Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

on

2,3-Heteroaromatic ring-fused cyclohexanones via heteroaromatic homo-Nazarov cylcization of donor-acceptor substituted cyclopropanes

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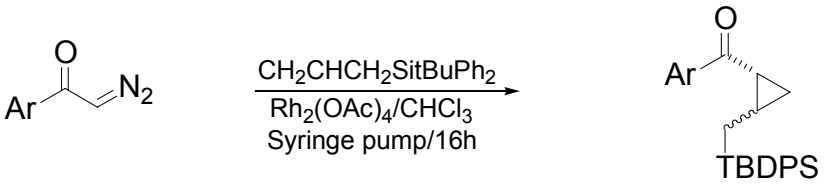
General. ^{1}H, ^{13}C, COSY and nOe spectra were recorded on JEOL JNM-LA400 FTNMR and JEOL JNM-LA500 FTNMR instruments using solutions in $CDCl_3$. The ^{1}H and ^{13}C spectra were referred to, respectively, tetramethylsilane, used as an internal standard, and the central line for $CDCl_3$. IR spectra were recorded on a BRUKER-VERTEX 70 FTIR Spectrometer**.** Mass spectra were recorded on Waters ESI-Q^{TOF} instrument. Elemental analyses were done using a ThermoQuest EA1110 instrument. All the reactions were carried out under dry nitrogen using freshly distilled dry solvents. Column chromatography was performed over silica gel (100-200 mesh, Acme Chemicals) using mixtures of hexanes and EtOAc as the eluent. The products were separated by radial chromatography using plates coated with silica gel PF_{254} (E-Merck). Solvents were removed under reduced pressure on a rotovap. The organic extracts were dried using anhydrous Na_2SO_4.

Procedure for the preparation of 2-(*t*-butyldiphenylsilylmethyl)cyclopropyl-3-furyl ketones 1a and 1b. A solution of 3-furyl diazoketone (1.0 g, 7.35 mmol) in anhydrous $CHCl_3$ (6 mL) was added to a stirred solution of allyl *tert*-butyldiphenylsilane (4.1 g, 14.7 mmol) and $Rh_2(OAc)_4$ (150 mg, 0.03 mmol) in anhydrous $CHCl_3$ (2 mL) over a period of 10 h using a syringe pump under nitrogen. The reaction mixture was stirred further for 5 h and the solvent was removed. The residue was chromatographed over silica gel to obtain *trans*-**1b**, 1.2 g, and *cis*-**1a**, 0.482 g, in a combined 70% yield.

Typical procedure for the $SnCl_4$-induced heteroaromatic homo-Nazarov reaction of 1a and 1b in dichloroethane. A solution of **1a** and **1b** (194 mg, 0.5 mmol), in dichloroethane (80 mL) was taken in a round bottom flask and mixed with a solution of $SnCl_4$ (237 μL, 2.0 mmol) in dichloroethane (10 mL) using a syringe. The reaction was heated to 80 °C and stirred for 12 hours before quenching with saturated aqueous $NaHCO_3$ (20 mL). The content was stirred vigorously for 10 min. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic solution was washed with brine, dried, filtered, and concentrated. The crude material was purified by radial chromatography to obtain the product **3** (159 mg, 82%) as a light yellow liquid.

Trasformation of the TBDPS function into a hydroxy function by oxidative cleavage of the carbon-silicon bond in 24a/24b. *t*-BuOOH (70%, 95 μL, 0.99 mmol) was added dropwise to an ice-cold suspension of KH (50 mg, 1.23 mmol, 30% dispersion in mineral oil, washed with 3 x 2 mL of hexanes) in DMF (2 mL). After 10 min, a solution of **24a/24b** (a mixture of *cis*- and *trans*-isomers, 66 mg, 0.123 mmol) in DMF (3 mL) was added. The mixture was stirred at 70 °C for 60 h and quenched by adding solid $Na_2S_2O_3$ (300 mg). The reaction mixture was stirred for 30 min and partitioned between water (5 mL) and diethyl ether (10 mL). The aqueous layer was extracted with diethyl ether (3 x 10 mL) and dried. The crude material was purified by column chromatography over silica gel to obtain the pure products **25a/25b** (a mixture of *cis*- and *tran*-isomers), 22 mg, 60%, colorless liquid.

Preparation of 2-*t*-butyldiphenylsilylmethylcyclopyl heteroaryl ketones



	cis : *trans*[a]
Ar = 3-furyl [1]	**1a** (20) : **1b** (50)
Ar = 2- furyl [1]	**3a** (17) : **3b** (51)
Ar = 3-thiofuryl [1]	**5a** (22) : **5b** (40)
Ar = 2-thiofuryl[1]	**7a** (16) : **7b** (32)
Ar = 2-indolyl [1]	**9a** (12) : **9b** (45)
Ar = 3-indolyl [2]	**11a** (7) : **11b** (42)[b]
Ar = 5-bromo-2-furyl [1]	**13a** (30) : **13b** (45)
Ar = 5-(2,4-dichlorophenyl)-2-furyl [1]	**15a** (20) : **15b** (50)
Ar = 5-(2-nitro-4-chlorophenyl)-2-furyl [1]	**17a** (18) : **17b** (54)

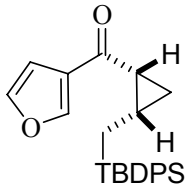
[a] All the ratios are of the isolated yields.

[b] The ratio was determined from the realative ^{1}H integrals.

The diazo reactants were prepared by following literature methods.

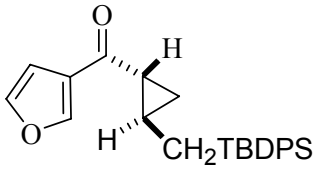
(1) N. R. Rosenquist, O. L. Chapman, *J. Org. Chem.*, 1976, **41**, 3326.

(2) R. L. Danheiser, R. F. Miller, R. G. Brisbois, S. G. Park, *J. Org. Chem.*, 1990, **55**, 1959.



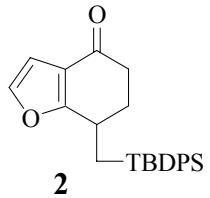
1a

Yellow solid, mp 69-71 °C. ^{1}H NMR (400 MHz) δ 7.90 (1H, bs), 7.68 (2H, dd, *J* = 7.8, 1.7 Hz), 7.60 (2H, dd, *J* = 7.8, 1.7 Hz), 7.42–7.26 (7H, m), 6.76 (1H, dd, *J* = 1.7, 1.0 Hz), 2.26 (1H, m), 1.51–1.44 (2H, m), 1.35–1.32 (1H, m), 1.14 (1H, m), 1.04 (9H, s), 0.92 (1H, m). ^{13}C NMR (100 MHz) δ 193.0, 146.7, 143.8, 136.2, 136.0, 134.7, 129.4, 129.0, 127.5, 108.7, 27.8, 25.9, 22.1, 18.1, 16.7, 7.3. IR (KBr) ν_{max}/cm^{-1} 3126, 3072, 2995, 2961, 2891, 2853, 1653, 1560, 1509, 1429, 1280, 1186, 1150, 1107, 910, 731, 703. Calcd *m/z* for $C_{25}H_{29}O_2Si$ $[M + H]^+$ = 389.1937; Found 389.1933.



