Supporting information.

Developing asymmetric iron and ruthenium-based cyclone complexes; complex factors influence the asymmetric induction in the transfer hydrogenation of ketones.

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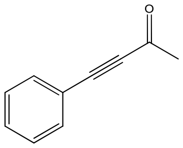
Contents:

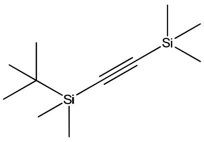
1) Synthesis of ligands and applications to reduction reactions:

General experimental details follow those previously reported.[1]



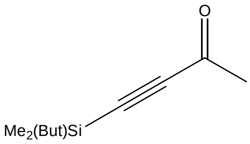
4-Phenyl-3-butyne-2-one 2[1,2]

n-BuLi (1.6M in hexanes, 37.5 cm^3, 60 mmol) was added to phenyl acetylene (6.58 cm^3, 6.12 g, 60 mmol) in THF (60 cm^3) at -78 °C and the mixture left to stir for 30 min. EtOAc (5.86 cm^3, 5.29 g, 60 mmol) in THF (90 cm^3) was added over 10 min followed by addition of $BF_3.Et_2O$ (9.03 cm^3, 10.15 g, 71.5 mmol). The mixture was kept at -78 °C for 30 min before being allowed to warm to room temperature and after 30 min was quenched with saturated $NH_4Cl_{(aq)}$ (100 cm^3). Following extraction with EtOAc (2 x 50 cm^3) the organics were washed with brine (50 cm^3) and dried over Na_2SO_4 and the was solvent removed in vacuo. Short path distillation (125 °C, 5.7 mbar) afforded the ketone[2] as a rich brown oil (4.86 g, 33.8 mmol, 56%); *m/z* (ESI) 167 $[M +23]^+$, 145 $[M +1]^+$; (Found (ESI): M+H 145.0652, $C_{10}H_9O$ requires 145.0648); ν_{max} 2195, 2124, 1665, 1487, 1355, 1274 and 1153 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.59-7.55 (2H, m, Ar), 7.48-7.43 (1H, m, Ar), 7.41-7.35 (2H, m, Ar), 2.45 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 184.40 (C=O), 132.88 (CH, Ar) 130.60 (CH, Ar), 128.49 (CH, Ar), 119.73 (ipso, Ar), 90.14 (C≡C), 88.12 (C≡C), 32.58 (CH_3).



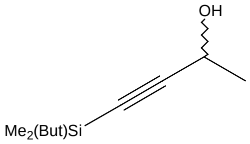
1-(t-Butyldimethylsilyl)-2-(trimethylsilyl)ethyne.[3]

To trimethysilylacetylene (10.0 g, 14.1 cm^3, 0.102 mmol) in THF (160 cm^3) was added ^{n}BuLi (40 cm^3, 2.5M, 0.1 mmol, 0.98 eq.) at -78 °C over 5 min. After 15 min the -78 °C ice bath was replaced with a 0 °C ice bath for 8 min after which the -78 °C bath was again reinstated. To the reaction mixture was added TBDMSCl (15.07 g, 0.1 mmol, 0.98 eq.) in THF (20 cm^3) over 15 min. The ice bath was subsequently removed and the reaction mixture allowed to warm to room temperature over night (18.5 h). In air the reaction was quenched using saturated NH_4Cl solution (100 cm^3) and extracted using Et_2O (2 x 100 cm^3) the combined fractions were further washed with brine (40 cm^3) and dried over $MgSO_4$. Removal of the solvent *in vacuo* afforded a yellow oil (20.619 g, 0.097 mmol, 95% yield); δ_H (300 MHz, $CDCl_3$) 0.91 (9H, s, C(C*H*$_3$)$_3$), 0.14 (9H, s, Si(C*H*$_3$)$_3$), 0.07 (6H, s, Si(C*H*$_3$)$_2$); δ_C (75 MHz, $CDCl_3$) 114.58 (quat., C≡C), 112.13 (quat., C≡C) 26.00 (CH_3, C(*C*H$_3$)$_3$), 16.43 (quat., *C*(CH$_3$)$_3$), 0.06 (CH_3, Si(*C*H$_3$)) -4.68 (CH_3, Si(*C*H$_3$)); δ_{Si} (99 MHz, $CDCl_3$) -9.26 (*Si*(CH$_3$)$_2$C(CH$_3$)$_3$), -19.27 (*Si*(CH$_3$)$_3$).



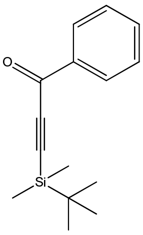
4-(t-Butyldimethylsilyl)-but-3-yn-2-one.[4]

To a suspension of $AlCl_3$ (4.059 g, 30.66 mmol, 1.3 eq.) in DCM (50 cm^3) was added dropwise a solution of 1-(t-butyldimethylsilyl)-2-(trimethylsilyl)ethyne (5.00 g, 23.59 mmol, 1 eq.) and acetylchloride (1.68 cm^3, 1.85 g, 23.6 mmol 1 eq.) in DCM (32 cm^3) over 10 min at 0 °C. The reaction mixture was allowed to warm to room temperature over ½ hours before being cooled to 0 °C and quenched using HCl(aq) (1N, 80 cm^3, 80 mmol) and extracted using DCM (2 x 20 cm^3). The combined organic fractions were further washed with brine solution (30 cm^3) and dried over $MgSO_4$. Removal of the solvent *in vacuo* afforded a yellow oil (3.66 g, 20.110 mmol, 85 % crude yield). Purification by column chromatography (hexane/EtOAc) afforded a colourless oil (3.1645g, 17.387 mmol, 74 % yield); *m/z* (ESI) 183.1 [M + 1]$^+$, 205.0 [M + 23]$^+$; (Found (ESI): M+H 183.1204. $C_{10}H_{19}O$ requires 183.1200); δ_H (400 MHz, $CDCl_3$) 2.32 (3H, s, C=OC*H*$_3$), 0.94 (9H, s, C(C*H*$_3$)$_3$), 0.15 (6H, s, Si(C*H*$_3$)$_2$); δ_C (100 MHz, $CDCl_3$) 184.14 (C=O), 103.17 (C≡C), 96.13 (C≡C) 32.57 (CH_3, C=O*C*H$_3$) 25.89 (CH_3, C(*C*H$_3$)$_3$), 16.47 (*C*(CH$_3$)$_3$), -5.27 (CH_3, Si(*C*H$_3$)); $\square_{Si}$ (99 MHz, $CDCl_3$) -5.37 (*Si*(CH$_3$)$_2$C(CH$_3$)$_3$).



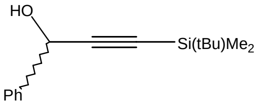
Racemic alcohol 11b.[5]

To 4-[(t-butyl)dimethylsilyl]-but-3-yn-2-one (0.100 g, 0.55 mmol, 1 eq) in methanol (3 cm^3) was added sodiumborohydride (42 mg, 1.10 mmol, 2 eq.) portion wise at 0 °C. After 30 min the reaction was quenched using saturated $NH_4Cl_{(aq)}$ (5 cm^3) and the methanol carefully evaporated and the remaining aqueous suspension extracted using Et_2O (3 x 5 cm^3). The combined organic extractions were then dried over $MgSO_4$ and the solvent removed in vacuo to afford a colourless oil (0.070 g, 0.3804 mmol, 69 % crude yield); *m/z* 207.1 $[M+23]^+$; (Found (ESI): M+Na 207.1179. $C_{10}H_{20}NaOSi$ requires 207.1176); δ_H (400 MHz, $CDCl_3$) 4.53 (1H, q, *J* 6.5, C*H*(OH)C*H*$_3$), 1.78 (1H, bs, O*H*), 1.46 (3H, d, *J* 6.5, CH(OH)C*H*$_3$), 0.94 (9H, s, SiC(C*H*$_3$)$_3$), 0.11 (6H, s,



3-(t-Butyldimethylsilyl)-1-phenyl-prop-2-yn-1-one.

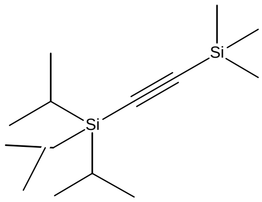
To a suspension of $AlCl_3$ (8.11 g, 61.32 mmol, 1.3 eq.) in DCM (100 cm^3) was added dropwise a solution of 1-(t-butyldimethylsilyl)-2-(trimethylsilyl)ethyne (10.00 g, 47.17 mmol, 1 eq.) and benzoylchloride (5.48 cm^3, 6.63 g, 47.2 mmol 1 eq.) in DCM (75 cm^3) over 10 min at 0 °C. The reaction mixture was allowed to warm to room temperature over 30 min. before being cooled to 0 °C and quenched using HCl(aq) (1N, 150 cm^3, 150 mmol) and extracted using DCM (2 x 40 cm^3). The combined organic fractions were further washed with brine solution (60 cm^3), dried over $MgSO_4$. Removal of the solvent in vacuo afforded a yellow oil (11.07 g, 45.36 mmol, 96 % crude yield). Purification by column chromatography (hexane/EtOAc) afforded a colourless oil (8.43 g, 34.55 mol, 73.4 % yield); *m/z* (ESI) 245.1 $[M+1]^+$, 267.0 $[M+23]^+$; (Found (ESI): M+H 245.1367. $C_{15}H_{21}OSi$ requires 245.1356); ν_{max} 2952, 2928, 2885, 2857, 2115, 1774 and 1643 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.15 (2H, d, *J* 8.2, Ar), 7.61 (1H, t, *J* 7.5, Ar), 7.48 (2H, t, *J* 7.5, Ar), 1.03 (9H, s, SiC(C*H*$_3$)$_3$), 0.26 (6H, s, Si(C*H*$_3$)$_2$); δ_C (100 MHz, $CDCl_3$) 177.48 (ipso, C=O), 136.53 (ipso, Ar), 134.08 (CH, Ar), 129.51 (CH, Ar), 128.91 (CH, Ar), 101.61 (quat., C≡C), 99.26 (quat., C≡C), 26.01 (CH_3, SiC(*C*H$_3$)$_3$), 16.64 (quat., Si*C*(CH$_3$)$_3$), -5.12 (CH_3, Si(*C*H$_3$)$_2$); δ_{Si} (99 MHz, $CDCl_3$) -5.14 (s, $Si(CH_3)_2C(CH_3)_3$).



Racemic alcohol 11d.

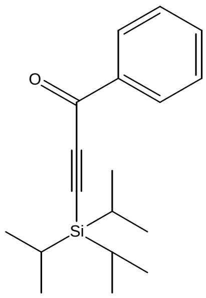
To 3-(t-butyldimethylsilyl)-1-phenyl-prop-2-yn-1-one, (2.762 g, 11.32 mmol, 1 eq) in methanol (80 cm^3) was added sodium borohydride (0.8603 g, 22.64 mmol, 2 eq.) in

10 portions at 0 °C. After 30 min the reaction was quenched using saturated $NH_4Cl_{(aq)}$ (135 cm^3), the methanol carefully evaporated and the remaining aqueous suspension extracted using Et_2O (3 x 67 cm^3). The combined organic extracts were then dried over $MgSO_4$ and the solvent removed in vacuo to afford **11d** as a colourless oil (1.41 g, 5.7317 mmol, 51 % crude yield); *m/z* 269.2 $[M+ 23]^+$; (Found (ESI): M+Na 269.1333. $C_{15}H_{22}NaOSi$ requires 269.1332); ν_{max} 3362 (OH), 2926, 2857, 1671, 1446 and 1003 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.568 (2H, d, *J* 7.1 Ar), 7.36 (3H, m, Ar), 5.47 (1H, s, Ar), 0.99 (9H, s, $SiC(CH_3)_3$), 0.17 (6H, s, $Si(CH_3)_2$); δ_C (100 MHz, $CDCl_3$) 140.36 (ipso, Ar), 128.49 (CH, Ar), 128.26 (CH, Ar), 126.70 (CH, Ar), 105.69 (quat., C≡C), 89.81 (quat., C≡C), 64.90 (CH(OH)), 26.03 ($SiC(CH_3)_3$), 16.50 (quat., $SiC(CH_3)_3$), -4.71 ($Si(CH_3)_2$); δ_{Si} (99 MHz, $CDCl_3$) -7.64 (s, $Si(CH_3)_2C(CH_3)_3$).



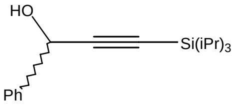
1-(Triisopropylsilyl)-2-(trimethylsilyl)-ethyne.[6]

To trimethysilylacetylene (10.385 g, 0.1057 mol) in THF (160 cm^3) was added nBuLi (64.9 cm^3, 1.6M, 0.1038 mol, 0.98 eq.) at -78 °C over 10 min. After 15 min the -78 °C ice bath was replaced with a 0 °C ice bath for 10 min after which the -78 °C bath was again reinstated. To the reaction mixture was added TIPSCl (20.012 g, 22.2 cm^3, 0.1038 mol, 0.98 eq.) over 5 min. The ice bath was subsequently removed and the reaction mixture allowed to warm to room temperature over night. In air the reaction was quenched using saturated $NH_4Cl_{(aq)}$ solution (100 cm^3) and extracted using Et_2O (2 x 100 cm^3), the combined fractions were washed with brine solution (40 cm^3). Removal of the solvent in vacuo afforded a yellow oil (26.23 g, 0.1033 mol, 98% yield); δ_H (400 MHz, $CDCl_3$) 1.12-1.01 (21H, m, $Si(CH(CH_3)_2)_3$) 0.17 (9H, s, $Si(CH_3)_3$).



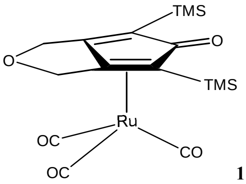
3-(Tri(isopropyl)silyl)-1-phenyl-prop-2-yn-1-one.

