Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information.

Synthesis and Applications to Catalysis of Novel Cyclopentadienone Iron Tricarbonyl Complexes.

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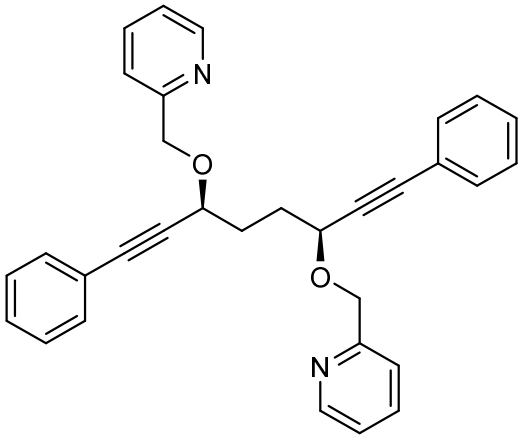
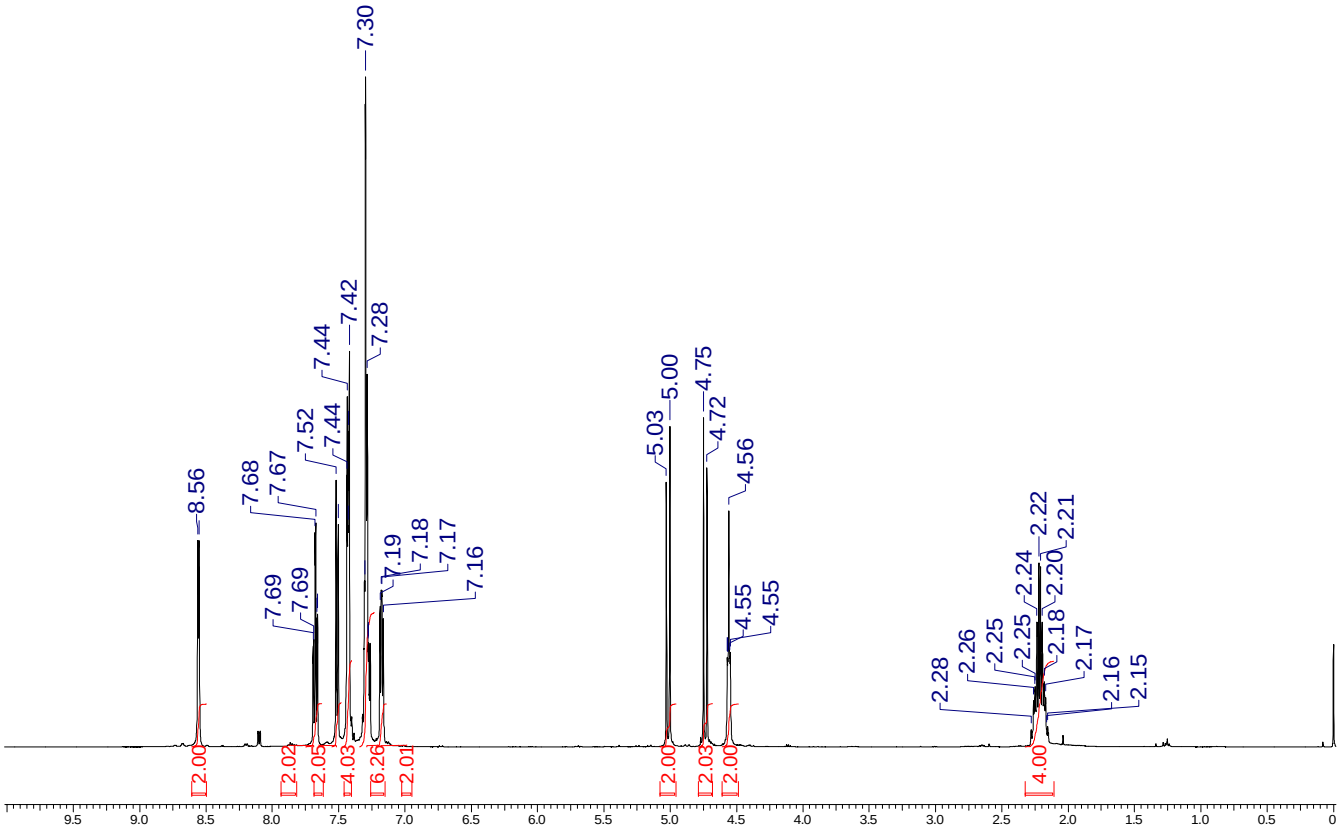
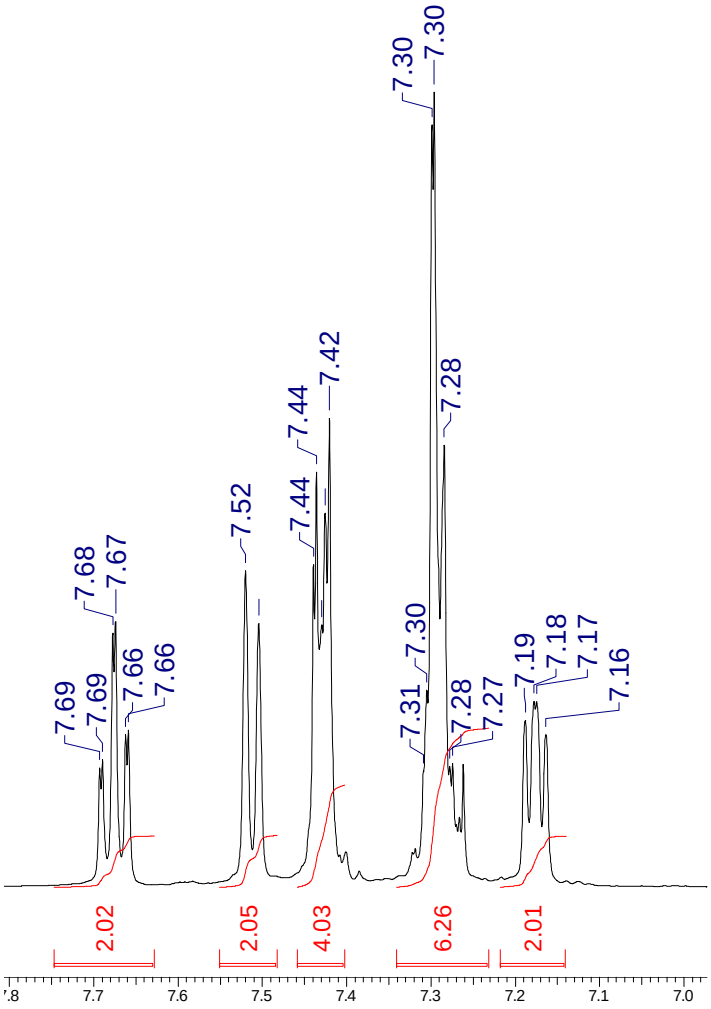
2,2'-((((3*S*,6*S*)-1,8-Diphenylocta-1,7-diyne-3,6-diyl)bis(oxy))bis(methylene))dipyridine 16: ADG93.



^{1}H NMR (500 MHz, $CDCl_3$)

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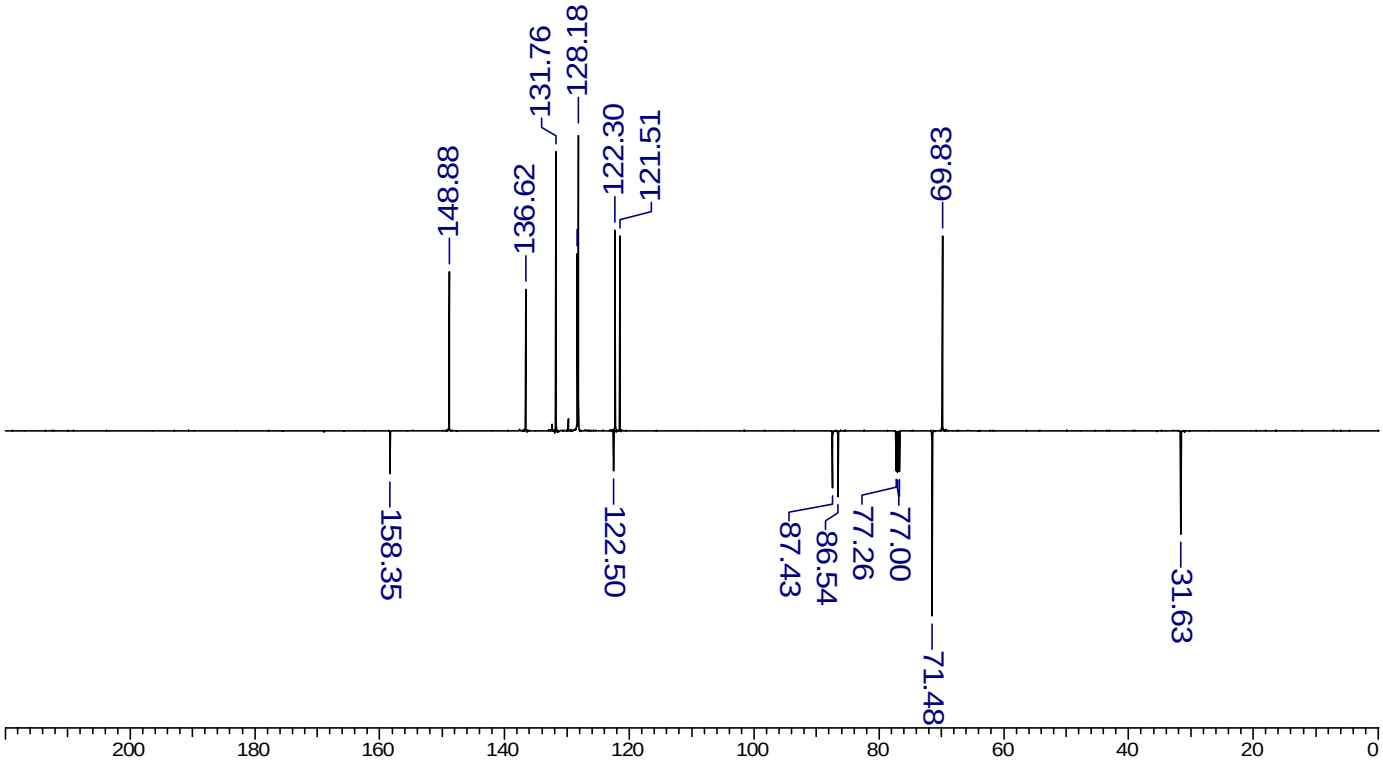
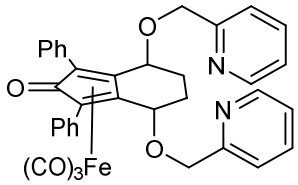
7.28
7.28
7.27
7.19
7.18
7.17
7.16
2.02
2.05
4.03
6.26
2.01
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0

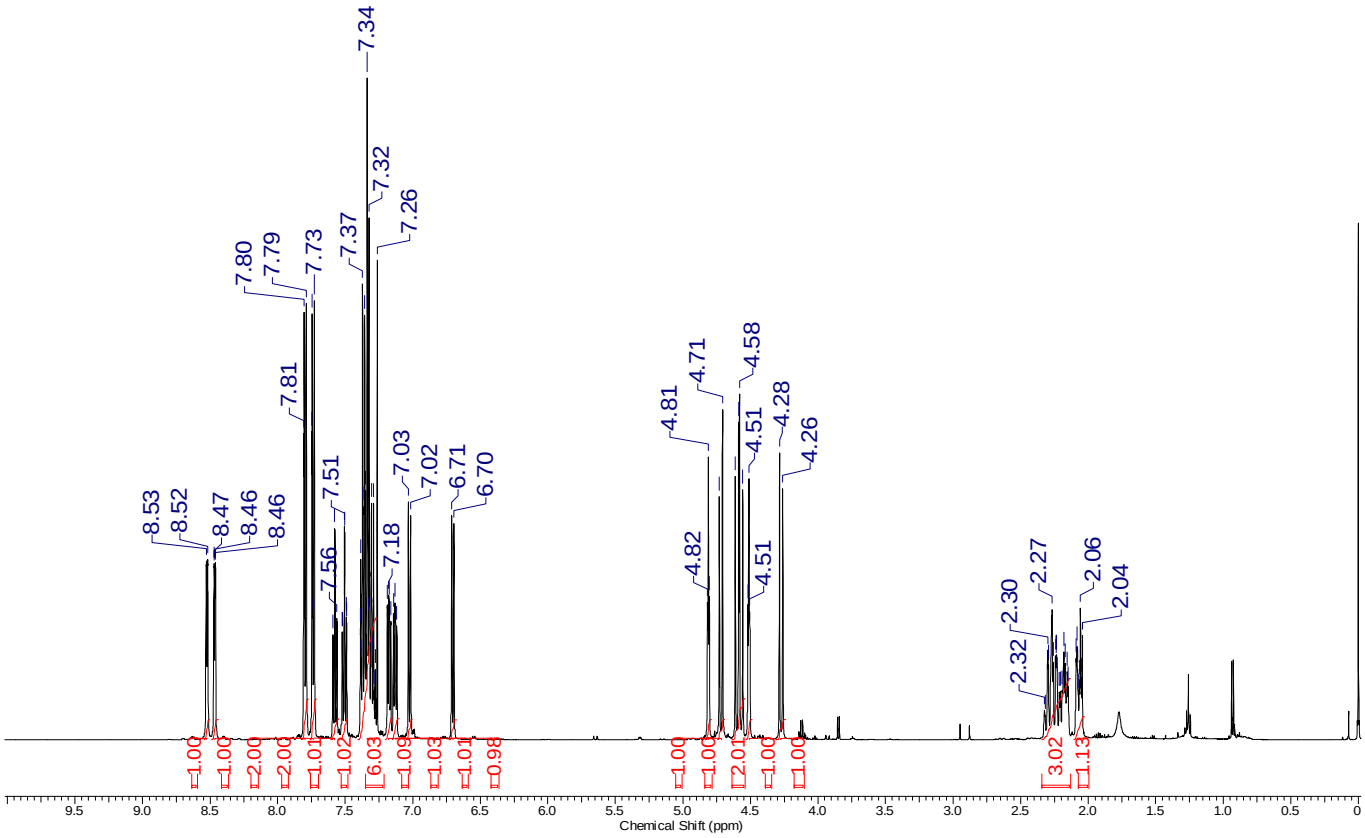
^{13}C NMR (125 MHz, $CDCl_3$)

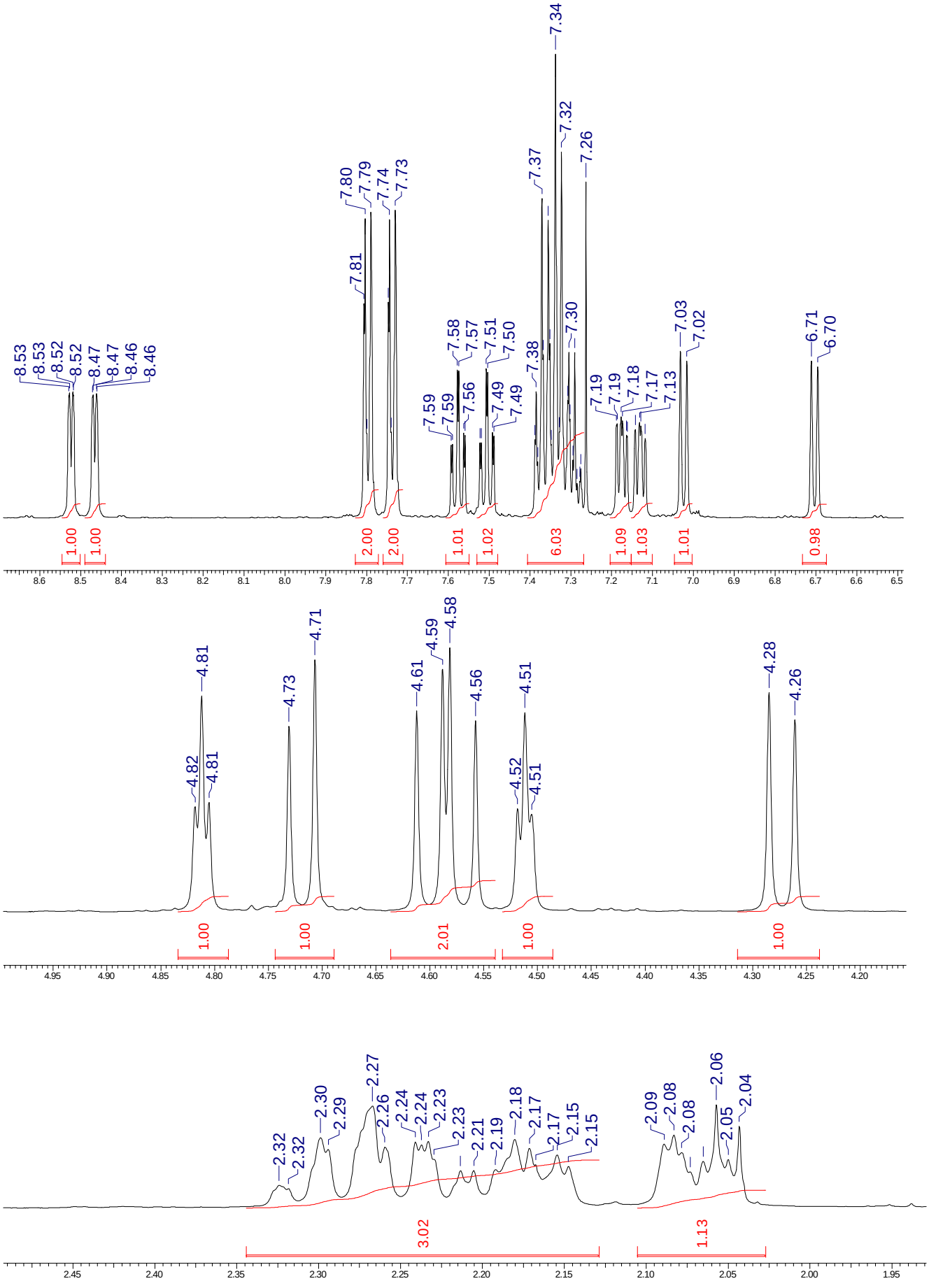


Tricarbonyl-((4*S*,7*S*)-1,3-diphenyl-4,7-bis(pyridin-2-ylmethoxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one) iron 14: ADG38.



^{1}H NMR (500 MHz, $CDCl_3$)

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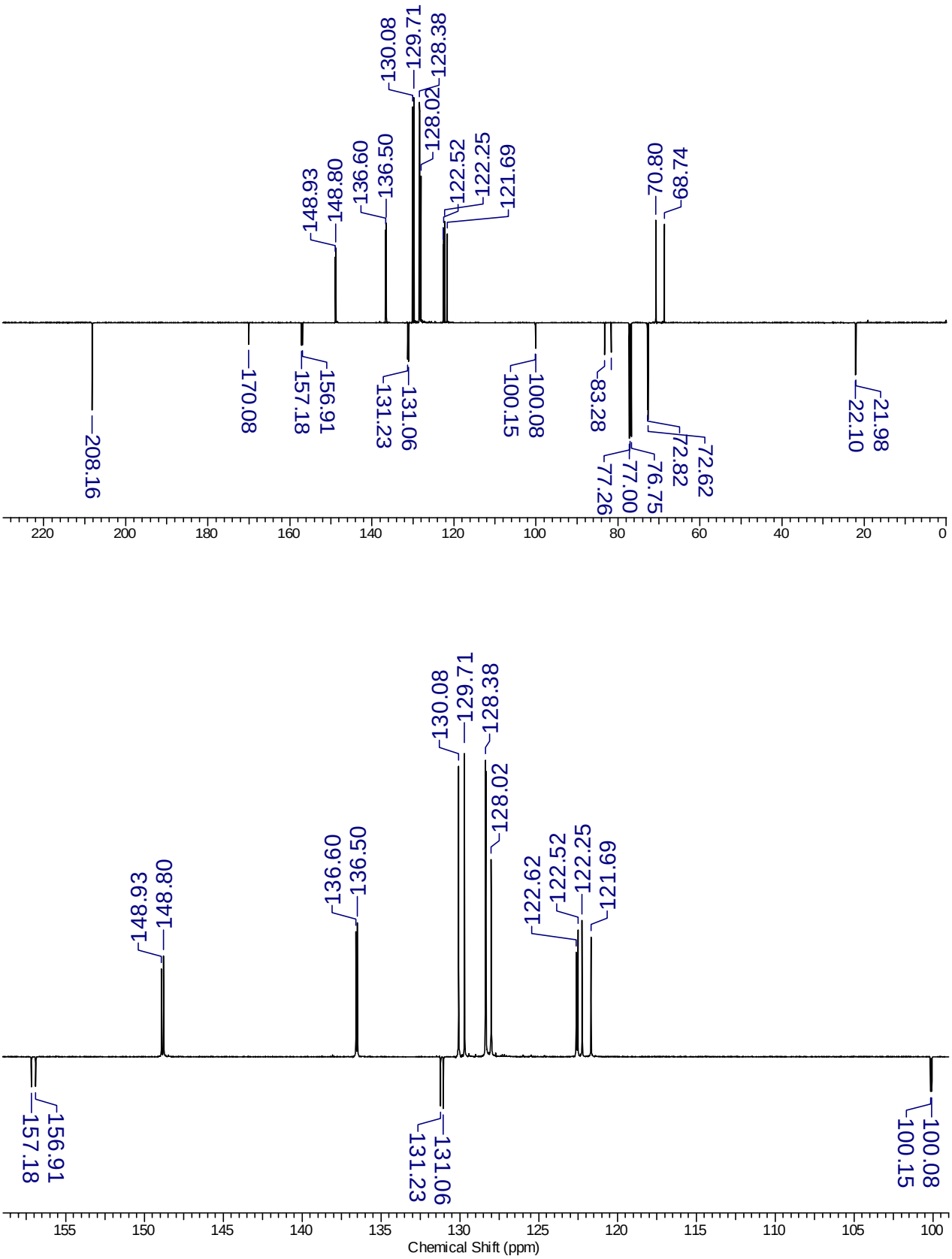
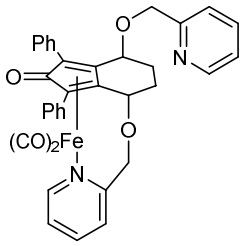
7.51
7.50
7.49
7.49
7.38
7.37
7.34
7.32
7.30
7.26
7.19
7.19
7.18
7.17
7.13
7.03
7.02
6.71
6.70
1.00
1.00
2.00
2.00
1.01
1.02
6.03
1.09
1.03
1.01
0.98
4.82
4.81
4.81
4.73
4.71
4.61
4.59
4.58
4.56
4.52
4.51
4.51
4.28
4.26
1.00
1.00
2.01
1.00
1.00
2.32
2.32
2.30
2.29
2.27
2.26
2.24
2.24
2.23
2.23
2.21
2.19
2.18
2.17
2.17
2.15
2.15
2.09
2.08
2.08
2.06
2.05
2.04
3.02
1.13

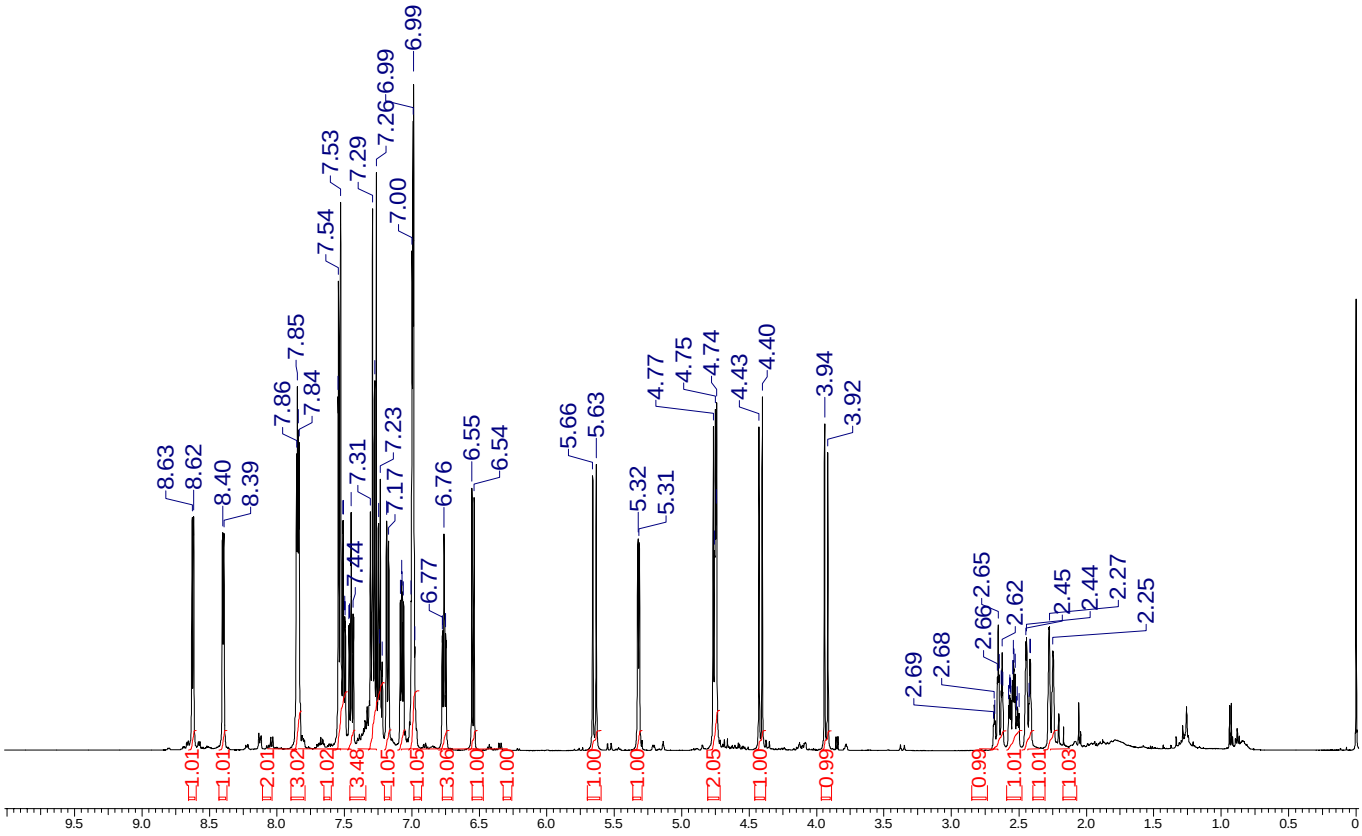
^{13}C NMR (125 MHz, $CDCl_3$)

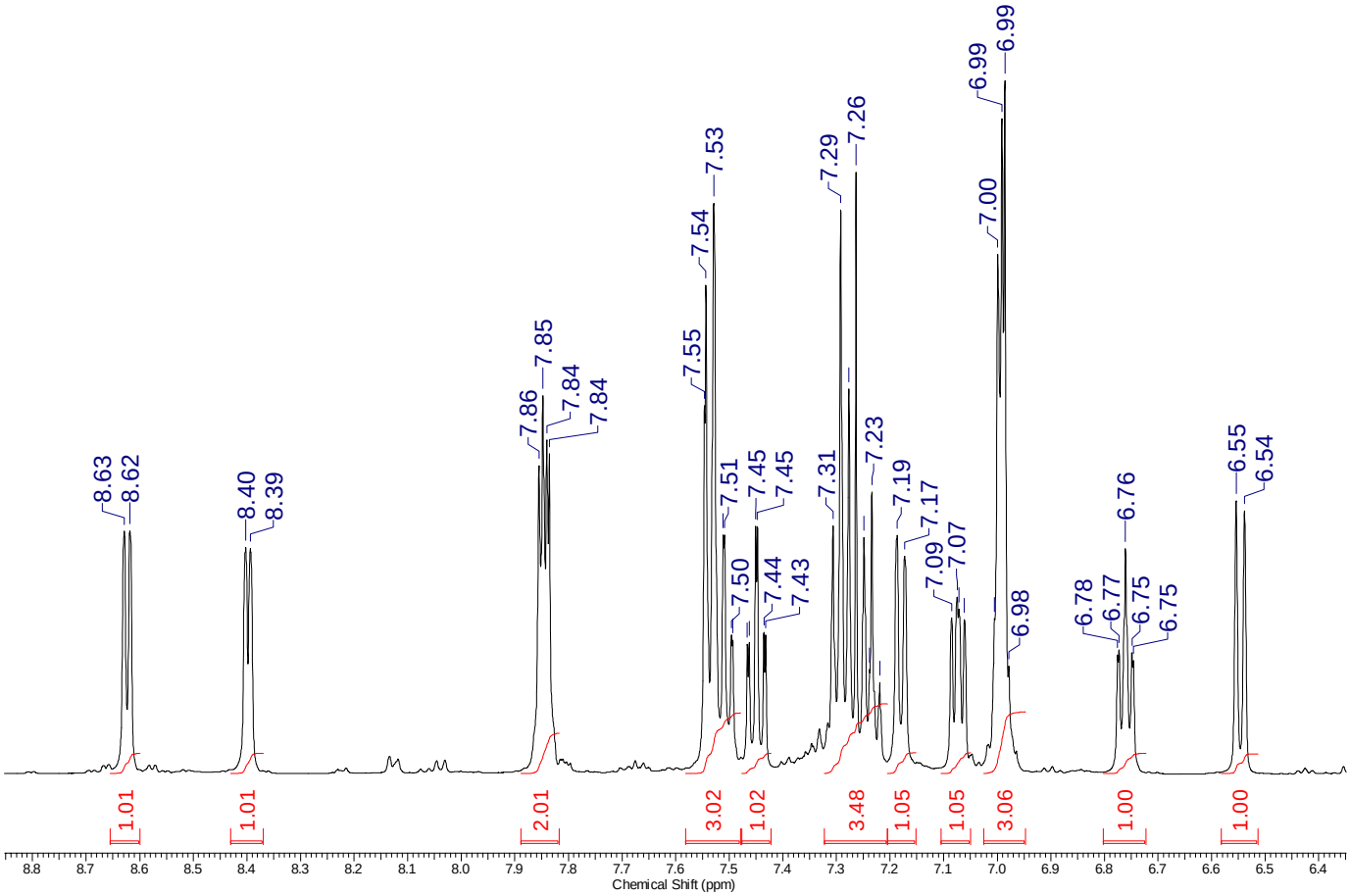


Dicarbonyl-((4*S*,7*S*)-1,3-diphenyl-4,7-bis(pyridin-2-ylmethoxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one) Iron 17: ADG58.



^{1}H NMR (500 MHz, $CDCl_3$)

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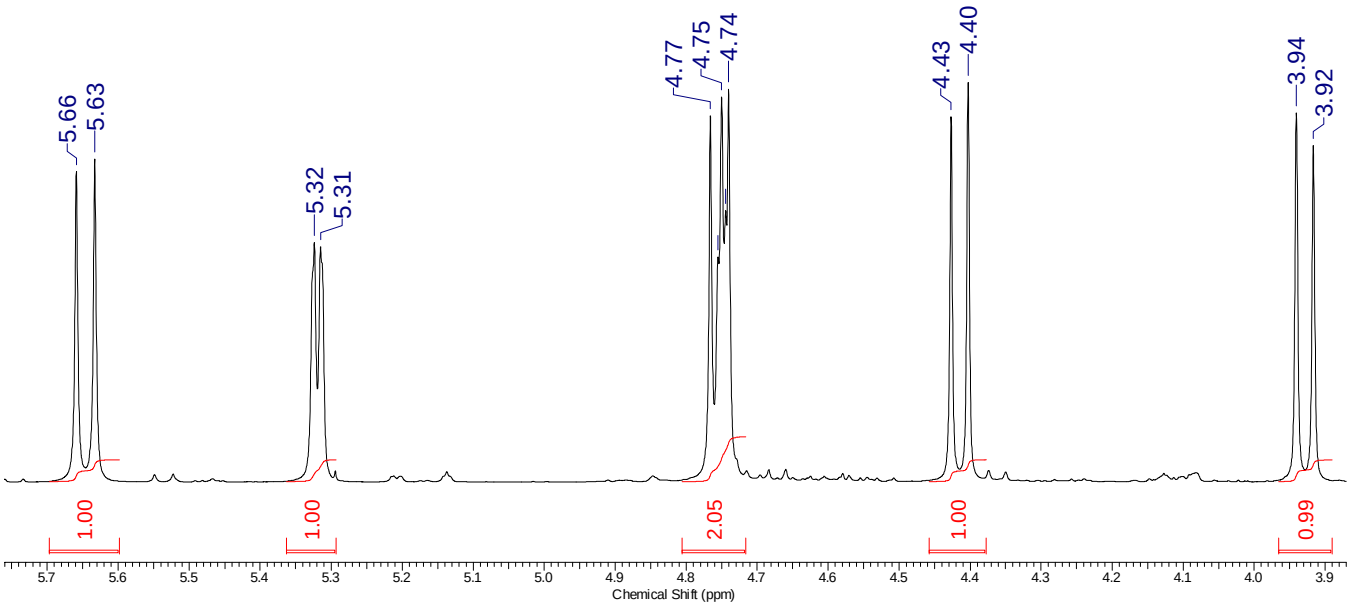
7.50
7.45
7.45
7.44
7.43
7.31
7.29
7.26
7.23
7.19
7.17
7.09
7.07
6.99
6.99
7.00
6.98
6.78
6.77
6.76
6.75
6.75
6.55
6.54
1.01
1.01
2.01
3.02
1.02
3.48
1.05
1.05
3.06
1.00
1.00
Chemical Shift (ppm)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5.63
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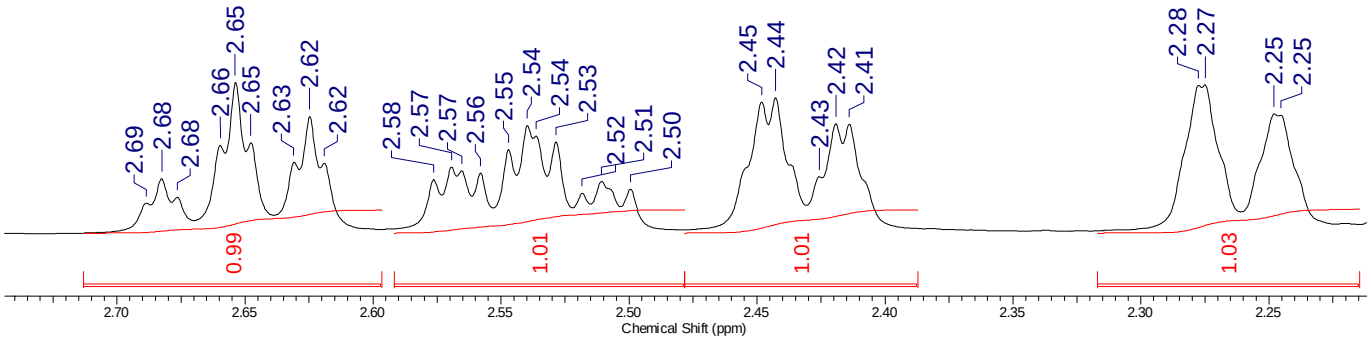
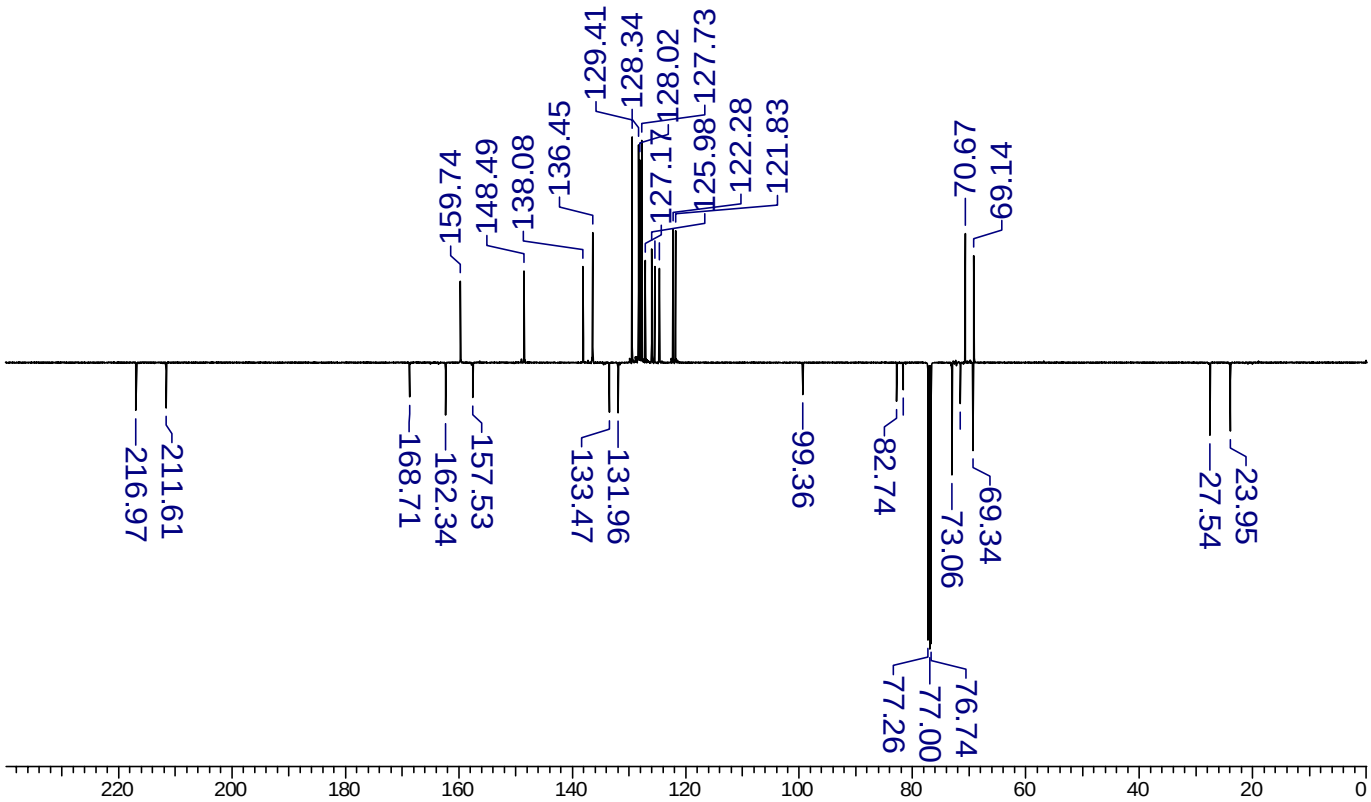
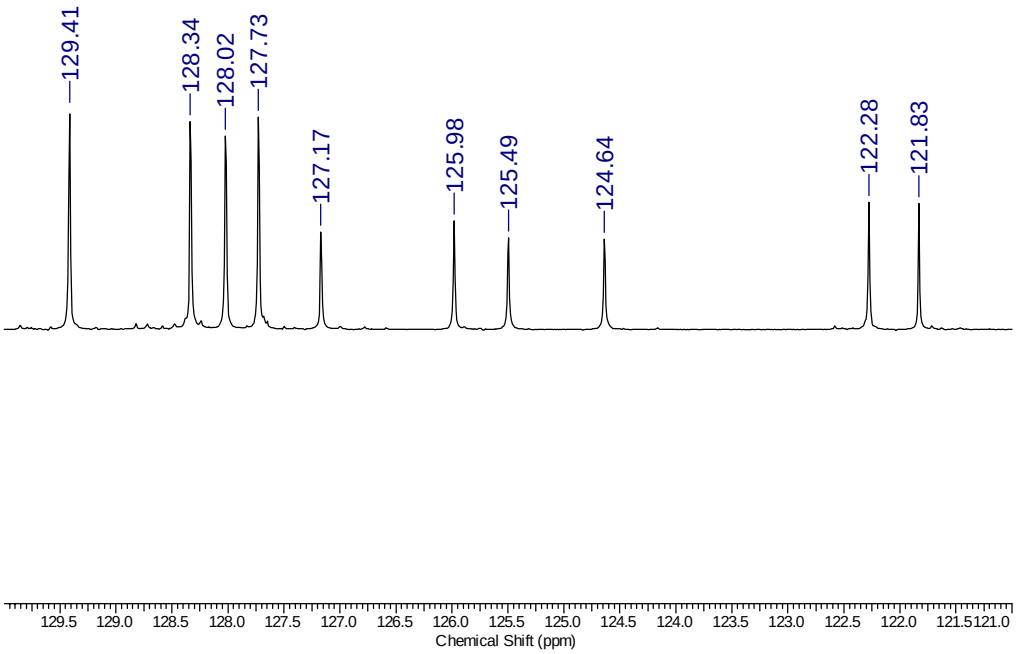
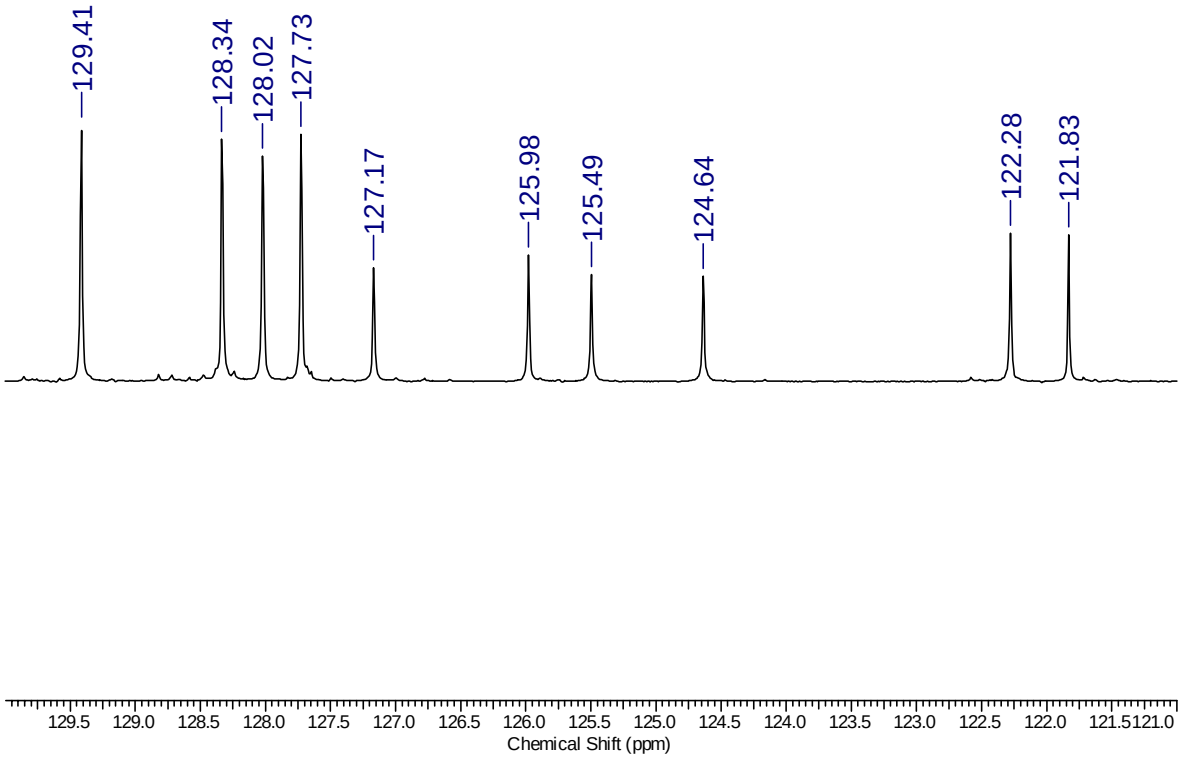
1.00
0.99
Chemical Shift (ppm)