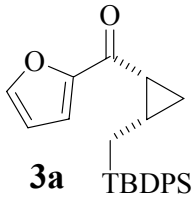
1b

Dense yellow liquid. ^{1}H NMR (400 MHz) δ 7.60–7.53 (5H, m), 7.40–7.25 (7H, m), 6.60 (1H, t, *J* = 1.0 Hz), 1.82 (1H, m), 1.60–1.55 (1H, m), 1.40 (1H, dd, *J* = 15.1, 6.6 Hz), 1.32 (1H, m), 1.25 (1H, dd, *J* = 15.1, 7.3 Hz), 1.04 (9H, s), 0.70 (1H, m). ^{13}C NMR (100 MHz) δ 193.9, 146.7, 143.6, 136.0, 134.7, 134.3, 129.1, 128.4, 127.6, 108.5, 29.3, 27.9, 22.4, 21.0, 18.0, 15.8. IR (neat) ν_{max}/cm^{-1} 3134, 3071, 3048, 2959, 2929, 2887, 2857, 1660, 1563, 1510, 1427, 1408, 1156, 1106, 895, 873, 730, 701. Calcd *m/z* for $C_{25}H_{29}O_2Si$ $[M + H]^+$ = 389.1937; Found 389.1933.



2

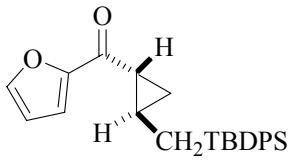
Wine-red dense liquid. ^{1}H NMR (400 MHz) δ 7.70–7.66 (4H, m), 7.42–7.34 (6H, m), 7.24 (1H, d, *J* = 2.0 Hz), 6.60 (1H, d, *J* = 2.0 Hz), 3.00 (1H, m), 2.36 (1H, ddd, *J* = 17.1, 6.5, 4.1 Hz), 2.12 (1H, ddd, *J* = 17.1, 10.5, 4.4), 2.01 (1H, dd, *J* = 15.1, 3.4 Hz), 1.73 (1H, m), 1.53 (1H, m), 1.30 (1H, dd, *J* = 15.1, 10.2 Hz), 1.05 (9H, s). ^{13}C NMR (100 MHz) δ 194.6, 170.9, 142.3, 136.0, 134.4, 133.5, 129.4, 127.8, 119.7, 106.5, 36.8, 31.3, 30.8, 27.8, 18.3, 12.3. IR (neat) ν_{max}/cm^{-1} 3133, 3070, 3048, 2959, 2929, 2889, 2857, 1660, 1568, 1468, 1427, 1392, 1248, 1106, 1037, 1011, 883, 820, 755, 737, 702. Calcd *m/z* for $C_{25}H_{29}O_2Si$ $[M + H]^+$ = 389.1937; Found 389.1930. Anal Calcd for $C_{25}H_{28}O_2Si$: C, 77.27; H, 7.26. Found: C, 77.23; H, 7.30.



3a

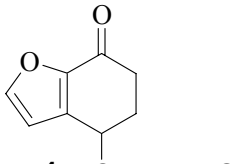
Yellow dense liquid. ^{1}H NMR (400 MHz) δ 7.60–7.55 (4H, m), 7.50 (1H, bs), 7.40–7.24 (6H, m), 6.89 (1H, d, *J* = 3.6 Hz), 6.45 (1H, dd, *J* = 3.5, 1.7 Hz), 2.16 (1H, m), 1.61 (1H, m), 1.42–1.27 (3H, m), 1.05 (9H, s), 0.73 (1H, dt, *J* = 6.8, 3.7 Hz). ^{13}C NMR (100 MHz) δ 188.5, 153.2, 146.1, 145.8, 136.0, 135.9, 134.5, 134.3, 129.1, 129.0, 127.6, 116.0, 111.9, 27.9, 22.8, 21.3, 18.1, 15.9. IR (neat) ν_{max}/cm^{-1} 3070, 3048,

2997, 2958, 2929, 2889, 2856, 1658, 1568, 1468, 1427, 1257, 1107, 1012, 883, 820, 739, 702. Calcd *m/z* for $C_{25}H_{29}O_2Si$ $[M + H]^+$ = 389.1937; Found 389.1933.



3b

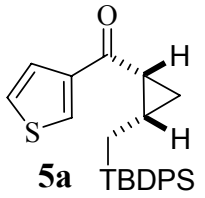
Yellow dense liquid. ^{1}H NMR (400 MHz) δ 7.71 (2H, dd, J = 7.5, 1.7 Hz), 7.57 (3H, dd, *J* = 13.0, 7.8 Hz), 7.50 (1H, bs), 7.42–7.24 (5H, m), 6.89 (1H, d, *J* = 3.4 Hz), 6.45 (1H, dd, *J* = 3.4, 1.7 Hz), 2.15 (1H, m), 2.08 (1H, m), 1.61 (1H, m), 1.42–1.27 (2H, m), 1.05 (9H, s), 0.73 (1H, dt, *J* = 6.8, 3.7 Hz). ^{13}C NMR (100 MHz) δ 188.5, 145.8, 136.0, 135.9, 134.8, 129.6, 129.1, 129.0, 127.7, 127.6, 127.5, 115.9, 111.9, 27.9, 26.6, 22.8, 21.3, 18.1, 15.9. IR (neat) ν_{max}/cm^{-1} 3048, 2958, 2929, 2890, 2856, 1748, 1658, 1568, 1469, 1428, 1247, 1109, 1012, 883, 820, 739, 702. Calcd *m/z* for $C_{25}H_{29}O_2Si$ $[M + H]^+$ = 389.1937; Found 389.1933.