To a suspension of $AlCl_3$ (8.00 g, 60.423 mmol, 1.3 eq.) in DCM (100 cm^3) was added dropwise a solution of 1-(triisopropylsilyl)-2-(trimethylsilyl)-ethyne (11.8057 g, 46.479 mmol, 1 eq.) and benzoylchloride (5.40 cm^3, 6.533 g, 46.4792 mmol 1 eq.) in DCM (70 cm^3) over 10 min at 0 °C. The reaction mixture was allowed to warm to room temperature over 30 min. before being cooled to 0 °C and quenched using $HCl_{(aq)}$ (1N, 150 cm^3, 150 mmol) and extracted using DCM (2 x 40 cm^3). The combined organic fractions were further washed with brine solution (60 cm^3), dried over $MgSO_4$. Removal of the solvent in vacuo afforded a yellow oil (12.45 g, 43.54 mmol, 94 % crude yield); *m/z* 287.2 [M$^+$ +1]; (Found (ESI): M+Na 309.1640 $C_{18}H_{26}NaOSi$ requires 309.1645); δ_H (400 MHz, $CDCl_3$) 8.18 (2H, d, *J* 7.1, Ar) 7.61 (1H, t, *J* 7.4, Ar), 7.54-7.46 (3H, m, Ar), 1.24-1.15 (21H, m, $Si(CH(CH_3)_3)$; δ_C (100 MHz, $CDCl_3$) 177.55 (quat., C=O), 136.76 (ipso, Ar), 132.42 (CH, Ar), 129.42 (CH, Ar), 128.57 (CH, Ar), 103.05 (quat., C≡C), 98.02 (quat., C≡C), 18.59 ($Si(CH(\mathit{C}H_3)_2)_3$), 11.15 ($Si(\mathit{C}H(CH_3)_2)_3$).



Racemic alcohol 11e. JPH137

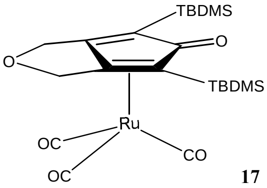
3-(Tri(isopropyl)silyl)-1-phenyl-prop-2-yn-1-one, (1.00 g, 3.4965 mmol, 1 eq.) in methanol (25 cm^3) was added sodium borohydride (0.266 g, 6.9930 mmol, 2 eq.) in small portions at 0 °C. After 30 min the reaction was quenched using saturated $NH_4Cl_{(aq)}$ (50 cm^3), the methanol carefully evaporated and the remaining aqueous suspension extracted using Et_2O (3 x 25 cm^3). The combined organic extracts were then dried over $MgSO_4$ and the solvent removed in vacuo to afford **11e** as a colourless oil in quantitative yield;



16

Complex 16.[7]

A pressure tube was charged with 1,1'-(oxydi-1-propyne-3,1-diyl)bis[1,1,1-trimethyl-silane, (0.100 g, 0.4302 mmol 1 eq.), toluene (2 cm^3) and $Ru_3(CO)_{12}$ (0.2686 g, 0.4202 mmol, 1 eq.) and purged under a steady stream of N_2. The tube was then sealed and heated to 105 ^oC. After 3 d the reaction mixture was cooled, carefully depressurised and the solvent removed in vacuo. The resulting black semisolid was dissolved in DCM (2 cm^3) and filtered through a cotton wool plug and loaded onto a short silica column (EtOAc/Hexane 0 to 20 %) to afford an orange solid (0.1110 g, 0.2461 mmol, 59 %); *m/z* 453.0 $[M+1]^+$, 474.9 $[M+23]^+$; (Found (ESI): 474.9945 M+Na $C_{16}H_{22}NaO_5RuSi_2$ requires 474.9945); δ_H (400 MHz, $CDCl_3$) 4.78 (4H, s, C*H*$_2$) 0.25 (18H, s, Si(C*H*$_3$)); δ_C (100 MHz, $CDCl_3$) 193.89 (quat., C=O), 185.72 (quat., C=O), 144.12 (quat.), 68.12 (quat.), 65.72 (quat.), -0.43 (CH_3); δ_{Si} (99 MHz, $CDCl_3$), -4.03.

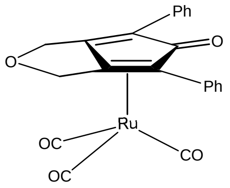


17

Complex 17.

A pressure tube was charged with (oxydi-1-propyne-3,1-diyl)bis[(1,1-dimethylethyl)dimethyl-silane (0.5535 g, 1.7189 mmol 3 eq.), acetonitrile (3 cm^3) and $Ru_3(CO)_{12}$ (0.3661 g, 0.5730 mmol, 1 eq.) and purged under a steady stream of N_2. The tube was then sealed and heated to 100 ^oC. After 2 d the reaction mixture was cooled, carefully depressurised and the solvent removed in vacuo. The resulting black semisolid was dissolved in DCM (2 cm^3) and filtered through a cotton wool plug and loaded onto a short silica column (EtOAc/Hexane 0 to 5 %) to afford an orange solid (0.5454 g, 1.0194 mmol, 59 %); *m/z* 537.1 $[M+1]^+$; (Found (ESI): M+H 537.1068 $C_{22}H_{35}O_5RuSi_2$ requires 537.1066); ν_{max} 2926, 2853, 2073, 2007 and1638 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.81 (2H, d, *J* 11.3, C*H*H), 4.76 (2H, d, *J* 11.3, CH*H*), 0.96 (18H, s, SiC(C*H*$_3$)$_3$), 0.36 (6H, s, Si(C*H*$_3$)), 0.06 (6H, s, Si(C*H*$_3$)); δ_C (100 MHz, $CDCl_3$)

193.78 (quat., C=O), 184.64 (quat., C=O), 115.11 (quat.), 68.50 (quat./CH_2), 65.67 (quat./CH_2), 27.27 (SiC(CH_3)$_3$), 18.51 (Si*C*(CH_3)$_3$), -4.01 (Si(*C*H_3)), -4.99 (Si(*C*H_3)); δSi (99 MHz, $CDCl_3$), -4.01.



18

Complex 18.[7]

A pressure tube was charged with 1,1'-(oxydi-1-propyne-3,1-diyl)bis-benzene (0.4901 g, 1.9922 mmol 3 eq.), acetonitrile (3.5 cm^3) and $Ru_3(CO)_{12}$ (0.4244 g, 0.6641 mmol, 1 eq.) and purged under a steady stream of N_2. The tube was then sealed and heated to 100 ^oC. After 2 d the reaction mixture was cooled, carefully depressurised and the solvent removed in vacuo. The resulting black semisolid was dissolved in DCM (2 cm^3) and filtered through a cotton wool plug and loaded onto a short silica column (EtOAC/Hexane 0 to 20 %) to afford a yellow solid (0.1263 g, 0.2752 mmol, 14 %); δ_H (400 MHz, $CDCl_3$) 7.86 (4H, d, *J* 8.0, Ar), 7.44-7.28 (6H, m, Ar), 5.30 (2H, d, *J* 11.0, C*H*H), 5.15 (2H, d, *J* 11.0, CH*H*).

Data for Ru-hydrides formed from tricarbonyl complexes.

Experiment code in which Ru-H was formed.	**Complex used.**	***m/z***	**δ_H hydride shift ($CDCl_3$)**
JPH115, JPH160, jph223	TBS*-TMS phenyl **15b**	*m/z* 543.0 $[M^+]$;	300 MHz, -10.32 (1H, s), -10.48 (0.25H, s).
JPH154, jph164	TBS*-TIPS phenyl **15a**	*m/z* 627 $[M^+]$;	400 MHz, -10.31 (1H, s), -10.36 (0.06H, s).
Jph145, jph161	TBS*-Ph phenyl **15c**		400 MHz, -10.33 (1H, s), -10.39 (0.04H, s).
Jph155, 224	TIPS*-TMS phenyl **15d**		400 MHz, -10.01 (1H, s), -10.16 (0.02H, s), -10.40 (0.33H, s).
Jph168	TIPS*-TBS phenyl **15f**		400 MHz, -9.93 (1H, s), -10.36 (0.6H, s).
Jph163, jph152	TIPS*-Ph phenyl **15e**	*m/z* 589 $[M^+]$;	400 MHz, -10.14 (1H, s), -10.25(0.04H, s-10.39 (0.63H, s), -19.06 (0.03H, s).
JPH146, jph159	TBS-TBS sym **17**	*m/z* 509 $[M^+]$;	400 MHz, -10.44 (1H, s).
Jph114, jph158	TMS-TMS sym **16**	*m/z* 425 $[M^+]$;	400 MHz, -10.51 (1H, s).
Jph153,jph169	Ph-Ph sym **18**	*m/z* 433 $[M^+]$;	300 MHz -17.33 (1H, s).

Jph225 major	Ph*-TMS methyl major **12a**		400 MHz, -10.34 (1H, s).
JPH226-minor	Ph*-TMS- methyl minor **12b**	*m/z* 443 [M$^+$];	400 MHz, -10.49 (0.2H, s), -19.20 (1H, s).
Jph251	Ph*-TIPS- methyl major **12c**	*m/z* 568 [M$^+$ +K];	400 MHz, -10.38 (1H, s).
Jph229	Ph*-Ph- methyl major **12e**	*m/z* 447 [M$^+$];	300 MHz, -17.80 (1H, s).
Jph252	Ph*-TBS*- methyl-methyl **13a/b**	*m/z* 540 [M$^+$ +K];	300 MHz, -10.47 (1H, s).

The results for complexes **12**, **13**, **16-18** are given in the main paper. The results for complexes **15** are given in a table below.

Table 1; Asymmetric reduction of acetophenone using complexes 15a-15f.

Complex	Conditions by expt no.	time	Conv/%	Ee (R/S)
15a (3:1)	**154** iPrOH 60 °C	166	14	19.7 (*S*)
	154 FA/TEA 60 °C	140	18	21 (*S*)
	164a iPrOH 60 °C	168	14	20 (*S*)
	164b FA/TEA 60 °C	168	25 (17% alc)	21 (*S*)
15b (3:1)	**115** iPrOH 60 °C	162	10	2 (*R*)
	115 FA/TEA 60 °C	238	26	2 (*R*)
	160a iPrOH 60 °C	168	57	1.6 (*R*)
	160b FA/TEA 60 °C	168	41 (35% alc)	0
15c (4:1)	**145** iPrOH 60 °C	168	94	4 (*R*)
	145 FA/TEA 60°C	165h	72	6.2 (*R*)
	161a iPrOH 60 °C	168	90	4.5 (*R*)
	161b FA/TEA 60 °C	168	71 (67% alc)	5.2 (*R*)
15d (7:3)	**155** iPrOH 60 °C	92	12	10 (*R*)
	155 FA/TEA 60 °C	92	8.5	12.0 (*R*)
15e (3:2)	**152** iPrOH 60	166	76	6 (*R*)
	152 FA/TEA 60°C	168	44	7 (*R*)
	163a iPrOH 60 °C	168	78	5.9 (*R*)
	163b FA/TEA 60 °C	168	61 (55% alc)	6.6 (*R*)
15f (3:2)	**168** iPrOH 60 °C	168	10	4.9 (*R*)
	168 FA/TEA 60 °C	168	15	9.4 (*R*)

Formate ees for reactions with FA/TEA;**160** (6% formate, 0% ee), **161** (4% formate, 5% ee *R*) **163** (6% formate, 7.8% ee *R*), **164** (8% formate, 21.2% ee, *S*). The RuH complex was formed and characterised prior to use.

References.

1) T. C. Johnson, G. J. Clarkson and M. Wills, *Organometallics* 2011, **30**, 1859-1868.

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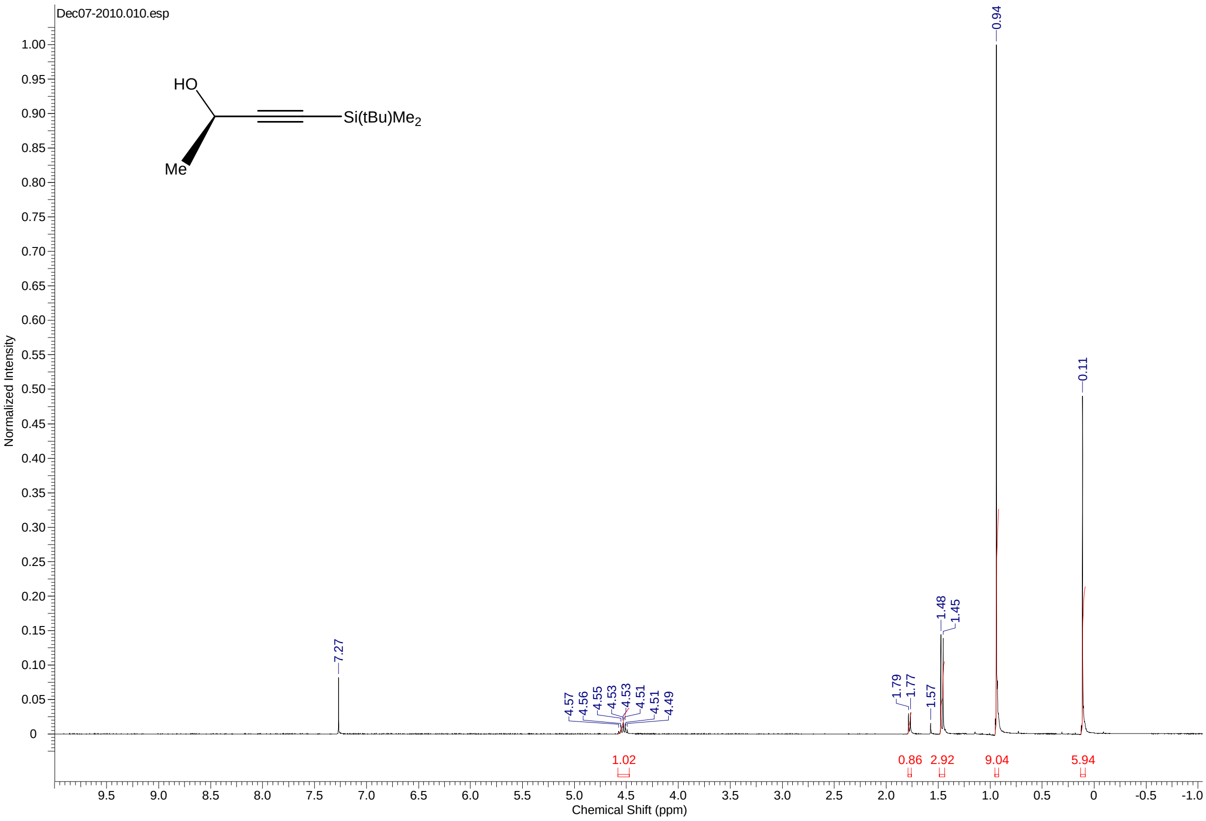
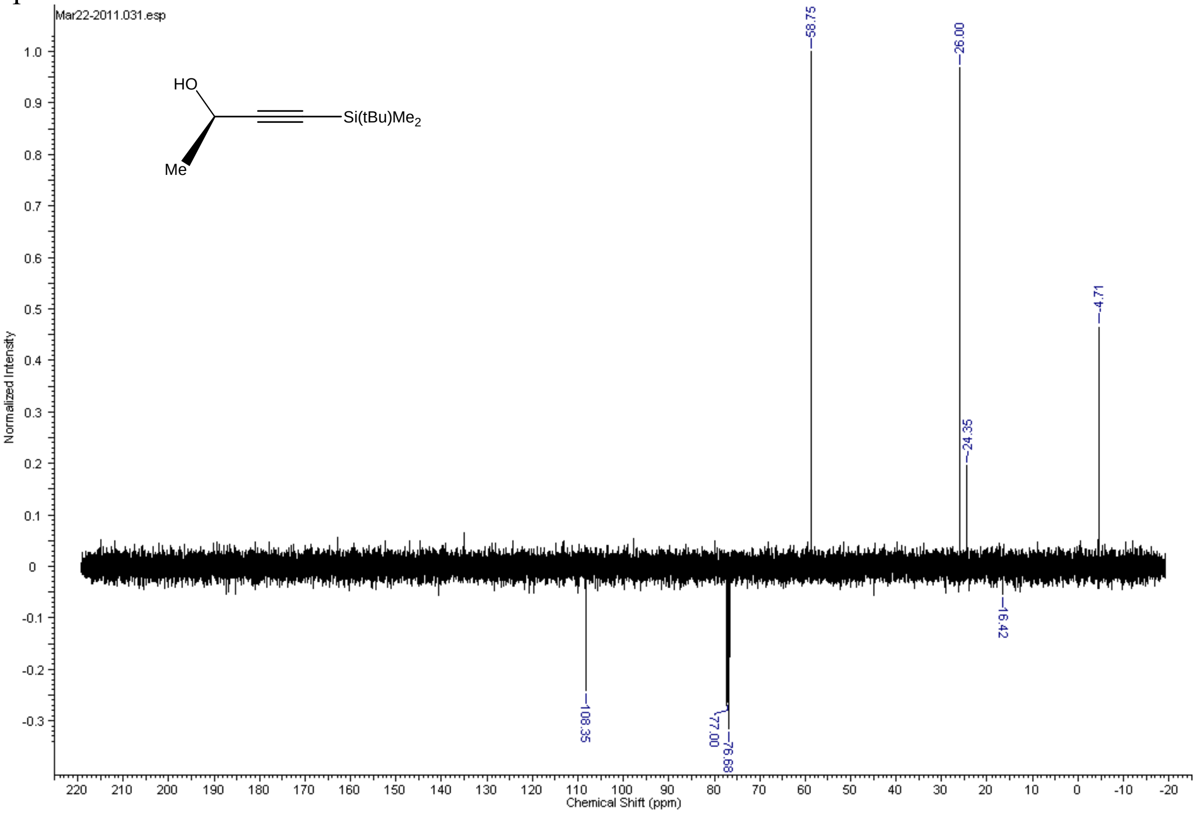
7) Y. Yamamoto, Y. Miyabe and K.Itoh, *Eur. J. Inorg. Chem.* **2004**, 3651-3661.