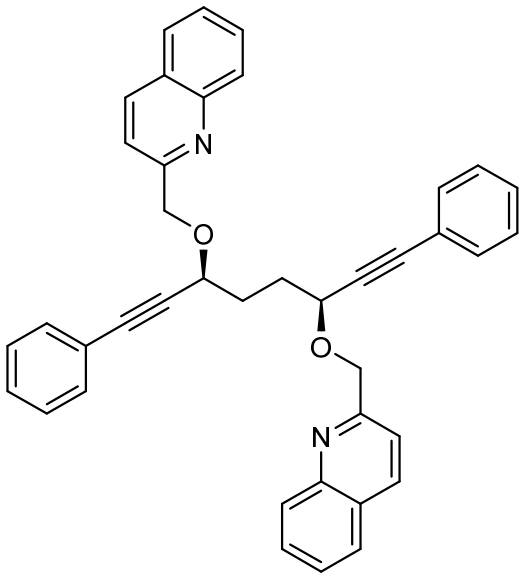
^{13}C NMR (125 MHz, $CDCl_3$)



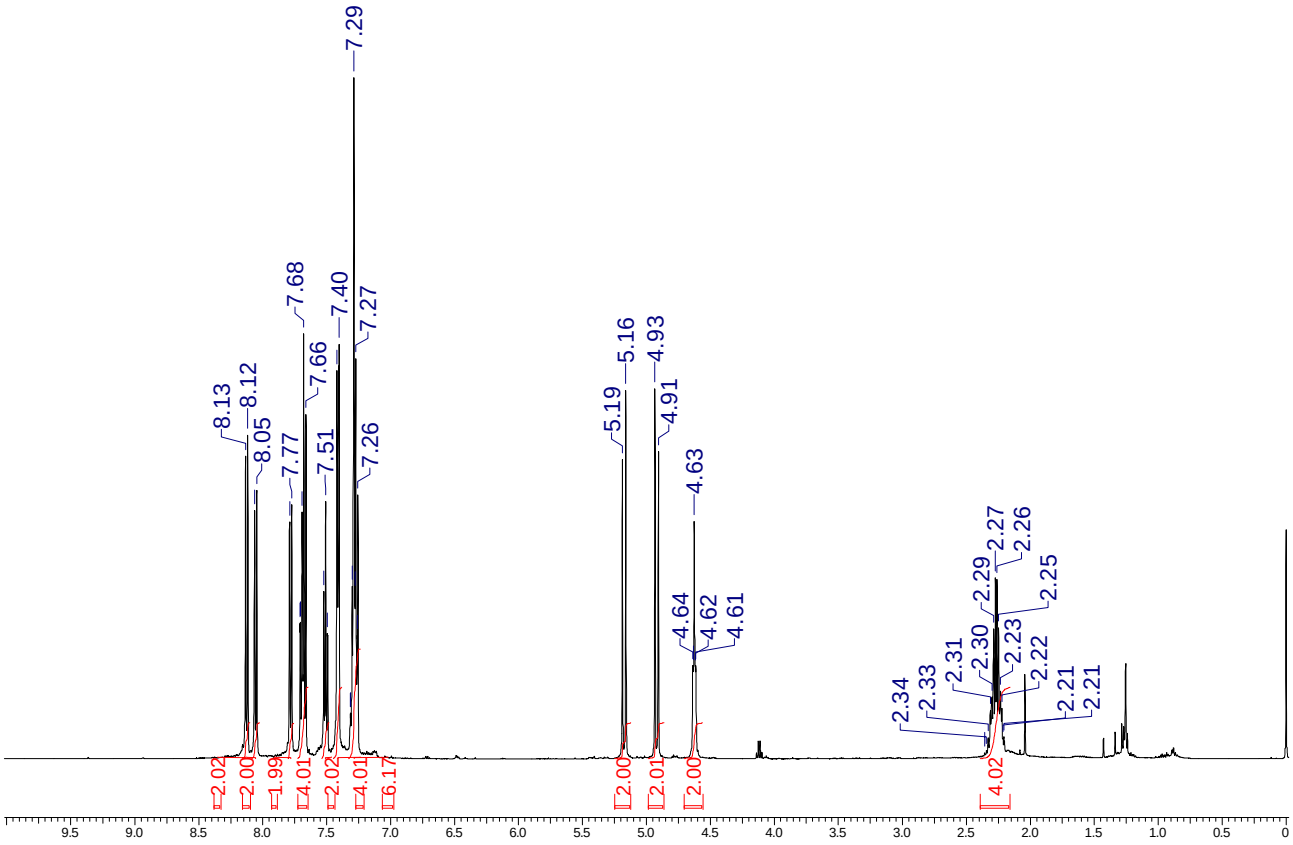

129.41
128.34
128.02
127.73
127.17
125.98
125.49
124.64
122.28
121.83
129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0 122.5 122.0 121.5 121.0
Chemical Shift (ppm)

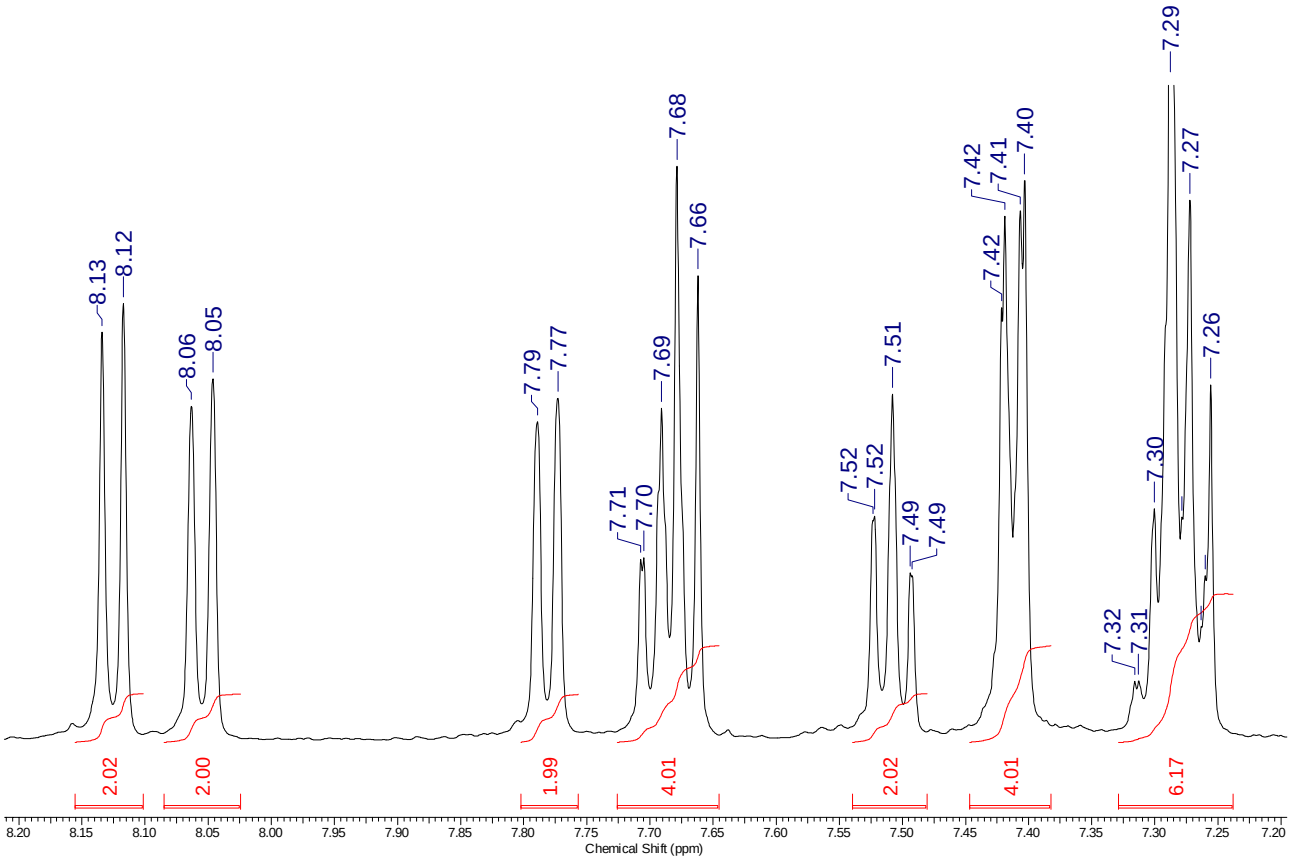

129.41
128.34
128.02
127.73
127.17
125.98
125.49
124.64
122.28
121.83
129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0 122.5 122.0 121.5 121.0
Chemical Shift (ppm)

2,2'-((((3*S*,6*S*)-1,8-Diphenylocta-1,7-diyne-3,6-diyl)bis(oxy))bis(methylene))diquinoline
19: ADG159.

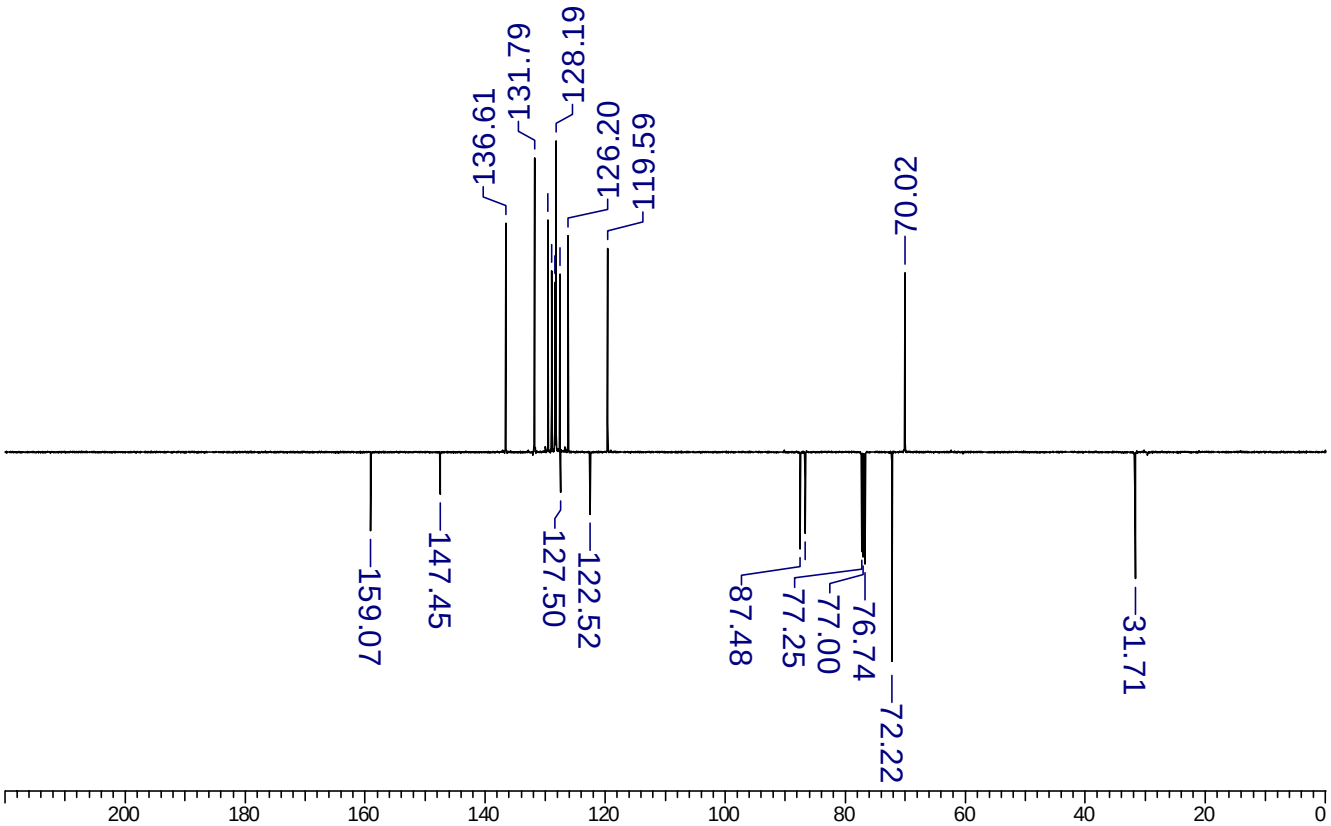


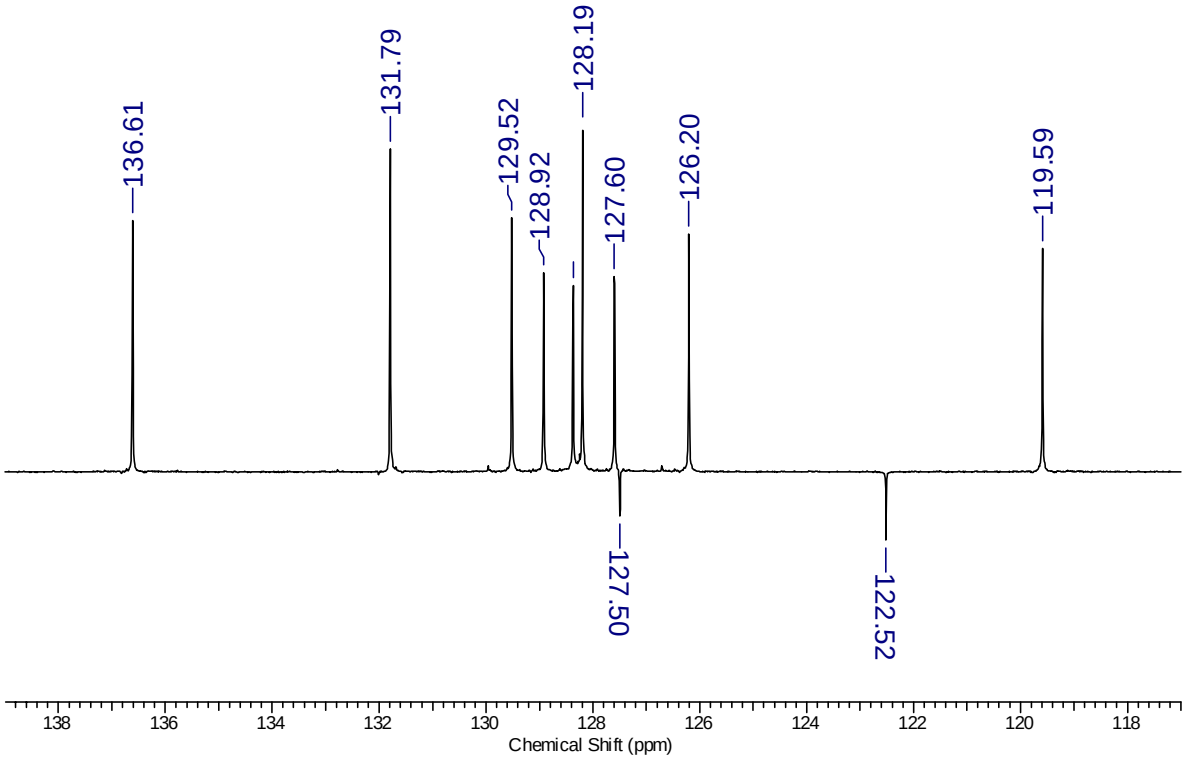
^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)




136.61
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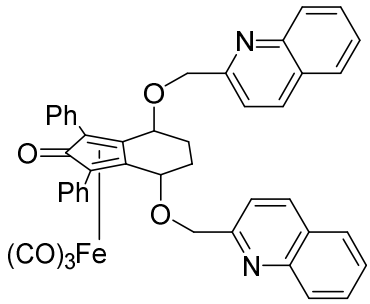
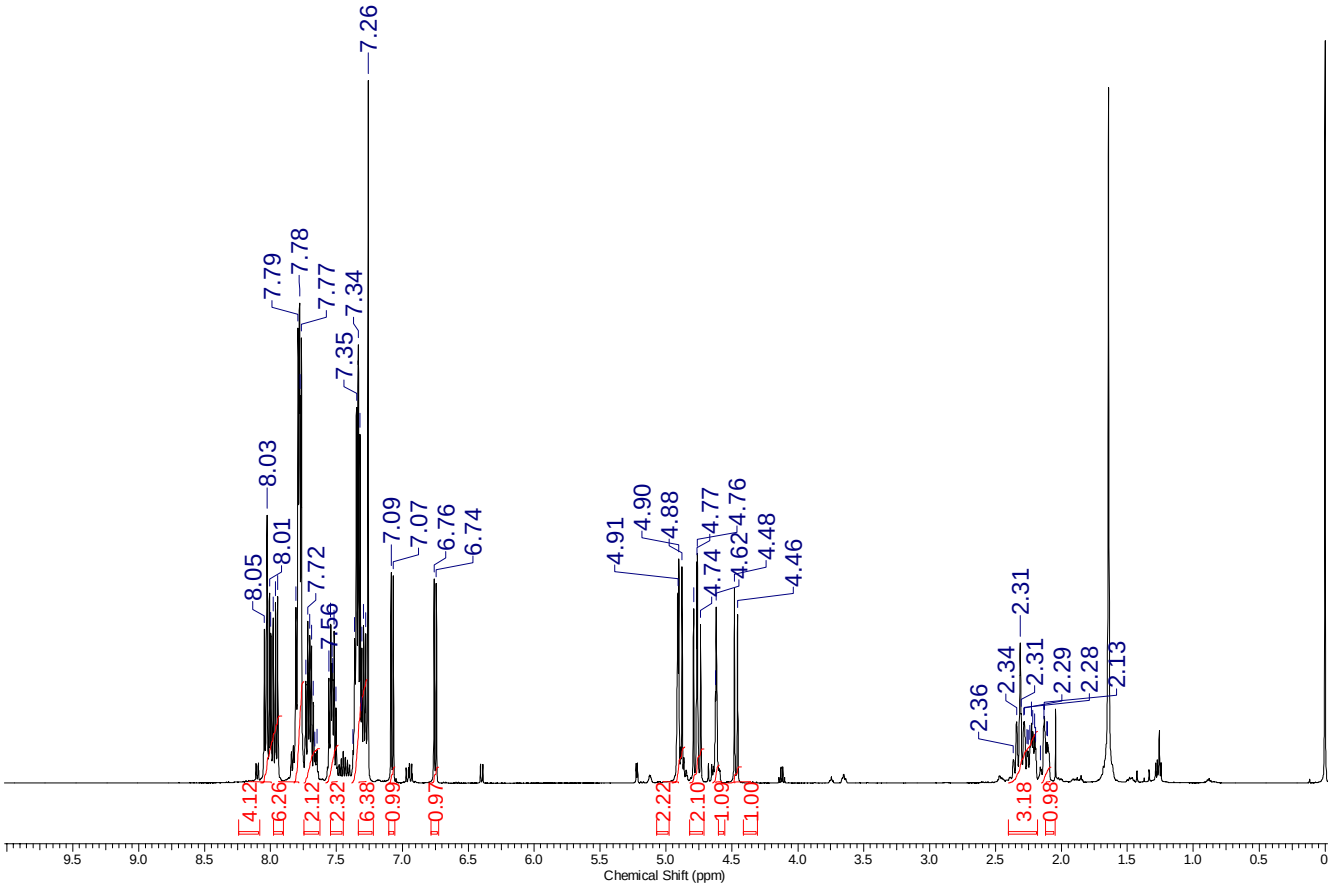
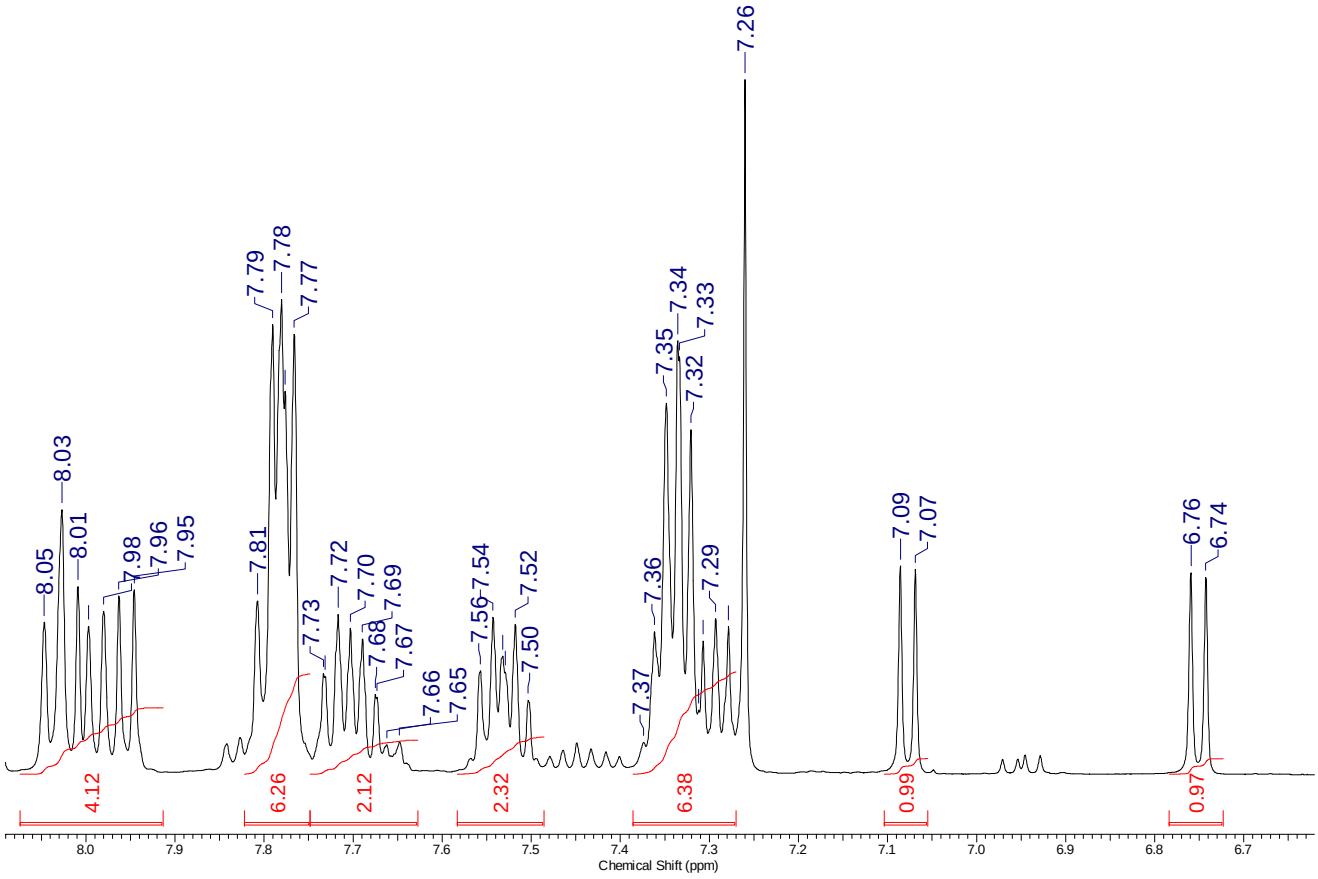
128.92
128.19
127.60
127.50
126.20
122.52
119.59
138
136
134
132
130
128
126
124
122
120
118
Chemical Shift (ppm)

Tricarbonyl-(4*S*,7*S*)-1,3-diphenyl-4,7-bis(quinolin-2-ylmethoxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron 18: ADG232.



^{1}H NMR (500 MHz, $CDCl_3$)

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7.77
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7.69
7.68
7.67
7.66
7.65
7.56
7.54
7.52
7.50
7.37
7.36
7.35
7.34
7.33
7.32
7.29
7.26
7.09
7.07
6.76
6.74
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6.26
2.12
2.32
6.38
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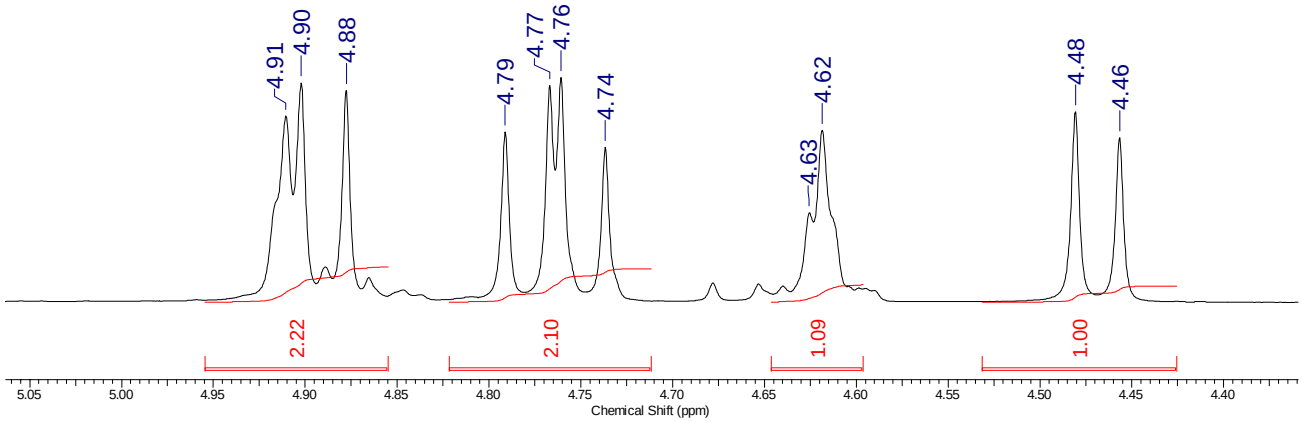
0.97
Chemical Shift (ppm)


4.91
4.90
4.88
4.79
4.77
4.76
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4.63
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4.48
4.46
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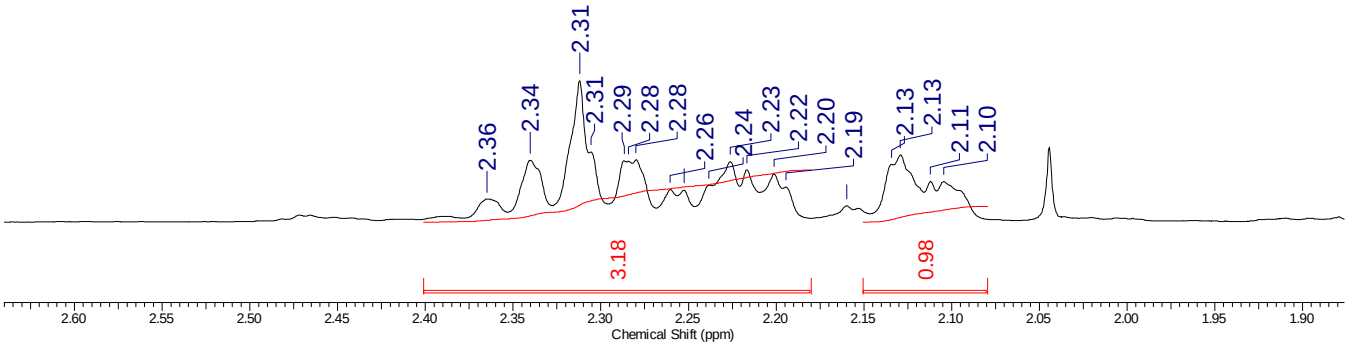
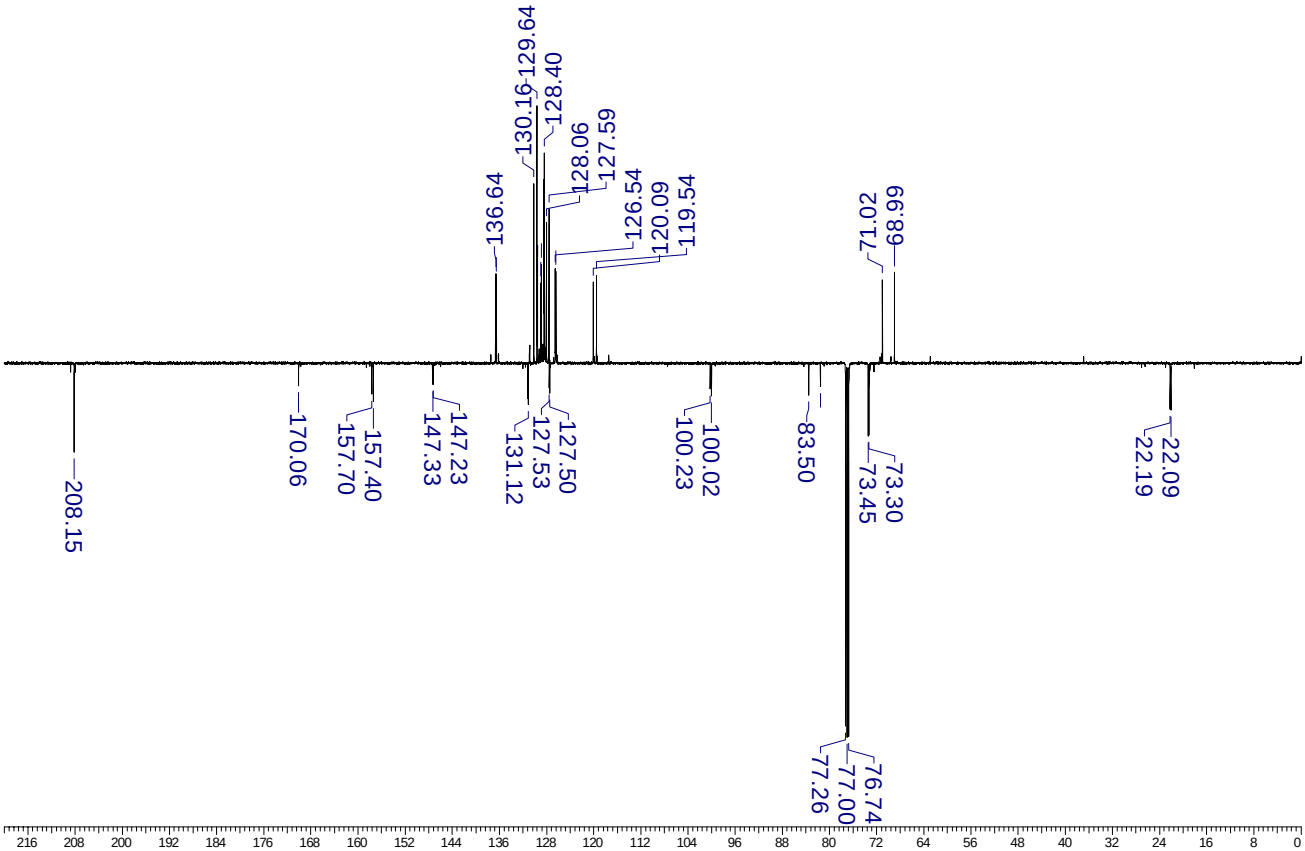
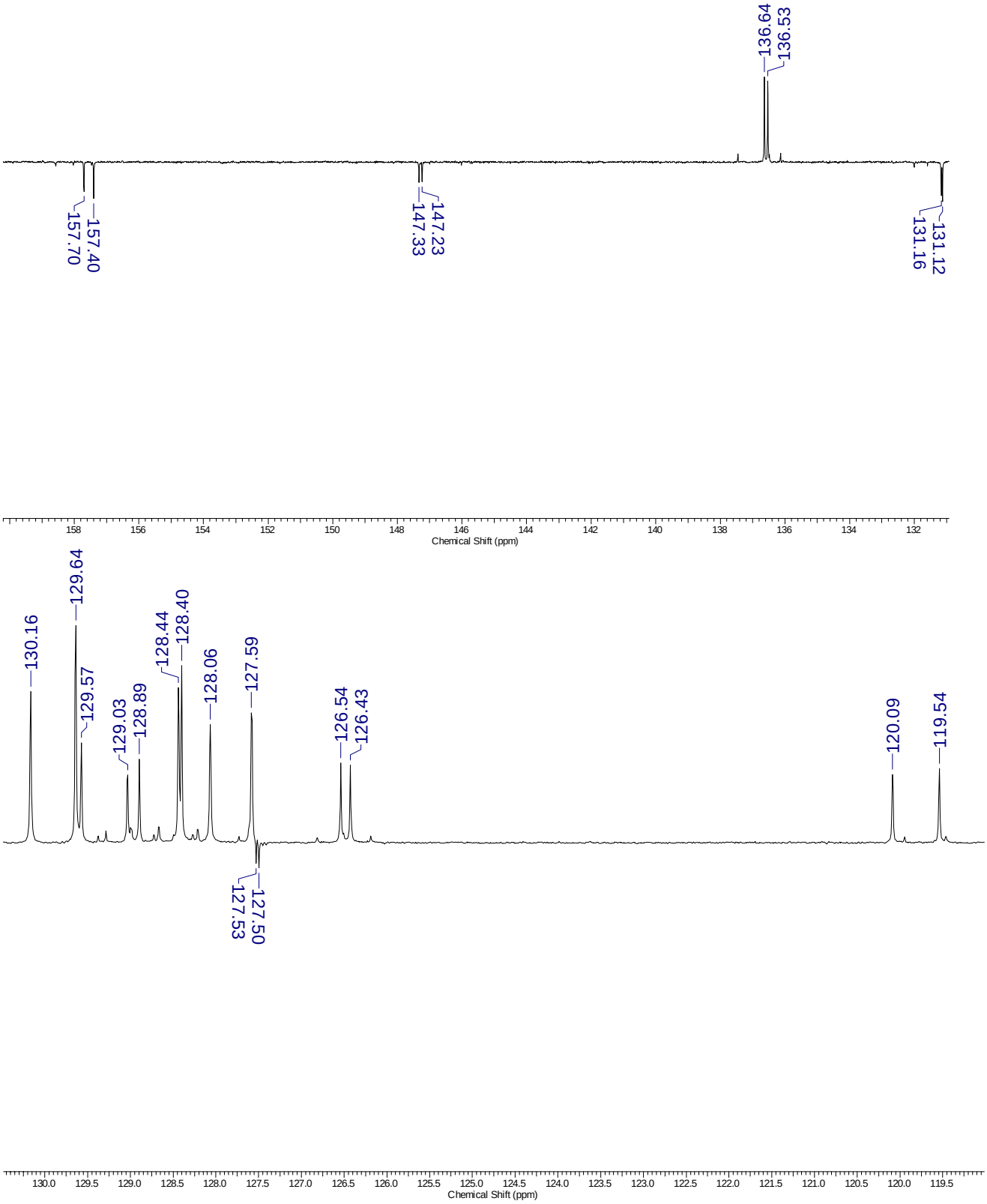
2.10
1.09
1.00
Chemical Shift (ppm)



^{13}C NMR (125 MHz, $CDCl_3$)




136.64
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157.70
157.40
147.23
147.33
131.12
131.16
158
156
154
152
150
148
146
144
142
140
138
136
134
132
Chemical Shift (ppm)
130.16
129.64
129.57
129.03
128.89
128.44
128.40
128.06
127.59
126.54
126.43
120.09
119.54
127.53
127.50
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
125.5
125.0
124.5
124.0
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123.0
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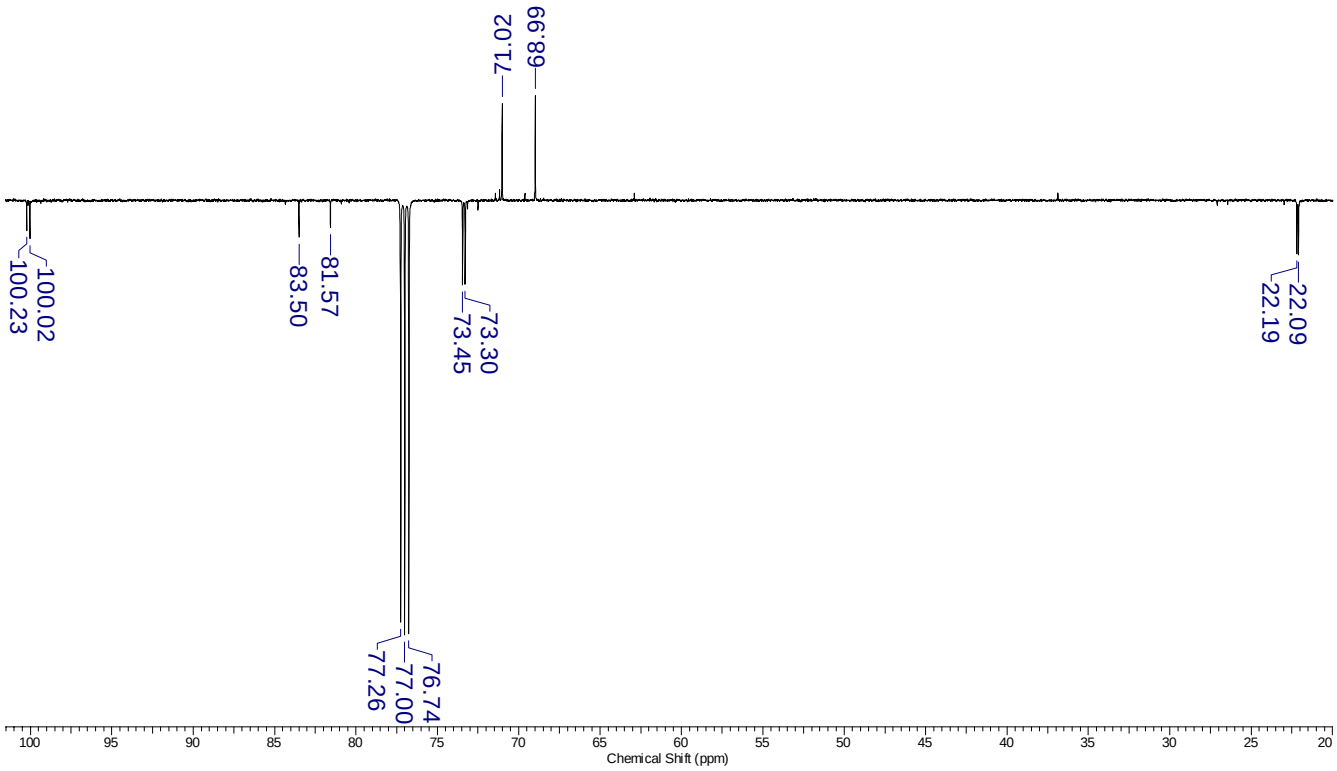
122.0
121.5
121.0
120.5
120.0
119.5
Chemical Shift (ppm)


71.02
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83.50
81.57
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77.00
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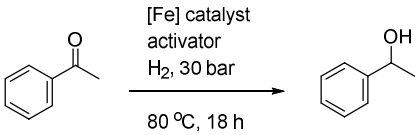
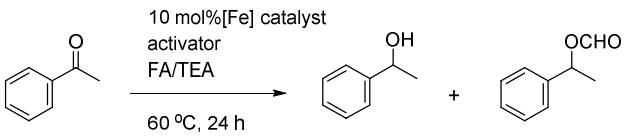
73.45
73.30
22.19
22.09
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
Chemical Shift (ppm)

Full Table S1; Hydrogenation of acetophenone using complexes **14 (dipy)**, **17 (cyc py)** and **18 (quin)**.



