Supporting Information for:

Direct Imidation of Lactones via Catalytic Oxo/Imido Heterometathesis

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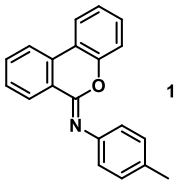
General. The catalyst **Ti/SiO$_2$** was prepared as described before.[1] Catalytic runs were performed under argon atmosphere using standard Schlenk techniques. Toluene for catalytic runs was distilled from Na/benzophenone and stored over activated 3 Å MS. Workup of the reactions and further manipulations with imidates were performed in air using reagent grade solvents. $CDCl_3$ and C_6D_6 were distilled from CaH_2 and Na/benzophenone, respectively, and stored over 3 Å MS. *N*-sulfinylanilines were prepared according to standard procedures using Merck $SOCl_2$ ("for synthesis" grade) and freshly distilled or recrystallized anilines.[2] *t*BuN=S=N*t*Bu was prepared according to literature method.[3] Lactones were either purchased or prepared according to standard procedures; liquid lactones were distilled and dried with 3 Å MS; solid lactones were sublimed in vacuum.

^{1}H, ^{13}C, ^{19}F NMR spectra were recorded using Bruker Avance 400 and 300 spectrometers. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. ^{1}H chemical shifts were referenced relative to the residual solvent peak: 7.26 ($CDCl_3$), 7.16 (C_6D_6). ^{13}C chemical shifts were referenced relative to the solvent peak: 77.16 ($CDCl_3$). ^{19}F spectra were referenced externally to $CFCl_3$. GC/FID was performed using Chromatec Crystal 5000.2 gas chromatograph equipped with a Restek RTX-35 column. IR spectra were recorded using Shimadzu IRPrestige-21 spectrometer equipped with MIRacle single reflection ATR accessory from Pike Technologies. Wavenumbers are given in cm^{-1}. High resolution mass spectra were recorded on Bruker micrOTOF II instrument in the *m/z* range 50–1600 using simultaneous electrospray ionisation. Elemental analysis was performed at the Laboratory of Microanalysis of the INEOS RAS.

General procedure for the preparation of imidates. A double-neck Schlenk flask was charged under argon with **Ti/SiO$_2$** (5 mol% Ti considering the Ti content in the catalyst of 0.23 mmolTi/g as determined from elemental analysis), lactone, toluene and *N*-sulfinylamine, and the mixture was stirred under reflux. The reaction was monitored with GC by taking aliquots of the solution. For the reactions listed in Table 1 C_6Me_6 was used as an internal standard and the conversions of the reagents were determined by GC from their consumption with respect to the internal standard. After the end of the reaction the catalyst was filtered off using a glass filter, the solvent evaporated, and the product purified as described below. Coumarin and 3,4-benzocoumarin are poorly soluble in aliphatic solvents and thus it is usually more convenient to use slight excess of RNSO (that in most cases can be easily washed out during workup) to ensure full conversion of lactone. Products are typically also poorly soluble in aliphatic solvents and can be washed without losing the yield, however in certain cases washing should be careful.

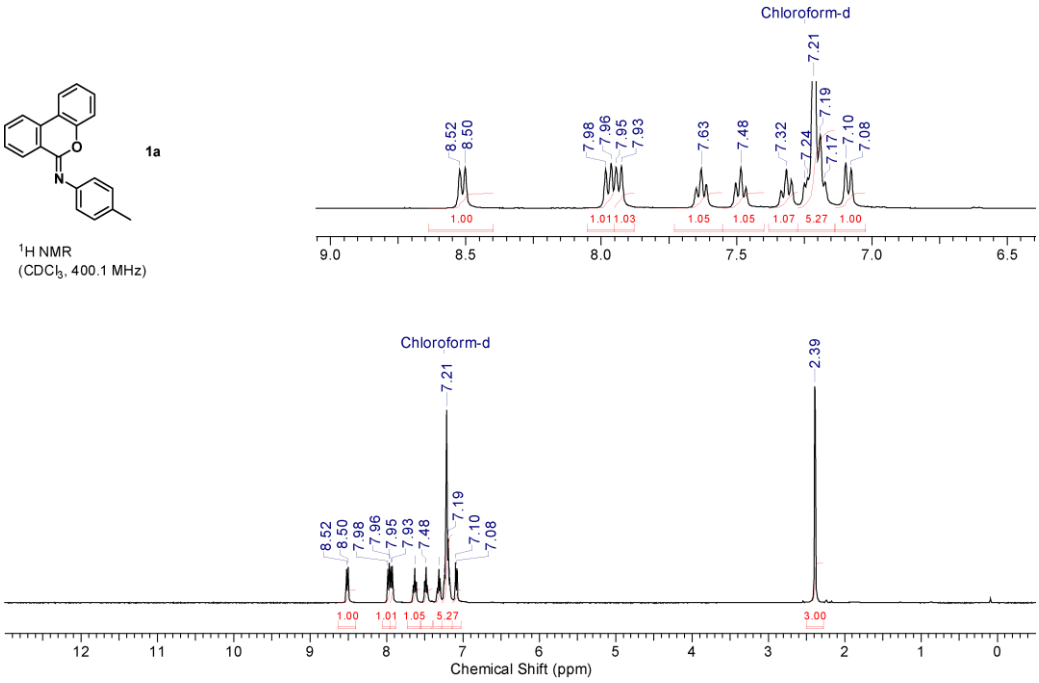


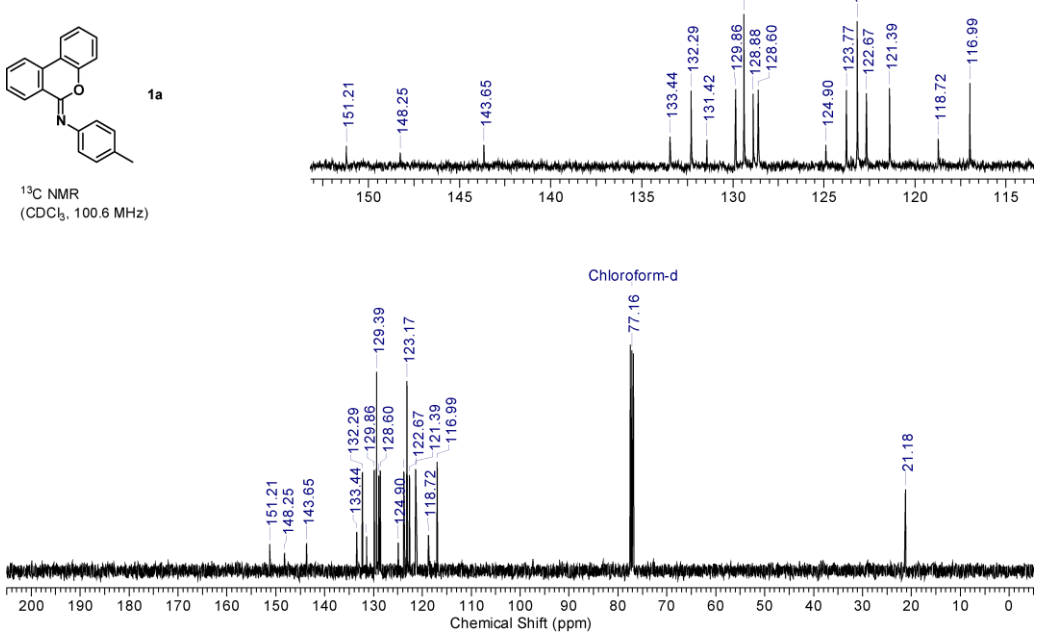
1a

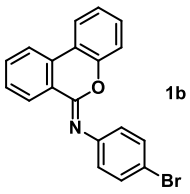
Loading: **Ti/SiO_2** (84 mg, 19 µmol Ti), 3,4-benzocoumarin (76 mg, 0.39 mmol), *N*-sulfinyl-4-methylaniline (55 µL, 0.41 mmol), toluene (3 mL). Reaction time 4 h. Crude product was triturated in heptane, decanted, washed with heptane, and isolated as tan powder after drying in vacuum. Yield 107 mg (96%); mp 104–105 °C. It can also be recrystallized from toluene to give off-white crystals. **IR**: *v* 1643 (C=N). **HRMS (ESI)**: *m/z* calcd for $C_{20}H_{16}NO^+$ $[M+H]^+$ 286.1226; found 286.1226.

^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 8.51 (d, ^3J = 8.0, 1H), 7.97 (d, ^3J = 8.0, 1H), 7.94 (d, ^3J = 8.0, 1H), 7.63 (t, ^3J = 7.6, 1H), 7.48 (t, ^3J = 7.6, 1H), 7.32 (t, ^3J = 7.6, 1H), 7.24–7.17 (m, 5H), 7.09 (d, ^3J = 8.0, 1H), 2.39 (s, 3H, CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): *δ* 151.2 (quat), 148.3 (quat), 143.7 (quat), 133.4 (quat), 132.3 (*C*H), 131.4 (quat), 129.9 (*C*H), 129.4 (*C*H), 128.9 (*C*H), 128.6 (*C*H), 124.9 (quat), 123.8 (*C*H), 123.2 (*C*H), 122.7 (*C*H), 121.4 (*C*H), 118.7 (quat), 117.0 (*C*H), 21.2 (*C*H_3).



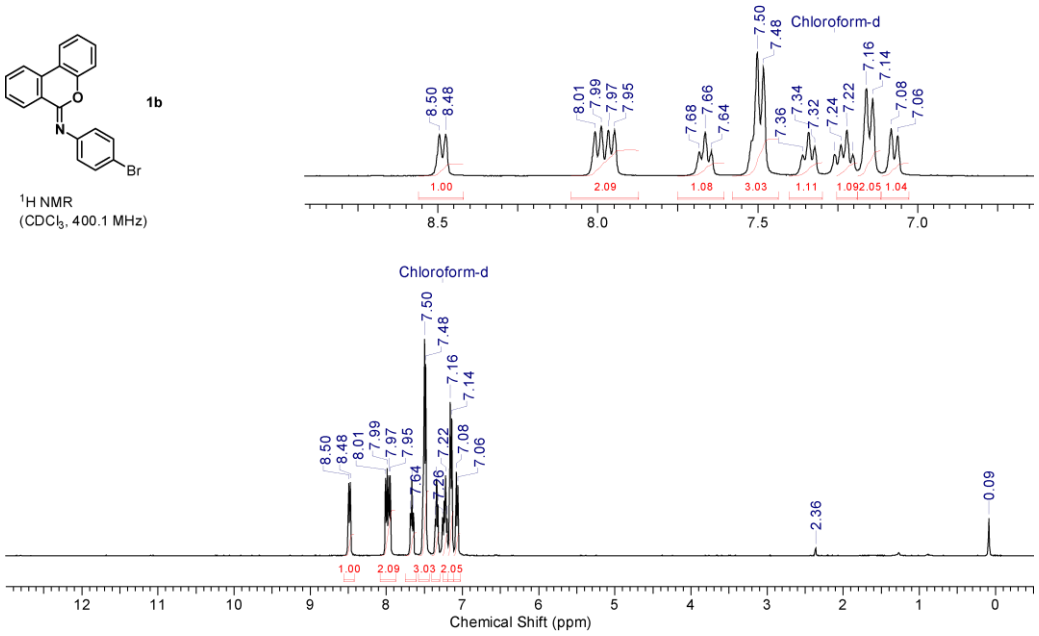


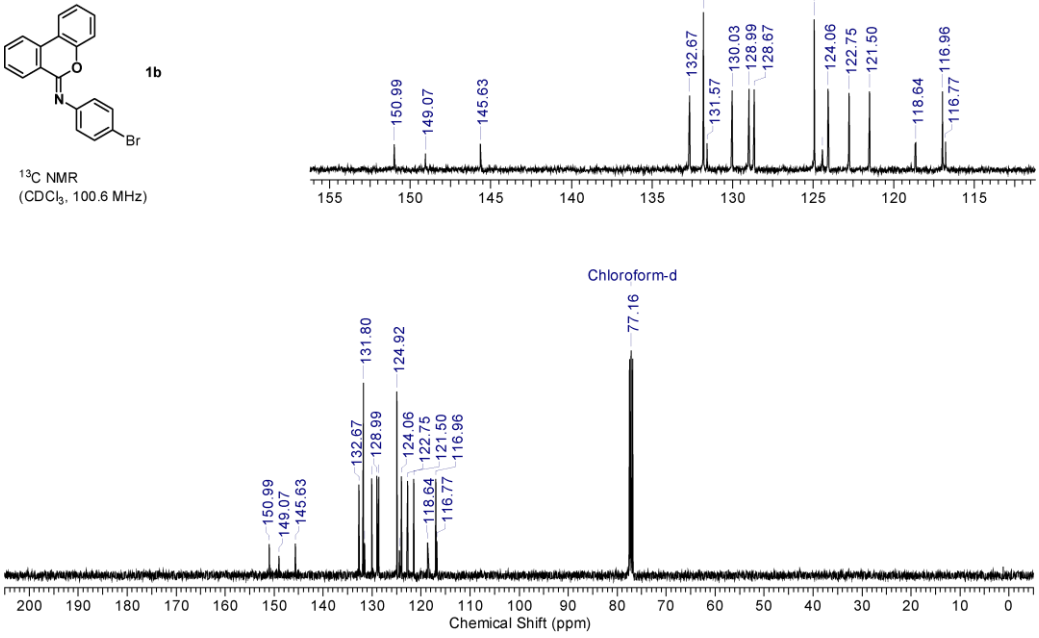


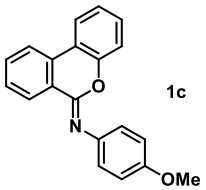
Loading: **Ti/SiO_2** (77 mg, 18 µmol Ti), 3,4-benzocoumarin (70 mg, 0.36 mmol), *N*-sulfinyl-4-bromoaniline (85 mg, 0.39 mmol), toluene (2 mL). Reaction time 2 h. Crude product was triturated in heptane, decanted, washed with heptane, and isolated as yellow powder after drying in vacuum. Yield 121 mg (98%); mp 146–147 °C. It can also be recrystallized from toluene to give orange crystals. **IR**: *v* 1654 (C=N). **HRMS (ESI)**: *m/z* calcd for $C_{19}H_{13}BrNO^+$ $[M+H]^+$ 350.0175; found 350.0171.

^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 8.49 (d, ^3J = 8.0, 1H), 8.00 (d, ^3J = 8.0, 1H), 7.96 (d, ^3J = 7.8, 1H), 7.66 (t, ^3J = 7.6, 1H), 7.52–7.47 (m, 3H), 7.34 (t, ^3J = 7.6, 1H), 7.22 (t, ^3J = 7.6, 1H), 7.15 (d, ^3J = 7.8, 2H), 7.07 (d, ^3J = 8.2, 1H).

^{13}C NMR (100.6 MHz, $CDCl_3$): *δ* 151.0 (quat), 149.1 (quat), 145.6 (quat), 132.7 (*C*H), 131.8 (*C*H), 131.6 (quat), 130.0 (*C*H), 129.0 (*C*H), 128.7 (*C*H), 124.9 (*C*H), 124.4 (quat), 124.1 (*C*H), 122.8 (*C*H), 121.5 (*C*H), 118.6 (quat), 117.0 (*C*H), 116.8 (quat).