4

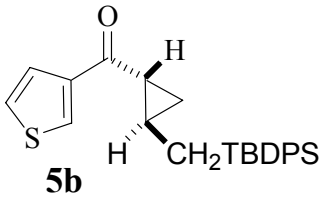
Pale yellow solid, mp 108-110 °C. ^{1}H NMR (500 MHz) δ 7.70-7.66 (4H, m), 7.44-7.35 (6H, m), 7.24 (1H, d, *J* = 2.0 Hz), 6.59 (1H, d, *J* = 2.0 Hz), 3.0 (1H, m), 2.36 (1H, ddd, *J* = 16.5, 6.0, 4.0 Hz), 2.12 (1H, ddd, *J* = 16.5, 10.0, 4.5 Hz), 2.01 (1H, dd, *J* = 15.0, 3.5 Hz), 1.73 (1H, m), 1.52 (1H, m), 1.28 (1H, dd, *J* = 15.0, 10.0 Hz), 1.05 (9H, s). ^{13}C NMR (125 MHz) δ 194.6, 170.9, 142.3, 136.0, 134.4, 133.4, 129.4,

127.8, 127.7, 119.7, 106.5, 36.8, 31.3, 30.8, 27.8, 18.3, 12.3. IR (KBr) ν_{max}/cm^{-1} 3124, 3046, 2930, 2857, 1667, 1446, 1425, 1244, 1104, 1011, 979, 930, 824. Calcd *m/z* for $C_{25}H_{29}O_2Si$ $[M + H]^+$ = 389.1937; Found 389.1934. Anal Calcd for $C_{25}H_{28}O_2Si$: C, 77.27; H, 7.26. Found: C, 77.20; H, 7.27.



5a

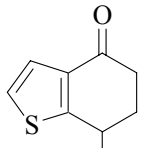
White solid, mp 72-74 °C. ^{1}H NMR (400 MHz) δ 7.95 (1H, dd, *J* = 3.0, 1.2 Hz), 7.68 (1H, t, *J* = 1.7 Hz), 7.66 (1H, t, *J* = 2.0 Hz), 7.59 (1H, t, *J* = 1.5 Hz), 7.57 (1H, t, *J* = 1.5 Hz), 7.53 (1H, dd, *J* = 4.9, 1.2 Hz), 7.41–7.26 (7H, m), 2.47 (1H, q, *J* = 7.8 Hz), 1.55–1.42 (2H, m), 1.32 (1H, m), 1.15 (1H, q, *J* = 5.5 Hz), 1.02 (9H, s), 0.92 (1H, m). ^{13}C NMR (100 MHz) δ 192.8, 144.2, 136.2, 136.0, 134.7, 131.1, 129.0, 127.5, 127.0, 125.9, 27.8, 25.5, 22.3, 18.1, 16.9, 7.5. IR (KBr) ν_{max}/cm^{-1} 3103, 3071, 2957, 2927, 2889, 2855, 1642, 1426, 1326, 1233, 1104, 876, 799, 736, 701. Calcd *m/z* for $C_{25}H_{29}OSSi$ $[M + H]^+$ = 405.1708; Found 405.1704.



5b

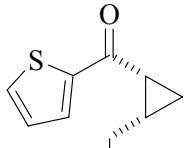
White solid, mp 78-80 °C.^{1}H NMR (400 MHz) δ 7.61–7.54 (5H, m), 7.37–7.21 (8H, m), 2.08 (1H, m), 1.57 (1H, m), 1.39 (1H, dd, *J* = 15.1, 6.6 Hz), 1.35–1.28 (2H, m), 1.05 (9H, s), 0.73 (1H, m). ^{13}C NMR (100 MHz) δ 193.7, 143.1, 136.0, 134.7, 134.3, 131.2, 129.2, 129.1, 127.6, 126.9, 125.7,

28.8, 27.9, 22.8, 21.4, 18.1, 15.9. IR (KBr) ν_{max}/cm^{-1} 3103, 3072, 3004, 2929, 2856, 1643, 1422, 1231, 1104, 1024, 916, 874, 797, 734, 699. Calcd *m/z* for $C_{25}H_{29}OSSi$ $[M + H]^+$ = 405.1708; Found 405.1704.



6 CH_2TBDPS

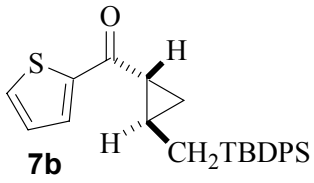
Pale yellow solid, mp 90-92 °C.^{1}H NMR (400 MHz) δ 7.73 (2H, dd, *J* = 7.3, 1.7 Hz), 7.68 (2H, dd, *J* = 7.6, 1.0 Hz), 7.44-7.37 (6H, m), 7.34 (1H, d, *J* = 5.4 Hz), 7.05 (1H, d, *J* = 5.4 Hz), 3.14 (1H, m), 2.40 (1H, td, *J* = 17.1, 4.1 Hz), 2.14 (1H, ddd, *J* = 17.1, 11.5, 4.1 Hz), 1.83 (1H, dd, *J* = 15.2, 2.9 Hz), 1.78 (1H, m), 1.64–1.58 (2H, m), 1.05 (9H, s). ^{13}C NMR (100 MHz) δ 193.0, 164.9, 136.1, 136.0, 134.3, 133.6, 129.5, 127.9, 127.7, 125.2, 122.8, 37.2, 33.5, 32.6, 27.8, 18.3, 18.0. IR (KBr) ν_{max}/cm^{-1} 3067, 3042, 2929, 2856, 1660, 1425, 1400, 1266, 1104, 907, 824, 744, 730, 703. Calcd *m/z* for $C_{25}H_{29}OSSi$ $[M + H]^+$ = 405.1708; Found 405.1709. Anal Calcd for $C_{25}H_{28}OSSi$: C, 74.21; H, 6.97; S, 7.72. Found: C, 74.25; H, 7.02; S, 7.95.



7a TBDPS

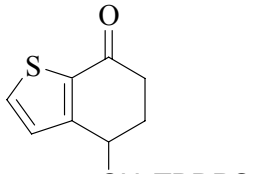
Wine-red dense liquid.^{1}H NMR (500 MHz) δ 7.66–7.58 (4H, m), 7.54 (1H, d, *J* = 4.9 Hz), 7.41–7.25 (7H, m), 7.03 (1H, dt, *J* = 4.3, 0.6 Hz), 2.14 (1H, m), 1.65 (1H, m), 1.39–1.35 (3H, m), 1.08 (9H, s), 0.76 (1H, dt, *J* = 7.5, 4.0 Hz,). ^{13}C

NMR (125 MHz) δ 192.3, 145.2, 136.2, 136.1, 134.6, 134.4, 133.0, 131.4, 129.3, 129.2, 128.0, 127.8, 28.6, 28.0, 23.1, 21.6, 18.3, 15.9. IR (neat) ν_{max}/cm^{-1} 3049, 3015, 2957, 2927, 2856, 1726, 1698, 1466, 1427, 1263, 1107, 820, 738, 701. Calcd *m/z* for $C_{25}H_{29}OSSi$ $[M + H]^+$ = 405.1708; Found 405.1706.



