Electronic Supporting Information

Accessing the antipodal series in microbial arene oxidation: a novel diene rearrangement induced by tricarbonyliron(0) complexation

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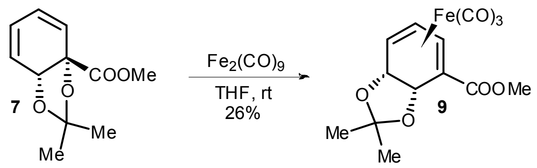
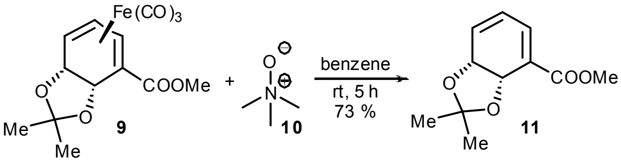
General Procedures and Instrumentation. Reactions were carried out under an atmosphere of nitrogen. Nonacarbonyldiiron was dispensed in a glovebox, but all subsequent isolation and purification procedures were performed in a fumehood, open to the atmosphere. Solvents were dried and degassed by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. Petrol refers to petroleum ether, bp 40-60 °C. TLCs were performed using aluminum-backed plates precoated with Alugram®SIL G/UV and visualized by UV light (254 nm) and/or $KMnO_4$ followed by gentle warming. Flash column chromatography was carried out using Davisil LC 60Å silica gel (35-70 micron) purchased from Fisher Scientifics. All reagents were purchased from Sigma-Aldrich and used as received. IR spectra were recorded on Perkin-Elmer 1600 FT IR spectrometer with absorbances quoted as ν in cm^{-1}. NMR spectra were run in $CDCl_3$ on Brüker Avance 300, 400 or 500 MHz instruments at 298 K, unless otherwise specified. Mass spectra were recorded with a micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Brüker Daltonik). Specific rotations were recorded on an Optical Activity AA-10 Automatic polarimeter with a path length of 1 dm. Concentrations (c) are quoted in g/100 mL. Elemental analysis was performed using an Exeter Analytical CE 440 analyzer.

Synthesis of (+)-(1*R*)-Tricarbonyl(η^4-(2*R*,3*S*)-methyl 2,3-isopropylidenedioxycyclohexa-4,6-dienecarboxylate)iron(0) 9



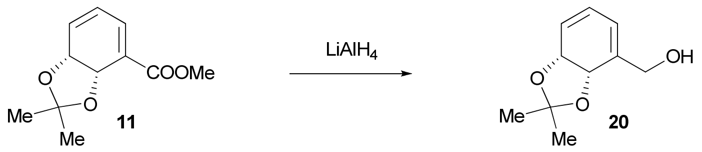
To known[1] acetonide **7** (183 mg, 0.872 mmol, 1.00 equiv) in a glove box was added diiron nonacarbonyl (348 mg, 0.957 mmol, 1.09 equiv). THF (100 mL) was added and the reaction mixture was stirred at rt for 7 d. The reaction mixture was then added to an additional portion of diiron nonacarbonyl (409 mg, 1.29 equiv) via cannula. The reaction mixture was stirred at rt for an additional 9 d, then concentrated under reduced pressure (***Care! Toxic pentacarbonyliron distilled over at this point***). The crude brown oil was pre-adsorbed on silica and purified by chromatography (10% EtOAc-petroleum) to give *(+)-(1*R*)-tricarbonyl(*η^4*-(2*R*,3*S*)-methyl 2,3-isopropylidenedioxycyclohexa-4,6-dienecarboxylate)iron(0)* **9** (80.4 mg, 26%) as a yellow foam; crystals suitable for x-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of **9**; R_f 0.44 (10% EtOAc-petroleum); mp 81-84 ºC; $[\alpha]_D^{25}$ +80º (c 0.1, CH_2Cl_2); δ_H (300 MHz, $CDCl_3$, 298 K) 6.36 (1H, d, *J* 5.0 Hz, H-6) 5.70 (1H, t, *J* 5.0 Hz, H-5) 5.12 (1H, d, *J* 8.5 Hz, H-2) 4.70 (1H, dd, *J* 8.5, 3.5 Hz, H-3) 3.72 (3H, s, $-COOCH_3$) 3.11 (1H, t, *J* 5.0 Hz, H-4) 1.34 (3H, s, $-OCH_3$) 1.22 (3H, s, $-OCH_3$); δ_C (100 MHz, toluene-d_8, 228 K) [212.8, 206.7, 204.8] ($Fe(CO)_3$), 171.4 (-*C*OOCH$_3$), 114.6 (H$_3$C-*C*-CH$_3$), 89.8 (C-6), 86.7 (C-5), 75.6 (C-3), 73.9 (C-2), 59.0 (C-4), 55.5 ($-OCH_3$), 52.3 (C-1), 26.4 ($-CH_3$), 24.6 ($-CH_3$); ν_{max} (film) 2989, 2954, 2059, 1978, 1710, 1460, 1436, 1380, 1372, 1278, 1244, 1204, 1161, 1043, 1006, 961, 916, 891, 802, 732, 667 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{14}FeO_7+H)^+$, 351.0167, found 351.0164; calcd for $(C_{14}H_{14}FeO_7+Na)^+$, 372.9986, found 372.9979. (Found: C, 47.6; H, 4.03. $C_{14}H_{14}FeO_7$ requires C, 48.0; H, 4.03 %).

Synthesis of (–)-(2*S*,3*R*)-methyl 2,3-isopropylidenedioxycyclohexa-4,6-dienecarboxylate 11



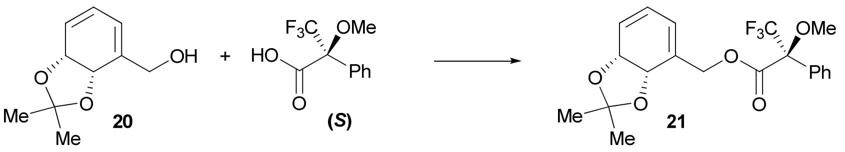
To iron complex **9** (123 mg, 0.350 mmol, 1.0 equiv) and trimethylamine-*N*-oxide **10** (1.05 g, 14.0 mmol, 39.9 equiv) under N_2 was added benzene (50 mL). The reaction mixture was stirred at rt for 5 h. Diethyl ether (50 mL) was then added and precipitate was thoroughly dislodged from the flask walls with a spatula. The reaction mixture was transferred to a separating funnel and extracted with H_2O (2 × 70 mL). The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and dried under high vacuum to give *(–)-(2S,3R)-methyl 2,3-isopropylidenedioxycyclohexa-4,6-dienecarboxylate* **11** (54 mg, 73%) as a light brown oil; R_f 0.48 (20% EtOAc-hexane); $[\alpha]_D^{25}$ -108° (c 1.0, CH_2Cl_2); δ_H (400 MHz, $CDCl_3$, 298 K) 7.14 (1H, d, *J* 5.0 Hz, H-6), 6.12 (1H, dd, *J* 10.0, 2.5 Hz, H-4), 6.09 (1H, dd, *J* 10.0, 5.0 Hz, H-5), 4.93 (1H, d, *J* 8.5 Hz, H-2), 4.87 (1H, dd, *J* 8.5, 2.5 Hz, H-3), 3.82 (3H, s, $-OCH_3$), 1.46 (3H, s, $-CCH_3$), 1.39 (3H, s, $-CCH_3$); data in agreement with those reported previously;[2] δ_C (75.5 MHz, $CDCl_3$, 298 K) 166.7 ($-\mathit{C}OOCH_3$), 134.0 (C-4), 133.9 (C-6), 126.1 (C-1), 121.3 (C-5), 105.6 (H_3C-*C*-CH_3), 72.5 (C-3), 68.1 (C-2), 52.1 ($-OCH_3$), 26.7 ($-C\mathit{C}H_3$), 25.1 ($-C\mathit{C}H_3$); ν_{max} (film) 2988, 2921, 1715, 1589, 1437, 1371, 1297, 1259, 1161, 1108, 1082, 1030, 864, 707 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{11}H_{14}O_4+Na)^+$, 233.0790, found 233.0779.

Synthesis of (–)-(2*S*,3*R*)-(2,3-isopropylidenedioxycyclohexa-4,6-dienyl)methanol 20



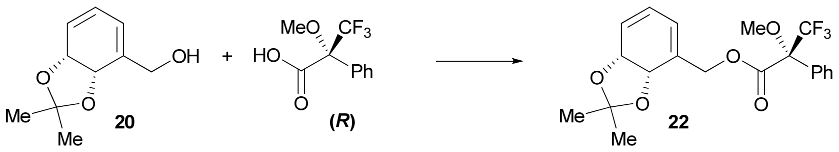
Ester **11** (92 mg, 0.438 mmol, 1.0 equiv) was dissolved in diethyl ether (10 mL) under N_2 at -78 °C. Lithium aluminium hydride (33.2 mg, 0.875 mmol, 2.0 equiv) in diethyl ether (10 mL) was added dropwise via cannula to the reaction mixture. The reaction mixture was stirred at 15 mins, then the dry ice/acetone bath was removed. The reaction mixture was then stirred for 10 mins, after which the reaction mixture was placed in an ice bath and ethyl acetate (2 mL) was added dropwise by syringe. The reaction mixture was stirred for a further 10 mins, then a saturated aqueous solution of Rochelle's salt (30 mL) was added dropwise by syringe. The biphasic mixture was stirred vigorously and the ice bath was removed. After 1 h, an additional portion of diethyl ether (20 mL) was added and the mixture was transferred to a separating funnel. The layers were separated and the aqueous layer was extracted with additional portions of diethyl ether (4 × 30 mL). Combined organic phases were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and purified by chromatography (30% EtOAc-hexane) to give *(–)-(2*S*,3*R*)-(2,3-isopropylidenedioxycyclohexa-4,6-dienyl)methanol* **20** (42.0 mg, 53%) as a colourless oil; R_f 0.21 (30% EtOAc-hexane); $[\alpha]_D^{25}$ -75° (c 0.1, CH_2Cl_2); δ_H (400 MHz, $CDCl_3$, 298 K) 6.03 (1H, dd, *J* 9.5, 5.5 Hz, H-5), 5.97 (1H, dq, *J* 5.5, 1.0 Hz, H-6), 5.89 (1H, ddd, *J* 9.5, 1.5, 1.0 Hz, H-4), 4.73 (1H, d, *J* 7.5 Hz, H-2 or H-3), 4.70 (1H, d, *J* 9.5 Hz, H-2 or H-3), 4.32 (1H, d, *J* 14.0 Hz, -C*H*HOH), 4.29 (1H, d, *J* 14.0 Hz, -CH*H*OH), 2.11 (1H, br s, -OH), 1.41 (3H, s, $-CH_3$), 1.41 (3H, s, $-CH_3$); δ_C (75.5 MHz, $CDCl_3$, 298 K) 136.1 (C-1), 124.6 (C-4), 124.0 (C-5), 119.5 (C-6), 105.5 (H_3C-*C*-CH_3), 71.8 (C-2), 71.0 (C-3), 64.6 ($-CH_2OH$), 26.8 (-C*C*H_3), 24.8 (-C*C*H_3); ν_{max} (film) 3575, 3416, 3044, 2985, 2930, 1611, 1541, 1406, 1371, 1304, 1246, 1207, 1158, 1033, 950, 877, 820, 791, 756, 718, 694 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{10}H_{14}O_3+Na)^+$, 205.0841, found 205.0834.