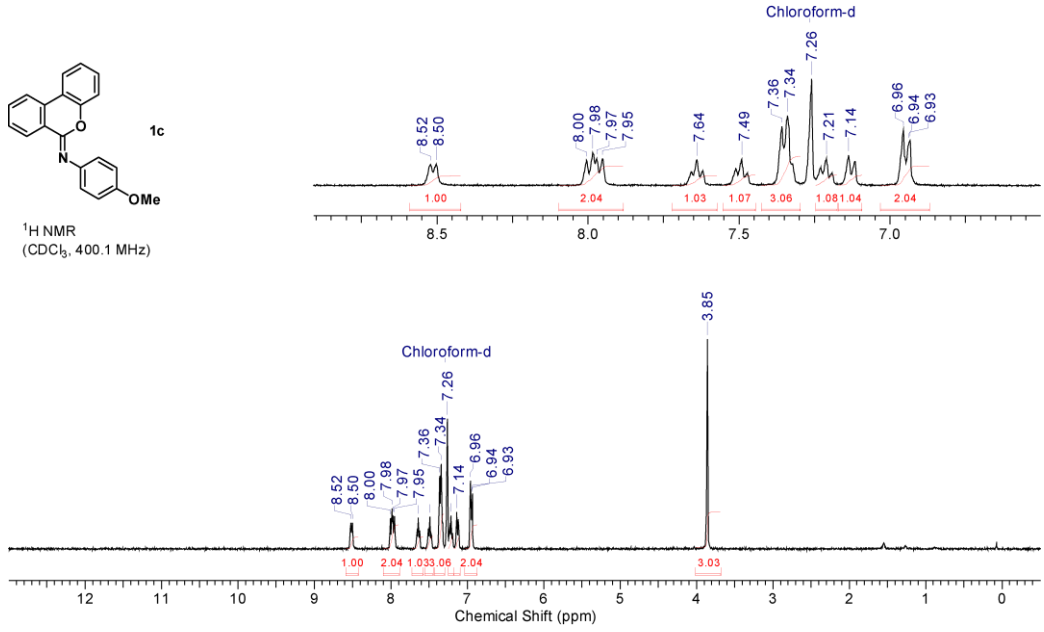


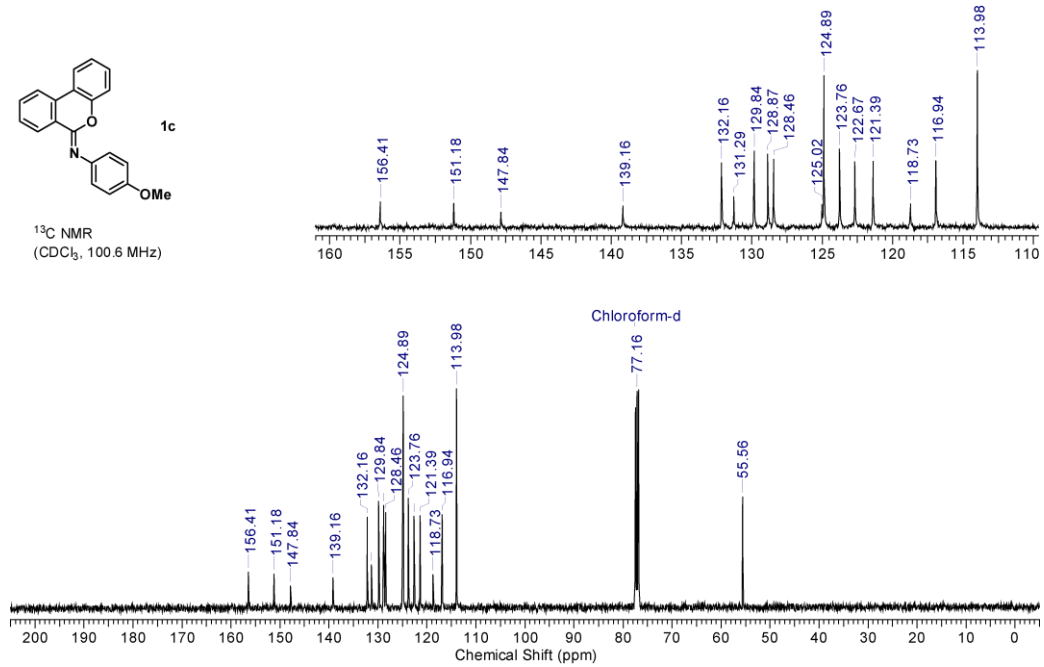


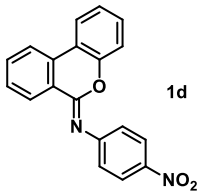
Loading: **Ti/SiO_2** (60 mg, 14 µmol Ti), 3,4-benzocoumarin (54 mg, 0.28 mmol), *N*-sulfinyl-4-methoxyaniline (37 µL, 0.28 mmol), toluene (2 mL). Reaction time 4 h. Crude product was recrystallized from boiling heptane, washed with heptane, and isolated as tan powder after drying in vacuum. Yield 78 mg (94%); mp 99–101 °C. **IR**: *v* 1653 (C=N). **HRMS (ESI)**: *m/z* calcd for $C_{20}H_{16}NO_2^+$ $[M+H]^+$ 302.1176; found 302.1172.

^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 8.51 (d, ^3J = 8.0, 1H), 7.99 (d, ^3J = 8.2, 1H), 7.96 (d, ^3J = 8.0, 1H), 7.64 (t, ^3J = 7.6, 1H), 7.49 (t, ^3J = 7.6, 1H), 7.37–7.32 (m, 3H), 7.21 (t, ^3J = 7.6, 1H), 7.13 (d, ^3J = 8.2, 1H), 6.95 (d, ^3J = 8.7, 2H), 3.85 (s, 3H, OCH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): *δ* 156.4 (quat *C*OMe), 151.2 (quat), 147.8 (quat), 139.2 (quat), 132.2 (*C*H), 131.3 (quat), 129.8 (*C*H), 128.9 (*C*H), 128.5 (*C*H), 125.0 (quat), 124.9 (*C*H), 123.8 (*C*H), 122.7 (*C*H), 121.4 (*C*H), 118.7 (quat), 116.9 (*C*H), 114.0 (*C*H), 55.6 (O*C*H$_3$).



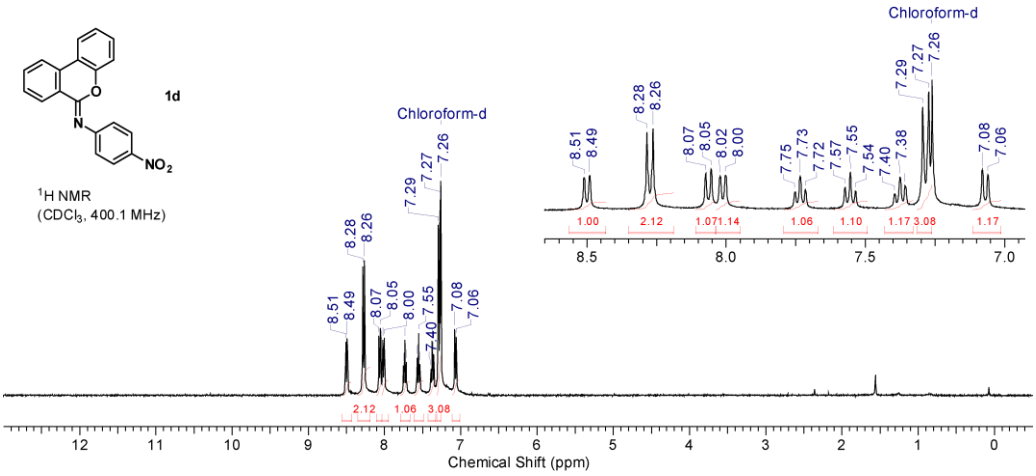


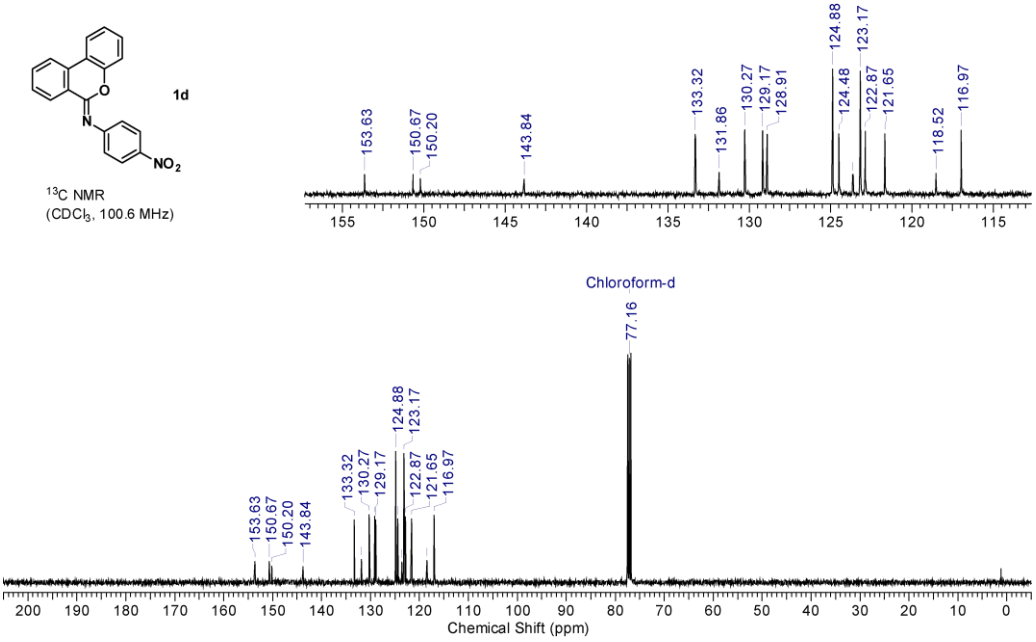


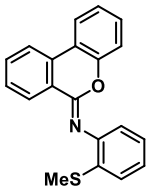
Loading: **Ti/SiO_2** (60 mg, 14 µmol Ti), 3,4-benzocoumarin (54 mg, 0.28 mmol), *N*-sulfinyl-4-nitroaniline (53 mg, 0.29 mmol), toluene (2 mL). Reaction time 4 h. Product precipitates from reaction mixture, after the reaction *ca.* 10 mL of CH_2Cl_2 was added to dissolve it before filtration of the catalyst. The product was further recrystallized from boiling toluene and obtained as bright-orange powder. Yield 71 mg (82%); mp 197–198 °C. **IR**: *v* 1638 (C=N), 1572 (asym NO_2), 1332 (sym NO_2). **HRMS (ESI)**: *m/z* calcd for $C_{19}H_{13}N_2O_3^+$ $[M+H]^+$ 317.0921; found 317.0919.

^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 8.50 (d, ^3J = 7.6, 1H), 8.27 (d, ^3J = 8.9, 2H), 8.06 (d, ^3J = 8.0, 1H), 8.01 (d, ^3J = 8.0, 1H), 7.73 (t, ^3J = 8.0, 1H), 7.55 (t, ^3J = 8.0, 1H), 7.38 (t, ^3J = 8.0, 1H), 7.30–7.25 (m, 3H), 7.07 (d, ^3J = 8.3, 1H).

^{13}C NMR (100.6 MHz, $CDCl_3$): *δ* 153.6 (quat), 150.7 (quat), 150.2 (quat), 143.8 (quat), 133.3 (*C*H), 131.9 (quat), 130.3 (*C*H), 129.2 (*C*H), 128.9 (*C*H), 124.9 (*C*H), 124.5 (*C*H), 123.6 (quat), 123.2 (*C*H), 122.9 (*C*H), 121.7 (*C*H), 118.5 (quat), 117.0 (*C*H).





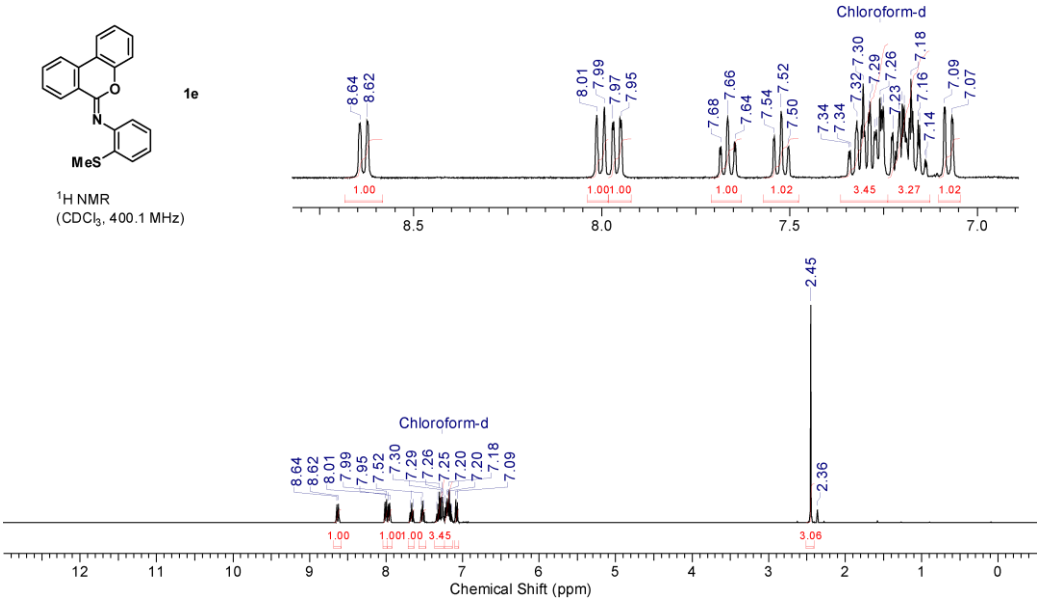


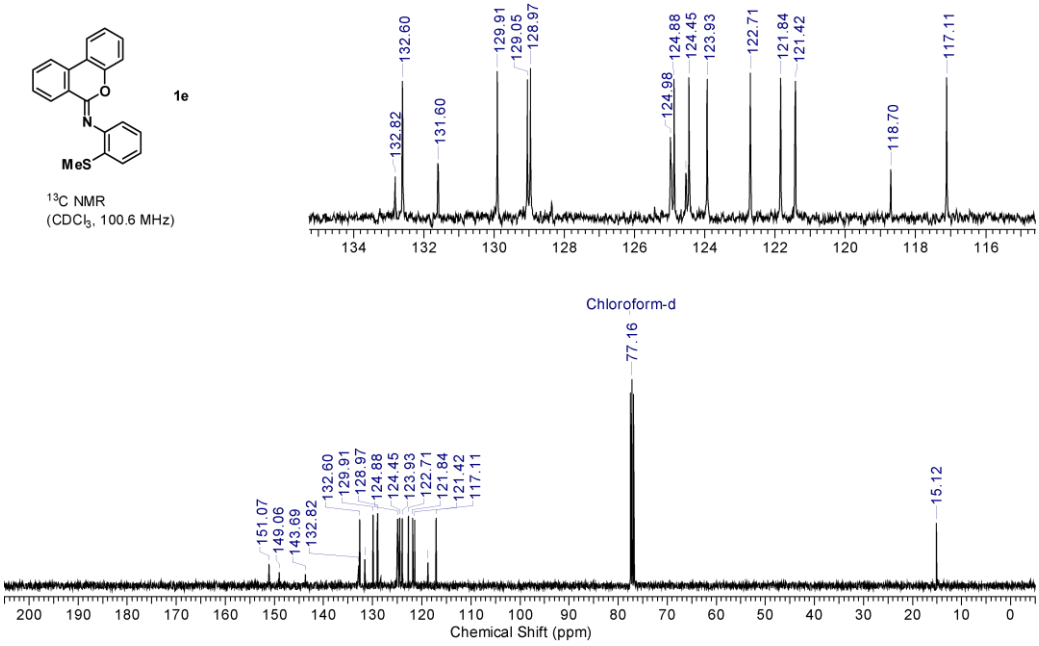
1e

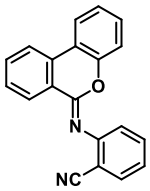
Loading: **Ti/SiO_2** (74 mg, 17 µmol Ti), 3,4-benzocoumarin (67 mg, 0.34 mmol), *N*-sulfinyl-2-methylthioaniline (63 mg, 0.34 mmol), toluene (2 mL). Reaction time 6 h. Crude product was recrystallized from toluene, washed with heptane, and isolated as red crystals after drying in vacuum. Yield 76 mg (70%); mp 148–150 °C. **IR**: *v* 1641 (C=N). **HRMS (ESI)**: *m/z* calcd for $C_{20}H_{16}NOS^+$ $[M+H]^+$ 318.0947; found 318.0952.

^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 8.63 (d, ^3J = 8.0, 1H), 8.00 (d, ^3J = 8.0, 1H), 7.96 (d, ^3J = 8.0, 1H), 7.66 (t, ^3J = 7.6, 1H), 7.52 (t, ^3J = 7.6, 1H), 7.34–7.25 (m, 3H), 7.23–7.14 (m, 3H), 7.08 (d, ^3J = 8.2, 1H), 2.45 (s, 3H, SCH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): *δ* 151.1 (quat), 149.1 (quat), 143.7 (quat), 132.8 (quat), 132.6 (*C*H), 131.6 (quat), 129.9 (*C*H), 129.1 (*C*H), 129.0 (*C*H), 125.0 (*C*H), 124.9 (*C*H), 124.5 (quat), 124.4 (*C*H), 123.9 (*C*H), 122.7 (*C*H), 121.8 (*C*H), 121.4 (*C*H), 118.7 (quat), 117.1 (*C*H), 15.1 (S*C*H_3).