7b

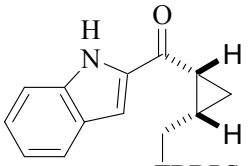
Colorless dense liquid. ^1H NMR (500 MHz) δ 7.68 (2H, dd, J = 7.8, 1.4 Hz), 7.66 (1H, dd, 3.8, 0.9), 7.61-7.57 (2H, m), 7.11 (1H, dd, *J* = 4.9, 3.8 Hz), 2.52 (1H, m), 1.52–1.47 (2H, m), 1.37 (1H, m), 1.17 (1H, m), 1.07 (1H, m), 1.00 (9H, s), 0.96 (1H, dt, J = 7.8, 4.3 Hz). ^{13}C NMR (125 MHz) δ 191.4, 146.4, 136.3, 136.1, 134.7, 134.6, 132.8, 131.3, 129.2, 129.1, 128.1, 127.6, 27.9, 25.3, 22.7, 18.3, 17.3, 7.5. IR (neat) ν_{max}/cm^{-1} 3048, 2959, 2929, 2887, 2856, 1645, 1418, 1391, 1237, 1226, 1106, 998, 896, 859, 820, 725, 701. Calcd *m/z* for $C_{25}H_{29}OSSi$ $[M + H]^+$ = 405.1708; Found 405.1706.



8

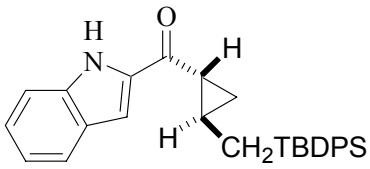
Yellow solid, mp 81-83 °C. ^1H NMR (500 MHz) δ 7.67 (4H, d, *J* = 5.6 Hz), 7.45–7.31 (7H, m), 6.49 (1H, s), 2.97 (1H, m), 2.36 (1H, ddd, *J* = 17.0, 6.5, 4.0 Hz), 2.12 (1H, ddd, *J* = 17.0, 10.5, 4.5 Hz), 1.95 (1H, dd, *J* = 15.5, 4.0 Hz), 1.76 (1H, m), 1.55 (1H, m), 1.32 (1H, dd, *J* = 15.0, 10 Hz), 1.05 (9H, m). ^{13}C NMR (100 MHz) δ 193.2, 171.8, 136.0, 135.9,

134.2, 133.3, 129.5, 127.9, 127.7, 123.2, 108.1, 36.4, 31.1, 30.9, 27.8, 18.3, 12.4. IR (KBr) ν_{max}/cm^{-1} 3044, 2924, 2854, 1737, 1659, 1465, 1422, 1398, 1264, 1180, 1103, 741, 702. Calcd *m/z* for $C_{25}H_{29}OSSi$ $[M + H]^+$ = 405.1708; Found 405.1701. Anal Calcd for $C_{25}H_{28}OSSi$: C, 74.21; H, 6.97; S, 7.92. Found: C, 74.25; H, 7.00; S, 7.90.



9a

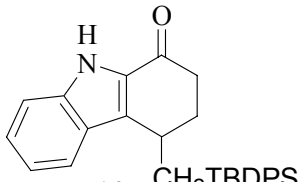
Yellow dense liquid. ^{1}H NMR (400 MHz) δ 9.18 (1H, bs), 7.65 (1H, d, *J* = 8.0 Hz), 7.61–7.55 (4H, m), 7.36–7.25 (8H, m), 7.13 (1H, t, *J* = 7.8 Hz), 6.81 (1H, s), 2.27 (1H, m), 1.64 (1H, m), 1.45–1.33 (3H, m), 1.06 (9H, s), 0.79 (1H, m). ^{13}C NMR (100 MHz) δ 191.9, 137.0, 136.0, 135.9, 134.5, 134.3, 129.1, 127.6, 125.8, 122.9, 120.6, 112.1, 108.9, 28.0, 27.8, 23.1, 21.3, 18.1, 15.8. IR (neat) ν_{max}/cm^{-1} 3297, 3070, 2997, 2959, 2856, 1629, 1522, 1426, 1400, 1343, 1231, 1168, 1141, 1106, 737, 701. Calcd *m/z* for $C_{29}H_{32}NOSi$ $[M + H]^+$ = 438.2253; Found 438.2253.



9b

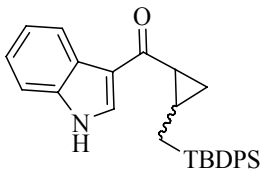
Yellow solid, mp 128-130 °C. ^{1}H NMR (400 MHz) δ 9.90 (1H, bs), 7.70-7.66 (3H, m), 7.55 (2H, dd, *J* = 7.5, 1.9 Hz), 7.46 (1H, d, J = 8.3 Hz), 7.40-7.20 (7H, m), 7.13 (2H, dt, *J* = 6.3, 0.7 Hz), 2.65 (1H, m), 1.57–1.50 (2H, m), 1.42 (1H, m), 1.24 (1H, m), 1.05 (9H, s), 1.02 (1H, m). ^{13}C NMR

(100 MHz) δ 191.3, 137.2, 136.9, 136.1, 136.0, 134.5, 134.4, 129.0, 128.9, 127.6, 127.5, 127.4, 125.9, 122.8, 120.6, 112.3, 109.0, 27.7, 24.6, 22.7, 18.1, 17.3, 7.7. IR (KBr) ν_{max}/cm^{-1} 3300, 3078, 2960, 2927, 2890, 2855, 1622, 1520, 1426, 1402, 1232, 1167, 1140, 1109, 925, 826, 797, 699. Calcd *m/z* for $C_{29}H_{32}NOSi$ $[M + H]^+$ = 438.2253; Found 438.2253.



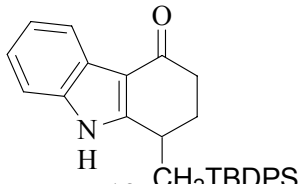
10

Yellow dense liquid. ^1H NMR (500 MHz) δ 8.83 (1H, bs), 7.82-7.78 (2H, m), 7.69-7.67 (2H, m), 7.59 (1H, dd, *J* = 8.0, 1.5 Hz), 7.45-7.33 (8H, m), 7.13 (1H, m), 3.37 (1H, m), 2.62 (1H, ddd, *J* = 17.5, 12.0, 4.5 Hz), 2.22 (1H, td, *J* = 17.5, 4.5 Hz), 1.93 (1H, m), 1.82 (1H, dd, *J* = 15.0, 2.5 Hz), 1.69 (1H, ddd, *J* = 13.5, 8.5, 4.5 Hz), 1.62 (1H, dd, *J* = 15.0, 12.0 Hz), 1.06 (9H, s). ^{13}C NMR (125 MHz) δ 191.2, 137.9, 136.1, 136.0, 135.7, 134.9, 134.0, 129.9, 129.4, 129.3, 127.9, 127.7, 126.8, 125.0, 121.6, 120.4, 112.6, 34.2, 30.1, 28.4, 27.8, 18.4, 14.7. IR (neat) ν_{max}/cm^{-1} 3276, 3071, 2927, 2856, 1648, 1470, 1427, 1333, 1255, 1078, 740, 702. Calcd *m/z* for $C_{29}H_{32}NOSi$ $[M + H]^+$ = 438.2253; Found 438.2250. Anal Calcd for $C_{29}H_{31}NOSi$: C, 79.59; H, 7.14; N, 3.20. Found: C, 79.62; H, 7.16; N, 3.20.