Synthesis of (–)-(2’*S*,3’*R*)-(2’,3’-isopropylidenedioxycyclohexa-4’,6’-dienyl)methyl (2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate 21



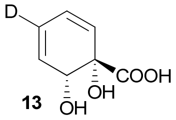
Alcohol **20** (21.2 mg, 0.116 mmol, 1.0 equiv) and (2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate[3] (54.5 mg, 0.233 mmol, 2.00 equiv, Aldrich #155616, 95% *e.e.*) were dissolved in CH_2Cl_2 (1.2 mL) at rt. *N*,*N*-Dimethylaminopyridine (2.5 mg, 0.020 mmol, 0.09 equiv) in CH_2Cl_2 (0.3 mL) was added by syringe, followed by *N*,*N*’-diisopropylcarbodiimide (29.4 mg, 0.233 mmol, 2.00 equiv). The reaction mixture was stirred at rt for 17 h, then concentrated under reduced pressure. A ^{1}H-NMR spectrum of the crude was acquired, then purification by chromatography (30% EtOAc-hexane) gave *(–)-(2’*S*,3’*R*)-(2’,3’-isopropylidenedioxycyclohexa-4’,6’-dienyl)methyl (2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate* **21** (40 mg, 87%) as a white gum; R$_f$ 0.68 (30% EtOAc-hexane); $[\alpha]_D^{25}$ -30º (c 0.1, CH_2Cl_2); δ_H (400 MHz, $CDCl_3$, 298 K) 7.53-7.52 (2H, m, Ar-H), 7.41-7.34 (3H, m, Ar-H), 6.01-5.97 (2H, m, H’-5, H’-6), 5.94-5.91 (1H, m, H’-4), 5.05 (1H, d, *J* 13.0 Hz, -C*H*H-O-), 4.89 (1H, d, *J* 13.0 Hz, -CH*H*-O-), 4.65 (1H, dd, *J* 9.0, 3.5 Hz, H’-3), 4.52 (1H, d, *J* 9.0 Hz, H’-2), 3.56 (3H, s, $-OCH_3$), 1.37 (6H, s, 2× $C-CH_3$); δ_C (125.8 MHz, $CDCl_3$, 298 K) 166.3 (C=O), 132.2, 130.8, 130.1, 129.6, 128.7, 127.4, 126.9, 125.9, 123.3, 123.3 (q, $^1J_{CF}$ 287 Hz, $-CF_3$), 122.7, 105.6 (H_3C-*C*-CH_3), 84.7 (q, $^2J_{CF}$ 27 Hz, *C*CF_3), 70.7, 70.5, 66.6 ($-CH_2O-$), 55.5 ($-OCH_3$), 26.7 (-C*C*H_3), 24.7 (-C*C*H_3); δ_F (376.5 MHz, $CDCl_3$, 298 K) -71.5; ν_{max} (film) 2968, 1754, 1452, 1372, 1171, 1122, 1017, 719, 642 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{20}H_{21}F_3O_5+Na)^+$, 421.1239, found 421.1238.

Synthesis of (+)-(2'*S*,3'*R*)-(2',3'-isopropylidenedioxycyclohexa-4',6'-dienyl)methyl (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate 22



Alcohol **20** (20.1 mg, 0.111 mmol, 1.0 equiv) and (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate[3] (60.0 mg, 0.256 mmol, 2.31 equiv, Aldrich #155268, 99% *e.e.*) were dissolved in CH_2Cl_2 (1.2 mL) at rt. *N*,*N*-Dimethylaminopyridine (2.0 mg, 0.016 mmol, 0.15 equiv) in CH_2Cl_2 (0.3 mL) was added by syringe, followed by *N*,*N*'-diisopropylcarbodiimide (28.0 mg, 0.222 mmol, 2.00 equiv). The reaction mixture was stirred at rt for 17 h, then concentrated under reduced pressure. A ^{1}H-NMR spectrum of the crude was acquired, then purification by chromatography (20% EtOAc-hexane) gave *(–)-(2'*S*,3'*R*)-(2',3'-isopropylidenedioxycyclohexa-4',6'-dienyl)methyl (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionate* **22** (32 mg, 72%) as a white gum; R$_f$ 0.58 (20% EtOAc-hexane); $[\alpha]_D^{25}$ +10° (c 0.1, CH_2Cl_2); δ_H (400 MHz, $CDCl_3$, 298 K) 7.57-7.52 (2H, m, Ar-H), 7.44-7.36 (3H, m, Ar-H), 6.02-5.99 (2H, m, H'-5, H'-6), 5.95-5.92 (1H, m, H'-4), 4.99 (1H, d, *J* 13.0 Hz, -C*H*H-O-), 4.94 (1H, d, *J* 13.0 Hz, -CH*H*-O-), 4.62 (1H, dd, *J* 9.0, 3.5 Hz, H'-3), 4.51 (1H, d, *J* 9.0 Hz, H'-2), 3.58 (3H, s, -OCH_3), 1.37 (3H, s, C-CH_3), 1.36 (3H, s, C-CH_3); δ_C (100.6 MHz, $CDCl_3$, 298 K) 166.3 (C=O), 132.3, 130.7, 129.7, 129.6, 128.8, 127.3, 126.8, 125.8 (q, $^1J_{CF}$ 276 Hz, -CF_3), 125.8, 123.4, 122.9, 105.6 (H_3C-*C*-CH_3), 84.7 (q, $^2J_{CF}$ 27 Hz, -*C*CF_3), 70.6, 70.4, 66.7 (-CH_2O-), 55.6 (-OCH_3), 26.7 (-C*C*H_3), 24.7 (-C*C*H_3); δ_F (376.5 MHz, $CDCl_3$, 298 K) -71.5; ν_{max} (film) 2988, 1749, 1672, 1498, 1452, 1372, 1236, 1168, 1122, 1018, 766, 710, 655 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{20}H_{21}F_3O_5+Na)^+$, 421.1239, found 421.1240.

Spectroscopic data for (1*S*,2*R*)-4-deutero-1,2-dihydroxycyclohexa-4,6-dienecarboxylic acid 13 (deuterated analogue of **4**)



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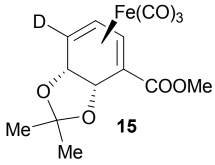
$[\alpha]_D^{25}$ -90 (c 0.1, CH_3OH); δ_H (300 MHz, CD_3OD); 6.09 (1H, d, *J* 7.5 Hz, H-5), 5.80-5.78 (2H, m, H-3, H-6), 4.85 (1H, br s, H-2); δ_C (100 MHz, CD_3OD) 178.4, 133.9, 127.7, 127.5, 123.7 (t, $^1J_{CD}$ 33.0 Hz), 75.9, 72.8; ν_{max} (film) 3281, 3060, 2879, 1695, 1576, 1397, 1357, 1330, 1309, 1267, 1221, 1171, 1150, 1078, 1050, 1008, 976, 912, 877, 861, 803, 766, 750, 656 cm^{-1}; HRMS (-ve ESI-TOF) m/z calcd for $(C_7H_7DO_4–H)^-$, 156.0413; found 156.0412.

Spectroscopic data for (+)-(1*R*)-Tricarbonyl(*η*^{4}-(2*R*,3*S*)-methyl 4-deutero-2,3-isopropylidenedioxycyclohexa-4,6-dienecarboxylate)iron(0) 15 (deuterated analogue of **9**)



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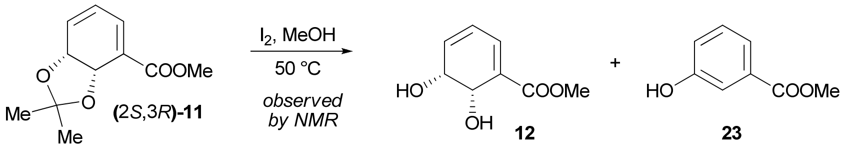
δ_H (300 MHz, $CDCl_3$); 6.36 (1H, d, *J* 4.5 Hz, H-6), 5.71 (1H, d, *J* 4.5 Hz, H-5), 5.13 (1H, d, *J* 8.5 Hz, H-2), 4.71 (1H, d, *J* 8.5, H-3), 3.73 (3H, s, $-COOCH_3$), 1.35 (3H, s, $C-CH_3$), 1.23 (3H, s, $C-CH_3$); δ_C (75.4 MHz, $CDCl_3$) 171.2, 114.8, 89.7, 86.7, 76.3, 74.6, 60.3, 52.0, 27.0, 25.4; ν_{max} (film) 2988, 2936, 2060, 1982, 1713, 1458, 1437, 1373, 1338, 1318, 1298, 1262, 1244, 1205, 1160, 1095, 1064, 1012, 961, 905, 878, 814, 661 cm^{-1}; HRMS (+ve ESI-TOF) m/z calcd for $(C_{14}H_{13}DFeO_7Na)^+$, 374.0044; found 374.0048.

Formation of (2*S*,3*R*)-methyl 2,3-dihydroxycyclohexa-4,6-dienecarboxylate **11** observed by NMR.



Isopropylidene **11** (22.0 mg, 0.105 mmol, 1.0 equiv) was dissolved in CD_3OD (1 mL) in a Young's NMR tube. Iodine (15.4 mg, 0.0607 mmol, 0.58 equiv) was added. The NMR sample was heated to 50 °C and ^{1}H-NMR spectra were acquired at five minute intervals (Fig. S1, diagnostic regions shown). Formation of diol **12** was observed, but before all isopropylidene **11** had been consumed, aromatic dehydration byproduct **23** was observed to form. Subsequently all material was converted to **23**.

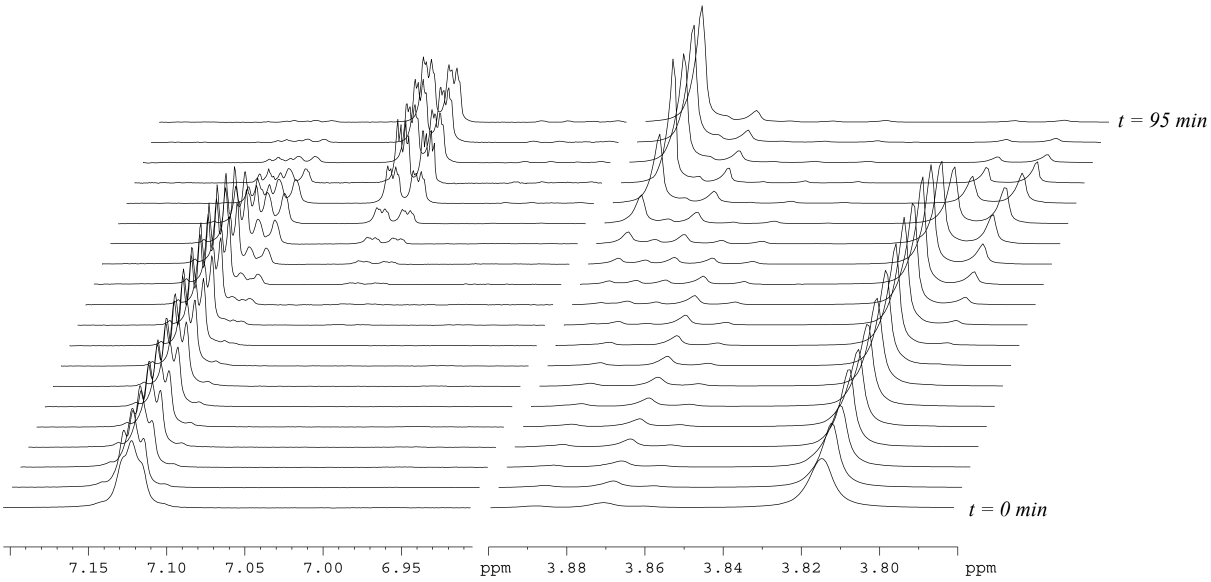


Fig. S1 Dynamic NMR of iodine-mediated deprotection of **11**. Spectra are at 5 min intervals.