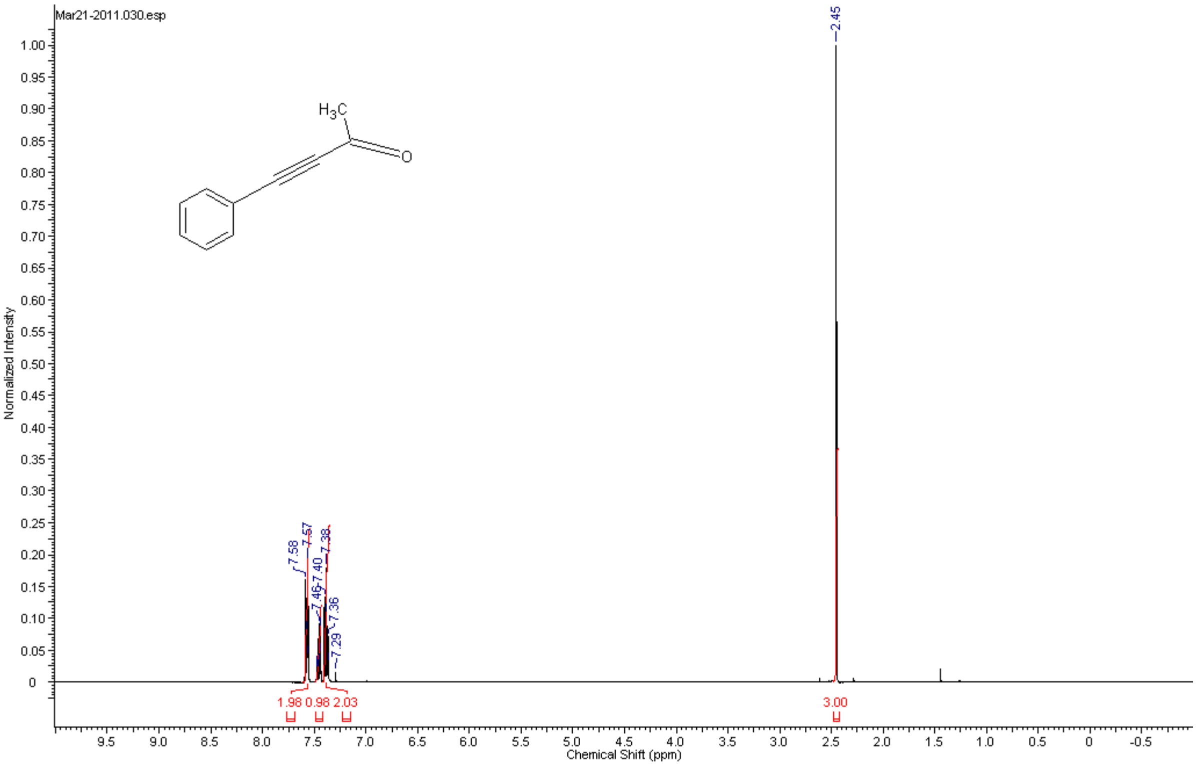
3) NMR spectra of novel Ru cyclone complexes and precursors.



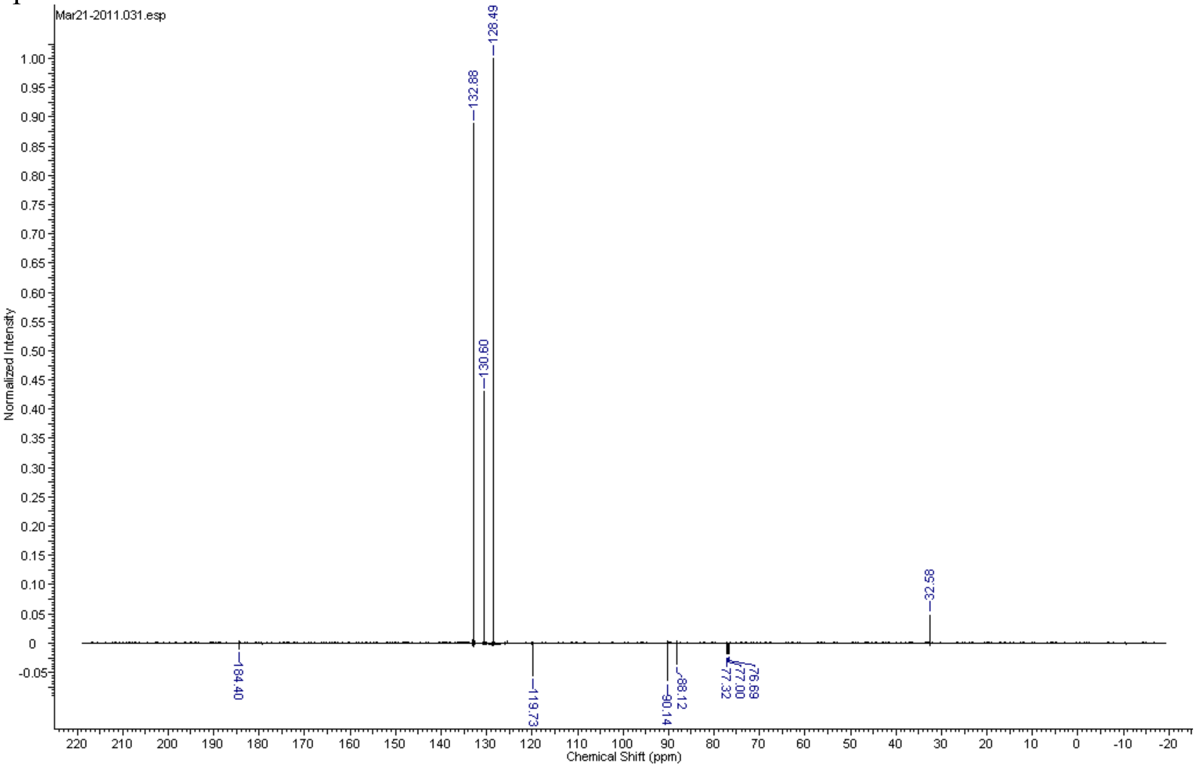
Jph200 TBS-Me-OH- 11b



JPH200 C13



Jph241



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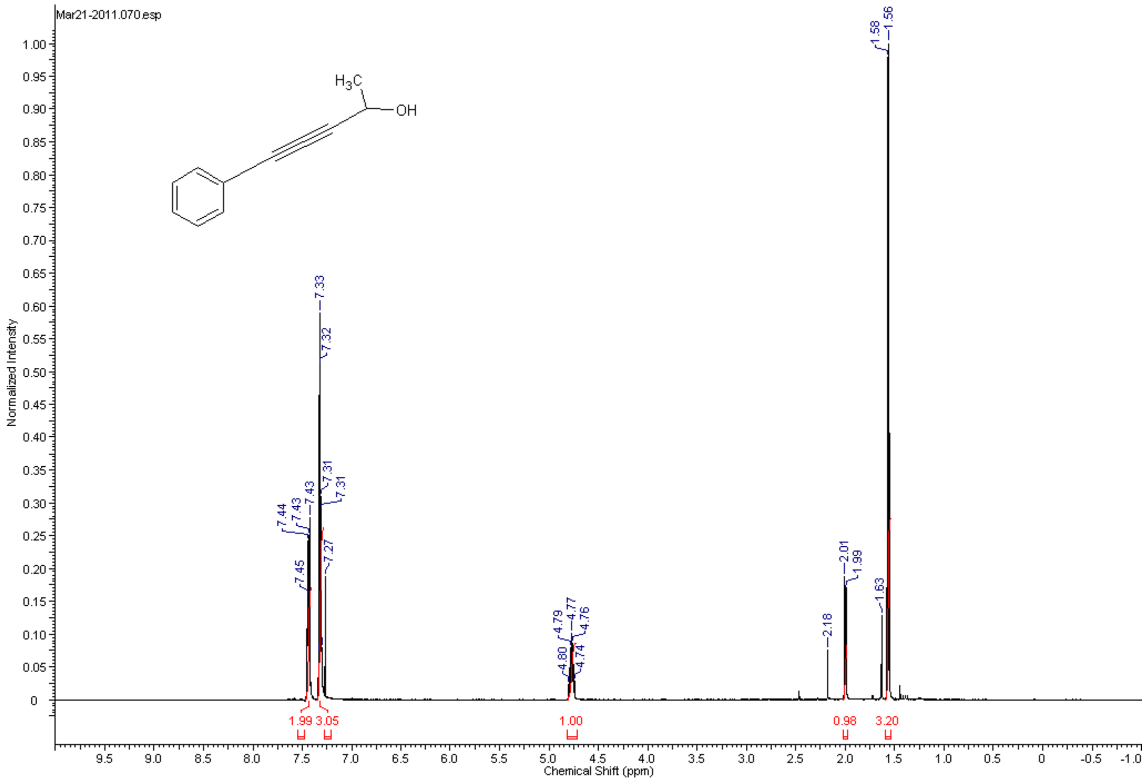
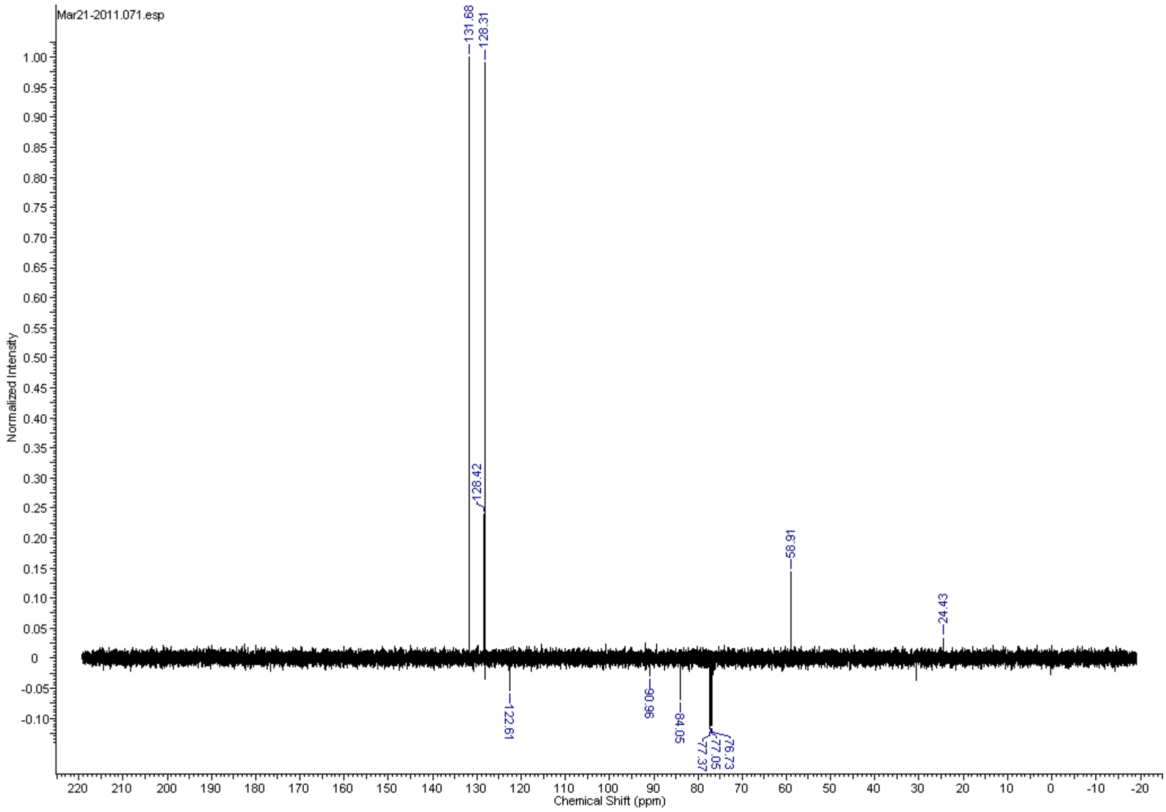


