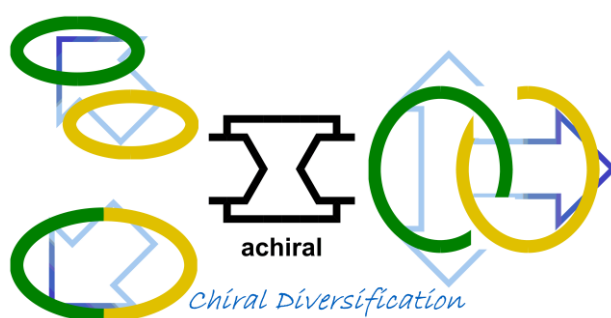


Supplementary Information 2

Chiral diversification through the assembly of achiral phenylacetylene macrocycles with a two-fold bridge

Ryo Katoono,* Keiichi Kusaka, Yuki Saito, Kazuki Sakamoto and Takanori Suzuki

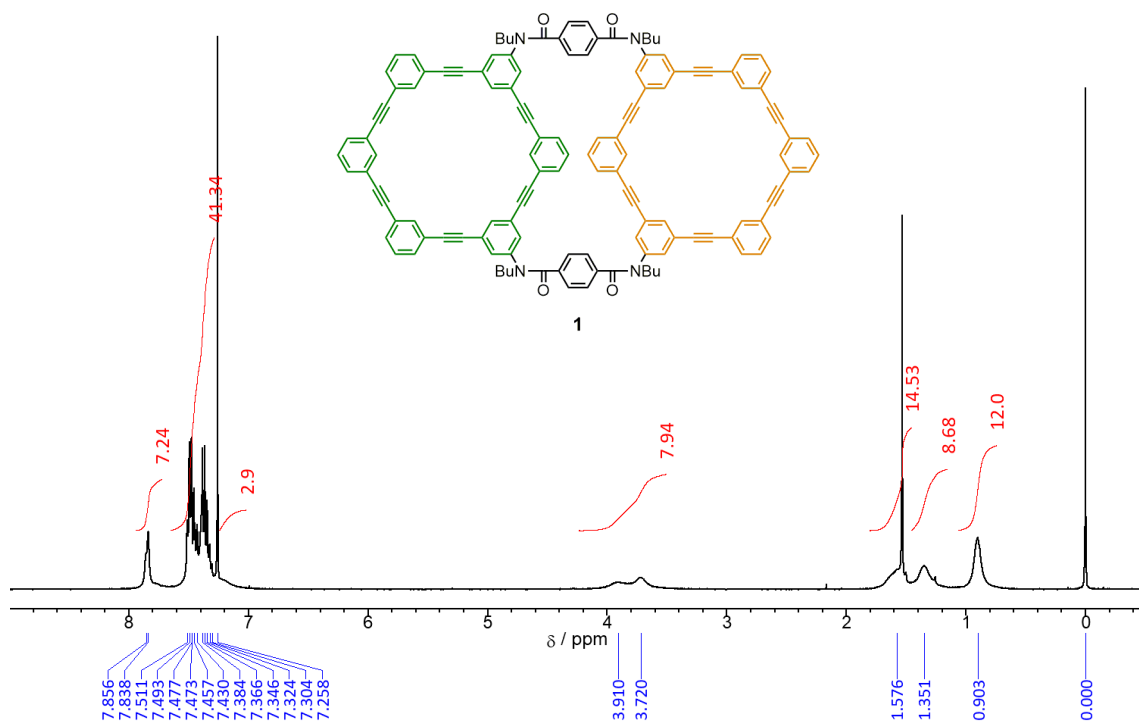
Department of Chemistry, Faculty of Science, Hokkaido University



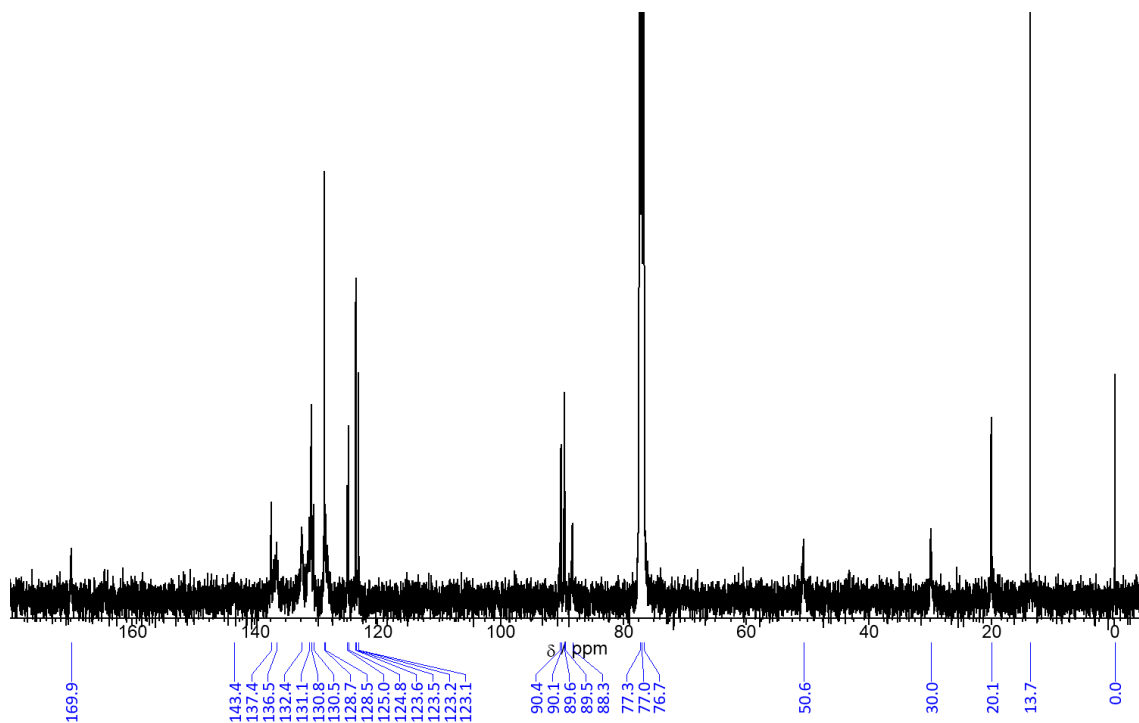
Contents

Copies of ^1H and ^{13}C NMR, IR and mass spectra of new compounds	S40-S76
Copies of ^1H NMR spectrum of new compounds (unprotected)	S77-S80
Copies of chiral HPLC traces	S81

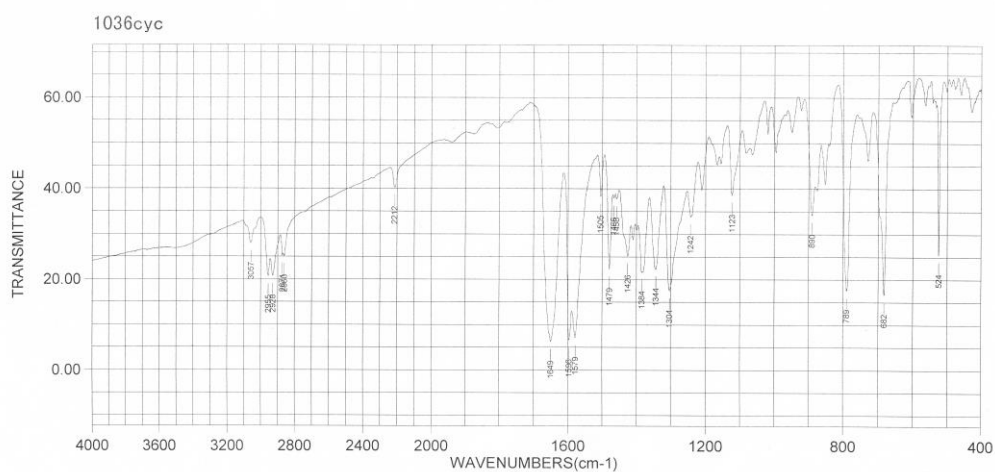
^1H and ^{13}C NMR spectra of new compounds



^1H NMR (400 MHz) spectrum of **1**, measured in chloroform-*d* at 303 K.



^{13}C NMR (100 MHz) spectrum of **1**, measured in chloroform-*d* at 313 K.



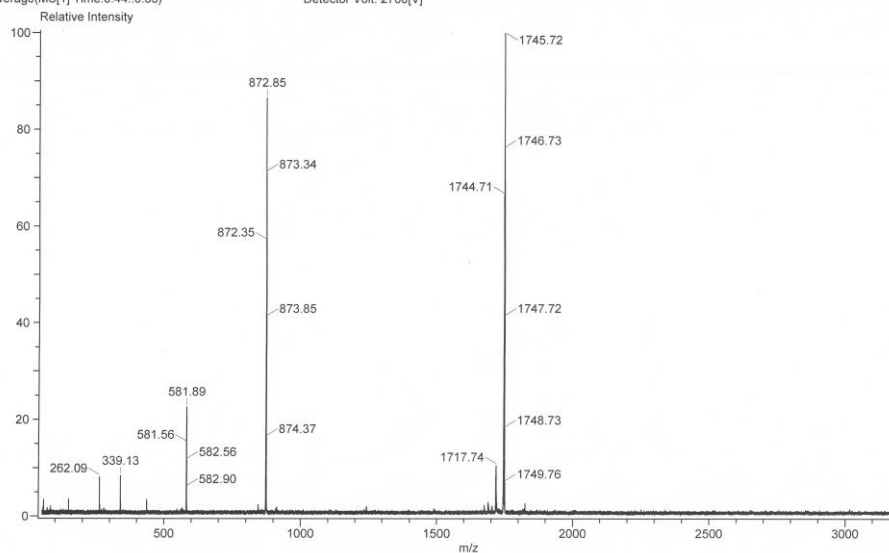
RESOL	: 2 cm-1	3057.62	27.99	1479.15	22.39	789.72	17.71
SCANS	: 5	2955.41	20.71	1466.62	38.01	682.69	16.73
AMP GAIN	: x1	2928.41	20.78	1458.90	37.87	524.55	25.55
P. INT	: 1 cm-1	2871.52	25.26	1426.12	25.26		
BEAM	: single	2860.92	25.21	1384.66	21.65		
S. SPEED	: TGS	2212.94	40.34	1344.16	22.33		
M. DATE	: 11/2/18	1649.92	6.33	1304.62	17.57		
F. NAME	: 測定中のデータ	1596.79	6.63	1242.91	33.93		
		1579.43	7.15	1123.35	38.64		
		1505.19	38.39	890.96	34.26		

IR spectrum of 1.

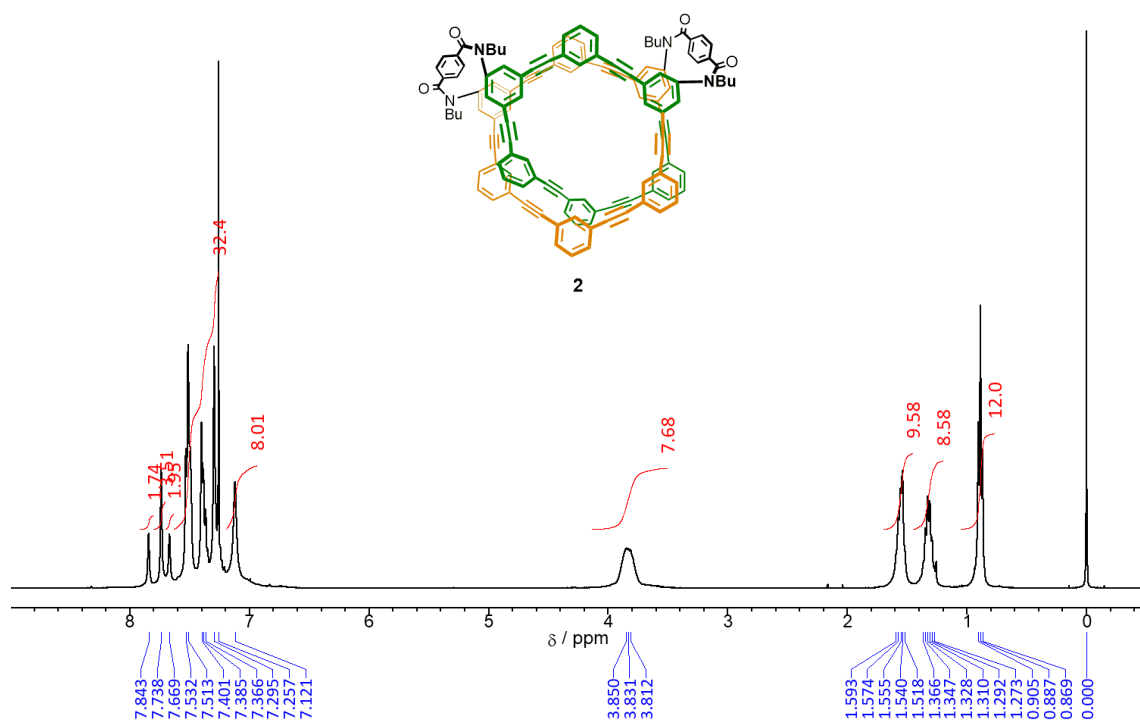
Data: common/Nov06:a00359-7
 Sample: 3396 Katono / 1036 cyc
 Experiment Date/Time: 2018/11/06 14:01:57
 Average[MS(1)] Time:0.44,0.55

Instrument Configuration: FD700-J,JMS-T100GCV
 Ionization Mode: FD+
 Acquired m/z Range: 50.00,3200.00
 Detector Volt: 2700[V]

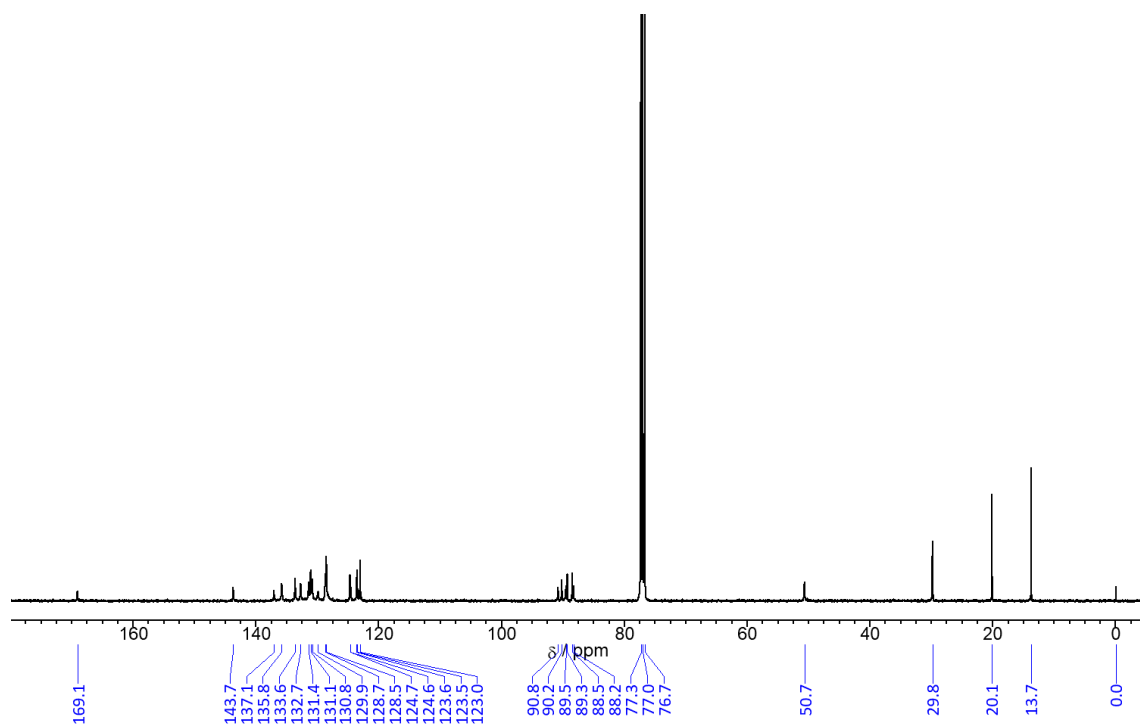
MS Tune Method Name: FD
 Agilent7890A Method Name: -



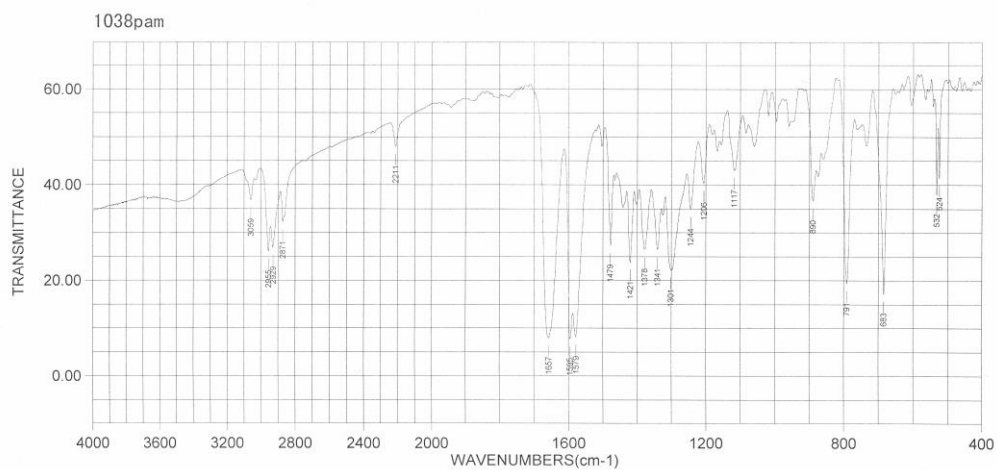
Mass spectrum (FD) of 1.



^1H NMR (400 MHz) spectrum of **2**, measured in chloroform-*d* at 303 K.

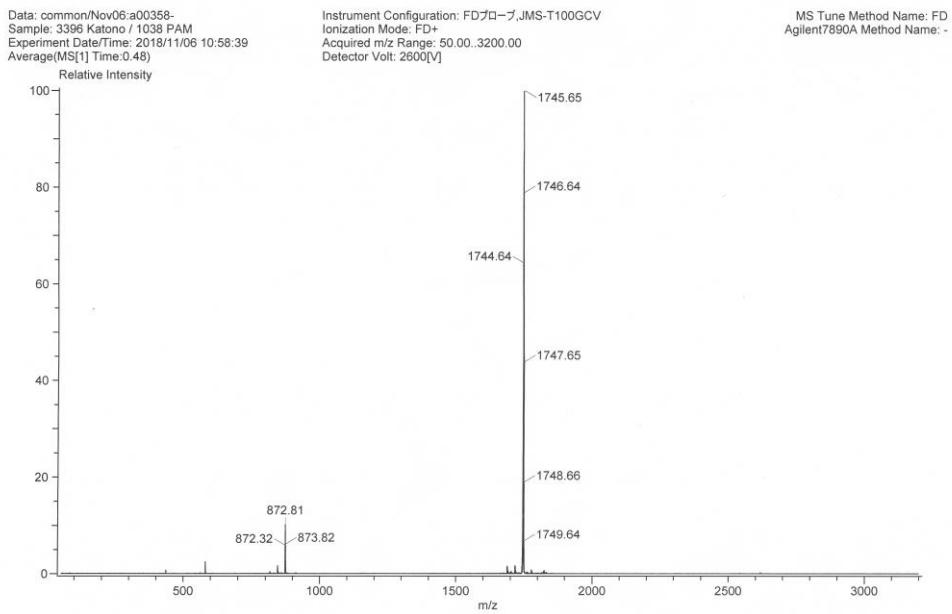


^{13}C NMR (100 MHz) spectrum of **2**, measured in chloroform-*d* at 313 K.