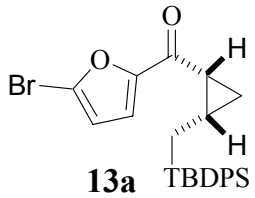
11a /11b

Pale yellow dense liquid. ^{1}H NMR (400 MHz) δ 8.56 (bs), 8.44 (bs), 8.34-8.32 (m), 7.78 (d, *J* = 2.7 Hz), 7.68 (d, *J* = 6.3 Hz), 7.60–7.56 (m), 7.40–7.23 (m), 2.47-2.41 (m), 2.05–2.01 (m), 1.45–1.20 (m), 1.05 (s), 1.01 (s), 0.92–0.83 (m), 0.68–0.64 (m). ^{13}C NMR (100 MHz) δ 194.6, 193.8, 136.3, 136.1, 136.0, 135.1, 134.7, 130.5, 130.4, 129.0, 128.9, 128.8, 127.6, 127.5, 127.4, 125.6, 123.5, 122.6, 122.4, 111.1, 111.0, 29.7, 28.7, 27.9, 25.7, 21.1, 20.7, 19.9, 18.1, 16.0, 15.4, 7.8. Calcd *m/z* for $C_{29}H_{32}NOSi$ $[M + H]^+$ = 438.2253; Found 438.2250.



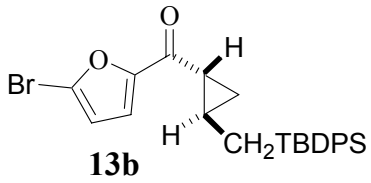
12

Light brown dense liquid. ^{1}H NMR (500 MHz) δ 8.63 (1H, s), 7.83-7.80 (2H, m), 7.71-7.68 (2H, m), 7.61 (1H, d, *J* = 8.0 Hz), 7.47-7.35 (8H, m), 7.15 (1H, m), 3.38 (1H, m), 2.63 (1H, ddd, *J* = 17.2, 12.0, 4.5 Hz), 2.23 (1H, td, *J* = 17.2, 4.6 Hz), 1.94 (1H, m), 1.84 (1H, dd, *J* = 15.5, 2.3 Hz), 1.70 (1H, ddd, *J* = 13.8, 8.6, 4.5 Hz), 1.64 (1H, dd, *J* = 15.5, 12.0 Hz), 1.07 (9H, s). ^{13}C NMR (125 MHz) δ 191.2, 137.8, 136.1, 136.0, 135.6, 134.8, 134.0, 129.9, 129.4, 129.3, 127.9, 127.7, 126.8, 125.0, 121.6, 120.5, 112.5, 34.1, 30.1, 28.3, 27.8, 18.4, 14.7. IR (neat) ν_{max}/cm^{-1} 3275, 3070, 2927, 2856, 1648, 1536, 1469, 1427, 1333, 1255, 1104, 820, 785, 741, 702. Calcd *m/z* for $C_{29}H_{32}NOSi$ $[M + H]^+$ = 438.2253; Found 438.2254. Anal Calcd for $C_{29}H_{31}NOSi$: C, 79.59; H, 7.14; N, 3.20. Found: C, 79.65; H, 7.15; N, 3.21.



13a

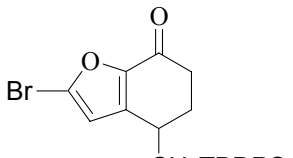
Yellow dense liquid. ^{1}H NMR (400 MHz) δ 7.66 (2H, dd, *J* = 7.6, 1.7 Hz), 7.58 (2H, dd, *J* = 7.8, 1.5 Hz), 7.41–7.25 (6H, m), 6.97 (1H, d, *J* = 3.5 Hz), 6.42 (1H, d, *J* = 3.5 Hz), 2.47 (1H, m), 1.59–1.48 (2H, m), 1.35 (1H, m), 1.14 (1H, m), 1.02 (9H, s), 0.98 (1H, m). ^{13}C NMR (100 MHz) δ 186.2, 155.7, 136.1, 136.0, 134.4, 129.0, 128.9, 127.5, 127.2, 117.5, 114.1, 27.8, 23.8, 23.1, 18.1, 17.5, 7.3. IR (neat) ν_{max}/cm^{-1} 3071, 3048, 2958, 2829, 2890, 2856, 1659, 1572, 1460, 1427, 1391, 1240, 1106, 1067, 1012, 820, 738, 702. Calcd *m/z* for $C_{25}H_{28}BrO_2Si$ $[M + H]^+$ = 467.1042; Found 467.1043.



13b

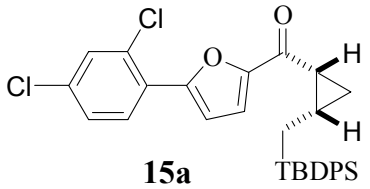
White solid, mp 68-70 °C. ^{1}H NMR (400 MHz) δ 7.60 (4H, ddd, *J* = 14.6, 7.6, 1.5 Hz), 7.40–7.24 (6H, m), 6.81 (1H, d, *J* = 3.5 Hz), 6.40 (1H, d, *J* = 3.5 Hz), 2.07 (1H, dt, *J* = 8.0, 4.1 Hz), 1.65 (1H, m), 1.40 (1H, dd, *J* = 15.2, 6.6 Hz), 1.35–1.25 (2H, m), 1.05 (9H, s), 0.76 (1H, dt, *J* = 6.6, 4.1 Hz). ^{13}C NMR (100 MHz) δ 187.4, 154.9, 136.0, 134.4, 134.2, 129.1, 129.0, 127.6, 127.2, 117.5, 114.1, 27.9, 27.4, 23.1, 21.6, 18.1, 15.8. IR (KBr) ν_{max}/cm^{-1} 3142, 3099, 3070, 3047,

2928, 2855, 1651, 1462, 1426, 1399, 1257, 1106, 1021, 954, 925, 891, 819, 803, 734, 716, 711. Calcd *m/z* for $C_{25}H_{28}BrO_2Si$ $[M + H]^+$ = 467.1042; Found 467.1043.