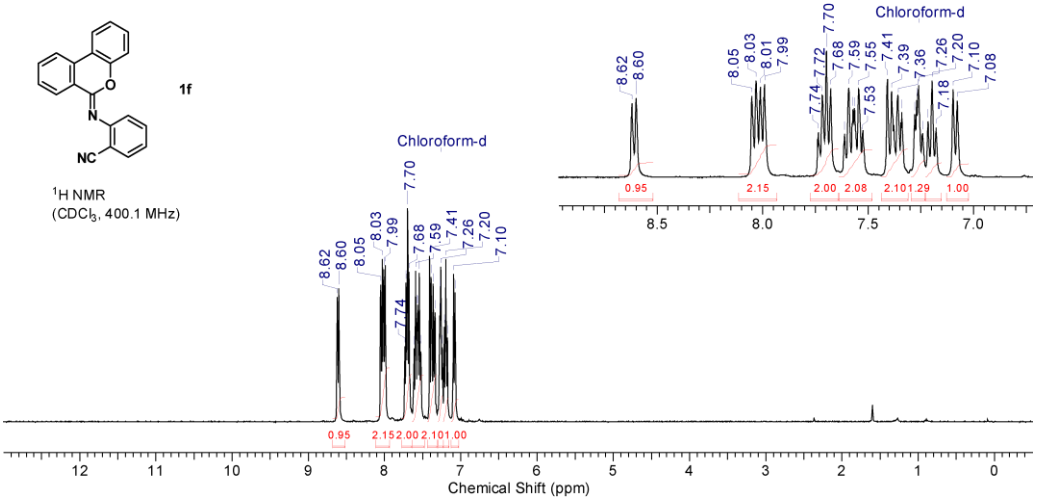


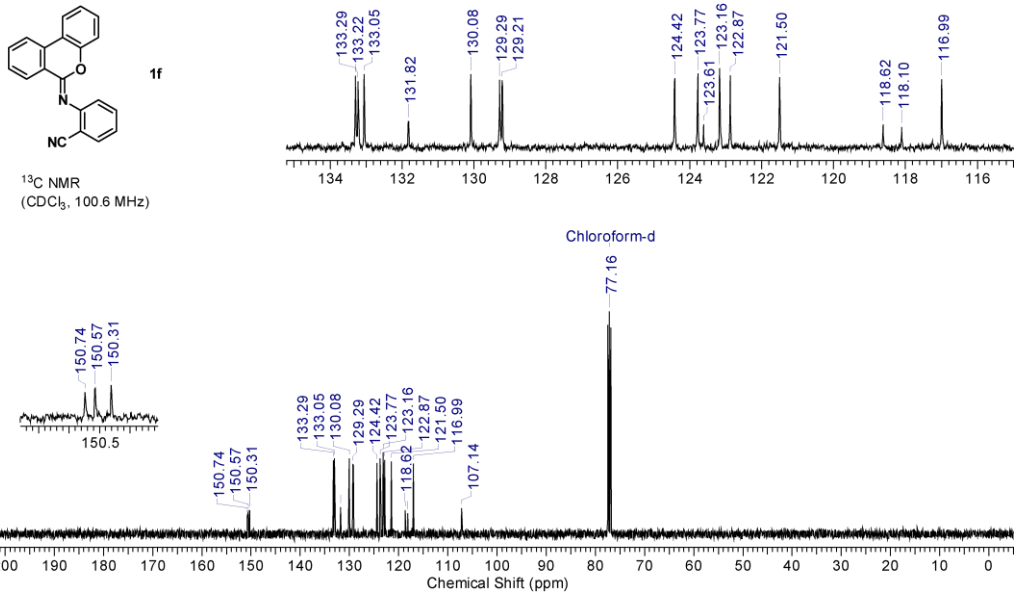
1f

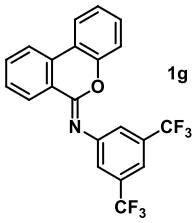
Loading: **Ti/SiO$_2$** (121 mg, 28 µmol Ti), 3,4-benzocoumarin (109 mg, 0.56 mmol), *N*-sulfinyl-2-aminobenzonitrile (91 mg, 0.55 mmol), toluene (4 mL). Reaction time 12 h. The product was isolated as pale orange crystals in several crops by recrystallization from toluene. Yield 144 mg (87%); mp 136–137 °C. **IR**: *v* 2225 (C≡N), 1647 (C=N). **HRMS (ESI)**: *m/z* calcd for $C_{20}H_{13}N_2O^+$ $[M+H]^+$ 297.1022; found 297.1022.

^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 8.61 (d, ^3J = 8.0, 1H), 8.06 (d, ^3J = 8.2, 1H), 8.00 (d, ^3J = 8.0, 1H), 7.74–7.68 (m, 2H), 7.61–7.53 (m, 2H), 7.41–7.34 (m, 2H), 7.28–7.24 (m, 1H), 7.20 (t, ^3J = 7.6, 1H), 7.09 (d, ^3J = 8.2, 1H).

^{13}C NMR (100.6 MHz, $CDCl_3$): *δ* 150.7 (quat), 150.6 (quat), 150.3 (quat), 133.3 (*C*H), 133.2 (*C*H), 133.1 (*C*H), 131.8 (quat), 130.1 (*C*H), 129.3 (*C*H), 129.2 (*C*H), 124.4 (*C*H), 123.8 (*C*H), 123.6 (quat), 123.2 (*C*H), 122.9 (*C*H), 121.5 (*C*H), 118.6 (quat), 118.1 (quat), 117.0 (*C*H), 107.1 (quat).





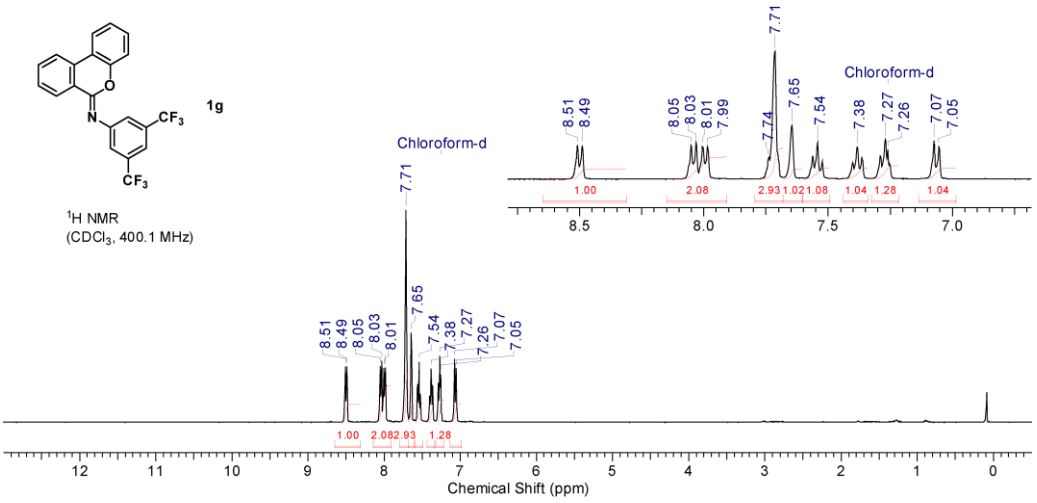


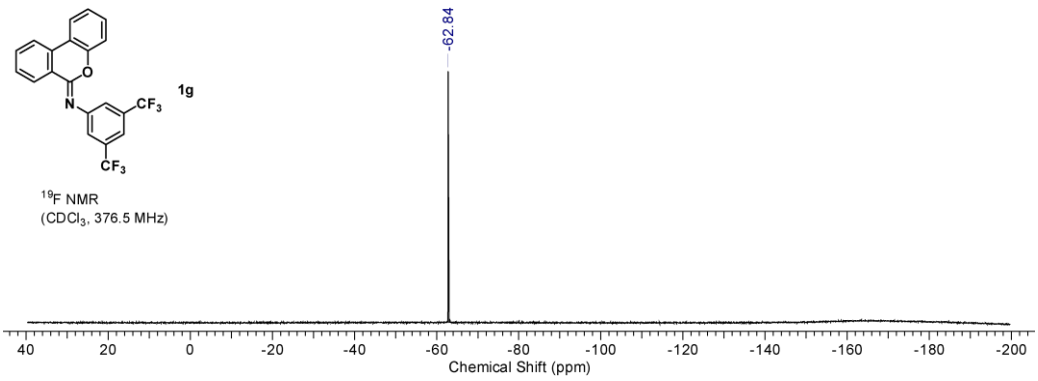
Loading: **Ti/SiO_2** (92 mg, 21 µmol Ti), 3,4-benzocoumarin (83 mg, 0.42 mmol), *N*-sulfinyl-3,5-*bis*(trifluoromethyl)aniline (86 µL, 0.42 mmol), toluene (3 mL). Reaction time 4 h. Crude product was triturated in heptane, decanted, washed with heptane, and isolated as brown crystals after drying in vacuum. Yield 126 mg (73%); mp 133–134 °C. **IR**: *v* 1645 (C=N). **HRMS (ESI)**: *m/z* calcd for $C_{21}H_{12}F_6NO^+$ $[M+H]^+$ 408.0818; found 408.0815.

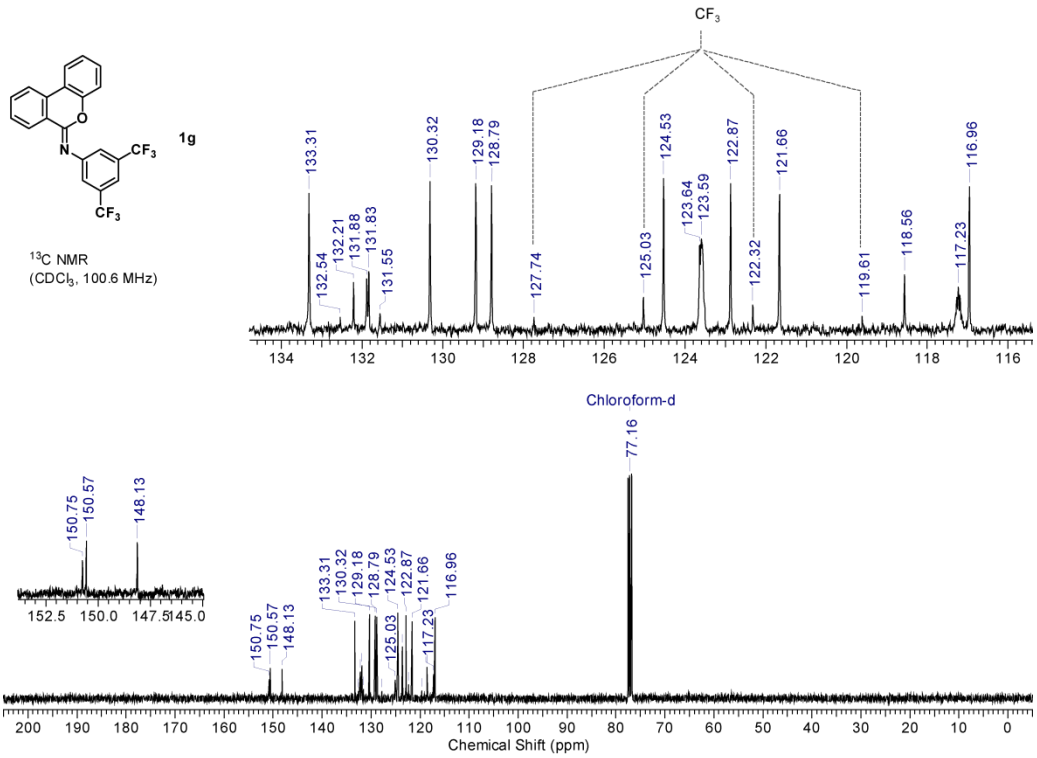
^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 8.50 (d, ^3J = 8.0, 1H), 8.04 (d, ^3J = 8.0, 1H), 8.00 (d, ^3J = 8.0, 1H), 7.73 (t, ^3J = 7.3, 1H), 7.71 (s, 2H, *o*-$C_6H_3(CF_3)_2$), 7.65 (s, 1H, *p*-$C_6H_3(CF_3)_2$), 7.54 (t, ^3J = 7.3, 1H), 7.38 (t, ^3J = 8.0, 1H), 7.27 (t, ^3J = 8.0, 1H), 7.06 (d, ^3J = 8.2, 1H).

^{13}C NMR (100.6 MHz, $CDCl_3$): *δ* 150.8 (quat), 150.6 (quat), 148.1 (quat), 133.3 (*C*H), 132.0 (q, $^2J_{CF}$ = 33.0, quat *C*CF_3), 131.8 (quat), 130.3 (*C*H), 129.2 (*C*H), 128.8 (*C*H), 124.5 (*C*H), 123.7 (q, $^1J_{CF}$ = 272, *C*F_3), 123.6 (quat), 123.6 (m, *o*-$C_6H_3(CF_3)_2$), 122.9 (*C*H), 121.7 (*C*H), 118.6 (quat), 117.2 (sept, $^3J_{CF}$ ~4, *p*-$C_6H_3(CF_3)_2$), 117.0 (*C*H).

^{19}F NMR (376.5 MHz, $CDCl_3$): *δ* −62.84.



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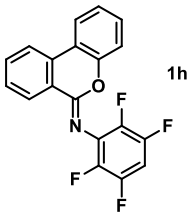
^{13}C NMR
($CDCl_3$, 100.6 MHz)
CF3
133.31
132.54
132.21
131.88
131.83
131.55
130.32
129.18
128.79
127.74
125.03
124.53
123.64
123.59
122.87
122.32
121.66
119.61
118.56
117.23
116.96
Chloroform-d
77.16
150.75
150.57
148.13
125.03
117.23
Chemical Shift (ppm)