JPF244 H



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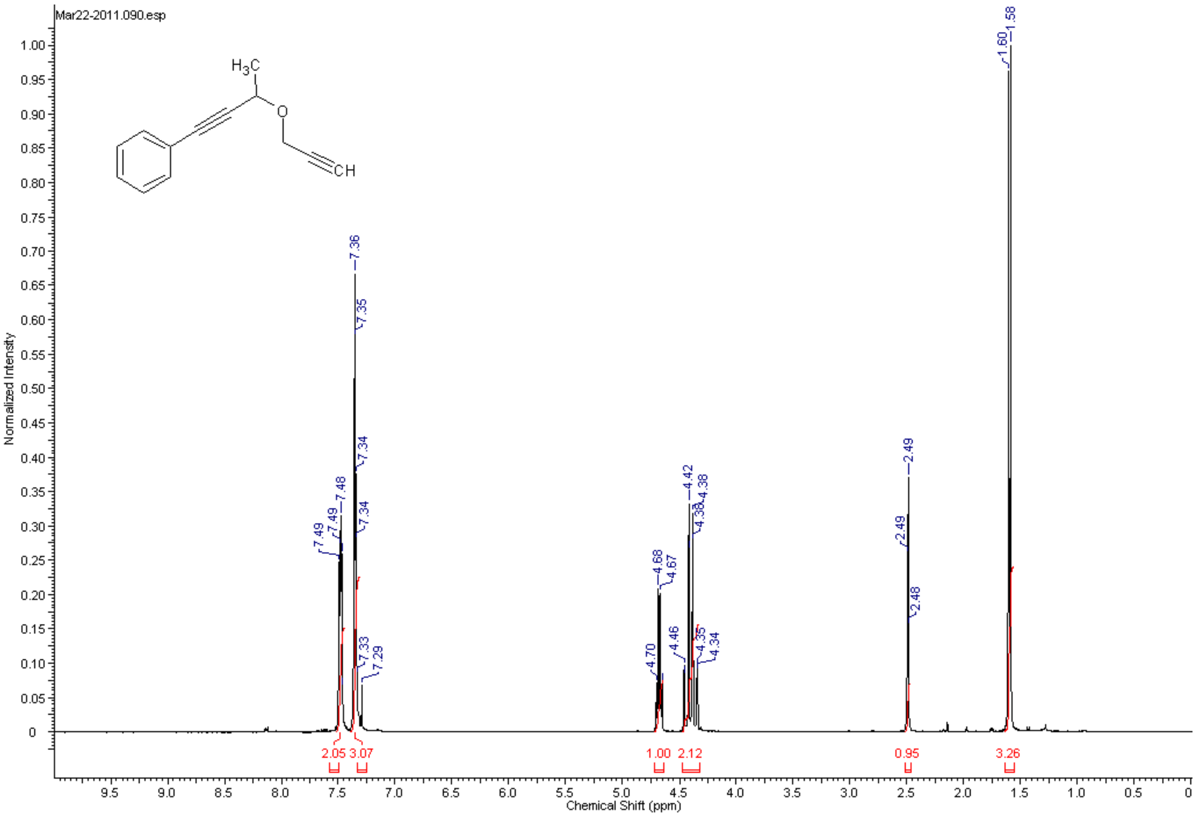

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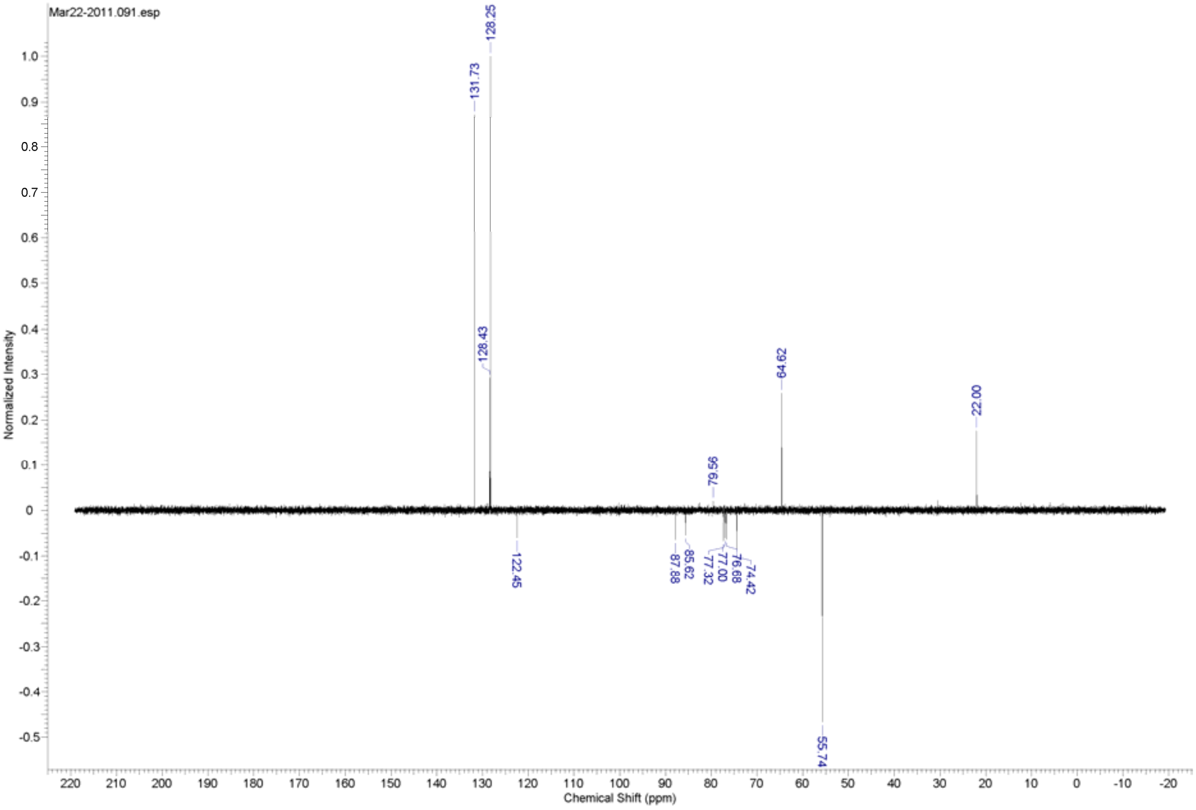

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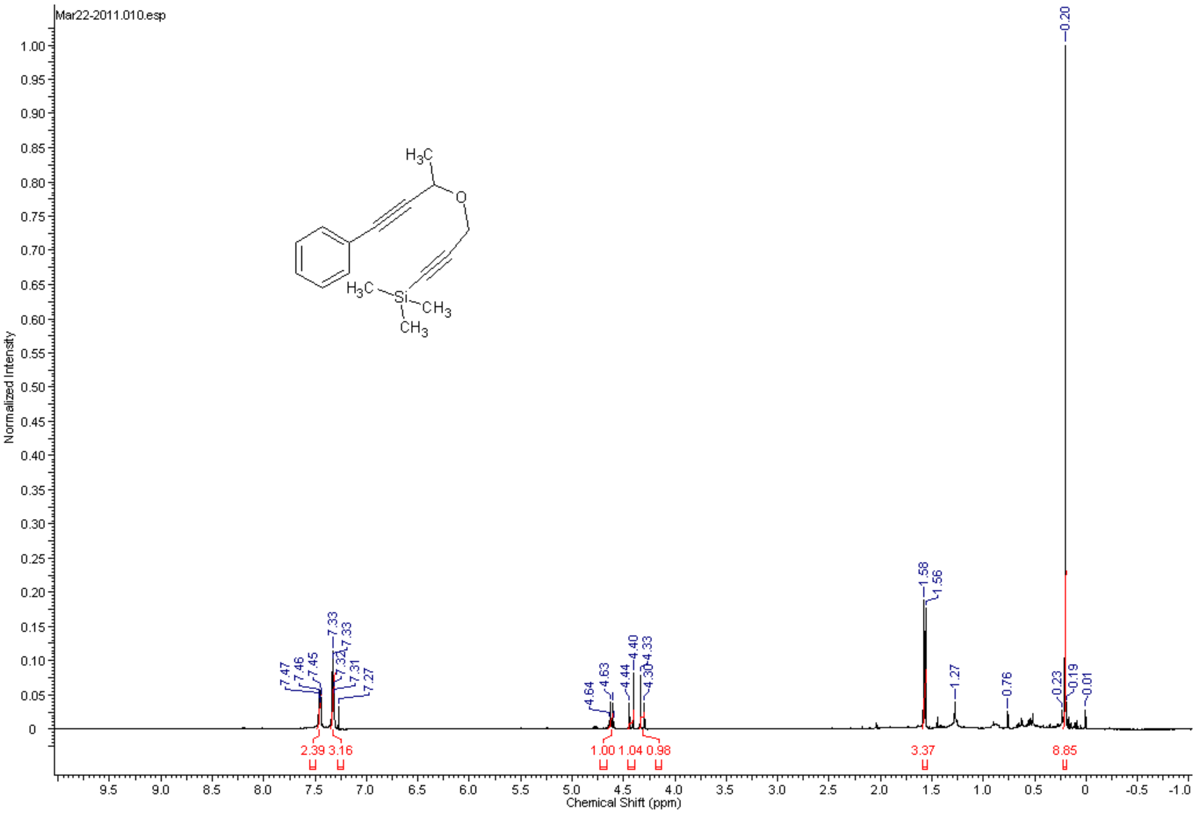

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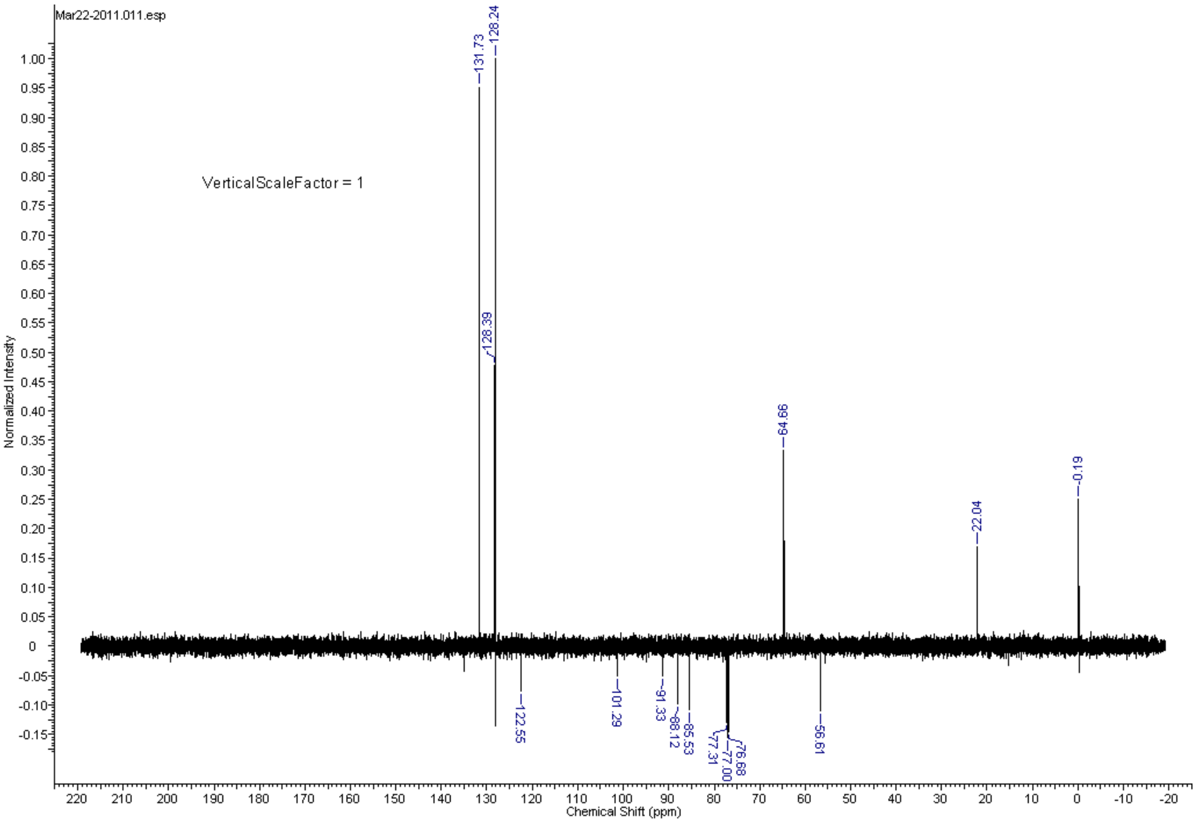
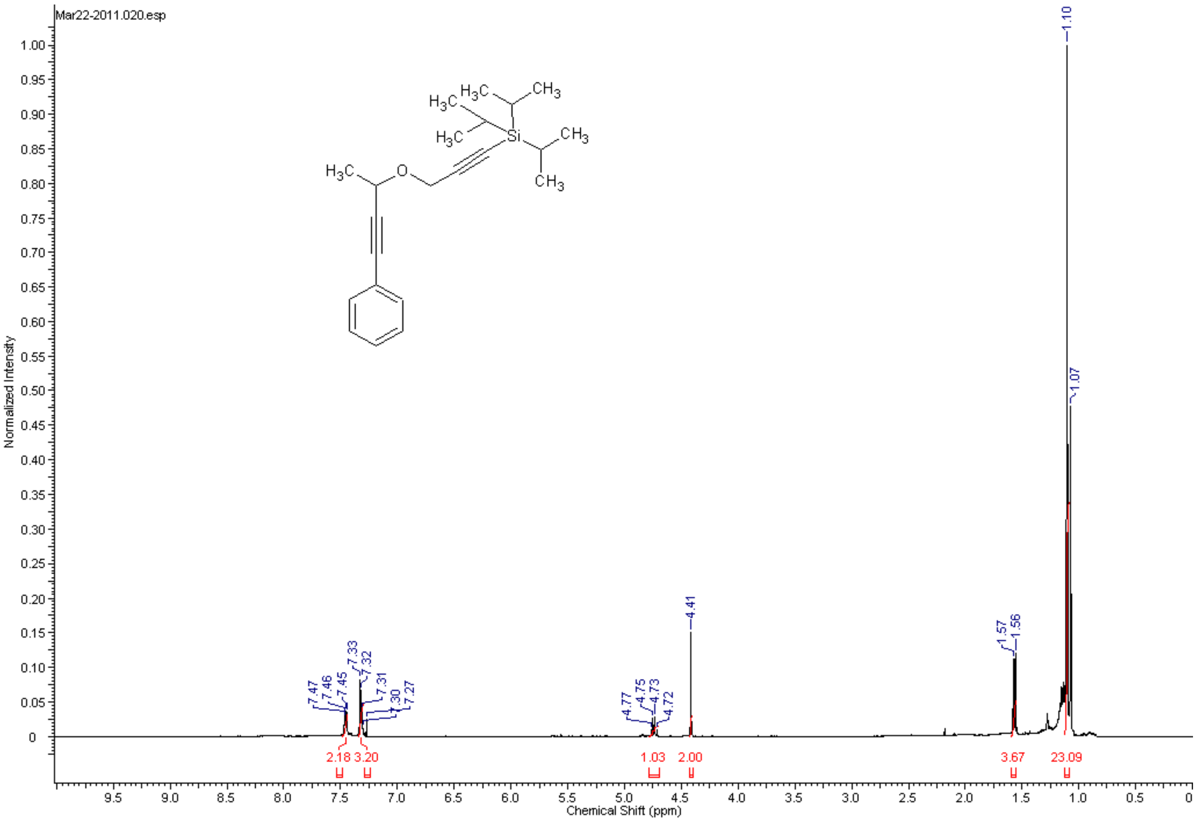