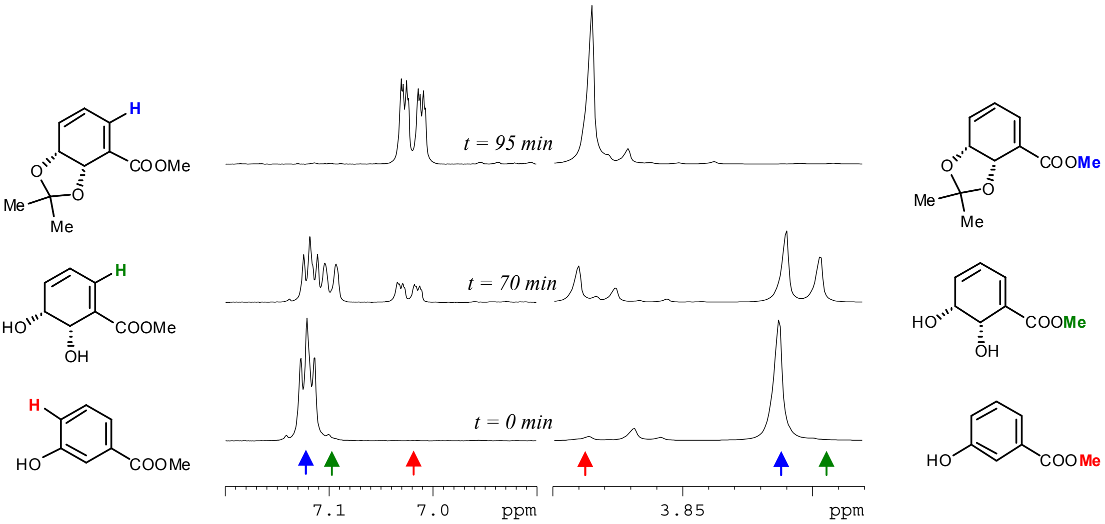


Fig. S2 NMR spectra of iodine-mediated deprotection of **11** at specific time points. Peak assignments shown.

VT-NMR Calculations

Variable temperature $^{13}C\{^{1}H\}$ spectra for lineshape analysis were acquired on a Brüker Avance 400 MHz spectrometer, operating at 100.6 MHz for ^{13}C, using toluene-d_8 as solvent and allowing at least 15 minutes for equilibration at each temperature. Spectra were calibrated to internal solvent at 20.4 ppm. Temperatures were calibrated using an external sample of either methanol or ethylene glycol,[4] acquired under identical conditions. Spectra were simulated using DNMR (Brüker)[5] and gNMR,[6] assuming a tripodal rotation and using the CO_2Me resonance to provide an estimate for the natural linewidth in the absence of exchange. At and above the coalescence temperature the chemical shifts for the 3 exchanging carbonyl ligands were estimated from their variation below the coalescence temperature:[7] the resonance at *ca.* 208 ppm was found to have a linear dependence on temperature, which was extrapolated to temperatures above coalescence; the resonances at *ca.* 214 and 206 ppm did not show a well-defined change with temperature and were fixed (to within 0.08 ppm) of the chemical shift below coalescence.

The rate constants, *k*, obtained from the simulations (**Fig. S3**) were used in plots (**Fig. S4**) of ln(k) versus T and ln (k/T) versus T to obtain values for the activation parameters, as described elsewhere.[7]

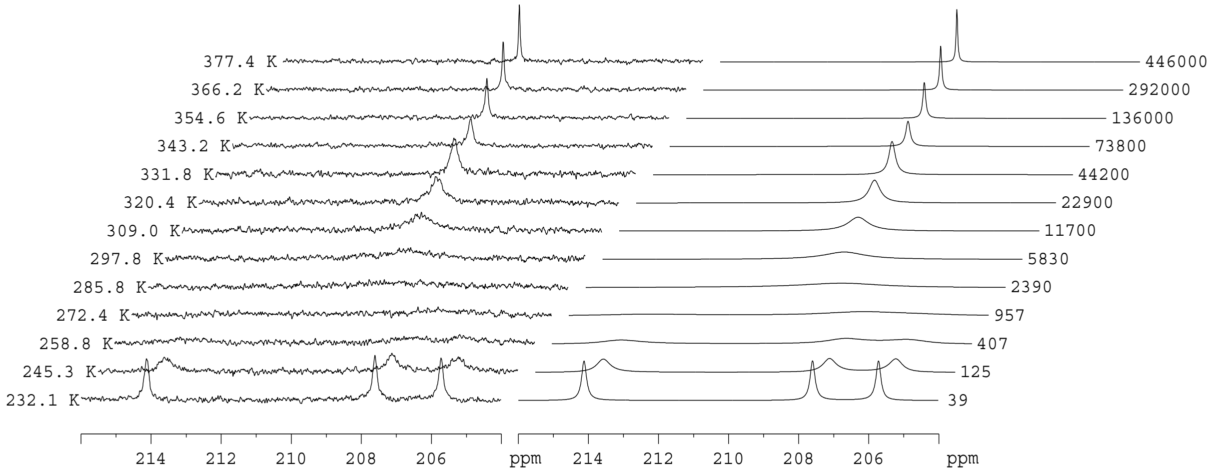


Fig. S3 Experimental (*left*) and simulated (*right*) variable temperature $^{13}C\{^{1}H\}$ NMR spectra of complex **9**, at 100.6 MHz in toluene-d_8, showing the iron carbonyl region only. Rate constants (in s^{-1}) are given alongside the simulated spectra.

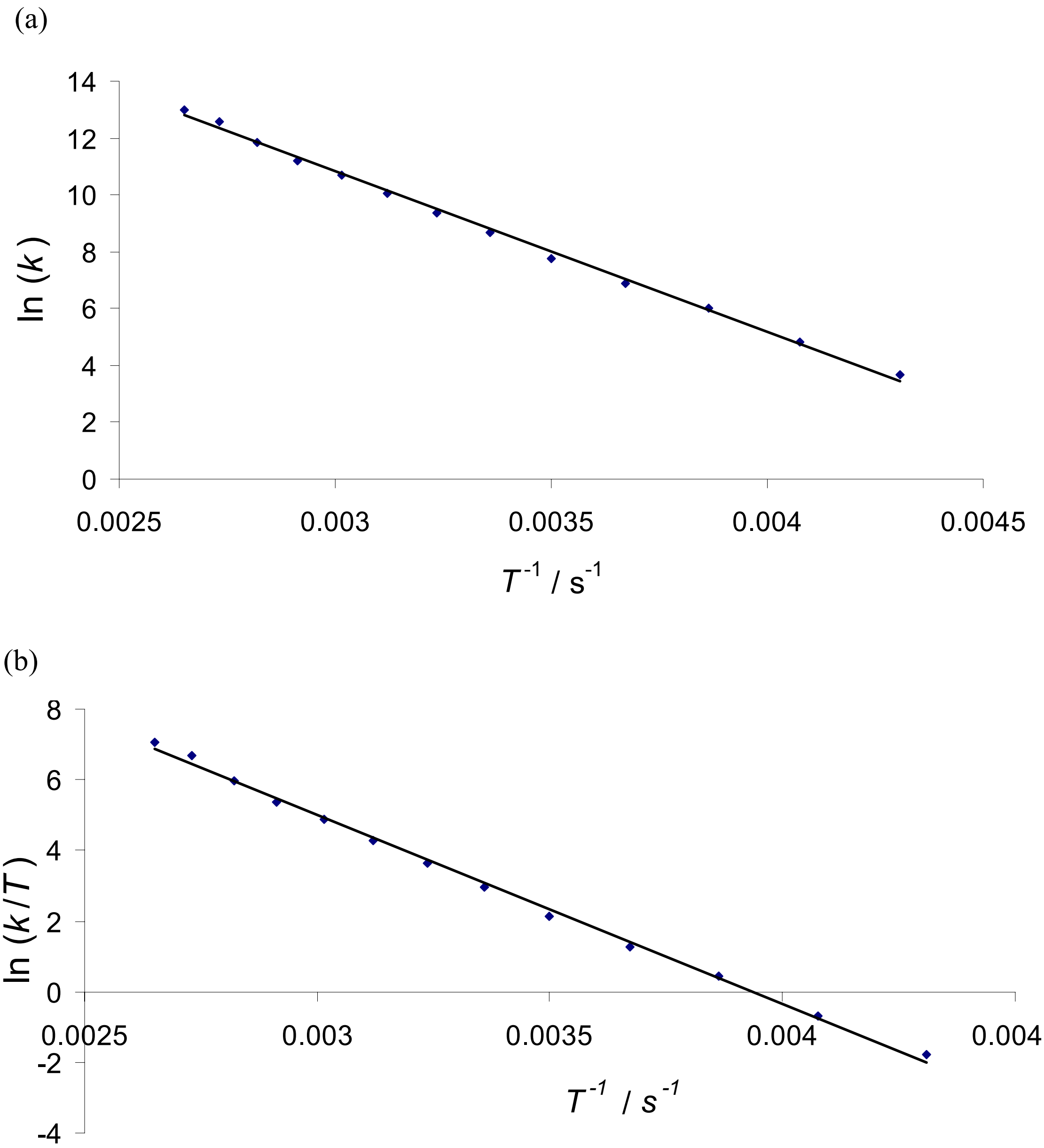


Fig S4 Plots of (a) ln (*k*) vs T^{-1} and (b) ln (*k*/*T*) vs T^{-1} for the carbonyl exchange in complex **9**.

Crystal Data for **9**.

Table S1. Crystal data and structure refinement for **9**.

Empirical formula	C14 H14 Fe O7	
Formula weight	350.10	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.1710(4) Å	α= 90°.
	b = 7.2170(4) Å	β= 110.426(3)°.
	c = 10.6320(6) Å	γ = 90°.
Volume	731.36(6) Å^3	
Z	2	
Density (calculated)	1.590 Mg/m^3	
Absorption coefficient	1.063 mm^{-1}	
F(000)	360	
Crystal size	0.22 x 0.17 x 0.13 mm^3	
Theta range for data collection	8.57 to 30.45°.	
Index ranges	-14<=h<=14, -10<=k<=10, -15<=l<=15	
Reflections collected	6719	
Independent reflections	3638 [R(int) = 0.0689]	
Completeness to theta = 30.45°	93.2 %	
Absorption correction	None	
Max. and min. transmission	0.8742 and 0.7998	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3638 / 1 / 203	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.1027	
R indices (all data)	R1 = 0.0398, wR2 = 0.1044	
Absolute structure parameter	-0.007(16)	
Extinction coefficient	0.068(13)	
Largest diff. peak and hole	0.362 and -0.628 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	-1413(1)	1264(1)	-8094(1)	19(1)
O(1)	816(2)	-1126(3)	-6359(2)	38(1)
O(2)	-49(3)	4784(3)	-6994(3)	43(1)
O(3)	-582(2)	1747(4)	-10467(2)	45(1)
O(4)	-2697(2)	-3869(3)	-9759(2)	28(1)
O(5)	-2932(2)	-1312(3)	-11033(2)	25(1)
O(6)	-4069(2)	-723(3)	-6164(2)	26(1)
O(7)	-4312(2)	-2720(3)	-7869(2)	22(1)
C(1)	-48(3)	-209(4)	-7052(3)	25(1)
C(2)	-585(3)	3437(4)	-7463(3)	27(1)
C(3)	-933(3)	1515(5)	-9584(3)	28(1)
C(11)	-2873(2)	-915(3)	-8810(2)	18(1)
C(12)	-3521(2)	871(3)	-9169(2)	19(1)
C(13)	-3358(2)	2093(3)	-8080(2)	21(1)
C(14)	-2557(2)	1388(4)	-6781(2)	22(1)
C(15)	-2767(2)	-574(3)	-6411(2)	19(1)
C(16)	-2952(2)	-1913(3)	-7588(2)	19(1)
C(17)	-2817(2)	-2210(3)	-9881(2)	19(1)
C(18)	-2957(3)	-2487(4)	-12142(3)	28(1)
C(19)	-4666(3)	-2481(3)	-6694(2)	22(1)
C(20)	-6245(3)	-2363(4)	-7108(3)	32(1)
C(21)	-4036(3)	-4034(4)	-5700(2)	30(1)

Table S3. Bond lengths [Å] and angles [°] for **9**.