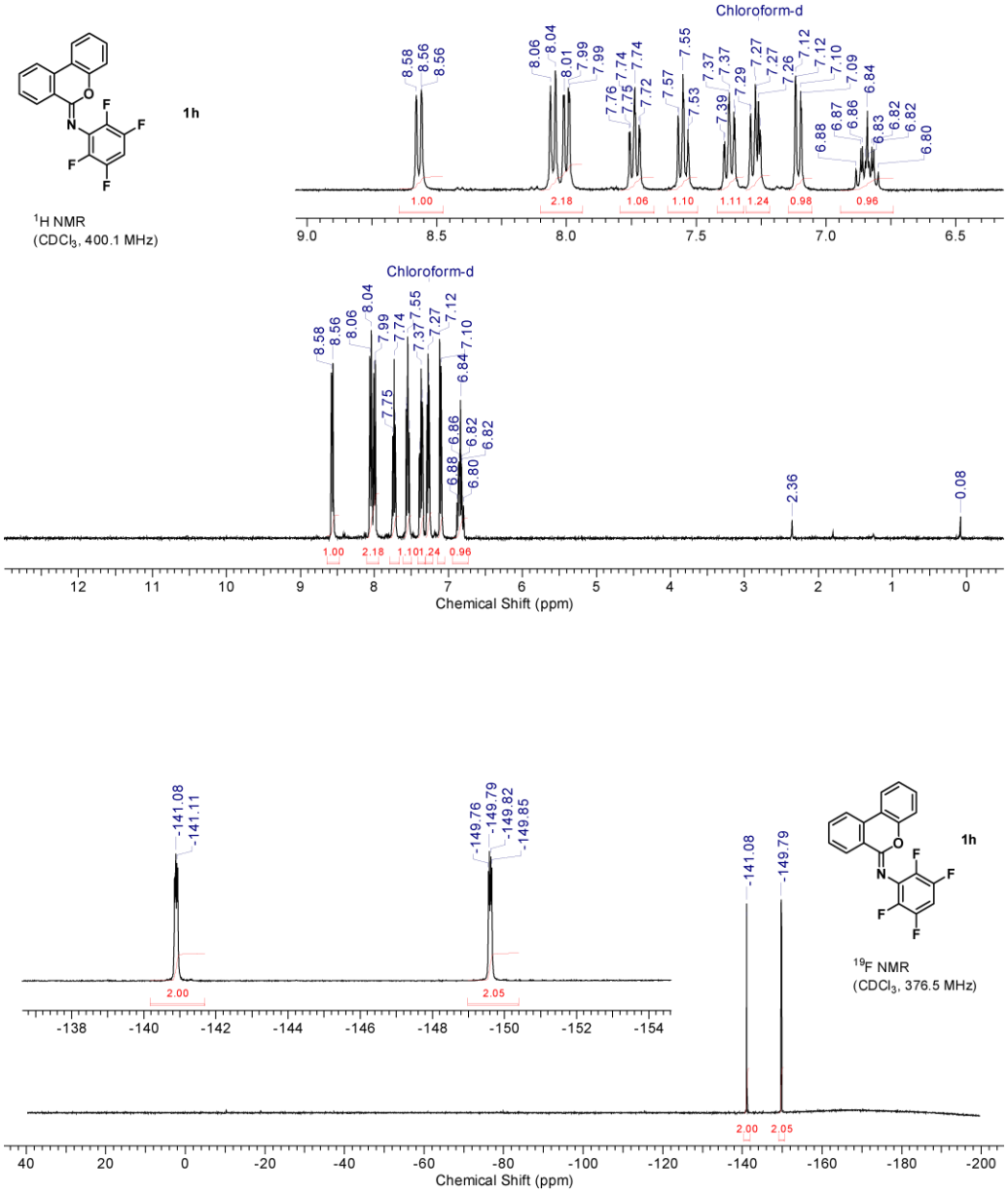


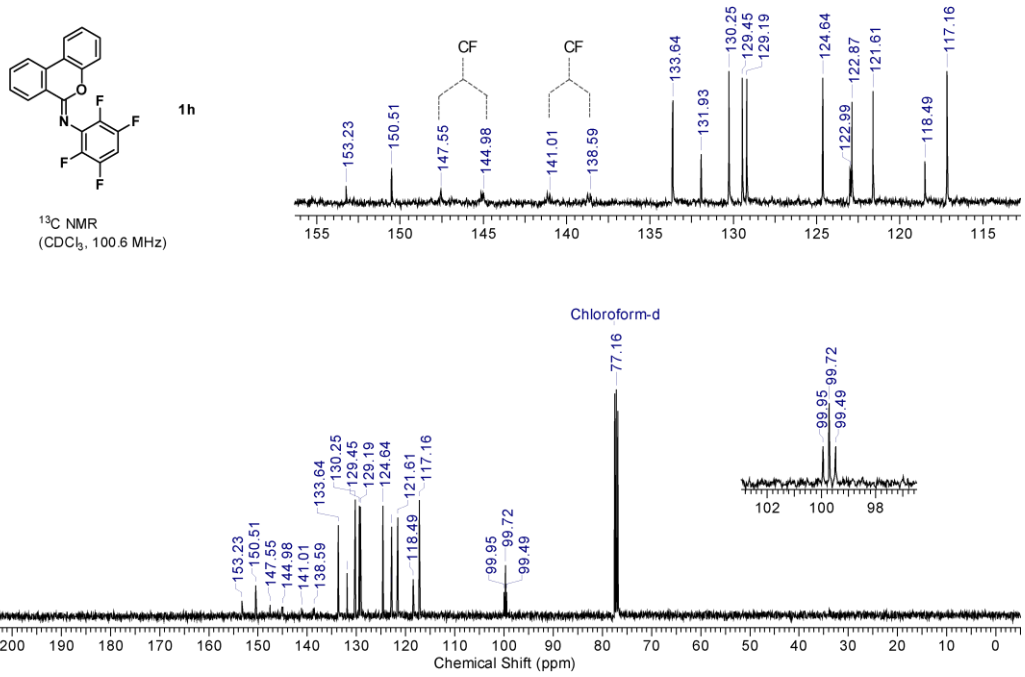
Loading: **Ti/SiO$_2$** (50 mg, 12 µmol Ti), 3,4-benzocoumarin (47 mg, 0.24 mmol), *N*-sulfinyl-2,3,5,6-tetrafluoroaniline (37 µL, 0.28 mmol), toluene (2 mL). Reaction time 6 h. Crude product was triturated in heptane, decanted, washed with heptane, and isolated as off-white powder after drying in vacuum. Yield 59 mg (72%); mp 165–166 °C. **IR**: two bands are observed in the C=N region at *ν* 1658 (likely C=N) and 1634 (probably due to aromatic ring stretching vibrations). **HRMS (ESI)**: *m/z* calcd for $C_{19}H_{10}F_4NO^+$ $[M+H]^+$ 344.0693; found 344.0689.

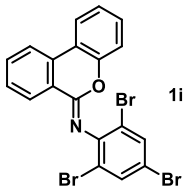
^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 8.57 (d, ^3J = 8.0, 1H), 8.05 (d, ^3J = 8.0, 1H), 8.00 (d, ^3J = 8.0, 1H), 7.74 (t, ^3J = 7.6, 1H), 7.55 (t, ^3J = 7.6, 1H), 7.37 (t, ^3J = 7.6, 1H), 7.27 (t, ^3J = 7.6, 1H), 7.11 (d, ^3J = 8.2, 1H), 6.84 (tt, $^3J_{HF}$ = 10.0, $^4J_{HF}$ = 7.0, 1H, C_6F_4H).

^{13}C NMR (100.6 MHz, $CDCl_3$): *δ* 153.2 (quat), 150.5 (quat), 146.3 (d, $^1J_{CF}$ ~245, quat *C*F), 139.8 (d, $^1J_{CF}$ ~245, quat *C*F), 133.6 (*C*H), 131.9 (quat), 130.3 (*C*H), 129.5 (*C*H), 129.2 (*C*H), 124.6 (*C*H), 123.0 (quat), 122.9 (*C*H), 121.6 (*C*H), 118.5 (quat), 117.2 (*C*H), 99.7 (t, $^2J_{CF}$ = 23.5, *p*-C_6F_4H); quat *C*–N difficult to assign.

^{19}F NMR (376.5 MHz, $CDCl_3$): *δ* −141.10 (dd, $^{3,5}J_{FF}$ = 11, 2F), −149.80 (dd, $^{3,5}J_{FF}$ = 11, 2F).




1h
^{13}C NMR
($CDCl_3$, 100.6 MHz)
CF
CF
153.23
150.51
147.55
144.98
141.01
138.59
133.64
131.93
130.25
129.45
129.19
124.64
122.87
121.61
122.99
118.49
117.16
Chloroform-d
77.16
99.95
99.72
99.49
Chemical Shift (ppm)

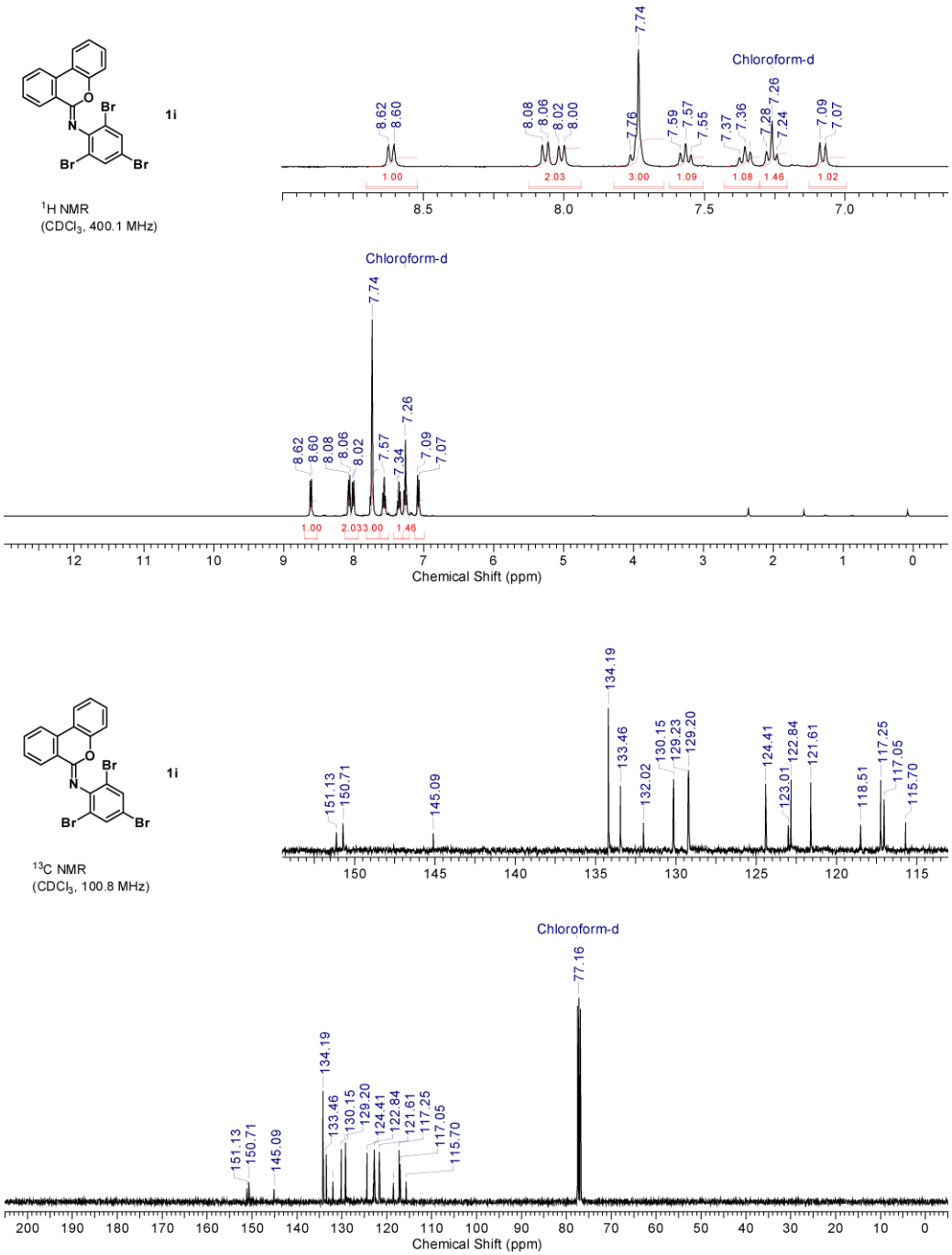


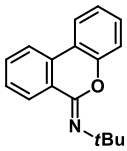
1i

Loading: **Ti/SiO$_2$** (78 mg, 18 µmol Ti), 3,4-benzocoumarin (71 mg, 0.36 mmol), *N*-sulfinyl-2,4,6-tribromoaniline (135 mg, 0.36 mmol), toluene (2 mL). Reaction time 24 h. Crude product was triturated in heptane, decanted, washed with heptane, and then recrystallized from toluene to give yellow-orange crystals. Yield 127 mg (70%); mp 187–189 °C. **IR**: *v* 1653 (C=N). **HRMS (ESI)**: *m/z* calcd for $C_{19}H_{11}Br_3NO^+$ $[M+H]^+$ 505.8385; found 505.8387.

^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 8.61 (d, ^3J = 8.0, 1H), 8.07 (d, ^3J = 8.0, 1H), 8.01 (d, ^3J = 8.0, 1H), 7.75 (t, ^3J = 8.0, 1H), 7.74 (s, 2H, $C_6H_2Br_3$), 7.57 (t, ^3J = 7.6, 1H), 7.36 (t, ^3J = 7.3, 1H), 7.26 (t, ^3J = 7.5, 1H), 7.08 (d, ^3J = 8.3, 1H).

^{13}C NMR (100.6 MHz, $CDCl_3$): *δ* 151.1 (quat), 150.7 (quat), 145.1 (quat), 134.2 (*C*H), 133.5 (quat), 132.0 (quat), 130.2 (*C*H), 129.2 (2x*C*H), 124.4 (*C*H), 123.0 (quat), 122.8 (*C*H), 121.6 (*C*H), 118.5 (quat), 117.3 (*C*H), 117.1 (*C*H), 115.7 (quat).





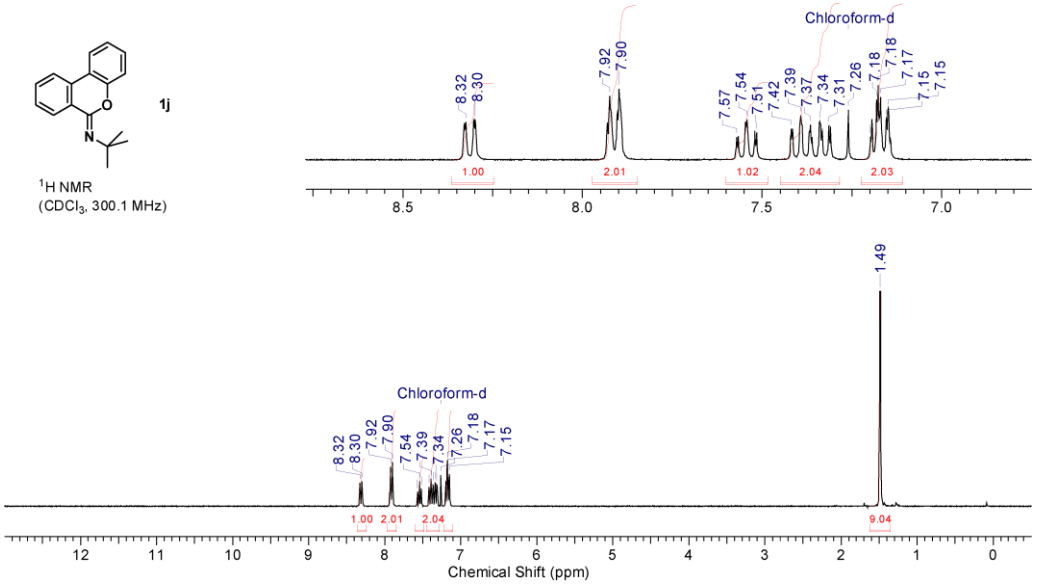
1j

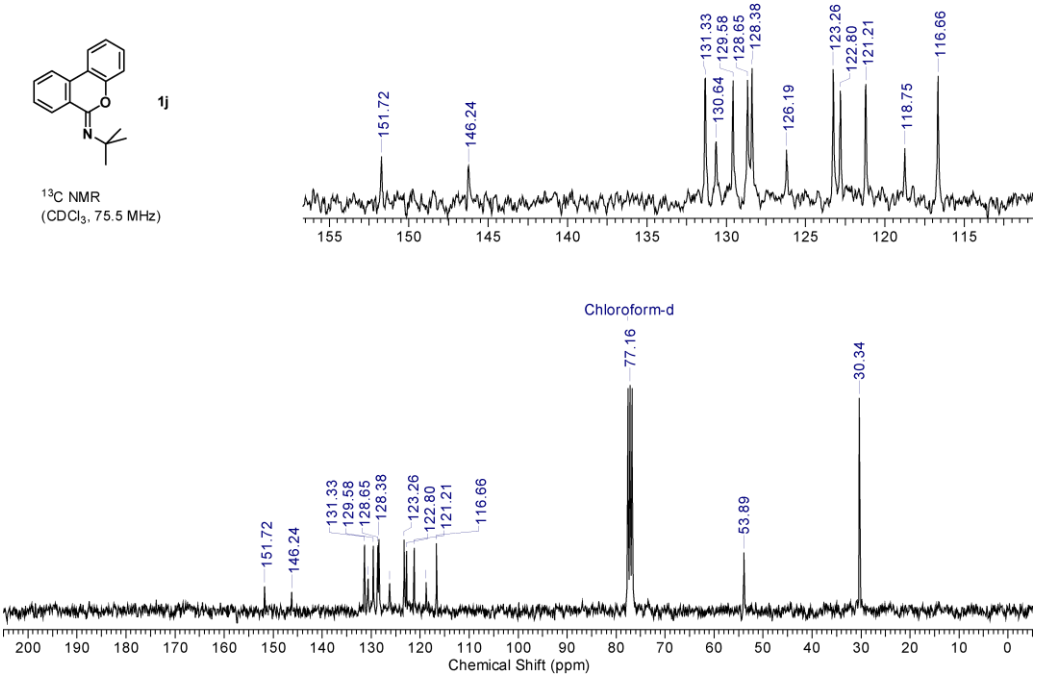
Loading: **Ti/SiO$_2$** (143 mg, 33 µmol Ti), 3,4-benzocoumarin (65 mg, 0.33 mmol), di-*tert*-butylsulfurdiimine (60 µL, 0.33 mmol), toluene (2.5 mL). Reaction time 3 days. Conversion *ca.* 80% (GC). The product was purified by column chromatography on silica (eluent: petr. ether – ethyl acetate (5:1) with 3% NEt_3 to prevent hydrolysis on silica) to afford colorless liquid that solidifies at RT into white waxy solid. Yield 40 mg (48%); mp 53–54 °C. **IR**: *v* 1666 (C=N) with a shoulder at 1645. **HRMS (ESI)**: *m/z* calcd for $C_{17}H_{18}NO^+$ $[M+H]^+$ 252.1383; found 252.1390.

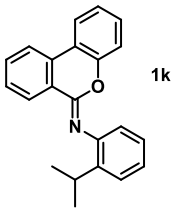
^{1}H NMR (300.1 MHz, $CDCl_3$): *δ* 8.31 (dd, ^3J = 7.9, ^4J = 1.0, 1H), 7.91 (apparent d, ^3J = 8.0, 2H), 7.54 (td, ^3J = 7.6, ^4J = 1.4, 1H), 7.42–7.31 (m, 2H), 7.20–7.14 (m, 2H), 1.49 (s, 9H, NC*Me$_3$*).