14

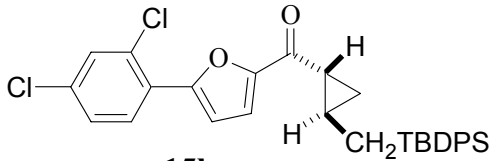
White solid, mp 97-99 °C. ^{1}H NMR (400 MHz) δ 7.67 (4H, d, *J* = 6.8 Hz), 7.44–7.36 (6H, m), 6.50 (1H, s), 2.98 (1H, m), 2.36 (1H, ddd, *J* = 17.1, 6.6, 4.1 Hz), 2.12 (1H, ddd, J = 17.1, 10.3, 4.4 Hz), 1.95 (1H, dd, *J* = 15.4, 4.1 Hz), 1.77 (1H, m), 1.56 (1H, m), 1.33 (1H, dd, *J* = 15.4, 10 Hz), 1.06 (9H, s). ^{13}C NMR (100 MHz) δ 193.2, 171.8, 136.0, 135.9, 134.2, 133.3, 129.5, 128.9, 127.7, 123.2, 108.1, 36.4, 31.1, 30.9, 27.8, 18.3, 12.4. IR (neat) ν_{max}/cm^{-1} 3070, 3049, 2957, 2929, 2856, 1667, 1470, 1427, 1112, 1008, 820, 740, 701. Calcd *m/z* for $C_{25}H_{28}BrO_2Si$ $[M + H]^+$ = 467.1042; Found 467.1046. Anal Calcd for $C_{25}H_{27}BrO_2Si$: C, 64.23; H, 5.82. Found: C, 64.27; H, 5.85.



15a

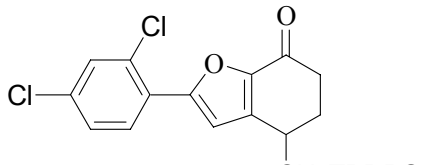
Yellow dense liquid. ^{1}H NMR (400 MHz) δ 7.89 (1H, d, *J* = 8.6 Hz), 7.67 (2H, dd, *J* = 7.3, 1.7 Hz), 7.58 (2H, dd, *J* = 7.3, 2.2 Hz), 7.50 (1H, d, *J* = 2.2 Hz), 7.38 (3H, t, *J* = 7.6 Hz), 7.33 (1H, dd, *J* = 8.5, 2.2 Hz), 7.30–7.22 (3H, m), 7.21 (1H, d, *J* = 3.6 Hz), 7.16 (1H, d, *J* = 3.6 Hz), 2.56 (1H, dd, *J* = 13.7, 8.0 Hz), 1.58–1.52 (2H, m), 1.39 (1H,

m), 1.18 (1H, dd, *J* = 9.8, 6.6 Hz), 1.03 (1H, m), 1.03 (9H, s). ^{13}C NMR (100 MHz) δ 187.3, 152.9, 151.9, 136.2, 136.0, 134.7, 134.6, 131.7, 130.7, 129.5, 129.0, 128.9, 127.5, 126.8, 117.6, 113.2, 27.8, 24.3, 23.1, 18.1, 17.5, 7.4. IR (neat) ν_{max}/cm^{-1} 2923, 2853, 1600, 1460, 1420, 1121, 1090, 1020. Calcd *m/z* for $C_{31}H_{31}Cl_2O_2Si$ $[M + H]^+$ = 533.1470; Found 533.1480.



15b

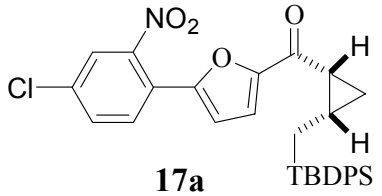
Yellow dense liquid. ^{1}H NMR (400 MHz) δ 7.81 (1H, d, *J* = 8.6 Hz), 7.60–7.54 (4H, m), 7.50 (1H, d, *J* = 2.0 Hz), 7.35 (1H, d, *J* = 2.0 Hz), 7.33-7.29 (2H, m), 7.26 (1H, s), 7.24–7.20 (3H, m), 7.17 (1H, d, *J* = 3.7 Hz), 6.97 (1H, d, *J* = 3.7 Hz), 2.14 (1H, m), 1.66 (1H, m), 1.43 (1H, dd, *J* = 15.2, 6.6 Hz), 1.36 (1H, m), 1.30 (1H, dd, *J* = 15.2, 7.6 Hz), 1.05 (9H, s), 0.79 (1H, m). ^{13}C NMR (100 MHz) δ 188.2, 152.0, 136.0, 135.9, 134.7, 134.5, 134.3, 131.7, 130.6, 129.6, 129.1, 129.0, 127.6, 127.5, 127.4, 126.8, 117.6, 113.1, 28.0, 27.9, 23.0, 21.6, 18.1, 15.9. Calcd *m/z* for $C_{31}H_{31}Cl_2O_2Si$ $[M + H]^+$ = 533.1470; Found 533.1480.



16

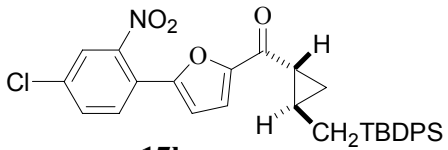
Wine-red dense liquid. ^{1}H NMR (400 MHz) δ 7.71 (1H, d, *J* = 1.5 Hz), 7.70 (1H, d, *J* = 1.5 Hz), 7.64 (1H, d, *J* = 1.9 Hz), 7.63 (1H, d, *J* = 1.9 Hz), 7.45 (1H, d, *J* = 2.2 Hz),

7.43–7.30 (7H, m), 7.26 (1H, bs), 7.22 (1H, bs), 3.12 (1H, m), 2.52 (1H, ddd, *J* = 17.2, 7.6, 4.4 Hz), 2.25 (1H, ddd, *J* = 17.2, 9.2, 4.0 Hz), 2.00 (1H, dd, *J* = 15.2, 4.8 Hz), 1.94 (1H, m), 1.69 (1H, m), 1.42 (1H, dd, *J* = 15.2, 8.8 Hz), 1.06 (9H, s). ^{13}C NMR (100 MHz) δ 194.2, 170.2, 149.2, 136.0, 135.9, 134.1, 133.7, 133.5, 131.1, 130.5, 129.5, 129.4, 128.6, 127.8, 127.2, 121.7, 107.2, 36.2, 31.6, 30.6, 27.8, 18.3, 12.8. IR (neat) ν_{max}/cm^{-1} 3370, 2997, 2958, 2856, 1658, 1574, 1515, 1463, 1427, 1391, 1256, 1240, 1106, 1073, 913, 820, 805, 738, 702. Calcd *m/z* for $C_{31}H_{31}Cl_2O_2Si$ $[M + H]^+$ = 533.1470; Found 533.1476. Anal Calcd for $C_{31}H_{30}Cl_2O_2Si$: C, 69.78; H, 5.67. Found: C, 69.87; H, 5.70.