Entry/ Reaction	Catalyst (%)/code	Activator (%)	Additive	Solvent	Conv	Ee
ADG65	ADG38 (1%) dipy	-------	-	IPA/H_2O	2	2(R)
ADG175	ADG110 (1%) dipy	-------	-	IPA/H_2O	3.1	N/A
ADG68	ADG38 (1%) dipy	K_2CO_3 (5%)	-	IPA/H_2O	19	2(R)
ADG176	ADG110 (1%) dipy	K_2CO_3 (5%)	-	IPA/H_2O	20.6	4.2(R)
ADG67	ADG38 (1%) dipy	K_2CO_3 (3%)	-	IPA/H_2O	17.3	2 (R)
ADG66	ADG38 (1%) dipy	K_2CO_3 (2%)	-	IPA/H_2O	18.6	2.4(R)
ADG101	ADG56 (1%) dipy	TMAO (1%)	-	IPA/H_2O	34.1	3(R)
ADG177	ADG110 (1%) dipy	TMAO (1%)	-	IPA/H_2O	37.1	4.2(R)
ADG102	ADG56 (1%) dipy	TMAO (1%)	PPh_3 (1%)	IPA/H_2O	2.2	3(R)
ADG103	ADG56 (1%) dipy	TMAO (2%)	PPh_3 (1%)	IPA/H_2O	16	3(R)
ADG70	ADG58 (1%) cyc py	------	-------	IPA/H_2O	23.6	2.6(R)
ADG104	ADG58 (1%) cyc py	------	-------	IPA/H_2O	17.3	4.6(R)
ADG73	ADG58 (1%) cyc py	------	-------	Toluene	40.9	1(S)
ADG74	ADG58 (1%) cyc py	------	------	DCM	44.8	1.4(R)
ADG196	ADG121 (1%) cyc py	K_2CO_3 (5%)	------	IPA/H_2O	12.9	4(R)
ADG213	ADG121 (1%) cyc py	K_2CO_3 (5%)	------	IPA/H_2O	15.4	2.6(R)
ADG71	ADG58 (1%) cyc py	TMAO (1%)	-------	IPA/H_2O	30.6	2.8(R)
ADG197	ADG121 (1%) cyc py	TMAO (1%)	-------	IPA/H_2O	36.3	4.1(R)
ADG72	ADG58 (1%) cyc py	TMAO (2%)	-------	IPA/H_2O	30.3	3.6(R)
ADG105	ADG58 (1%) cyc py	------	PPh_3 (1%)	IPA/H_2O	2.2	2.8(R)
ADG106	ADG58 (1%) cyc py	TMAO (1%)	PPh_3 (1%)	IPA/H_2O	8.5	3.8(R)
ADG107	ADG58 (1%) cyc py	TMAO (2%)	PPh_3 (1%)	IPA/H_2O	4.2	2.8(R)
ADG147	ADG113 (1%) quin	-------		IPA/H_2O	69.8	4.2(R)
ADG154	ADG113 (1%) quin	-------		IPA/H_2O	70.9	5.4(R)
ADG148	ADG113 (1%) quin	K_2CO_3 (5%)		IPA/H_2O	53.5	3(R)
ADG155	ADG113 (1%) quin	K_2CO_3 (5%)		IPA/H_2O	51.2	5(R)
ADG115	ADG113 (1%) quin	TMAO (1%)		IPA/H_2O	99.7	4.6(R)
ADG149	ADG113 (1%) quin	TMAO (1%)		IPA/H_2O	99.8	7.6(R)
ADG116	ADG113 (1%) quin	TMAO (2%)		IPA/H_2O	99.7	5(R)
ADG117	ADG113 (1%) quin	TMAO (3%)		IPA/H_2O	99.8	4.6(R)

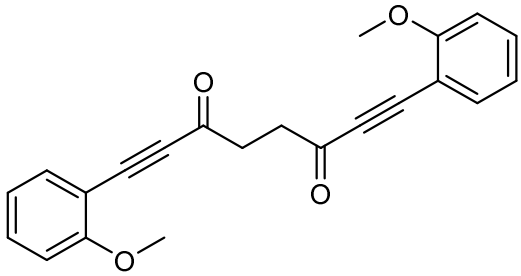
Full Table S2; Asymmetric transfer hydrogenation of acetophenone using complexes **14**, **17** and **18**.



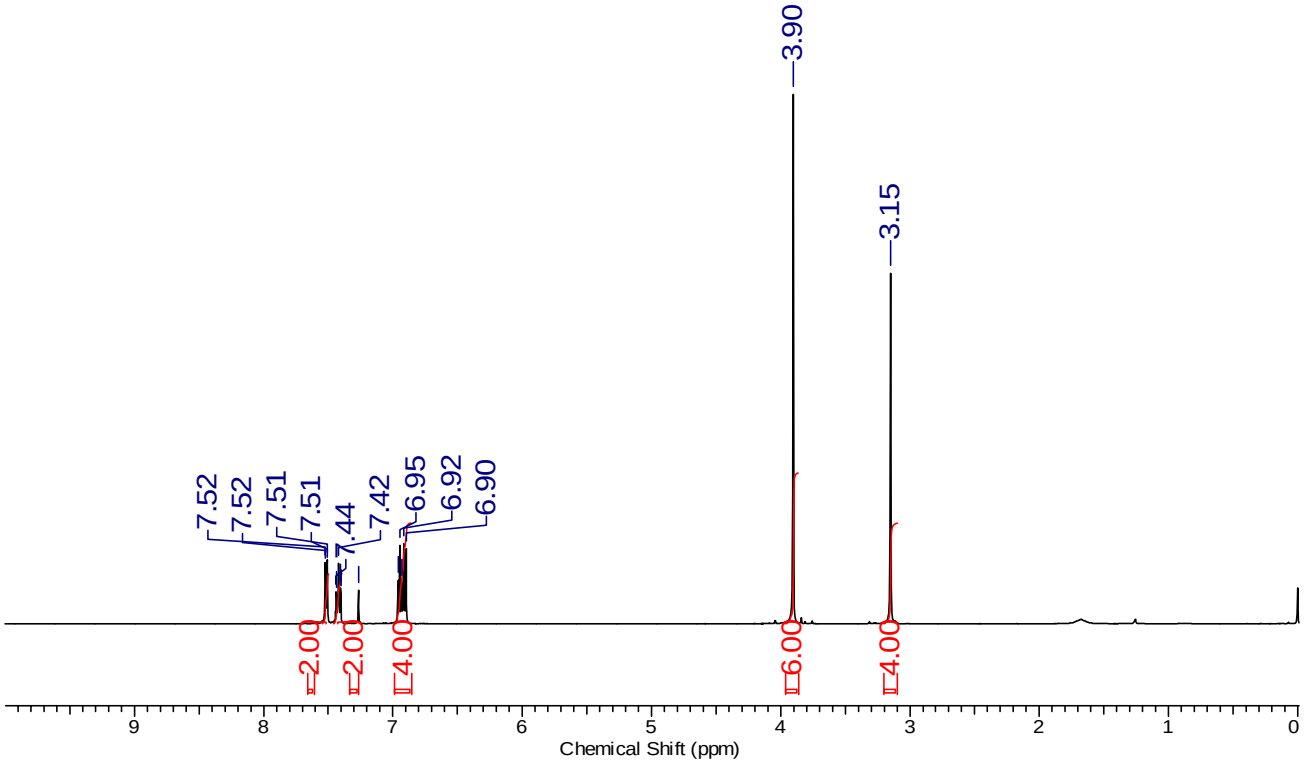
Reaction	Catalyst (%)	Activator (%)	Conv	Alcohol (ee)	Formate (ee)
ADG129	ADG110 dipy	---------	73.7	63.1 (2.4 R)	10.6 (2.6 R)
ADG118	ADG56 dipy	TMAO (10%)	99.7	90.8 (2 R)	8.9 (2.8 R)
ADG124	ADG121 cyc py	------	99.9	85.5 (4.2 R)	14.4 (3 R)
ADG125	ADG121 cyc py	TMAO (10%)	99.9	87.8 (3.4 R)	11.8 (3 R)
ADG119[a]	ADG56 quin	TMAO (10%)	58.1	45.4(3.4 R)	12.7 (5.2 R)

a: hetereogenous reaction (catalyst is not soluble)

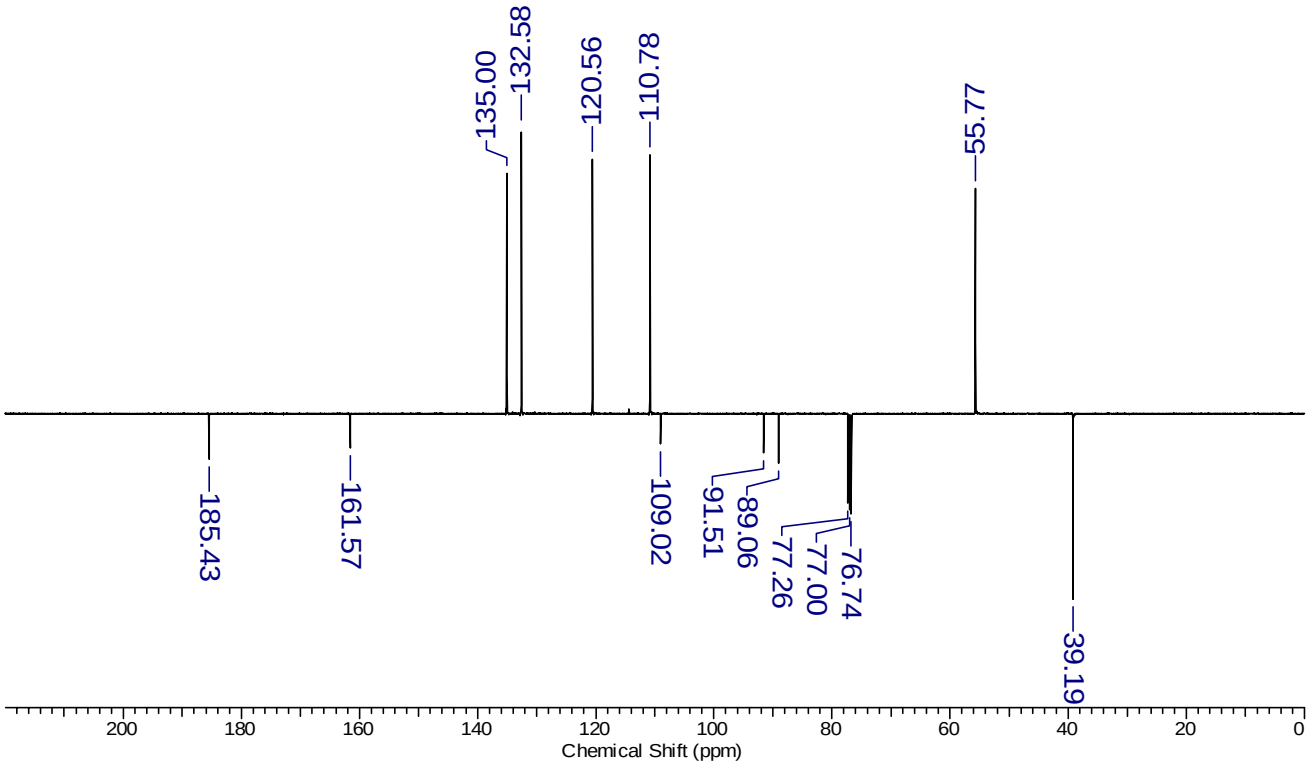
1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-dione 22: ADG220.



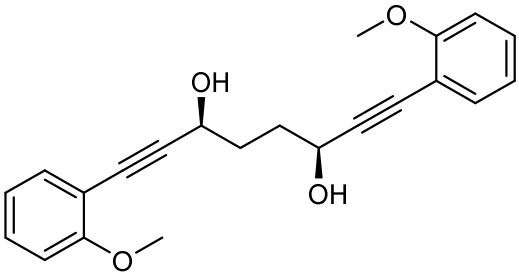
^{1}H NMR (500 MHz, $CDCl_3$)



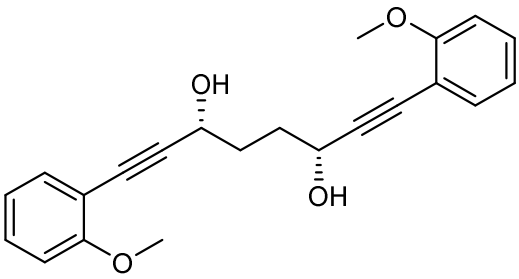
^{13}C NMR (125 MHz, $CDCl_3$)



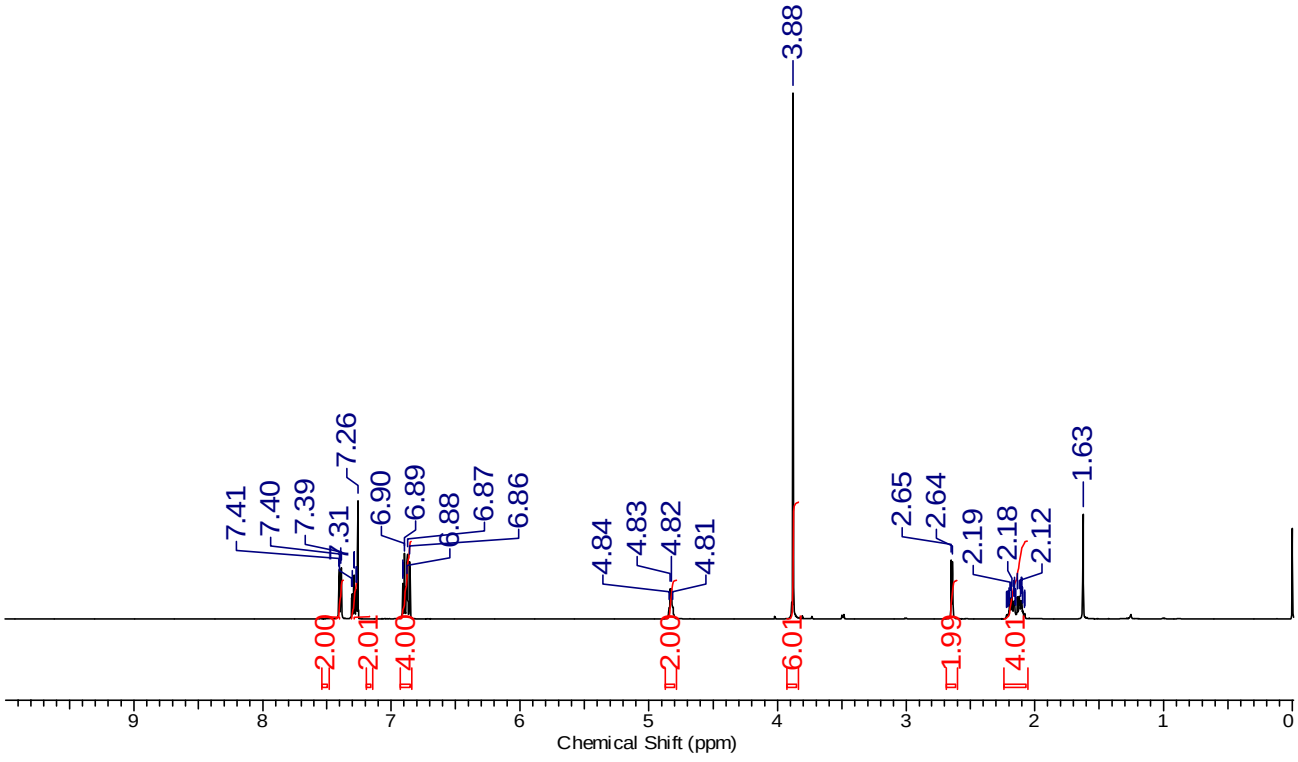
(3*S*,6*S*)-1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol 24: AEC019.



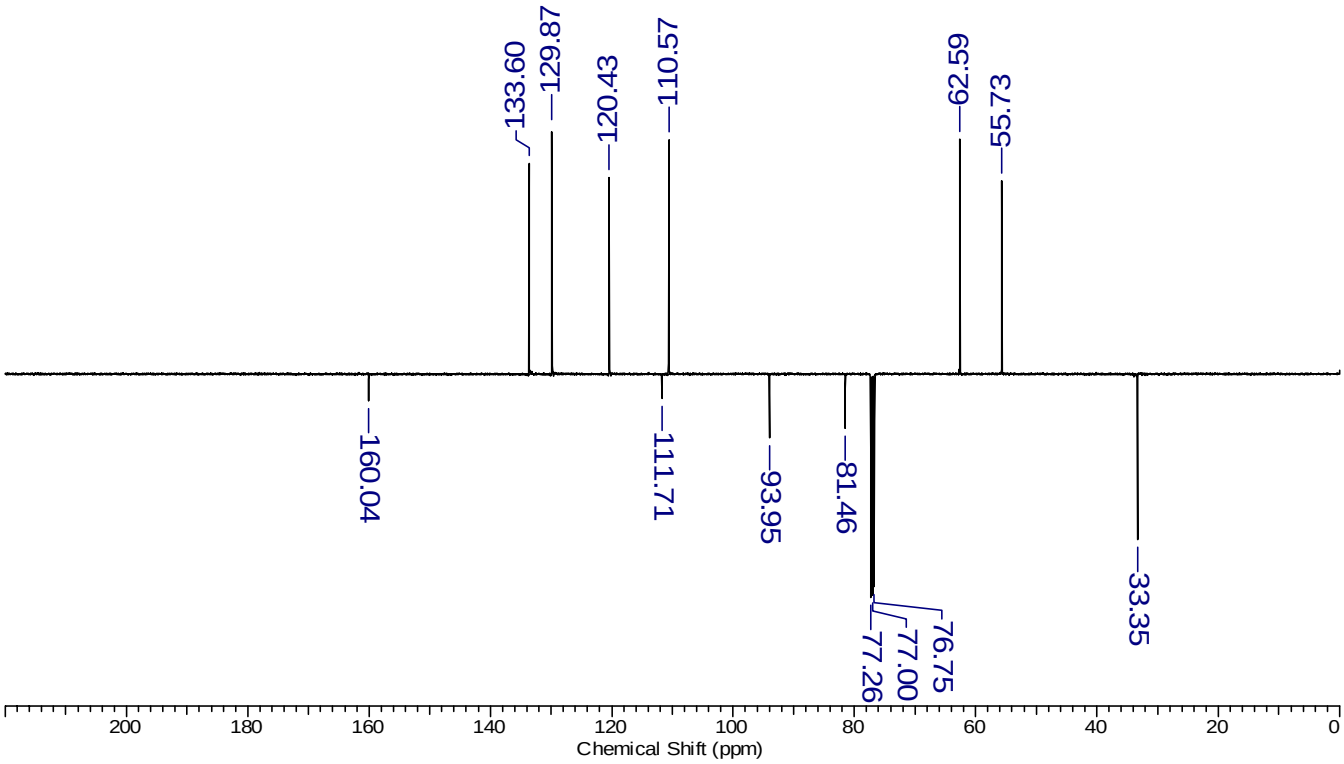
(3*R*,6*R*)-1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol 24: ADG188.



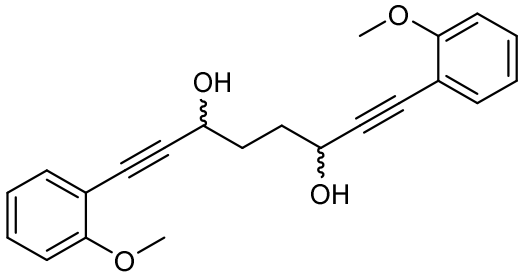
^{1}H NMR (500 MHz, $CDCl_3$).



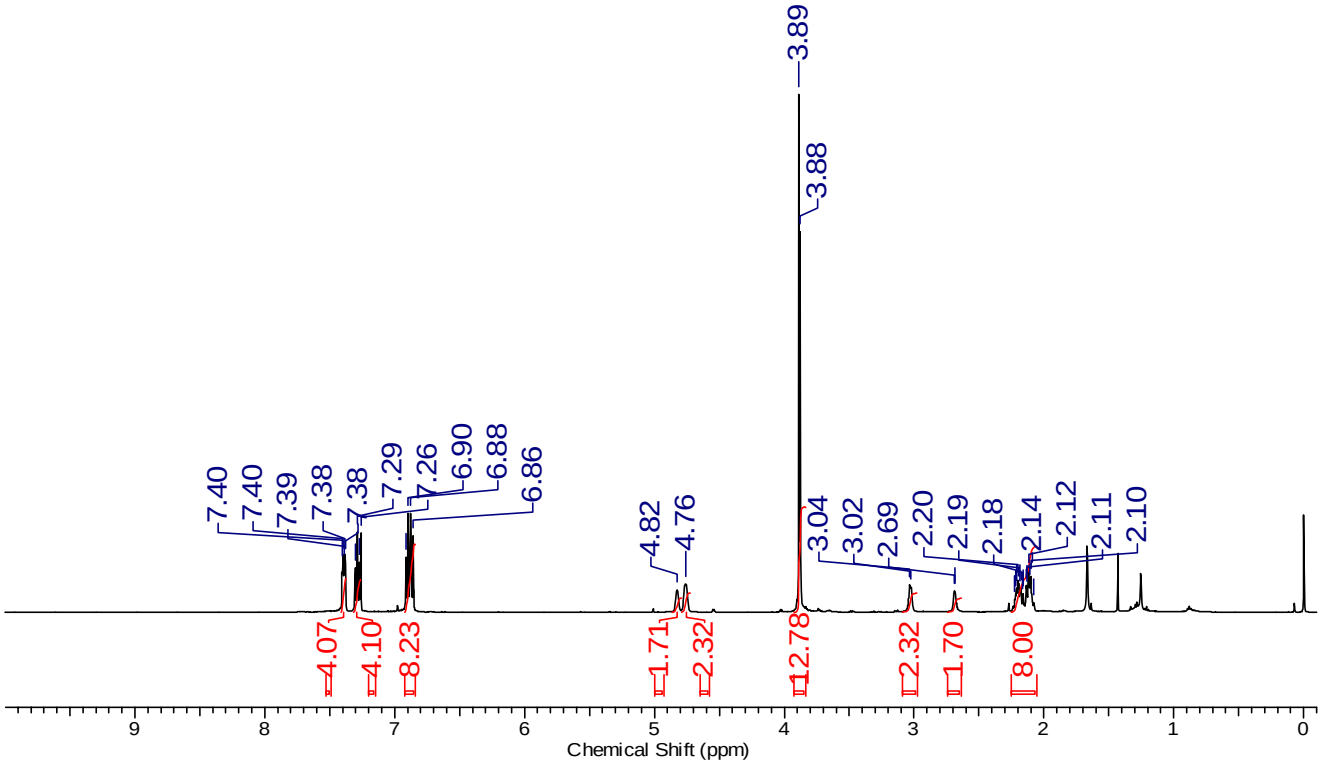
^{13}C NMR (125 MHz, $CDCl_3$)



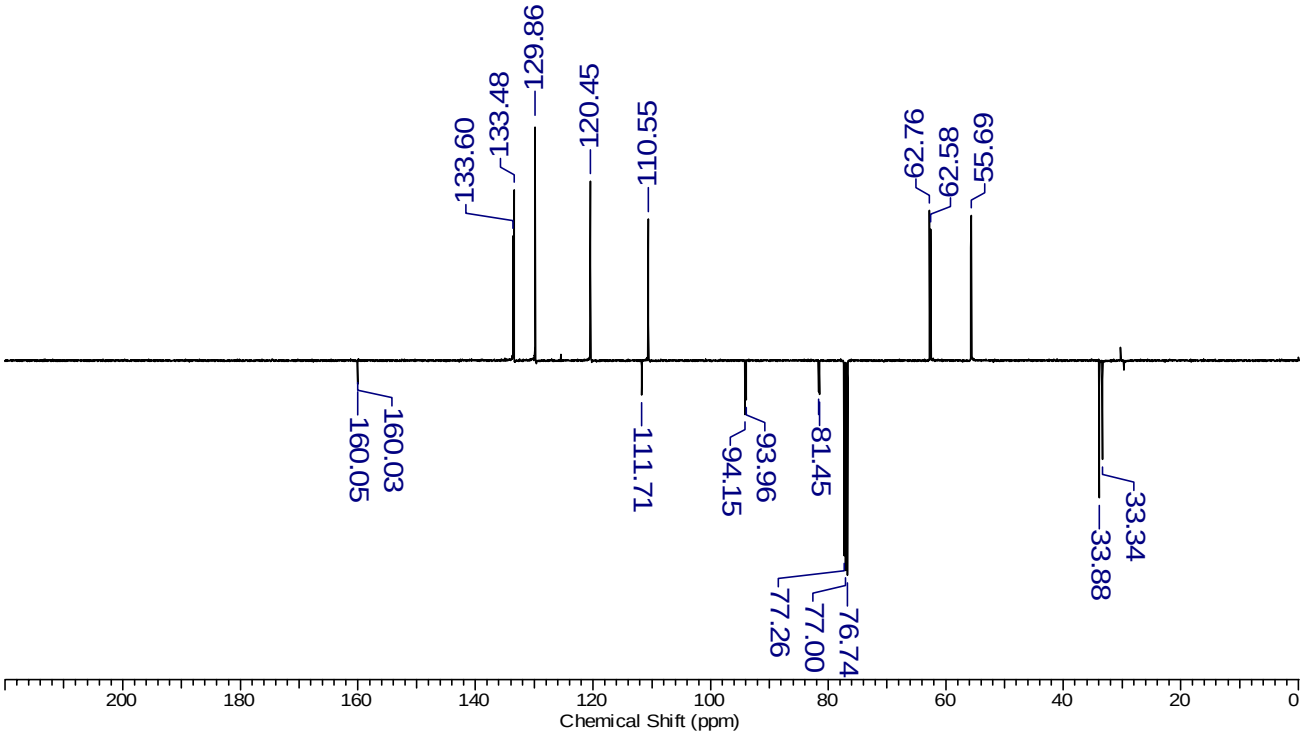
1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol 24: ADG187.



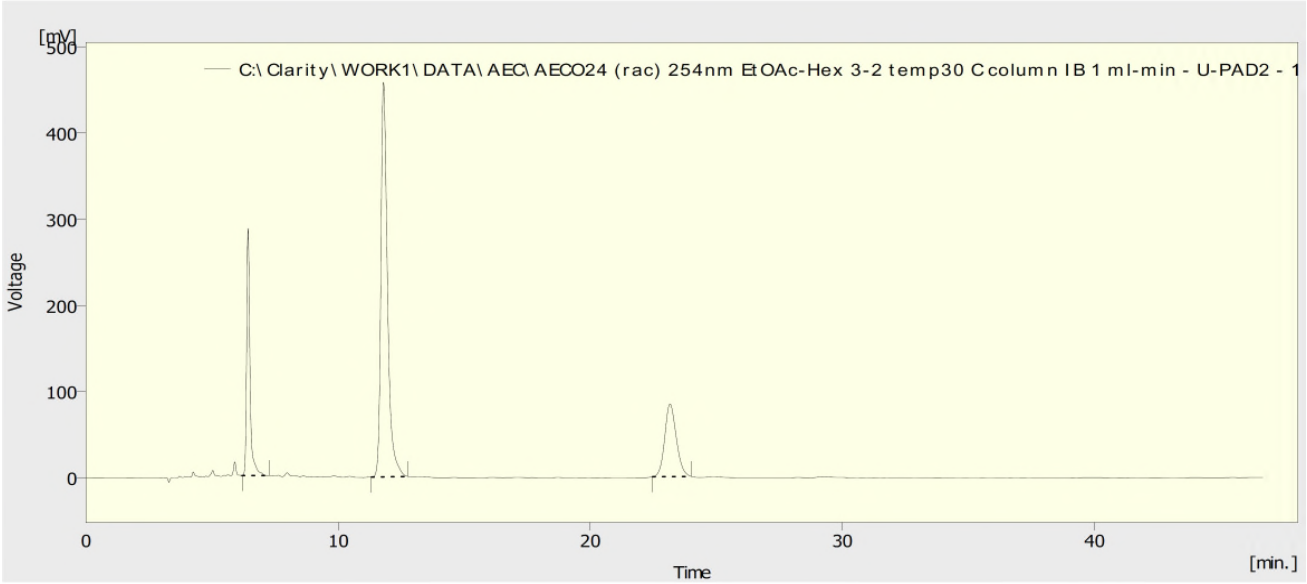
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



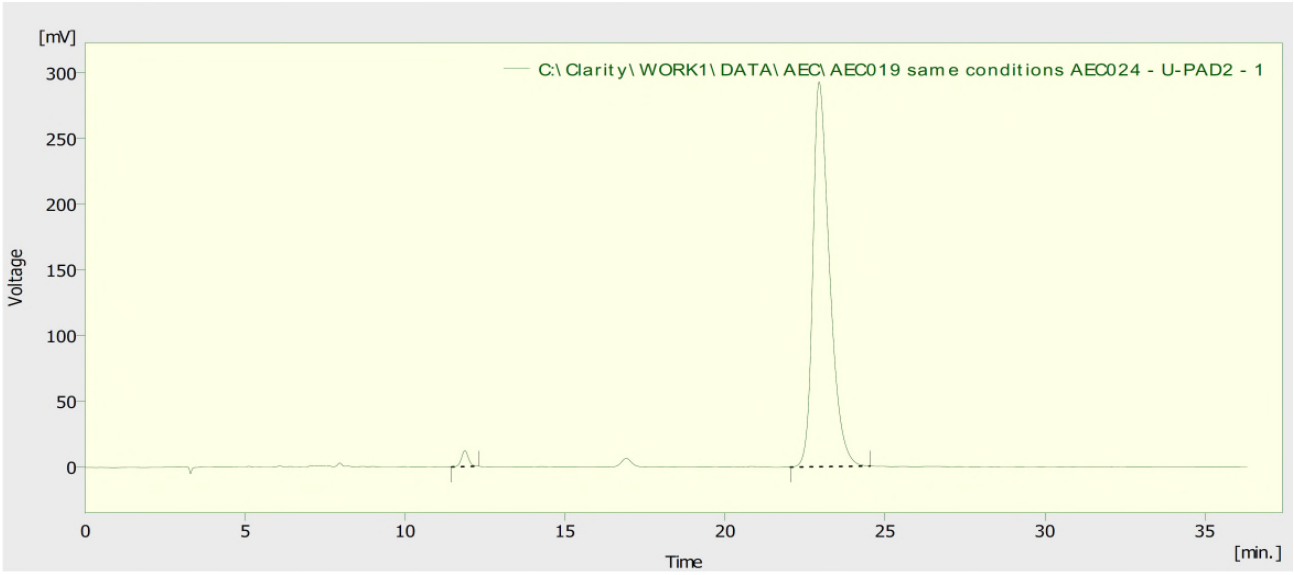
1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol 24 (racemic/meso mixture): HPLC analysis on ChiralPak IB Column: 0.46 cm x 25cm, Mobile phase EtOAc : Hexane 3 : 2, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.



Result Table (Uncal - C:\Clarity\WORK1\DATA\AEC\AECO24 (rac) 254nm EtOAc-Hex 3-2 temp30 C column IB 1 ml-min - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.424	2649.925	286.977	19.3	34.6	0.13	
2	11.796	8356.324	458.154	61.0	55.2	0.27	
3	23.160	2700.271	84.427	19.7	10.2	0.49	
	Total	13706.520	829.558	100.0	100.0		

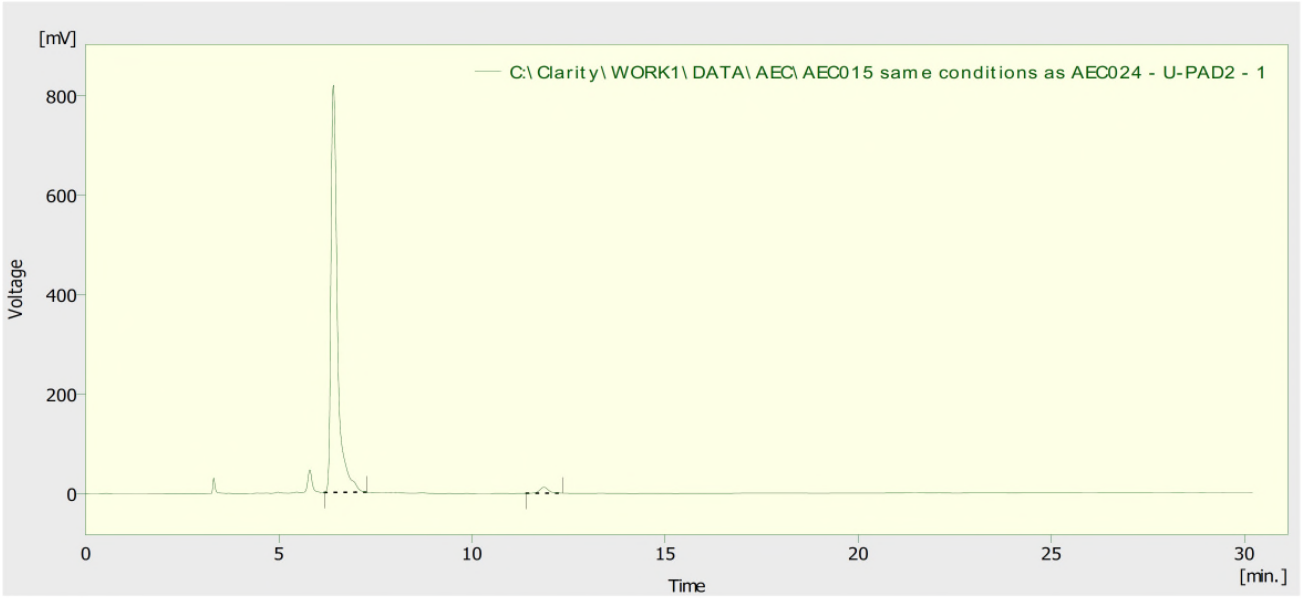
(3*S*,6*S*)-1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol 24: HPLC analysis on ChiralPak IB Column: 0.46 cm x 25cm, Mobile phase EtOAc : Hexane 3 : 2, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.



Result Table (Uncal - C:|Clarity|WORK1|DATA|AEC|AEC019 same conditions AEC024 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	11.864	187.821	12.241	1.7	4.0	0.23	
2	22.940	10653.850	292.814	98.3	96.0	0.54	
	Total	10841.671	305.055	100.0	100.0		

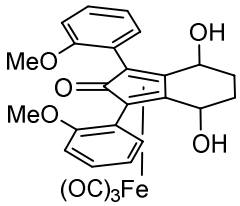
(3*S*,6*S*)-1,8-Bis(2-methoxyphenyl)octa-1,7-diyne-3,6-diol 24: HPLC analysis on ChiralPak IB Column: 0.46 cm x 25cm, Mobile phase EtOAc : Hexane 3 : 2, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.



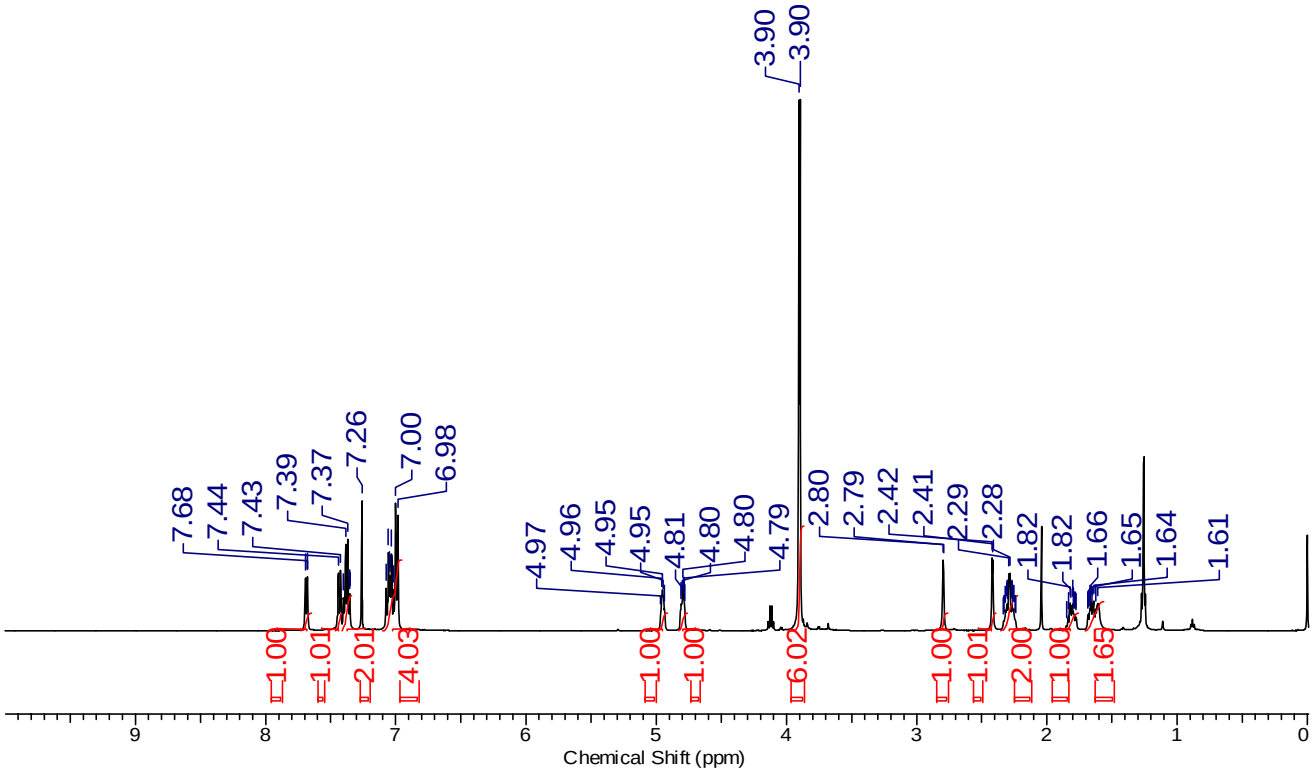
Result Table (Uncal - C:|Clarity|WORK1|DATA|AEC|AEC015 same conditions as AEC024 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.412	9654.039	819.322	98.1	98.5	0.17	
2	11.864	189.885	12.110	1.9	1.5	0.24	
	Total	9843.925	831.432	100.0	100.0		

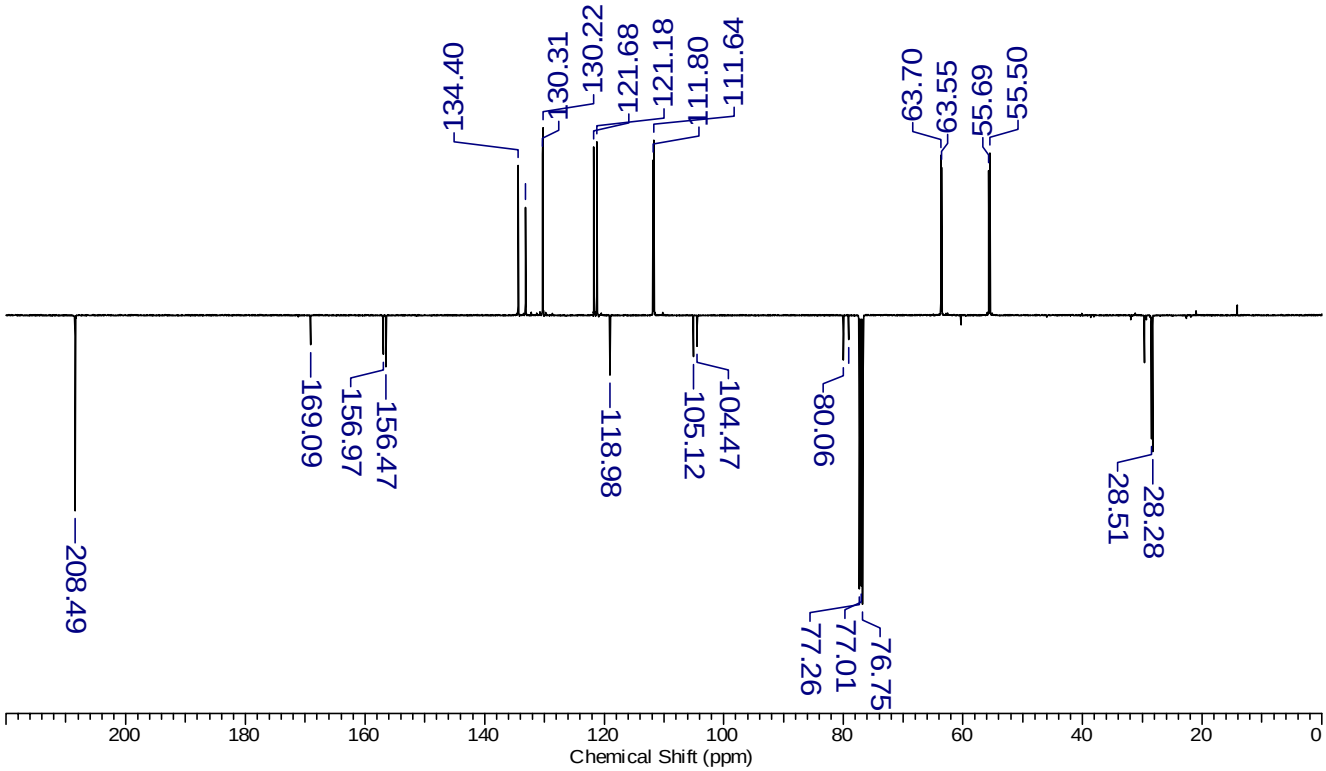
Tricarbonyl-(4*S*,7*S*)-4,7-dihydroxy-1,3-bis(2-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron 26: AEC25 (for X-ray), ADG167.