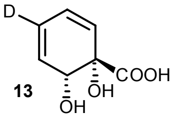
Fe(1)-C(1)	1.793(3)	C(12)-C(13)	1.418(3)
Fe(1)-C(2)	1.796(3)	C(12)-H(12)	0.9500
Fe(1)-C(3)	1.823(3)	C(13)-C(14)	1.430(3)
Fe(1)-C(12)	2.067(2)	C(13)-H(13)	0.9500
Fe(1)-C(13)	2.071(2)	C(14)-C(15)	1.505(4)
Fe(1)-C(14)	2.108(2)	C(14)-H(14)	0.9500
Fe(1)-C(11)	2.114(2)	C(15)-C(16)	1.540(3)
O(1)-C(1)	1.140(3)	C(15)-H(15)	1.0000
O(2)-C(2)	1.140(4)	C(16)-H(16)	1.0000
O(3)-C(3)	1.126(3)	C(18)-H(18A)	0.9800
O(4)-C(17)	1.206(3)	C(18)-H(18B)	0.9800
O(5)-C(17)	1.354(3)	C(18)-H(18C)	0.9800
O(5)-C(18)	1.445(3)	C(19)-C(20)	1.512(4)
O(6)-C(19)	1.434(3)	C(19)-C(21)	1.520(4)
O(6)-C(15)	1.441(3)	C(20)-H(20A)	0.9800
O(7)-C(19)	1.426(3)	C(20)-H(20B)	0.9800
O(7)-C(16)	1.433(3)	C(20)-H(20C)	0.9800
C(11)-C(12)	1.437(3)	C(21)-H(21A)	0.9800
C(11)-C(17)	1.490(3)	C(21)-H(21B)	0.9800
C(11)-C(16)	1.511(3)	C(21)-H(21C)	0.980

C(1)-Fe(1)-C(2)	97.24(13)	C(12)-Fe(1)-C(14)	70.51(8)
C(1)-Fe(1)-C(3)	102.18(12)	C(13)-Fe(1)-C(14)	40.01(9)
C(2)-Fe(1)-C(3)	90.29(13)	C(1)-Fe(1)-C(11)	94.38(10)
C(1)-Fe(1)-C(12)	133.68(10)	C(2)-Fe(1)-C(11)	164.42(11)
C(2)-Fe(1)-C(12)	125.97(11)	C(3)-Fe(1)-C(11)	97.38(11)
C(3)-Fe(1)-C(12)	94.25(10)	C(12)-Fe(1)-C(11)	40.19(8)
C(1)-Fe(1)-C(13)	134.66(10)	C(13)-Fe(1)-C(11)	70.44(9)
C(2)-Fe(1)-C(13)	93.99(12)	C(14)-Fe(1)-C(11)	77.85(10)
C(3)-Fe(1)-C(13)	121.59(11)	C(17)-O(5)-C(18)	115.3(2)
C(12)-Fe(1)-C(13)	40.09(9)	C(19)-O(6)-C(15)	106.55(17)
C(1)-Fe(1)-C(14)	95.96(11)	C(19)-O(7)-C(16)	106.81(16)
C(2)-Fe(1)-C(14)	90.62(12)	O(1)-C(1)-Fe(1)	178.1(3)
C(3)-Fe(1)-C(14)	161.58(11)	O(2)-C(2)-Fe(1)	176.3(3)

O(3)-C(3)-Fe(1)	176.0(3)	O(7)-C(16)-C(15)	105.04(18)
C(12)-C(11)-C(17)	119.72(19)	C(11)-C(16)-C(15)	111.78(19)
C(12)-C(11)-C(16)	119.90(19)	O(7)-C(16)-H(16)	109.8
C(17)-C(11)-C(16)	112.69(19)	C(11)-C(16)-H(16)	109.8
C(12)-C(11)-Fe(1)	68.15(12)	C(15)-C(16)-H(16)	109.8
C(17)-C(11)-Fe(1)	122.18(16)	O(4)-C(17)-O(5)	123.1(2)
C(16)-C(11)-Fe(1)	106.65(14)	O(4)-C(17)-C(11)	124.7(2)
C(13)-C(12)-C(11)	115.40(19)	O(5)-C(17)-C(11)	112.1(2)
C(13)-C(12)-Fe(1)	70.11(13)	O(5)-C(18)-H(18A)	109.5
C(11)-C(12)-Fe(1)	71.65(12)	O(5)-C(18)-H(18B)	109.5
C(13)-C(12)-H(12)	122.3	H(18A)-C(18)-H(18B)	109.5
C(11)-C(12)-H(12)	122.3	O(5)-C(18)-H(18C)	109.5
Fe(1)-C(12)-H(12)	127.8	H(18A)-C(18)-H(18C)	109.5
C(12)-C(13)-C(14)	115.6(2)	H(18B)-C(18)-H(18C)	109.5
C(12)-C(13)-Fe(1)	69.81(13)	O(7)-C(19)-O(6)	104.43(18)
C(14)-C(13)-Fe(1)	71.40(13)	O(7)-C(19)-C(20)	108.6(2)
C(12)-C(13)-H(13)	122.2	O(6)-C(19)-C(20)	109.0(2)
C(14)-C(13)-H(13)	122.2	O(7)-C(19)-C(21)	110.2(2)
Fe(1)-C(13)-H(13)	128.5	O(6)-C(19)-C(21)	111.2(2)
C(13)-C(14)-C(15)	120.2(2)	C(20)-C(19)-C(21)	113.0(2)
C(13)-C(14)-Fe(1)	68.60(13)	C(19)-C(20)-H(20A)	109.5
C(15)-C(14)-Fe(1)	107.10(16)	C(19)-C(20)-H(20B)	109.5
C(13)-C(14)-H(14)	119.9	H(20A)-C(20)-H(20B)	109.5
C(15)-C(14)-H(14)	119.9	C(19)-C(20)-H(20C)	109.5
Fe(1)-C(14)-H(14)	94.1	H(20A)-C(20)-H(20C)	109.5
O(6)-C(15)-C(14)	109.93(19)	H(20B)-C(20)-H(20C)	109.5
O(6)-C(15)-C(16)	103.99(17)	C(19)-C(21)-H(21A)	109.5
C(14)-C(15)-C(16)	111.52(18)	C(19)-C(21)-H(21B)	109.5
O(6)-C(15)-H(15)	110.4	H(21A)-C(21)-H(21B)	109.5
C(14)-C(15)-H(15)	110.4	C(19)-C(21)-H(21C)	109.5
C(16)-C(15)-H(15)	110.4	H(21A)-C(21)-H(21C)	109.5
O(7)-C(16)-C(11)	110.60(17)	H(21B)-C(21)-H(21C)	109.5

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3)for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	18(1)	17(1)	19(1)	0(1)	4(1)	-1(1)
O(1)	26(1)	34(1)	44(1)	8(1)	0(1)	4(1)
O(2)	40(1)	25(1)	54(1)	-5(1)	4(1)	-8(1)
O(3)	39(1)	67(2)	32(1)	1(1)	15(1)	-13(1)
O(4)	42(1)	19(1)	25(1)	-1(1)	14(1)	2(1)
O(5)	40(1)	21(1)	17(1)	-3(1)	12(1)	0(1)
O(6)	28(1)	24(1)	31(1)	-12(1)	16(1)	-6(1)
O(7)	25(1)	24(1)	16(1)	-3(1)	6(1)	-6(1)
C(1)	21(1)	24(1)	28(1)	-2(1)	7(1)	-4(1)
C(2)	27(1)	23(1)	30(1)	1(1)	8(1)	-2(1)
C(3)	22(1)	35(2)	27(1)	0(1)	7(1)	-4(1)
C(11)	20(1)	17(1)	15(1)	-2(1)	4(1)	-1(1)
C(12)	19(1)	17(1)	19(1)	-1(1)	6(1)	1(1)
C(13)	22(1)	18(1)	24(1)	-2(1)	7(1)	2(1)
C(14)	23(1)	22(1)	20(1)	-4(1)	6(1)	-4(1)
C(15)	21(1)	22(1)	16(1)	-3(1)	6(1)	-2(1)
C(16)	19(1)	18(1)	16(1)	-1(1)	4(1)	0(1)
C(17)	20(1)	20(1)	17(1)	-1(1)	6(1)	0(1)
C(18)	41(1)	26(1)	22(1)	-6(1)	15(1)	-1(1)
C(19)	25(1)	19(1)	23(1)	-6(1)	11(1)	-3(1)
C(20)	25(1)	24(1)	51(2)	-10(1)	18(1)	-2(1)
C(21)	39(1)	29(2)	22(1)	5(1)	12(1)	-2(1)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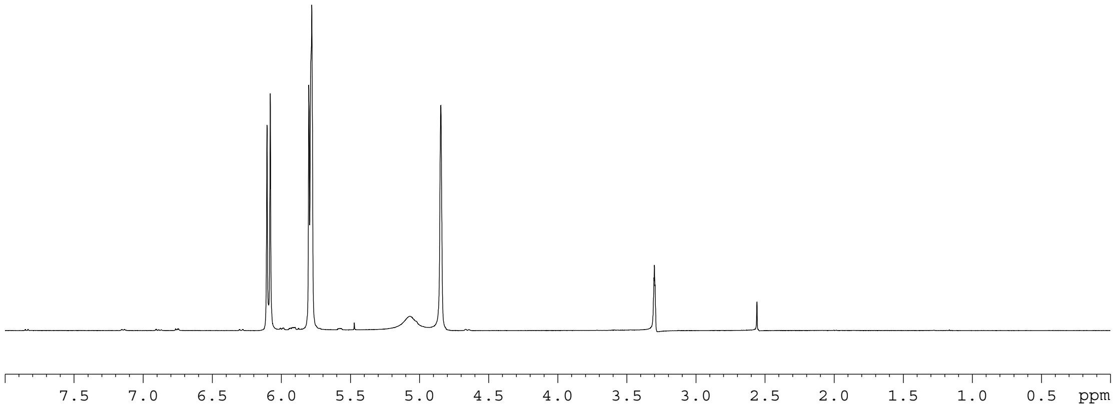
OH
OH