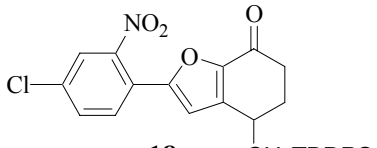
17a

Yellow dense liquid. ^{1}H NMR (400 MHz) δ 7.78 (1H, d, *J* = 8.6 Hz), 7.74 (1H, d, *J* = 2.0 Hz), 7.67-7.65 (2H, m), 7.62–7.57 (3H, m), 7.42–7.33 (3H, m), 7.30–7.25 (3H, m), 7.12 (1H, d, *J* = 3.6 Hz), 6.73 (1H, d, *J* = 3.6 Hz), 2.50 (1H, m), 1.56–1.47 (2H, m), 1.36 (1H, dd, *J* = 14.9, 4.4 Hz), 1.15 (1H, m), 1.03 (9H, s), 0.99 (1H, m). ^{13}C NMR (100 MHz) δ 187.4, 154.4, 149.5, 136.2, 136.0, 135.4, 134.6, 132.2, 130.4, 129.0, 128.9, 127.5, 124.2, 121.6, 117.0, 112.1, 27.8, 24.4, 23.4, 18.1, 17.6, 7.5. IR (neat) ν_{max}/cm^{-1} 3070, 3049, 2959, 2929, 2856, 1659, 1539, 1464, 1427, 1390, 1362, 1242, 1106, 1072, 1019, 913, 820, 738, 702, 607. Calcd *m/z* for $C_{31}H_{31}ClNO_4Si$ $[M + H]^+$ = 544.1711, Found 544.1710.



17b

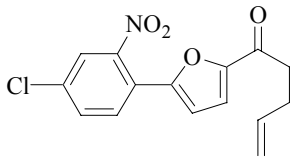
Yellow dense liquid. ^{1}H NMR (400 MHz) δ 7.73 (2H, d, *J* = 8.3 Hz), 7.62–7.54 (6H, m), 7.37–7.20 (5H, m), 6.94 (1H, d, *J* = 3.8 Hz), 6.69 (1H, d, *J* = 3.8 Hz), 2.10 (1H, m), 1.62 (1H, m), 1.37–1.33 (3H, m), 1.05 (9H, s), 0.78 (1H, dt, *J* = 7.6, 3.6 Hz). ^{13}C NMR (100 MHz) δ 188.3, 153.5, 149.6, 148.0, 136.0, 135.9, 135.4, 134.5, 134.3, 132.2, 130.3, 129.1, 129.0, 127.6, 127.5, 124.2, 121.6, 117.1, 112.0, 28.1, 27.9, 23.5, 21.6, 18.1, 15.8. IR (neat) ν_{max}/cm^{-1} 3070, 2997, 2958, 2856, 1660, 1580, 1538, 1463, 1427, 1392, 1240, 1106, 1024, 729, 702. Calcd *m/z* for $C_{31}H_{31}ClNO_4Si$ [M + H]$^{+}$ = 544.1711; Found 544.1710.



18

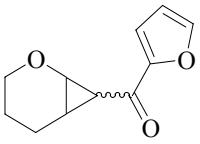
Pale yellow dense liquid. ^{1}H NMR (400 MHz) δ 7.73 (1H, d, *J* = 2.2 Hz), 7.69 (1H, bs), 7.67 (1H, d, *J* = 1.5 Hz), 7.65 (1H, d, *J* = 2.2 Hz), 7.63 (1H, d, *J* = 3.9 Hz), 7.55 (1H, dd, *J* = 8.6, 2.2 Hz), 7.47–7.36 (7H, m), 6.85 (1H, s), 3.05 (1H, m), 2.42 (1H, ddd, *J* = 16.8, 6.6, 4.1 Hz), 2.19 (1H, ddd, *J* = 16.8, 10.0, 4.4 Hz), 1.95 (1H, dd, *J* = 15.4, 3.9 Hz), 1.80 (1H, m), 1.57 (1H, m), 1.32 (1H, dd, *J* = 15.4, 9.5 Hz), 1.05 (9H, s). ^{13}C NMR (100 MHz) δ 193.9, 172.0, 147.7, 136.0, 134.7, 134.2, 133.3, 132.1, 130.0, 129.5, 127.9, 124.3, 121.8, 121.5, 106.3, 36.6, 31.1, 30.8, 27.7,

18.2, 12.6. IR (neat) ν_{max}/cm^{-1} 2957, 2928, 2856, 1682, 1538, 1450, 1363, 1137, 1106, 1005, 822, 728, 702. IR: ν_{max} 3079, 2922, 1679, 1538, 1460, 1360, 1155, 1117, 1024, 923, 806, 768. Calcd *m/z* for $C_{31}H_{31}ClNO_4Si$ $[M + H]^+$ = 544.1711; Found 544.1710. Anal Calcd for $C_{31}H_{30}ClNO_4Si$: C, 68.43; H, 5.56; N, 2.57. Found: C, 68.45; H, 5.57; N, 2.57.



3-butenyl 5-(4-chloro-2-nitrophenyl)-2-furyl ketone

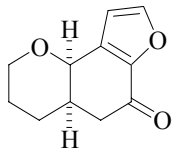
Brown solid, mp 120-122 °C. ^{1}H NMR (400 MHz) δ 7.78–7.74 (2H, m), 7.63 (1H, dd, *J* = 8.6, 2.2 Hz), 7.25 (1H, t, *J* = 3.7 Hz), 6.76 (1H, t, *J* = 3.7 Hz), 5.88 (1H, m), 5.10 (1H, dd, *J* = 17.1, 1.5 Hz), 5.02 (1H, d, *J* = 10.2 Hz), 2.93 (2H, t, *J* = 7.5 Hz), 2.51–2.45 (2H, m). ^{13}C NMR (100 MHz) δ 188.6, 153.1, 150.3, 148.0, 136.8, 135.7, 132.3, 130.5, 124.4, 121.5, 117.9, 115.6, 112.0, 37.7, 27.9. IR (KBr)) ν_{max}/cm^{-1} 3018, 2956, 2925, 2854, 1681, 1538, 1450, 1369, 1106, 1002, 745, 726, 702. Calcd *m/z* for $C_{15}H_{13}ClNO_4$ $[M + H]^+$ = 306.0533; Found 306.0530. Anal Calcd for $C_{15}H_{12}ClNO_4$: C, 58.93; H, 3.96; N, 4.58. Found: C, 58.96; H, 3.97; N, 4.60.