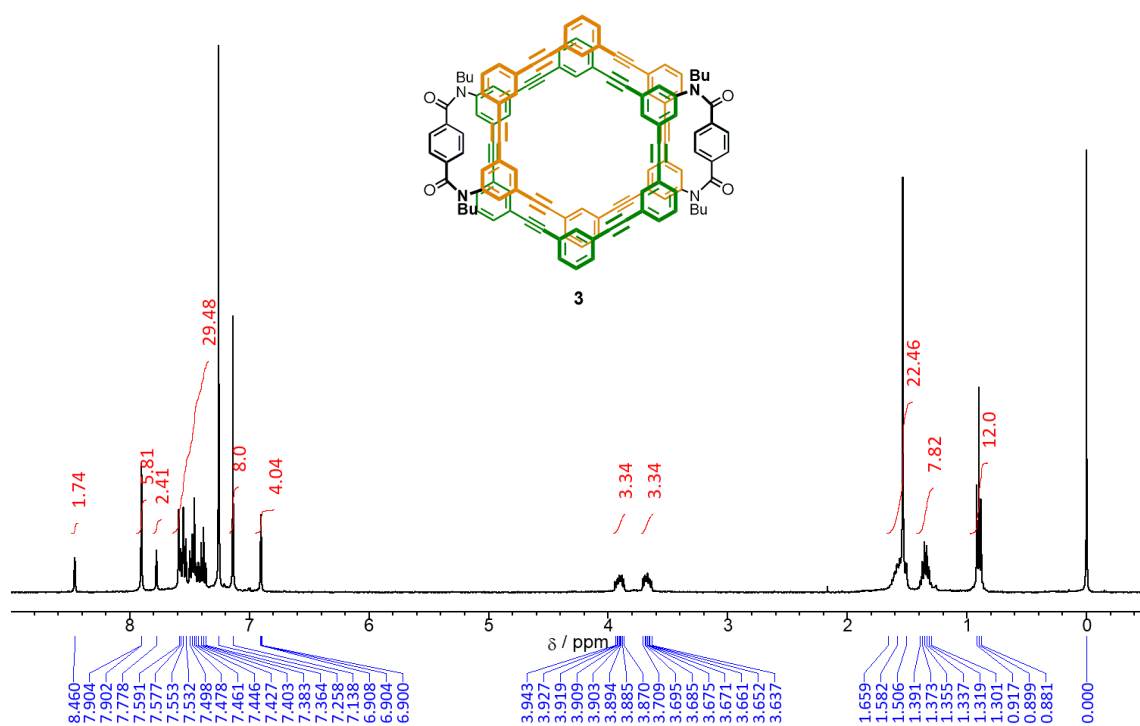


RESOL	: 2	cm-1	3059.55	36.89	1378.87	26.56	524.55	41.53
SCANS	: 5		2955.41	26.11	1341.26	26.55		
AMPGAIN	: x1		2929.38	26.97	1301.73	22.21		
P. INT	: 1	cm-1	2871.52	32.30	1244.84	34.95		
BEAM	: single		2211.98	48.06	1206.27	40.44		
S. SPEED	: TGS		1657.54	8.01	1117.56	43.07		
M. DATE	: 11/2/18		1595.83	7.80	890.96	36.70		
F. NAME	: 測定中のデータ		1579.43	8.22	791.65	19.40		
			1479.15	27.38	683.65	17.27		
			1421.30	23.87	532.26	38.10		

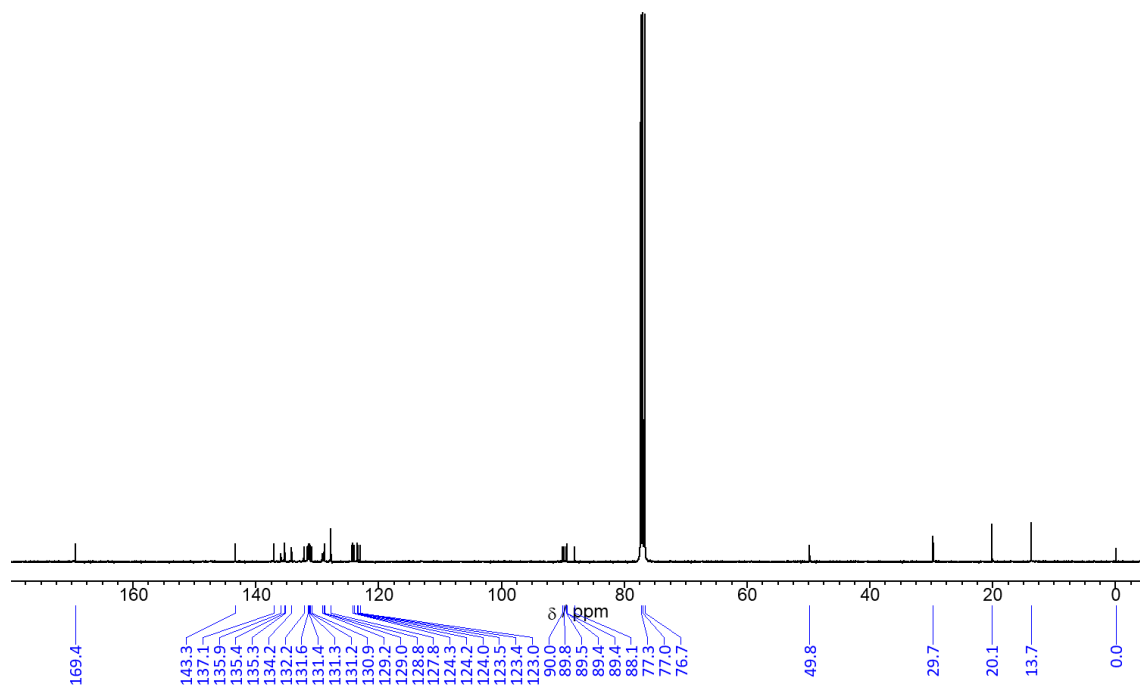
IR spectrum of 2.



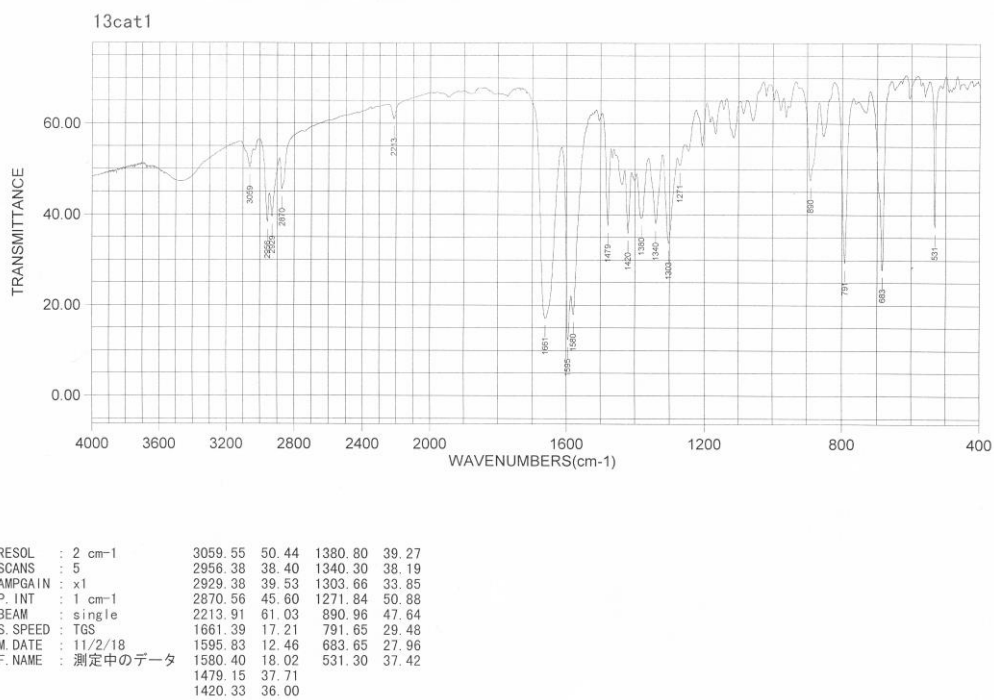
Mass spectrum (FD) of 2.



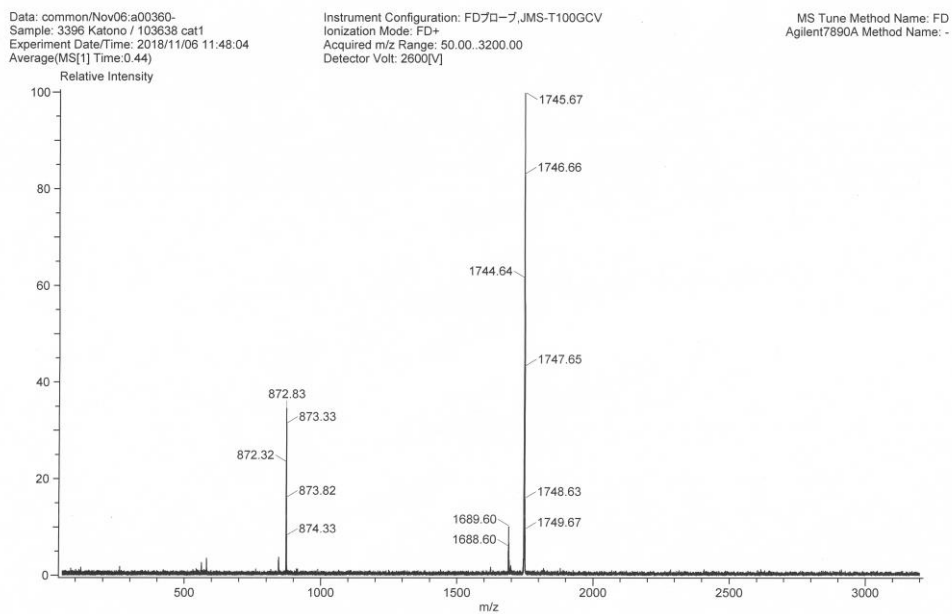
^1H NMR (400 MHz) spectrum of (\pm)-**3**, measured in chloroform-*d* at 303 K.



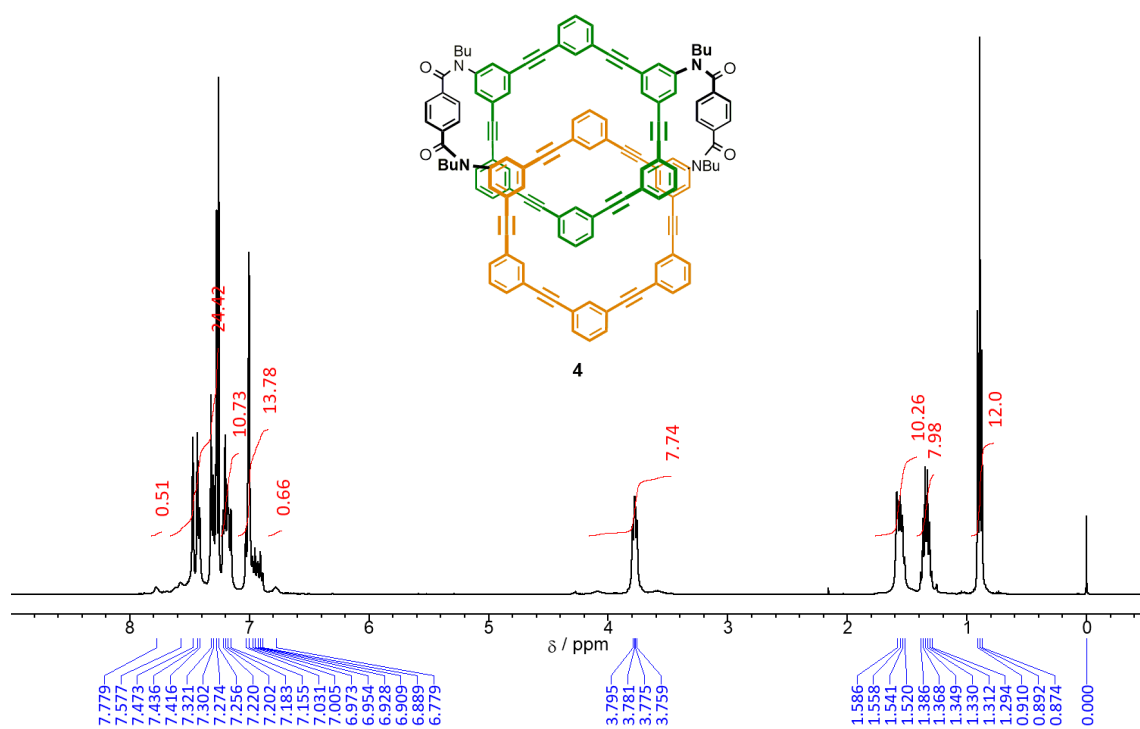
^{13}C NMR (100 MHz) spectrum of (\pm)-**3**, measured in chloroform-*d* at 313 K.



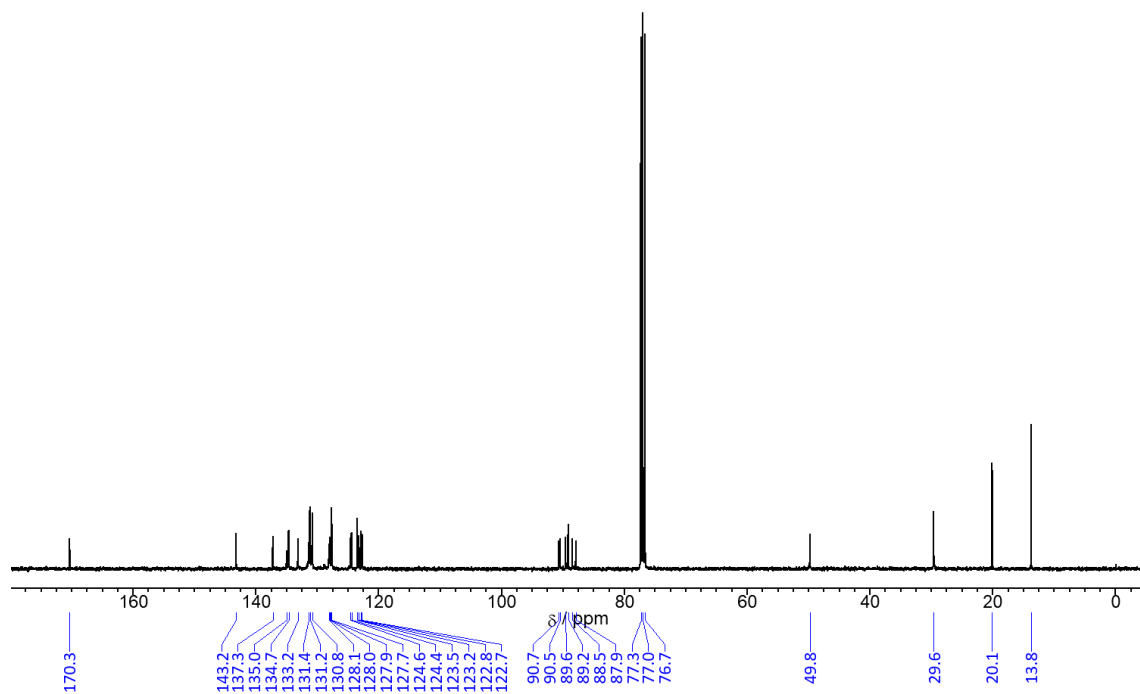
IR spectrum of (\pm)-3.



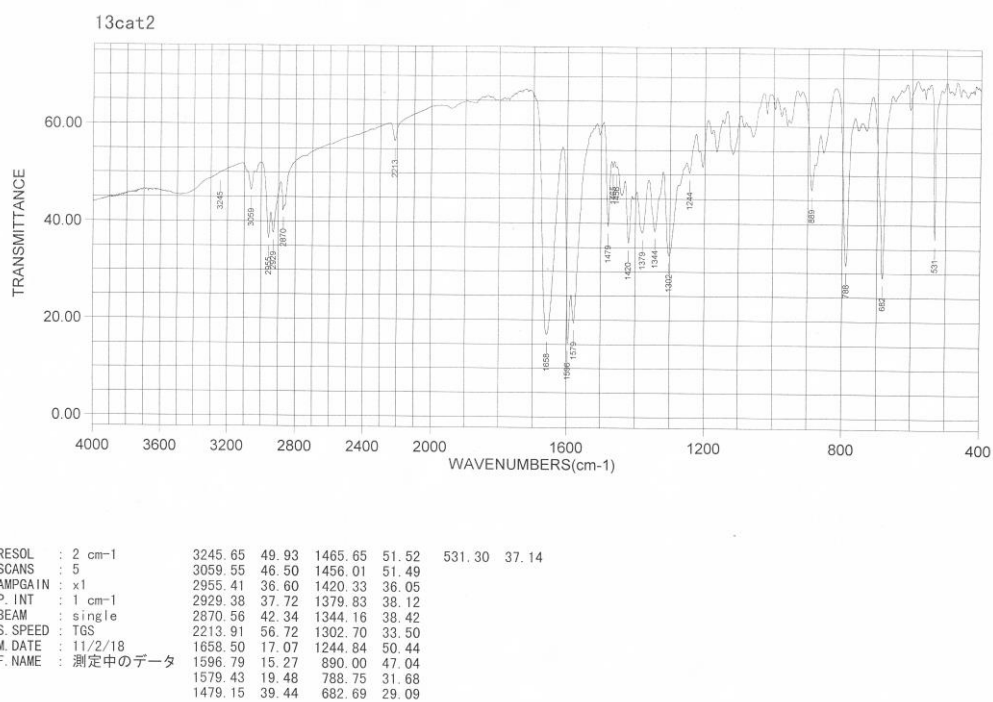
Mass spectrum (FD) of (\pm)-3.



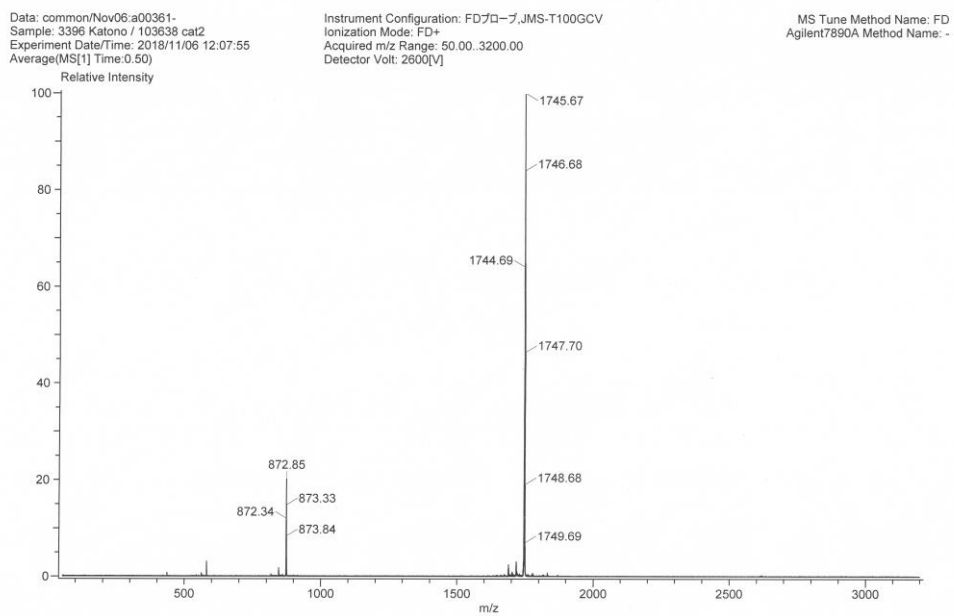
^1H NMR (400 MHz) spectrum of (\pm)-4, measured in chloroform-*d* at 303 K.



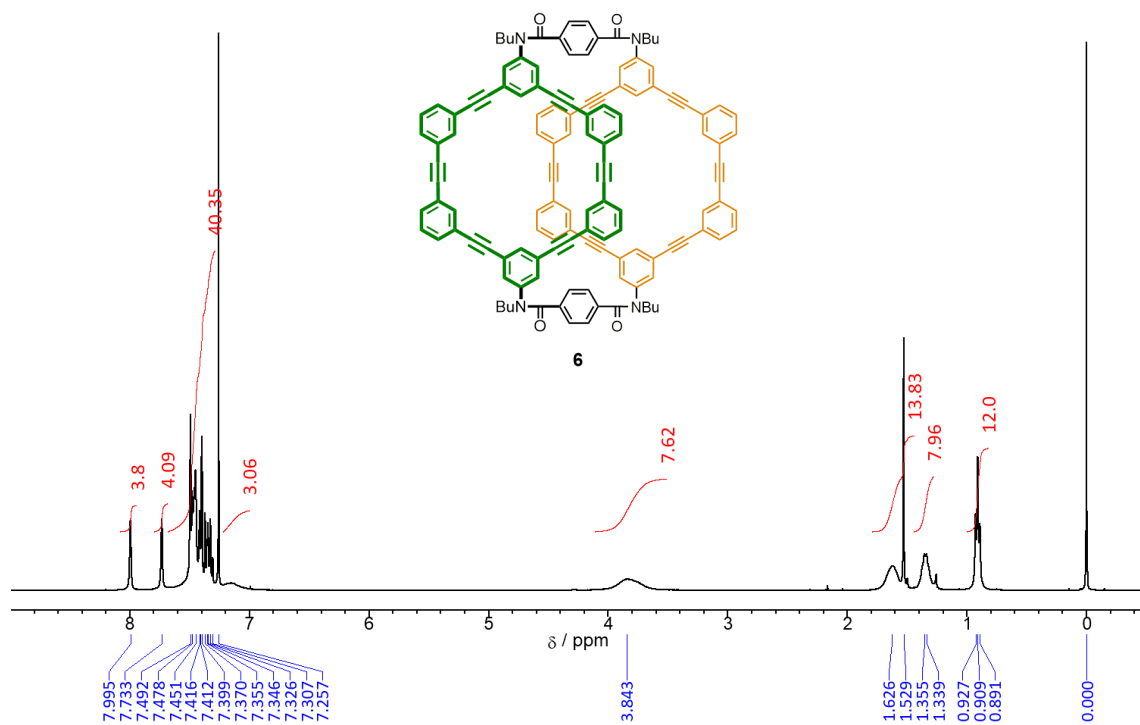
^{13}C NMR (100 MHz) spectrum of (\pm)-4, measured in chloroform-*d* at room temperature.



