40), 139.0 (100), 141.0 (71), 111.0 (69), 75.0 (36).

Phenyl 2-chlorobenzoate

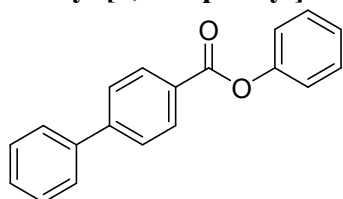


^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.7$ Hz, 1H), 7.46 – 7.39 (m, 2H), 7.39 – 7.28 (m, 3H), 7.19 (dd, $J = 15.3, 7.5$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 164.05, 150.65, 134.32, 133.12, 131.82, 131.29, 129.50, 129.35, 126.70, 126.07, 121.57.

GC-MS (EI, 70 eV): $m/z(\%)=232.0$ ($[\text{M}]^+$, 6), 232.0 (10), 141.0 (36), 139.0 (100), 111.0 (28), 75.0 (15).

Phenyl [1,1'-biphenyl]-4-carboxylate

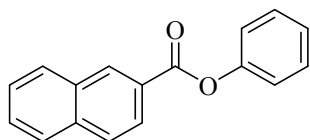


^1H NMR (400 MHz, CDCl_3) δ 8.25 – 8.15 (m, 2H), 7.71 – 7.60 (m, 2H), 7.57 (d, $J = 6.2$ Hz, 2H), 7.46 – 7.30 (m, 5H), 7.18 (d, $J = 12.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.05, 150.96, 146.28, 139.82, 130.67, 129.47, 128.95, 128.28, 128.23, 127.29, 127.20, 125.86, 121.71.

GC-MS (EI, 70 eV): $m/z(\%)=274.0$ ($[\text{M}]^+$, 6), 181.0 (100), 152.0 (41).

Phenyl 2-naphthoate

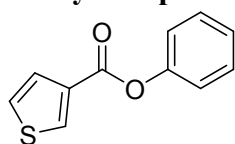


^1H NMR (400 MHz, CDCl_3) δ 8.81 (s, 1H), 8.22 (d, $J = 8.6$ Hz, 1H), 8.01 (d, $J = 8.1$ Hz, 1H), 7.98 – 7.90 (m, 2H), 7.61 (dt, $J = 14.9, 7.0$ Hz, 2H), 7.47 (t, $J = 7.8$ Hz, 2H), 7.31 (t, $J = 8.0$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.28, 151.00, 135.74, 132.43, 131.85, 129.46, 129.42, 128.55, 128.32, 127.77, 126.77, 126.71, 125.85, 125.39, 121.72.

GC-MS (EI, 70 eV): $m/z(\%)=248.0$ ($[\text{M}]^+$, 7), 248.0 (21), 155.0 (100), 127.0 (80).

Phenyl thiophene-3-carboxylate

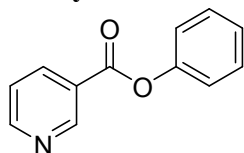


^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 2.1$ Hz, 1H), 7.66 (d, $J = 5.1$ Hz, 1H), 7.41 (t, $J = 7.7$ Hz, 2H), 7.36 (dd, $J = 4.6, 3.4$ Hz, 1H), 7.28 – 7.23 (m, 1H), 7.20 (d, $J = 7.8$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.00, 150.63, 133.96, 132.84, 130.12, 129.42, 128.52, 128.17, 126.32, 125.83, 121.65.

GC-MS (EI, 70 eV): $m/z(\%)=204.0$ ($[\text{M}]^+$, 5), 204.0 (30), 111.0 (100), 83.0 (26).

Phenyl nicotinate

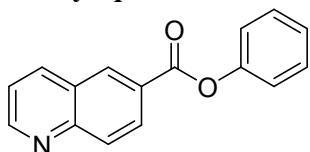


^1H NMR (400 MHz, CDCl_3) δ 9.40 (s, 1H), 8.85 (d, $J = 4.7$ Hz, 1H), 8.46 (d, $J = 8.0$ Hz, 1H), 7.54 – 7.39 (m, 3H), 7.32 – 7.17 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.60, 153.52, 150.92, 150.35, 137.71, 129.47, 126.12, 125.60, 123.47, 121.39.

GC-MS (EI, 70 eV): $m/z(\%)=199.0$ ($[\text{M}]^+$, 6), 199.0 (47), 106.0 (100), 78.0 (66), 51.0 (32).