13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3.0
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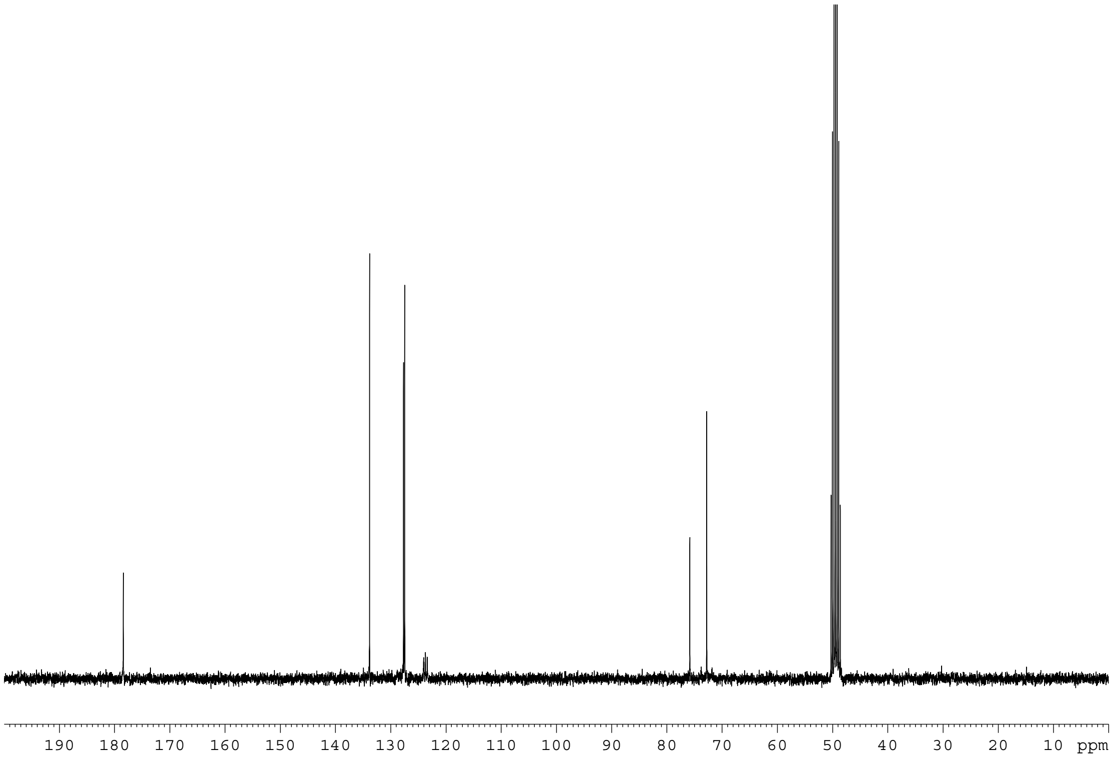
1.0
0.5
ppm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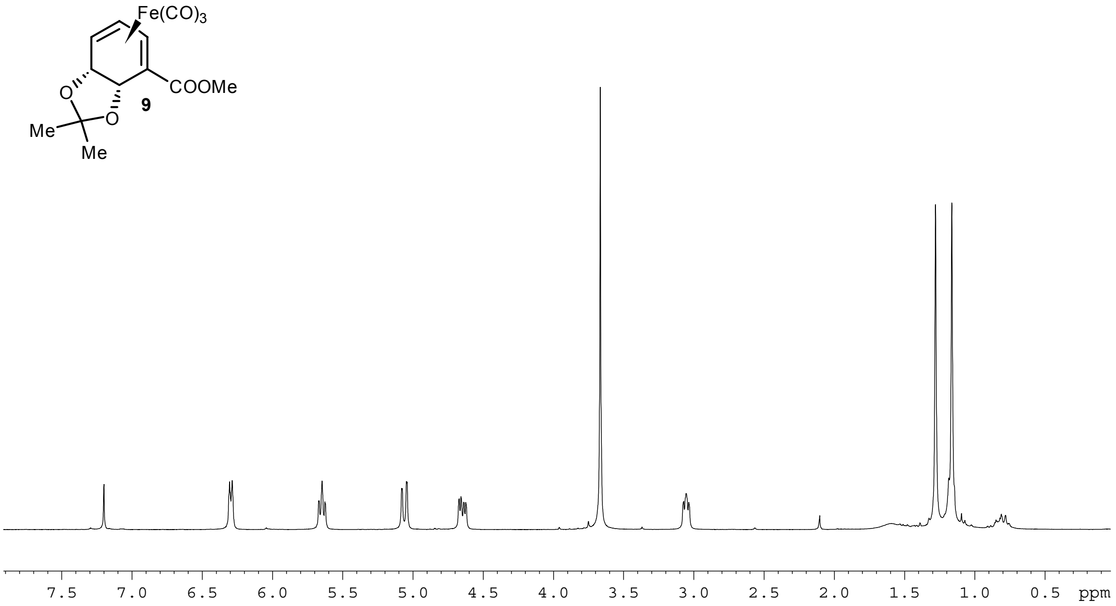
10
ppm


Fe(CO)$_3$
COOMe
O
O
Me
Me
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6.5
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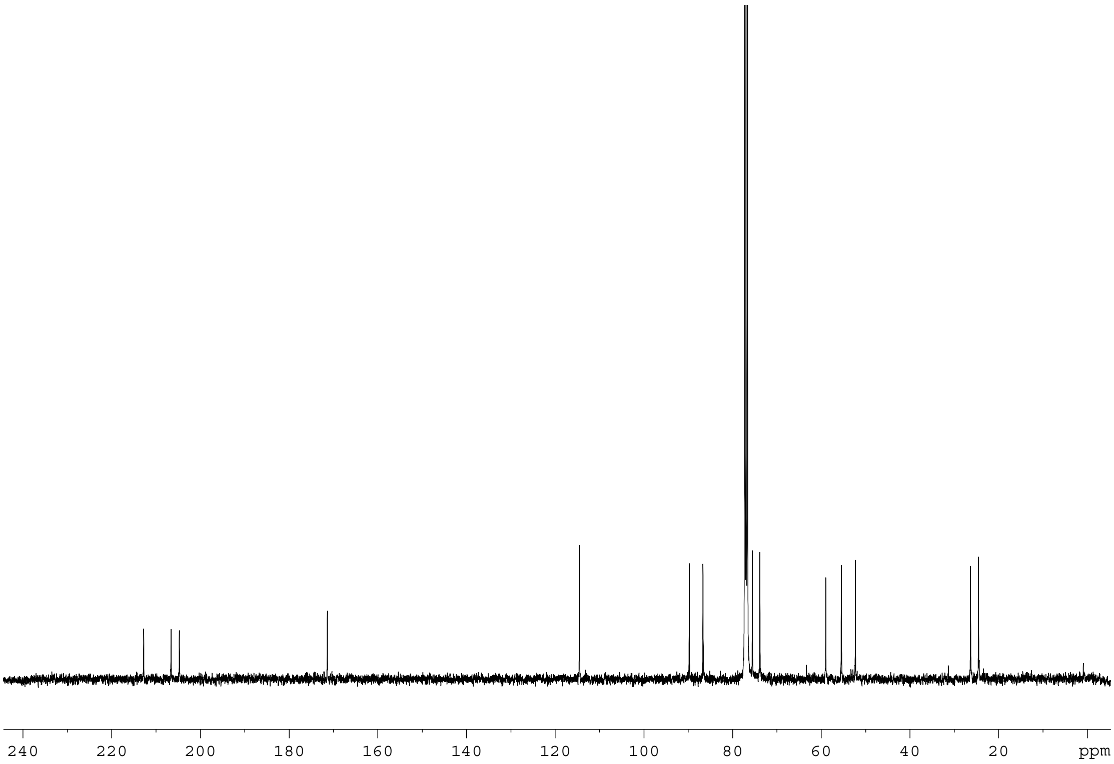
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

9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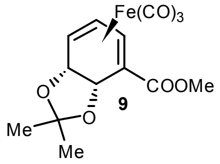
40
20
ppm

228 K


Fe(CO)3
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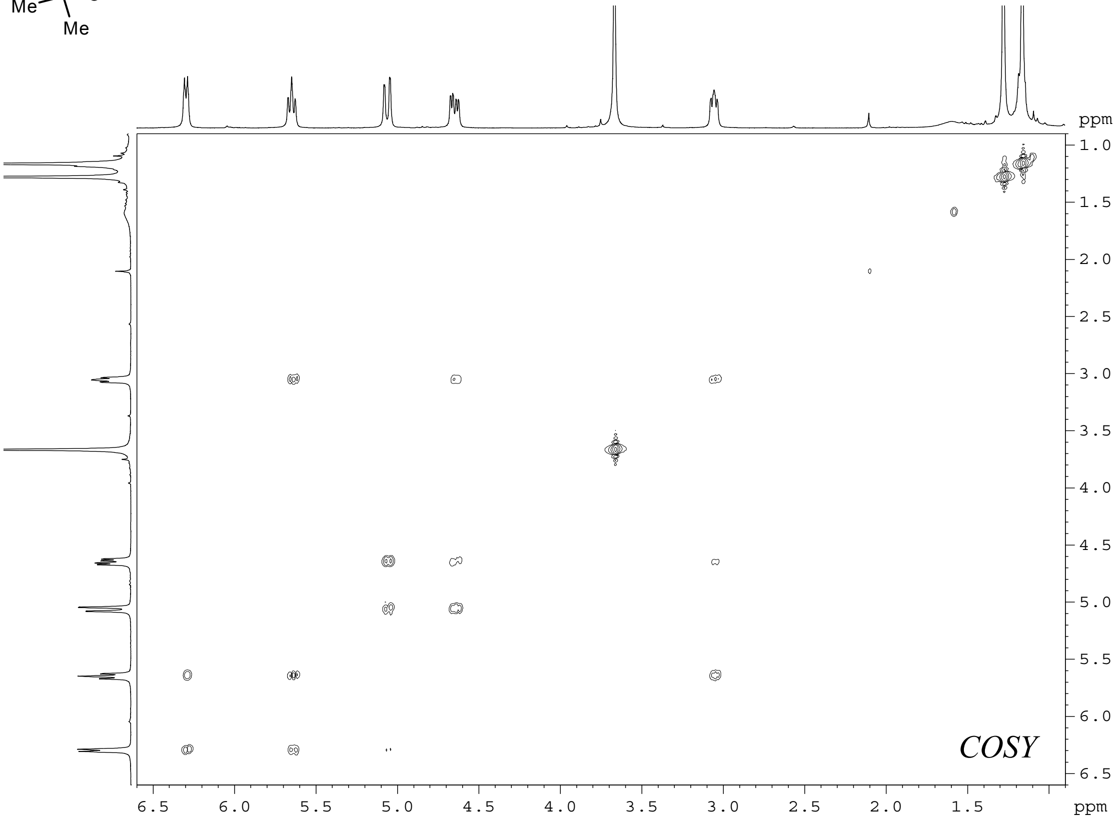
O
Me
Me