JPH218 C



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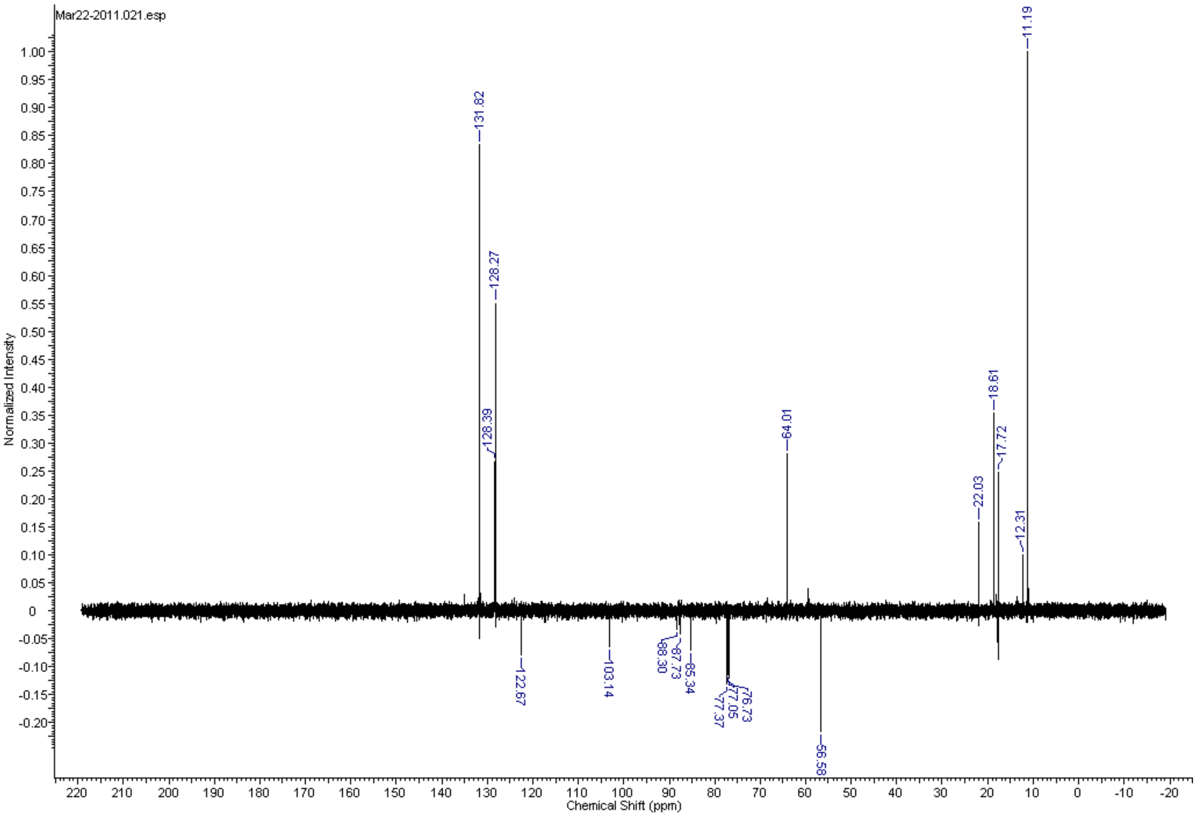

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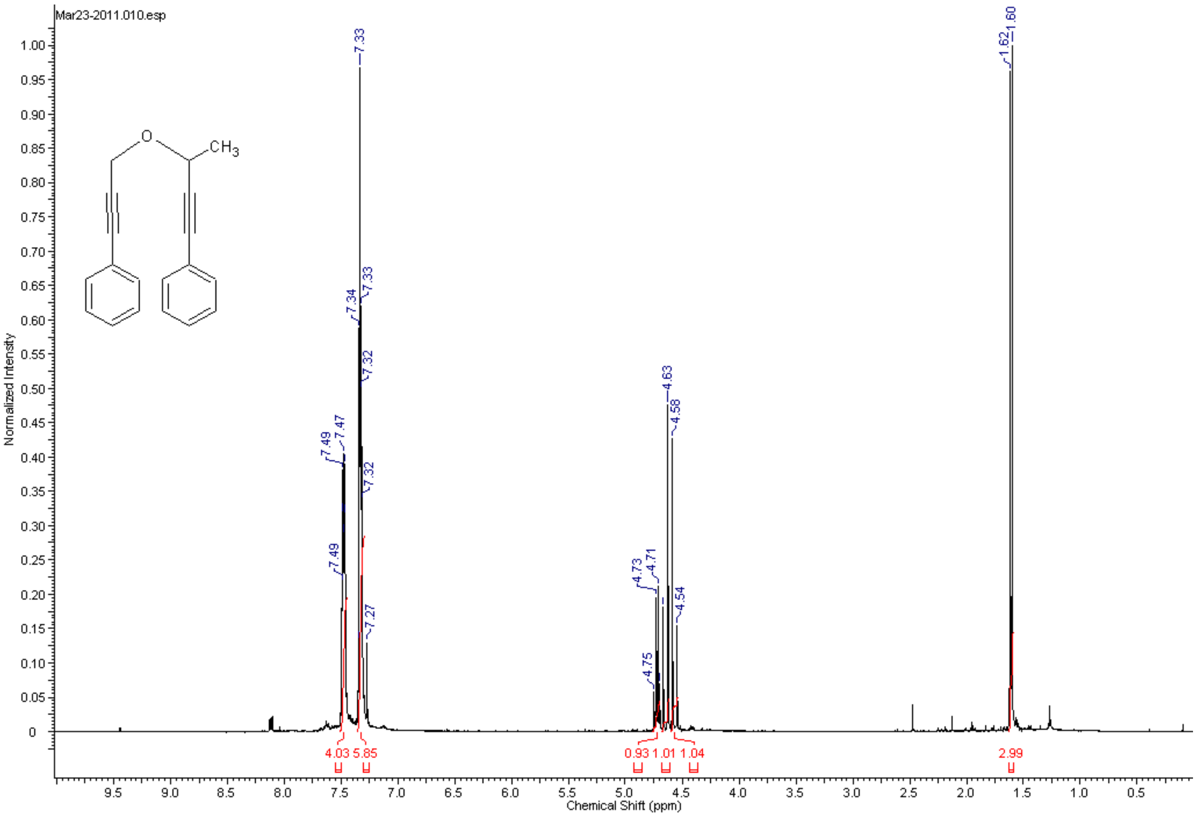

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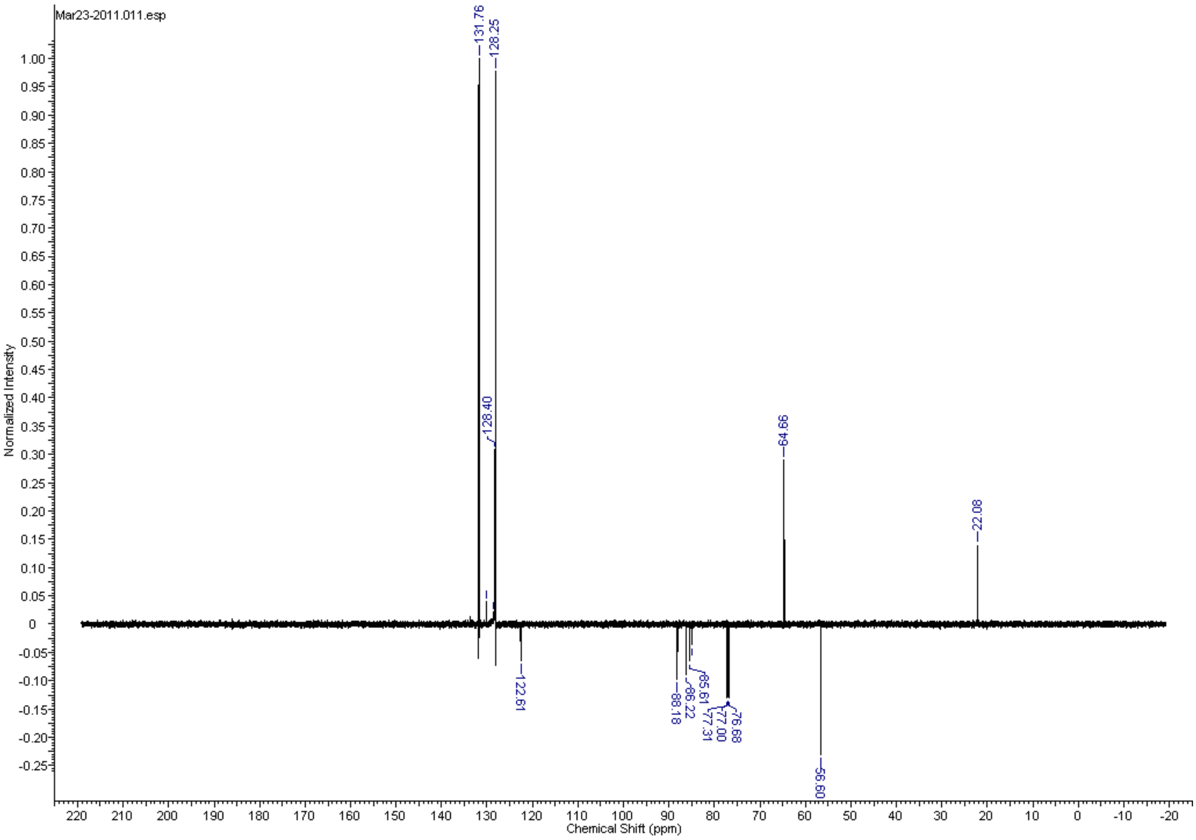

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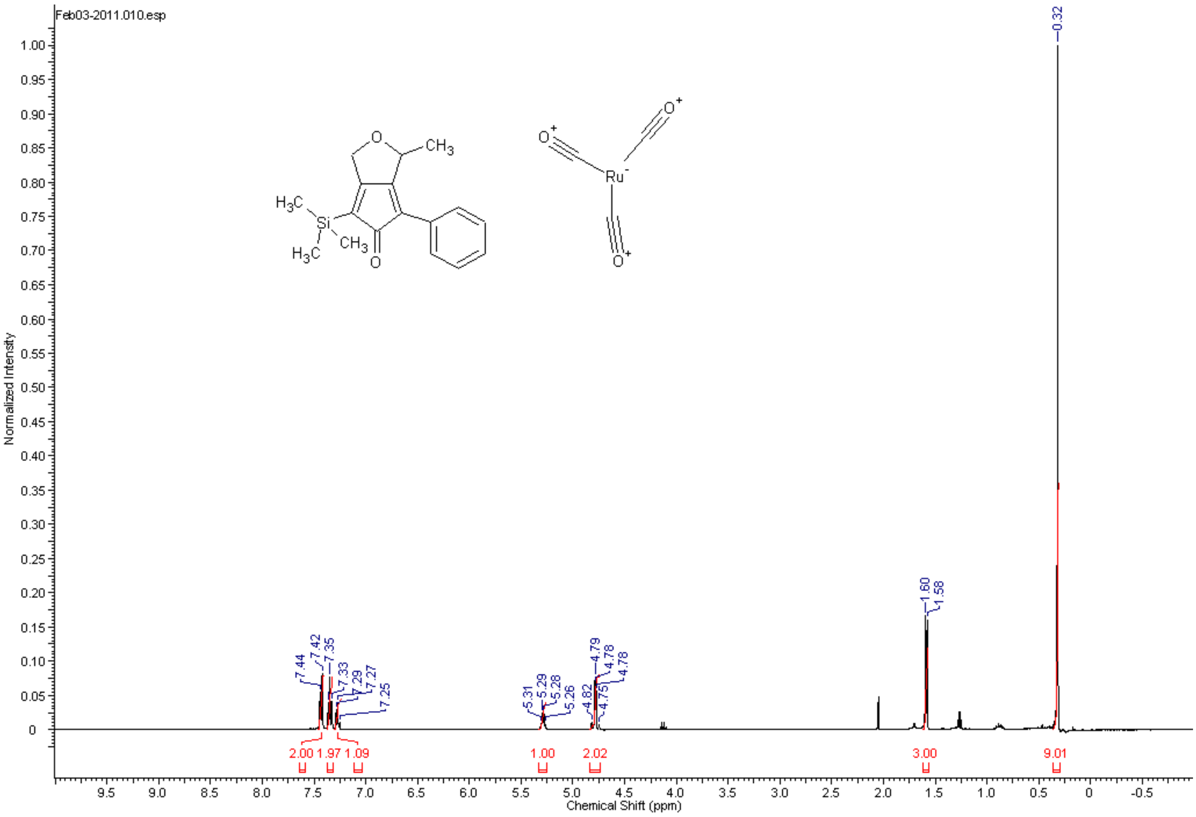