^{1}H NMR (400.1 MHz, C_6D_6): *δ* 8.61 (dd, ^3J = 8.0, ^4J = 1.0, 1H), 7.48 (d, ^3J = 7.7, 1H), 7.44 (d, ^3J = 7.7, 1H), 7.09 (t, ^3J = 7.7, ^4J = 1.6, 1H), 7.04 (t, ^3J = 7.7, 1H), 6.95 (t, ^3J = 7.7, 1H), 6.86 (d, ^3J = 8.2, 1H), 6.83 (t, ^3J = 7.7, 1H), 1.63 (s, 9H, NC*Me$_3$*).

^{13}C NMR (75.5 MHz, $CDCl_3$): *δ* 151.7 (quat), 146.2 (quat), 131.3 (*C*H), 130.6 (quat), 129.6 (*C*H), 128.7 (*C*H), 128.4 (*C*H), 126.2 (quat), 123.3 (*C*H), 122.8 (*C*H), 121.2 (*C*H), 118.8 (quat), 116.7 (*C*H), 53.9 (N*C*Me$_3$), 30.3 (NC*Me$_3$*).



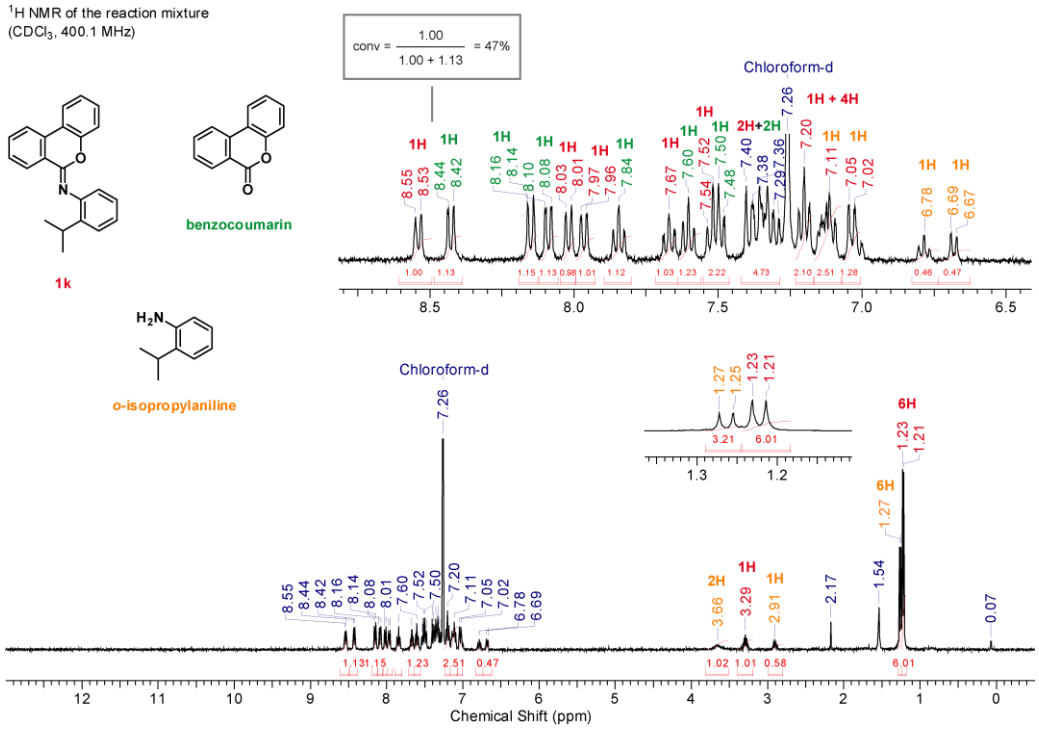


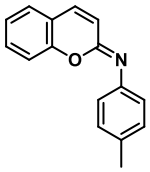


Loading: **Ti/SiO_2** (92 mg, 21 µmol Ti), 3,4-benzocoumarin (83 mg, 0.42 mmol), *N*-sulfinyl-2-isopropylaniline (70 µL, 0.42 mmol), toluene (3 mL).

After 24 h of reaction GC conversion was *ca.* 50% (based on consumption of lactone).

The reaction mixture was filtered from the catalyst and an aliquot was analysed with ^{1}H NMR. The conversion of 3,4-benzocoumarin into imidate was estimated as 47% (the remaining *N*-sulfinylamine hydrolysed to aniline as the workup and sample preparation was performed in air; low aniline content in the spectrum is due to its partial evaporation during drying the aliquot in vacuum; 3,4-benzocoumarin is not volatile under these conditions).





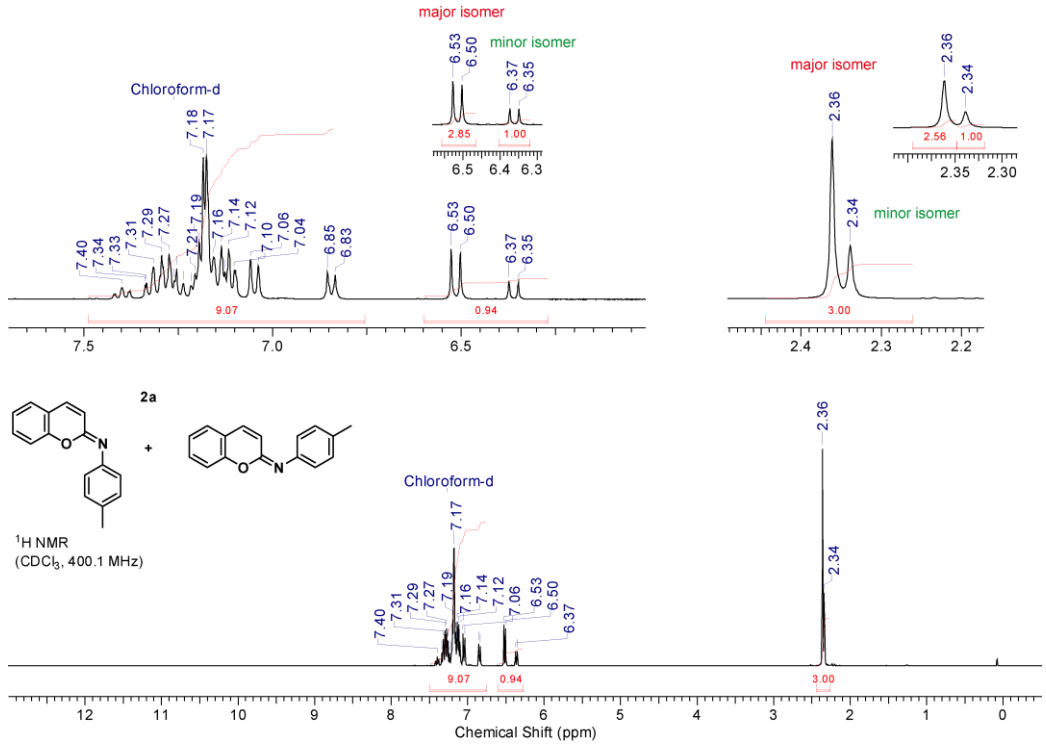
2a

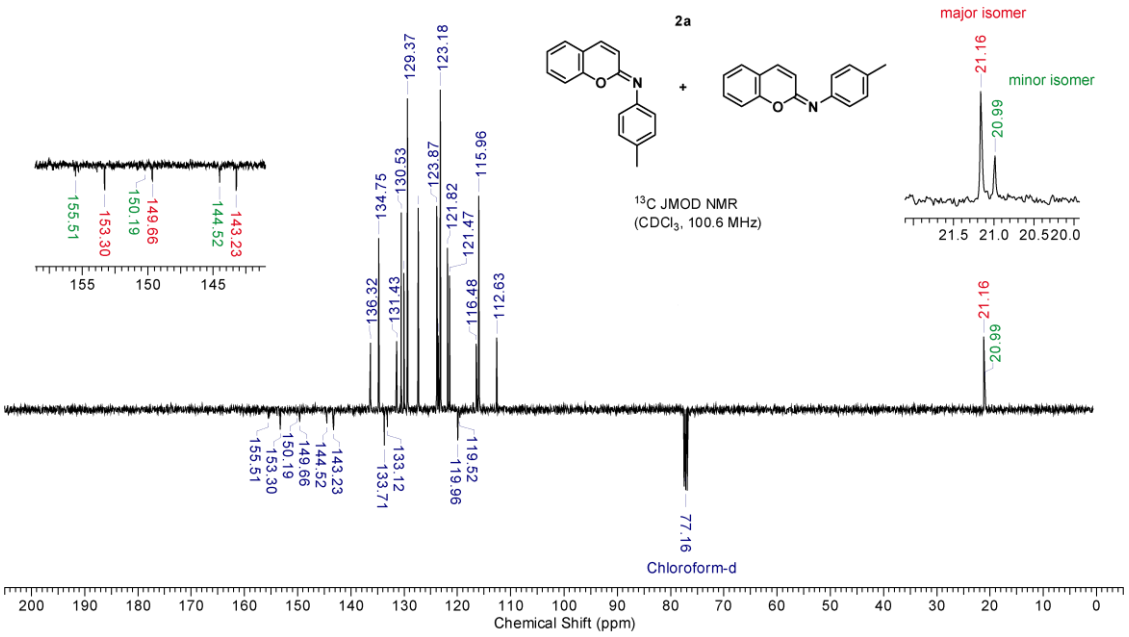
Loading: **Ti/SiO$_2$** (60 mg, 14 µmol Ti), coumarin (40 mg, 0.27 mmol), *N*-sulfinyl-4-methylaniline (45 µL, 0.33 mmol), toluene (3 mL). Reaction time 2 h. Crude product was triturated in petr. ether, decanted, washed with petr. ether, and isolated as yellow-orange powder after drying in vacuum. Yield 50 mg (78%); mp 71–72 °C. It can be recrystallized from toluene to give yellow crystals. **IR**: *v* 1638 (C=N). **HRMS (ESI)**: *m/z* calcd for $C_{16}H_{14}NO^+$ $[M+H]^+$ 236.1070; found 236.1069. **EA:** found (calcd for $C_{16}H_{13}NO$, %): C, 81.59 (81.68); H, 5.91 (5.57); N, 5.68 (5.95).

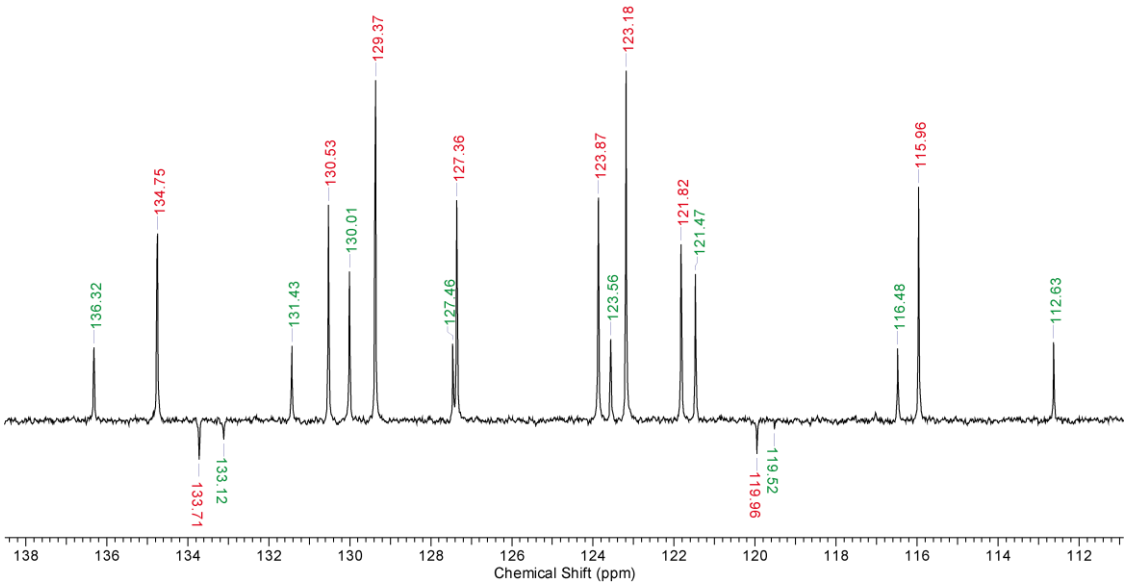
The identity of the compound is confirmed by the presence of a single molecular ion in HRMS and by elemental analysis. NMR spectra indicate that it is a mixture of *E* and *Z* isomers. Although the resonances corresponding to each isomer cannot be fully resolved in ^{1}H spectrum (based on the *p*-CH_3 groups the amount of minor isomer is *ca.* 30%), two sets of signals that can be assigned to major and minor isomers are observed in ^{13}C spectrum, each carbon atom being represented by a pair of signals.

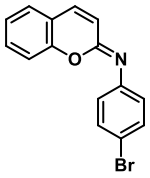
^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 7.45–7.00 (m, 9H), 6.51 and 6.36 (2 doublets, ^4J = 9.9, 1H in total), 2.36 and 2.34 (2 singlets, 3H in total).

^{13}C NMR (100.6 MHz, $CDCl_3$). Major isomer: *δ* 153.3 (quat), 149.7 (quat), 143.2 (quat), 134.8 (*C*H), 133.7 (quat), 130.5 (*C*H), 129.4 (*C*H), 127.4 (*C*H), 123.9 (*C*H), 123.2 (*C*H), 121.8 (*C*H), 120.0 (quat), 116.0 (*C*H), 21.2 (CH_3). Minor isomer: *δ* 155.5 (quat), 150.2 (quat), 144.5 (quat), 136.3 (*C*H), 133.1 (quat), 131.4 (*C*H), 130.0 (*C*H), 127.5 (*C*H), 123.6 (*C*H), 121.5 (*C*H), 119.5 (quat), 116.5 (*C*H), 112.6 (*C*H), 21.0 (CH_3).




2a
major isomer
minor isomer
^{13}C JMOD NMR
($CDCl_3$, 100.6 MHz)
Chloroform-d
Chemical Shift (ppm)


Chemical Shift (ppm)