Phenyl quinoline-6-carboxylate

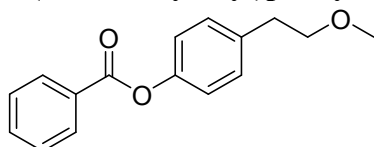


^1H NMR (400 MHz, CDCl_3) δ 9.06 (d, $J = 3.6$ Hz, 1H), 8.79 (s, 1H), 8.47 (d, $J = 8.8$ Hz, 1H), 8.36 (d, $J = 8.3$ Hz, 1H), 8.27 (d, $J = 8.8$ Hz, 1H), 7.54 (dd, $J = 8.3, 4.3$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 2H), 7.30 (dd, $J = 17.1, 7.8$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 164.56, 152.36, 150.82, 149.68, 137.97, 131.79, 129.60, 129.56, 129.46, 127.73, 127.47, 126.08, 122.01, 121.61.

GC-MS (EI, 70 eV): $m/z(\%)=249.0$ ($[\text{M}]^+$, 8), 249.0 (10), 156.0 (100), 128.0 (42), 101.0 (12).

4-(2-Methoxyethyl)phenyl benzoate

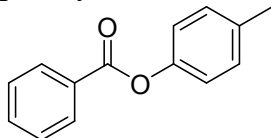


^1H NMR (400 MHz, CDCl_3) δ 8.24 – 8.18 (m, 2H), 7.63 (dd, $J = 10.5, 4.3$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 7.28 (t, $J = 7.8$ Hz, 2H), 7.15 (d, $J = 8.5$ Hz, 2H), 3.62 (t, $J = 7.0$ Hz, 2H), 3.37 (s, 3H), 2.91 (t, $J = 7.0$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.17, 149.26, 136.58, 133.45, 130.06, 129.77, 129.54, 128.46, 121.44, 73.40, 58.58, 35.54.

GC-MS (EI, 70 eV): $m/z(\%)=256.0$ ($[\text{M}]^+$, 6), 256.0 (13), 105.0 (100), 77.0 (34).

p-Tolyl benzoate

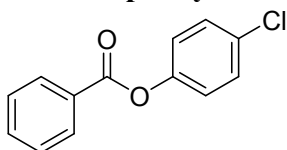


^1H NMR (400 MHz, CDCl_3) δ 8.24 – 8.18 (m, 2H), 7.63 (dd, $J = 10.5, 4.3$ Hz, 1H), 7.51 (t, $J = 7.7$ Hz, 2H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.36, 148.68, 135.49, 133.47, 130.12, 129.97, 129.66, 128.51, 121.34, 20.88.

GC-MS (EI, 70 eV): $m/z(\%)=212.0$ ($[\text{M}]^+$, 4), 212.0 (24), 105.0 (100), 77.0 (49), 51.0 (10).

4-Chlorophenyl benzoate.

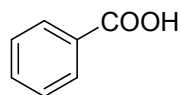


^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 7.9$ Hz, 2H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.7$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 8.6$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 164.82, 149.34, 133.70, 131.15, 130.10, 129.44, 129.09, 128.55, 123.03.

GC-MS (EI, 70 eV): $m/z(\%)=232.0$ ($[\text{M}]^+$, 5), 232.0 (26), 105.0 (100), 77.0 (68), 51.0 (28).

Benzoic acid

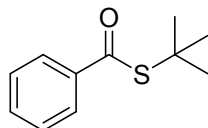


^1H NMR (400 MHz, CDCl_3) δ 13.03 (s, 1H), 8.14 (d, $J = 8.3$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 172.68, 133.80, 130.19, 129.30, 128.44.

GC-MS (EI, 70 eV): $m/z(\%)=122.0$ ($[\text{M}]^+$, 4), 122.0 (94), 105.0 (100), 77.0 (79), 51.0 (31).

S-(*tert*-Butyl) benzothioate

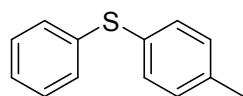


^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 7.2$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.40 (t, $J = 7.7$ Hz, 2H), 1.58 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 192.81, 138.23, 132.86, 128.40, 126.90, 48.09, 29.96.

GC-MS (EI, 70 eV): $m/z(\%)=194.0$ ($[\text{M}]^+$, 8), 194.0 (33), 138.0 (46), 105.0 (100), 77.0 (49), 57.1 (30).

Phenyl(*p*-tolyl)sulfane



^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 4.4$ Hz, 4H), 7.14 (s, 1H), 7.12 (d, $J = 6.5$ Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.58, 137.10, 132.25, 131.25, 130.04, 129.75, 129.02, 126.38, 21.11.

GC-MS (EI, 70 eV): $m/z(\%)=200.0$ ($[\text{M}]^+$, 12), 201.0 (18), 200.0 (100), 199.0 (36), 185.0 (46), 184.0 (45), 91.0 (26).