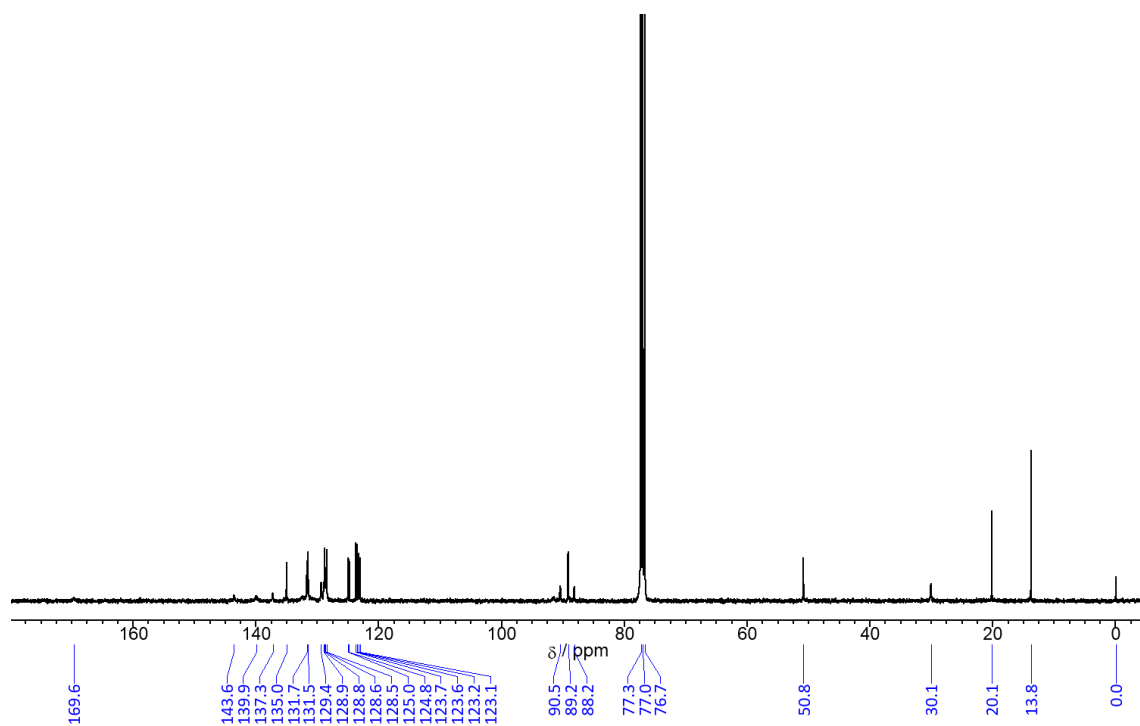
IR spectrum of (\pm)-4.



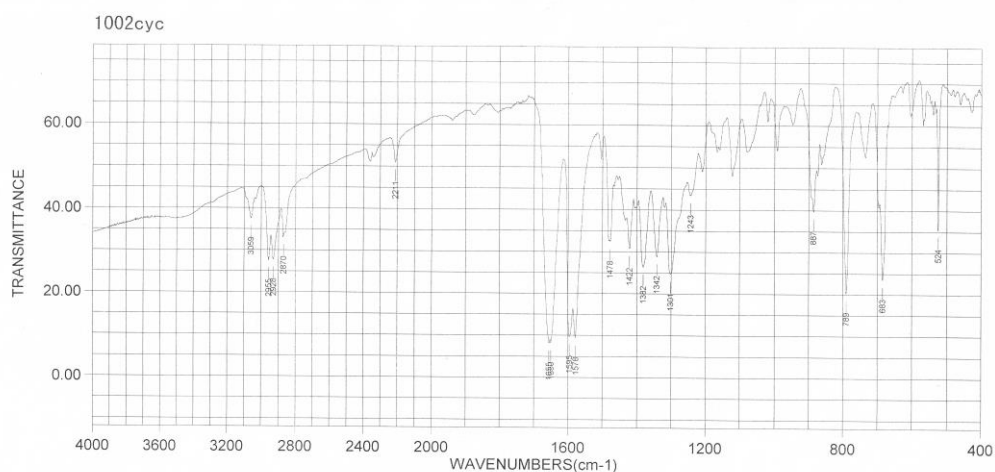
Mass spectrum (FD) of (\pm)-4.



¹H NMR (400 MHz) spectrum of **6**, measured in chloroform-*d* at 303 K.

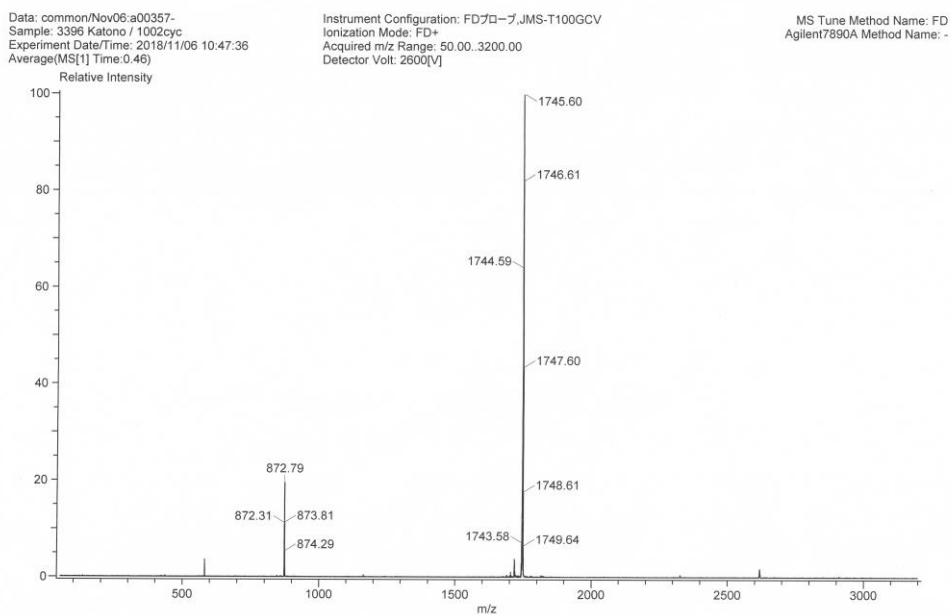


¹³C NMR (100 MHz) spectrum of **6**, measured in chloroform-*d* at 313 K.

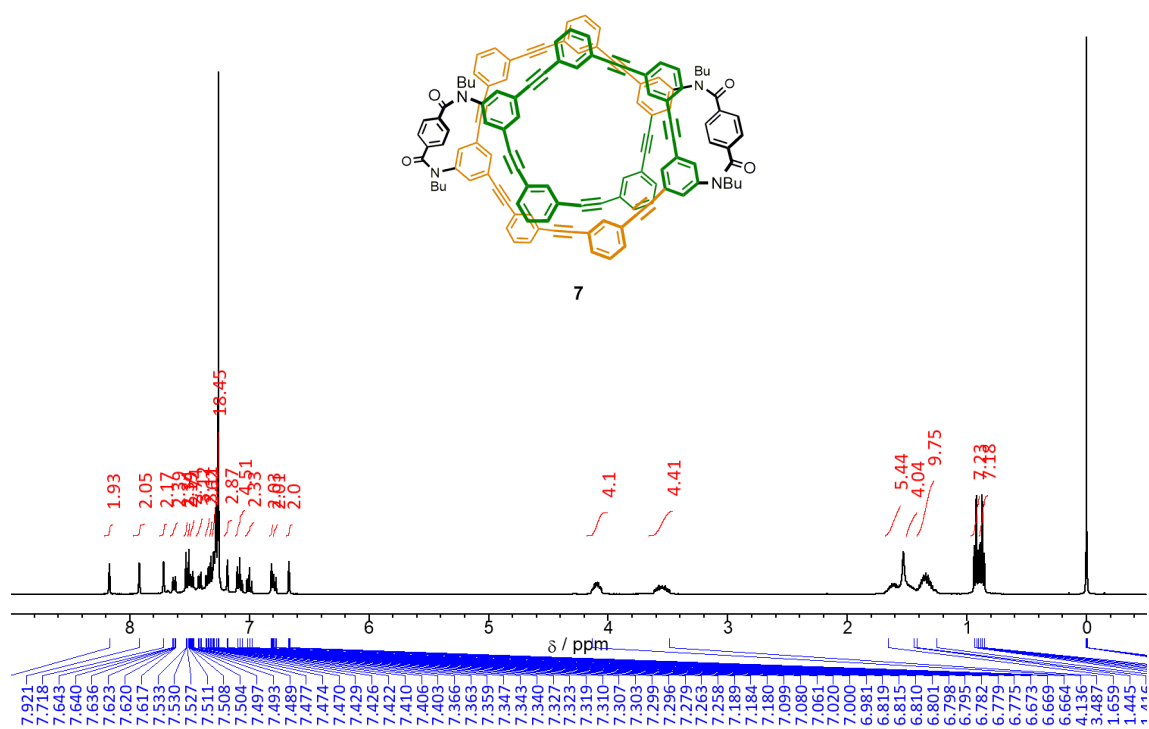


RESOL	: 2 cm-1	3059.55	37.59	1422.26	30.82
SCANS	: 5	2955.41	27.62	1382.73	26.47
AMP GAIN	: x1	2928.41	27.80	1342.23	28.88
P. INT	: 1 cm-1	2870.56	33.07	1301.73	24.77
BEAM	: single	2211.98	51.06	1243.88	43.43
S. SPEED	: TGS	1655.61	8.20	887.11	39.74
M. DATE	: 11/2/18	1650.79	8.31	789.72	20.39
F. NAME	: 測定中のデータ	1595.83	9.79	683.65	23.60
		1578.47	9.46	524.55	35.52
		1478.19	32.49		

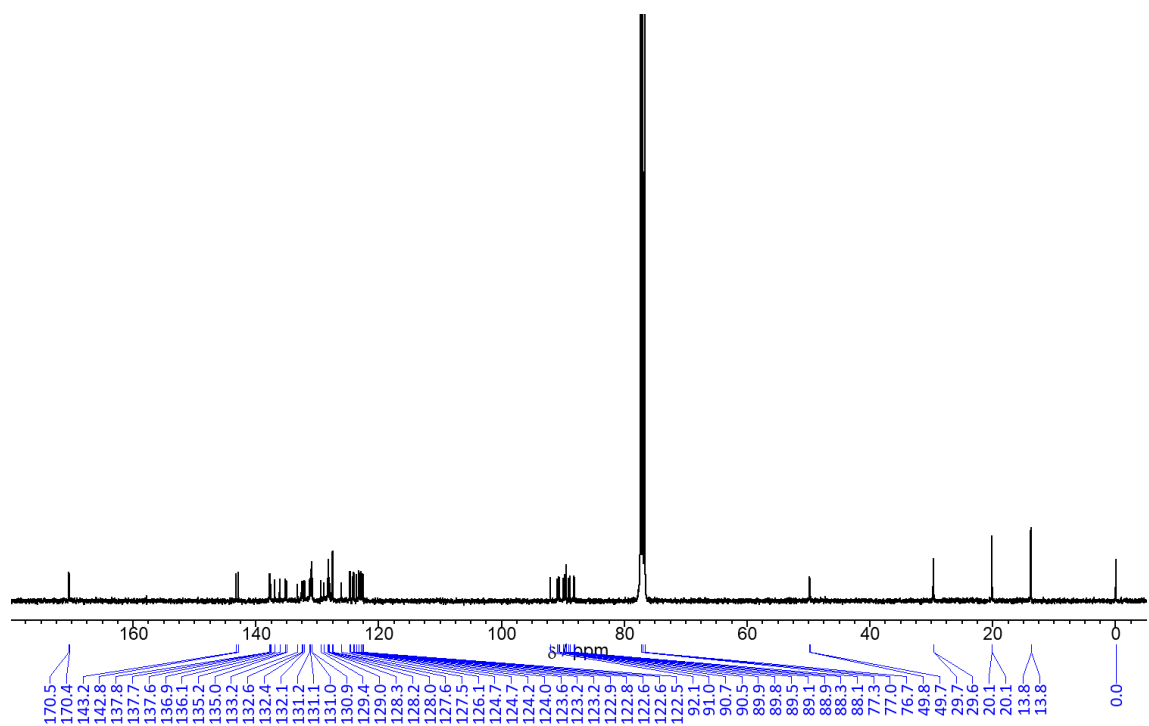
IR spectrum of 6.



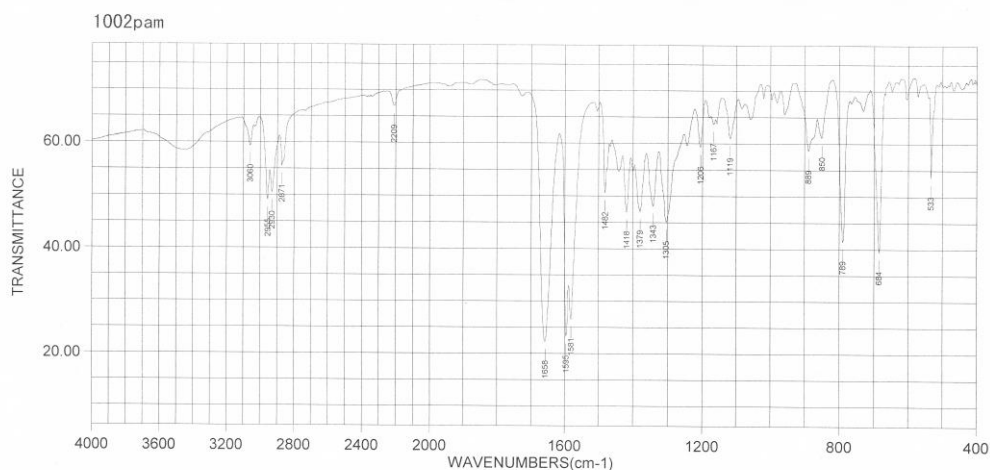
Mass spectrum (FD) of 6.



^1H NMR (400 MHz) spectrum of **7**, measured in chloroform-*d* at 303 K.

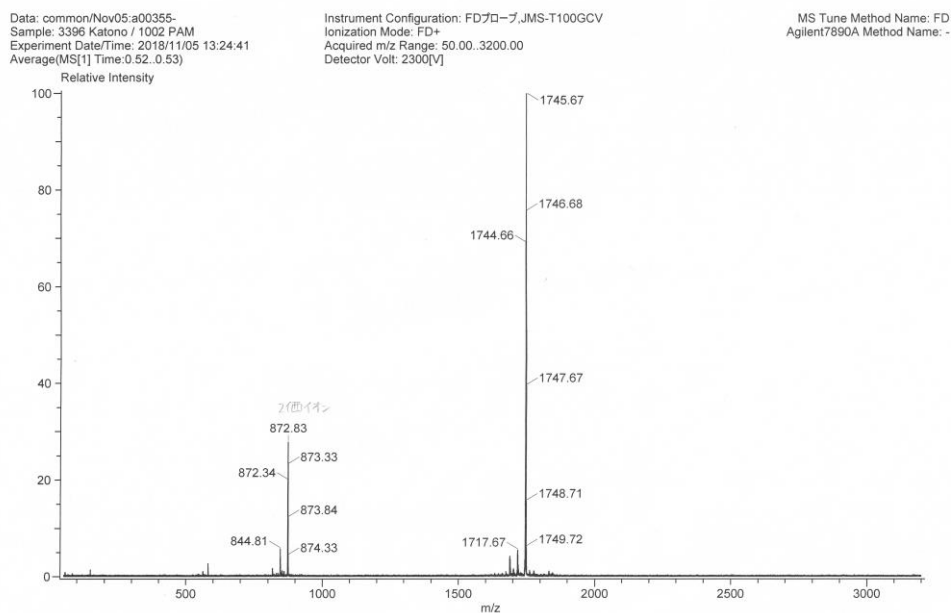


^{13}C NMR (100 MHz) spectrum of **7**, measured in chloroform-*d* at room temperature.

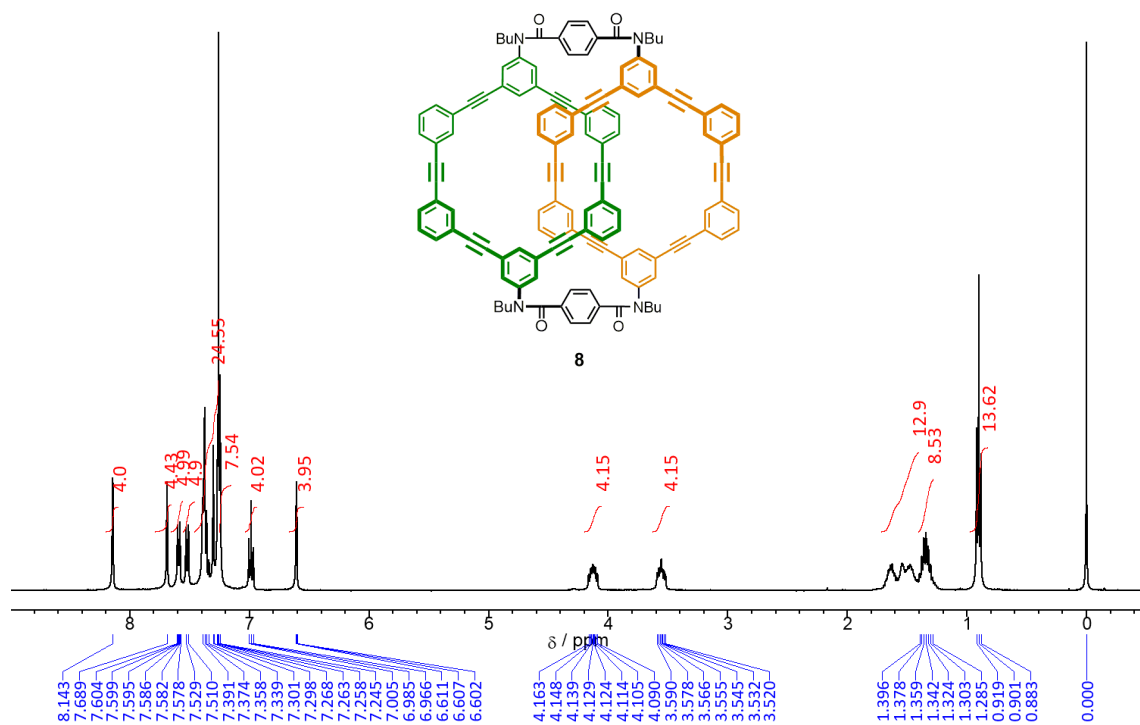


RESOL	: 2 cm ⁻¹	3060.51	59.30	1379.83	47.11	533.23	53.77
SCANS	: 5	2955.41	49.06	1343.19	48.12		
AMPGAIN	: x1	2930.34	50.44	1305.59	45.14		
P. INT	: 1 cm ⁻¹	2871.52	55.52	1206.27	59.32		
BEAM	: single	2209.09	66.94	1167.70	63.71		
S. SPEED	: TGS	1658.50	22.31	1119.49	60.97		
M. DATE	: 11/2/18	1595.83	23.34	889.03	58.69		
F. NAME	: 測定中のデータ	1581.36	26.55	850.46	61.14		
		1482.04	50.58	789.72	41.46		
		1418.40	47.01	684.61	39.52		

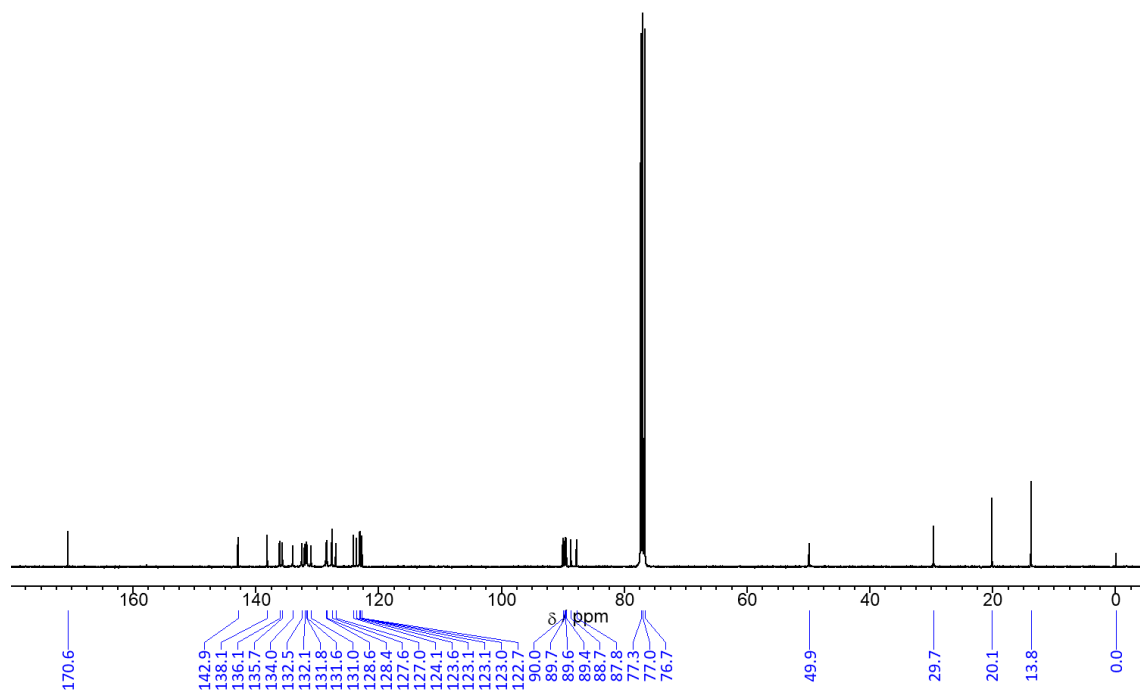
IR spectrum of 7.