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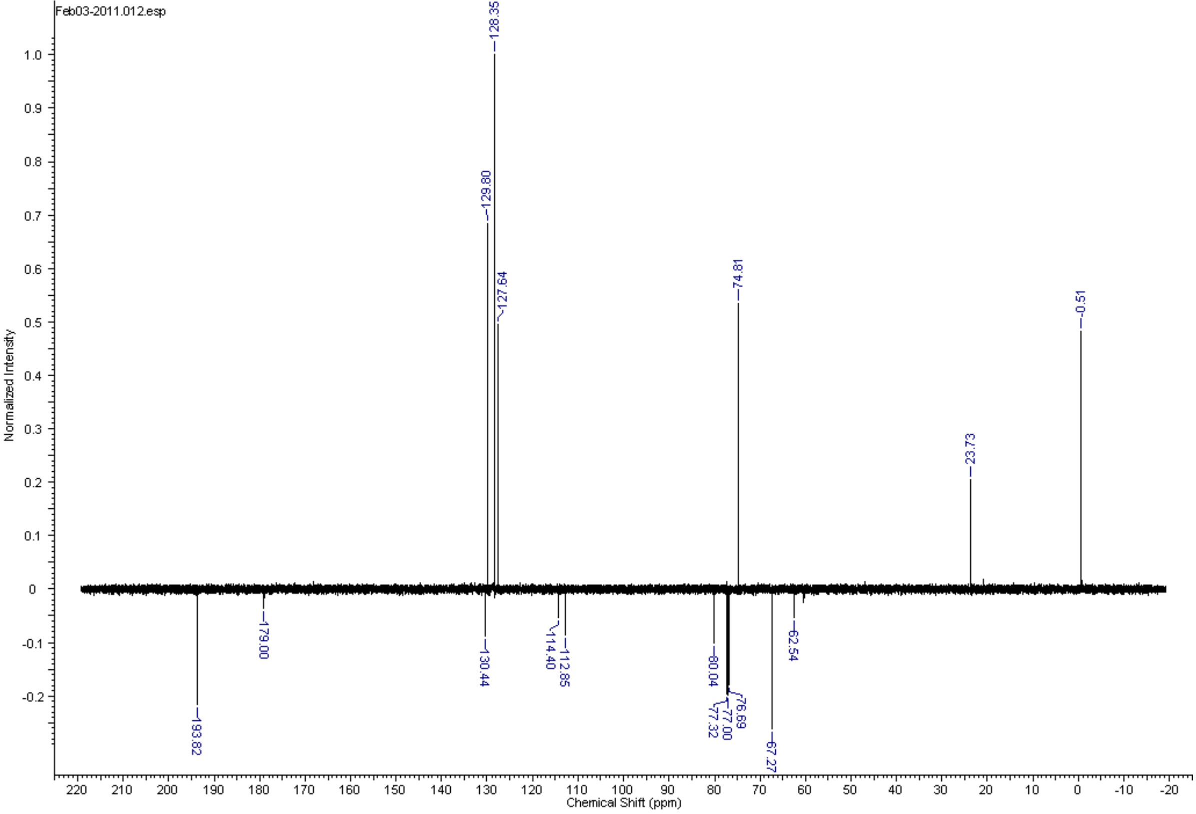

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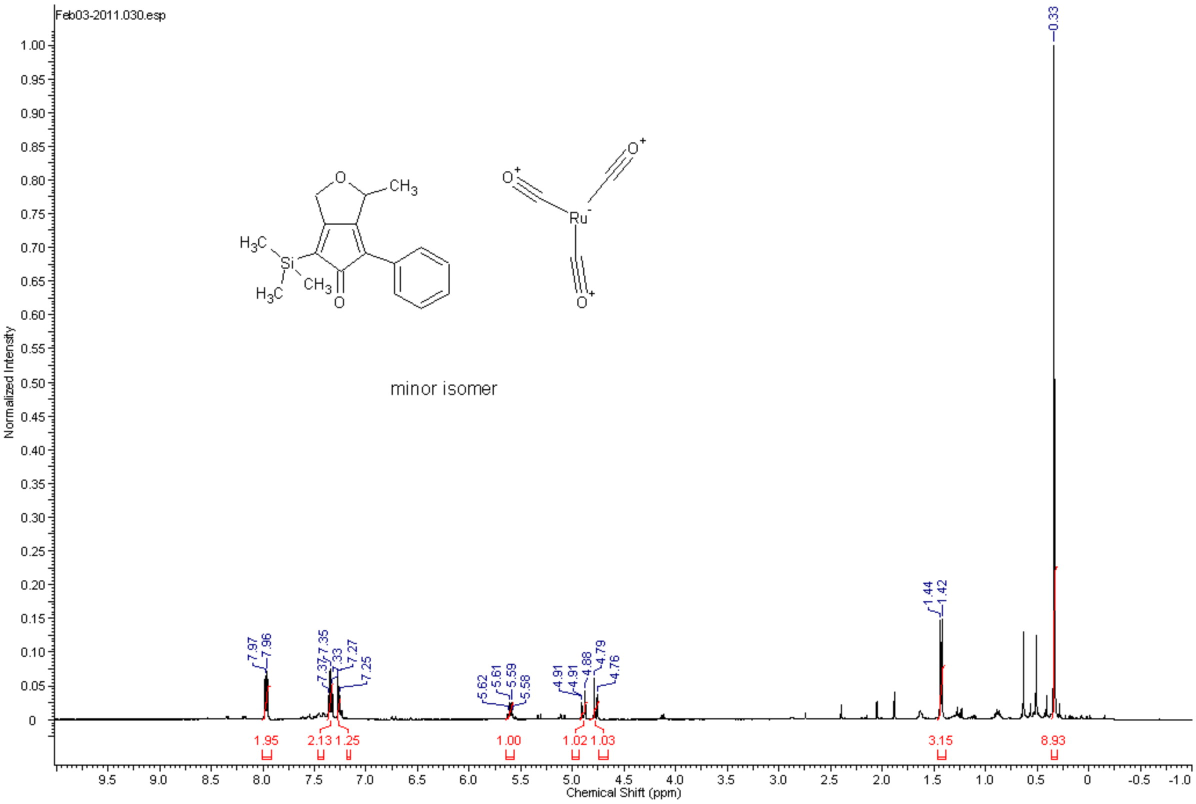

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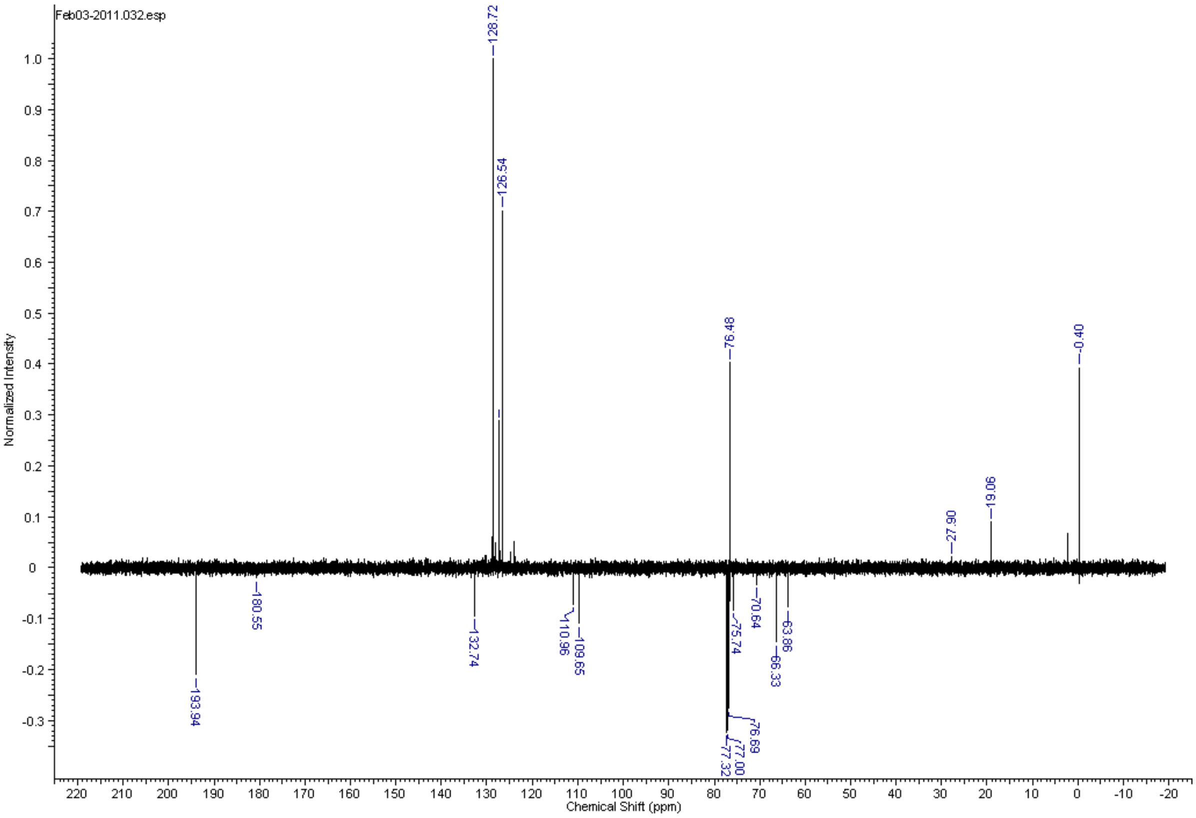

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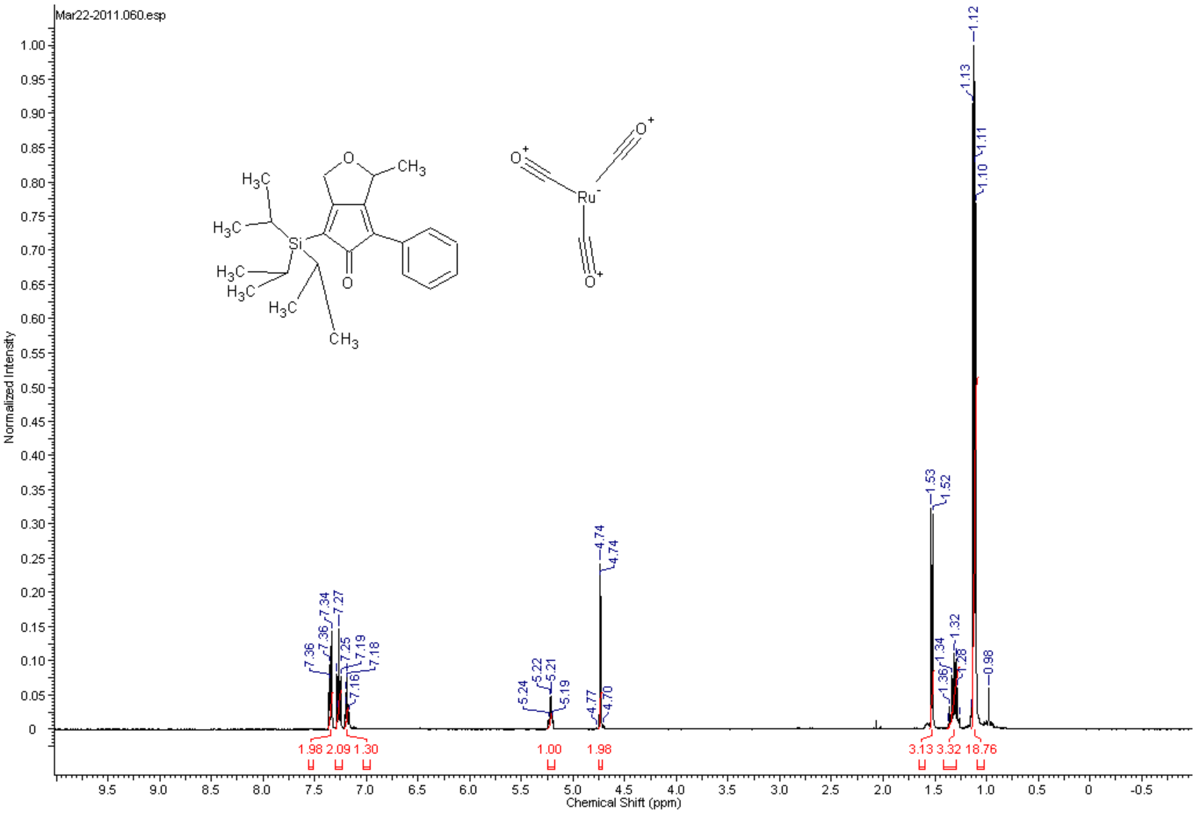
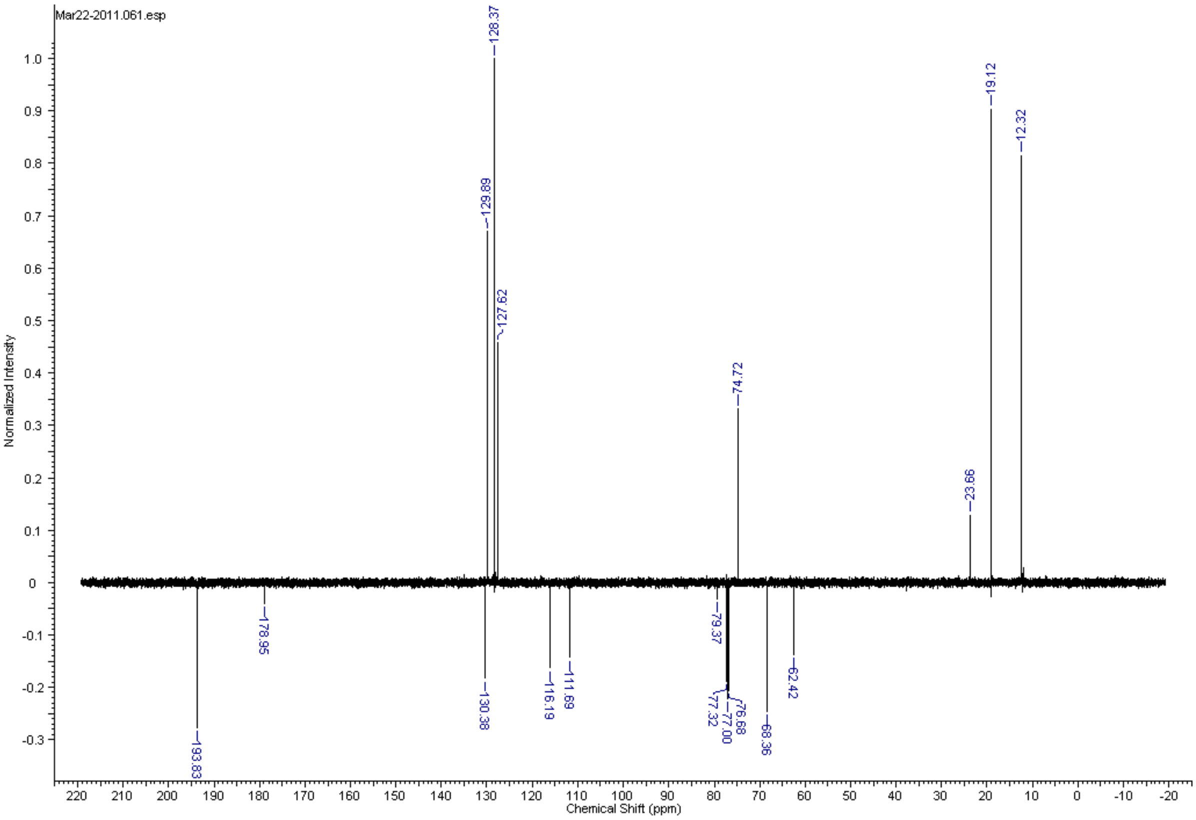
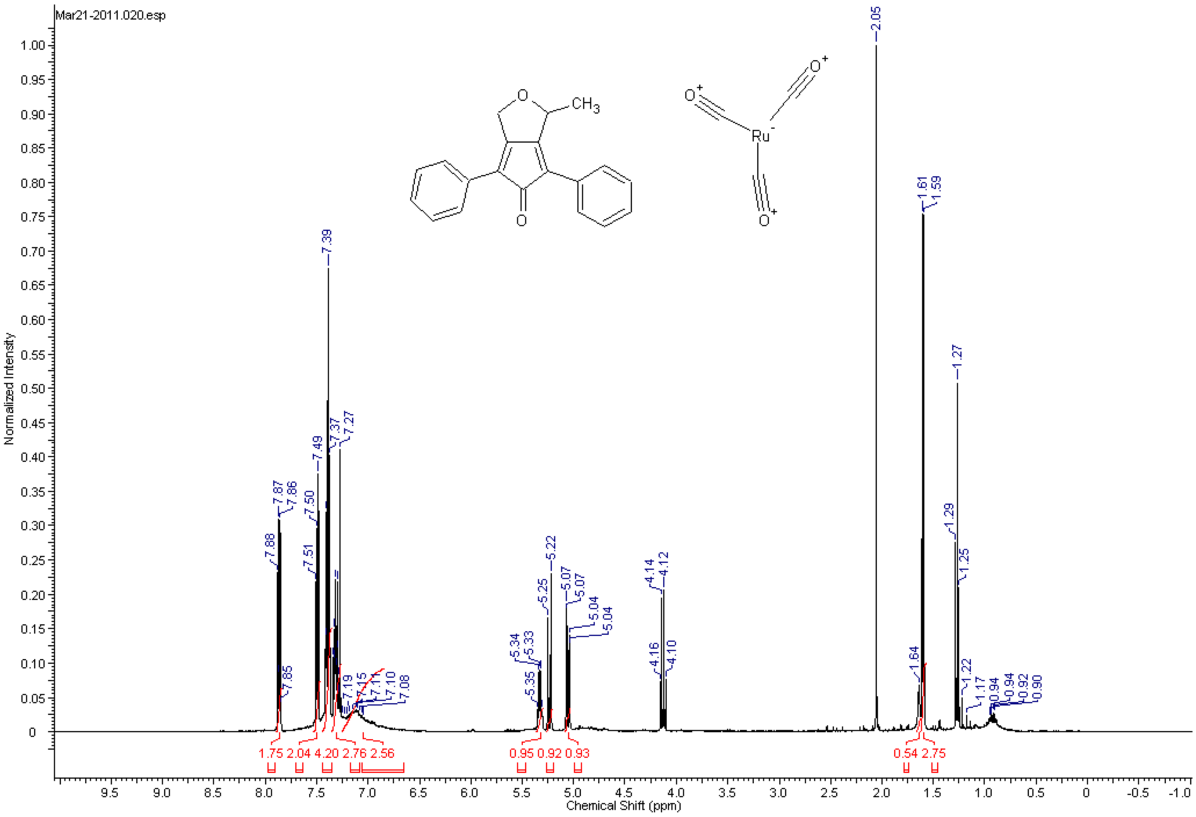