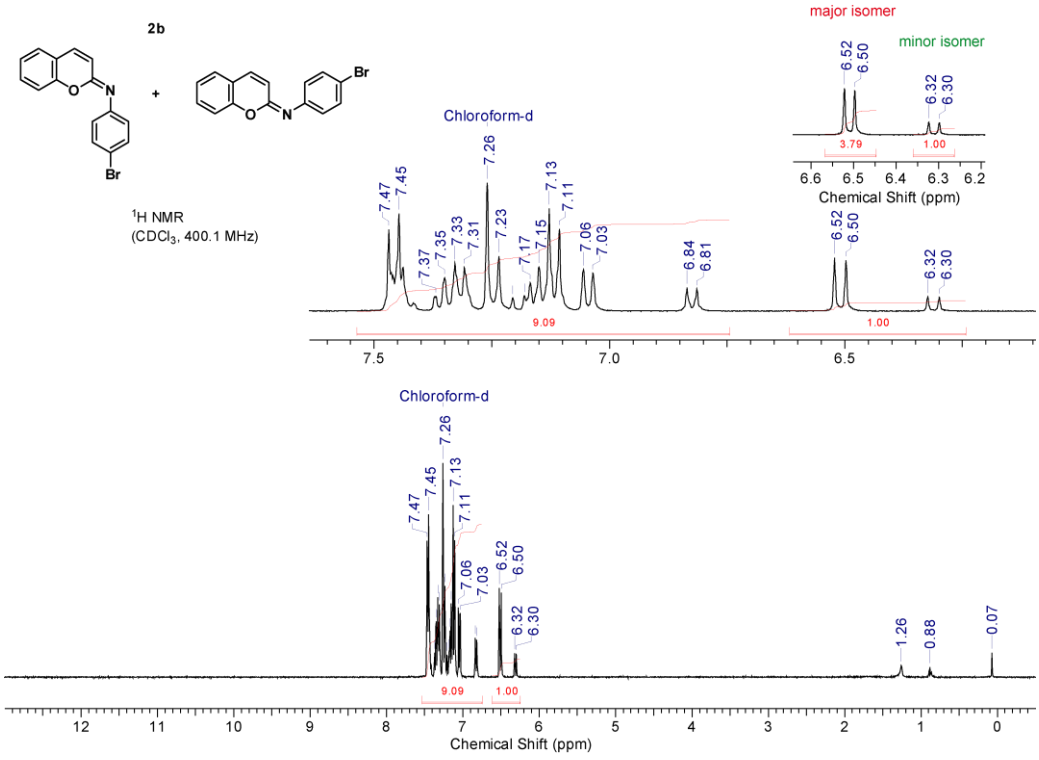


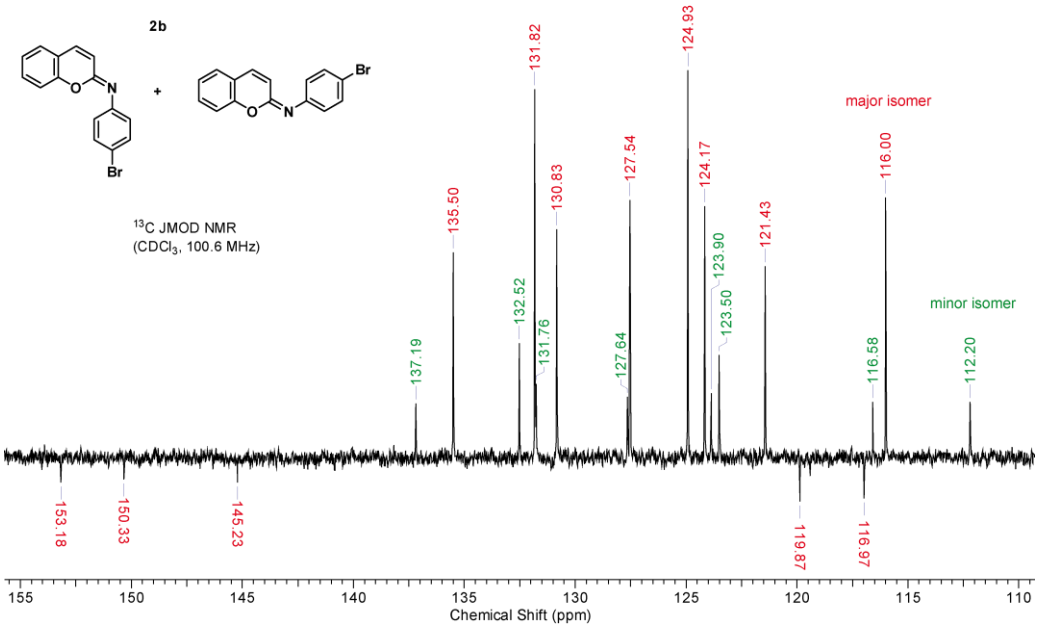
2b Loading: **Ti/SiO_2** (42 mg, 10 µmol Ti), coumarin (28 mg, 0.19 mmol), *N*-sulfinyl-4-bromoaniline (52 mg, 0.24 mmol), toluene (1 mL). Reaction time 2 h. Crude product was triturated in heptane, decanted, washed with heptane, and isolated as yellow powder after drying in vacuum. Yield 55 mg (96%); mp 117–118 °C. **IR**: *v* 1650 (C=N). **HRMS (ESI)**: *m/z* calcd for $C_{15}H_{11}BrNO^+$ $[M+H]^+$ 300.0019; found 300,0015.

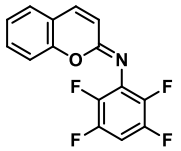
The identity of the compound is confirmed by the presence of a single molecular ion in HRMS. Similarly to **2a** the compound is a mixture of *E* and *Z* isomers (the amount of minor isomer is *ca.* 20%). Two sets of signals are observed in ^{13}C spectrum, however only for the main isomer all the resonances can be identified, while for the minor isomer quaternary carbons could not be observed due to its low abundance.

^1H NMR (400.1 MHz, $CDCl_3$): *δ* 7.50–6.80 (m, 9H), 6.51 and 6.31 (2 doublets, ^4J = 9.7 and 9.8, 1H in total).

^{13}C NMR (100.6 MHz, $CDCl_3$). Major isomer: *δ* 153.2 (quat), 150.3 (quat), 145.2 (quat), 135.5 (*C*H), 131.6 (*C*H), 130.8 (*C*H), 127.5 (*C*H), 124.9 (*C*H), 124.2 (*C*H), 121.4 (*C*H), 119.9 (quat), 117.0 (quat), 116.0 (*C*H). Minor isomer (only *C*H): *δ* 137.2, 132.5, 131.8, 127.6, 123.9, 123.5, 116.6, 112.2.




2b
Br
Br
^{13}C JMOD NMR
($CDCl_3$, 100.6 MHz)
major isomer
minor isomer
131.82
124.93
127.54
124.17
116.00
135.50
130.83
121.43
123.90
132.52
123.50
131.76
137.19
127.64
116.58
112.20
153.18
150.33
145.23
116.87
116.97
155
150
145
140
135
130
125
120
115
110
Chemical Shift (ppm)



2h

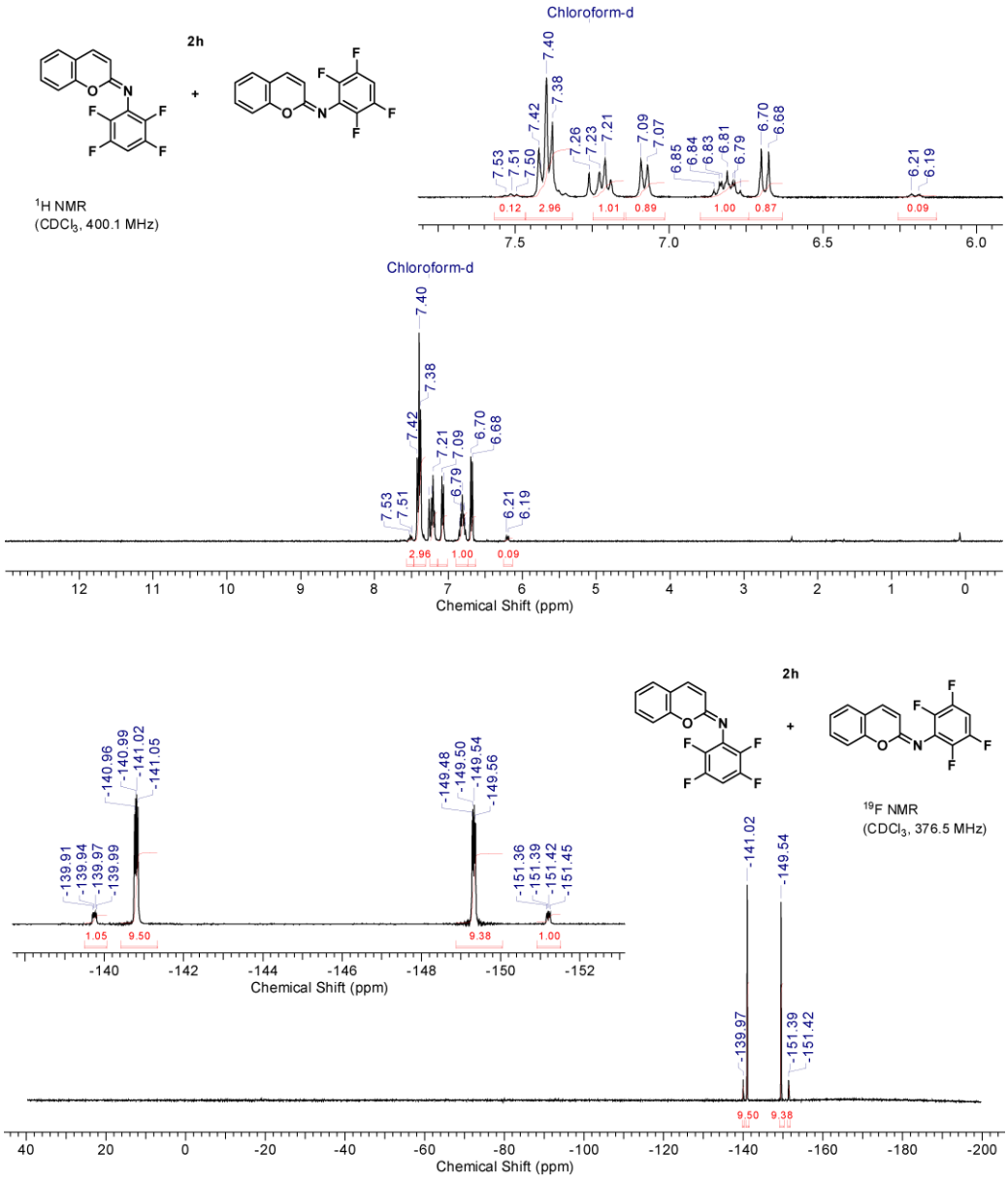
Loading: **Ti/SiO$_2$** (71 mg, 16 µmol Ti), coumarin (48 mg, 0.33 mmol), *N*-sulfinyl-2,3,5,6-tetrafluoroaniline (50 µL, 0.38 mmol), toluene (3 mL). Reaction time 2 h. Crude product was triturated in heptane, decanted, washed with heptane, and isolated as pale yellow-orange powder after drying in vacuum. Yield 92 mg (85%); mp 122–124 °C. **IR**: two bands are observed in C=N region at *v* 1655 (likely C=N) and 1632 (probably due to aromatic ring stretching vibrations). **HRMS (ESI)**: *m/z* calcd for $C_{15}H_8F_4NO^+$ $[M+H]^+$ 294.0537; found 294.0534.

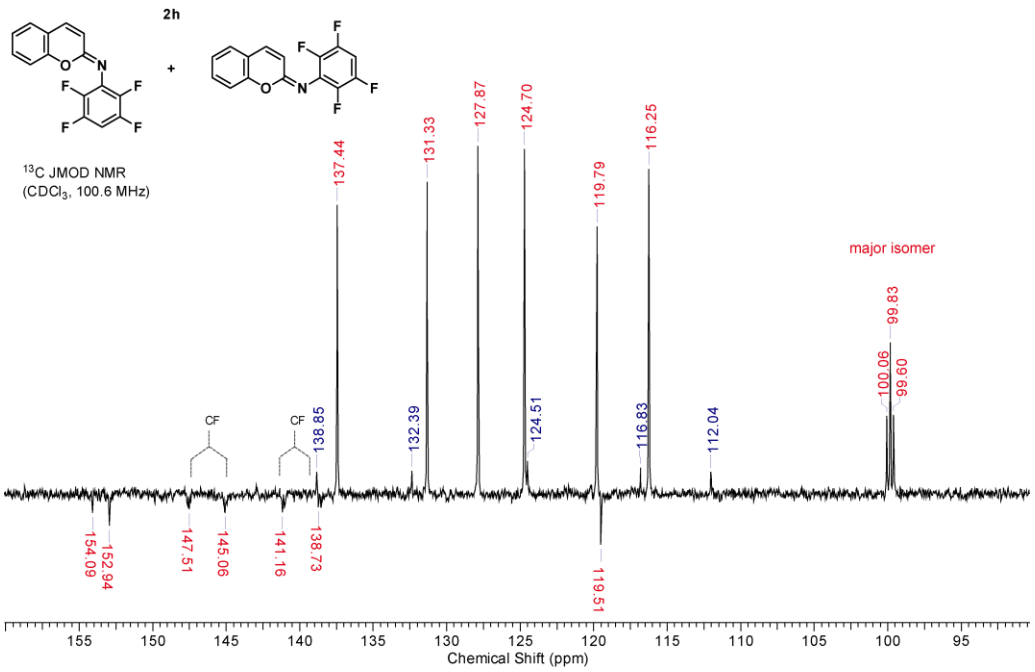
The identity of the compound is confirmed by the presence of a single molecular ion in HRMS. Similarly to **2a** the compound is a mixture of *E* and *Z* isomers (the amount of minor isomer can be estimated from ^{1}H and ^{19}F spectra as *ca.* 10%). Only the resonances of the main isomer could be fully identified in ^{1}H and ^{13}C spectra due to the low abundance of the minor isomer.

^{1}H NMR (400.1 MHz, $CDCl_3$). Main isomer: δ 7.43–7.37 (m, 3H), 7.21 (t, ^3J = 7.5, 1H), 7.09 (d, ^3J = 8.2, 1H), 6.81 (tt, $^3J_{HF}$ = 10.0, $^4J_{HF}$ = 7.3, 1H, C_6F_4H), 6.89 (d, ^3J = 9.5, 1H).

^{13}C NMR (100.6 MHz, $CDCl_3$). Main isomer: δ 154.1 (quat), 152.9 (quat), 146.2 (d, $^1J_{CF}$ ~245, quat *C*F), 139.7 (d, $^1J_{CF}$ ~245, quat *C*F), 137.4 (*C*H), 131.3 (*C*H), 127.9 (*C*H), 124.7 (*C*H), 119.8 (*C*H), 119.5 (quat), 116.3 (*C*H), 99.8 (t, $^2J_{CF}$ ~23, *p*-C_6F_4H); quat *C*–N not observed.

^{19}F NMR (376.5 MHz, $CDCl_3$). Main isomer: δ −141.00 (dd, $^{3,5}J_{FF}$ = 11, 2F), −149.52 (dd, $^{3,5}J_{FF}$ = 11, 2F). Minor isomer: δ −139.95 (dd, $^{3,5}J_{FF}$ = 11, 2F), −151.40 (dd, $^{3,5}J_{FF}$ = 11, 2F).




2h
+
^{13}C JMOD NMR
($CDCl_3$, 100.6 MHz)
major isomer
CF
CF
137.44
131.33
127.87
124.70
119.79
116.25
138.85
132.39
124.51
116.83
112.04
99.83
100.06
99.60
154.09
152.94
147.51
145.06
141.16
138.73
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155
150
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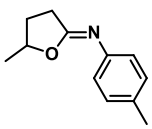
140
135
130
125
120
115
110
105
100
95
Chemical Shift (ppm)