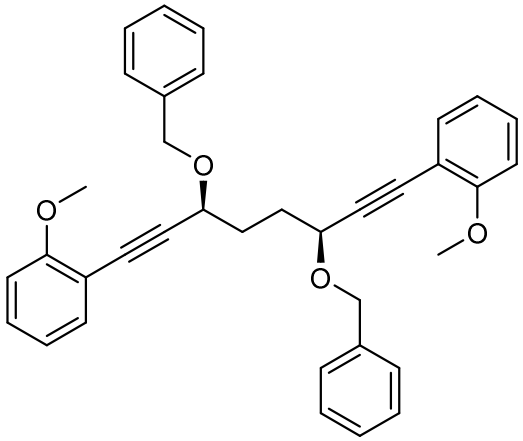
^{1}H NMR (500 MHz, $CDCl_3$)



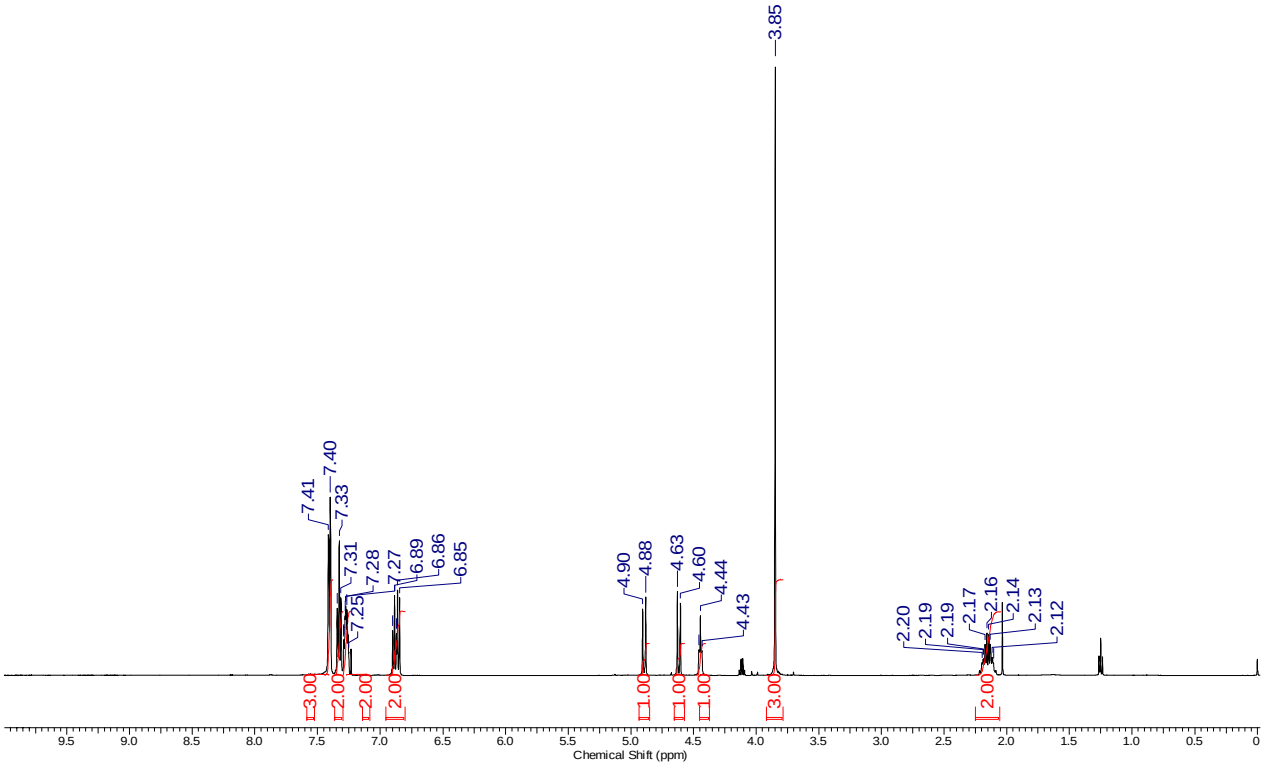
^{13}C NMR (125 MHz, $CDCl_3$)



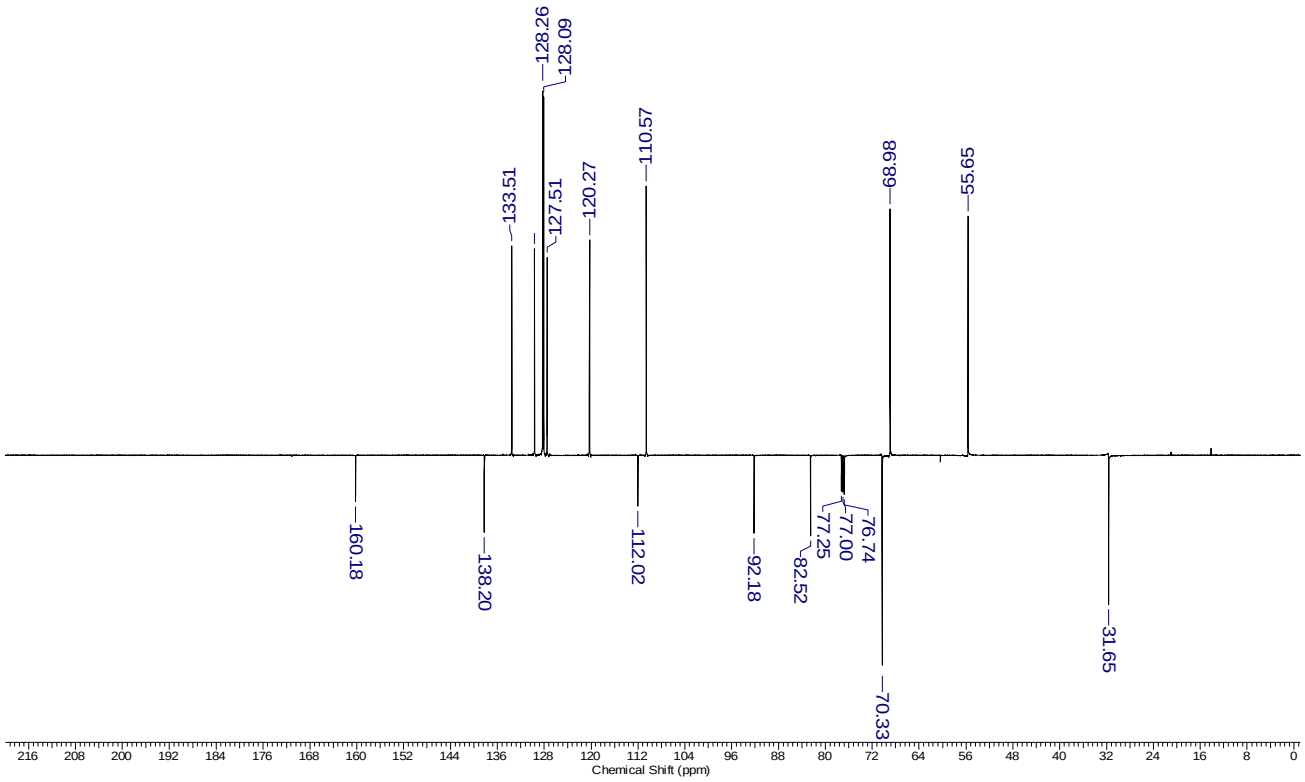
2,2'-((3*S*,6*S*)-3,6-bis(benzyloxy)octa-1,7-diyne-1,8-diyl)bis(methoxybenzene) 25: AEC26.



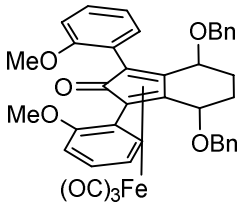
^{1}H NMR (500 MHz, $CDCl_3$)



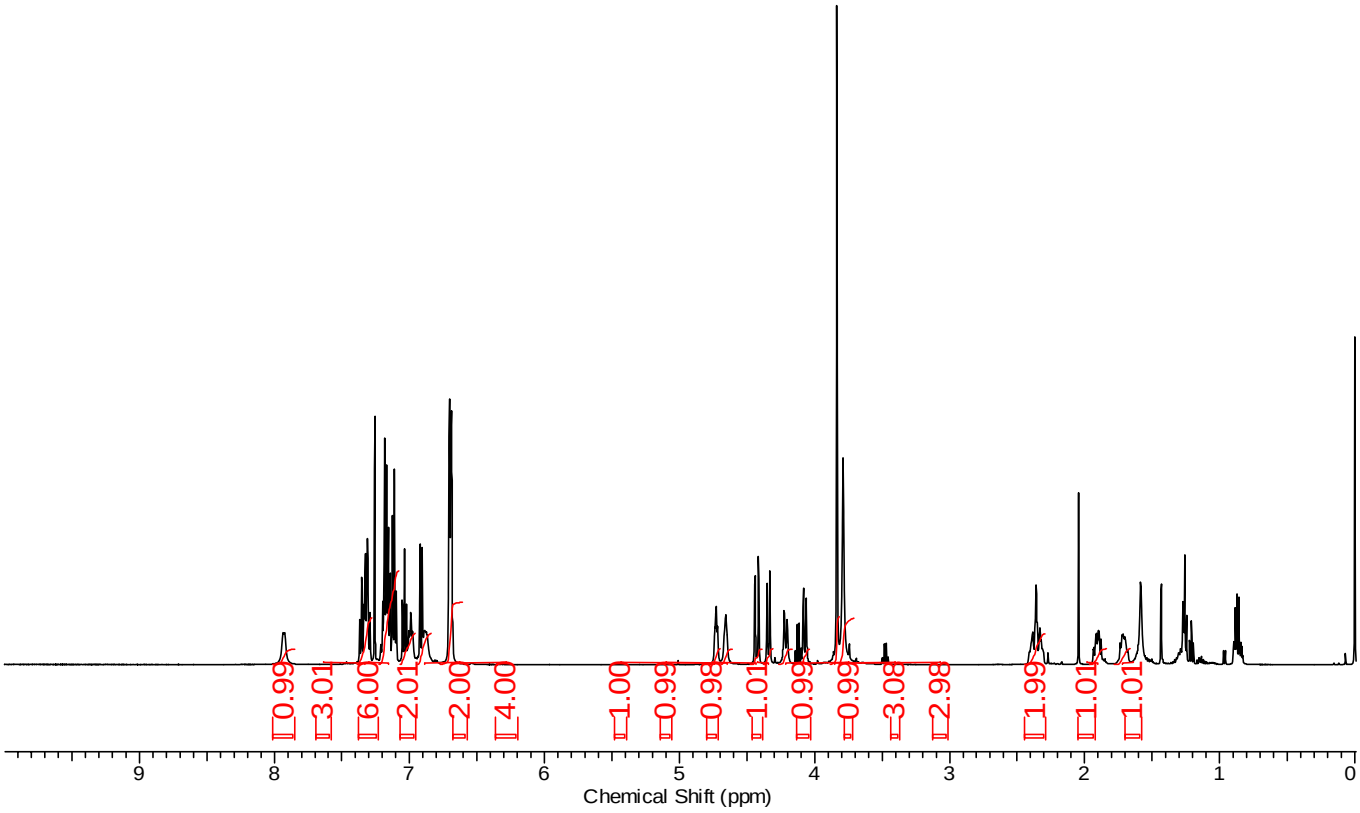
^{13}C NMR (125 MHz, $CDCl_3$)



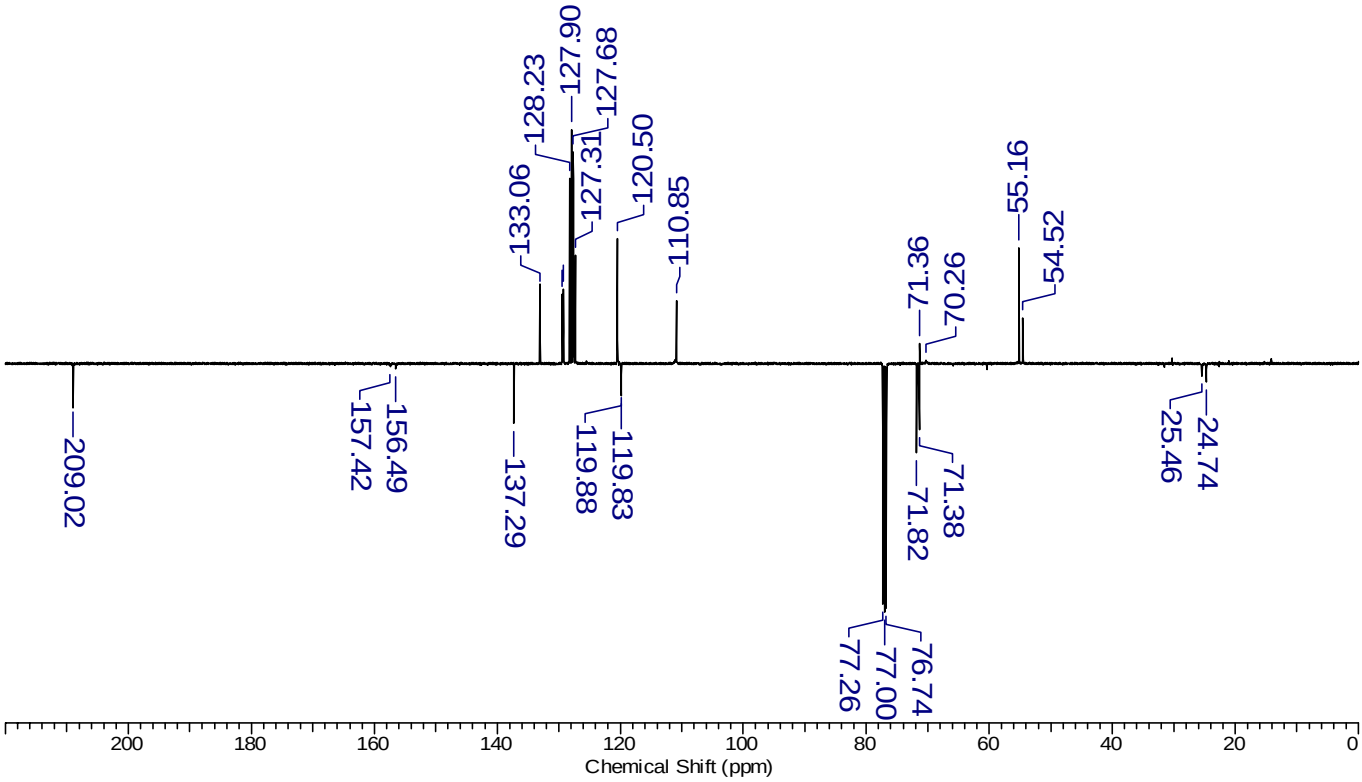
Tricarbonyl-(4*S*,7*S*)-4,7-bis(benzyloxy)-1,3-bis(2-methoxyphenyl)-4,5,6,7-tetrahydro-2-2*H*-inden-2-one iron 27: AEC33.



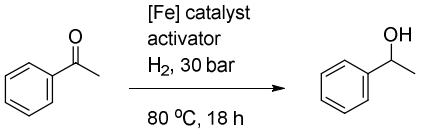
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

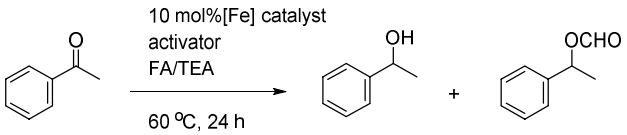


Full Table S3; Hydrogenation of acetophenone using complexes **26** and **27**.



Reaction	Catalyst (%) (acetophenone unless indicated otherwise,	Activator (%)	Solvent	Conv	ee
ADG172	ADG167 (1%) OH **26**	-------	IPA/H_2O	54.4	10(R)
ADG173	ADG167 (1%) OH **26**	K_2CO_3 (5%)	IPA/H_2O	19.5	9.2(R)
ADG174	ADG167 (1%) OH **26**	TMAO (1%)	IPA/H_2O	99.8	9.4(R)
AEC 027	AEC025 (1%) OH **26**	TMAO (1%)	IPA/H_2O 5:2	79.8	7.0 (R)
AEC 052	AEC025 (1%) OH **26** Rerun 027	TMAO (1%)	IPA/H_2O 5:2	100	7.6 R
AEC 028	AEC025 (1%) OH **26**	TMAO (1%)	IPA	89.3	3.6 (R)
AEC 029	AEC025 (1%) OH **26**	TMAO (1%)	H_2O	57.2	7.4 (R)
AEC 030	AEC025 (1%) OH **26**	TMAO (1%)	Toluene	98.1	2.2 (R)
AEC 031	AEC025 (1%) OH **26**	TMAO (1%)	Chlorobenzene	85.9	0.2 (R)
AEC 032	AEC025 (1%) OH **26**	TMAO (1%)	THF	98.6	9.4 (R)
AEC 034	AEC025 (1%) OH **26** 60 °C	TMAO (1%)	IPA/H_2O 5:2	87.5	9.0 (R)
AEC 035	AEC025 (1%) OH **26** 60 °C	TMAO (1%)	THF	61.4	13.8 (R)
AEC 036	AEC025 (1%) OH **26** 40 °C	TMAO (1%)	IPA/H_2O 5:2	21.8	12.0 R)
AEC 037	AEC025 (1%) OH **26** 40 °C	TMAO (1%)	THF	19.2	17.8 (R)
AEC 050	AEC025 (1%) OH **26** 2-OMe	TMAO (1%)	IPA/H_2O 5:2	>99	8.6 R
AEC 039	AEC025 (1%) OH **26** 4-OMe	TMAO (1%)	IPA/H_2O 5:2	91.6	6.0 S
AEC 040	AEC025 (1%) OH **26** 2-Cl	TMAO (1%)	IPA/H_2O 5:2	56.8	3.6 R
AEC 041	AEC025 (1%) OH **26** 4-Cl	TMAO (1%)	IPA/H_2O 5:2	96.6	10.2 S
AEC 044	AEC025 (1%) OH **26** 2-OMe	TMAO (1%)	THF	99.8	3.6 R
AEC 045	AEC025 (1%) OH **26** 4-OMe	TMAO (1%)	THF	80.9	5.8 R
AEC 046	AEC025 (1%) OH **26** 2-Cl	TMAO (1%)	THF	45.9	4.0 R
AEC 047	AEC025 (1%) OH **26** 4-Cl	TMAO (1%)	THF	99	9.4 S
AEC 052	AEC025 (1%) OH **26**	TMAO (1%)	IPA/H_2O 5:2	100	7.6 R
AEC 048	AEC033 (1%) OBn **27**	TMAO (1%)	IPA/H_2O 5:2	77.8	21.0 R
AEC 049	AEC033 (1%) OBn **27**	TMAO (1%)	THF	100	16.0 R

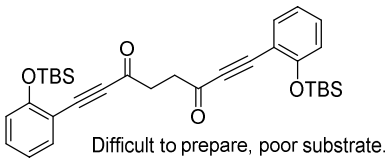
Full Table S4; Asymmetric transfer hydrogenation of acetophenone using complexes **26** and **27**.



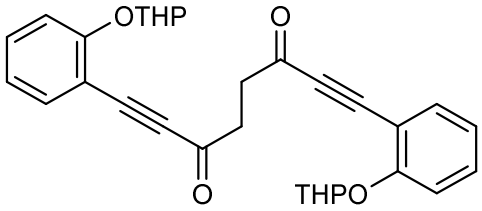
Reaction	Catalyst (%)	Activator (%)	Conv	Alcohol (ee)	Formate (ee)
ADG178	ADG167 (10%) OH **26**	---------	54.9	46.8 (28.4 *R*)	8.2 (25 *R*)
ADG179	ADG167 (10%) OH **26**	TMAO (10%)	99.6	87.2 (30.2 *R*)	12.3 (28 *R*)
AEC051	ADG025 (10%) OH **26**	TMAO (10%)	97.6	81.9 (27.4 *R*)	15.7 (n/a)
AEC054*	ADG025 (10%) OH **26** 30 °C 24h	TMAO (10%)	25.7	25.2 (35.2 *R*)	0.5 (n/a)
AEC054*	ADG025 (10%) OH **26** 30 °C 48h	TMAO (10%)	51.5	49.9 (34.4 *R*)	1.6 (n/a)
AEC054*	ADG025 (10%) OH **26** 30 °C 72h	TMAO (10%)	87.8	81.9 (34.6 *R*)	5.9 (n/a)
AEC053	AEC033 (10%)OBn **27**	TMAO (10%)	93.3	89.4 (28.0 *R*)	10.6 (29.3 *R*)

* 054 was followed over time and done at lower temp. of 30 °C.

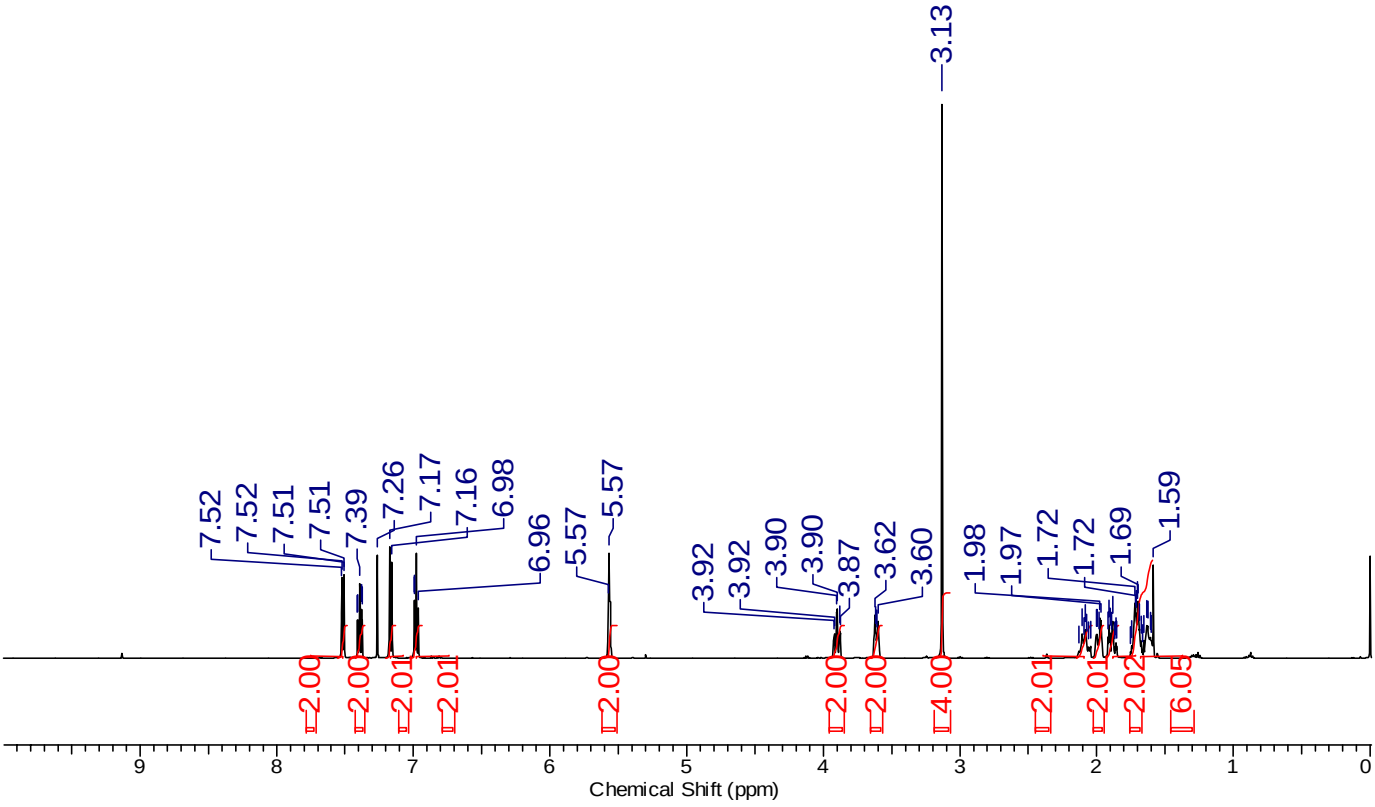
**Footnote: We also attempted to prepare bis-TBS dialkyne below via the diphenol following removal of the THP groups in 79% yield using PPTS. The reaction of TBSCl with this diphenol unfortunately gave only 58% bis TBS compound along with 28% mono protection. Subsequent reduction of this mixture using tethered catalyst gave only 4-5% of reduction products, indicating that the TBSs might have been lost



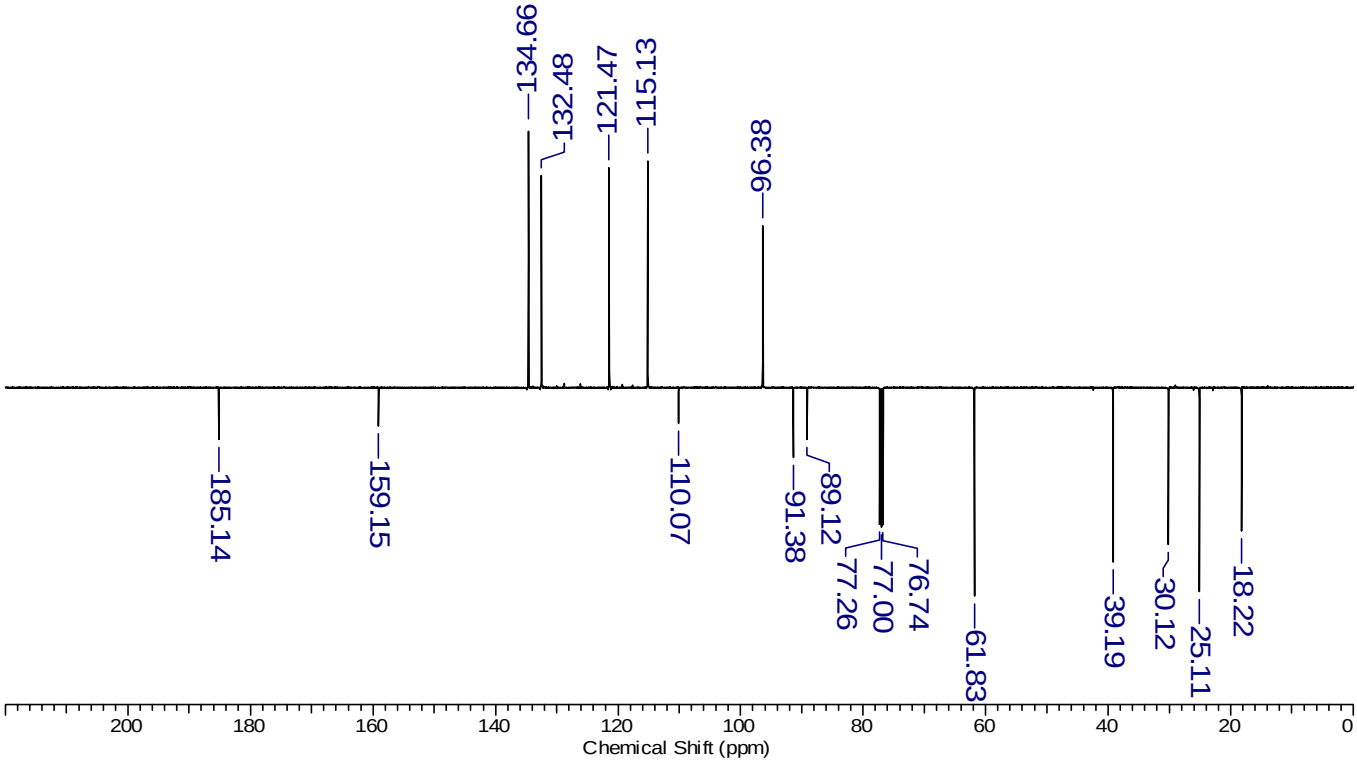
1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-dione 28: (ADG327).



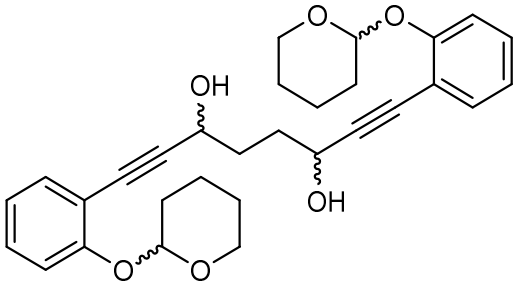
^{1}H NMR (500 MHz, $CDCl_3$)



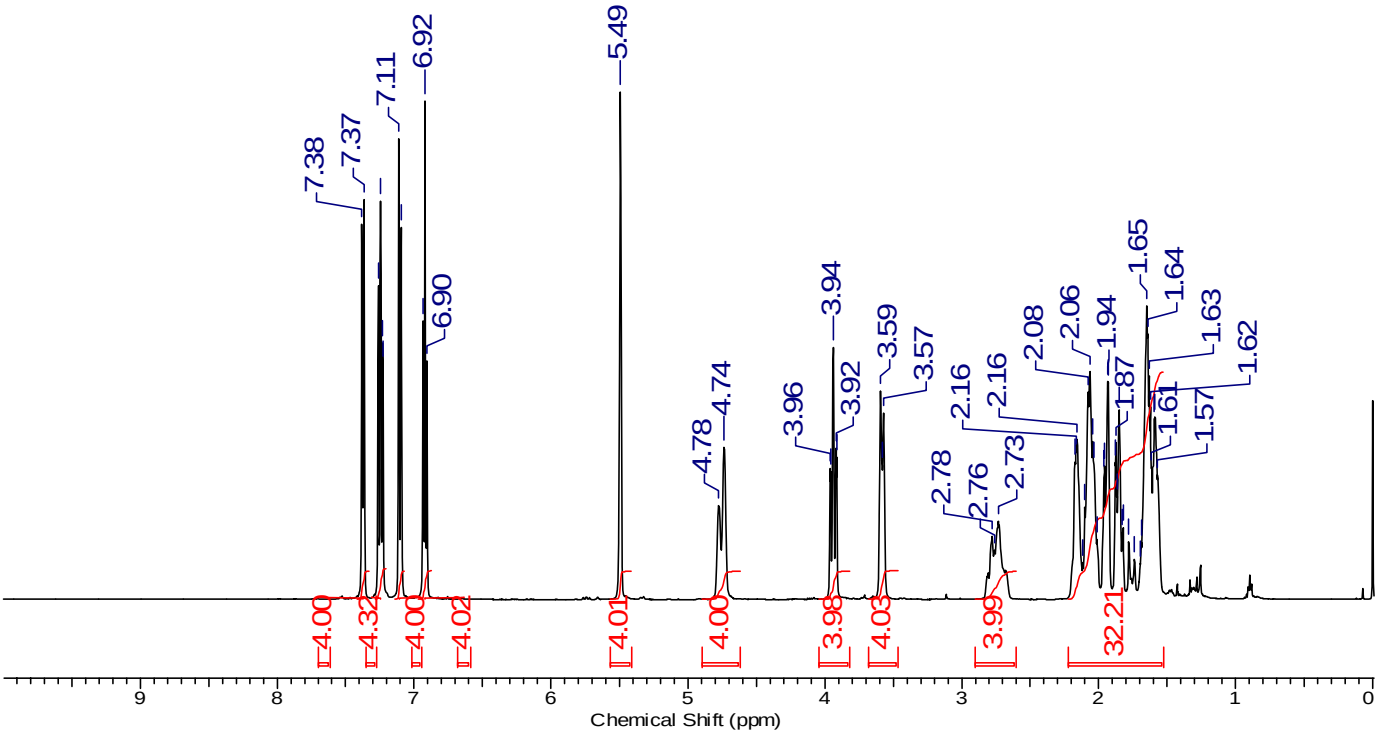
^{13}C NMR (125 MHz, $CDCl_3$)



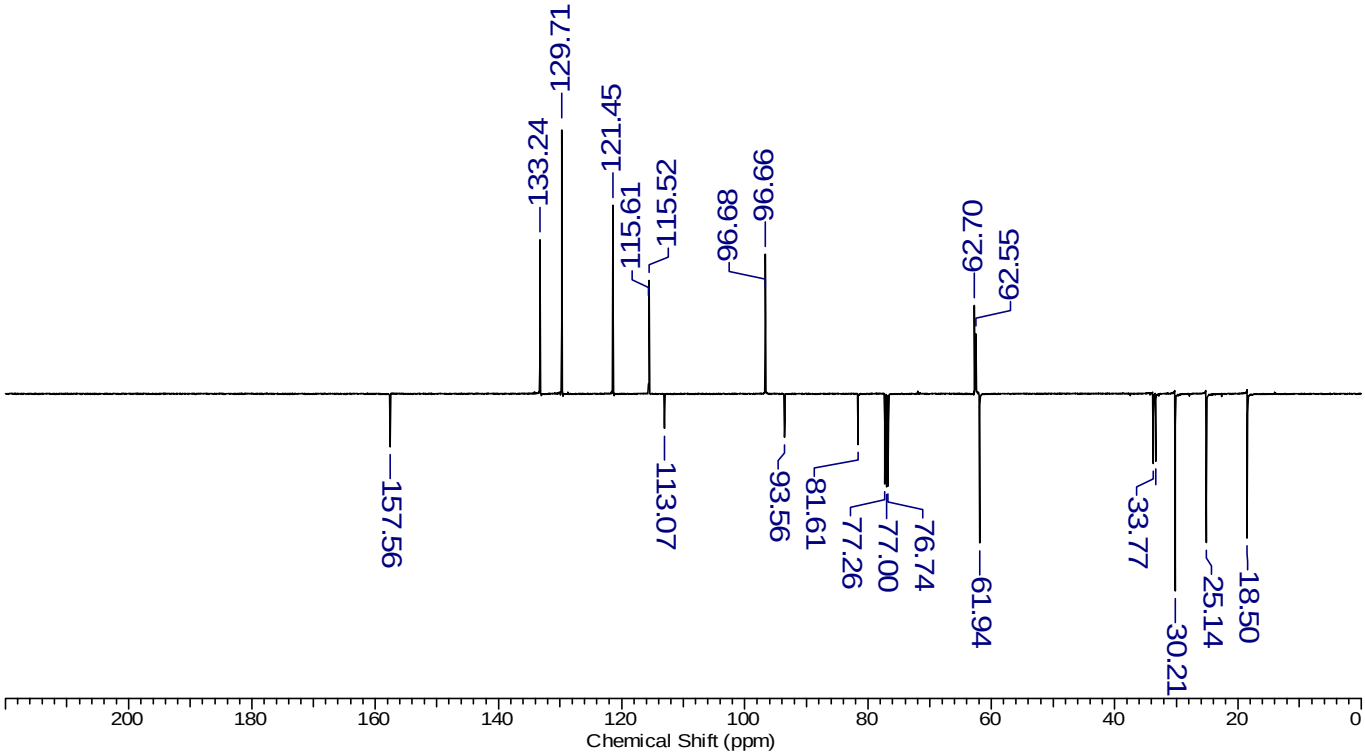
1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol 30: (ADG387).



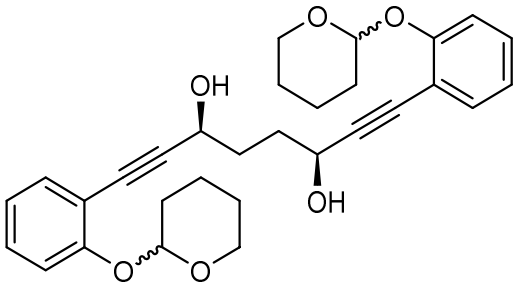
^{1}H NMR (500 MHz, $CDCl_3$)



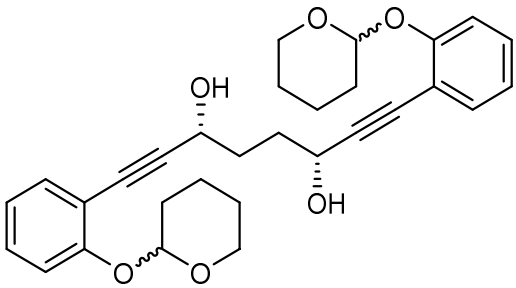
^{13}C NMR (125 MHz, $CDCl_3$)



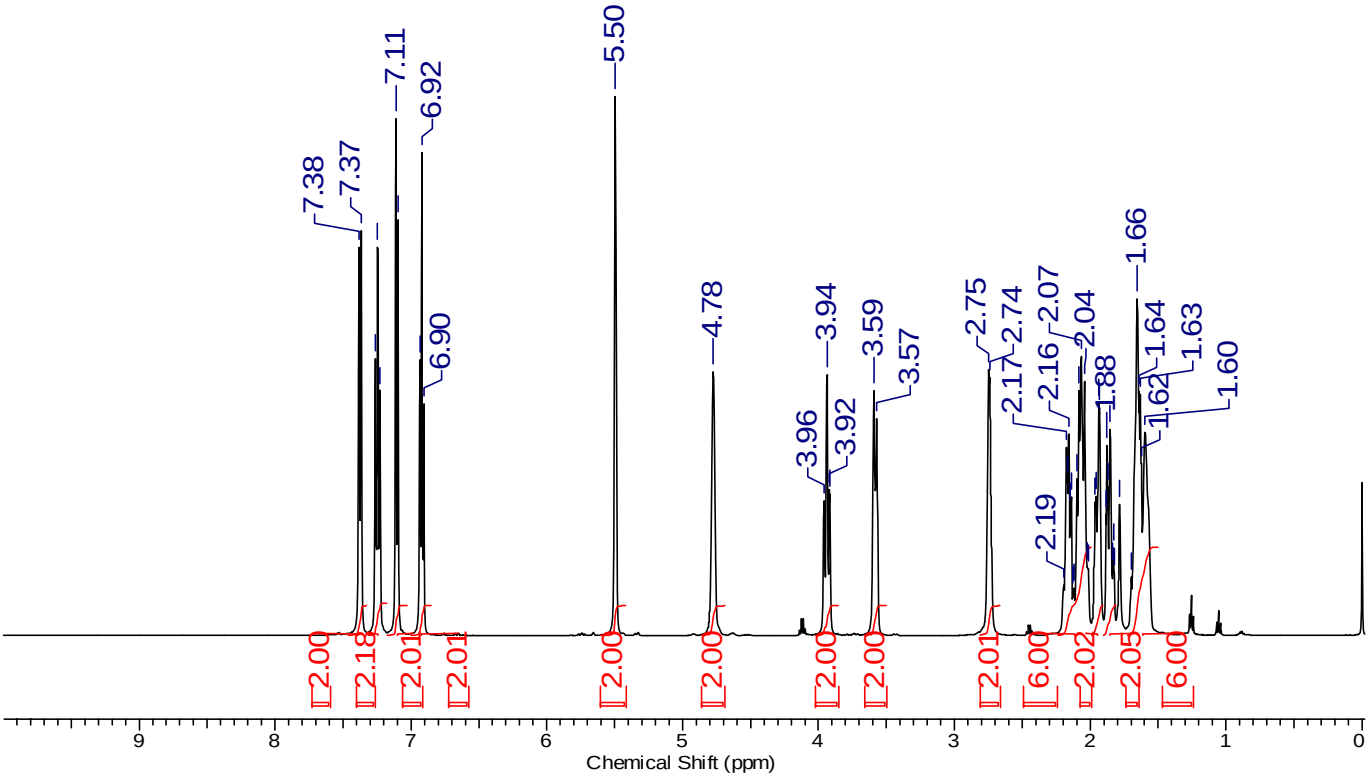
(3*S*,6*S*)-1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol 30 30: (ADG360).



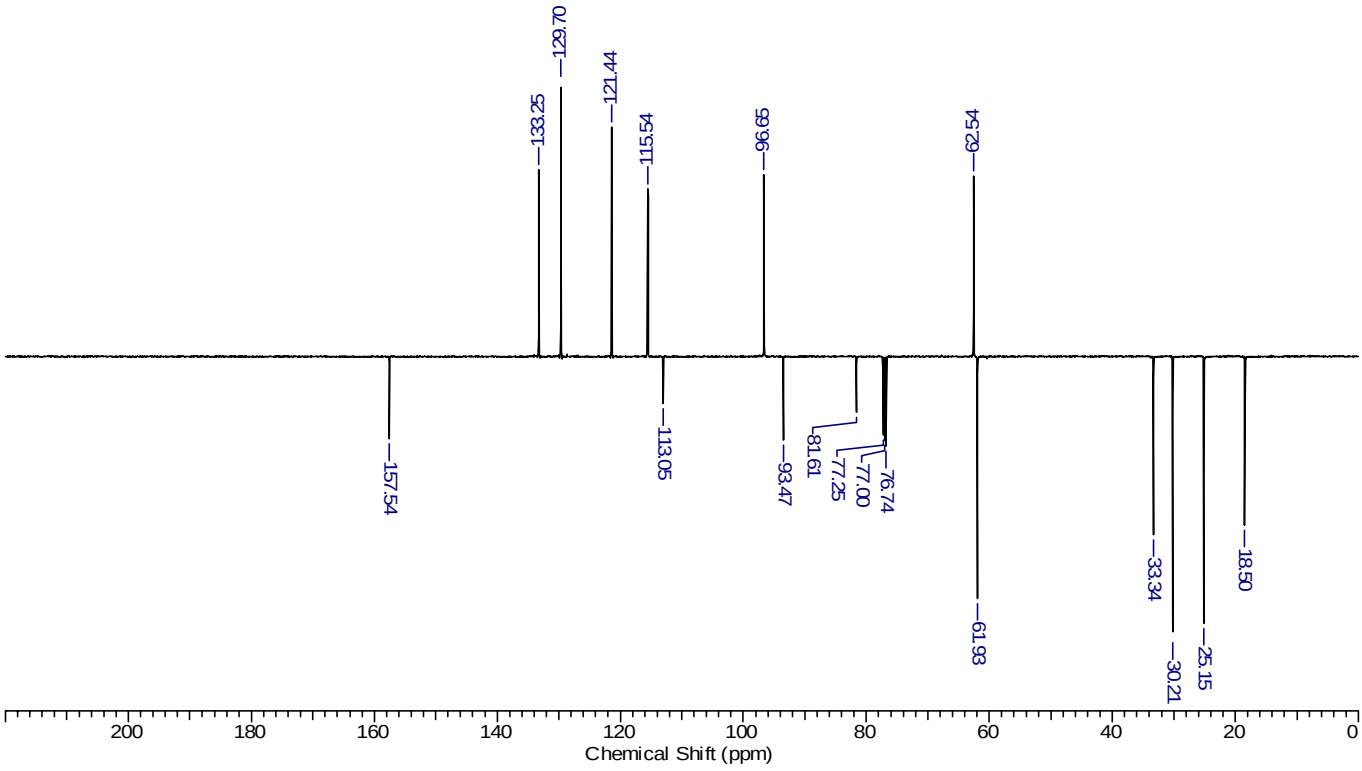
(3*R*,6*R*)-1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol 30: (ADG307).