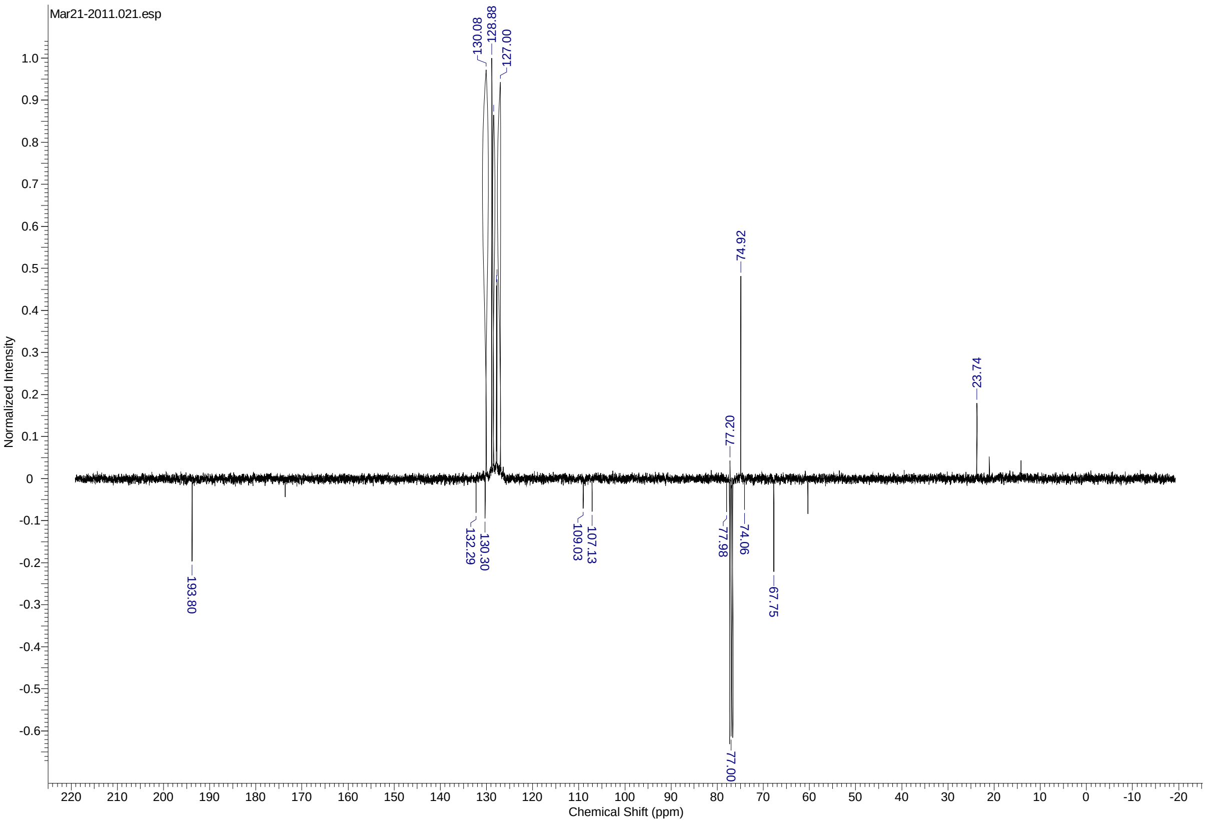
JPH222H **12c**



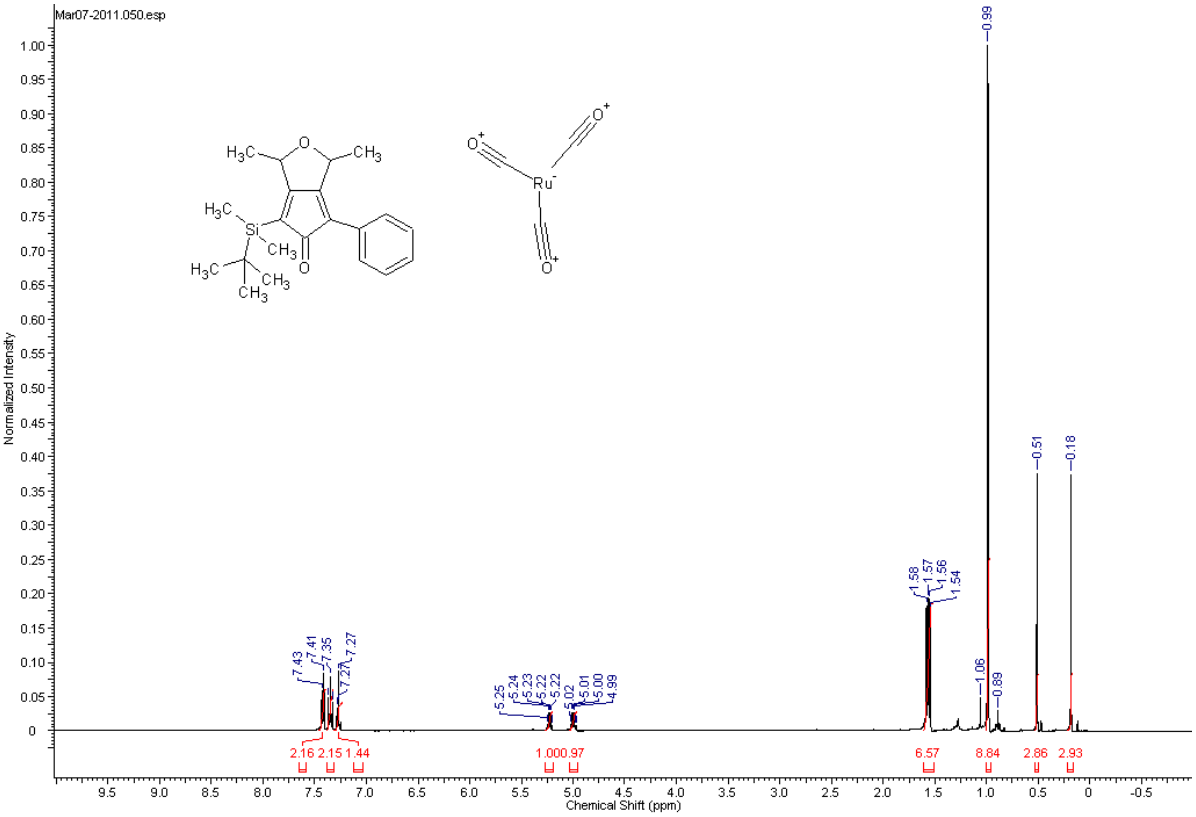
Jph222C **12c**



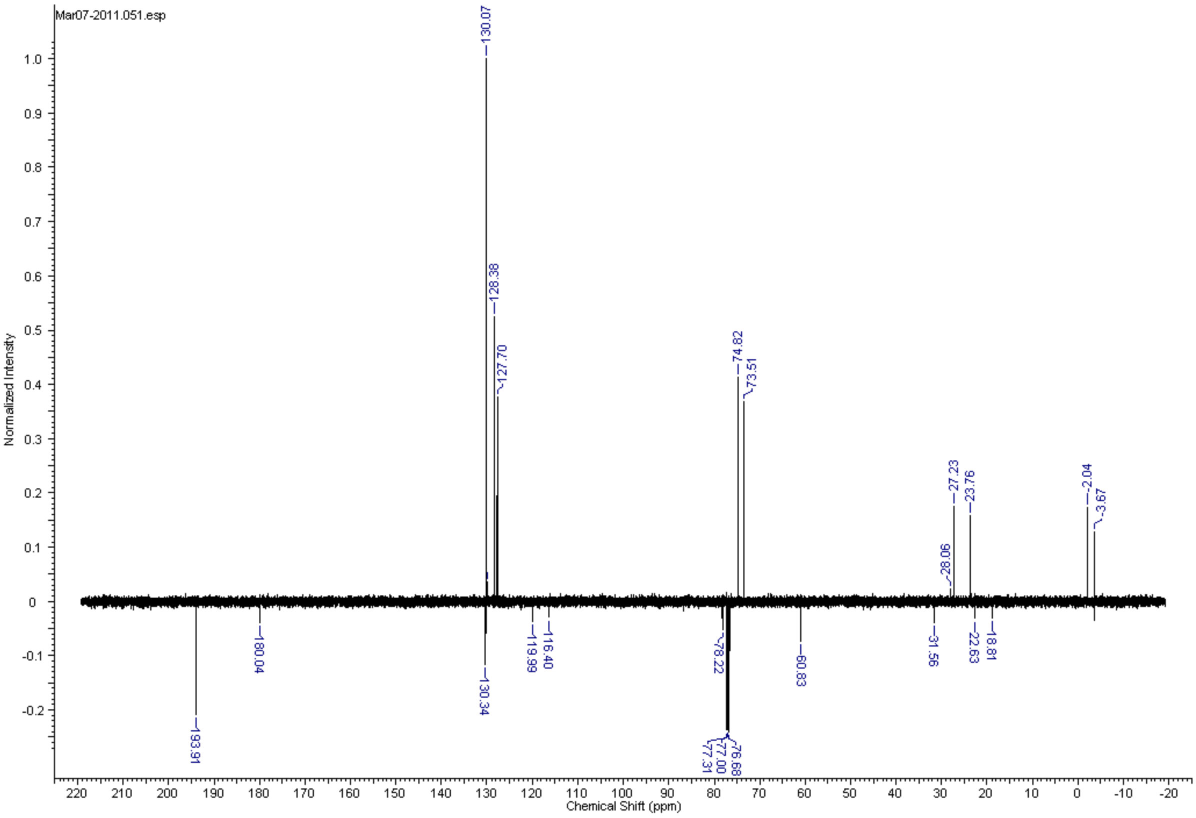
JPH228H **12e**



Jph228 **12e**.