9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5.5
6.0
6.5
COSY
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5.5
5.0
4.5
4.0
3.5
3.0
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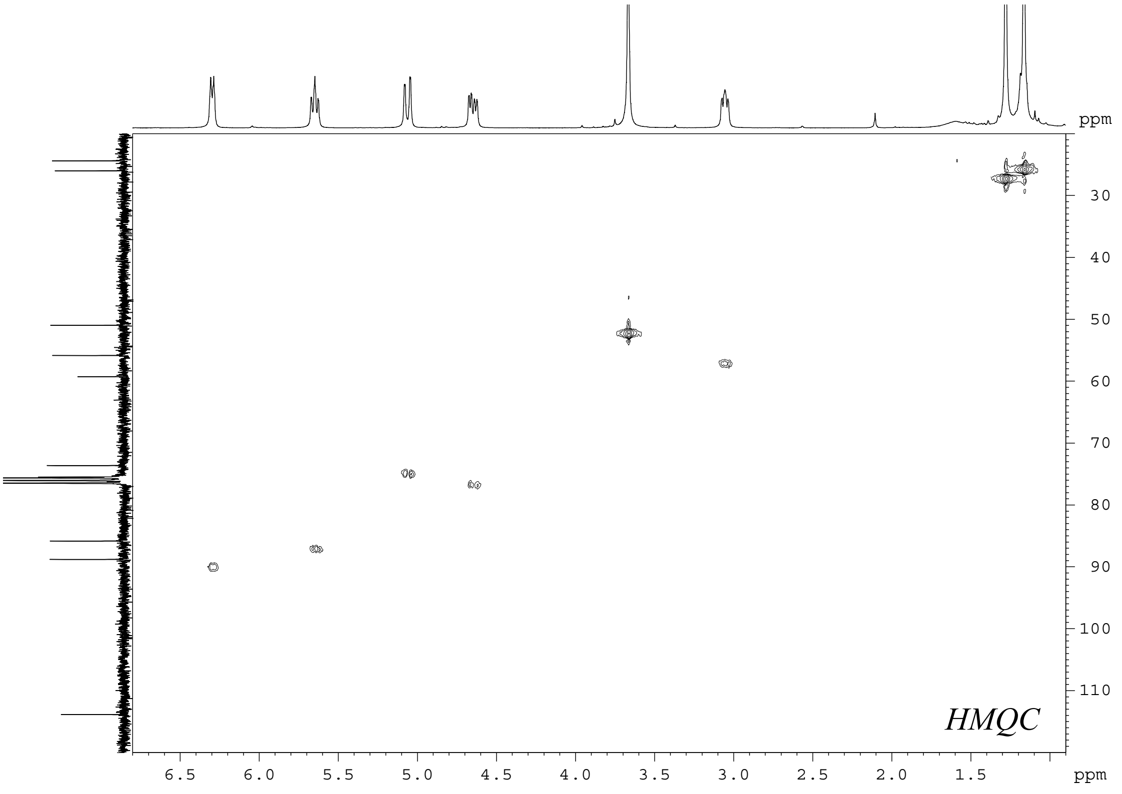
2.0
1.5
ppm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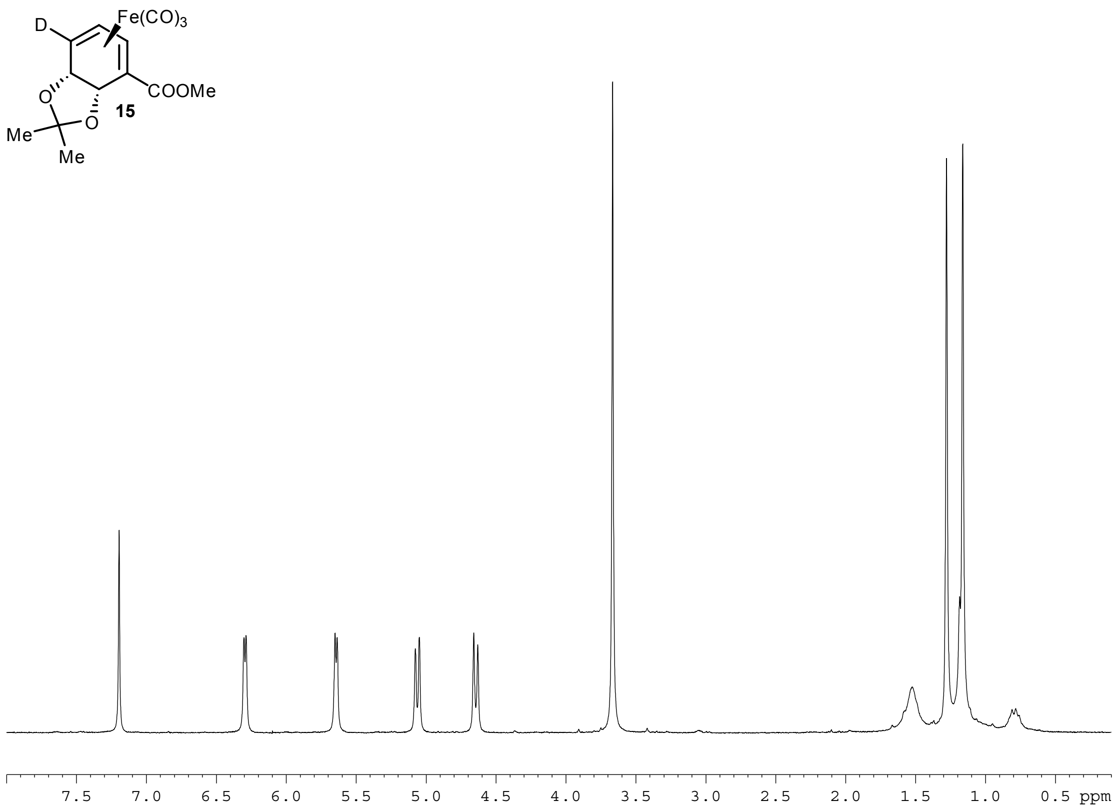
2.0
1.5
ppm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COOMe
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O
O
Me
Me
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4.0
3.5
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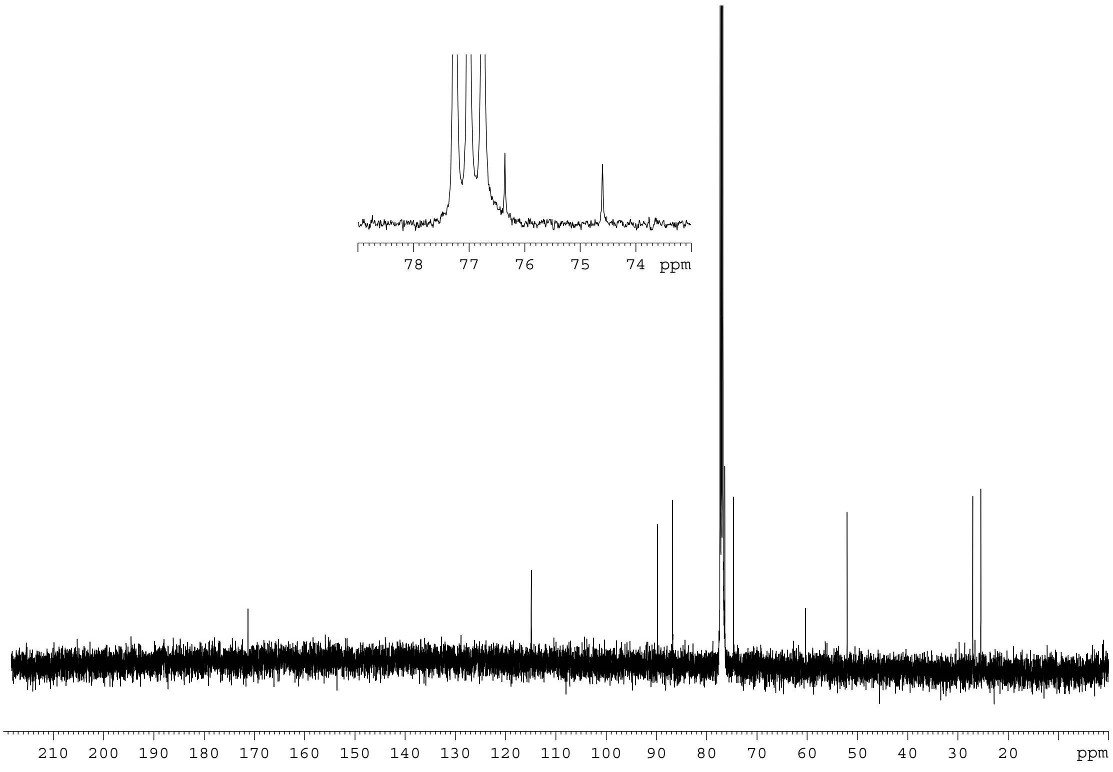
1.5
1.0
0.5 ppm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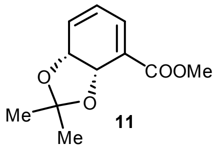
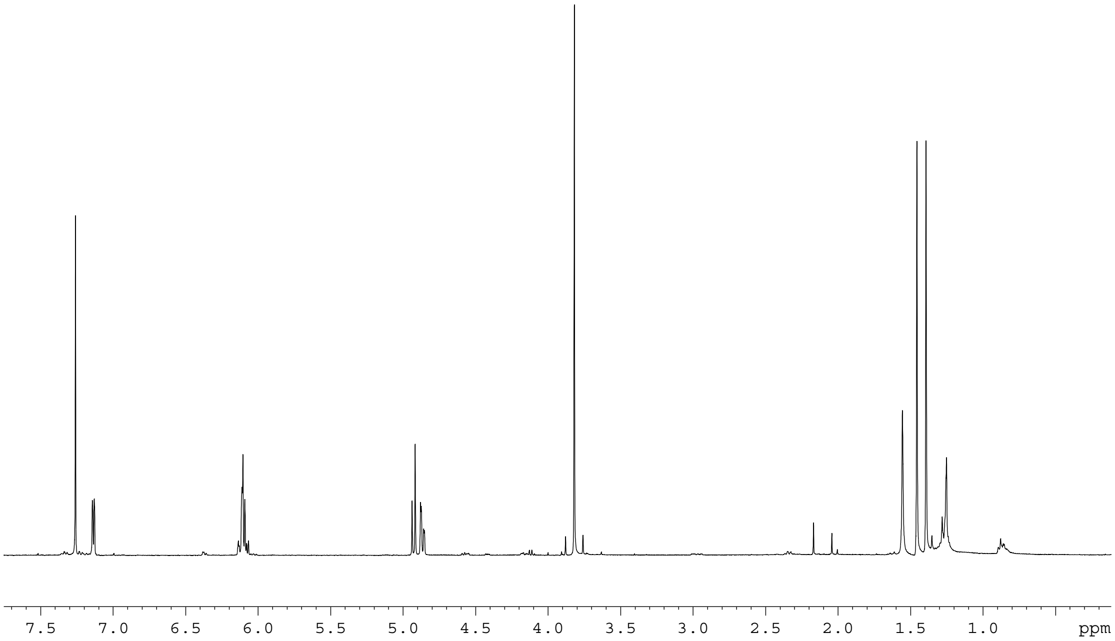
20
ppm


COOMe
O
O
Me
Me

11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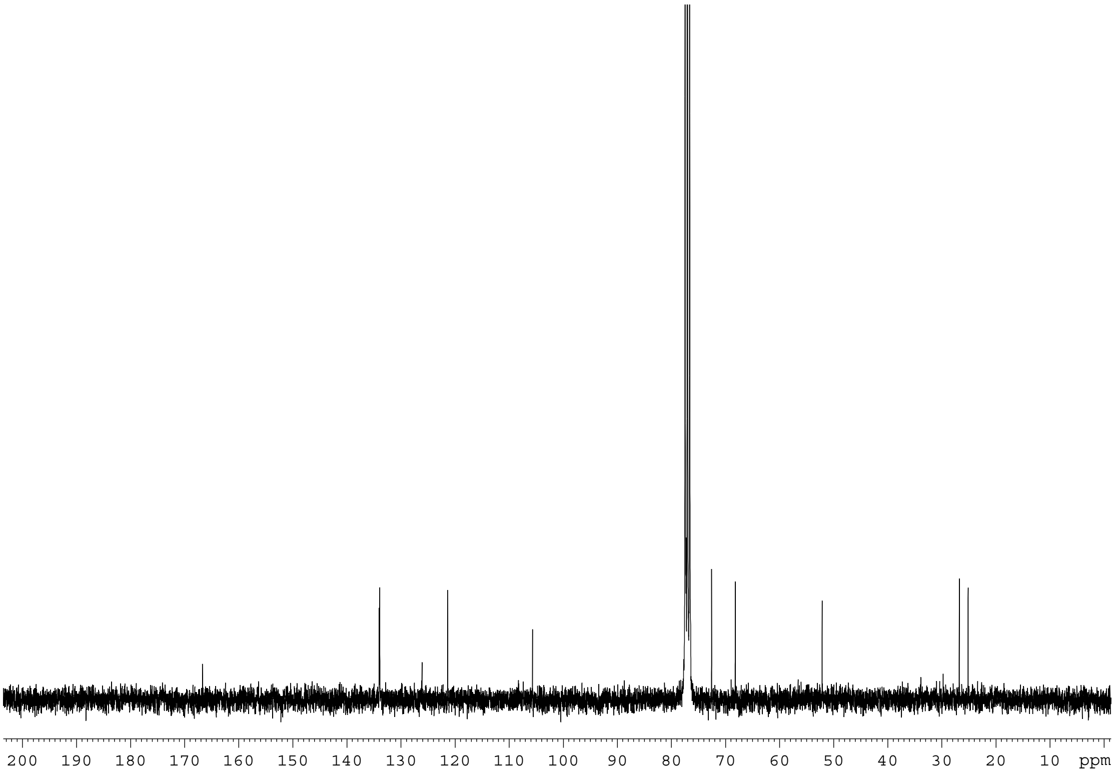
1.0
ppm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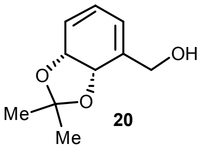
10
ppm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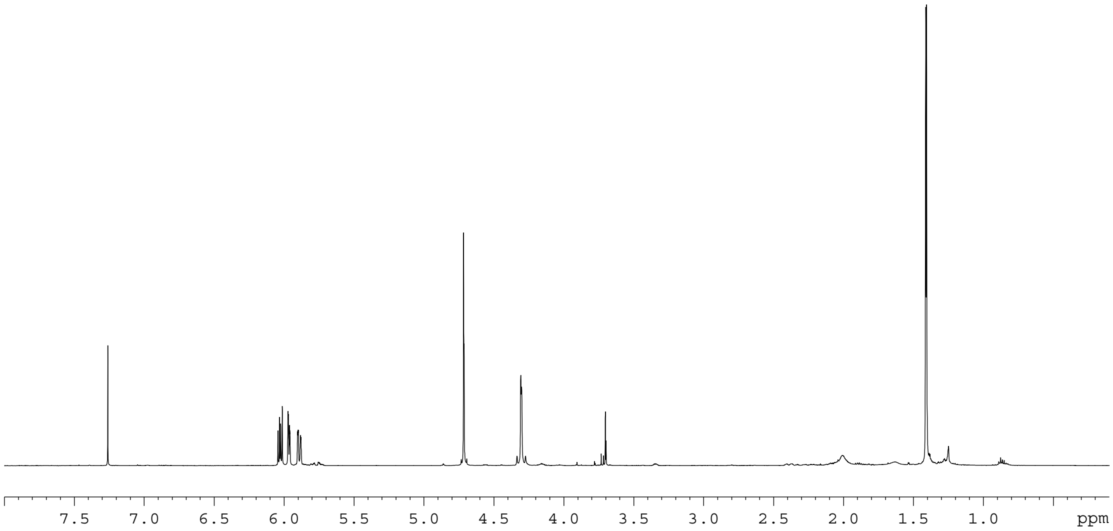
O
O
Me
Me