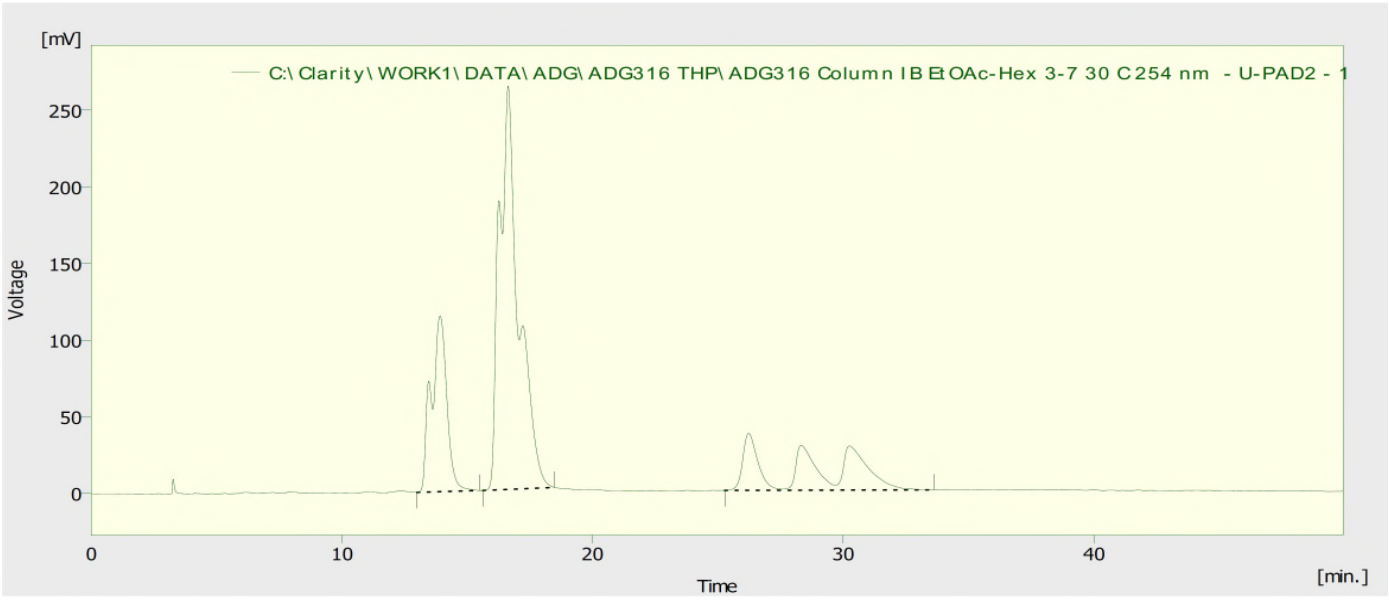
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



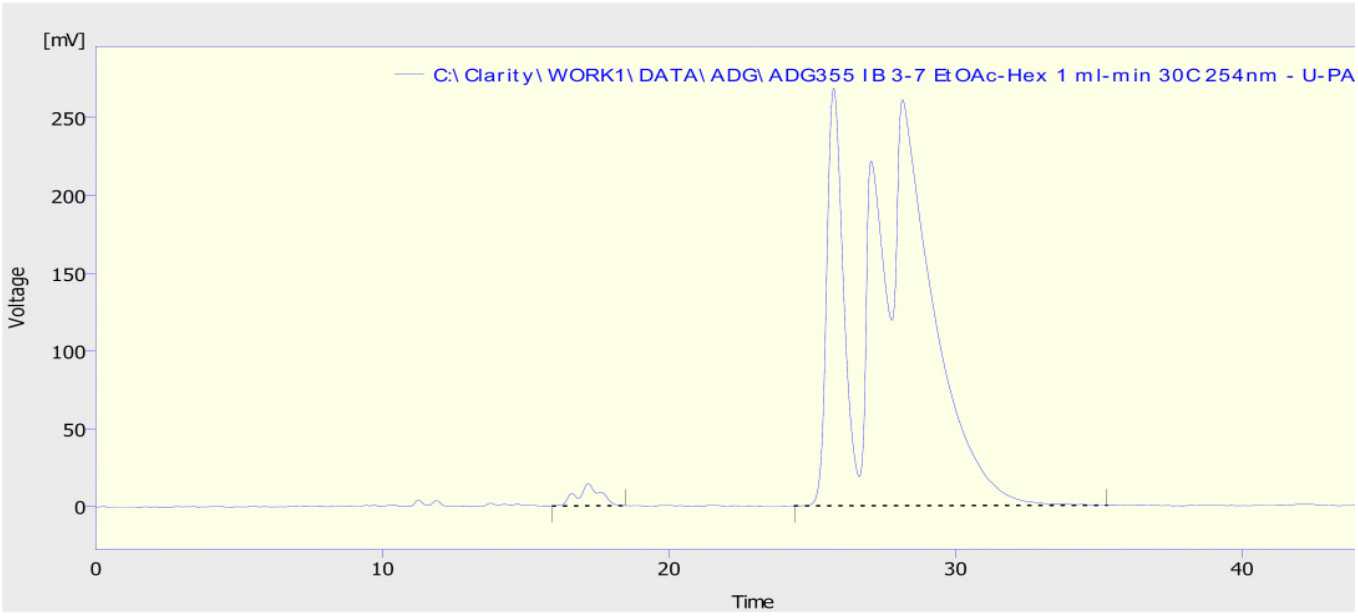
1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol 30 (racemic and meso)**:** HPLC analysis with a ChiralPak IB Column: 0.46 cm x 25cm, Mobile phase EtOAc : Hexane 7 : 3, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.



Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG316 THP\ADG316 Column IB EtOAc-Hex 3-7 30 C 254 nm - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	13.912	4963.239	114.567	20.4	27.6	0.54	
2	16.628	14154.540	263.211	58.3	63.4	0.78	
3	26.224	5160.932	37.322	21.3	9.0	0.62	
	Total	24278.711	415.100	100.0	100.0		

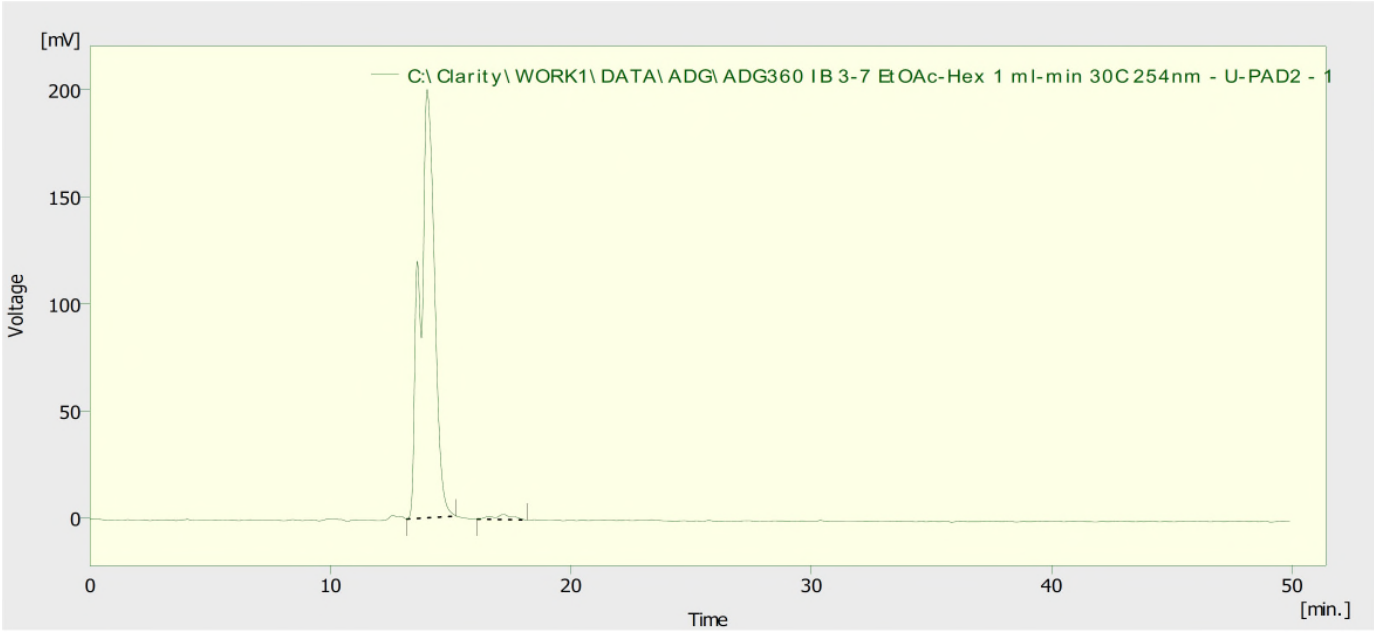
(3*S*,6*S*)-1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol 30: HPLC analysis with a ChiralPak IB Column: 0.46 cm x 25cm, Mobile phase EtOAc : Hexane 7 : 3, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.



Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG355 IB 3-7 EtOAc-Hex 1 ml-min 30C 254nm - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	17.180	794.447	14.318	1.7	5.1	0.80	
2	25.748	45089.665	268.464	98.3	94.9	0.62	
	Total	45884.112	282.782	100.0	100.0		

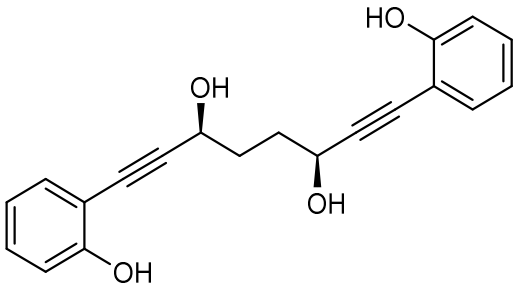
(3*R*,6*R*)-1,8-Bis(2-((tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)octa-1,7-diyne-3,6-diol 30: HPLC analysis with a ChiralPak IB Column: 0.46 cm x 25cm, Mobile phase EtOAc : Hexane 7 : 3, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.



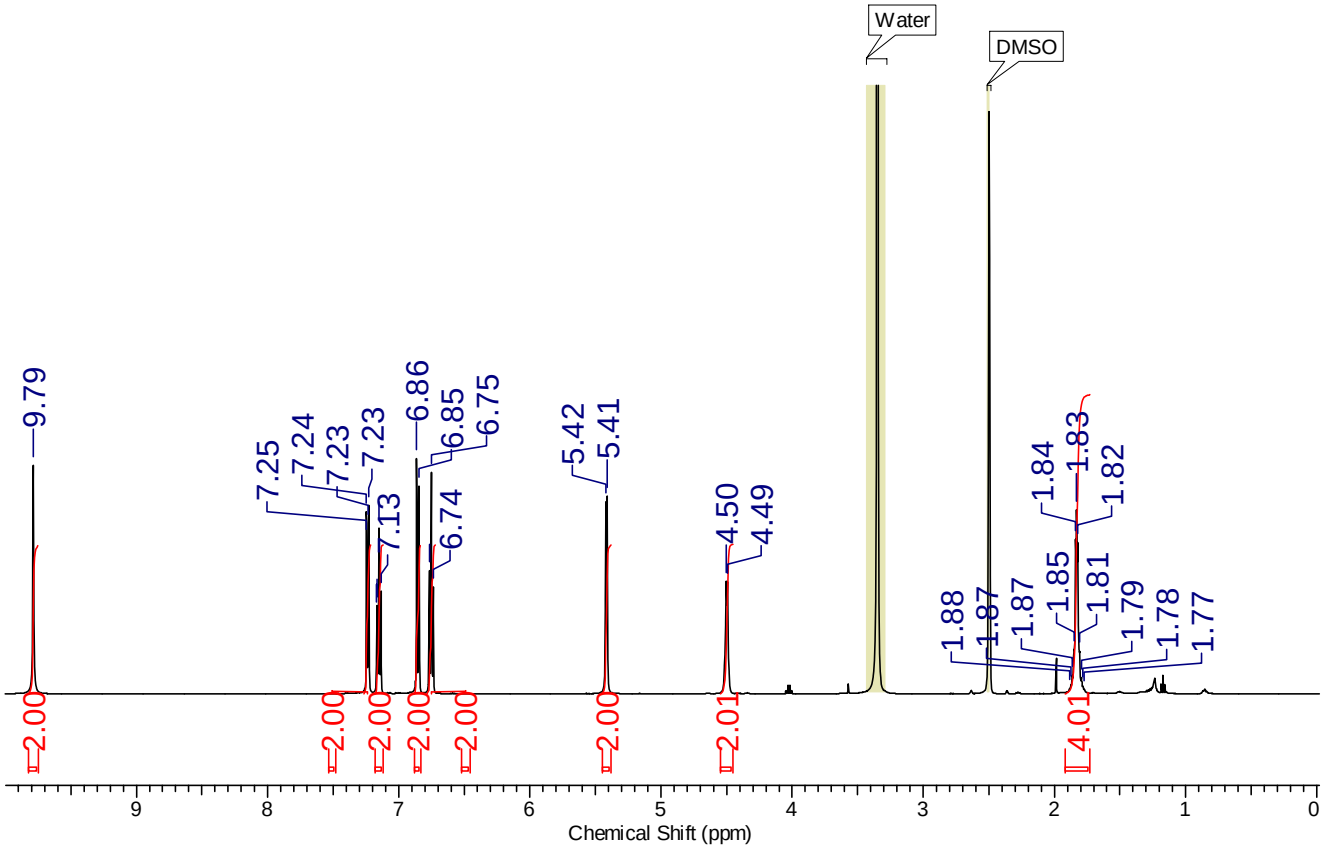
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|ADG\|ADG360 IB 3-7 EtOAc-Hex 1 ml-min 30C 254nm - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	14.016	8385.017	200.004	98.4	98.8	0.52	
2	17.196	134.406	2.410	1.6	1.2	0.76	
	Total	8519.423	202.415	100.0	100.0		

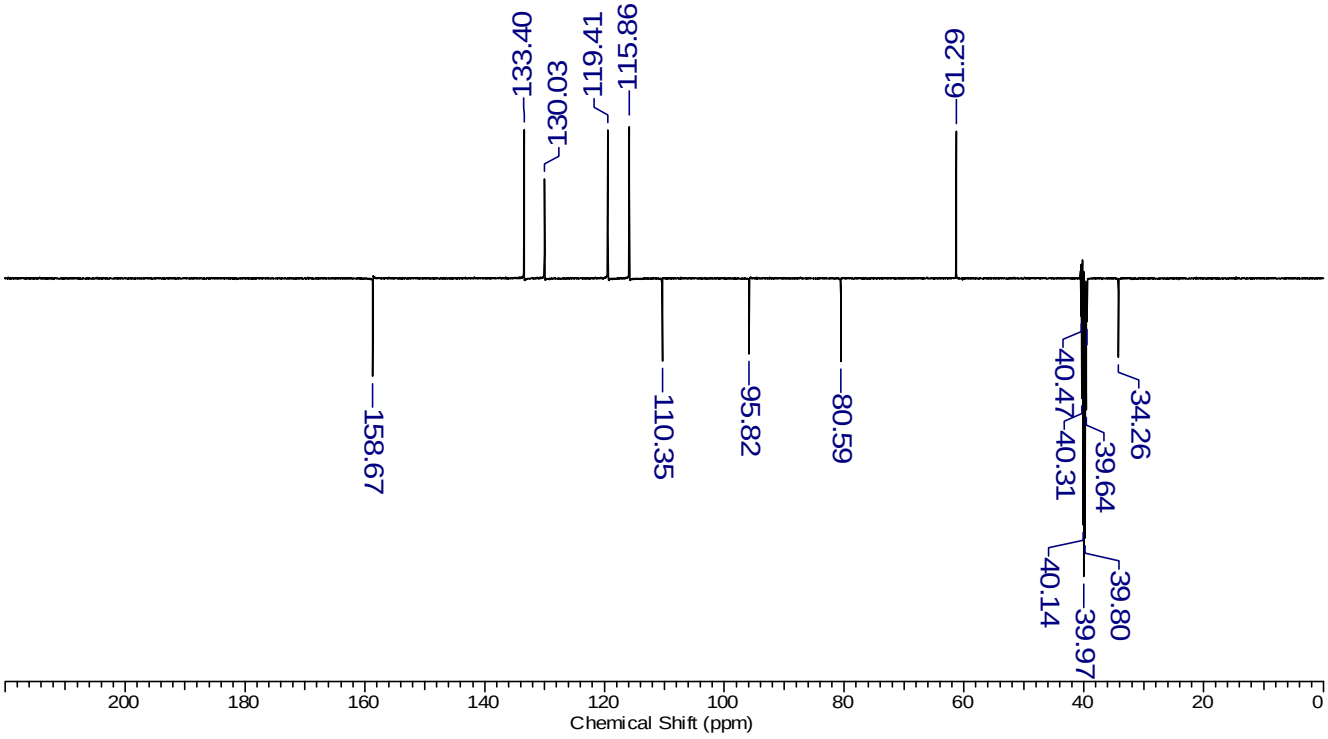
(3*S*,6*S*)-1,8-bis(2-hydroxyphenyl)octa-1,7-diyne-3,6-diol 31: ADG404.



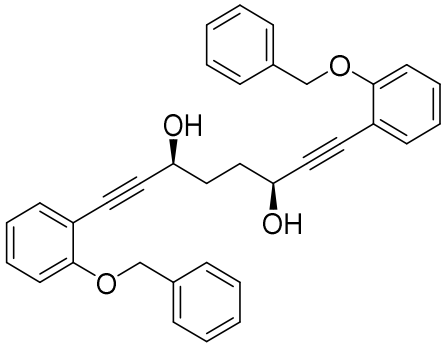
^{1}H NMR (500 MHz, $CDCl_3$)



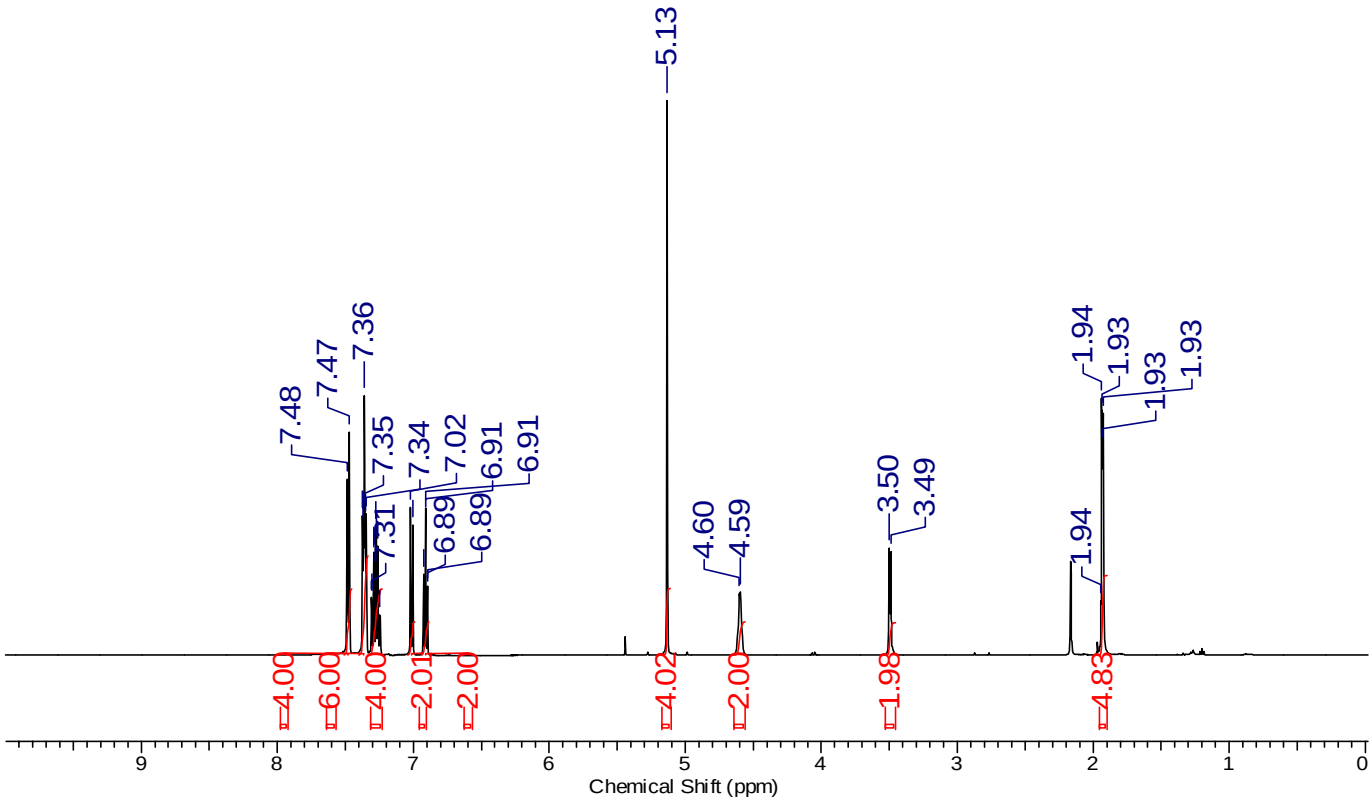
^{13}C NMR (125 MHz, $CDCl_3$)



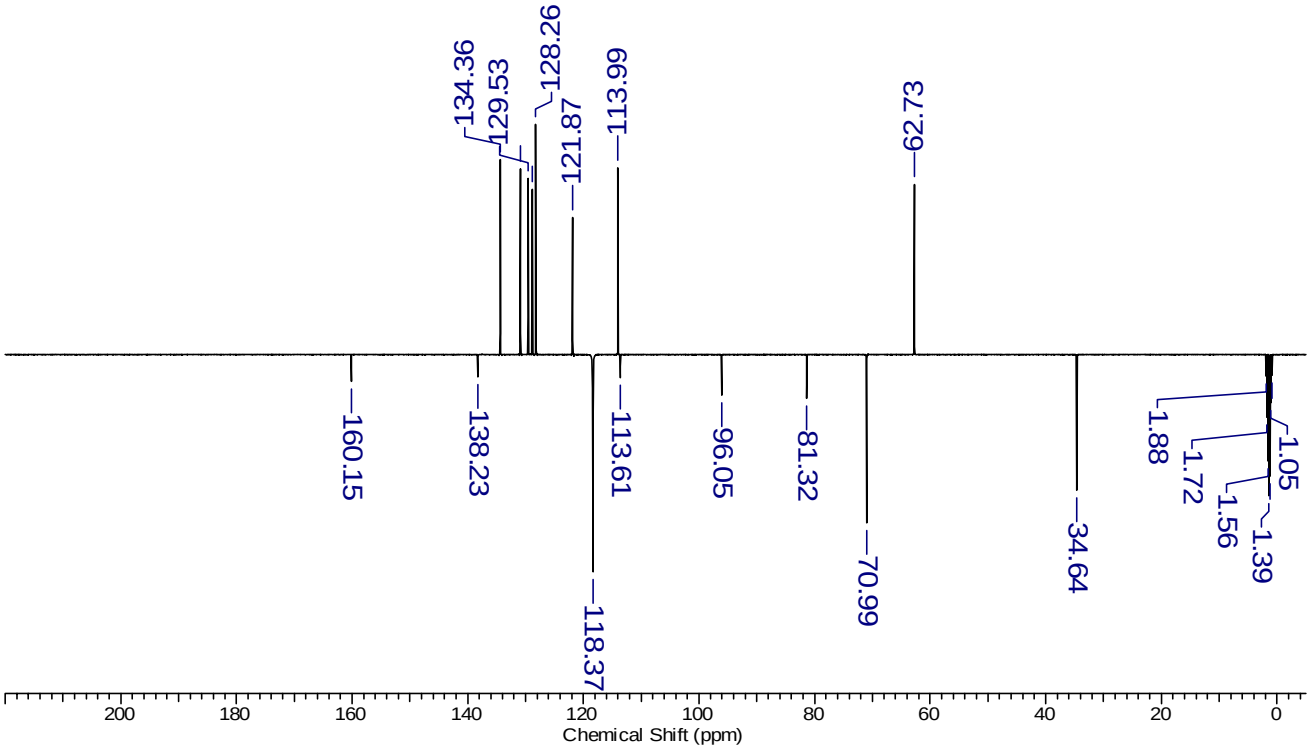
(3*S*,6*S*)-1,8-Bis(2-(benzyloxy)phenyl)octa-1,7-diyne-3,6-diol 32: ADG356.



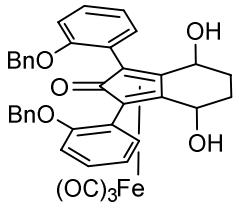
^{1}H NMR (500 MHz, $CDCl_3$)



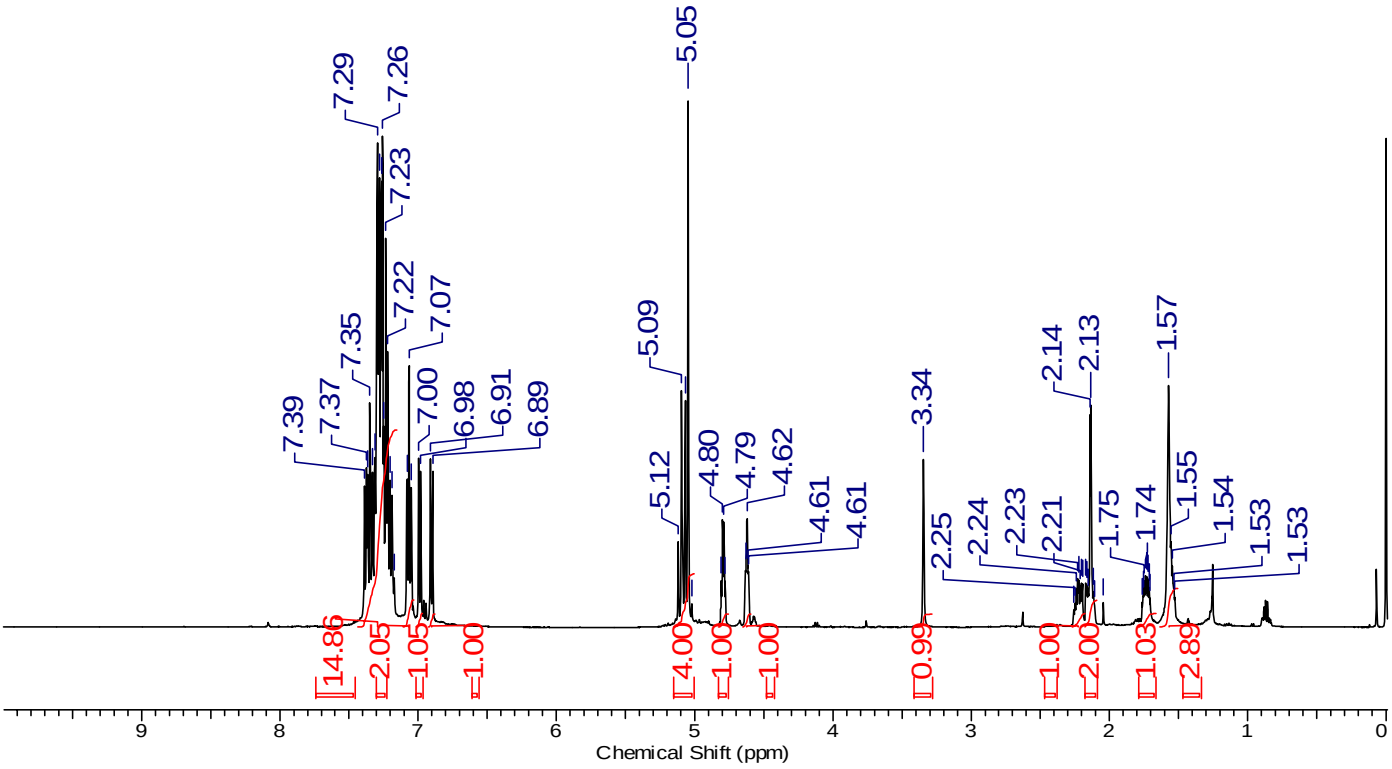
^{13}C NMR (125 MHz, $CDCl_3$)



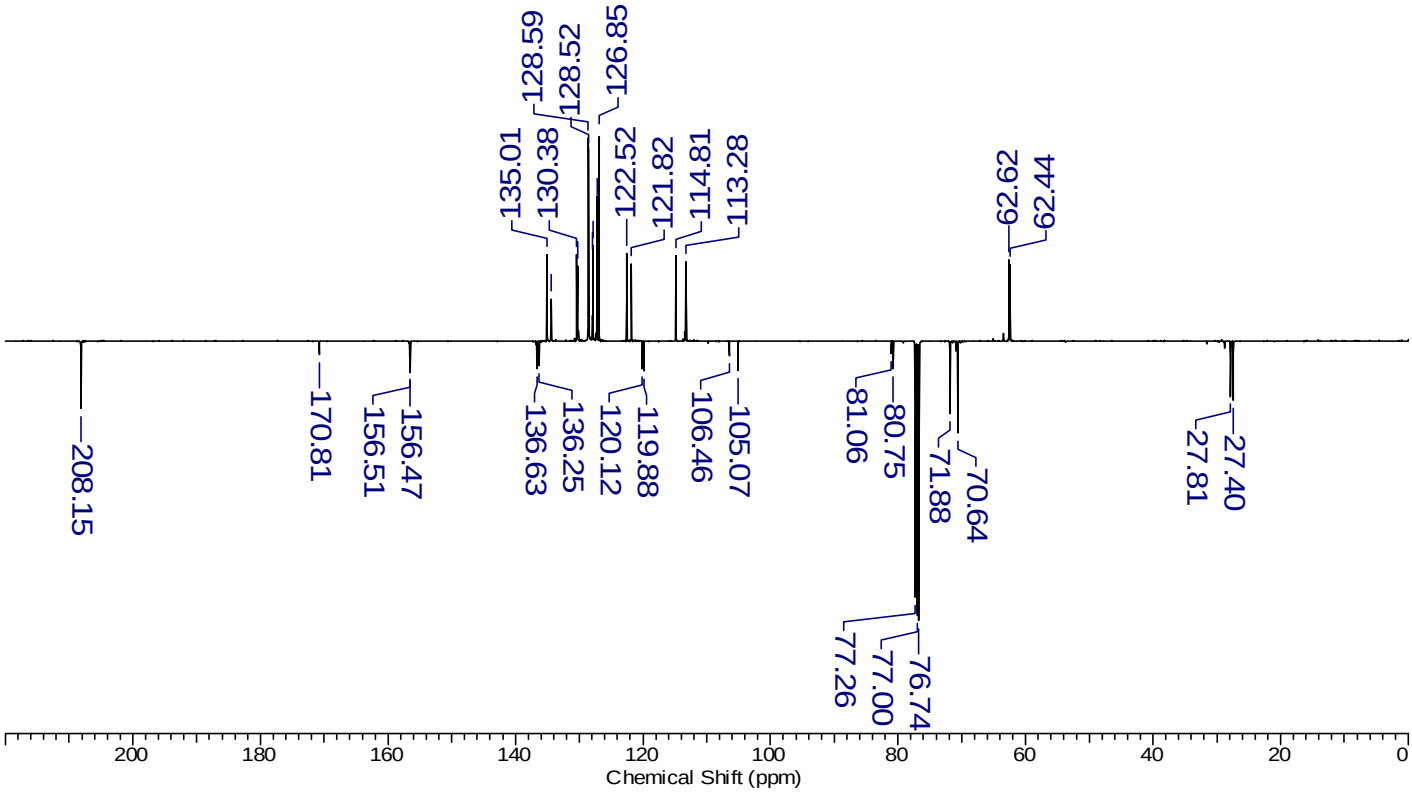
Tricarbonyl-(4*S*,7S)-1,3-bis(2-(benzyloxy)phenyl)-4,7-dihydroxy-4,5,6,7-tetrahydro-2*H*-inden-2-one iron 34: ADG535.



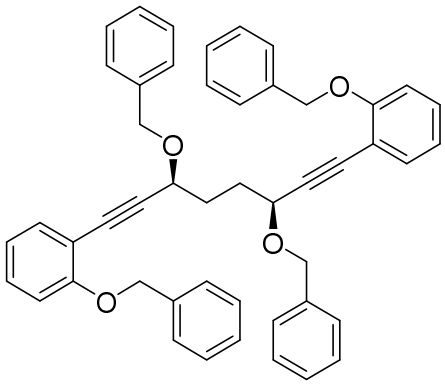
^{1}H NMR (500 MHz, $CDCl_3$)



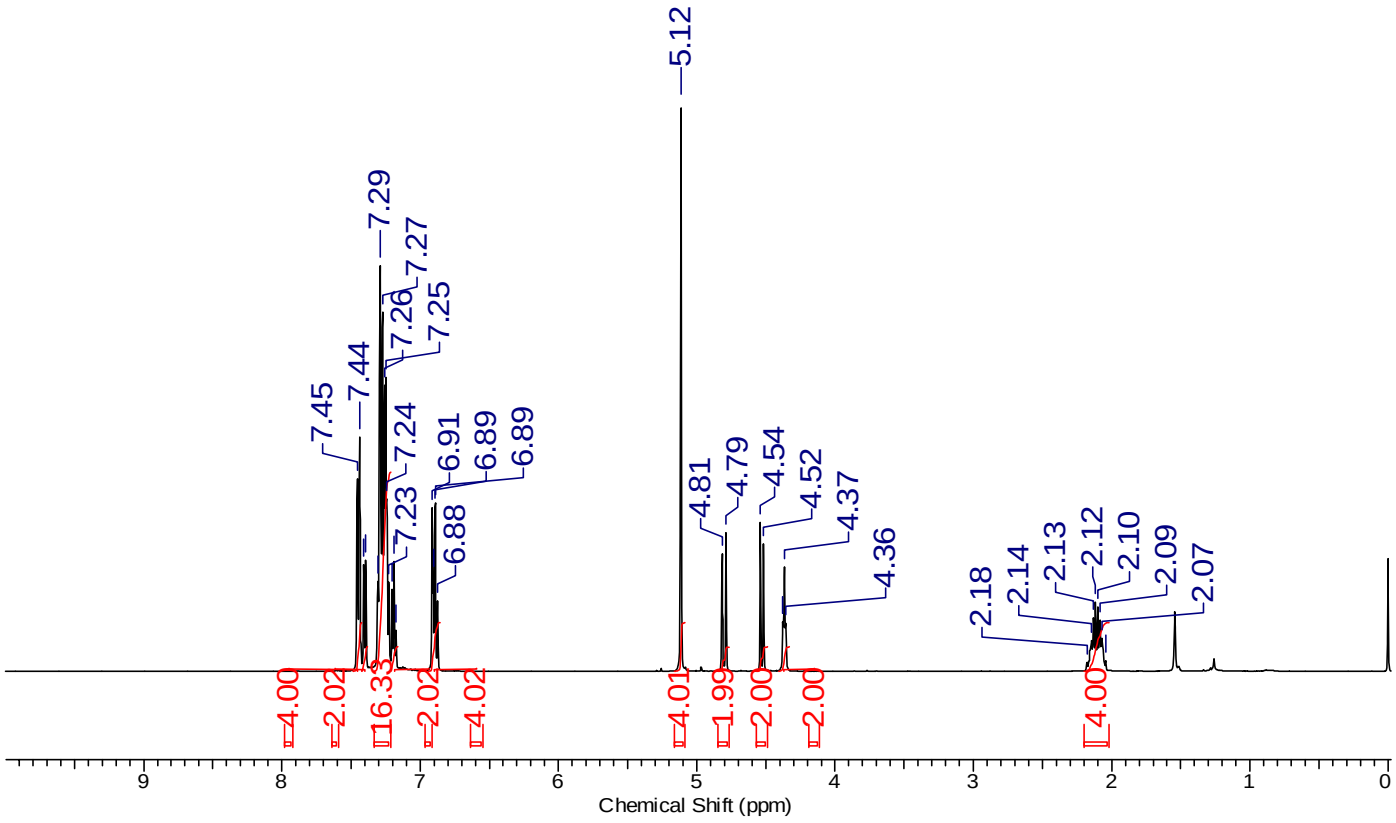
^{13}C NMR (125 MHz, $CDCl_3$)


128.59
128.52
126.85
135.01
130.38
122.52
121.82
114.81
113.28
62.62
62.44
208.15
170.81
156.51
156.47
136.63
136.25
120.12
119.88
106.46
105.07
81.06
80.75
71.88
70.64
27.81
27.40
77.26
77.00
76.74
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

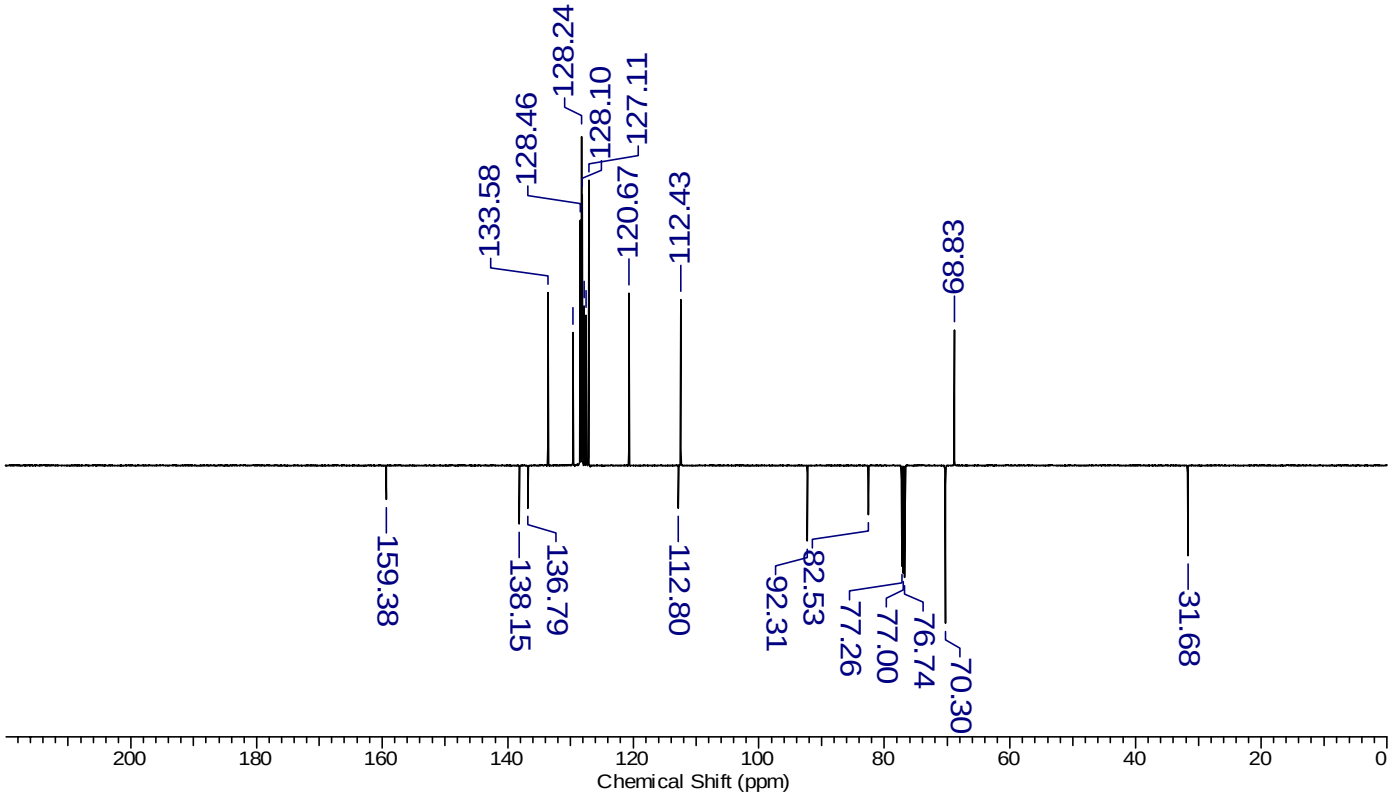
2,2'-((3*S*,6*S*)-3,6-Bis(benzyloxy)octa-1,7-diyne-1,8-diyl)bis((benzyloxy)benzene) 33: (ADG348)



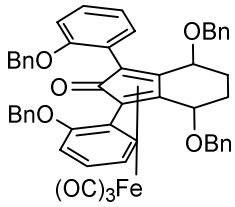
^{1}H NMR (500 MHz, $CDCl_3$)



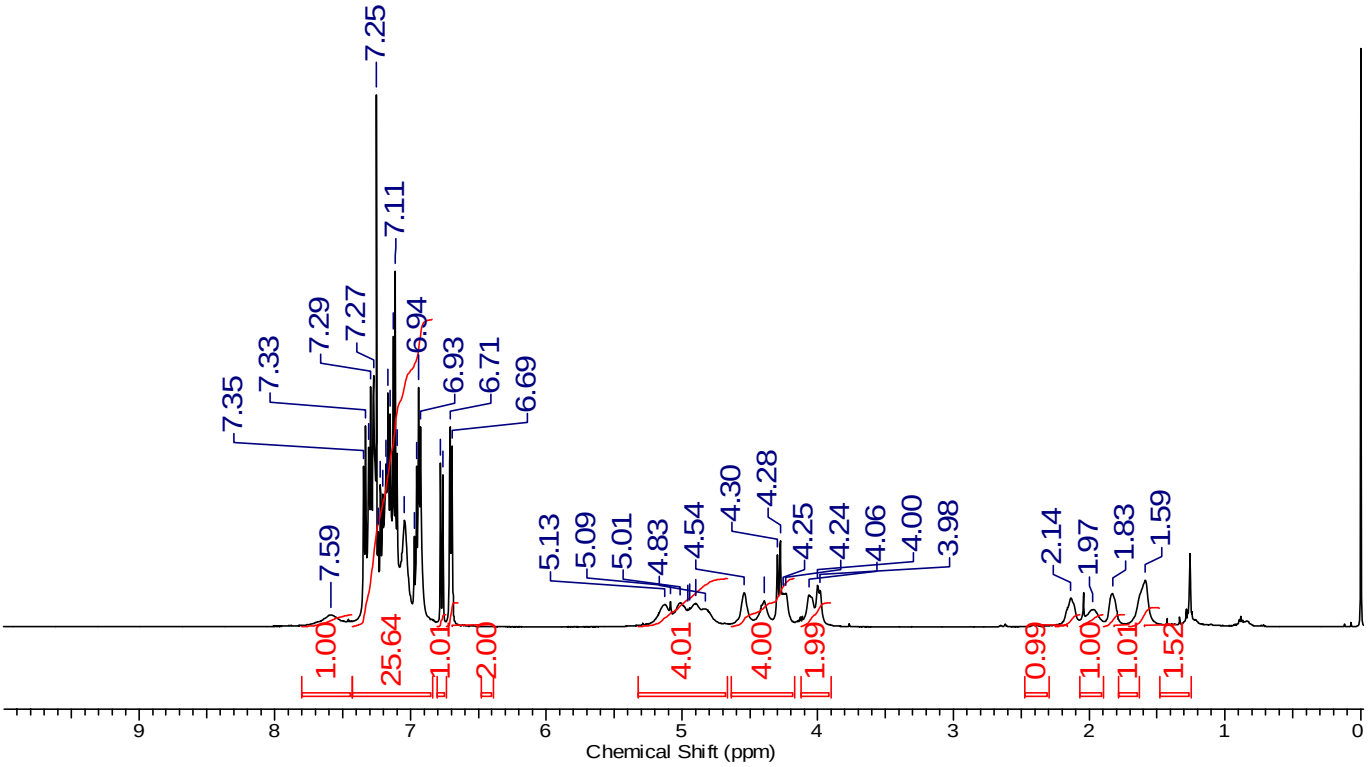
^{13}C NMR (125 MHz, $CDCl_3$)