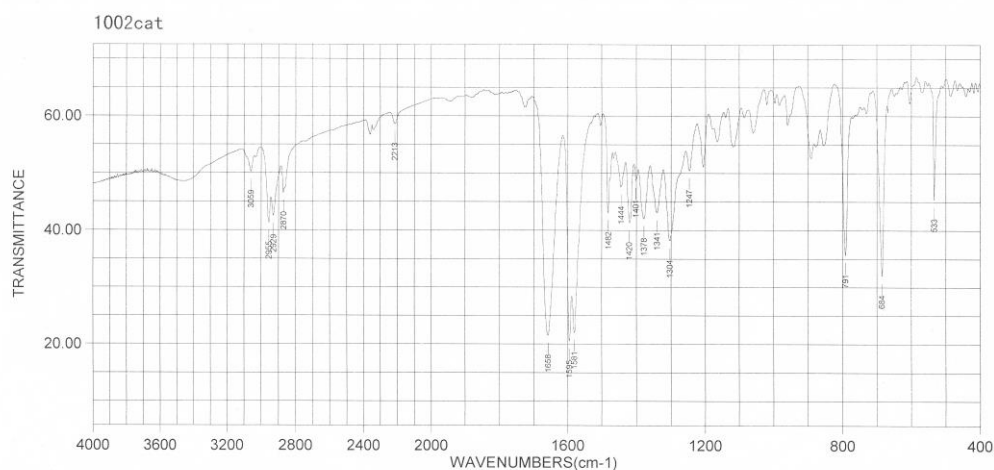
Mass spectrum (FD) of 7.



¹H NMR (400 MHz) spectrum of (\pm)-**8**, measured in chloroform-*d* at 303 K.

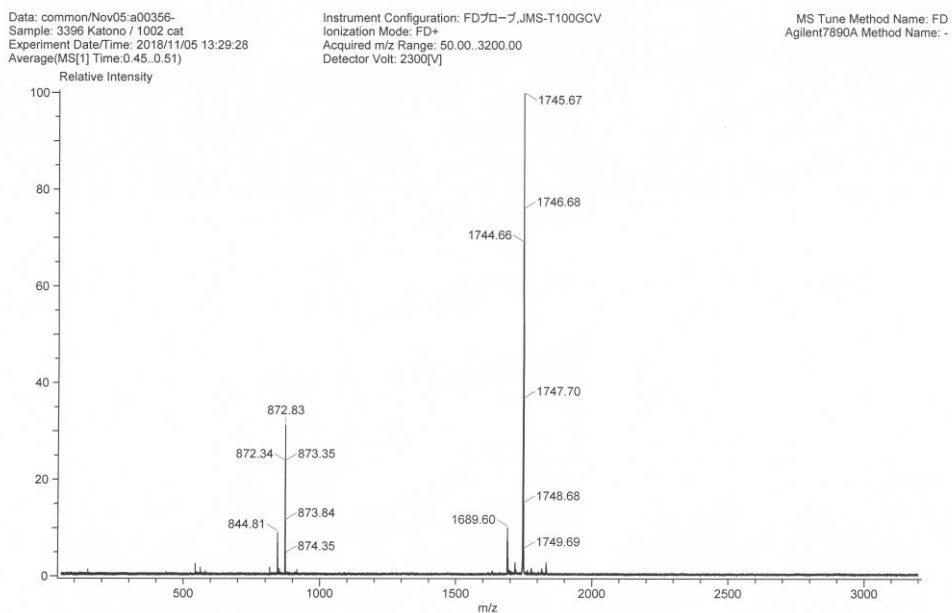


¹³C NMR (100 MHz) spectrum of (\pm)-**8**, measured in chloroform-*d* at room temperature.

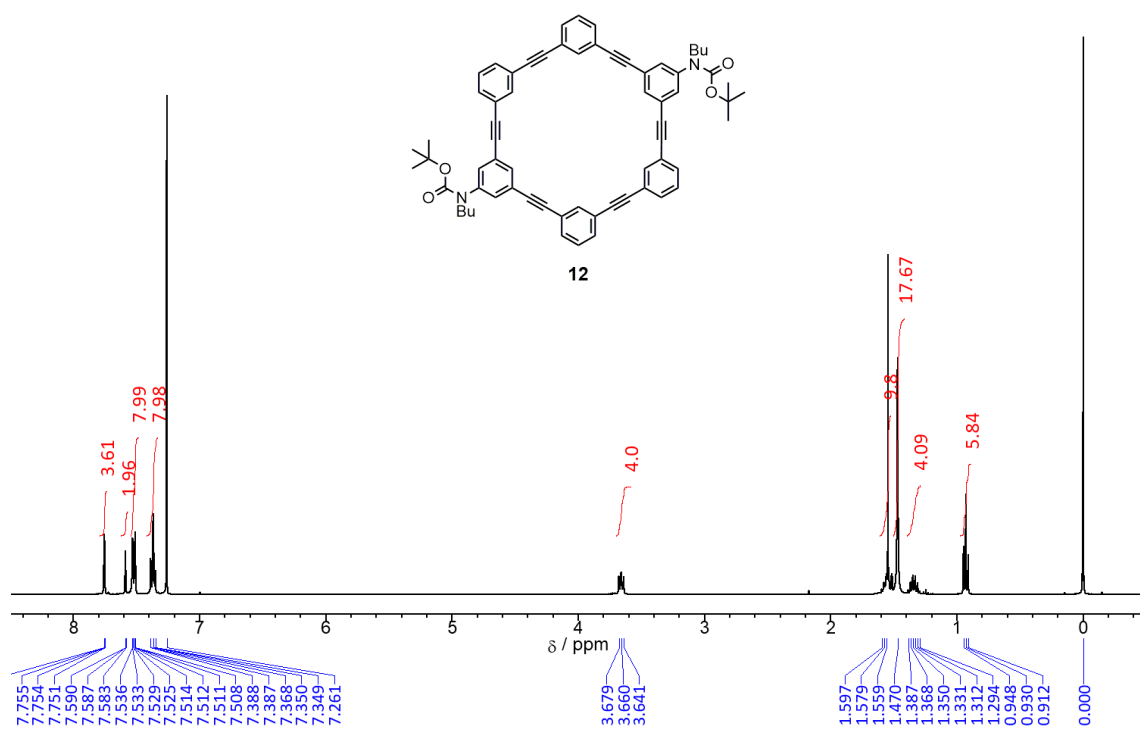


RESOL	: 2 cm-1	3059.55	50.29	1420.33	41.31
SCANS	: 5	2955.41	41.31	1401.05	48.78
AMPGAIN	: x1	2929.38	42.53	1378.87	42.06
P. INT	: 1 cm-1	2870.56	46.54	1341.26	43.09
BEAM	: single	2213.91	58.66	1304.62	38.20
S. SPEED	: TGS	1658.50	21.54	1247.73	50.51
M. DATE	: 11/2/18	1595.83	20.55	791.65	35.69
F. NAME	: 測定中のデータ	1482.04	43.11	533.23	45.47
		1444.44	47.59		

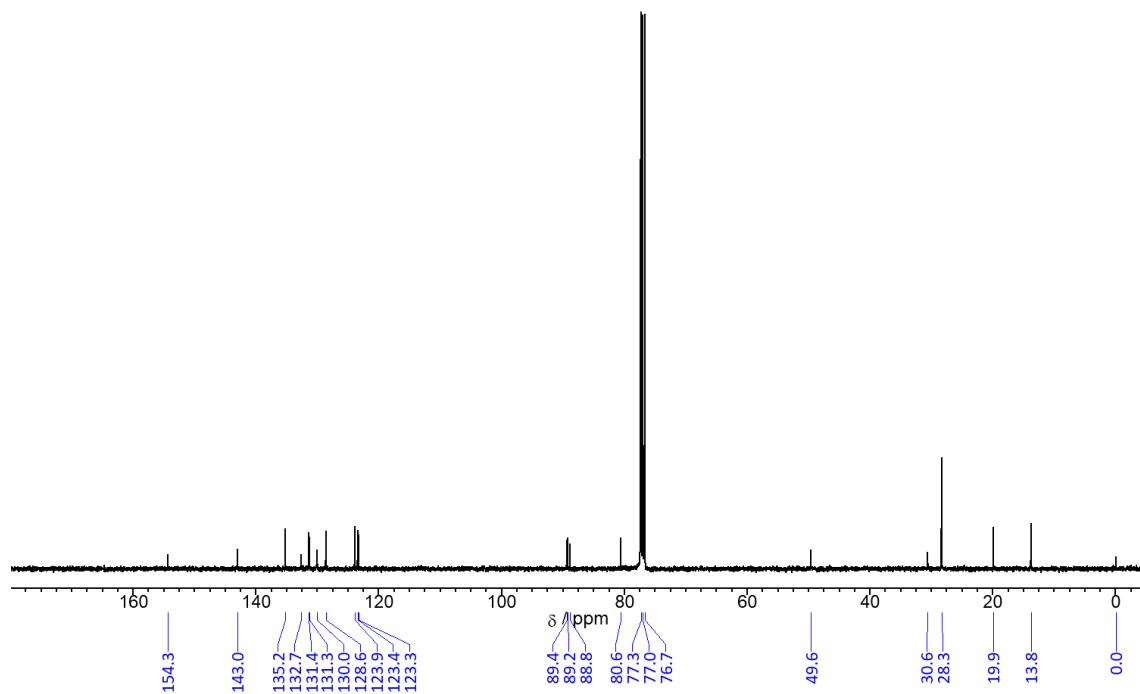
IR spectrum of (\pm)-8.



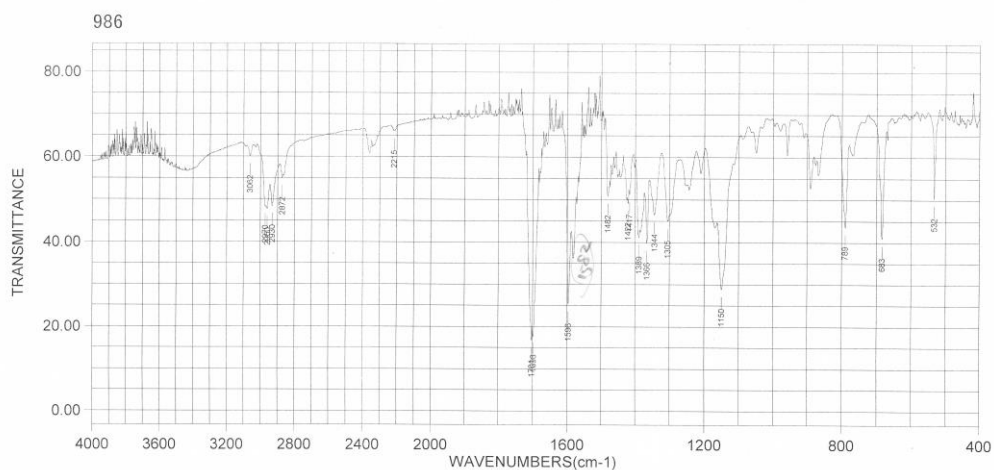
Mass spectrum (FD) of (\pm)-8.



^1H NMR (400 MHz) spectrum of **12**, measured in chloroform-*d* at room temperature.

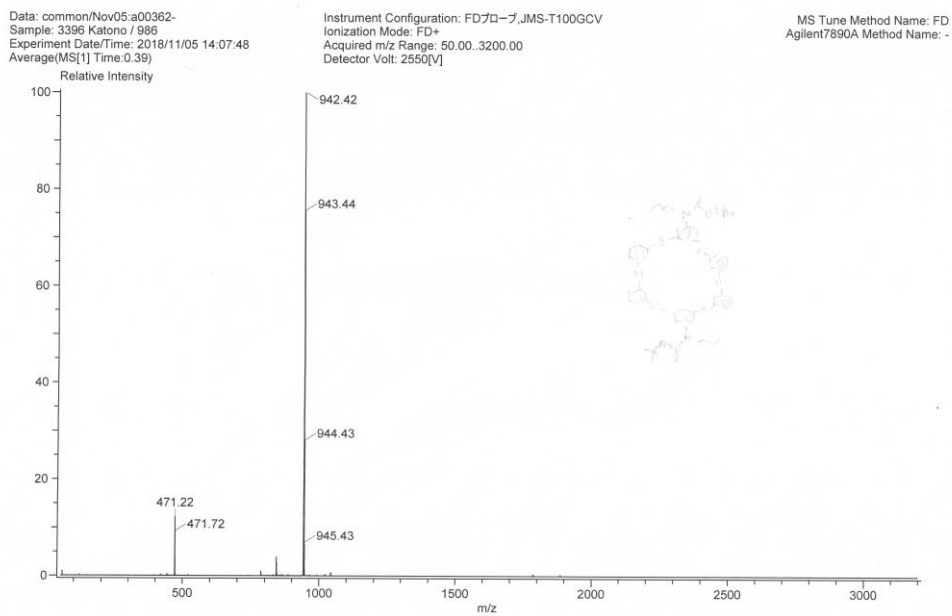


^{13}C NMR (100 MHz) spectrum of **12**, measured in chloroform-*d* at room temperature.

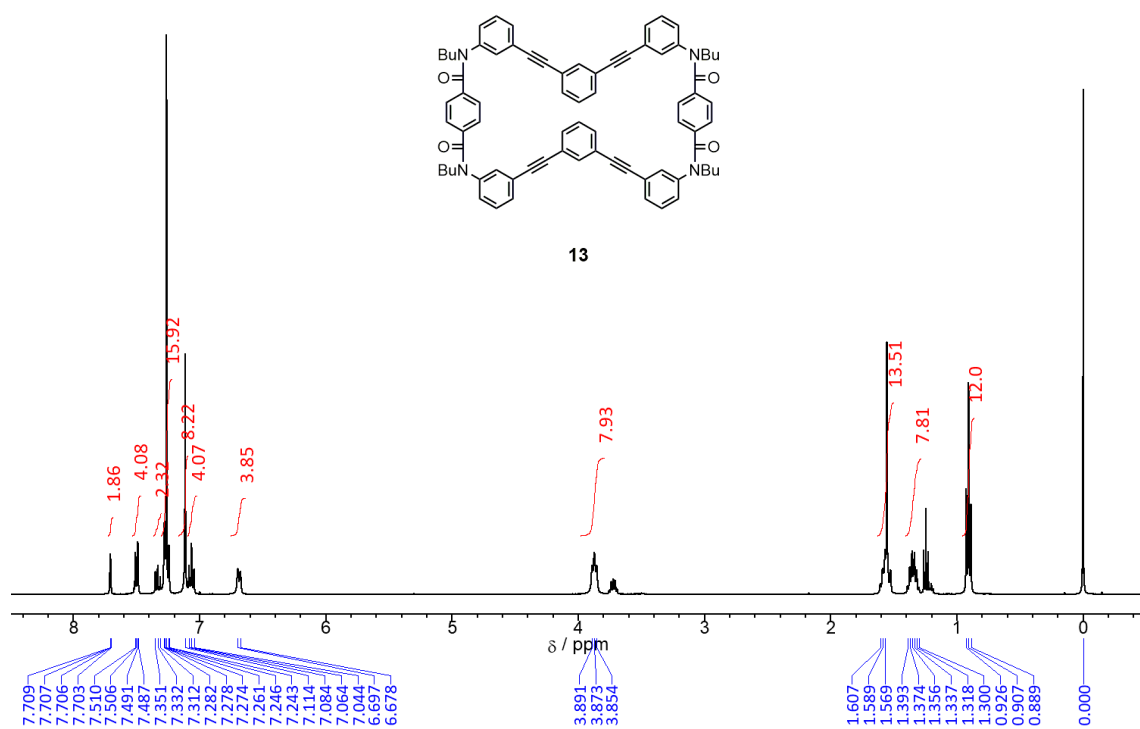


RESOL	: 2 cm-1	3062.44	60.12	1422.26	49.19
SCANS	: 5	2970.84	48.33	1417.44	51.22
AMP GAIN	: x1	2960.23	47.76	1389.48	41.19
P. INT	: 1 cm-1	2930.34	48.41	1366.34	39.81
BEAM	: single	2872.49	54.99	1344.16	46.55
S. SPEED	: TGS	2215.84	66.11	1305.59	45.01
M. DATE	: 11/2/18	1701.89	16.74	1150.34	28.91
F. NAME	: 測定中のデータ	1698.04	17.93	789.72	43.64
		1596.79	25.30	683.65	40.97
		1482.04	50.93	532.26	50.43

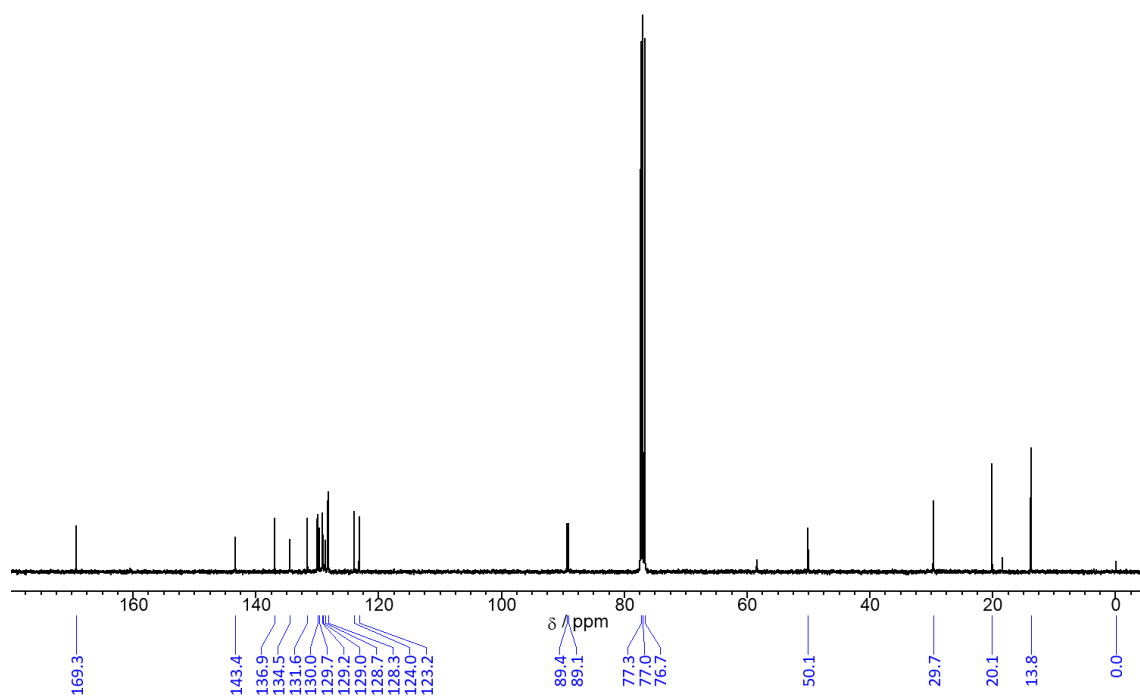
IR spectrum of **12**.