JPH240H **13a/b**

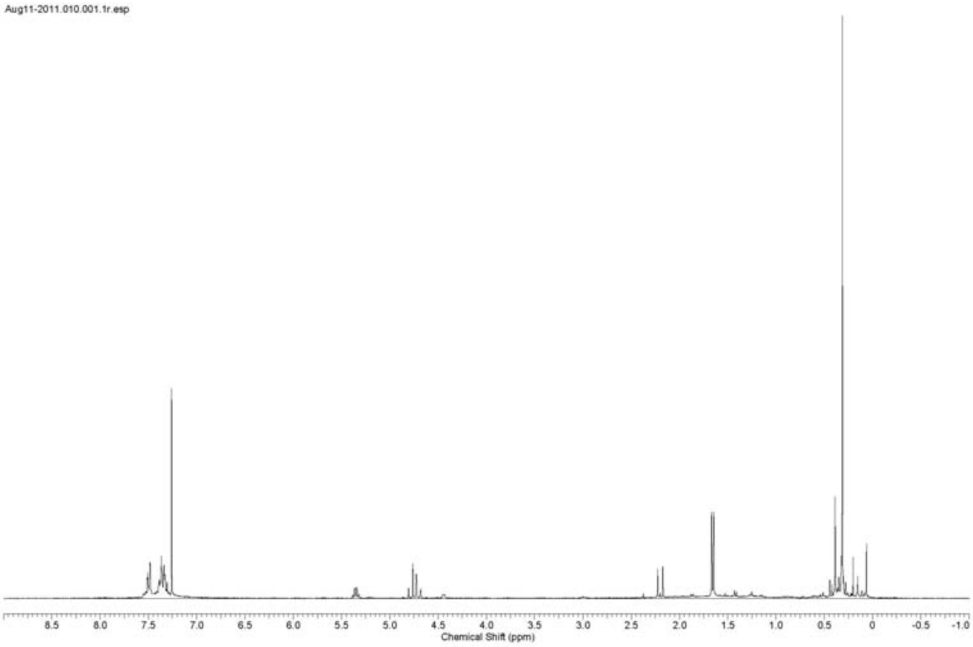


JPH240C

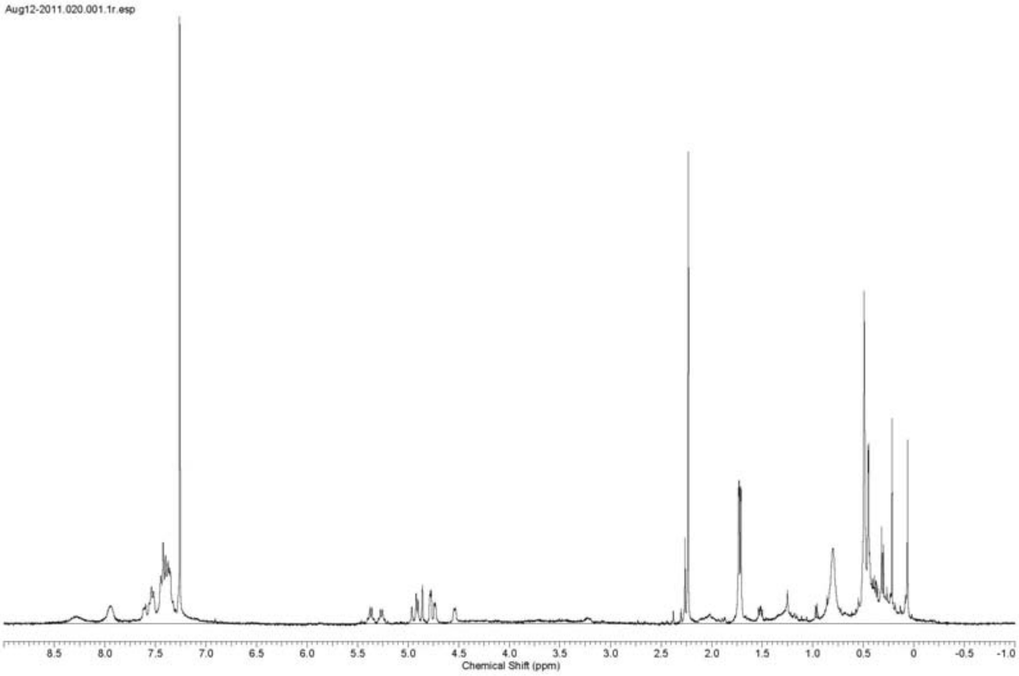
4) Shift reagent study on 7d to establish enantiomeric purity:

Chiral shift data for complex 7d using Europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate].

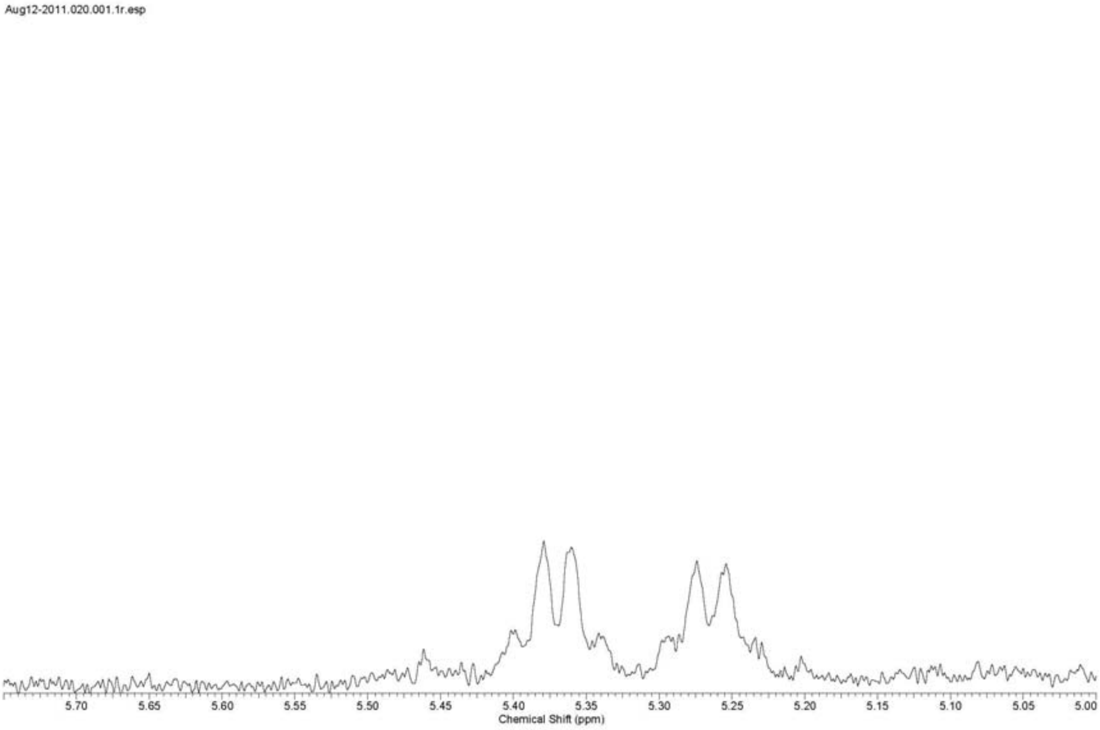
Racemic **7d** without Eu



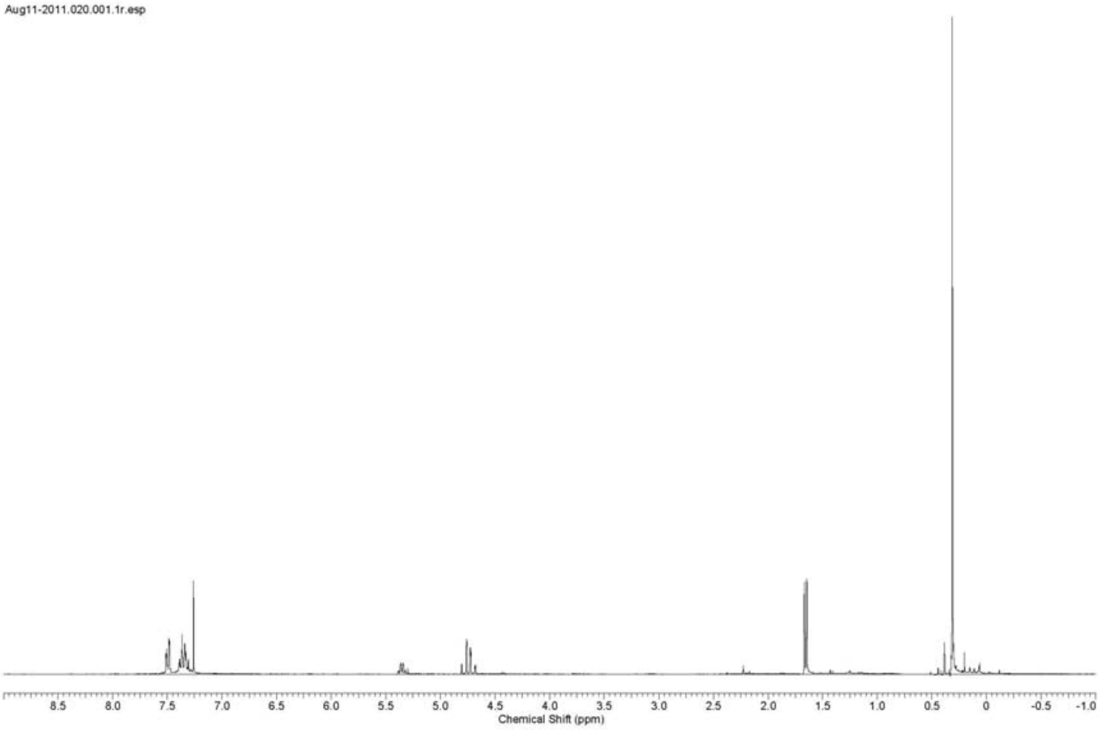
Racemic **7d** with Eu



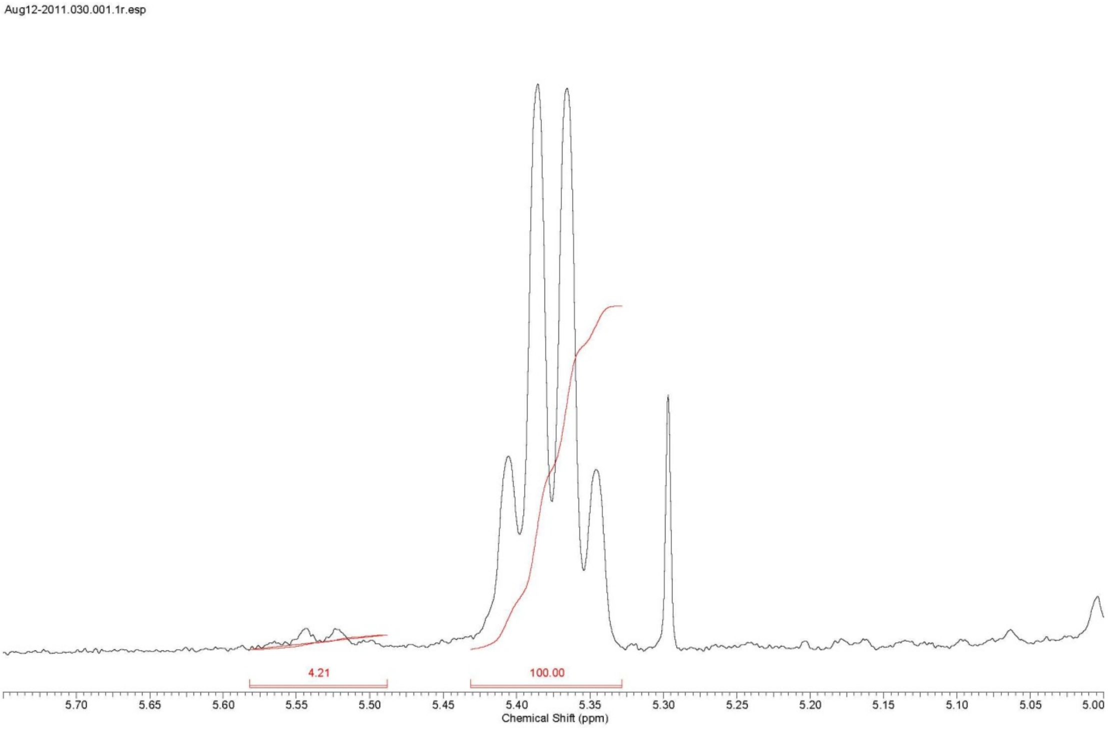
Expansion of racemic **7d** with Eu



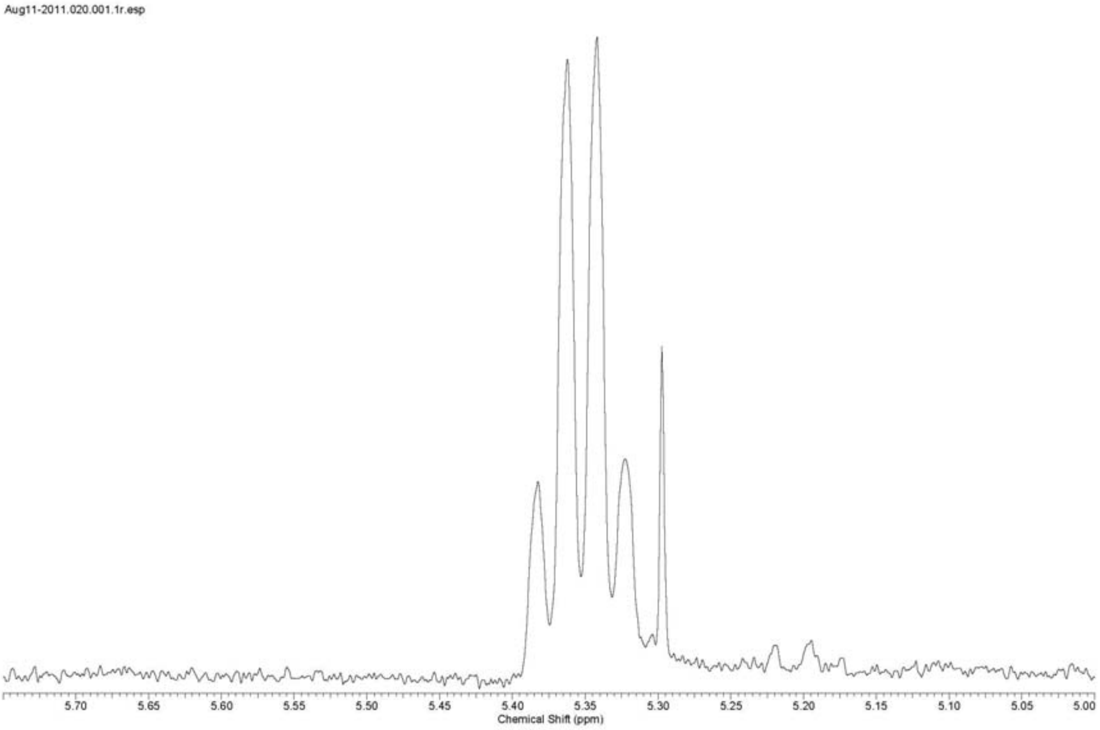
Asymmetric **7d** without Eu



Expansion of asymmetric **7d** with Eu



Expansion of asymmetric **7d** without Eu



Separation is clearly visible and integration of the peaks indicates a minimal enantiomeric purity of 7c of 92% ee.