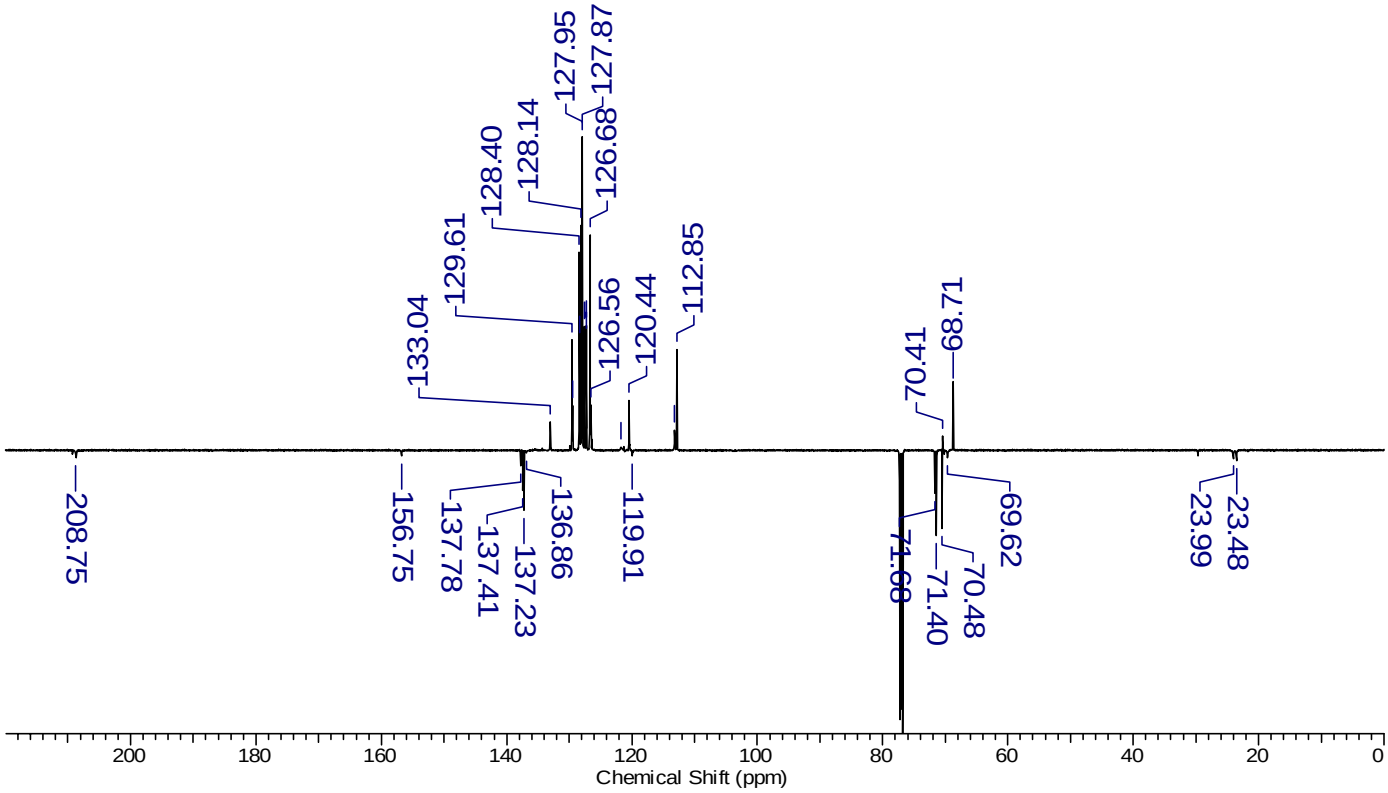
Tricarbonyl-(4*S*,7S)-4,7-bis(benzyloxy)-1,3-bis(2-(benzyloxy)phenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron 35: ADG358



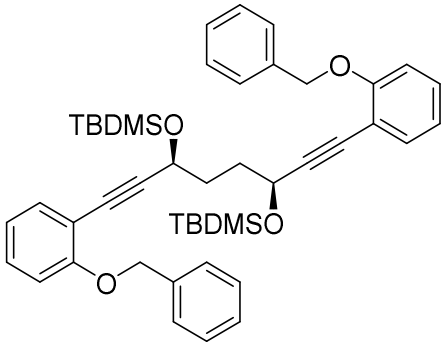
^{1}H NMR (500 MHz, $CDCl_3$)



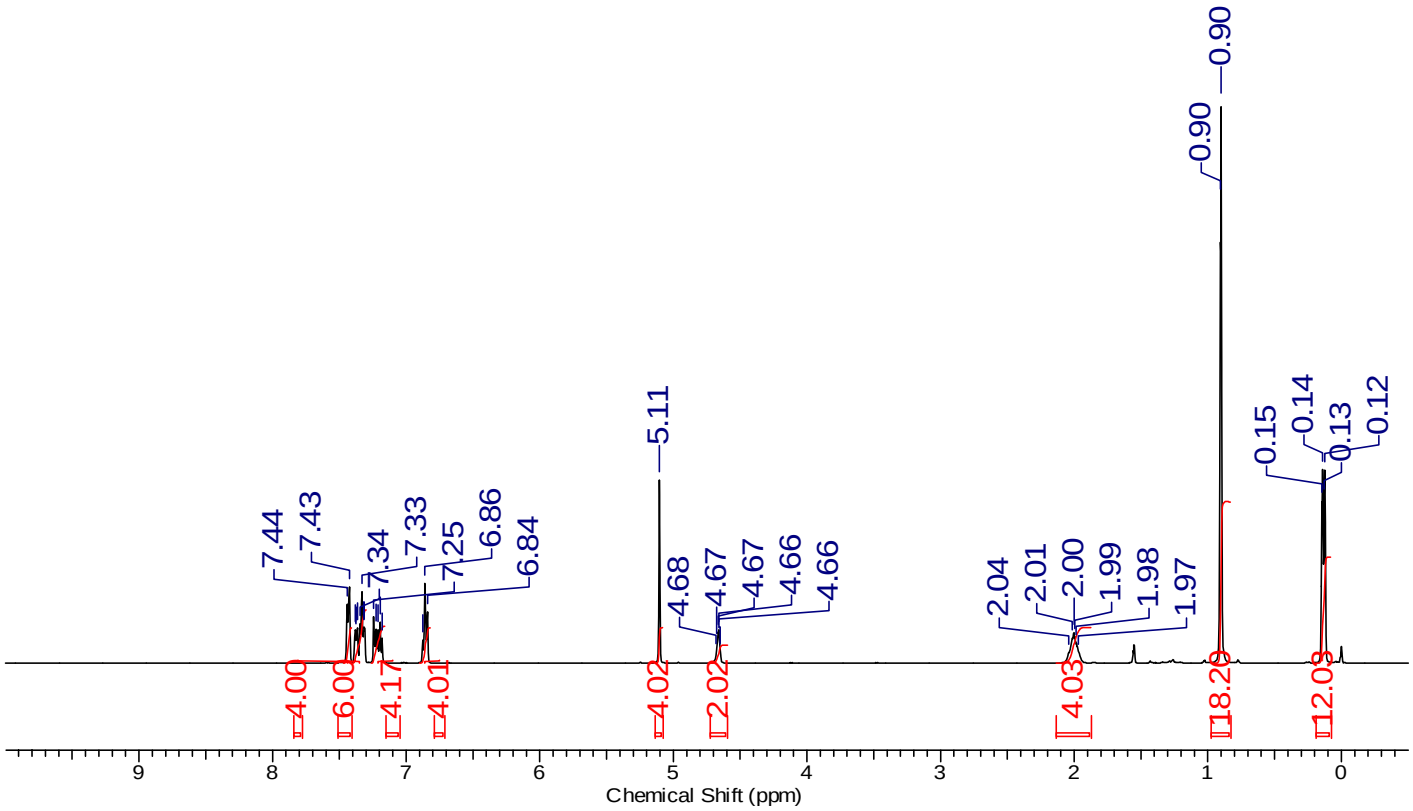
^{13}C NMR (125 MHz, $CDCl_3$)



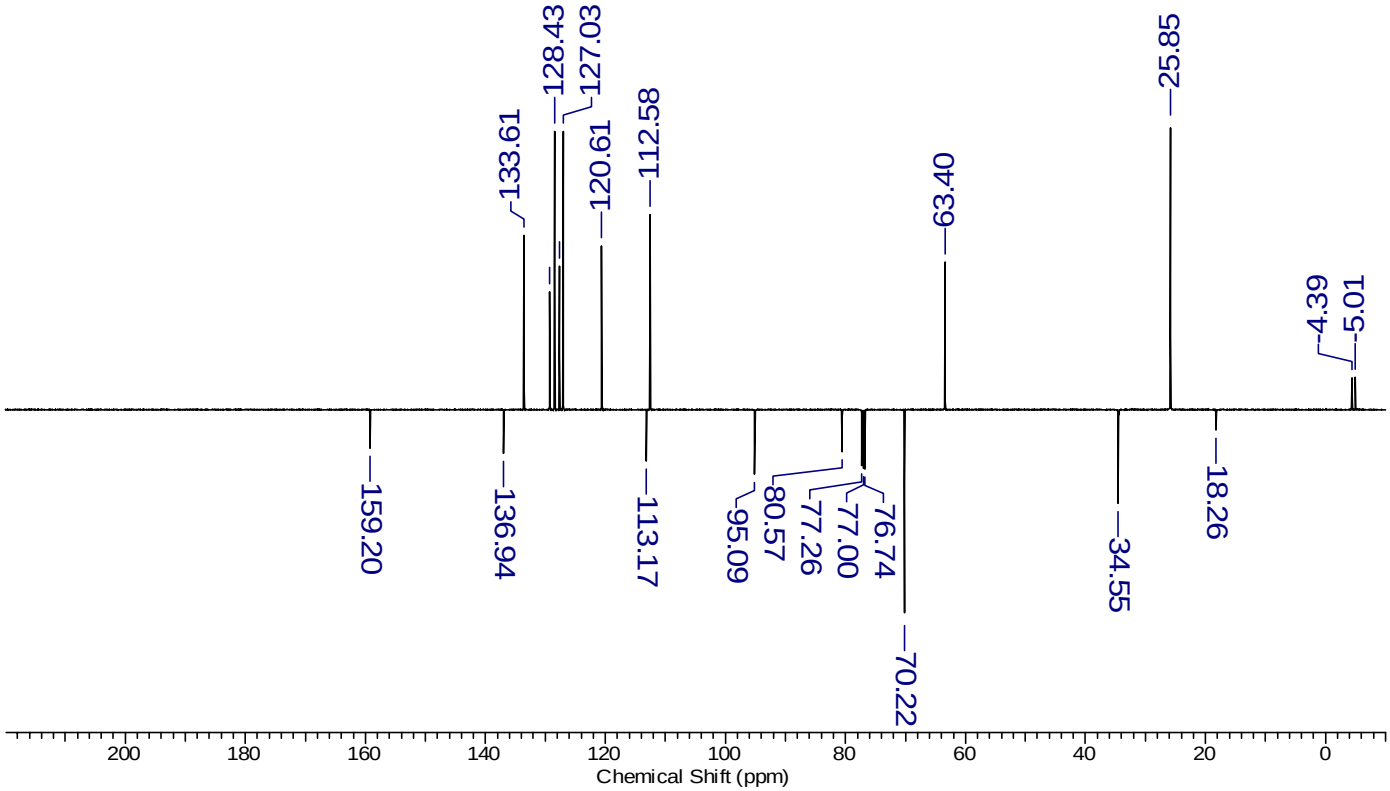
(5*S*,8*S*)-5,8-Bis((2-(benzyloxy)phenyl)ethynyl)-2,2,3,3,10,10,11,11-octamethyl-4,9-dioxa-3,10-disiladodecane 36: ADG410



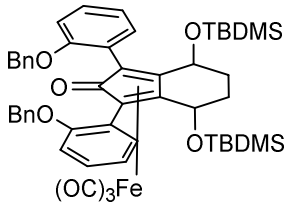
^{1}H NMR (500 MHz, $CDCl_3$)



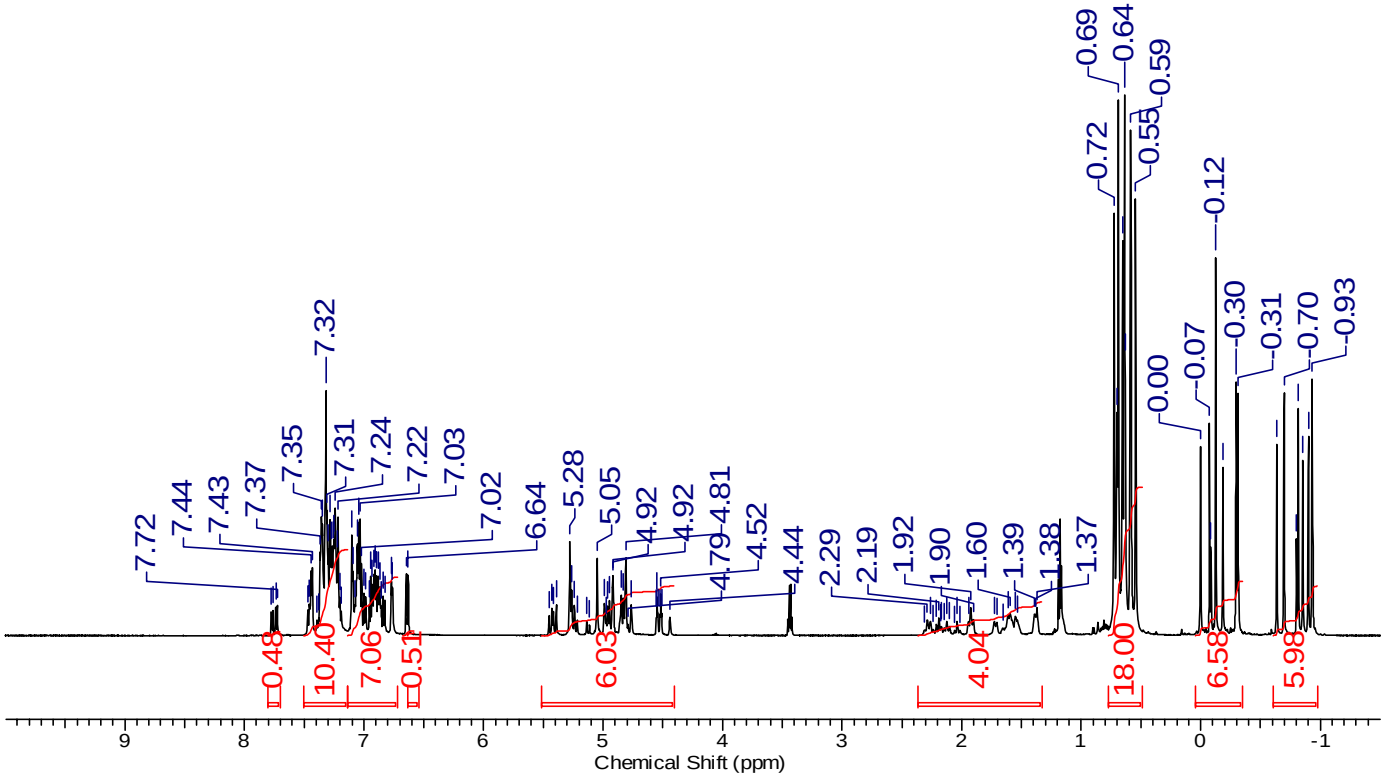
^{13}C NMR (125 MHz, $CDCl_3$)



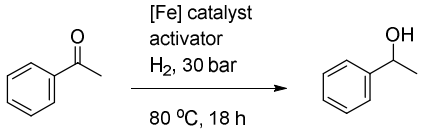
Tricarbonyl-(4*S*,7S)-1,3-bis(2-(benzyloxy)phenyl)-4,7-bis((*tert*-butyldimethylsilyl)oxy)-4,5,6,7-tetrahydro-2*H*-inden-2-one iron 37: ADG358.



^{1}H NMR (500 MHz, $CDCl_3$)

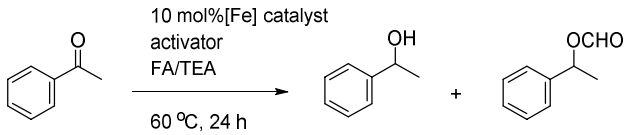


Full Table S5; Hydrogenation of acetophenone using complexes **34**, **35** and **35**.



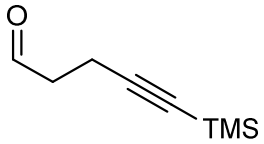
Reaction	Catalyst (%)	Activator (%)	Solvent	Conv	Ee
ADG364	ADG358 (1%) OBn4 **35**	-------	IPA/H_2O	4.8	25.2 (*R*)
ADG363	ADG358 (1%) OBn4 **35**	K_2CO_3 (5%)	IPA/H_2O	>99	23.2 (*R*)
ADG362	ADG358 (1%) OBn4 **35**	TMAO (1%)	IPA/H_2O	>99	23 (*R*)
ADG379	ADG372 (1%) OBn2 **34**	-------	IPA/H_2O	>99	3.4 (*R*)
ADG380	ADG372 (1%) OBn2 **34**	K_2CO_3 (5%)	IPA/H_2O	12	5.2 (*R*)
ADG381	ADG372 (1%) OBn2 **34**	TMAO (1%)	IPA/H_2O	>99	3.2 (*R*)
ADG421	ADG414 (1%) OBn OTBS **37**	TMAO 1%	IPA/H_2O	85.2%	12 (*R*)
436	ADG358 (1%) OBn4 **35**	1% TMAO	MeCN	1.6	34 (*R*)
437	ADG358 (1%) OBn4 **35**	1% TMAO	EtOAc	>99	24.5 (*R*)
438	ADG358 (1%) OBn4 **35**	1% TMAO	DMSO	3.4	31.8 (*R*)
439	ADG358 (1%) OBn4 **35**	1% TMAO	Toluene	54.2	16.2 (*R*)
440	ADG358 (1%) OBn4 **35**	1% TMAO	THF	91.6	25.2 (*R*)
441	ADG358 (1%) OBn4 **35**	1% TMAO	IPA	>99	19.2 (*R*)
442	ADG358 (1%) OBn4 **35**	1% TMAO	Neat	87.6	18.8 (*R*)
444	ADG358 (1%) OBn4 **35**	1% TMAO	tBuOH	98.8	19.6 (*R*)
445	ADG358 (1%) OBn4 **35**	1% TMAO	MeNO2	0	-
446	ADG358 (1%) OBn4 **35**	1% TMAO	DMF	35.9	35.6 (*R*)
447	ADG358 (1%) OBn4 **35**	1% TMAO	Dioxane	62.5	25.6 (*R*)
448	ADG358 (1%) OBn4 **35**	1% TMAO	Chlorobenz	27.2	15 (*R*)
449	ADG358 (1%) OBn4 **35**	1% TMAO	Cyclohex	28.4	14.8 (*R*)
450	ADG358 (1%) OBn4 **35** Repeat	1% TMAO	MeCN	16.8	35.6 (*R*)
453	ADG358 (1%) OBn4 **35**	1% TMAO	IPA 60 oC	64.2	24.8 (*R*)

Table S6; Asymmetric transfer hydrogenation of acetophenone using complexes **34**, **35** and **37**.

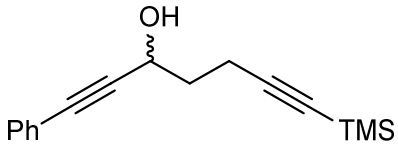


Reaction	Catalyst	Activator/%	Conv/%	Alcohol/% (ee/%)	Formate/% (ee/%)
ADG368	ADG358 (10%) OBn4 **35**	TMAO (10%)	55.7	47.9 (35.6 *R*)	7.8 (35.8 *R*)
ADG378	ADG372 (10%) OBn2 **34**	TMAO (10%)	96.2	88.3 (25.8 *R*)	7.9 (26.4 *R*)
ADG432	ADG414 (1%) OBn OTBS **37**	TMAO	98.6	91.1 (34.2 *R*)	8.5 (32.6 *R*)

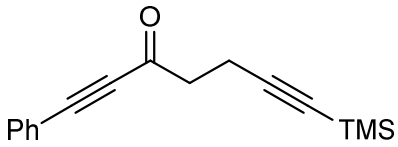
5-(Trimethylsilyl)pent-4-ynal: ADG269



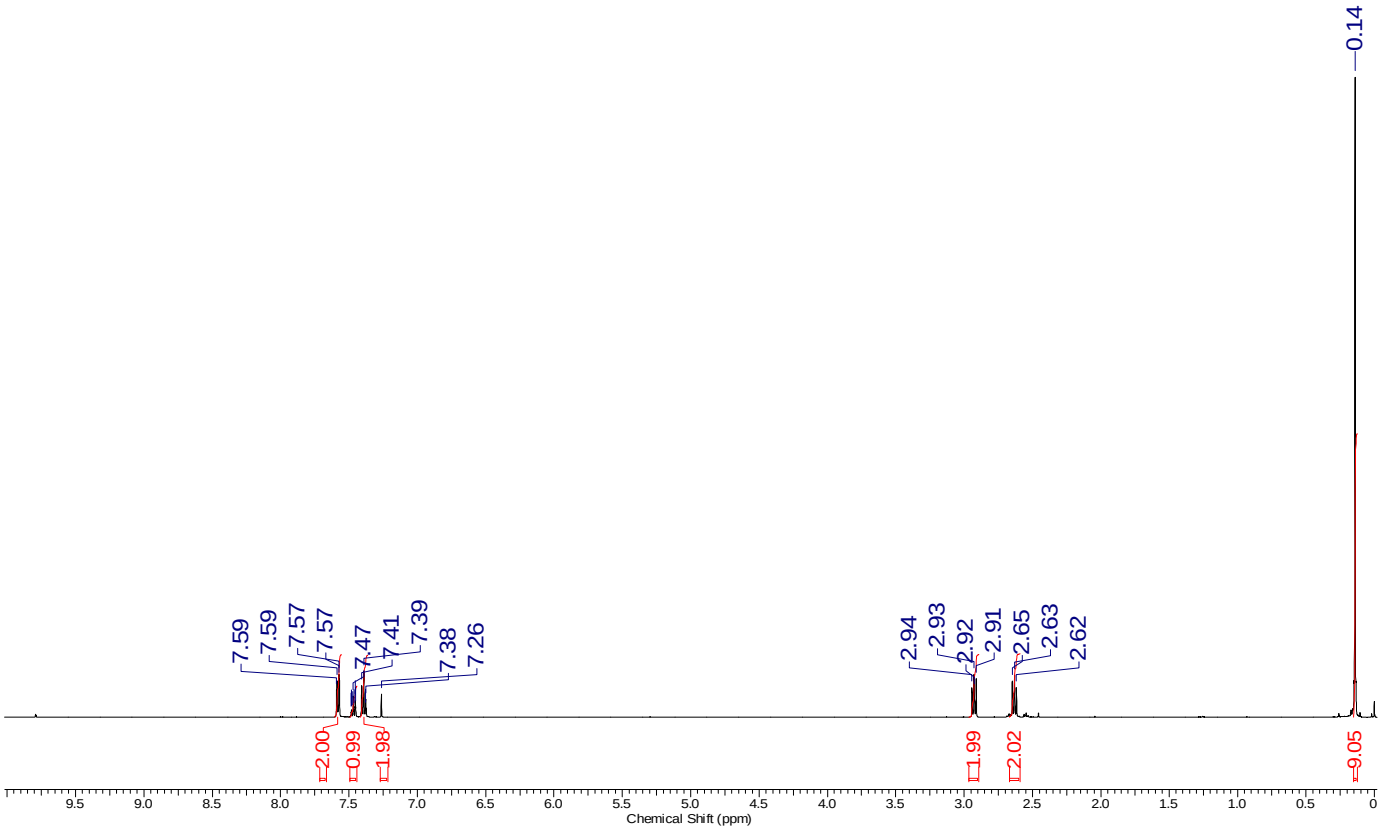
1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol 30: ADG270, ADG272.



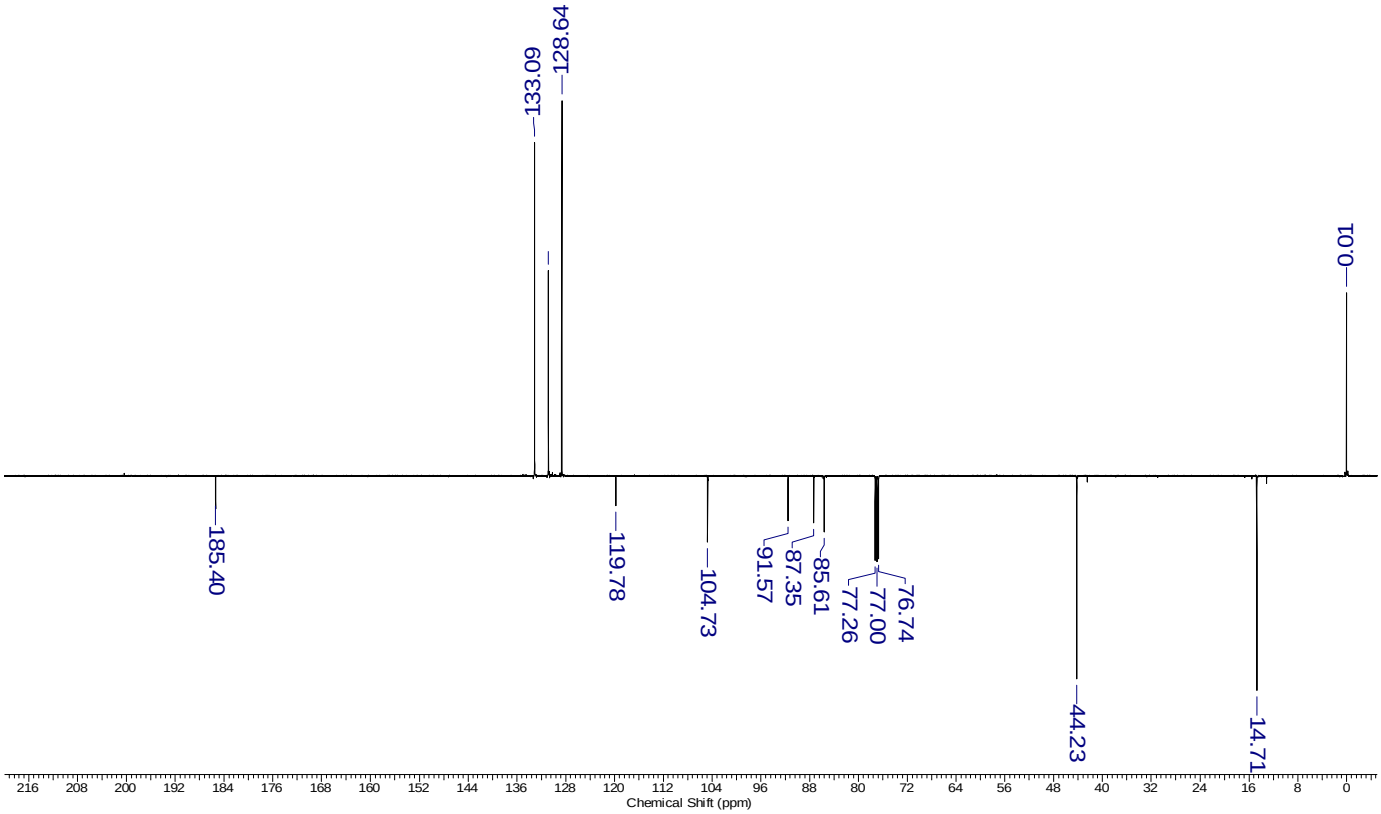
1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-one 38: ADG302



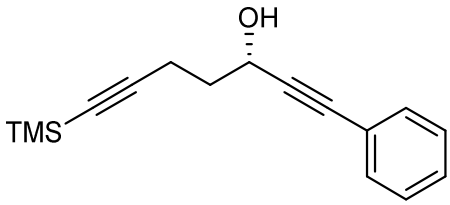
^{1}H NMR (500 MHz, $CDCl_3$)



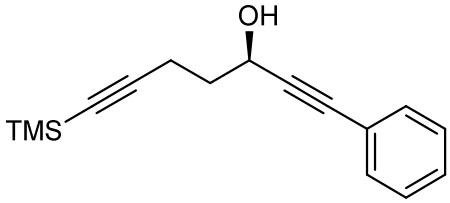
^{13}C NMR (125 MHz, $CDCl_3$)



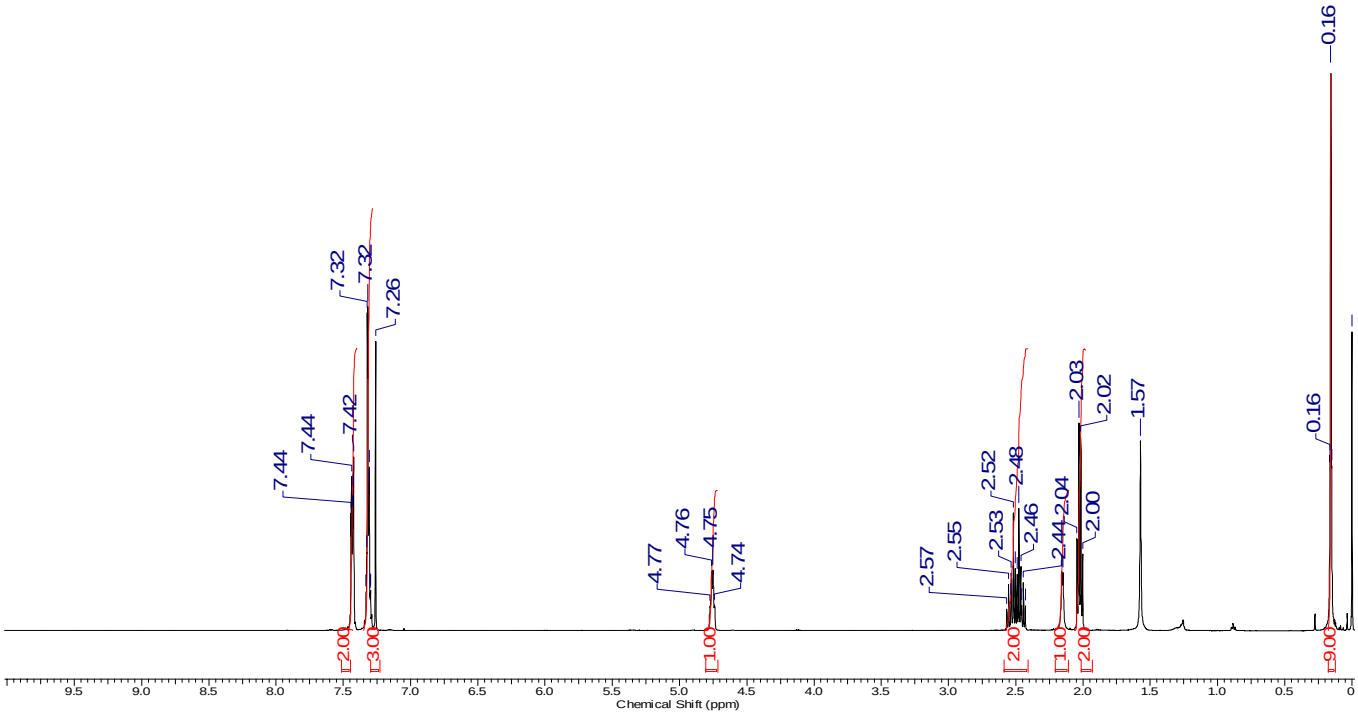
(*S*)-1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol 39: ADG273, ADG305



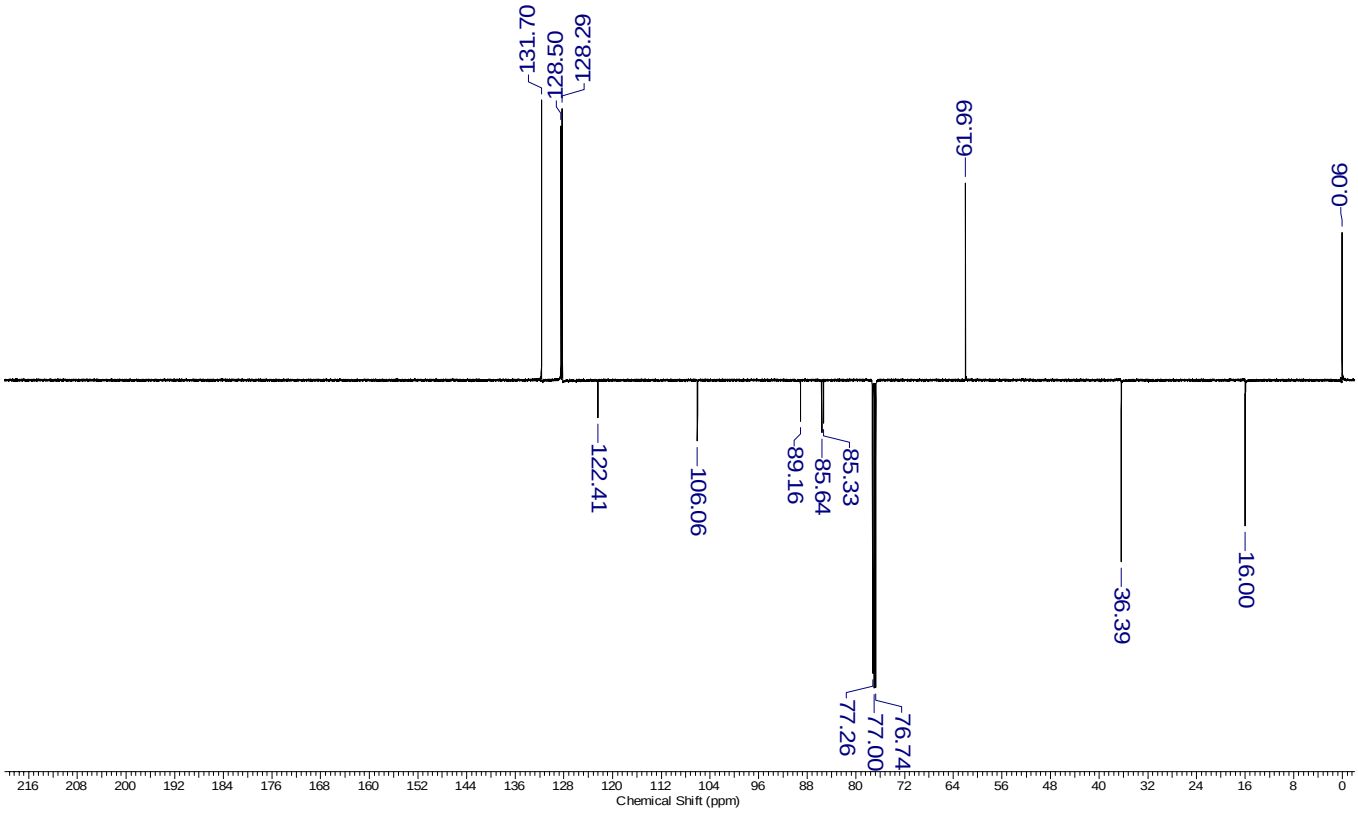
(*R*)-1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol 39: ADG272



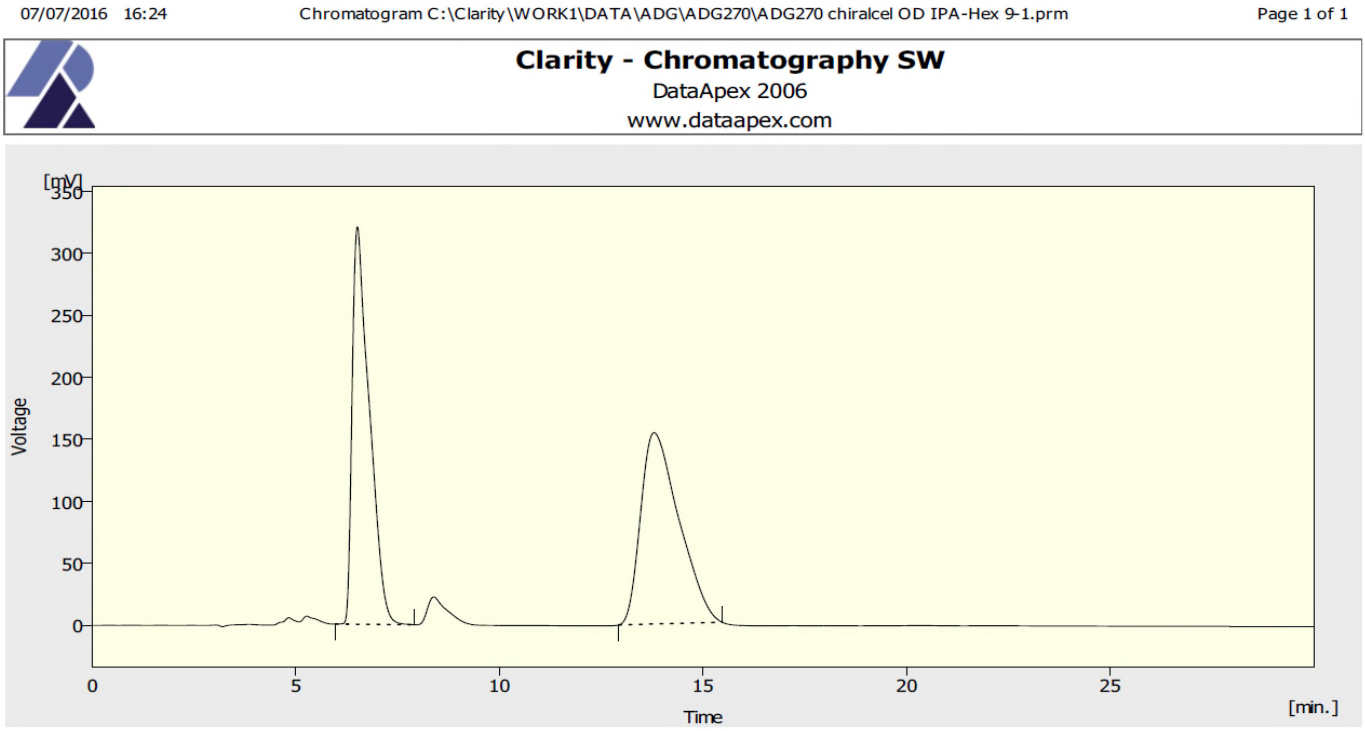
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



***Rac*-1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol 39:** ChiralPak OD Column: 0.46 cm x 25cm, Mobile phase *Iso*-propanol : Hexane 9 : 1, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.