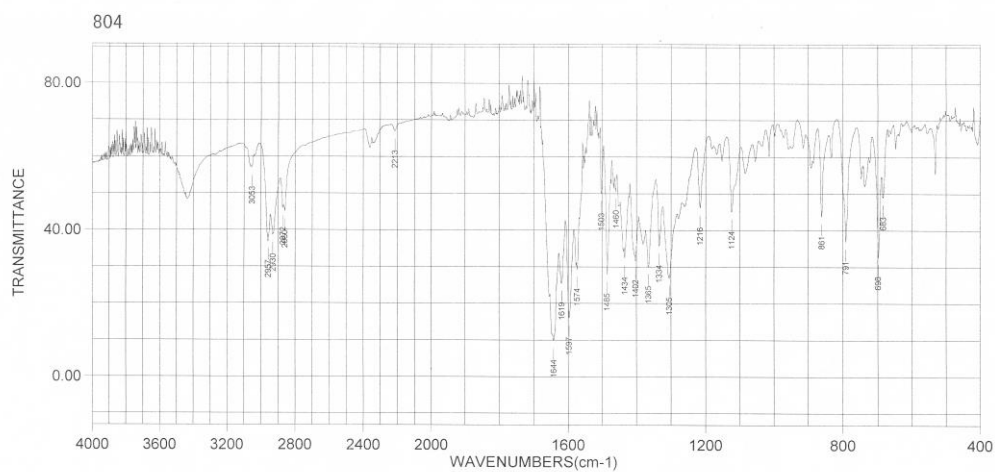
Mass spectrum (FD) of **12**.



^1H NMR (400 MHz) spectrum of **13** cont. ethanol, measured in chloroform-*d* at room temperature.

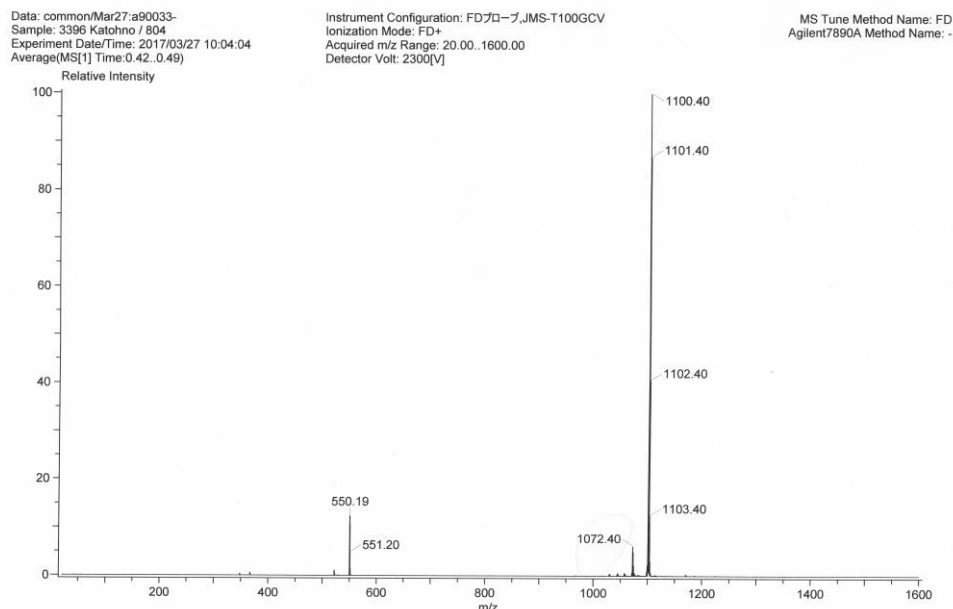


^{13}C NMR (100 MHz) spectrum of **13** cont. ethanol, measured in chloroform-*d* at room temperature.

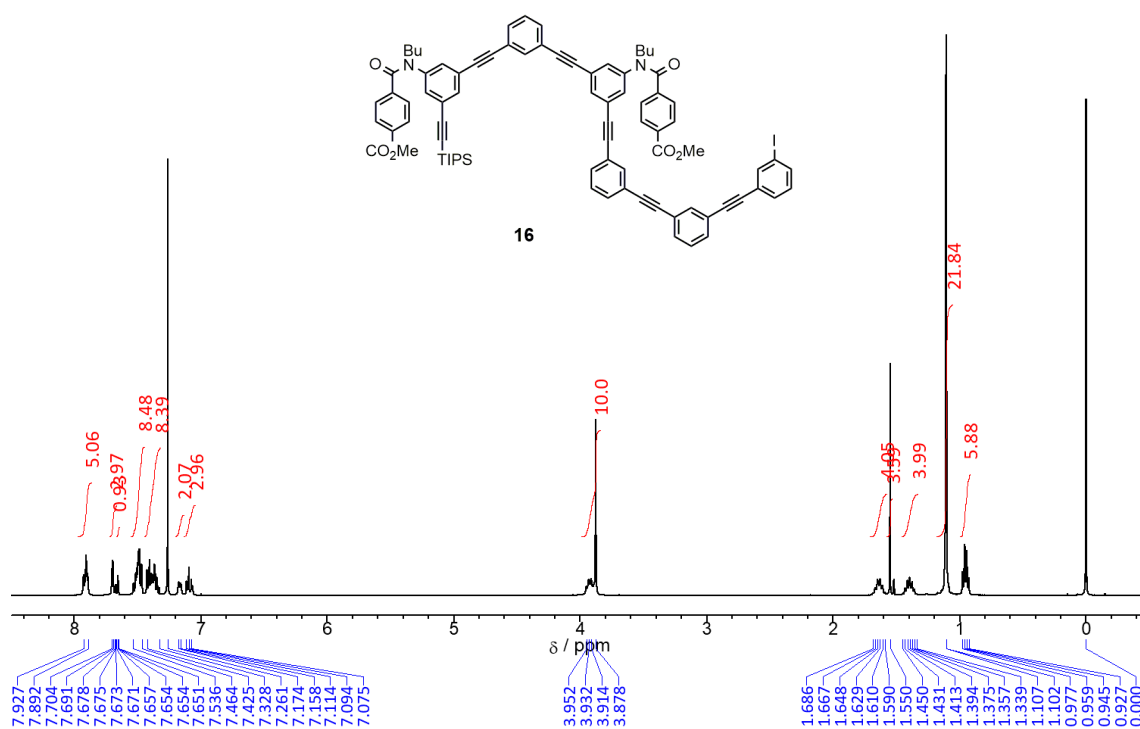


RESOL	: 2 cm-1	3053.76	57.01	1503.26	50.01	861.07	43.90
SCANS	: 5	2957.34	37.01	1485.90	28.10	791.65	37.04
AMP GAIN	: x1	2930.34	38.69	1460.83	50.72	698.11	32.82
P. INT	: 1 cm-1	2872.49	46.00	1434.80	32.57	683.65	49.04
BEAM	: single	2860.92	45.14	1402.98	31.84		
S. SPEED	: TGS	2213.91	66.96	1365.37	30.13		
M. DATE	: 11/2/18	1644.04	9.90	1334.52	35.83		
F. NAME	: 測定中のデータ	1619.93	25.61	1305.59	27.01		
		1597.75	16.16	1216.88	46.21		
		1574.61	29.39	1124.31	45.17		

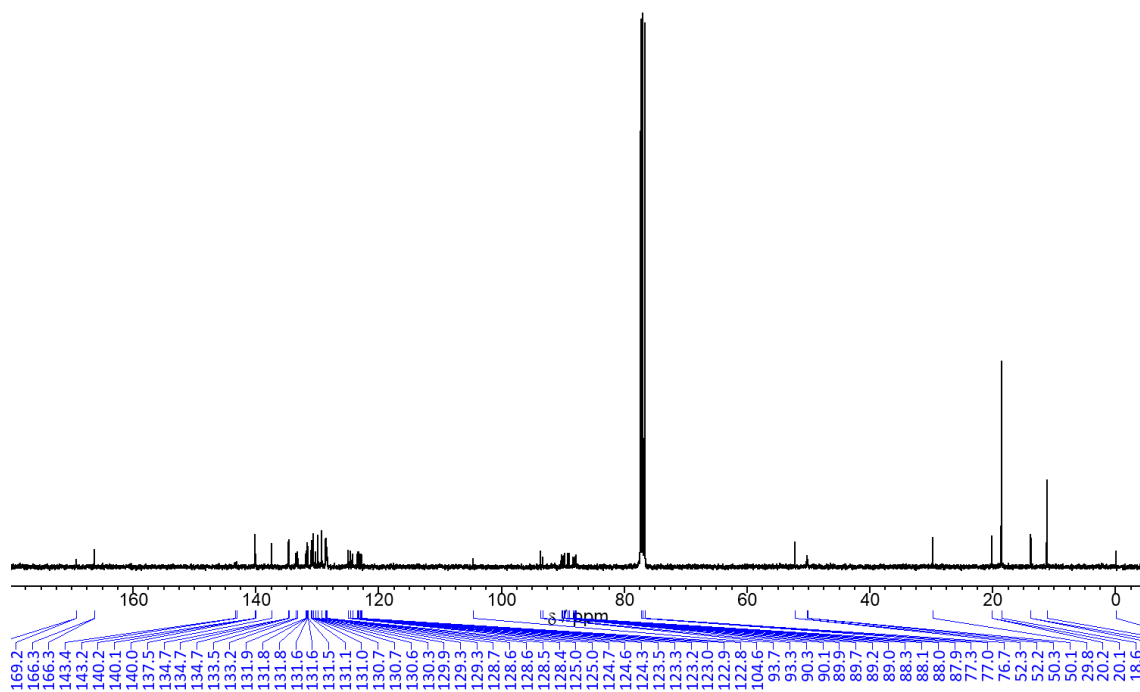
IR spectrum of **13**.



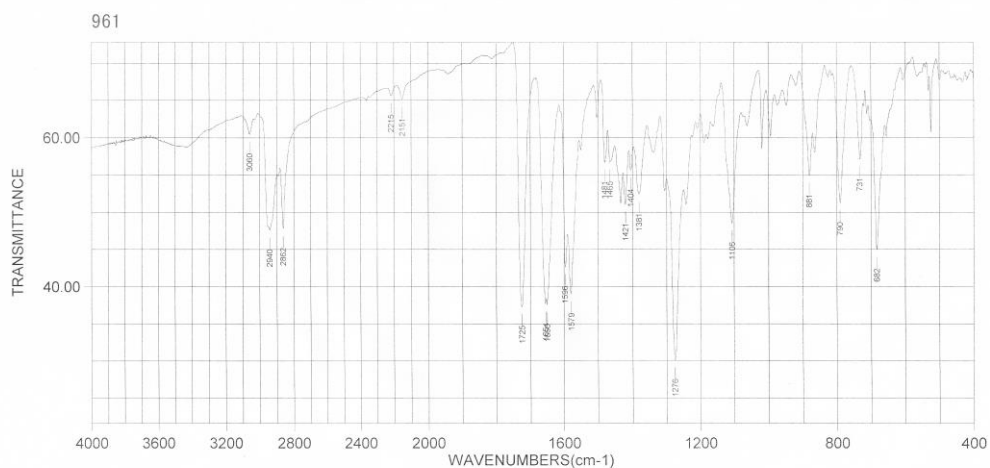
Mass spectrum (FD) of **13**.



¹H NMR (400 MHz) spectrum of **16**, measured in chloroform-*d* at room temperature.

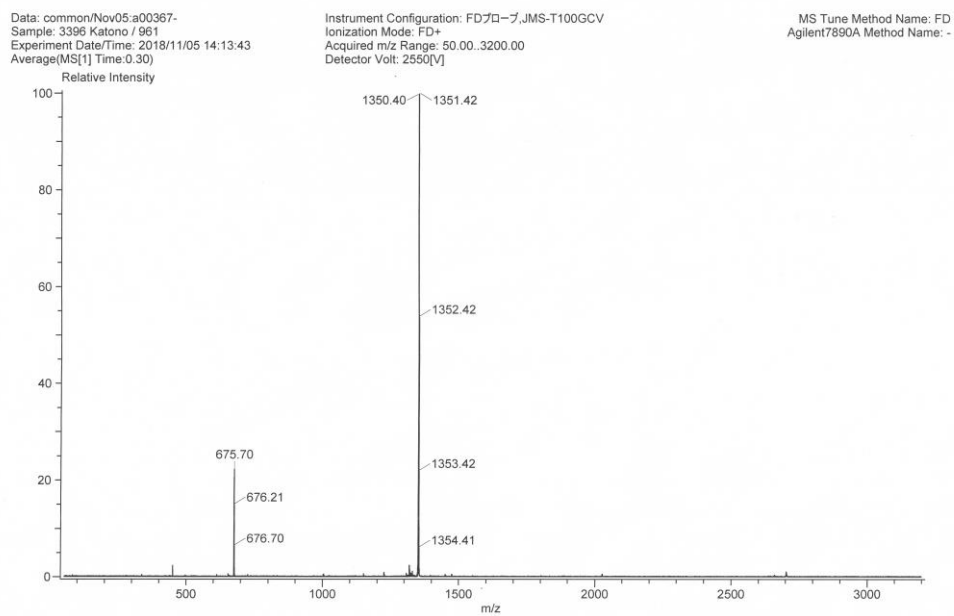


¹³C NMR (100 MHz) spectrum of **16**, measured in chloroform-*d* at room temperature.

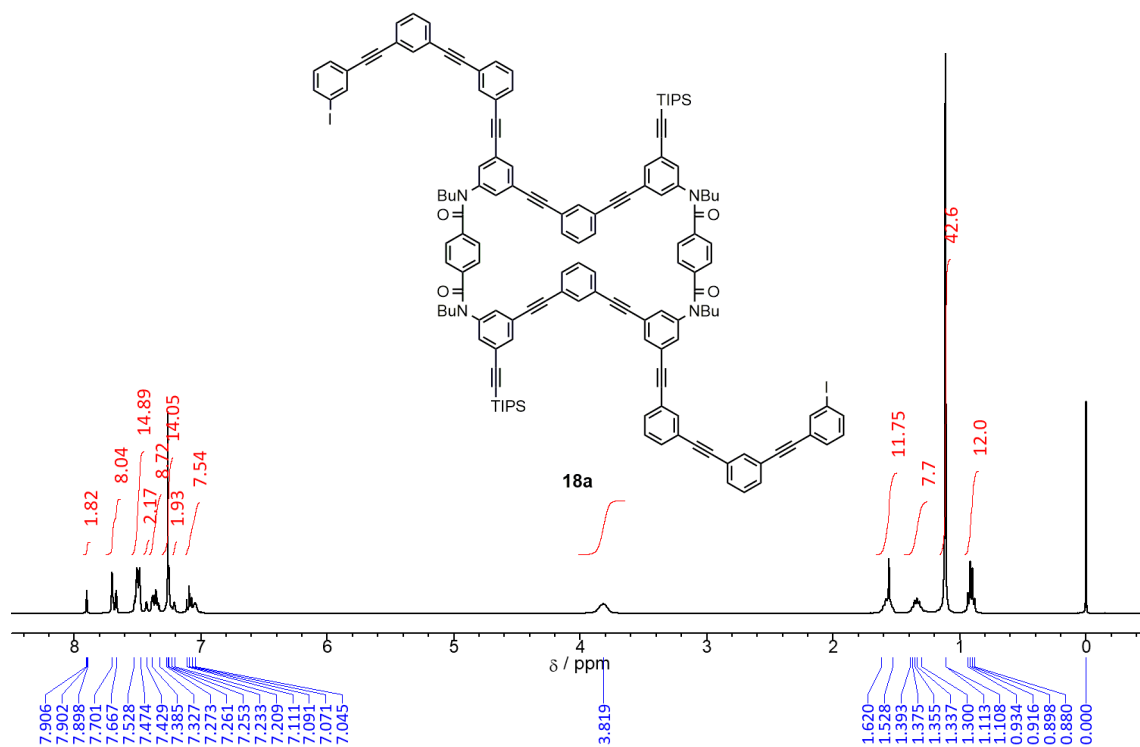


RESOL	: 2 cm-1	3060.51	60.52	1481.08	56.78	682.69	45.03
SCANS	: 5	2940.95	47.66	1465.65	56.77		
AMPGAIN	: x1	2862.84	47.87	1421.30	51.13		
P. INT	: 1 cm-1	2215.84	65.70	1404.91	55.71		
BEAM	: single	2151.23	65.22	1381.76	52.49		
S. SPEED	: TGS	1725.03	37.33	1276.66	30.14		
M. DATE	: 11/2/18	1654.64	37.70	1106.95	48.61		
F. NAME	: 測定中のデータ	1650.79	37.55	881.32	55.03		
		1596.79	42.71	790.68	51.30		
		1579.43	39.04	731.86	57.24		

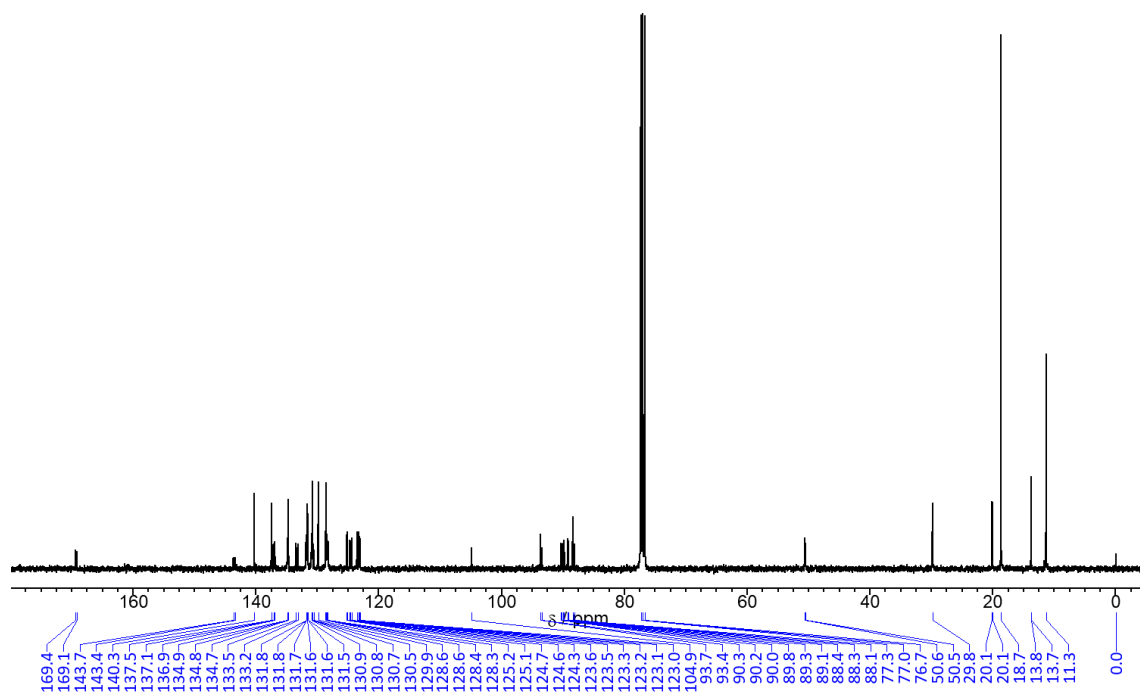
IR spectrum of 16.



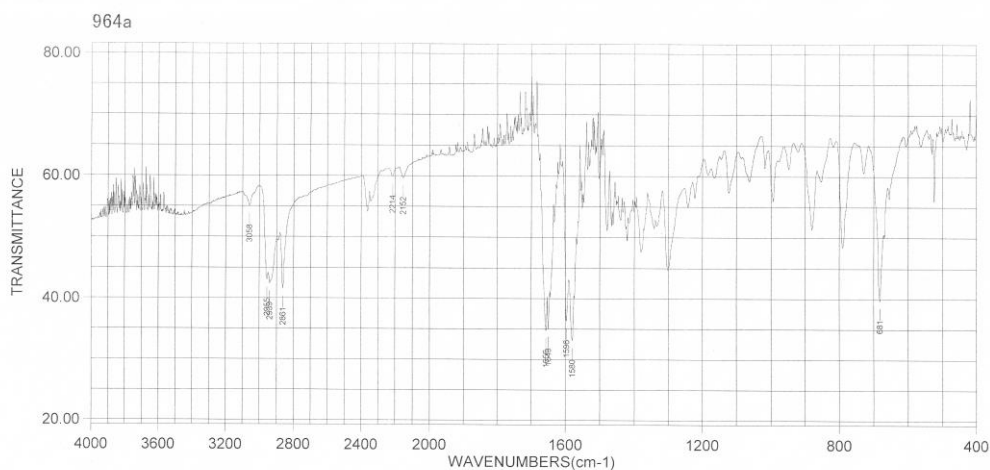
Mass spectrum (FD) of 16.