19a / **19b**

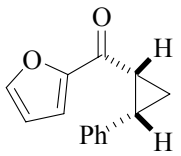
Light brown dense liquid. ^{1}H NMR (400 MHz) δ 7.60 (bs), 7.24 (d, *J* = 3.2 Hz), 6.55–6.53 (m), 5.12 (d, *J* = 2.0 Hz), 4.50–4.47 (m), 4.05–3.97 (m), 3.58–3.50 (m), 3.15 (dd, *J* = 16.4,

6.1 Hz), 2.99 (dd, *J* = 16.4, 6.6 Hz), 2.77 (dd, *J* = 16.6, 7.3 Hz), 2.70 (dd, *J* = 16.6, 7.1), 2.41 (bs), 2.15-2.11 (m), 1.97–1.93 (m), 1.68–1.52 (m), 1.40–1.20 (m). ^{13}C NMR (100 MHz) δ 188.7, 188.2, 152.7, 152.6, 146.4, 117.3, 112.1, 112.0, 99.1, 99.0, 98.3, 93.4, 93.3, 65.6, 65.5 60.2, 60.1, 40.3, 40.2, 39.6, 38.4, 36.2, 35.7, 29.5, 28.1, 26.5, 24.7, 24.5, 24.1. 23.7. IR (neat) ν_{max}/cm^{-1} 2929, 2854, 1670, 1568, 1467, 1394, 1291, 1126, 1077, 1022, 765. Calcd *m/z* for $C_{11}H_{13}O_3$ [M + H]$^+$ = 193.0865; Found 193.0861.



21

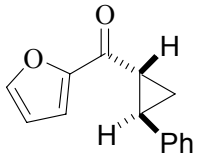
Colorless dense liquid. ^{1}H NMR (400 MHz) δ 7.44 (1H, d, *J* = 1.9 Hz), 6.70 (1H, d, *J* = 1.9 Hz), 4.69 (1H, d, *J* = 3.2 Hz), 3.95 (1H, d, *J* = 10.3 Hz), 3.67 (1H, dt, *J* = 10.8, 2.7 Hz), 2.95 (1H, dd, *J* = 16.1, 10.8 Hz), 2.45–2.34 (2H, m), 1.93–1.78 (3H, m), 0.87 (1H, m). ^{13}C NMR (125 MHz) δ 194.4, 163.4, 144.4,122.5, 106.4, 69.1, 67.4, 39.6, 34.3, 27.2, 21.1. IR (neat) ν_{max}/cm^{-1} 2924, 2852, 1678, 1456, 1194, 1138, 1019. Calcd *m/z* for $C_{11}H_{13}O_3$ [M + H]$^+$ = 193.0865; Found 193.0866. Anal Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.77; H, 6.31.



22a

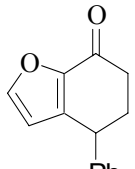
White solid, mp 85-87 °C. ^{1}H NMR (400 MHz) δ 7.52 (1H, bs), 7.25–7.13 (5H, m), 7.10 (1H, d, *J* = 3.6 Hz), 6.47 (1H, dd,

J = 3.4, 1.7 Hz), 3.05 (1H, m), 2.83 (1H, dd, *J* = 16.6, 8.3 Hz), 2.05 (1H, m), 1.45 (1H, dt, J = 7.8, 4.6 Hz). ^{13}C NMR (100 MHz) δ 184.8, 154.0, 145.8, 135.8, 129.3, 127.8, 126.6, 115.9, 112.0, 29.4, 26.1, 11.7. IR (KBr) ν_{max}/cm^{-1} 3289, 3139, 3108, 3036, 1653, 1565, 1465, 1411, 1346, 1258, 1084, 1043, 1021, 986, 917, 770, 734, 698. Calcd *m/z* for $C_{14}H_{13}O_2$ $[M + H]^+$ = 213.0915; Found 213.0913.



22b

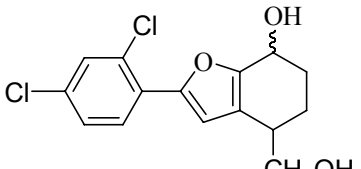
Brown solid, mp 64-66 °C. ^{1}H NMR (400 MHz) δ 7.58 (1H, m), 7.30 (2H, t, *J* = 7.6 Hz), 7.25–7.19 (2H, m), 7.15 (2H, bd, *J* = 8.8 Hz), 6.53 (1H, dd, *J* = 3.4, 1.7 Hz), 2.83 (1H, m), 2.72 (1H, m), 1.87 (1H, m), 1.52 (1H, m). ^{13}C NMR (100 MHz) δ 187.2, 153.2, 146.3, 140.3, 128.5, 126.5, 126.2, 116.6, 112.2, 29.3, 28.9, 18.9. IR (KBr) ν_{max}/cm^{-1} 3110, 2925, 1653, 1565, 1466, 1410, 1259, 1045, 775, 763, 738, 700. Calcd *m/z* for $C_{14}H_{13}O_2$ $[M + H]^+$ = 213.0915; Found 213.0913.



23

Yellow solid, mp 80-82 °C. ^{1}H NMR (400 MHz) δ 7.38–7.26 (4H, m), 7.14 (1H, d, *J* = 1.5 Hz), 7.12 (1H, bs), 6.75 (1H, d, *J* = 2.0 Hz), 4.29 (1H, dd, *J* = 7.6, 4.9 Hz), 2.65–2.48 (3H, m), 2.24 (1H, m). ^{13}C NMR (100 MHz) δ 194.1, 167.0, 143.3, 139.8, 128.8, 127.8, 127.4, 122.2, 106.5, 40.8, 36.3, 32.5. IR (KBr) ν_{max}/cm^{-1} 3153, 3119, 2953, 2922, 2855, 1671, 1584,

1449, 1406, 1287, 1241, 1120, 777, 729, 700. Calcd *m/z* for $C_{14}H_{13}O_2$ $[M + H]^+$ = 213.0915; Found 213.0915. Anal Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.24; H, 5.73.



25a/25b

Colorless dense liquid. ^{1}H NMR (400 MHz) δ 7.73-7.70 (m), 7.54 (d, *J* = 8.4 Hz), 7.45 (d, *J* = 2.4 Hz), 7.34 (d, *J* = 8.4 Hz), 7.29 (t, *J* = 4 Hz), 7.16 (s), 7.14 (s), 7.0 (s), 6.68 (s), 4.80-4.71(m), 3.95-3.81 (m), 3.17-2.90 (m), 2.18-2.14 (m), 1.95-1.94 (m), 1.76-1.68 (m), 0.90-0.86 (m). Calcd *m/z* for $C_{15}H_{14}Cl_2NaO_3$ $[M + Na]^+$ = 335.0218; Found 335.0220. Anal Calcd for $C_{15}H_{14}Cl_2O_3$: C, 57.53; H, 4.51. Found: C, 57.55; H, 4.52.