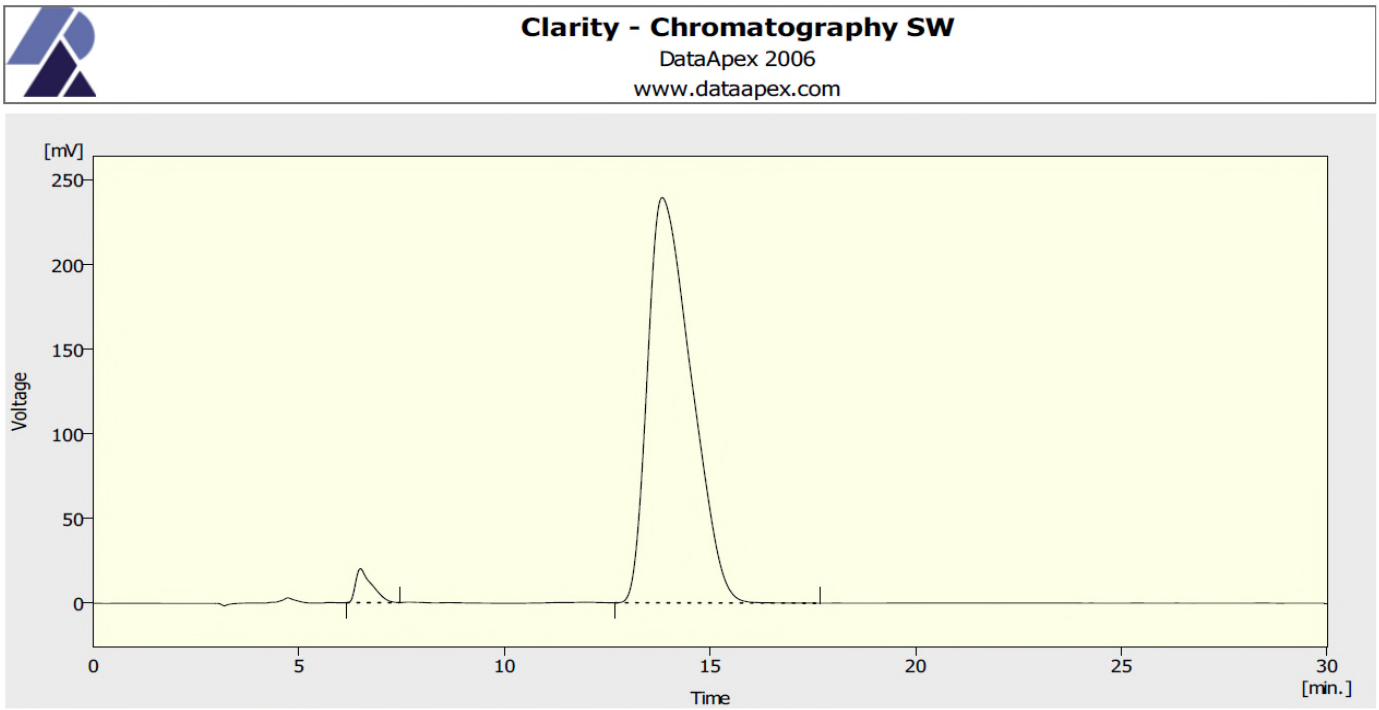


Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG270\ADG270 chiralcel OD IPA-Hex 9-1 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.508	9411.516	320.659	48.3	67.5	0.48	
2	13.800	10086.597	154.386	51.7	32.5	1.04	
	Total	19498.113	475.044	100.0	100.0		

(*S*)-1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol 39: ChiralPak OD Column: 0.46 cm x 25cm, Mobile phase *Iso*-propanol : Hexane 9 : 1, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm

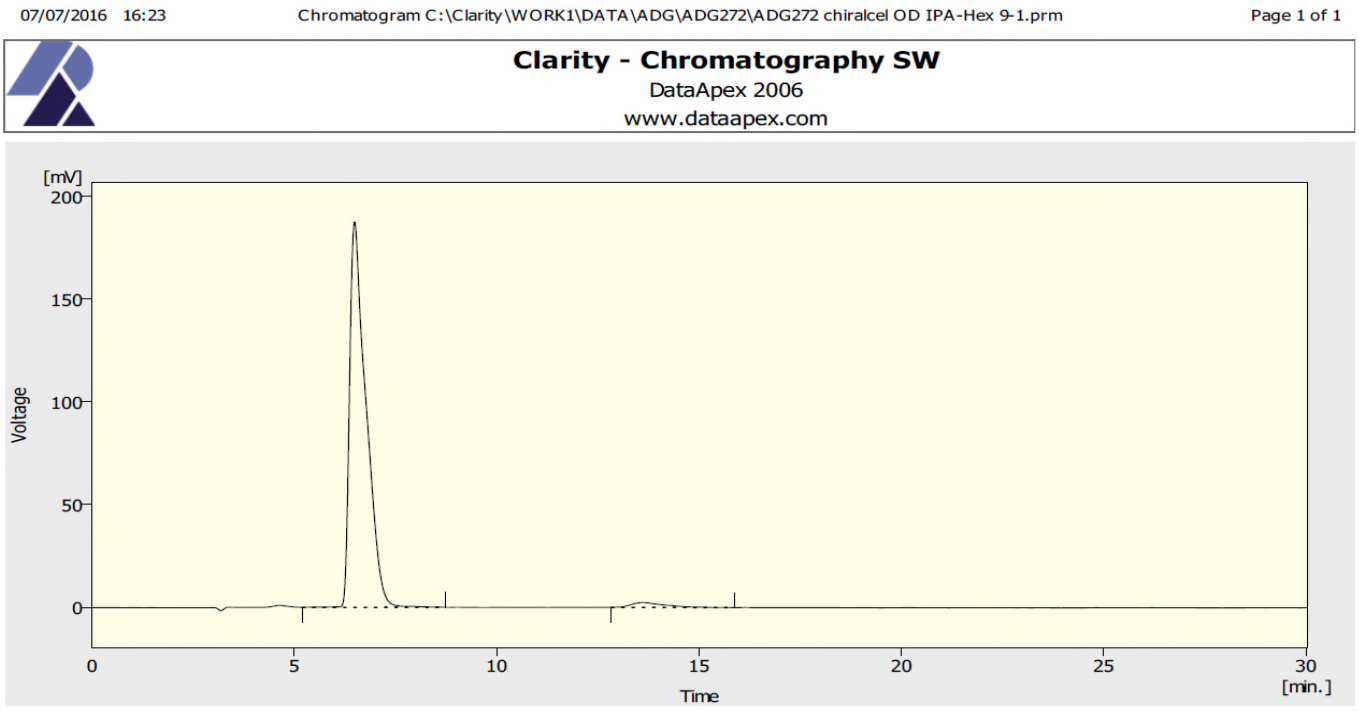
07/07/2016 16:24 Chromatogram C:\Clarity\WORK1\DATA\ADG\ADG273\ADG273 chiralcel OD IPA-Hex 9-1.prm Page 1 of 1



Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG273\ADG273 chiralcel OD IPA-Hex 9-1 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.496	549.852	20.106	3.0	7.7	0.44	
2	13.836	17641.028	239.322	97.0	92.3	1.18	
	Total	18190.880	259.428	100.0	100.0		

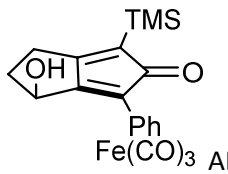
(*R*)-1-Phenyl-7-(trimethylsilyl)hepta-1,6-diyn-3-ol 39: ChiralPak OD Column: 0.46 cm x 25cm, Mobile phase *Iso*-propanol : Hexane 9 : 1, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm



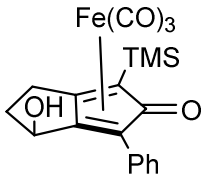
Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG272\ADG272 chiralcel OD IPA-Hex 9-1 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.492	5278.802	187.526	97.5	98.7	0.44	
2	13.608	136.070	2.377	2.5	1.3	0.85	
	Total	5414.872	189.903	100.0	100.0		

Compounds 40 and 41.

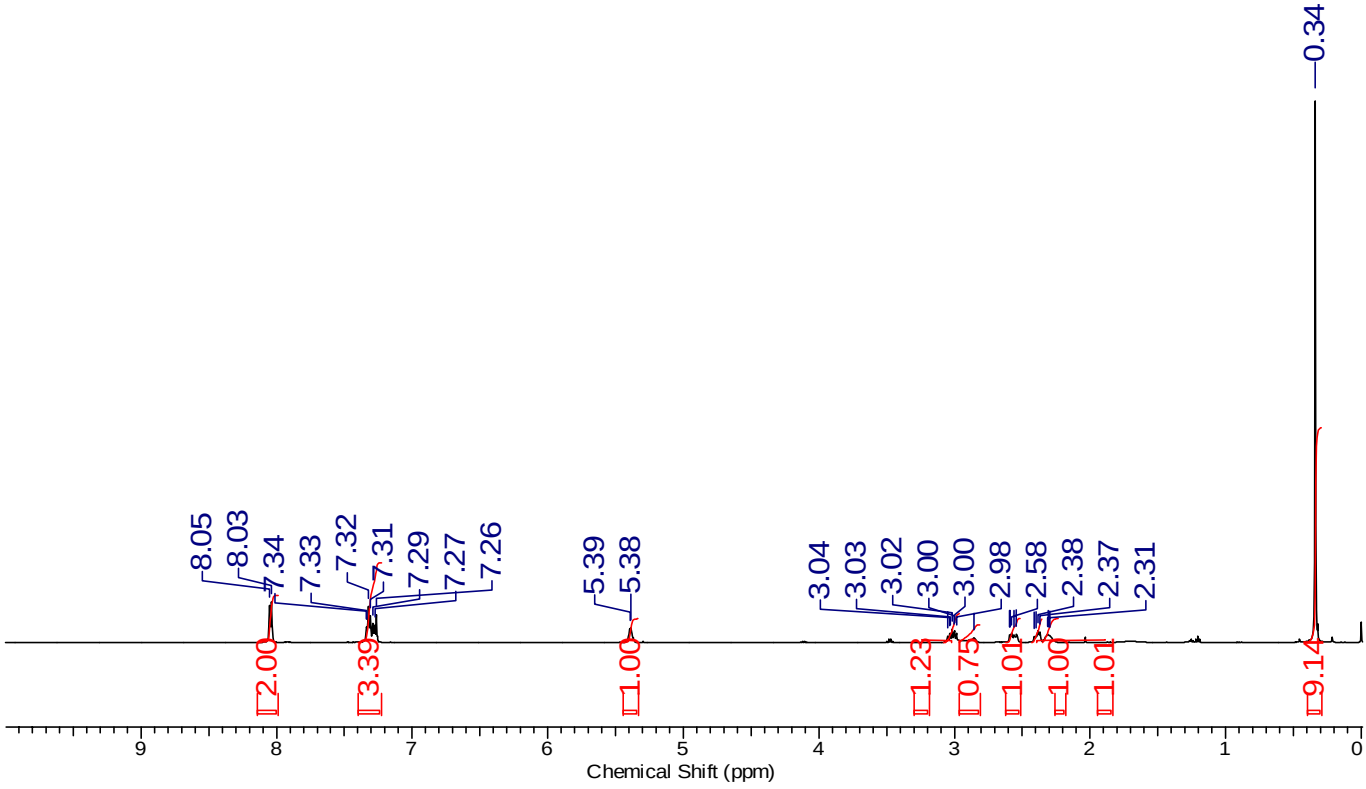


ADG274-1st

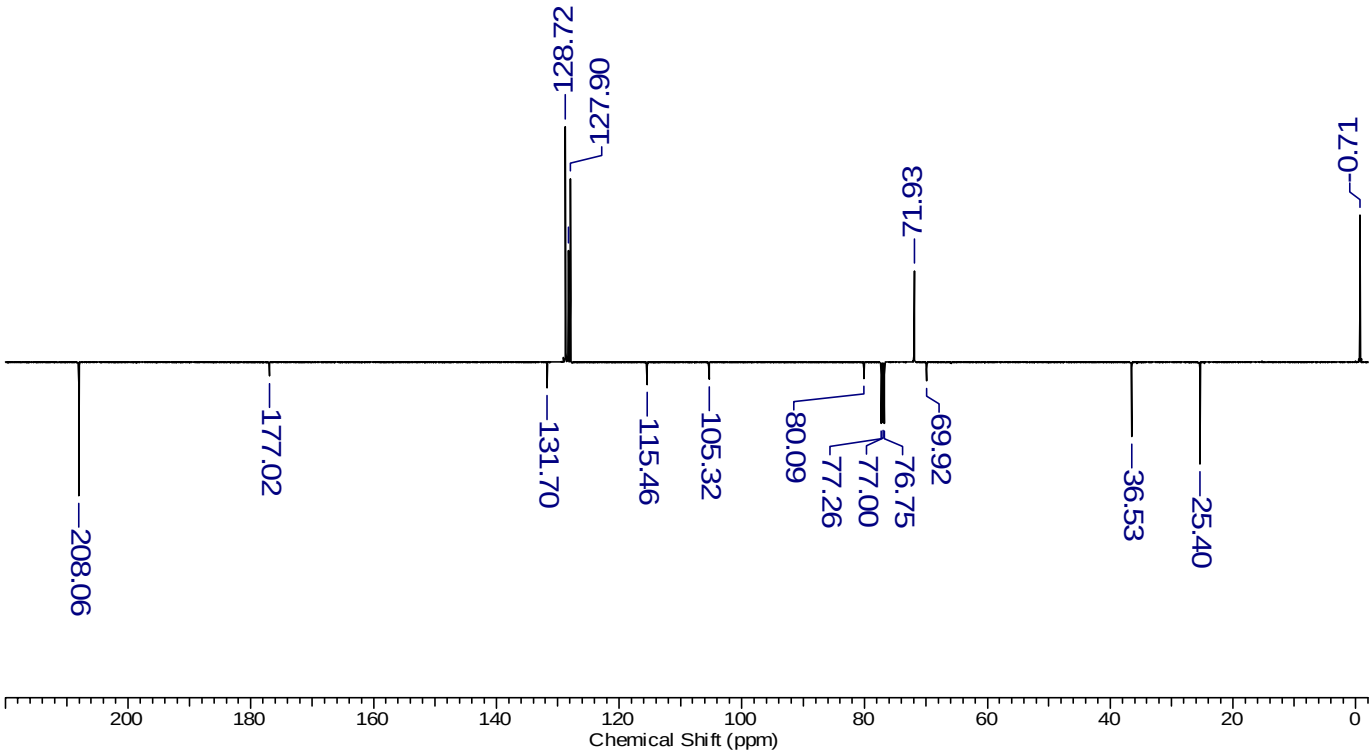


ADG274-2nd

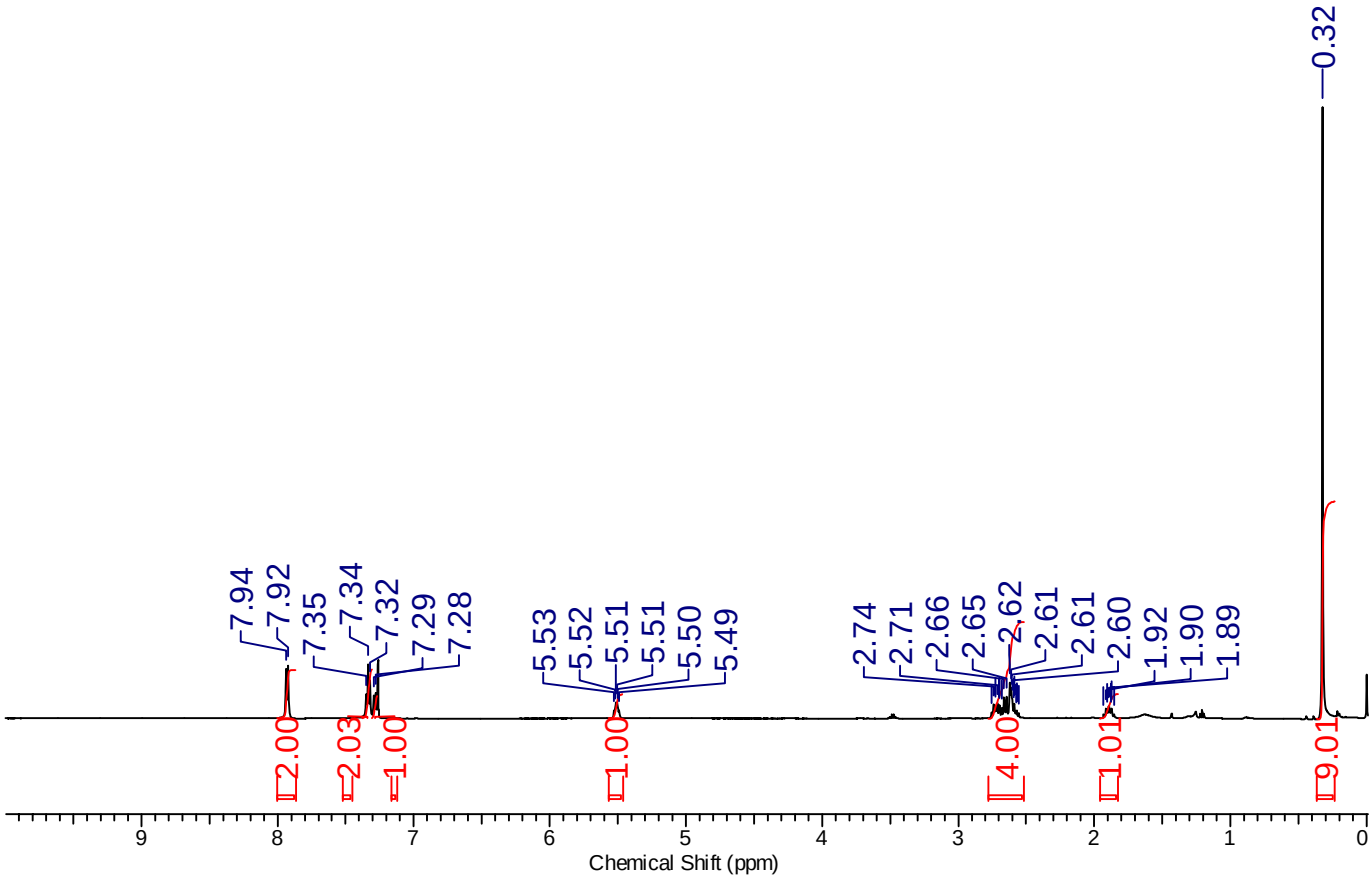
^{1}H NMR (500 MHz, $CDCl_3$) **40 ADG274-1st**



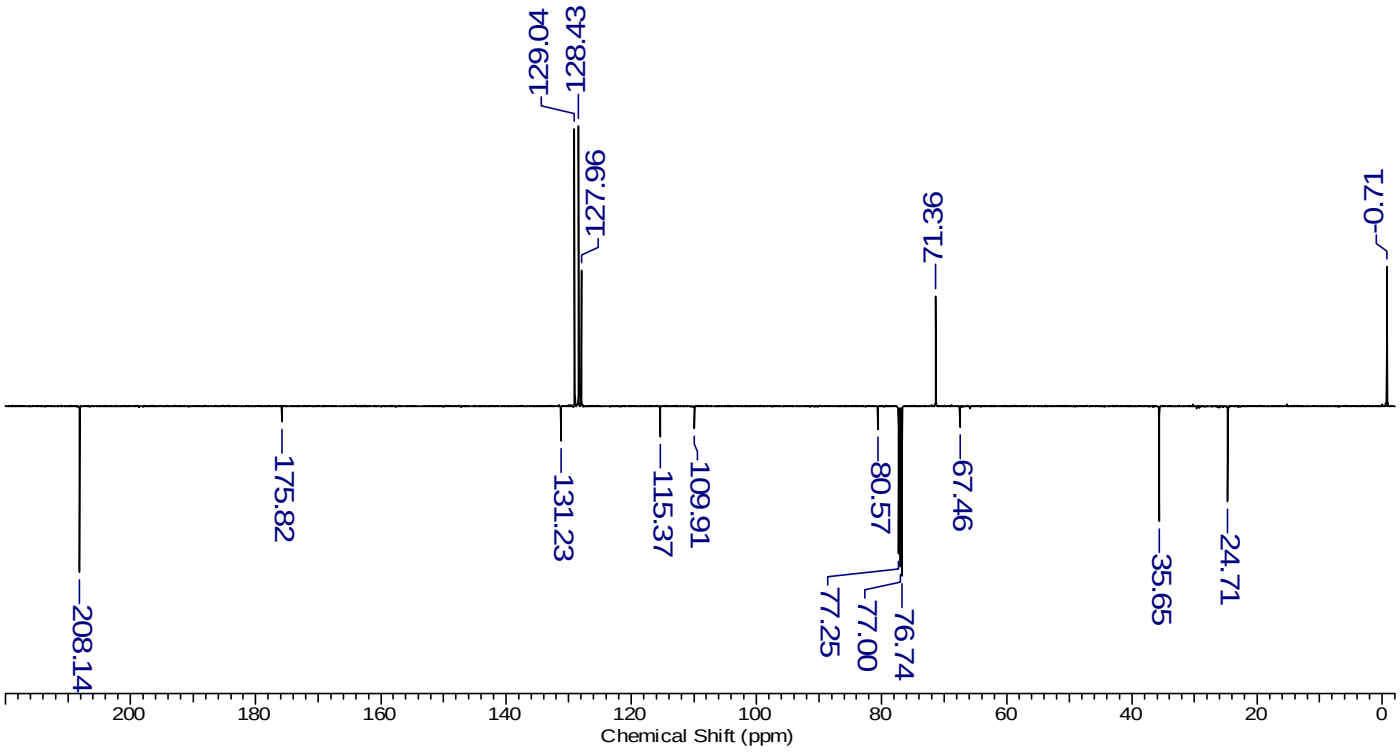
^{13}C NMR (125 MHz, $CDCl_3$)



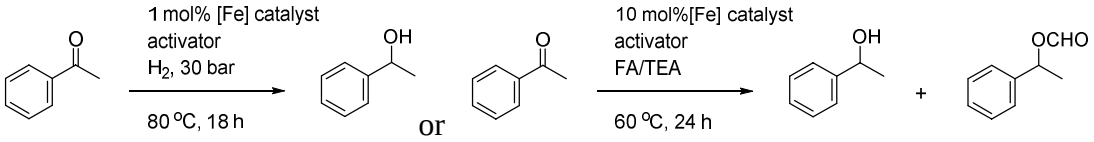
^{1}H NMR (500 MHz, $CDCl_3$) **41 ADG274-2nd**



^{13}C NMR (125 MHz, $CDCl_3$)

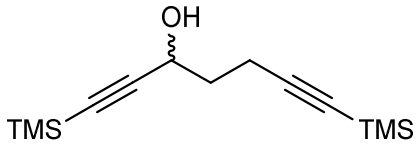


Full Table S7; Asymmetric hydrogenation (entries 1-6) and ATH (entries 7-8) of acetophenone using complexes **40** and **41**.

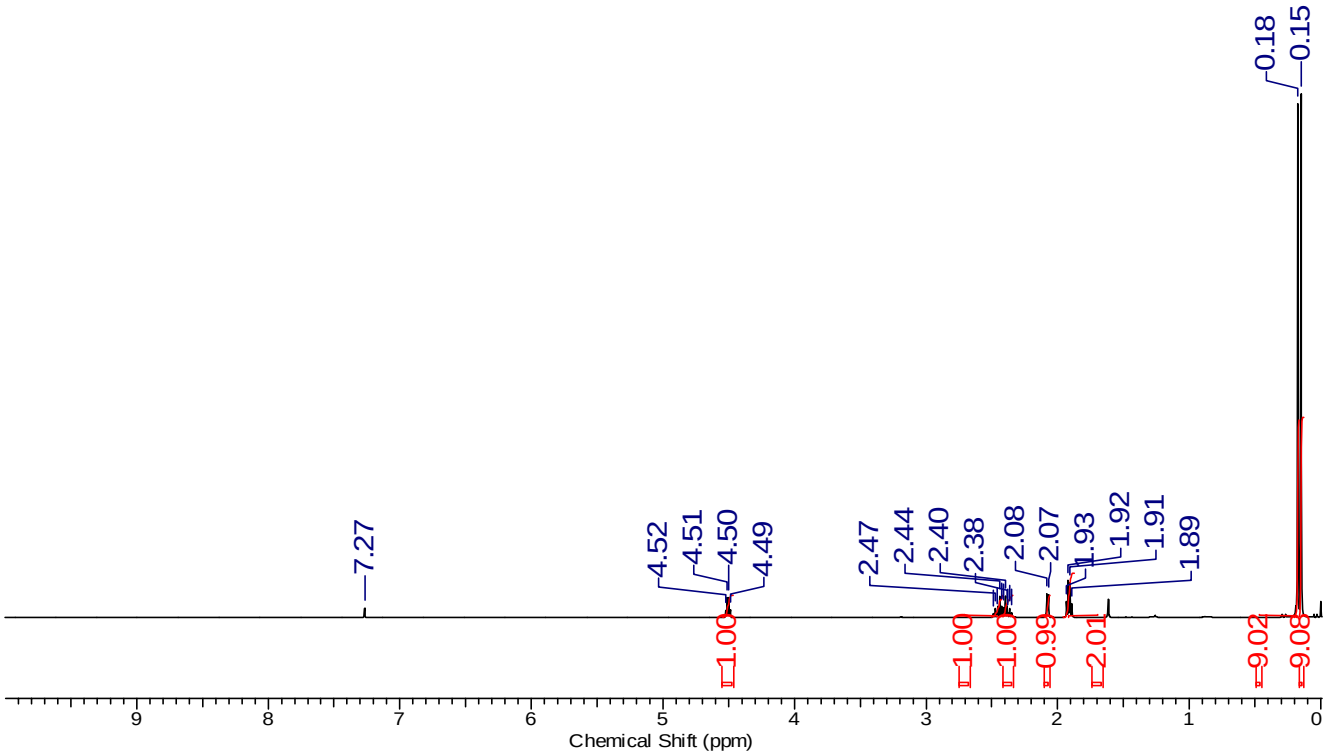


Reaction	**Catalyst**	**Activator/%**	**Solvent**	**Conv/%**	**Ee/%**
ADG277	ADG274 1st **40**	--	IPA/H_2O	4	5 (*R*)
ADG278	ADG274 1st **40**	K_2CO_3 (5%)	IPA/H_2O	68	7.4 (*R*)
ADG279	ADG274 1st **40**	TMAO (1%)	IPA/H_2O	99.7	6.2 (*R*)
ADG280	ADG274 2nd **41**	--	IPA/H_2O	11.9	11.4 (*S*)
ADG281	ADG274 2nd **41**	K_2CO_3 (5%)	IPA/H_2O	82.3	11.6 (*S*)
ADG282	ADG274 2nd **41**	TMAO (1%)	IPA/H_2O	99.8	12.2 (*S*)
Reaction	**Catalyst (%)**	**Activator/%**	**Solvent**	**Alcohol/% (ee/%)**	**Formate/% (ee/%)**
ADG365	ADG274 1st **40**	TMAO (10%)	FA/TEA	91.1 (3.8 *R*)	8.1 (4 *R*)
ADG366	ADG274 2nd **41**	TMAO (10%)	FA/TEA	88.4 (5.8 *S*)	9.9 (5.6 *S*)

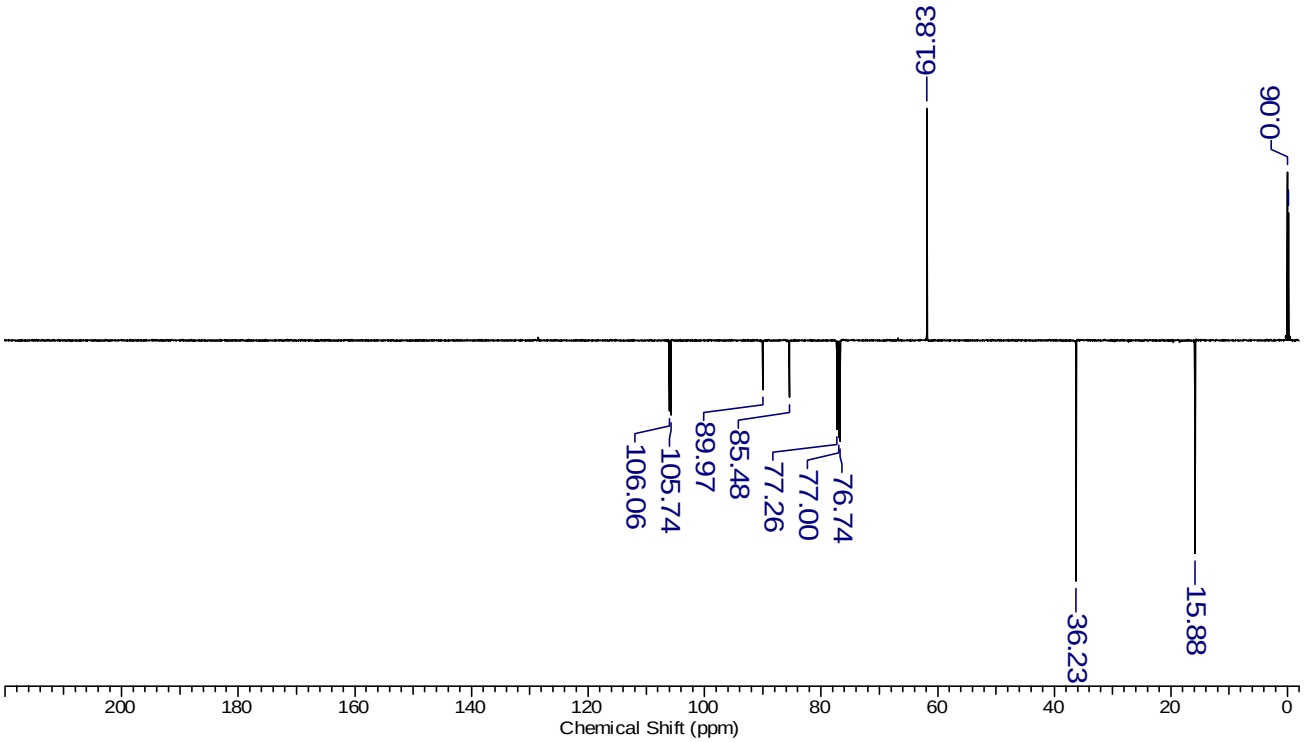
1,7-Bis(trimethylsilyl)hepta-1,6-diyn-3-ol: (ADG538)



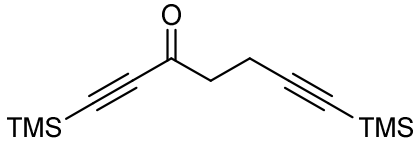
^{1}H NMR (500 MHz, $CDCl_3$)



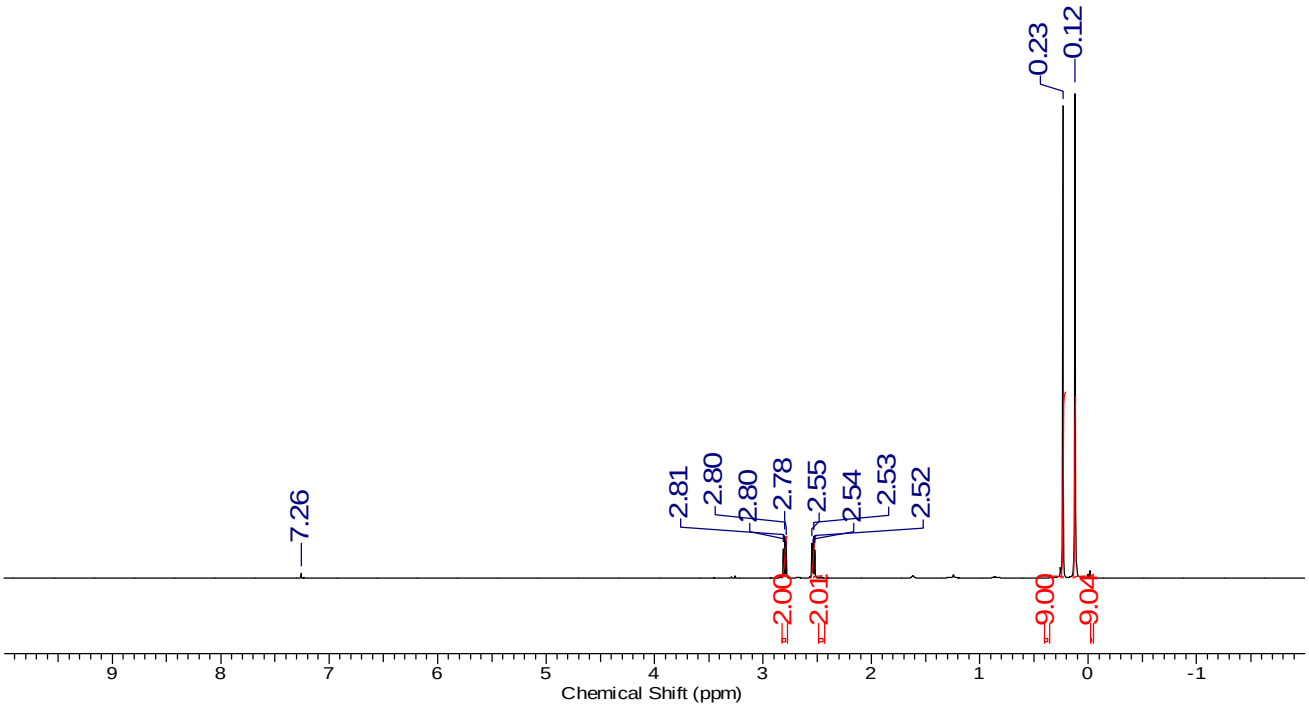
^{13}C NMR (125 MHz, $CDCl_3$)



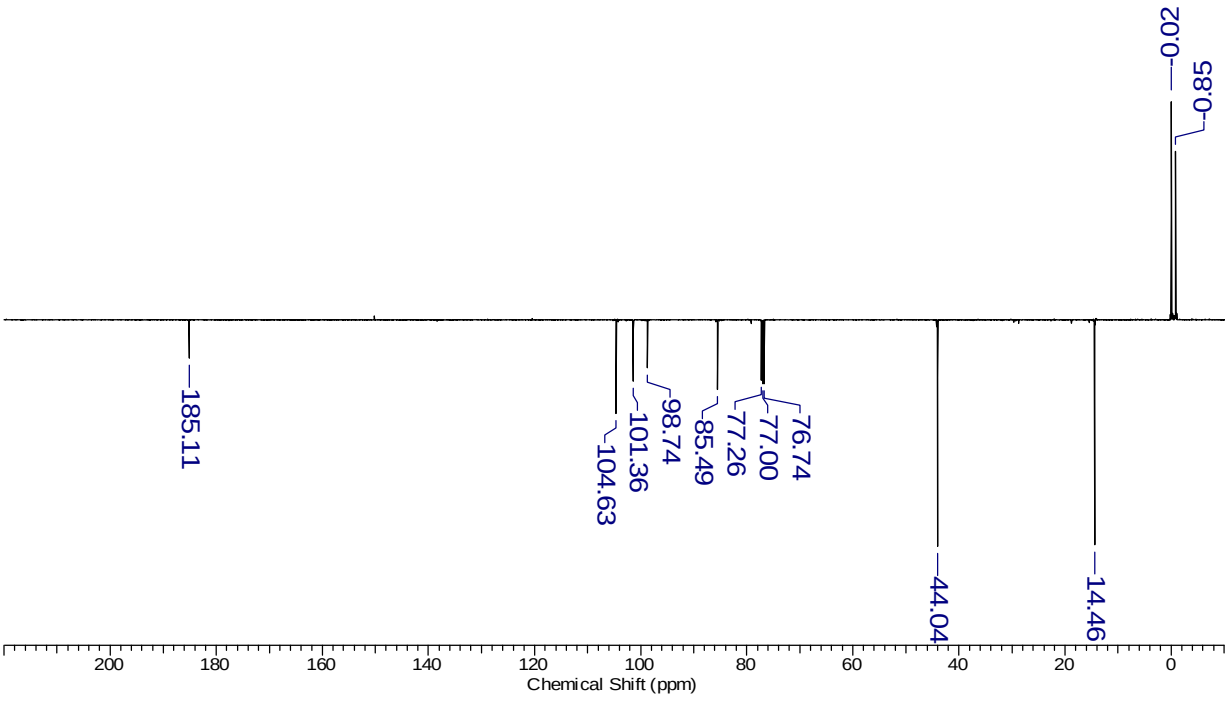
1,7-Bis(trimethylsilyl)hepta-1,6-diyn-3-one 44: ADG541



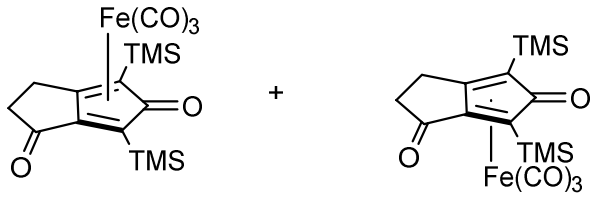
^{1}H NMR (500 MHz, $CDCl_3$)



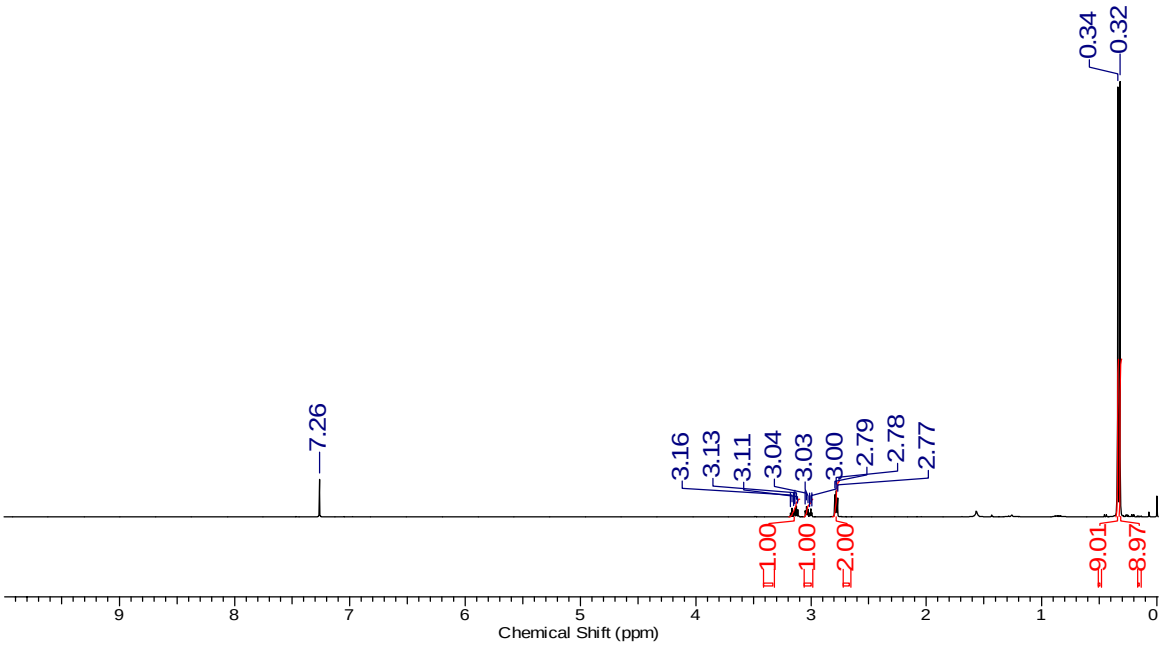
^{13}C NMR (125 MHz, $CDCl_3$)



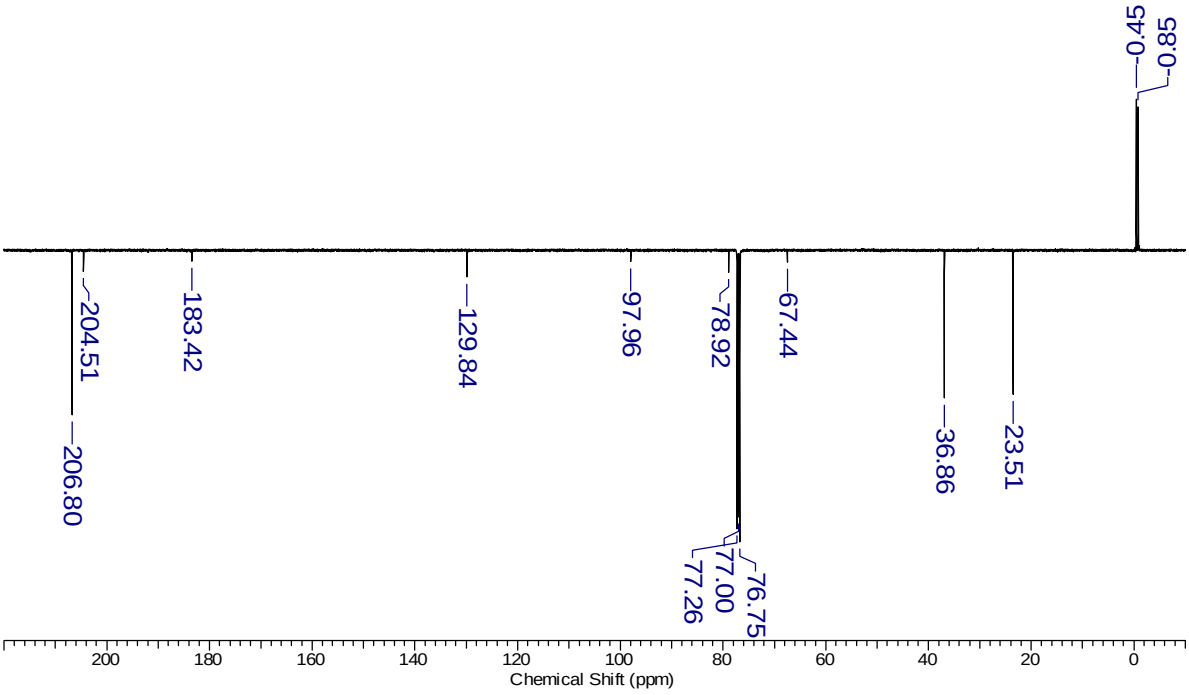
Tricarbonyl-4,6-bis(trimethylsilyl)-2,3-dihydropentalene-1,5-dione iron 42: (ADG189).