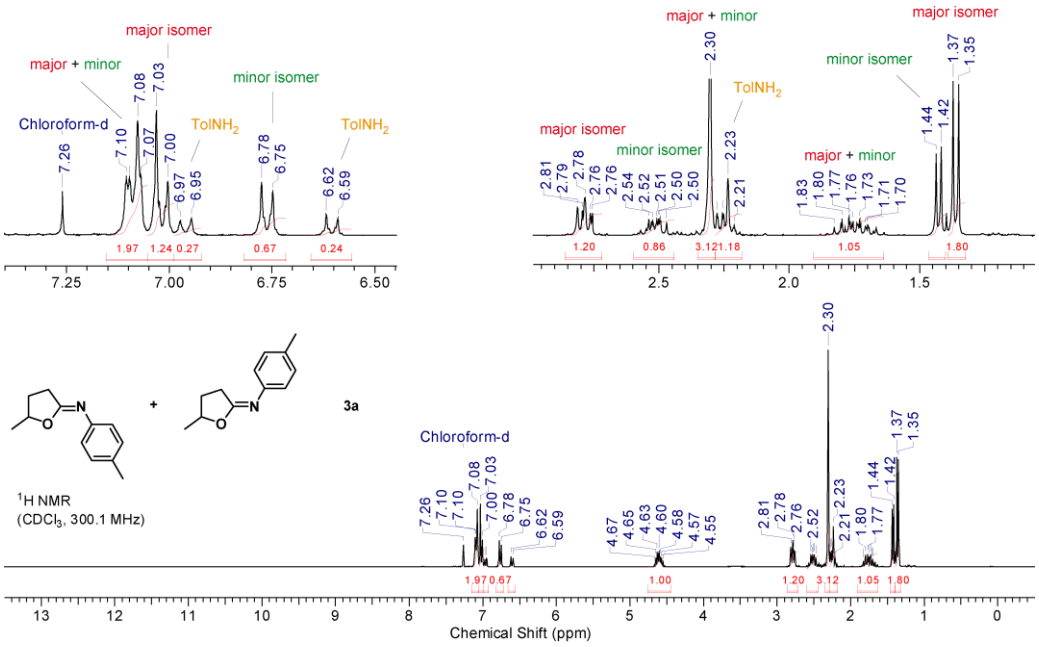
3a

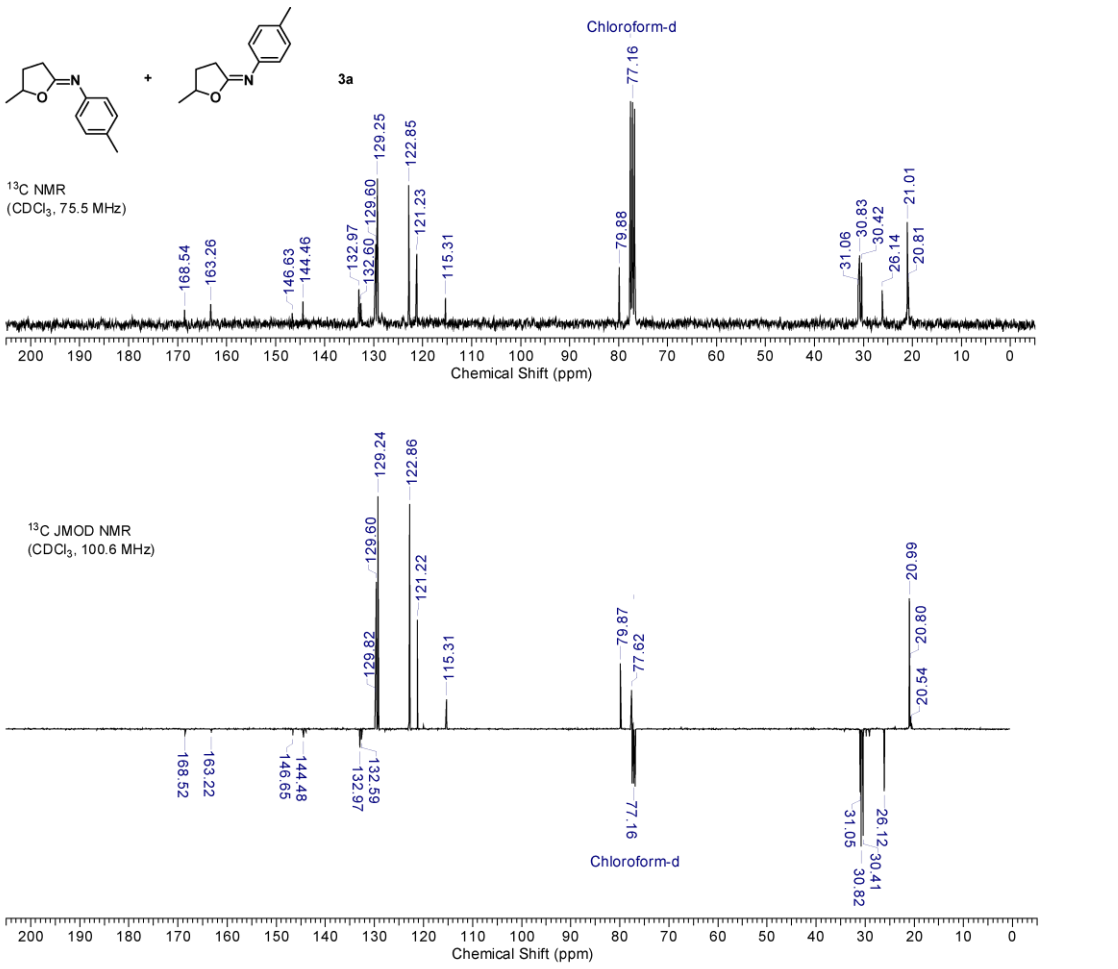
Loading: **Ti/SiO_2** (154 mg, 35 µmol Ti), γ-valerolactone (71 mg, 0.71 mmol), *N*-sulfinyl-4-methylaniline (110 µL, 0.83 mmol), toluene (5 mL). Reaction time 24 h. The reaction mixture was then filtered, the solvent was evaporated, and the resulting brown oil was distilled in vacuum to afford **3a** as yellow oil in purity sufficient for unambiguous spectroscopic characterization (it is still contaminated with *ca.* 10% of $TolNH_2$ that cannot be easily removed). Attempted chromatographic purification on silica failed even using eluent containing NEt_3. **IR** ($CHCl_3$): *v* 1691br (C=N).

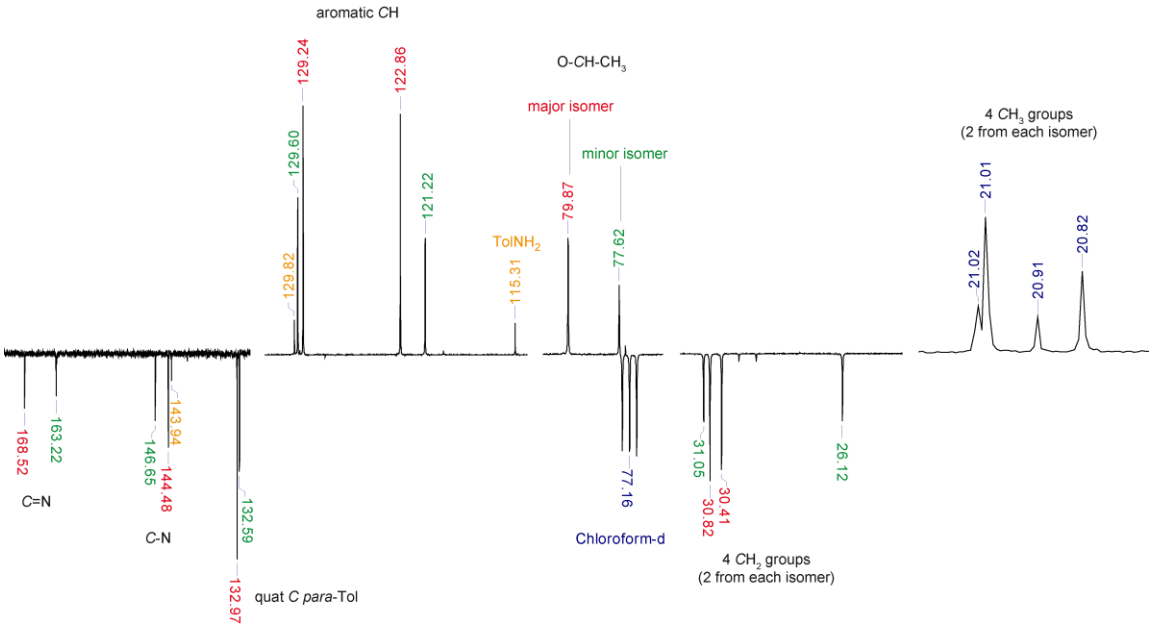
Similarly to coumarin derivatives (**2a**,**b**,**h**) the compound is a mixture of *E* and *Z* isomers in *ca.* 60 : 40 ratio. The isomers are not fully resolved in ^{1}H NMR but can be assigned in ^{13}C spectrum.

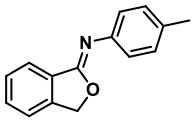
^{1}H NMR (300.1 MHz, $CDCl_3$): *δ* 7.10–7.07 (m, 2H, C_6H_4), 7.02 and 6.76 (2 doublets, ^3J = 8.2, 2H in total, C_6H_4), 4.67–4.65 (m, 1H, OC*H*Me), 2.81–2.76 and 2.57–2.47 (2 multiplets, 2H in total, CH_2CH_2C(=NTol)), 2.30 (s, 3H, C_6H_4Me), 2.30–2.20 (m, 1H, CH_2CH_2C(=NTol)), 1.83–1.65 (m, 1H, CH_2CH_2C(=NTol)), 1.43 and 1.36 (2 doublets, ^3J = 6.2, 3H in total, OCH*Me*).

^{13}C NMR (100.6 MHz, $CDCl_3$). Major isomer: *δ* 163.3 (quat *C*=N), 144.5 (quat *C*N), 133.0 (quat *p*-$C_6H_4CH_3$), 129.3 (CH_{Ar}), 122.9 (CH_{Ar}), 79.9 (OCH), 30.8 (CH_2), 30.4 (CH_2), 21.0 (2xCH_3). Minor isomer: *δ* 168.5 (quat *C*=N), 146.6 (quat *C*N), 132.6 (quat *p*-$C_6H_4CH_3$), 129.6 (CH_{Ar}), 121.2 (CH_{Ar}), 77.6 (OCH), 31.1 (CH_2), 26.1 (CH_2), 20.9 (CH_3), 20.8 (CH_3).




3a
Chloroform-d
77.16
129.25
122.85
129.60
121.23
132.97
132.60
115.31
79.88
168.54
163.26
146.63
144.46
31.06
30.83
30.42
26.14
21.01
20.81
^{13}C NMR
($CDCl_3$, 75.5 MHz)
Chemical Shift (ppm)
129.24
122.86
129.60
121.22
129.82
115.31
79.87
77.62
20.99
20.80
20.54
168.52
163.22
146.65
144.48
132.97
132.59
77.16
31.05
26.12
30.41
30.82
^{13}C JMOD NMR
($CDCl_3$, 100.6 MHz)
Chloroform-d
Chemical Shift (ppm)


aromatic CH
O-CH-CH$_3$
major isomer
minor isomer
4 CH$_3$ groups
(2 from each isomer)
129.24
122.86
129.60
121.22
129.82
TolNH$_2$
115.31
79.87
77.62
21.01
21.02
20.91
20.82
168.52
163.22
146.65
143.94
144.48
132.59
132.97
77.16
31.05
30.41
30.82
26.12
C=N
C-N
quat C para-Tol
Chloroform-d
4 CH$_2$ groups
(2 from each isomer)

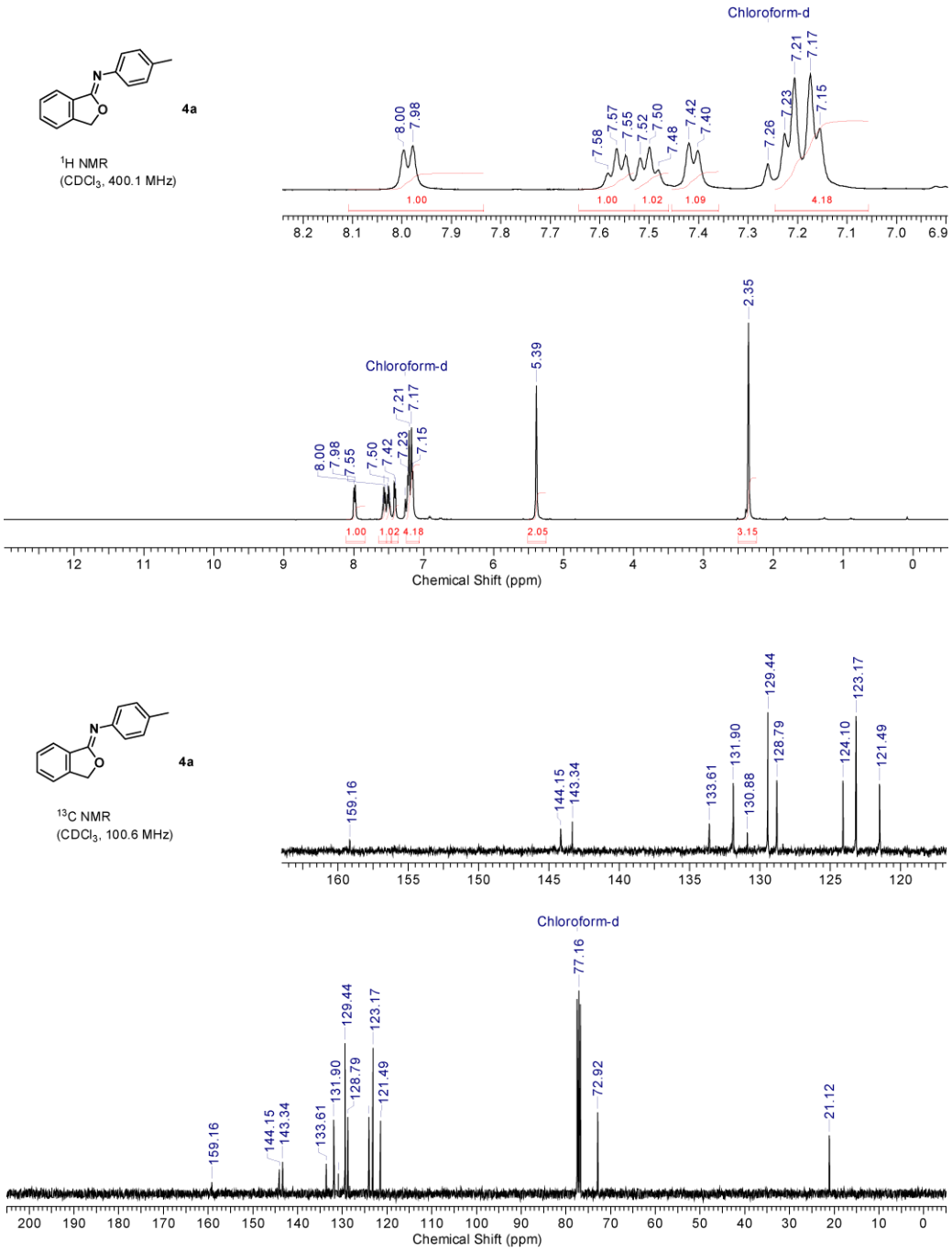


4a

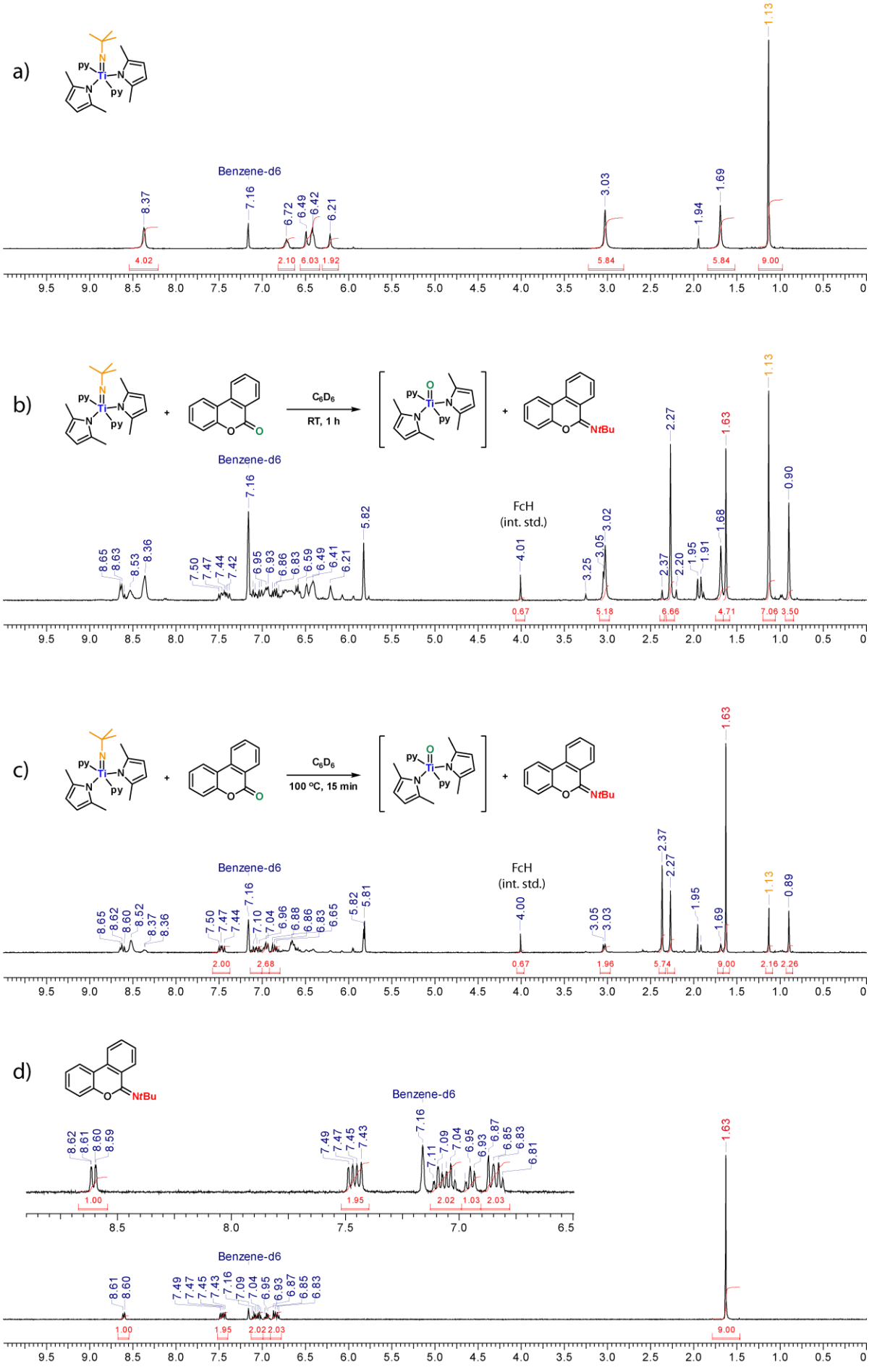
Loading: **Ti/SiO$_2$** (77 mg, 18 µmol Ti), phthalide (48 mg, 0.35 mmol), *N*-sulfinyl-4-methylaniline (48 µL, 0.35 mmol), toluene (2.5 mL). Reaction time 20 h. The product was isolated as off-white crystals in several crops by recrystallization from toluene. Yield 73 mg (92%); mp 119–120 °C. **IR**: *v* 1669 (C=N). **HRMS (ESI)**: *m/z* calcd for $C_{15}H_{14}NO^+$ $[M+H]^+$ 224.1070; found 224.1066. **EA:** found (calcd for $C_{15}H_{13}NO$, %): C, 80.64 (80.69); H, 5.77 (5.87); N, 6.29 (6.27).