¹H NMR (400 MHz) spectrum of **18a**, measured in chloroform-*d* at room temperature.

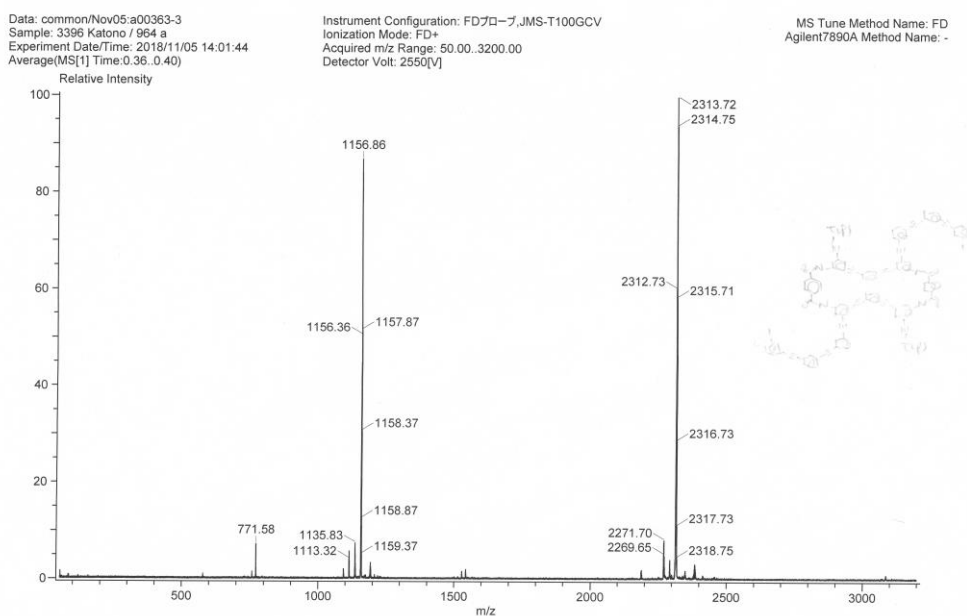


¹³C NMR (100 MHz) spectrum of **18a**, measured in chloroform-*d* at 313 K.

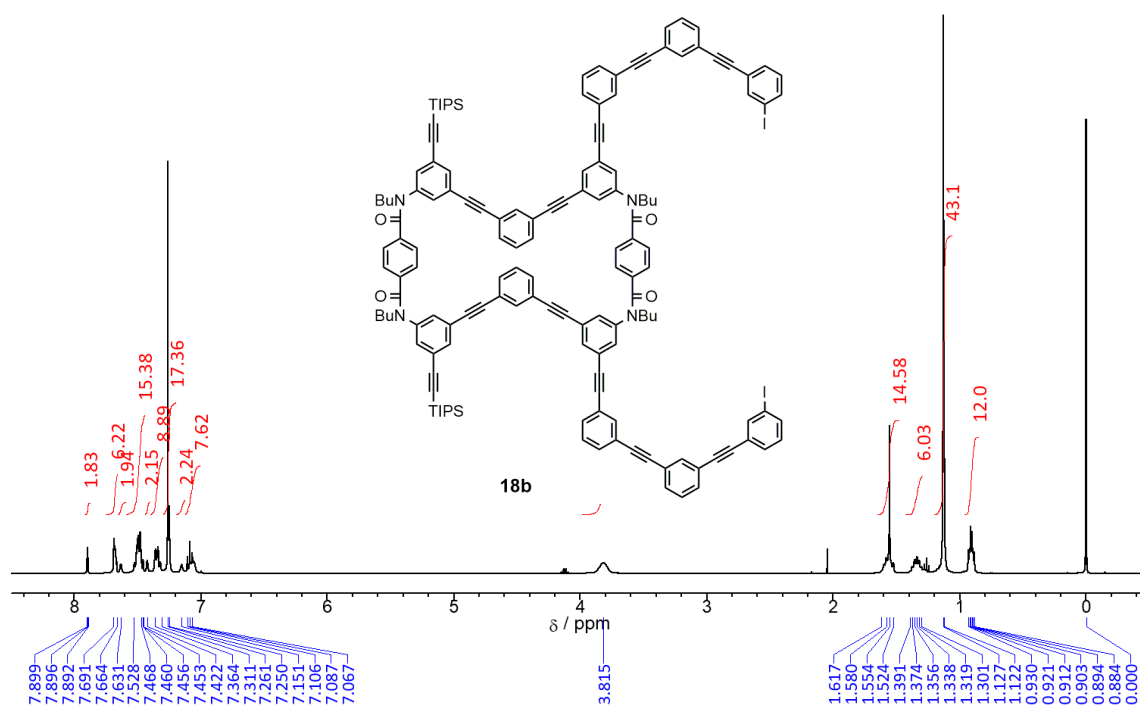


RESOL	: 2 cm ⁻¹	3058.59	55.16	681.72	39.70
SCANS	: 5	2955.41	43.06		
AMPGAIN	: x1	2939.02	42.42		
P. INT	: 1 cm ⁻¹	2861.88	41.55		
BEAM	: single	2214.87	59.94		
S. SPEED	: TGS	2152.20	59.71		
M. DATE	: 11/2/18	1656.57	34.77		
F. NAME	: 測定中のデータ	1649.82	34.99		
		1596.79	36.35		
		1580.40	33.13		

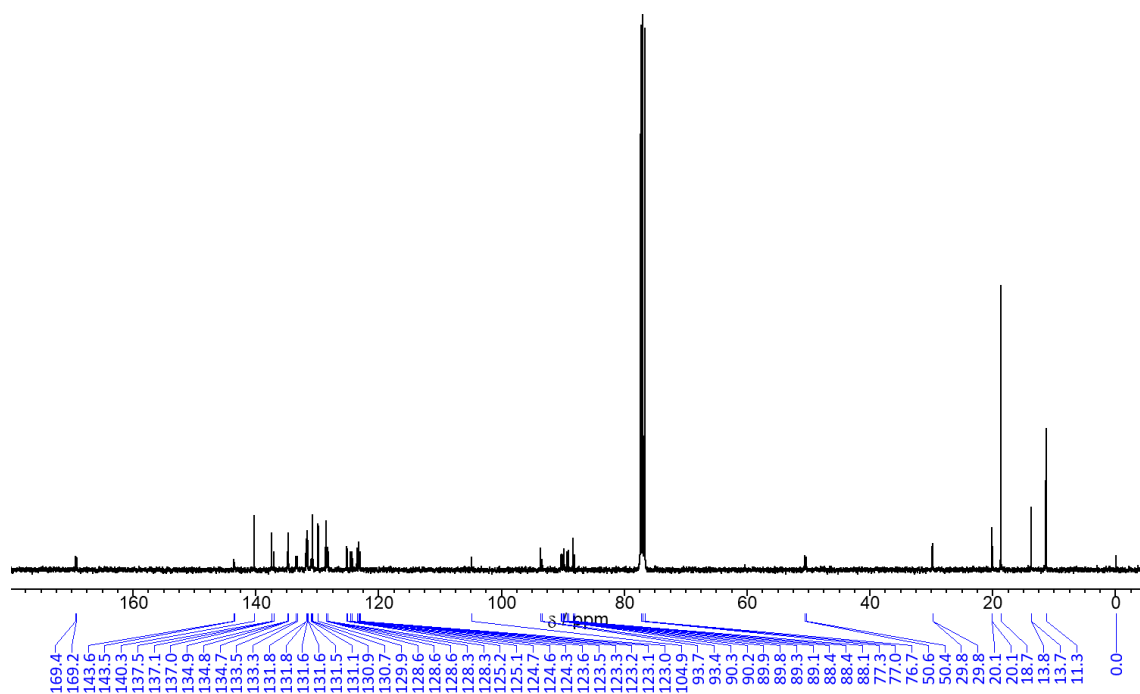
IR spectrum of **18a**.



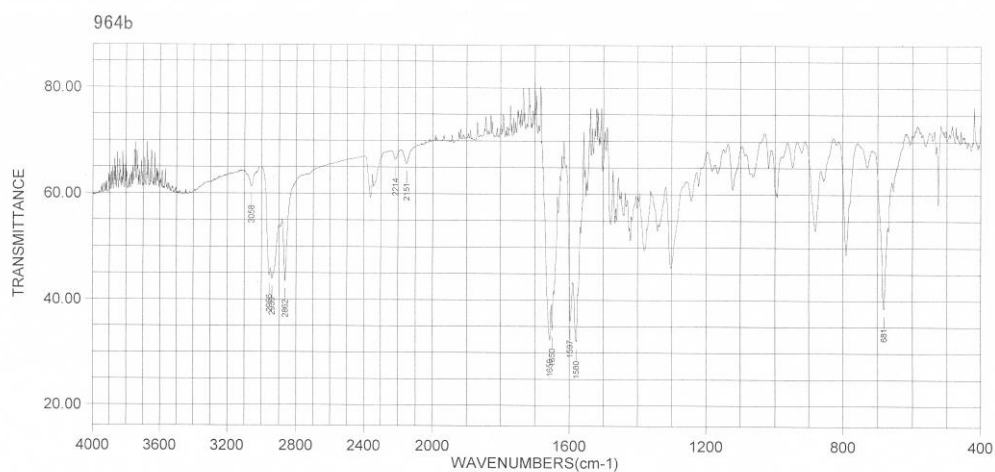
Mass spectrum (FD) of **18a**.



¹H NMR (400 MHz) spectrum of **18b** cont. residual solvent (ethyl acetate), measured in chloroform-*d* at room temperature.

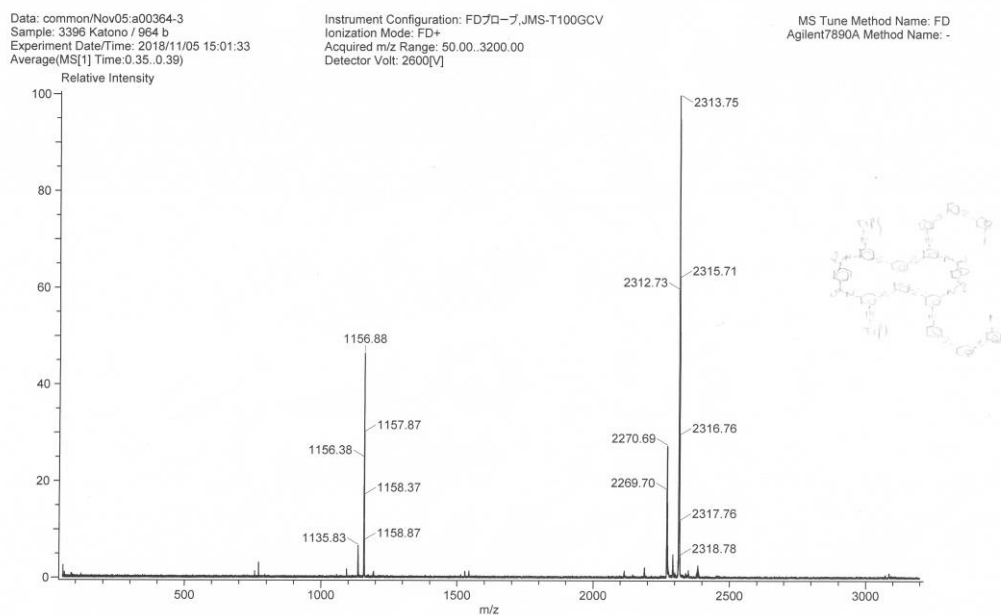


¹³C NMR (100 MHz) spectrum of **18b**, measured in chloroform-*d* at 313 K.

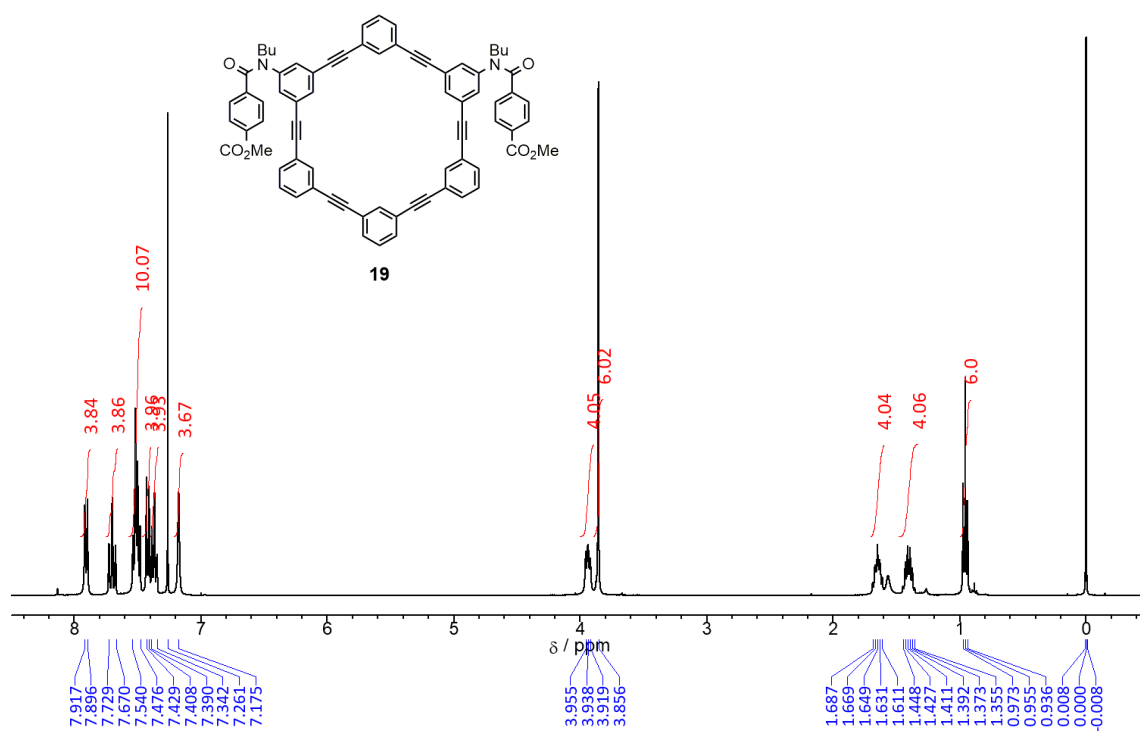


RESOL	: 2 cm-1	3058.59	61.36	681.72	38.48
SCANS	: 5	2956.38	44.51		
AMP GAIN	: x1	2939.98	43.95		
P. INT	: 1 cm-1	2862.84	43.46		
BEAM	: single	2214.87	66.52		
S. SPEED	: TGS	2151.23	65.70		
M. DATE	: 11/2/18	1656.57	32.45		
F. NAME	: 測定中のデータ	1650.79	34.39		
		1597.75	36.08		
		1580.40	32.14		

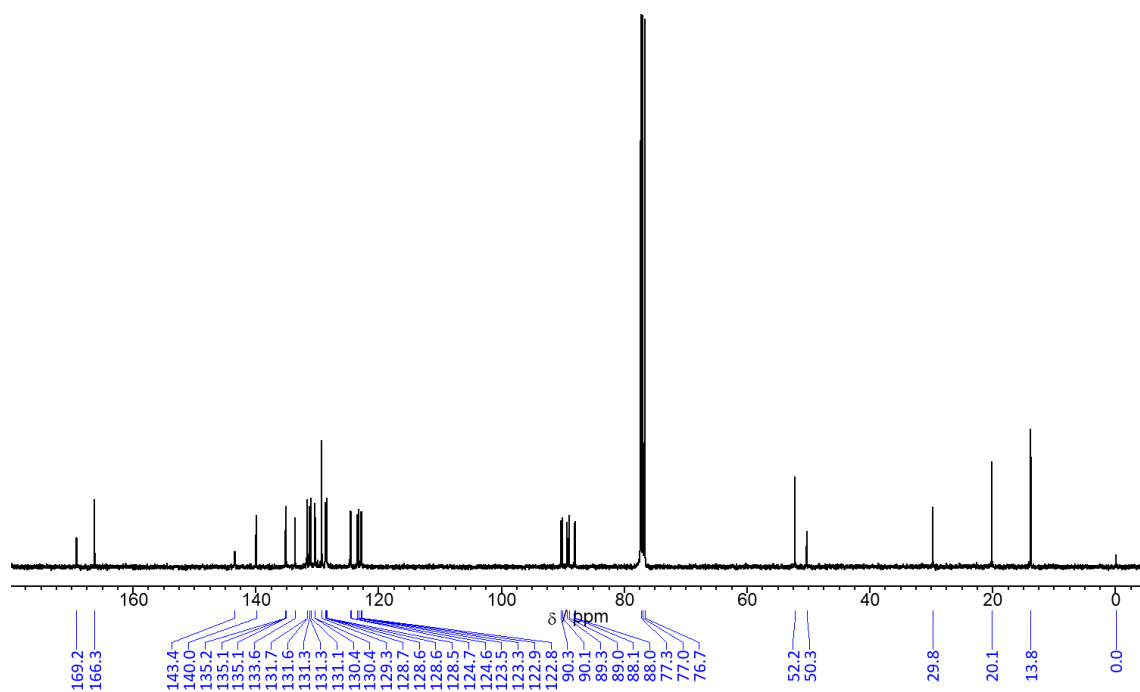
IR spectrum of **18b**.



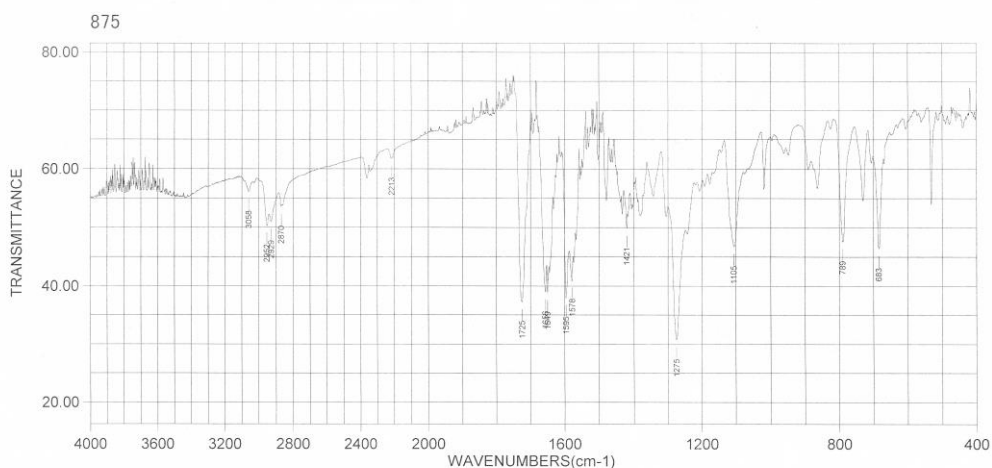
Mass spectrum (FD) of **18b**.



¹H NMR (400 MHz) spectrum of **19**, measured in chloroform-*d* at room temperature.

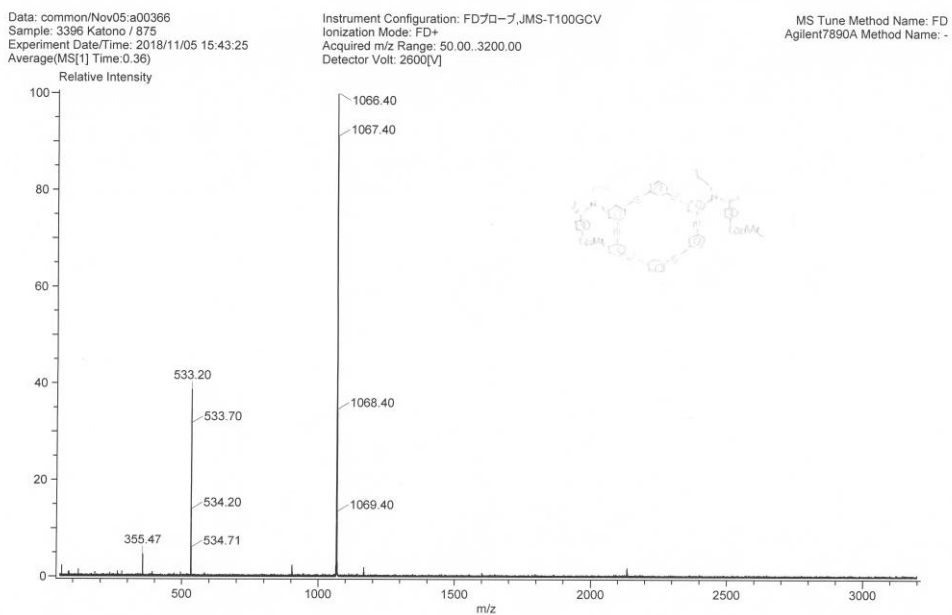


¹³C NMR (100 MHz) spectrum of **19**, measured in chloroform-*d* at room temperature.