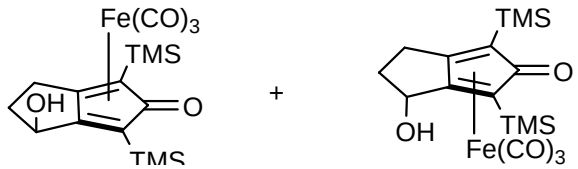
^{1}H NMR (500 MHz, $CDCl_3$)



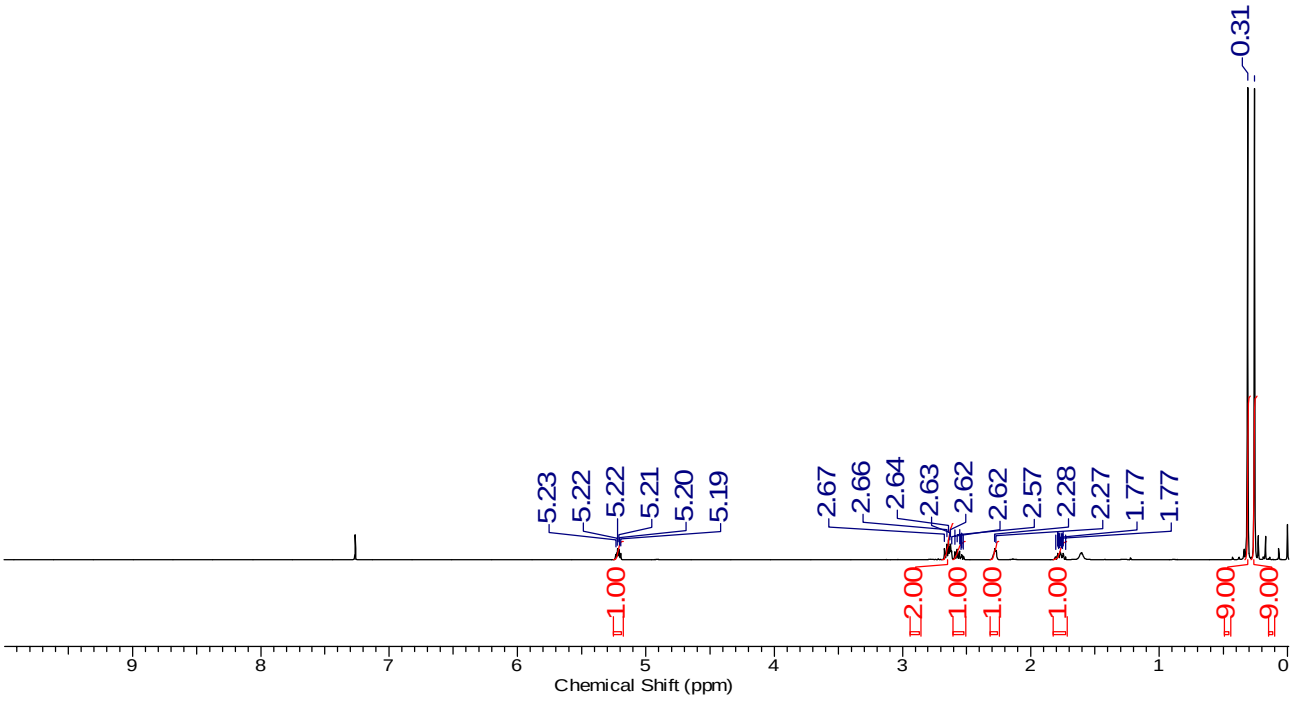
^{13}C NMR (125 MHz, $CDCl_3$)



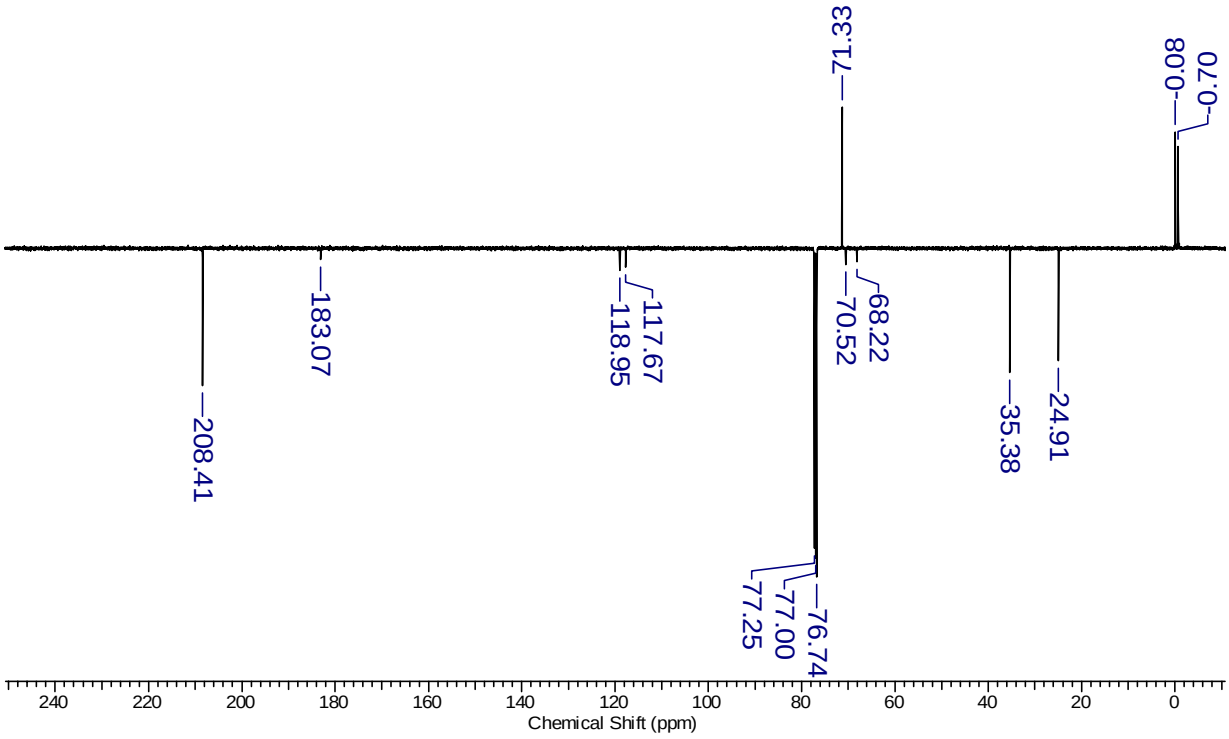
Tricarbonyl-4-hydroxy-1,3-bis(trimethylsilyl)-5,6-dihydropentalen-2(4*H*)-one iron 45: ADG146.



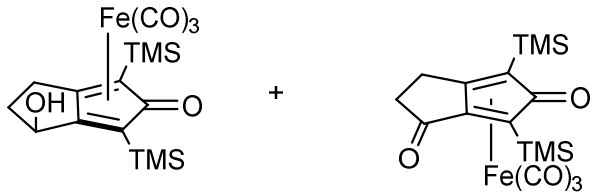
^{1}H NMR (500 MHz, $CDCl_3$)



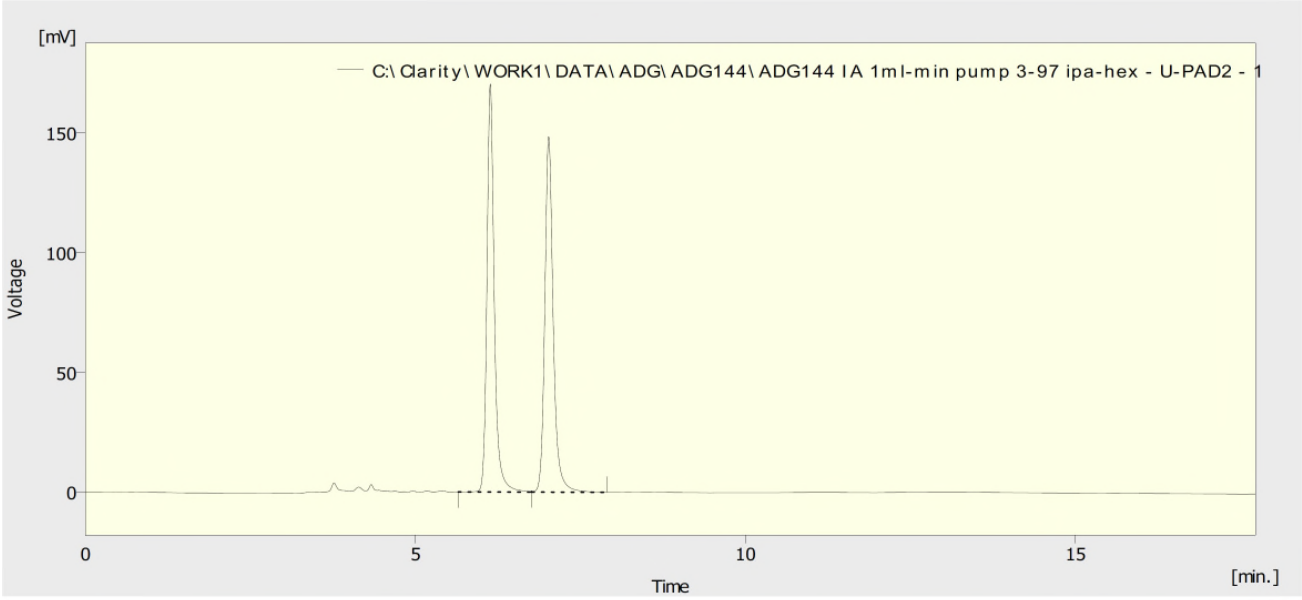
^{13}C NMR (125 MHz, $CDCl_3$)



(-)-45 and (+)-42.



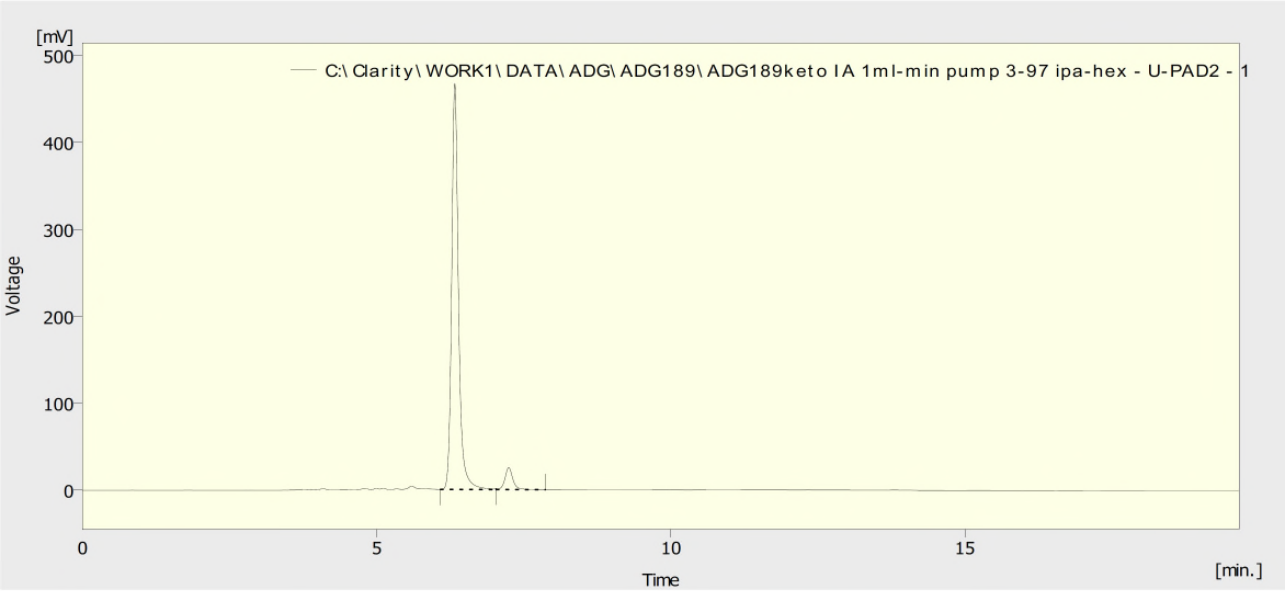
Tricarbonyl-4,6-bis(trimethylsilyl)-2,3-dihydropentalene-1,5-dione iron 42: HPLC analysis on ChiralPak IA Column: 0.46 cm x 25cm, Mobile phase *iso*-propanol : Hexane 3 : 97, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.



Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG144\ADG144 IA 1ml-min pump 3-97 ipa-hex - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.132	1321.781	170.331	50.0	53.4	0.12	
2	7.016	1321.666	148.424	50.0	46.6	0.13	
	Total	2643.447	318.755	100.0	100.0		

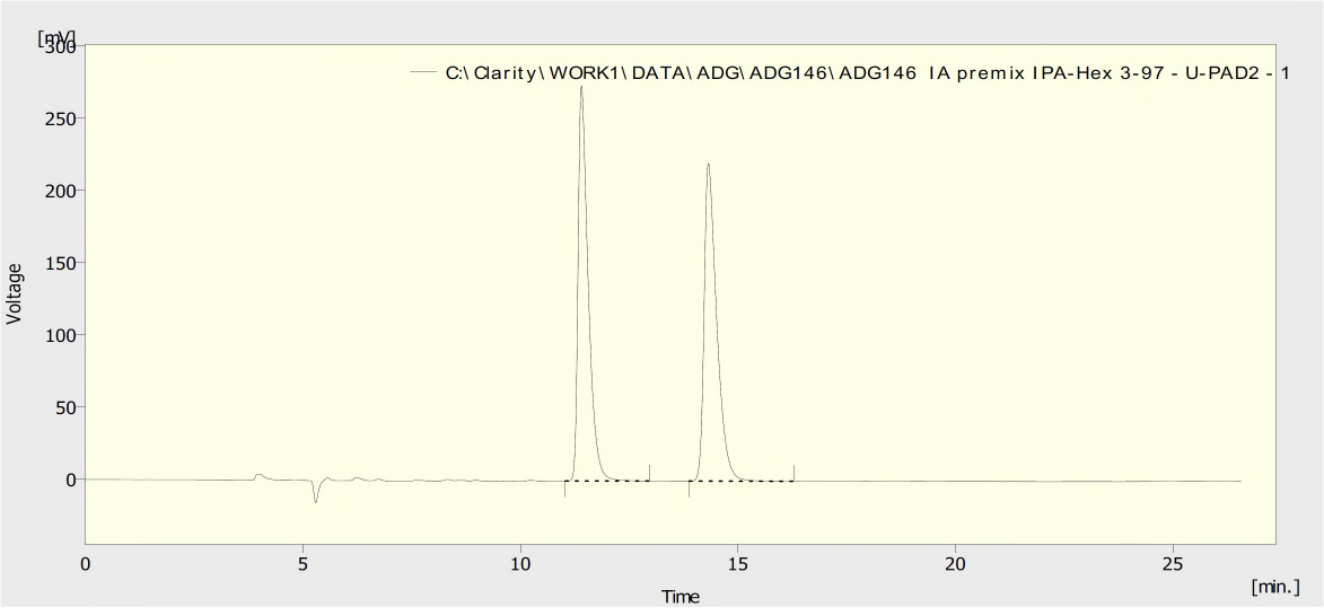
Chiral Tricarbonyl-4,6-bis(trimethylsilyl)-2,3-dihydropentalene-1,5-dione iron 42: HPLC analysis on ChiralPak IA Column: 0.46 cm x 25cm, Mobile phase *iso*-propanol : Hexane 3 : 97, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.



Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG189\ADG189keto IA 1ml-min pump 3-97 ipa-hex - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.328	3778.328	467.024	94.1	94.8	0.12	
2	7.244	237.905	25.517	5.9	5.2	0.14	
	Total	4016.234	492.541	100.0	100.0		

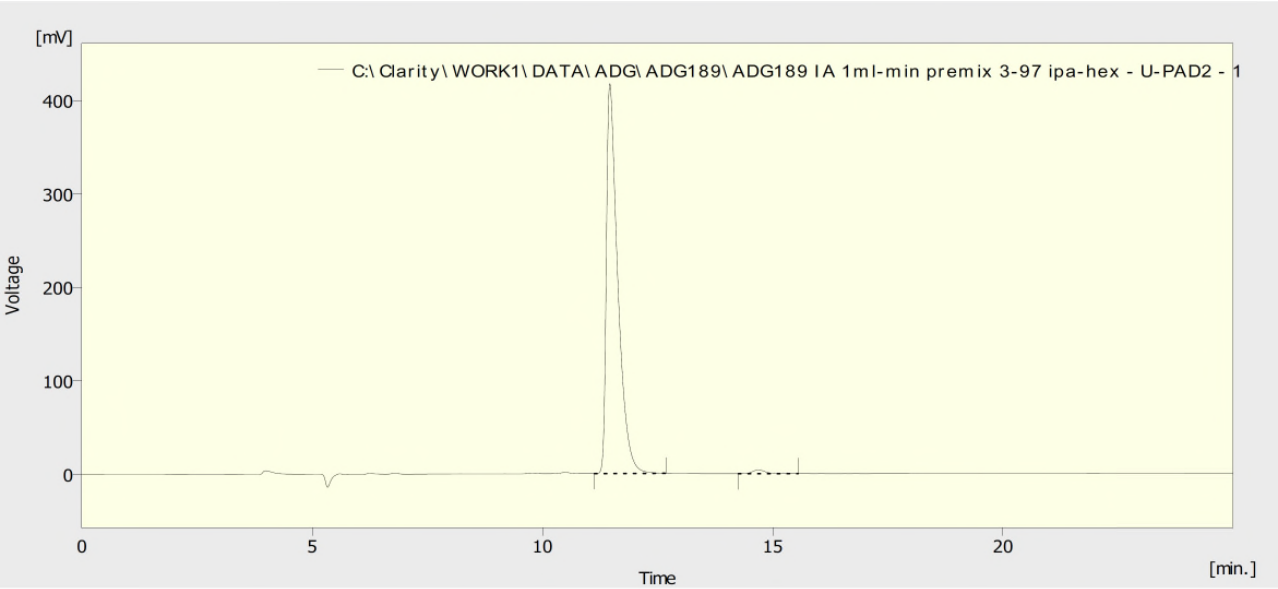
Tricarbonyl-4-hydroxy-1,3-bis(trimethylsilyl)-5,6-dihydropentalen-2(4*H*)-one iron 45: HPLC analysis on ChiralPak IA Column: 0.46 cm x 25cm, Mobile phase *iso*-propanol : Hexane 3 : 97, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.



Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG146\ADG146 IA premix IPA-Hex 3-97 - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	11.404	4432.110	273.542	50.0	55.4	0.24	
2	14.324	4439.087	219.861	50.0	44.6	0.30	
	Total	8871.197	493.403	100.0	100.0		

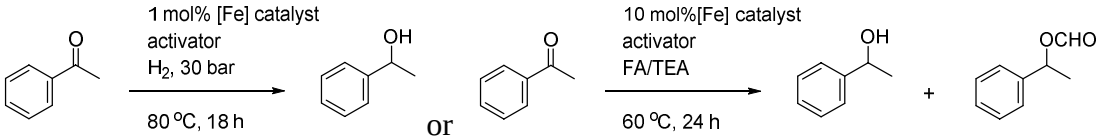
Chiral Tricarbonyl-4-hydroxy-1,3-bis(trimethylsilyl)-5,6-dihydropentalen-2(4*H*)-one iron 45: HPLC analysis on ChiralPak IA Column: 0.46 cm x 25cm, Mobile phase *iso*-propanol : Hexane 3 : 97, flow rate 1 mL/min, Temperature 30 ºC, UV detection at λ = 254 nm.



Result Table (Uncal - C:\Clarity\WORK1\DATA\ADG\ADG189\ADG189 IA 1ml-min premix 3-97 ipa-hex - U-PAD2 - 1)

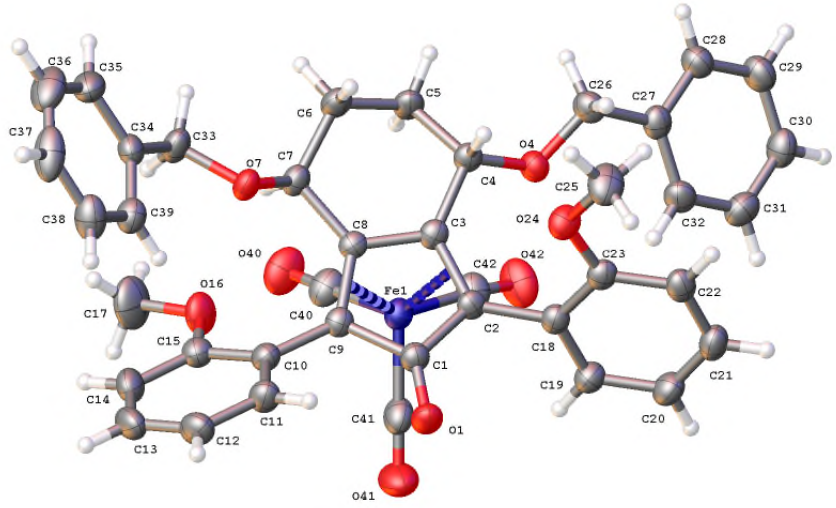
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	11.464	7182.580	417.531	98.9	99.0	0.26	
2	14.688	79.921	4.162	1.1	1.0	0.29	
	Total	7262.501	421.692	100.0	100.0		

Table S8. Asymmetric hydrogenation (entries 1-6) and ATH (entry 7) of acetophenone using **42** and **45**.



Reaction	Catalyst	Activator/%	Solvent	Conv/%	Ee/%
ADG192	ADG189 (1%) OH **45**	----------	IPA/H_2O	11.9	7.8 (*S*)
ADG206	ADG189 (1%) OH **45**	----------	IPA/H_2O	13.7	6.8 (*S*)
AD193	ADG189 (1%) OH **45**	K_2CO_3 (5%)	IPA/H_2O	99.5	2 (*S*)
ADG207	ADG189 (1%) OH **45**	K_2CO_3 (5%)	IPA/H_2O	99.4	9.4 (*S*)
ADG194	ADG189 (1%) OH **45**	TMAO (10%)	IPA/H_2O	99.6	4 (*S*)
ADG208	ADG189 (1%) OH **45**	TMAO (10%)	IPA/H_2O	99.6	4.2 (*S*)
ADG411	ADG189? (1%) C=O **42**	----------	IPA/H_2O	>99	3.8 (*R*)
ADG412	ADG189? (1%) C=O **42**	K_2CO_3 (5%)	IPA/H_2O	9.6	2.6 (*R*)
ADG413	ADG189? (1%) C=O **42**	TMAO (1%)	IPA/H_2O	>99	0.4 (*R*)
Reaction	**Catalyst (%)**	**Activator (%)**	**Solvent**	**Formate**	**Alcohol**
ADG 408	ADG189 **42**	TMAO 10%	FA/TEA	3.9 (3.8 ee *R*)	24.2 (4 ee *R*)

X-ray Crystallographic data for 27 (local code ADG11, CCDC 1567220).



Solid state structure of adg11/CCDC 1567220 with atom labeling and thermal ellipsoids drawn at 50% probability level.

Crystal structure determination of adg11/CCDC 1567220.

The asymmetric unit contains the complex, there are two in the unit cell. The Flack

parameter refined to -0.010(2) which is reasonably small with a low error so we are confident in the assignment of the stereochemistry of the crystal chosen, shown in the picture above.
Hooft y: -0.0086(19) Olex2
Flack x: -0.010(2) Shelx 2014

Experimental for adg11/CCDC 1567220.
Single crystals of $C_{40}H_{34}FeO_8$ were grown from DCM/hexane. A suitable crystal was selected and mounted on a Mitegen head with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.
1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

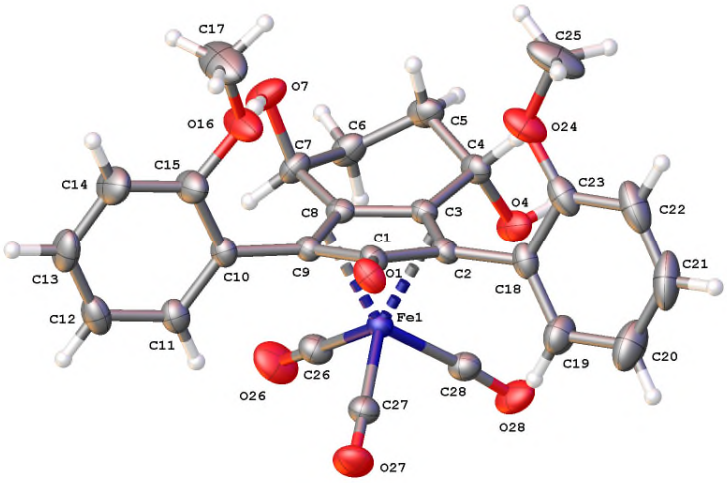
Crystal Data for $C_{40}H_{34}FeO_8$ (M =698.52 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 9.64408(12) Å, b = 8.04710(9) Å, c = 21.6608(2) Å, β = 92.7335(11)°, V = 1679.12(3) Å^3, Z = 2, T = 150(2) K, μ(CuKα) = 4.056 mm^{-1}, $Dcalc$ = 1.382 g/cm^3, 34729 reflections measured (8.172° ≤ 2Θ ≤ 156.536°), 7091 unique (R_{int} = 0.0567, R_{sigma} = 0.0399) which were used in all calculations. The final R_1 was 0.0381 (I > 2σ(I)) and wR_2 was 0.1002 (all data).

Table S9 Crystal data and structure refinement for adg11/CCDC 1567220**.**

Identification code	adg11
Empirical formula	$C_{40}H_{34}FeO_8$
Formula weight	698.52
Temperature/K	150(2)
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	9.64408(12)
b/Å	8.04710(9)
c/Å	21.6608(2)

α/°	90
β/°	92.7335(11)
γ/°	90
Volume/Å^3	1679.12(3)
Z	2
ρ_{calc}g/cm^3	1.382
μ/mm^{-1}	4.056
F(000)	728.0
Crystal size/mm^3	0.4 × 0.2 × 0.02 yellow block
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.172 to 156.536
Index ranges	-11 ≤ h ≤ 12, -10 ≤ k ≤ 10, -27 ≤ l ≤ 27
Reflections collected	34729
Independent reflections	7091 [R_{int} = 0.0567, R_{sigma} = 0.0399]
Data/restraints/parameters	7091/1/444
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.0961
Final R indexes [all data]	R_1 = 0.0420, wR_2 = 0.1002
Largest diff. peak/hole / e Å^{-3}	0.68/-0.24
Flack parameter	-0.010(2)

X-ray Crystallographic data for 26 (local code adg12, CCDC 1567221).



solid state structure of adg12/CCDC 1567221 with atom labeling and thermal ellipsoids drawn at 50% probability level.

Crystal structure determination of adg12/CCDC 1567221.

The asymmetric unit contains the Fe complex of the cyclopentadienyl cyclohexane diol. Four times this data are in the unit cell. The OHs were located in a difference map and allowed to refine with thermal parameters Uiso 1.5 x times Uequiv of the parent oxygen. O7-H7 was refined with a DFIX distance restraint. The OHs form short contacts tabulated below

Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
0.83(4)	1.98(4)	2.792(3)	166(4)	O4-H4...O1_$1
0.84(2)	2.10(3)	2.928(3)	171(4)	O7-H7...O16

Symmetry operator used to generate equivalent atoms in above contacts

$1 -x+1, y+1/2, -z+3/2

Flack parameter refined to a value of Flack x: -0.008(2) which is low with a reasonably low error so we are confident in the assignment of the stereochemistry of the crystal chosen, shown in the picture above.

Hooft y: -0.0063(13) Shelx 2014

Flack x: -0.008(2) Olex2

Experimental for adg12/CCDC 1567221.

Single crystals of $C_{26}H_{22}FeO_8$ were grown from DCM/hexane. A suitable crystal was selected

and mounted on a Mitegen head with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

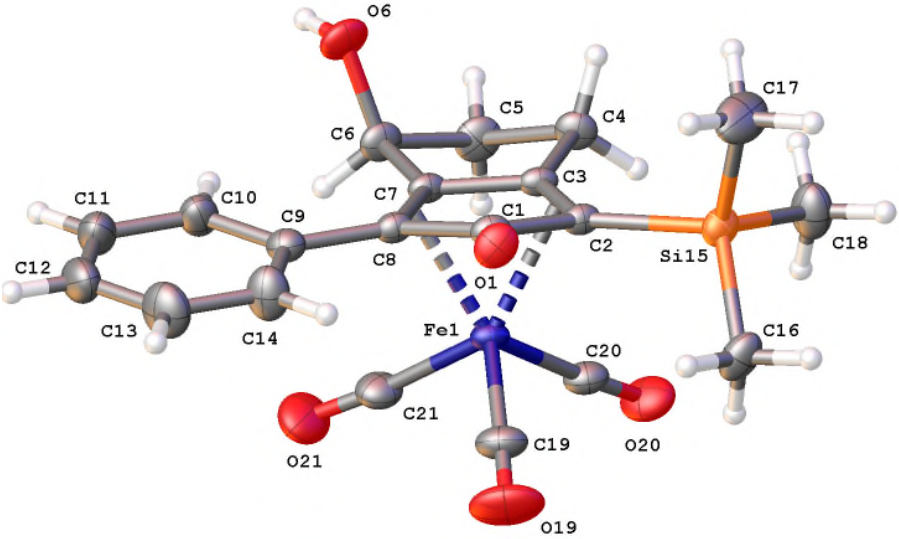
Crystal Data for $C_{26}H_{22}FeO_8$ (M =518.28 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 8.60374(7) Å, b = 14.16447(11) Å, c = 19.76246(18) Å, V = 2408.40(3) Å^3, Z = 4, T = 150(2) K, μ(CuKα) = 5.445 mm^{-1}, $Dcalc$ = 1.429 g/cm^3, 24973 reflections measured (7.68° ≤ 2Θ ≤ 156.408°), 5094 unique (R_{int} = 0.0374, R_{sigma} = 0.0253) which were used in all calculations. The final R_1 was 0.0271 (I > 2σ(I)) and wR_2 was 0.0720 (all data).

Table S10 Crystal data and structure refinement for adg12/CCDC 1567221**.**

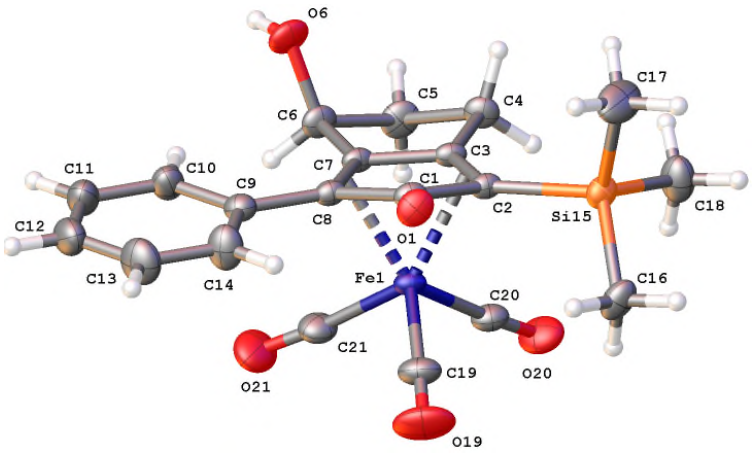
Identification code	adg12
Empirical formula	$C_{26}H_{22}FeO_8$
Formula weight	518.28
Temperature/K	150(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	8.60374(7)
b/Å	14.16447(11)
c/Å	19.76246(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2408.40(3)
Z	4
ρ_{calc}g/cm^3	1.429
μ/mm^{-1}	5.445

F(000)	1072.0
Crystal size/mm^3	0.24 × 0.2 × 0.08 yellow block
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.68 to 156.408
Index ranges	-10 ≤ h ≤ 10, -17 ≤ k ≤ 17, -23 ≤ l ≤ 24
Reflections collected	24973
Independent reflections	5094 [R_{int} = 0.0374, R_{sigma} = 0.0253]
Data/restraints/parameters	5094/1/324
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0271, wR_2 = 0.0716
Final R indexes [all data]	R_1 = 0.0276, wR_2 = 0.0720
Largest diff. peak/hole / e Å^{-3}	0.25/-0.23
Flack parameter	-0.0076(17)

X-ray Crystallographic data for 40 (local code adg7, CCDC 1567218)



solid state structure of adg7/CCDC 1567218 with atom labeling and thermal ellipsoids drawn at 50% probability Below; different view.



Crystal structure determination of adg7/CCDC 1567218 (least polar/first off the column). The asymmetric unit contains the iron complex, there are four in the unit cell.

The OH was located in a difference map and refined with a DFIX restraint and given thermal ellipsoids Uiso 1.5 times the Uequiv of the parent oxygen. It forms short contacts tabulated below.

Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)	
0.85(2)	1.98(2)	2.7868(17)	160(3)	O6-H6...O1_$1

Symmetry operator used to generate equivalent atoms in above contact was $1 2-X,-0.5+Y,0.5-Z. The angle between a mean planes through the carbonyl and a mean plane through the diene described by the atoms C8 C1 O1 C2 to C2 C3 C7 C8 is 13.689 (0.073) degrees. The angle between the diene and the phenyl described by mean planes through the atoms C2 C3 C7 C8 to C9 C10 C11 C12 C13 C14 is 5.249 (0.054) degrees. The flack parameter refines to -0.018(4) which is small with a low error so we can have confidence in the assignment of the handedness of the crystal chosen.

Flack x = -0.015(10) by classical fit to all intensities (Shelx 2014)

-0.018(4) from 2542 selected quotients (Parsons' method)

Hooft y: -0.018(3) Olex2

Experimental for adg7/CCDC 1567218.

Single crystals of $C_{20}H_{20}FeO_5Si$ were grown from DCM/hexane. A suitable crystal was selected and mounted on a Mitegen head with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K

during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

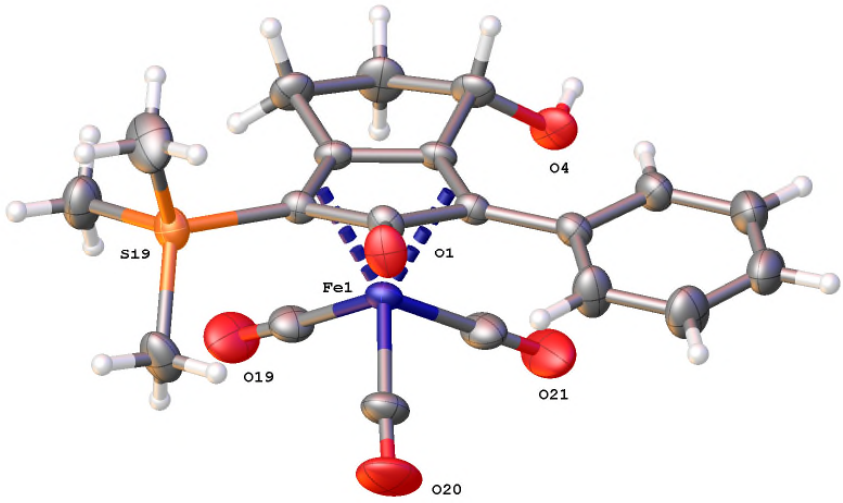
Crystal Data for $C_{20}H_{20}FeO_5Si$ (*M* =424.30 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 6.56456(12) Å, *b* = 15.9301(3) Å, *c* = 19.5077(4) Å, *V* = 2040.00(7) Å^3, *Z* = 4, *T* = 150(2) K, μ(MoKα) = 0.825 mm^{-1}, *Dcalc* = 1.381 g/cm^3, 38542 reflections measured (5.114° ≤ 2Θ ≤ 64.782°), 6932 unique (R_{int} = 0.0315, R_{sigma} = 0.0234) which were used in all calculations. The final R_1 was 0.0256 (I > 2σ(I)) and wR_2 was 0.0638 (all data).

Table S11 Crystal data and structure refinement for adg7/CCDC 1567218**.**

Identification code	adg7
Empirical formula	$C_{20}H_{20}FeO_5Si$
Formula weight	424.30
Temperature/K	150(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	6.56456(12)
b/Å	15.9301(3)
c/Å	19.5077(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2040.00(7)
Z	4
ρ_{calc}g/cm^3	1.381
μ/mm^{-1}	0.825
F(000)	880.0
Crystal size/mm^3	0.38 × 0.38 × 0.06 yellow block

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.114 to 64.782
Index ranges	$-9 \leq h \leq 9, -23 \leq k \leq 23, -26 \leq l \leq 28$
Reflections collected	38542
Independent reflections	6932 [R_{int} = 0.0315, R_{sigma} = 0.0234]
Data/restraints/parameters	6932/1/250
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0256, wR_2 = 0.0618
Final R indexes [all data]	R_1 = 0.0306, wR_2 = 0.0638
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.18
Flack parameter	-0.018(4)

X-ray Crystallographic data for 41 (local code adg10, CCDC 1567219).



Solid state structure of adg10/CCDC 1567219 with only key atoms labeled and thermal ellipsoids drawn at 50% probability level

Crystal structure determination of adg10/CCDC 1567219.

The asymmetric unit contains the complex, there are four in the unit cell.

OH located in a difference map but was placed at calculate position during refinement.

It forms a short contact to the C=O of a symmetry related complex tabulated below

Specified hydrogen bonds (with esds except fixed and riding H)

D-H	H...A	D...A	<(DHA)

0.84	1.91	2.7226(16)	161.5	O4-H4A...O1_$1

Symmetry operator used to generate equivalent atom in above contact
$1 2-X,-0.5+Y,1.5-Z

The pucker in the coordinated cyclopentadieneone ring is described by mean planes through the diene system and the atoms of the ketone and its alpha carbons described below
C2 C3 C7 C8 to O1 C1 C2 C8 is 15.761 (0.073) degrees

The Flack parameter as a measure of the confidence you can have in the assignment of the handedness of the crystal chosen. It is low with a low error so we can be confident in the stereochemistry shown.
Flack x: -0.012(4) Shelx 2014
Hooft y: -0.012(3) Olex2

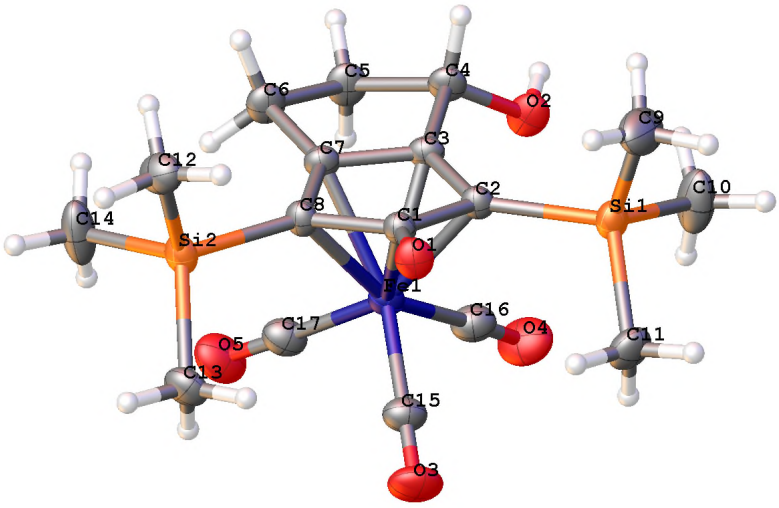
Experimental for adg10/CCDC 1567219.
Single crystals of $C_{20}H_{20}FeO_5Si$ were grown from DCM/hexane. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.
1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal Data for $C_{20}H_{20}FeO_5Si$ (M =424.30 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.66446(13) Å, b = 16.1511(3) Å, c = 19.2420(4) Å, V = 2071.18(7) Å^3, Z = 4, T = 150(2) K, μ(MoKα) = 0.812 mm^{-1}, *Dcalc* = 1.361 g/cm^3, 104348 reflections measured (6.47° ≤ 2Θ ≤ 75.62°), 10846 unique (R_{int} = 0.0506, R_{sigma} = 0.0249) which were used in all calculations. The final R_1 was 0.0324 (I > 2σ(I)) and wR_2 was 0.0796 (all data).

Table S12 Crystal data and structure refinement for adg10/CCDC 1567219**.**

Identification code	adg10
Empirical formula	$C_{20}H_{20}FeO_5Si$
Formula weight	424.30
Temperature/K	150(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	6.66446(13)
b/Å	16.1511(3)
c/Å	19.2420(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2071.18(7)
Z	4
ρ_{calc}g/cm^3	1.361
μ/mm^{-1}	0.812
F(000)	880.0
Crystal size/mm^3	0.6 × 0.4 × 0.06 yellow block
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.47 to 75.62
Index ranges	$-11 \leq h \leq 11$, $-26 \leq k \leq 27$, $-33 \leq l \leq 32$
Reflections collected	104348
Independent reflections	10846 [R_{int} = 0.0506, R_{sigma} = 0.0249]
Data/restraints/parameters	10846/0/248
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0753
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.0796
Largest diff. peak/hole / e Å^{-3}	0.38/-0.26
Flack parameter	-0.012(4)

X-ray Crystallographic data for (-)-45 (local code Adg3, CCDC 1567222)



Solid state structure of adg3/CCDC1567222 with atom labels and thermal ellipsoids at 50% probability level.

Experimental for **adg3**/CCDC 1567222.

Single crystals of $C_{17}H_{24}FeO_5Si_2$ were grown by evaporation of ethyl acetate under a flow of air. A suitable crystal was selected and mounted on a glass fibre with Fromblin oil on a Xcalibur, Ruby, Gemini diffractometer. The crystal was kept at 150(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of adg3/CCDC 1567222.

Crystal Data for $C_{17}H_{24}FeO_5Si_2$ (M =420.39 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.73153(6) Å, b = 16.18105(14) Å, c = 19.25027(18) Å, V = 2096.80(3) Å^3, Z = 4, T = 150(2) K, μ(CuKα) = 7.059 mm^{-1}, *Dcalc* = 1.332 g/cm^3, 15756 reflections measured (7.136° ≤ 2Θ ≤ 156.076°), 4439 unique (R_{int} = 0.0424, R_{sigma} = 0.0380) which were used in all calculations. The final R_1 was 0.0301 (I > 2σ(I)) and wR_2 was 0.0772 (all data).

Table S13 Crystal data and structure refinement for adg3/CCDC 1567222.

Identification code	adg3
Empirical formula	$C_{17}H_{24}FeO_5Si_2$
Formula weight	420.39
Temperature/K	150(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.73153(6)
b/Å	16.18105(14)
c/Å	19.25027(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2096.80(3)
Z	4
ρ_{calc}g/cm^3	1.332
μ/mm^{-1}	7.059
F(000)	880.0
Crystal size/mm^3	0.38 × 0.16 × 0.016
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.136 to 156.076
Index ranges	$-6 \leq h \leq 8$, $-20 \leq k \leq 20$, $-24 \leq l \leq 24$
Reflections collected	15756
Independent reflections	4439 [R_{int} = 0.0424, R_{sigma} = 0.0380]
Data/restraints/parameters	4439/0/233
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0301, wR_2 = 0.0764
Final R indexes [all data]	R_1 = 0.0311, wR_2 = 0.0772

Largest diff. peak/hole / e $Å^{-3}$	0.42/-0.23
Flack parameter	-0.010(2)