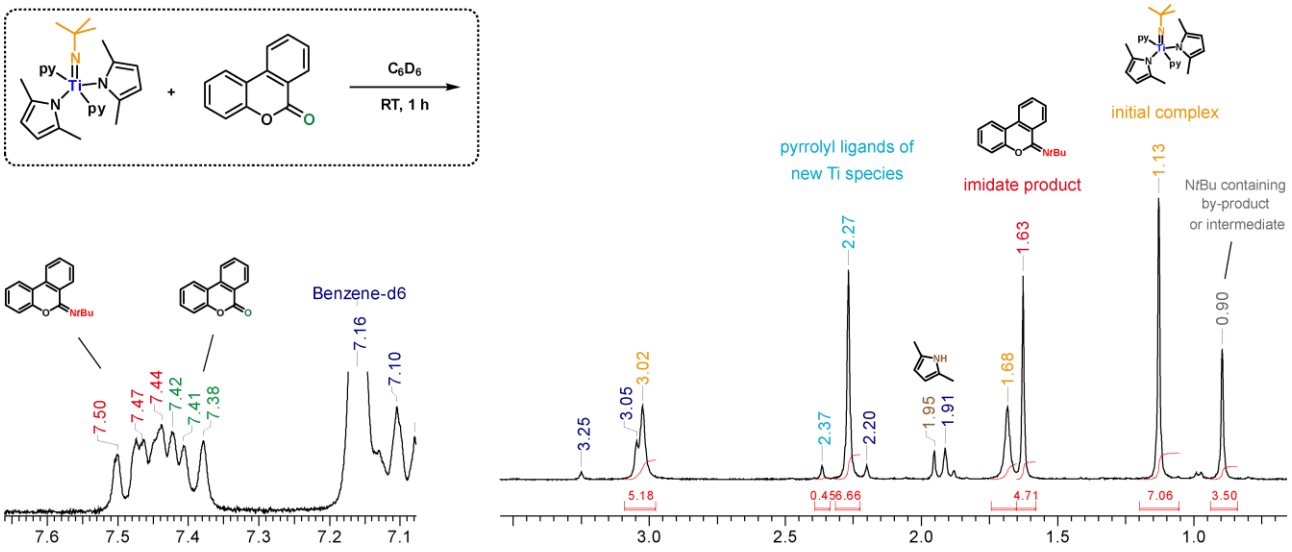
^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.99 (d, ^3J = 7.4, 1H), 7.57 (t, ^3J = 7.3, 1H), 7.50 (t, ^3J = 7.3, 1H), 7.41 (d, ^3J = 7.3, 1H), 7.22 (d, ^3J = 7.9, 2H), 7.16 (d, ^3J = 7.9, 2H), 5.39 (s, 2H, CH_2), 2.35 (s, 3H, CH_3).

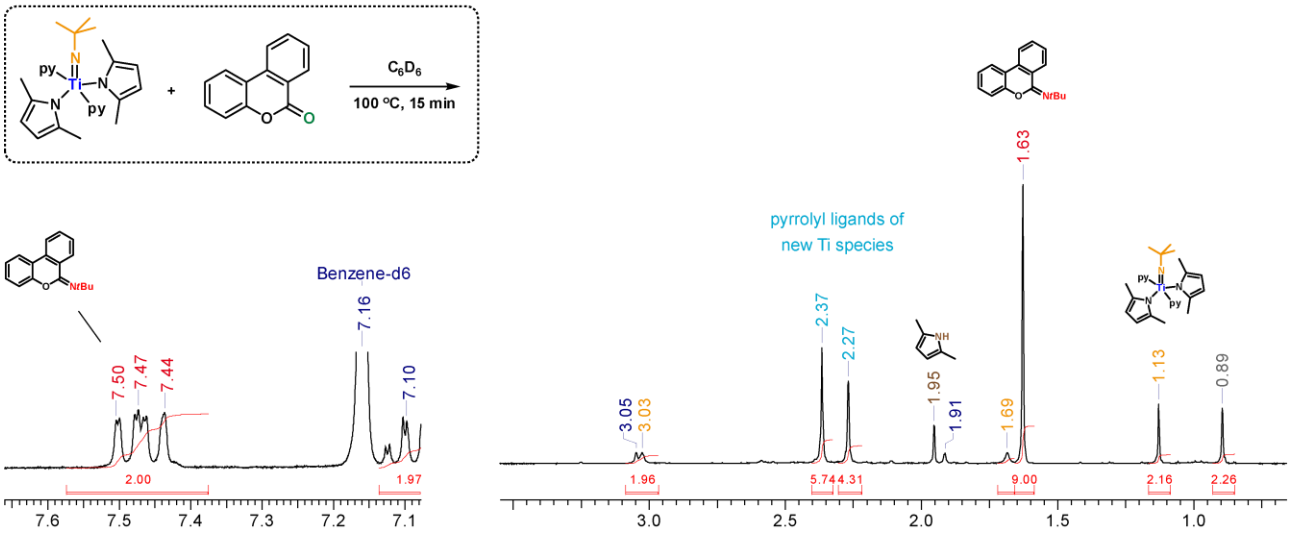
^{13}C NMR (100.6 MHz, $CDCl_3$): δ 159.2 (quat *C*=N), 144.2 (quat), 143.3 (quat), 133.6 (quat), 131.9 (*C*H), 130.9 (quat), 129.4 (*C*H), 128.8 (*C*H), 124.1 (*C*H), 123.2 (*C*H), 121.5 (*C*H), 72.9 (*C*H$_2$), 21.1 (*C*H$_3$).



Stoichiometric reaction of [Ti(=N*t*Bu)(Me$_2$Pyr)$_2$(py)$_2$] with lactone




C6D6
RT, 1 h
initial complex
pyrrolyl ligands of
new Ti species
imidate product
NtBu containing
by-product
or intermediate
Benzene-d6
7.50
7.47
7.44
7.42
7.41
7.38
7.16
7.10
3.25
3.05
3.02
2.37
2.27
2.20
1.95
1.91
1.68
1.63
1.13
0.90
5.18
0.45
6.66
4.71
7.06
3.50


C6D6
100 °C, 15 min
pyrrolyl ligands of
new Ti species
Benzene-d6
7.50
7.47
7.44
7.16
7.10
3.05
3.03
2.37
2.27
1.95
1.91
1.69
1.63
1.13
0.89
2.00
1.97
1.96
5.74
4.31
9.00
2.16
2.26

Computational details

DFT calculations (geometry optimization and thermochemistry) were performed with the Gaussian09 package[4] using the PBE0 functional[5] and Def2-TZVP basis set.[6] Reported reaction ΔH and ΔG were calculated using the thermal corrected enthalpies (H) and thermal corrected Gibbs free energies (G) at 298.15 K listed below.

	E_{el}, au	E_{el} + ZPE, au	H, au	G, au
$Ph_2C=O$	-576.155558	-575.963508	-575.951804	-576.001182
$Ph_2C=NPh$	-787.130255	-786.845586	-786.828982	-786.890636
PhCOOPh	-651.336371	-651.140233	-651.127524	-651.179883
PhC(=NPh)OPh	-862.306849	-862.018085	-862.000505	-862.065176
3,4-benzocoumarin	-650.168487	-649.992971	-649.981779	-650.029231
3,4-benzocoumarin phenyl imidate (**1a**)	-861.134684	-860.866682	-860.850487	-860.910957
PhNSO	-759.372329	-759.272375	-759.264643	-759.304426
SO_2	-548.410989	-548.403775	-548.399774	-548.427923

Optimized geometries

$Ph_2C=O$

C	2.66648	-1.51126	0.70792
C	3.77333	-0.90620	0.13161
C	3.64489	0.33036	-0.48893
C	2.41379	0.95944	-0.52907
C	1.29119	0.34759	0.02673
C	1.42708	-0.89222	0.64777
H	0.56601	-1.36236	1.10785
H	2.76803	-2.46780	1.20764
H	4.74001	-1.39565	0.17045
H	4.51053	0.80564	-0.93599
H	2.29753	1.93462	-0.98691
C	-0.00002	1.09525	0.00013
O	-0.00002	2.30877	0.00028
C	-1.29121	0.34756	-0.02666
C	-2.41397	0.95953	0.52871
C	-1.42692	-0.89241	-0.64741
C	-2.66629	-1.51151	-0.70768
C	-3.77329	-0.90632	-0.13181
C	-3.64504	0.33043	0.48842
H	-2.29781	1.93482	0.98632
H	-2.76769	-2.46819	-1.20715
H	-0.56574	-1.36266	-1.10717
H	-4.73996	-1.39580	-0.17075
H	-4.51081	0.80580	0.93512

$Ph_2C=NPh$

C	4.26920	0.09574	-0.46883
C	4.73373	-1.13216	-0.02410
C	3.83085	-2.09265	0.41612
C	2.47417	-1.82655	0.40894
C	1.99592	-0.59079	-0.03029
C	2.90941	0.36791	-0.46642
H	2.55318	1.32855	-0.81866
H	4.96726	0.84689	-0.82052
H	5.79742	-1.34213	-0.01884
H	4.18963	-3.05329	0.76817

H	1.75746	-2.56809	0.74001
C	0.53413	-0.33540	-0.05034
N	-0.24054	-1.34862	-0.06998
C	0.07554	1.08336	-0.06982
C	-0.80202	1.52888	-1.05531
C	0.51812	1.98287	0.89801
C	0.07516	3.29623	0.89301
C	-0.79612	3.73231	-0.09451
C	-1.22821	2.84702	-1.07178
H	-1.15037	0.83632	-1.81246
H	0.41555	3.98229	1.66031
H	1.20871	1.64737	1.66397
H	-1.13627	4.76156	-0.10420
H	-1.90452	3.18310	-1.84938
C	-1.63044	-1.27743	0.02297
C	-2.27891	-0.65492	1.09147
C	-3.66026	-0.69176	1.18772
C	-4.41859	-1.33462	0.22002
C	-3.77748	-1.96373	-0.83879
C	-2.39607	-1.95341	-0.92860
H	-1.88689	-2.46544	-1.73709
H	-4.35788	-2.48100	-1.59482
H	-1.69084	-0.15387	1.85124
H	-4.14817	-0.21021	2.02807
H	-5.49927	-1.35702	0.29714

PhCOOPh

C	2.42078	-0.83629	1.49567
C	3.38072	-1.26675	0.59215
C	3.40510	-0.73015	-0.68771
C	2.47072	0.21891	-1.06893
C	1.50866	0.63145	-0.15877
C	1.48521	0.11972	1.13028
H	0.74812	0.47088	1.84267
H	2.40178	-1.23898	2.50185
H	4.11222	-2.00964	0.88647
H	4.15809	-1.05144	-1.39822
H	2.47691	0.65231	-2.06199
O	0.64608	1.61956	-0.56473
C	-0.65053	1.68060	-0.13340
O	-1.11445	2.74749	0.14043
C	-1.44029	0.42067	-0.12473
C	-2.57650	0.38209	0.67998
C	-1.13630	-0.66459	-0.94203
C	-1.96110	-1.77741	-0.94979
C	-3.08044	-1.81999	-0.13104
C	-3.38681	-0.73944	0.68535
H	-2.81167	1.24551	1.29055
H	-1.72780	-2.61515	-1.59644
H	-0.26305	-0.63709	-1.58127
H	-3.71892	-2.69621	-0.13252
H	-4.26404	-0.76946	1.32110

PhC(=NPh)OPh

C	4.48226	1.03580	-0.26349
C	5.20200	-0.08132	0.13085
C	4.53711	-1.26952	0.41047
C	3.16157	-1.33952	0.29591
C	2.43084	-0.21772	-0.09793
C	3.10223	0.97045	-0.37895

H	2.53907	1.84116	-0.68835
H	4.99637	1.96449	-0.48281
H	6.28130	-0.02911	0.21950
H	5.09713	-2.14556	0.71709
H	2.62648	-2.25642	0.50919
C	0.96257	-0.30733	-0.20472
N	0.34229	-1.34284	0.16931
C	-0.65529	1.46267	-0.21651
C	-1.40940	2.25583	-1.06839
C	-0.93334	1.41514	1.14102
C	-1.98765	2.16569	1.63920
C	-2.75309	2.96006	0.79940
C	-2.45655	3.00281	-0.55550
H	-1.16344	2.27794	-2.12328
H	-2.20783	2.12718	2.69993
H	-0.33717	0.79578	1.79986
H	-3.57500	3.54238	1.19808
H	-3.04585	3.62128	-1.22284
C	-1.01415	-1.59831	-0.01584
C	-1.71731	-2.19000	1.03465
C	-3.05159	-2.52551	0.88692
C	-3.69829	-2.31193	-0.32252
C	-2.99566	-1.75431	-1.38107
C	-1.66759	-1.39097	-1.23303
H	-1.12365	-0.96016	-2.06493
H	-3.48744	-1.59621	-2.33451
H	-1.19539	-2.37901	1.96557
H	-3.58638	-2.97218	1.71769
H	-4.73942	-2.58755	-0.44272
O	0.41164	0.80797	-0.78195

3,4-benzocoumarin

C	1.26884	-1.92124	0.00001
C	2.64801	-1.96970	0.00000
C	3.40187	-0.79797	-0.00001
C	2.75915	0.42136	-0.00001
C	1.36637	0.47755	0.00001
C	0.59842	-0.69426	0.00001
H	0.70822	-2.84717	0.00002
H	3.14744	-2.93206	0.00000
H	4.48419	-0.84552	-0.00002
H	3.30807	1.35499	-0.00001
C	0.73548	1.80471	0.00004
O	1.32397	2.84840	-0.00007
C	-1.39838	0.71591	0.00002
C	-2.77040	0.92579	0.00001
C	-0.85114	-0.56796	0.00001
C	-1.74034	-1.64745	-0.00002
C	-3.10597	-1.45225	-0.00003
C	-3.62295	-0.15991	-0.00001
H	-3.13962	1.94392	0.00002
H	-1.35194	-2.65823	-0.00004
H	-3.77310	-2.30573	-0.00005
H	-4.69482	-0.00089	-0.00002
O	-0.62674	1.83701	0.00004

3,4-benzocoumarin phenyl imidate (1a)

C	3.38905	-1.44277	0.05622
C	3.33764	-2.81996	0.12024
C	2.11023	-3.47724	0.14823

C	0.94310	-2.74484	0.11226
C	0.98621	-1.35209	0.04723
C	2.21678	-0.68225	0.01802
H	4.35335	-0.95140	0.03546
H	4.25935	-3.38993	0.14882
H	2.07165	-4.55896	0.19844
H	-0.02789	-3.22291	0.13271
C	-0.27265	-0.60276	0.01360
N	-1.39488	-1.18873	0.01149
C	0.98394	1.42841	-0.07959
C	0.88868	2.81073	-0.14942
C	2.21490	0.77446	-0.05283
C	3.36423	1.56829	-0.09830
C	3.28581	2.94520	-0.16654
C	2.04271	3.56861	-0.19255
H	-0.09466	3.26434	-0.17164
H	4.33887	1.09679	-0.08094
H	4.19297	3.53623	-0.20116
H	1.97392	4.64864	-0.24788
C	-2.62598	-0.53414	0.02543
C	-2.95085	0.47648	0.93394
C	-4.22293	1.02441	0.94559
C	-5.18859	0.59026	0.04845
C	-4.87355	-0.41680	-0.85283
C	-3.61127	-0.98516	-0.85473
H	-3.36349	-1.78738	-1.54003
H	-5.62117	-0.77278	-1.55306
H	-2.20530	0.81903	1.64074
H	-4.46085	1.80130	1.66405
H	-6.18065	1.02640	0.05851
O	-0.19708	0.75484	-0.03736

PhNSO

C	2.36856	0.82898	0.00000
C	2.11848	2.19710	0.00000
C	0.81074	2.65647	0.00000
C	-0.24178	1.75658	0.00000
C	0.00000	0.38216	0.00000
C	1.32417	-0.07495	0.00000
H	1.53550	-1.13815	0.00000
H	3.38958	0.46490	0.00000
H	2.94389	2.89926	0.00000
H	0.60708	3.72096	0.00000
H	-1.27102	2.09384	0.00000
N	-1.13209	-0.43308	0.00000
S	-1.12275	-1.95243	0.00000
O	-2.44967	-2.53106	0.00000

SO_2

S	0.00000	0.00000	0.36384
O	0.00000	-1.23254	-0.36384
O	0.00000	1.23254	-0.36384

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