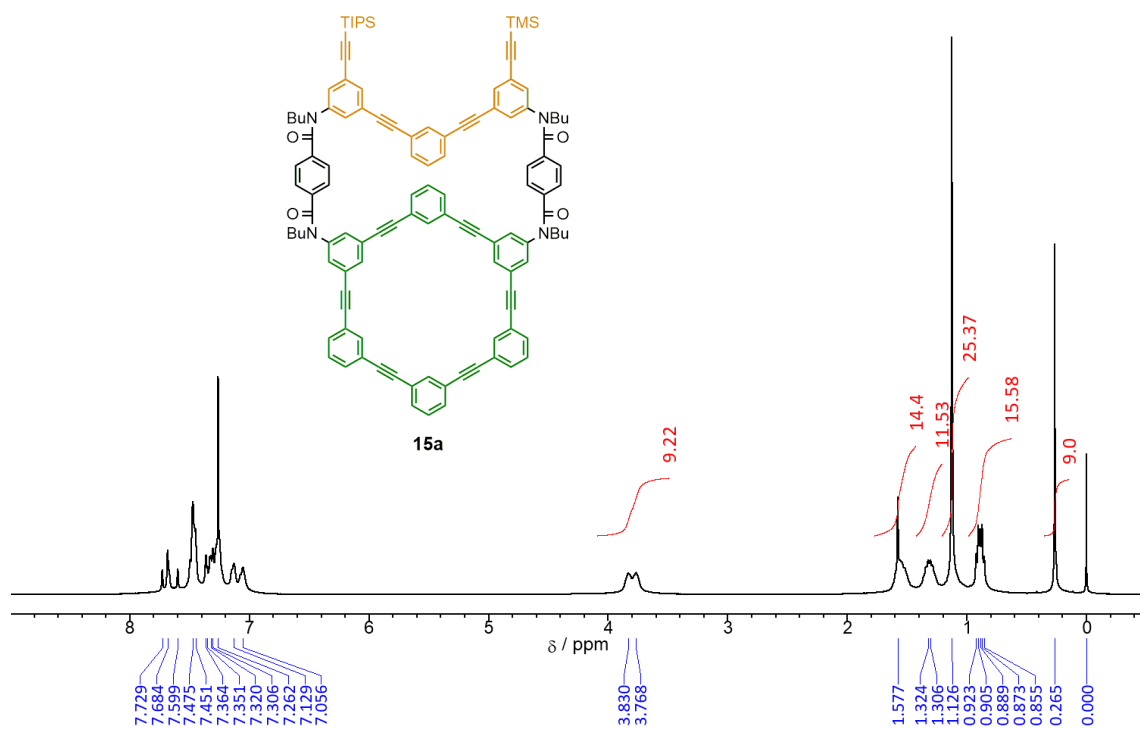


RESOL	: 2	cm-1	3058.59	56.15	1421.30	49.90
SCANS	: 5		2952.52	50.39	1275.70	30.79
AMP GAIN	: x1		2929.38	51.06	1105.99	46.76
P. INT	: 1	cm-1	2870.56	53.57	789.72	47.59
BEAM	: single		2213.91	61.81	683.65	46.45
S. SPEED	: TGS		1725.03	37.30		
M. DATE	: 11/2/18		1656.57	39.01		
F. NAME	: 測定中のデータ		1649.82	38.88		
			1595.83	38.01		
			1578.47	41.07		

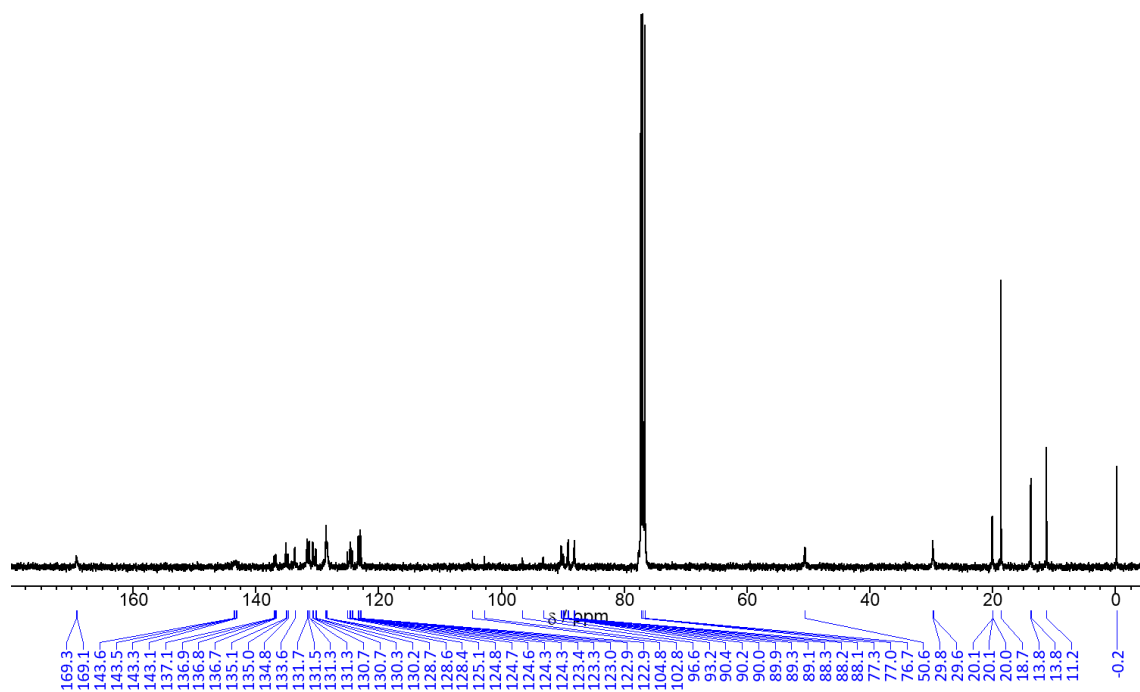
IR spectrum of 19.



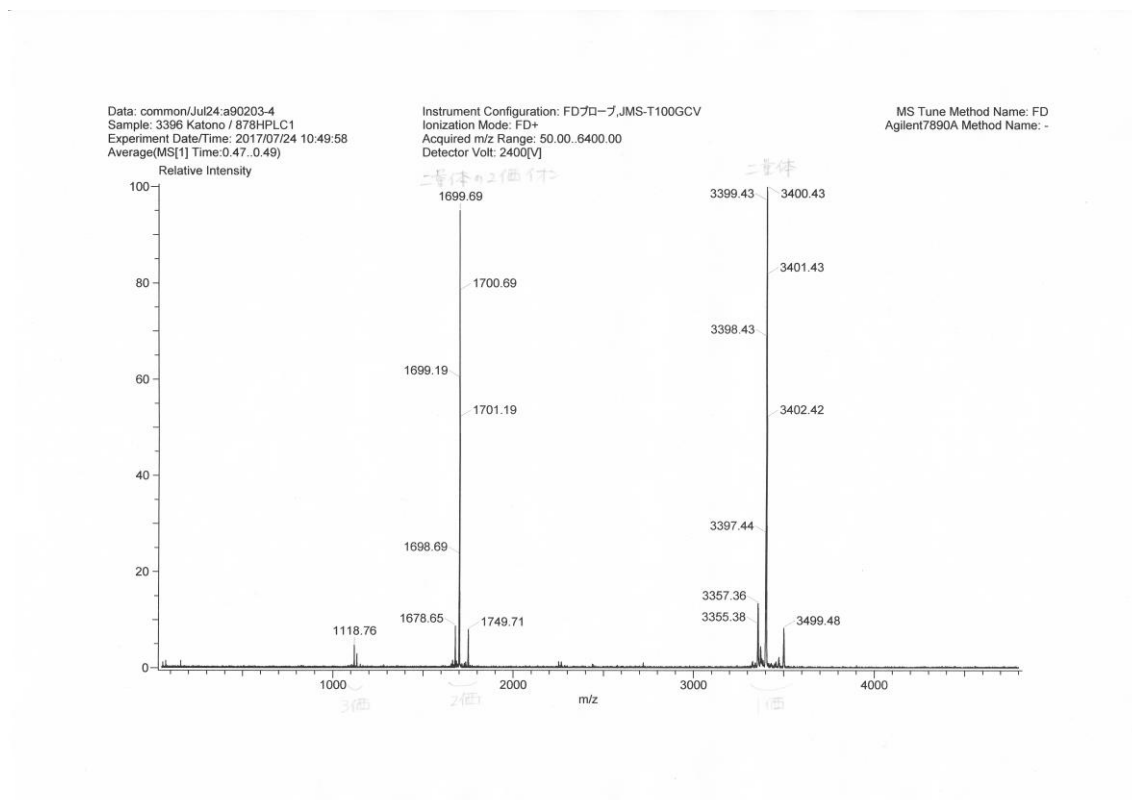
Mass spectrum (FD) of 19.



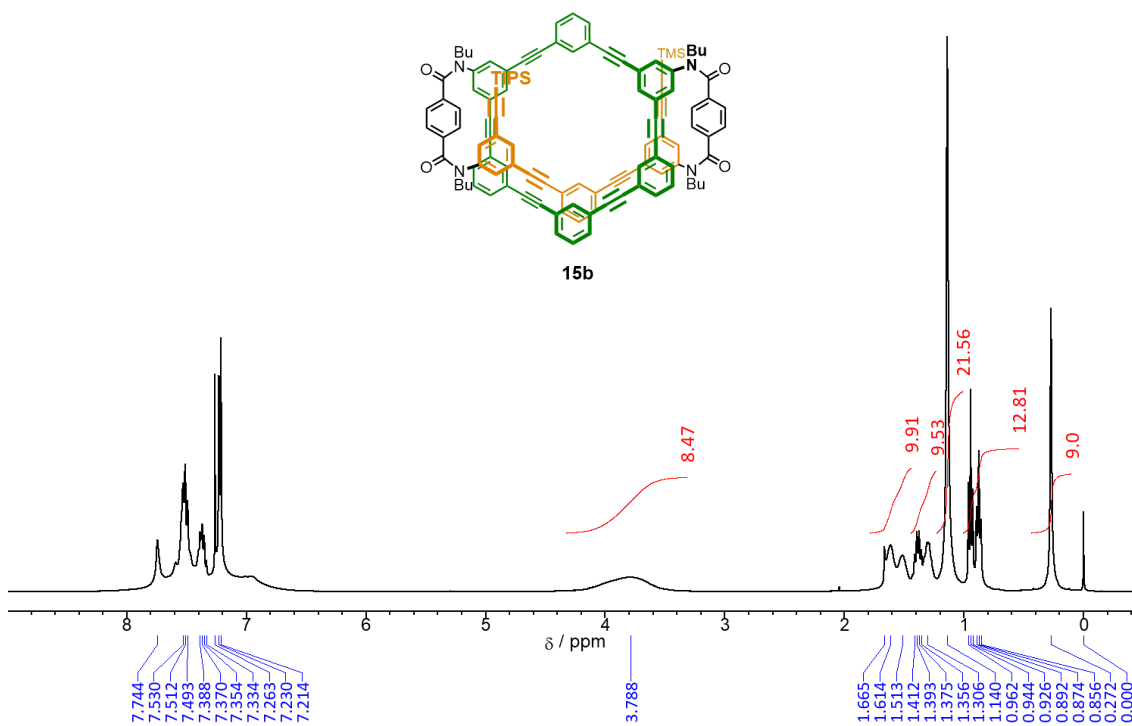
^1H NMR (400 MHz) spectrum of **15a**, measured in chloroform-*d* at room temperature.



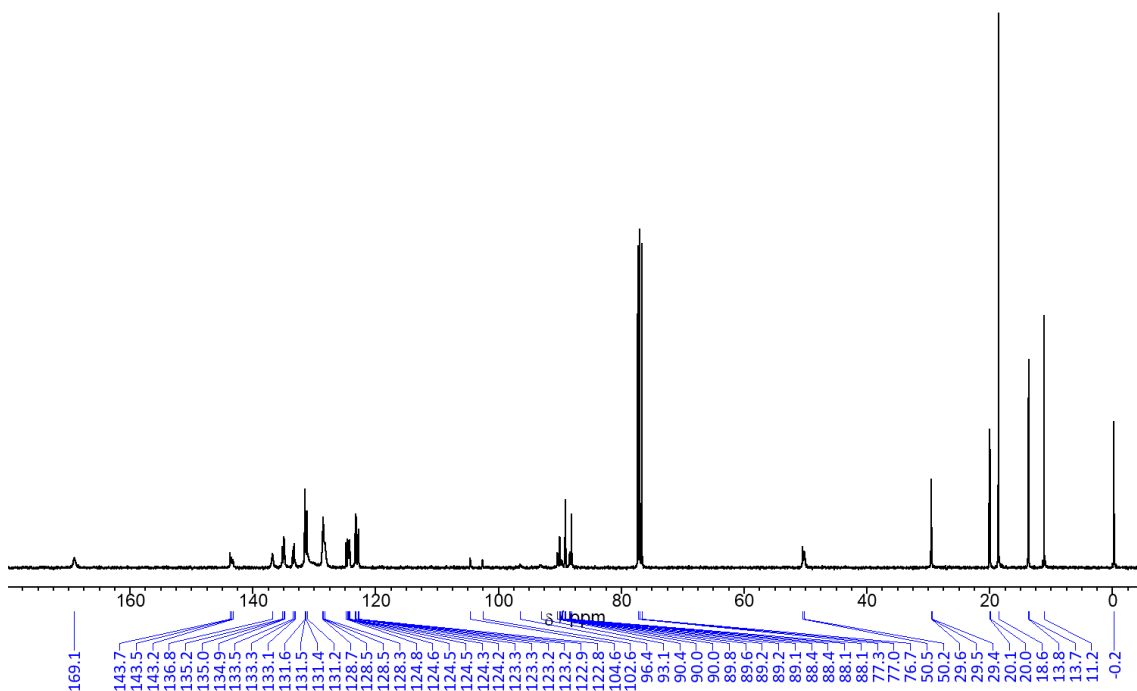
^{13}C NMR (100 MHz) spectrum of **15a**, measured in chloroform-*d* at room temperature.



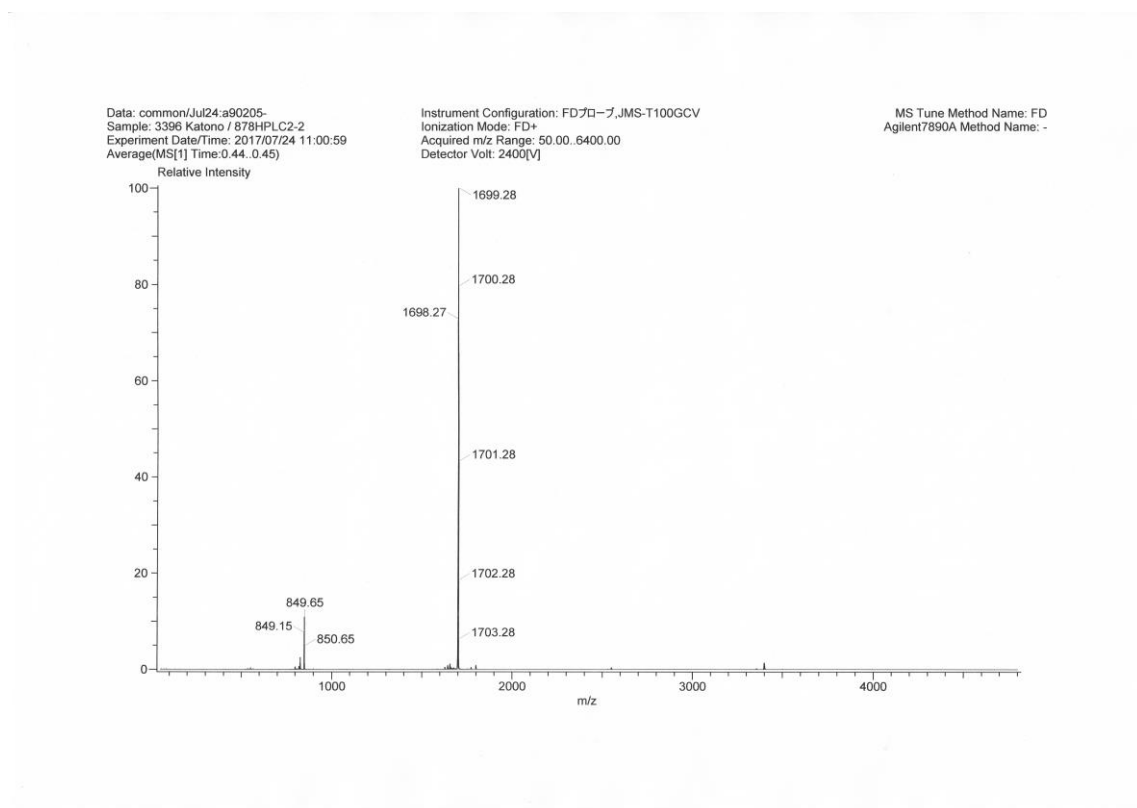
Mass spectrum (FD) of **15a**.



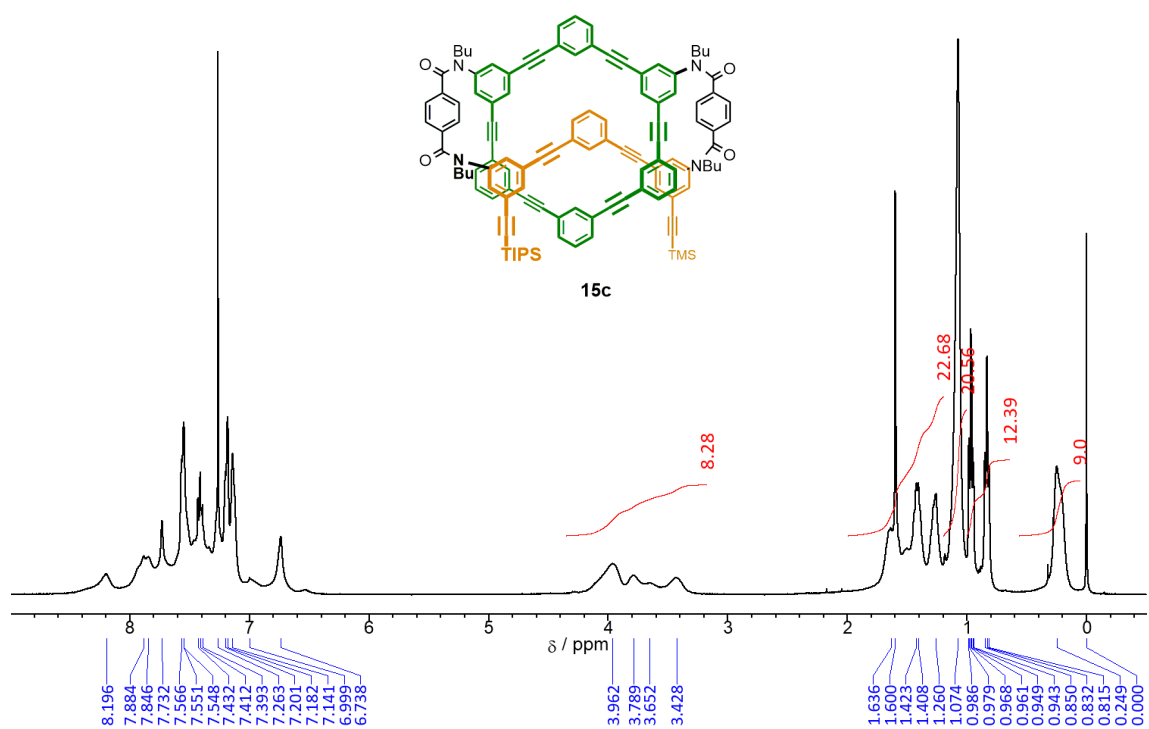
^1H NMR (400 MHz) spectrum of **15b**, measured in chloroform-*d* at room temperature.