20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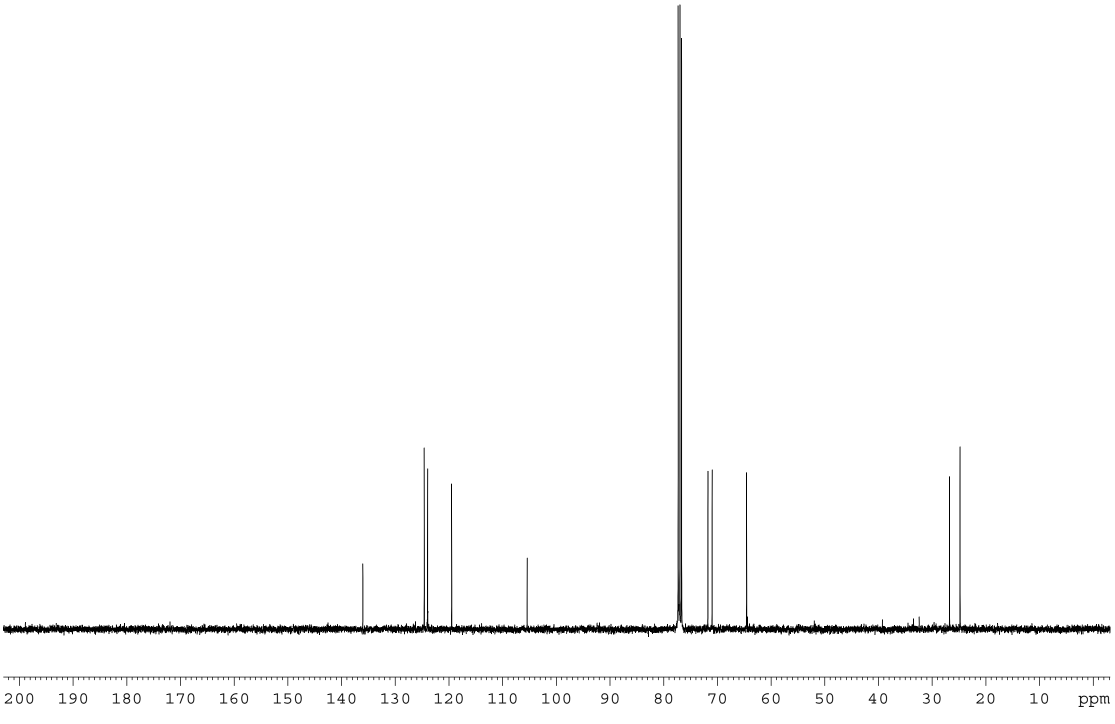
1.0
ppm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10
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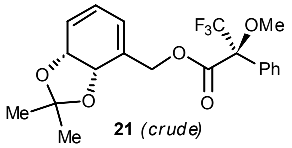
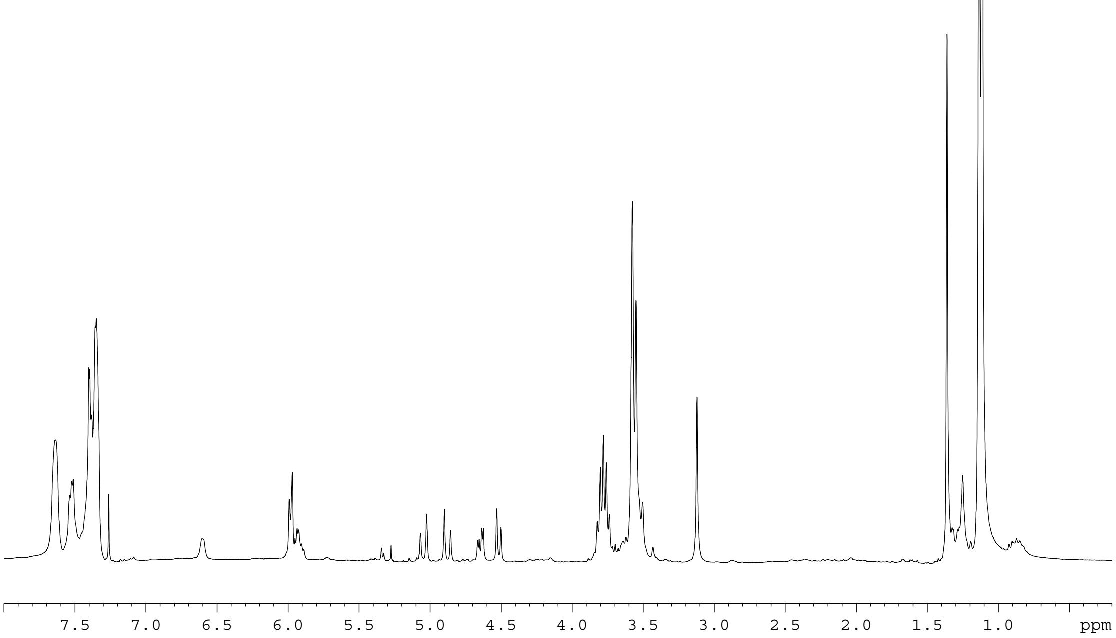
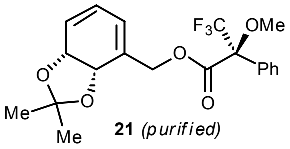
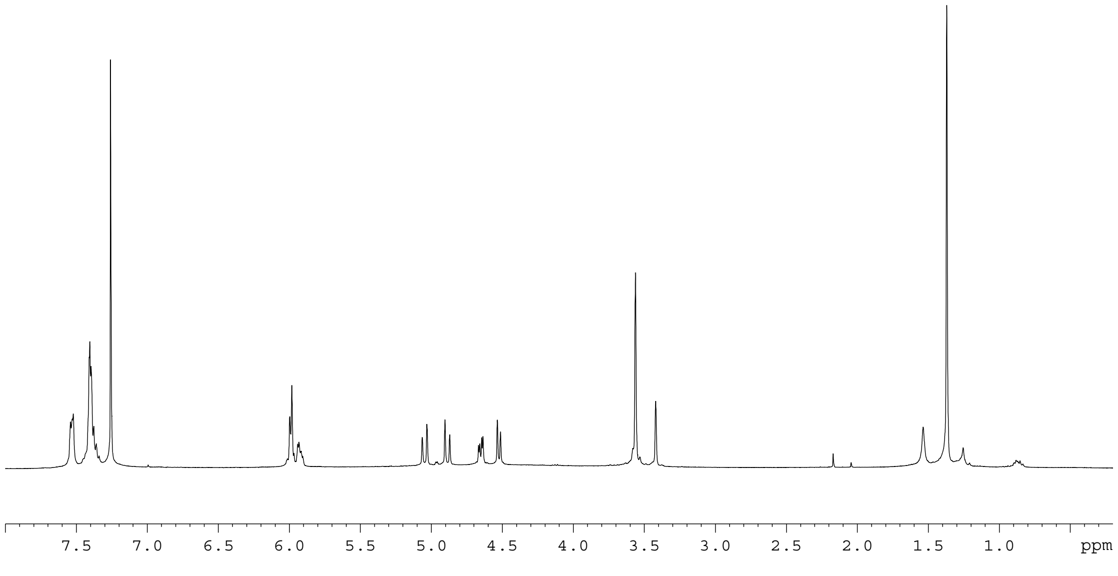


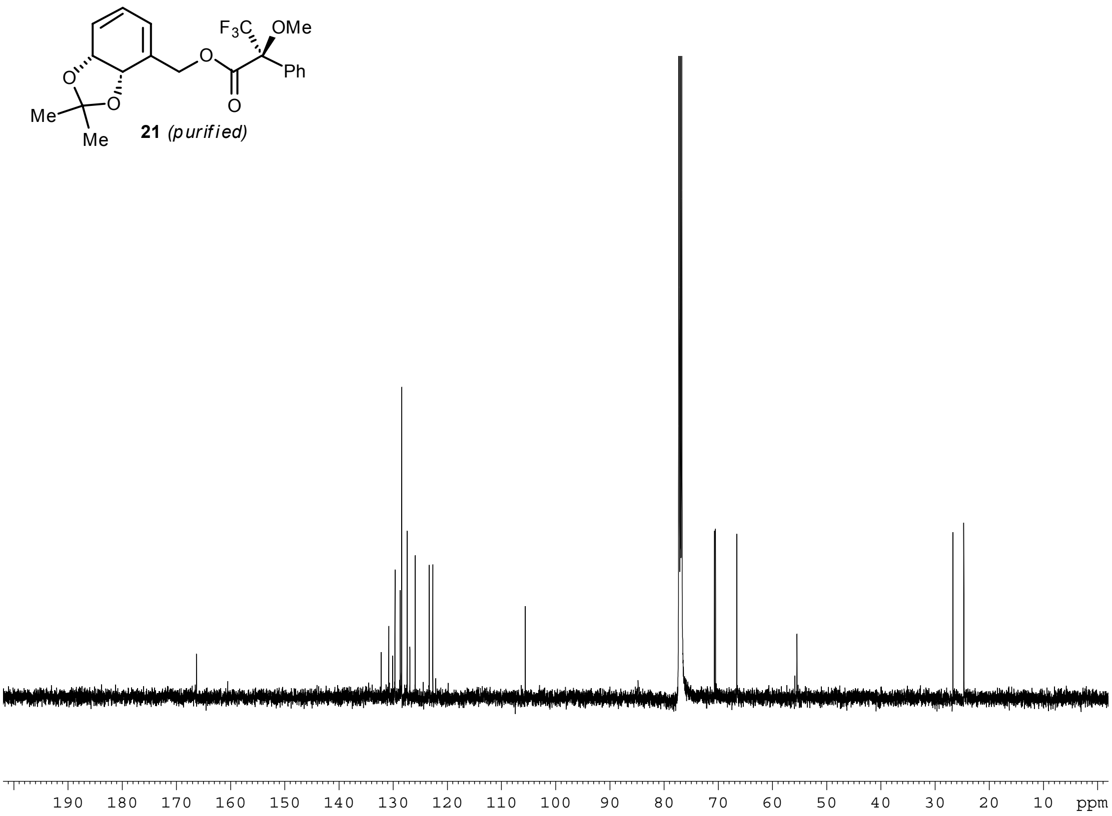
21 *(crude)*





21 *(purified)*





21 *(purified)*

F$_3$C
OMe
Ph
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O
O
O
Me
Me
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150
140
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90
80
70
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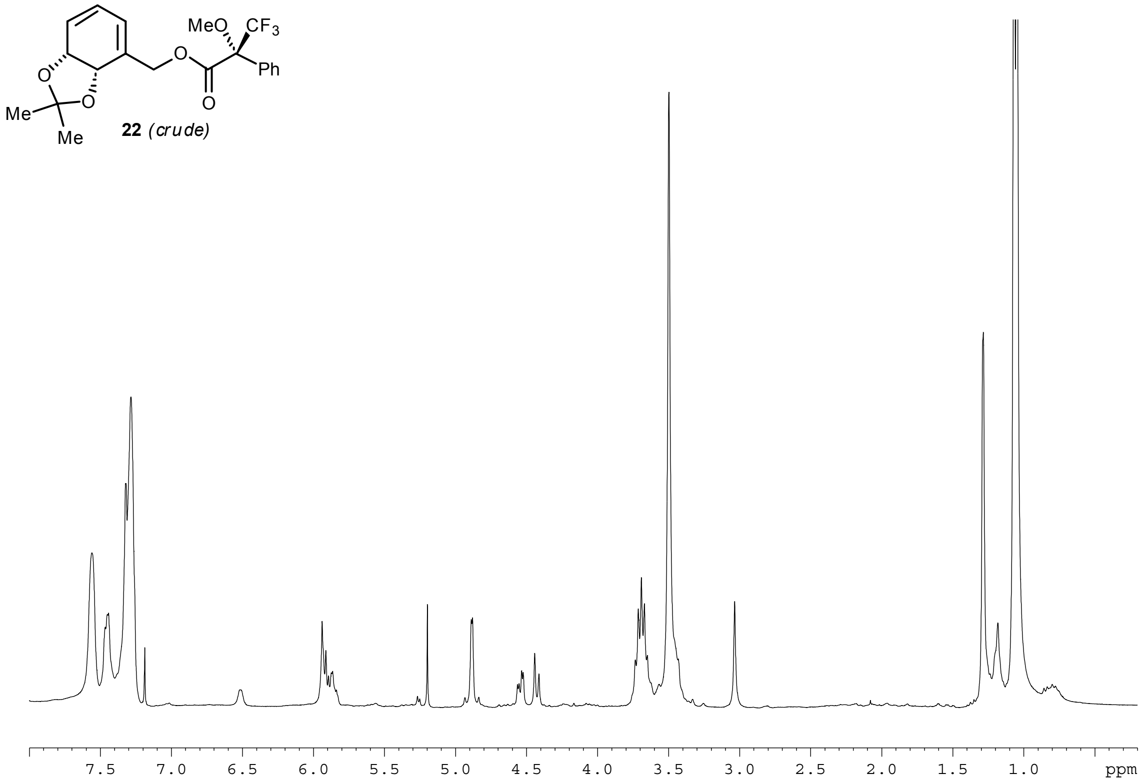
40
30
20
10
ppm



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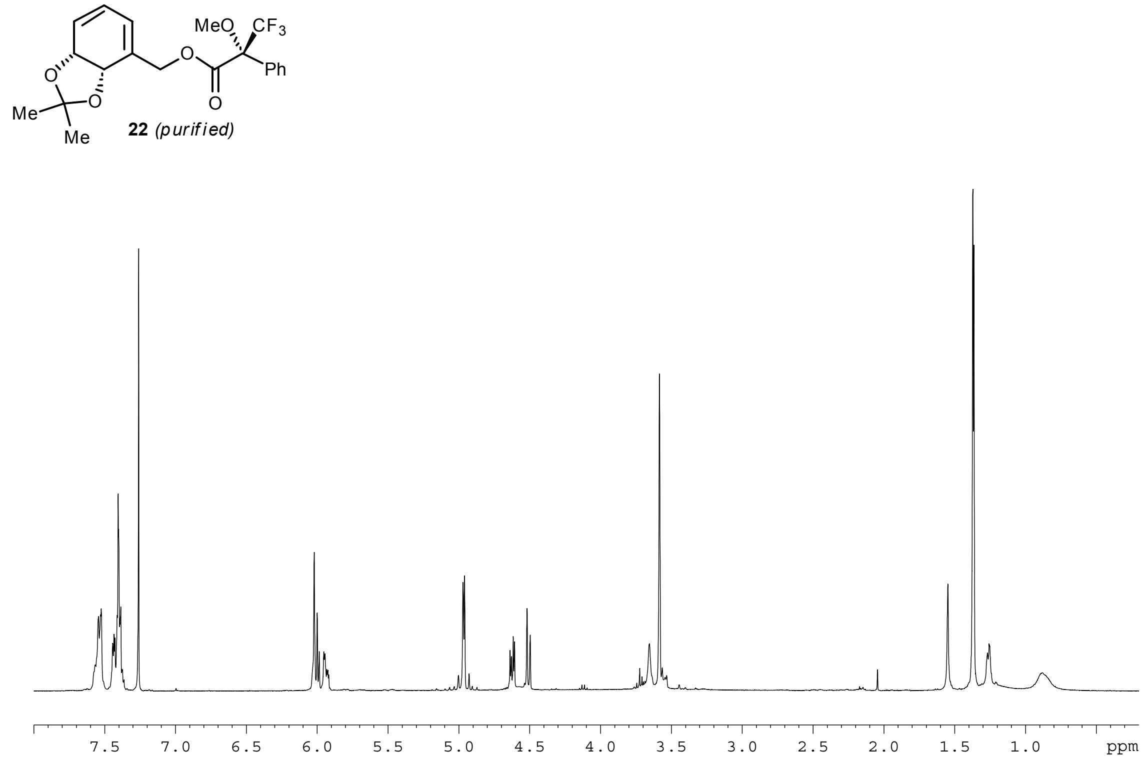

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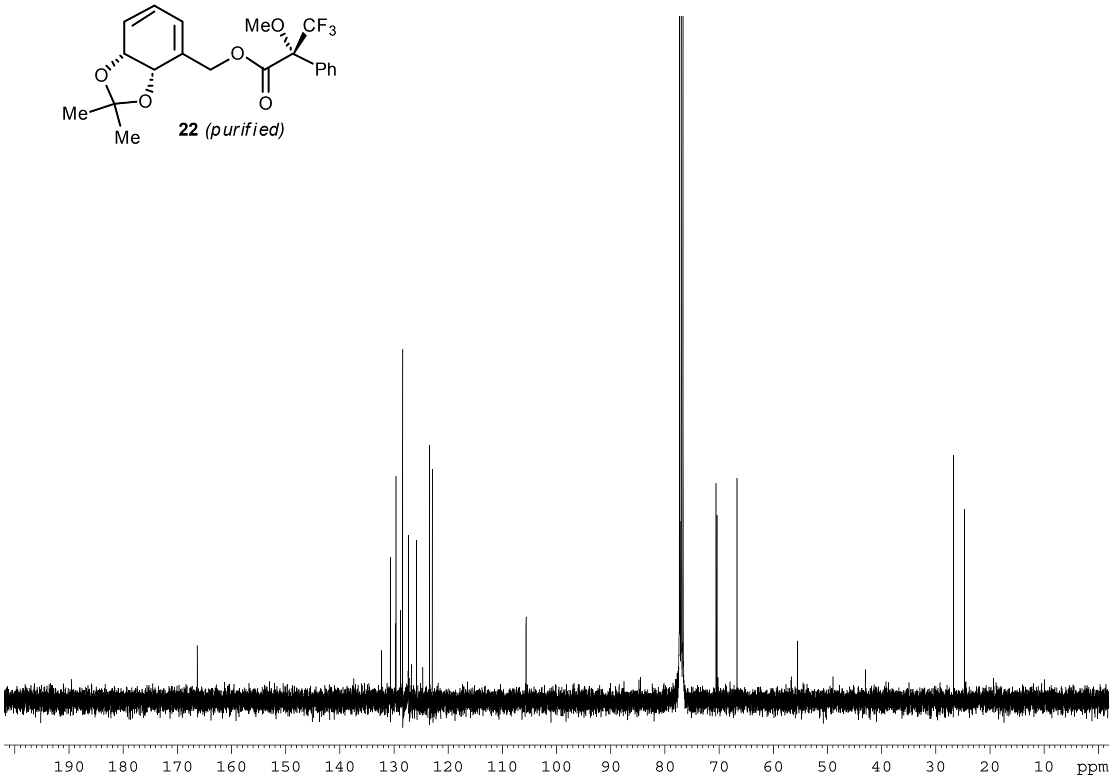
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CF3
Ph
O
O
O
O
O
Me
Me

22 *(purified)*

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180
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140
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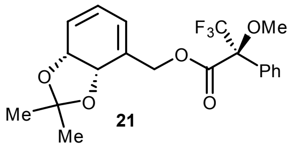
40
30
20
10
ppm



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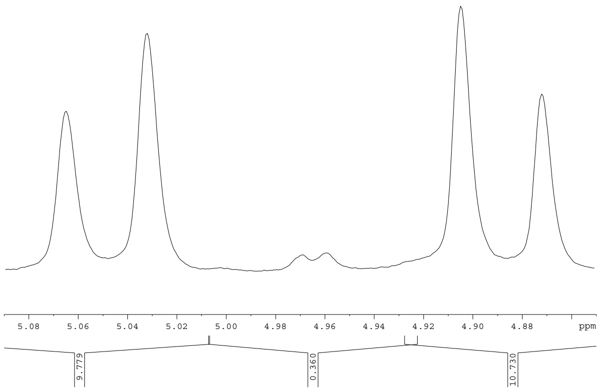
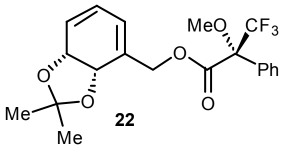
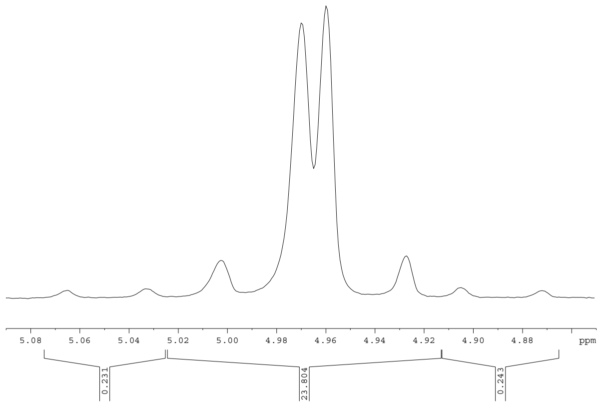
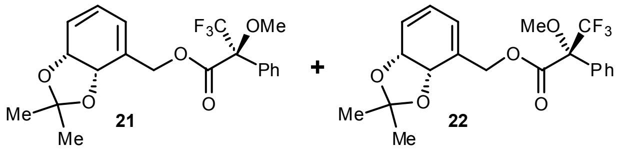


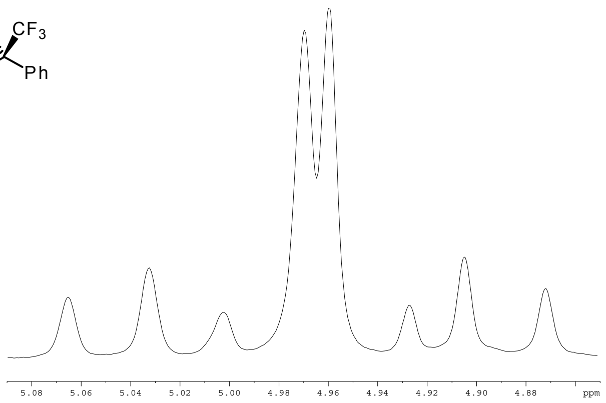


22





(mixture)



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