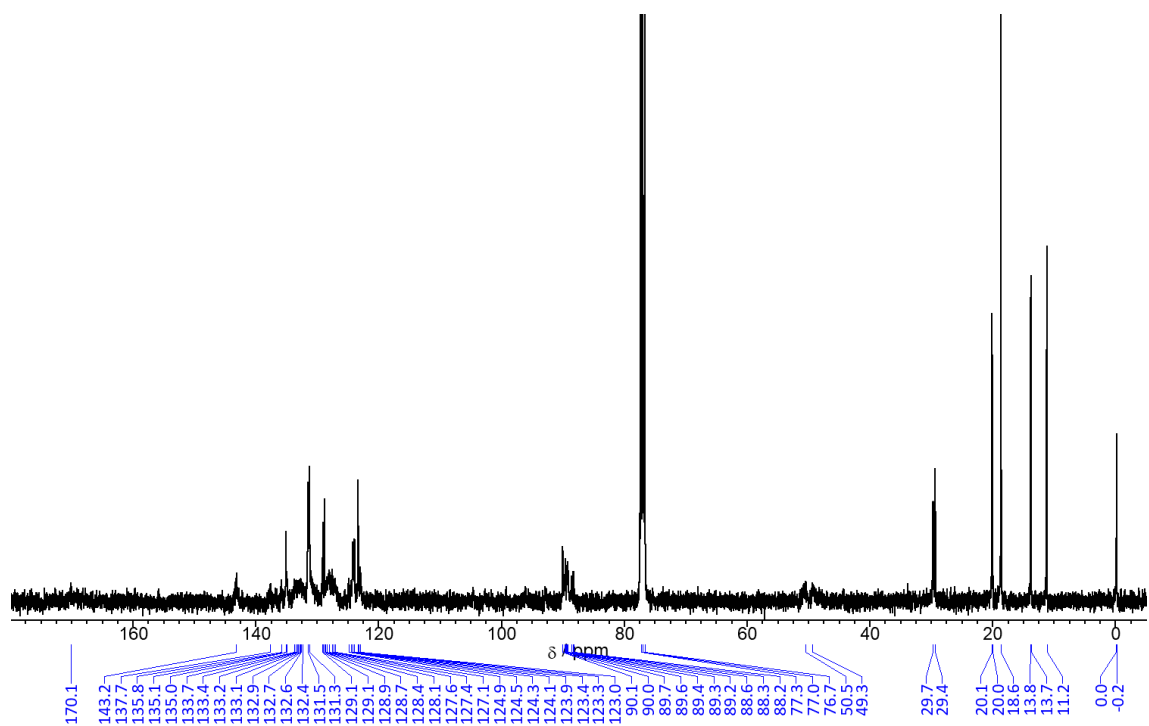
^{13}C NMR (100 MHz) spectrum of **15b**, measured in chloroform-*d* at room temperature.



Mass spectrum (FD) of **15b**.



¹H NMR (400 MHz) spectrum of **15c**, measured in chloroform-*d* at room temperature.

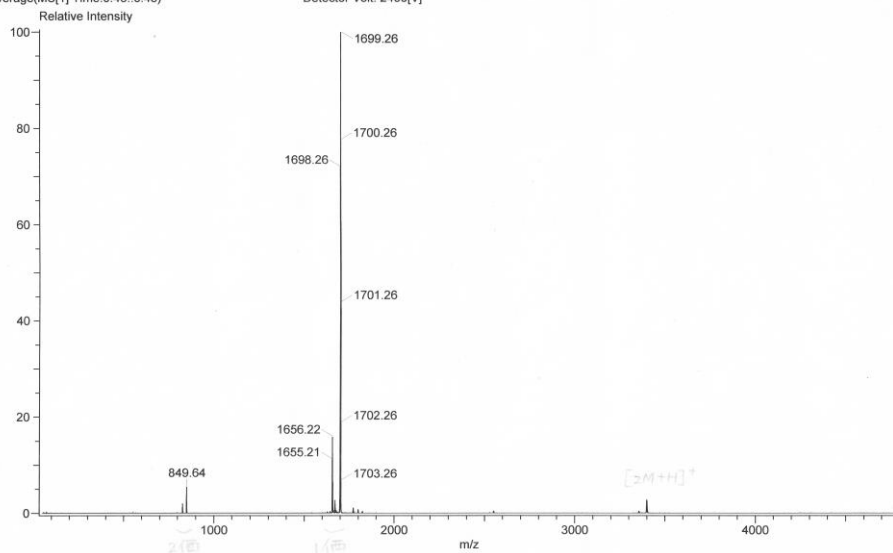


¹³C NMR (100 MHz) spectrum of **15c**, measured in chloroform-*d* at room temperature.

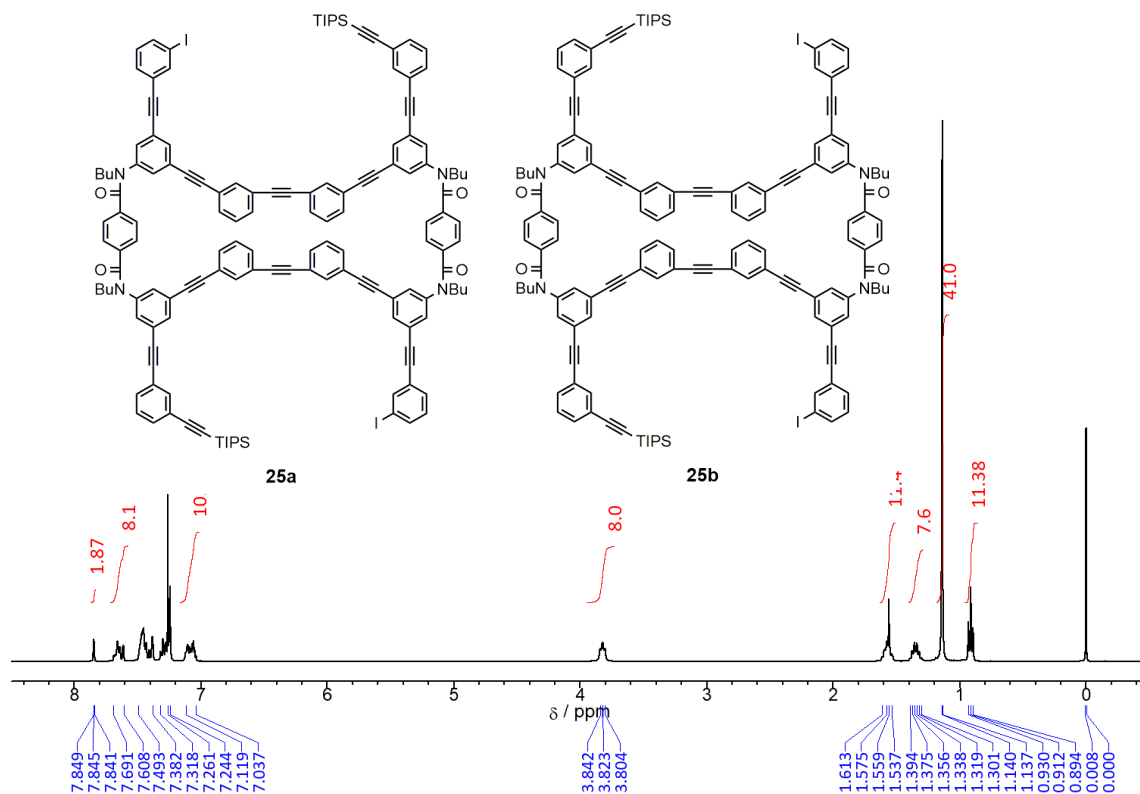
Data: common/Jul24:s90204-
Sample: 3396 Katono / 878HPLC2-1
Experiment Date/Time: 2017/07/24 10:54:58
Average(MS[1] Time:0.46..0.48)

Instrument Configuration: FDプローブ,JMS-T100GCV
Ionization Mode: FD+
Acquired m/z Range: 50.00..6400.00
Detector Volt: 2400[V]

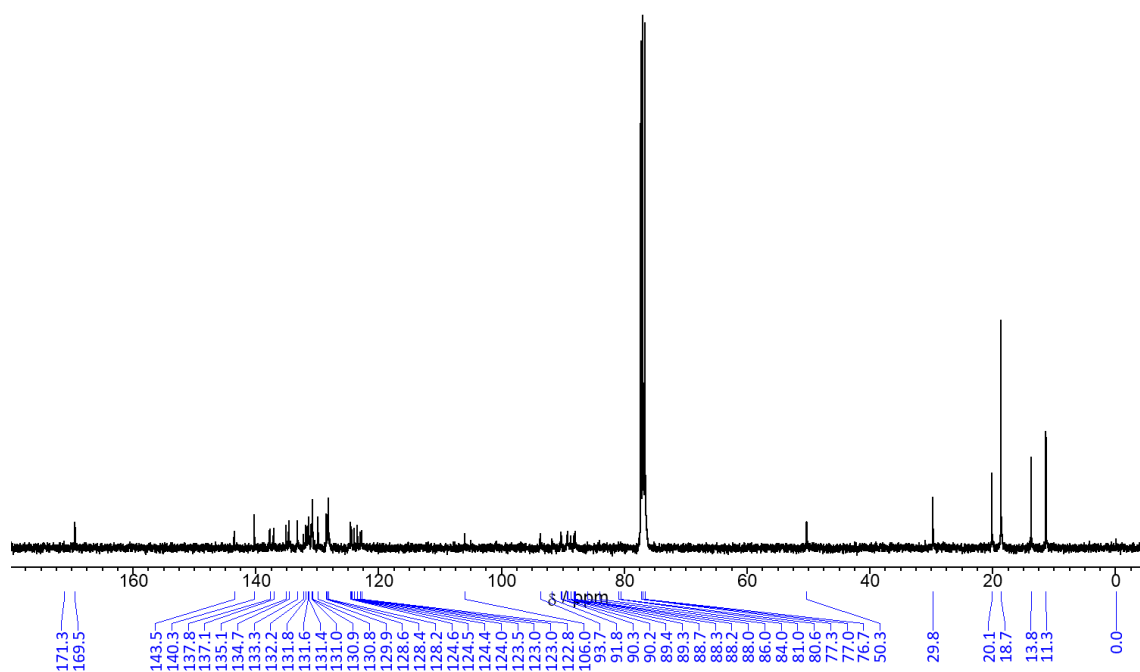
MS Tune Method Name: FD
Agilent7890A Method Name: -



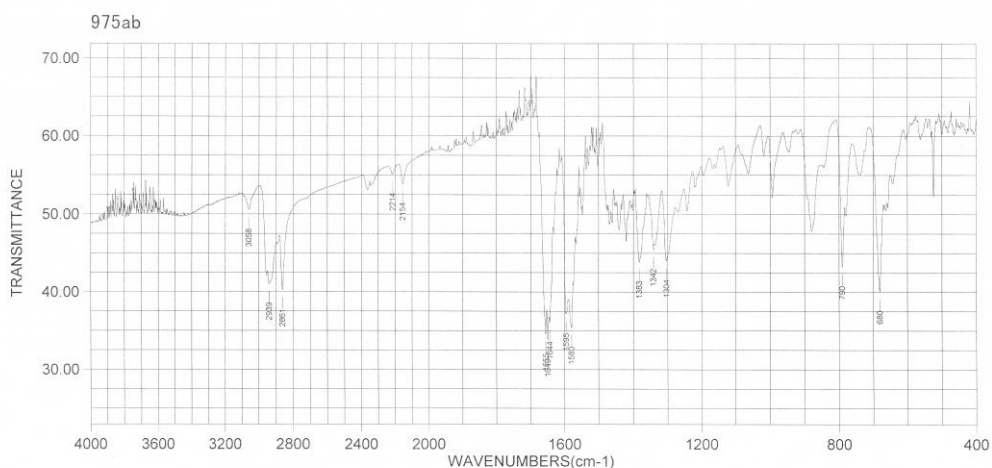
Mass spectrum (FD) of **15c**.



^1H NMR (400 MHz) spectrum of a mixture of **25a** and **25b**, measured in chloroform-*d* at room temperature.

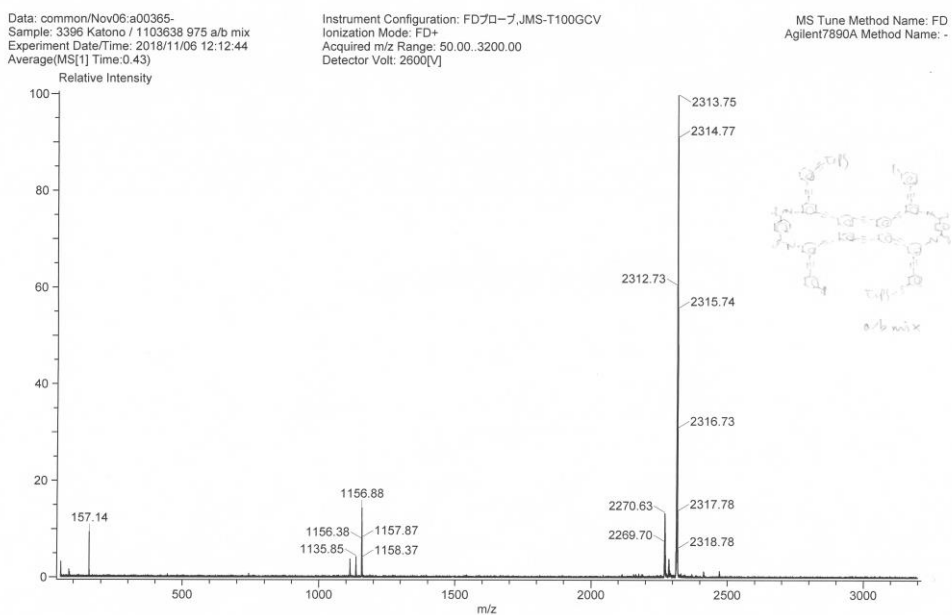


^{13}C NMR (100 MHz) spectrum of a mixture of **25a** and **25b**, measured in chloroform-*d* at 308 K.

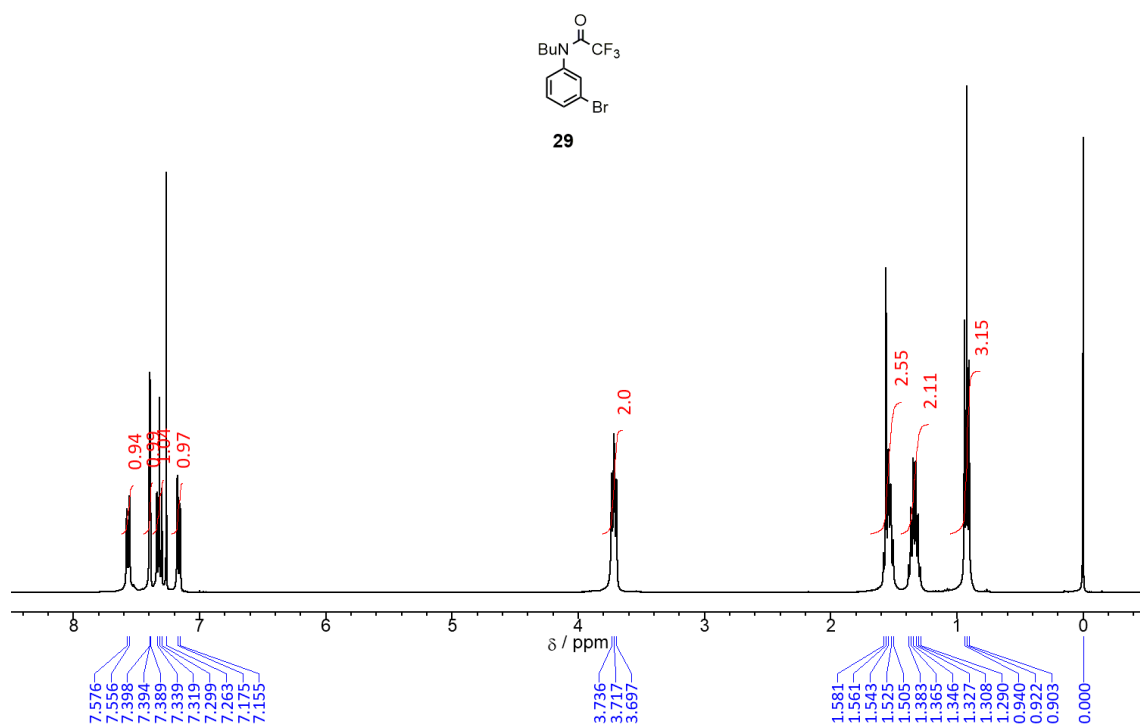


RESOL	: 2	cm-1	3058.59	50.58	1383.69	43.92
SCANS	: 5	2939.02	41.06	1342.23	45.46	
AMPGAIN	: x1	2861.88	40.26	1304.62	44.08	
P. INT	: 1	cm-1	2214.87	55.15	790.68	43.29
BEAM	: single	2154.12	53.87	680.76	40.09	
S. SPEED	: TGS	1655.61	34.58			
M. DATE	: 11/2/18	1649.82	33.84			
F. NAME	: 測定中のデータ	1644.04	36.08			
		1595.83	37.17			
		1580.40	35.44			

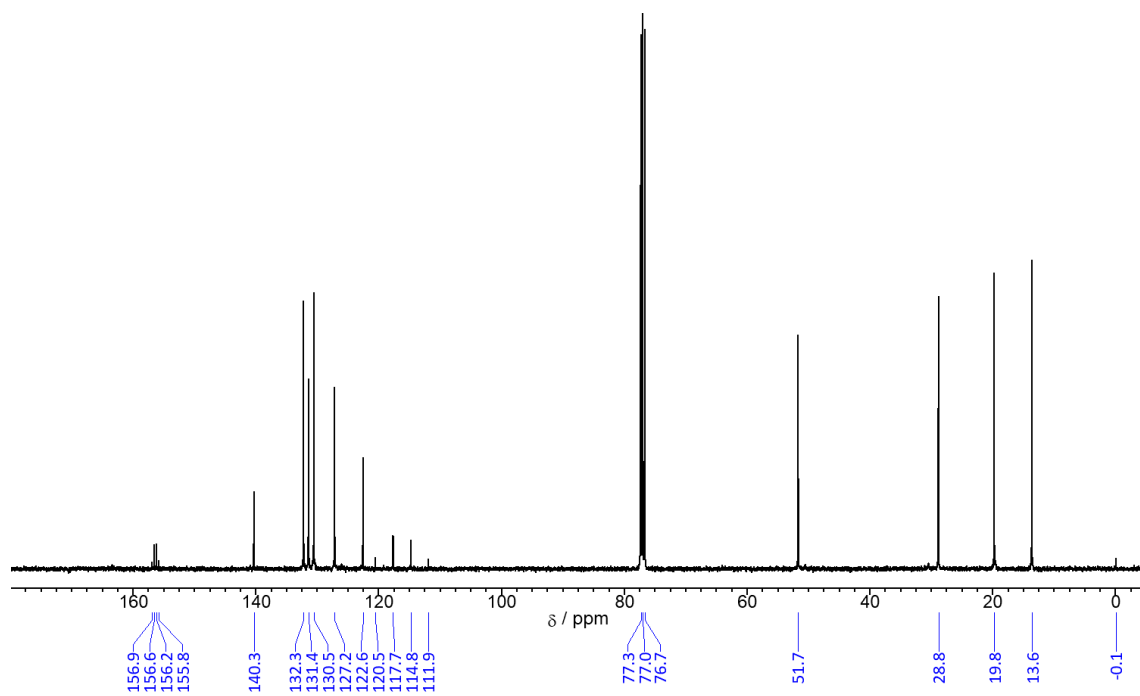
IR spectrum of a mixture of **25a** and **25b**.



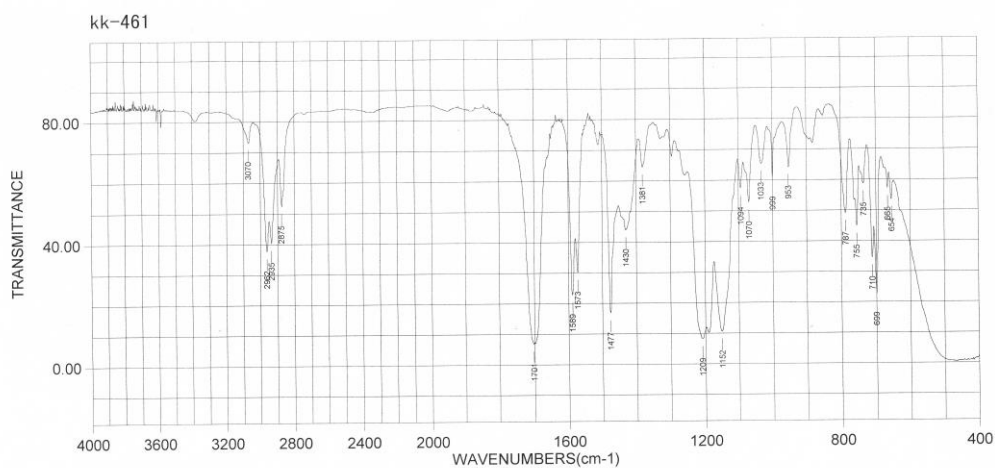
Mass spectrum (FD) of a mixture of **25a** and **25b**.



^1H NMR (400 MHz) spectrum of **29**, measured in chloroform-*d* at room temperature.

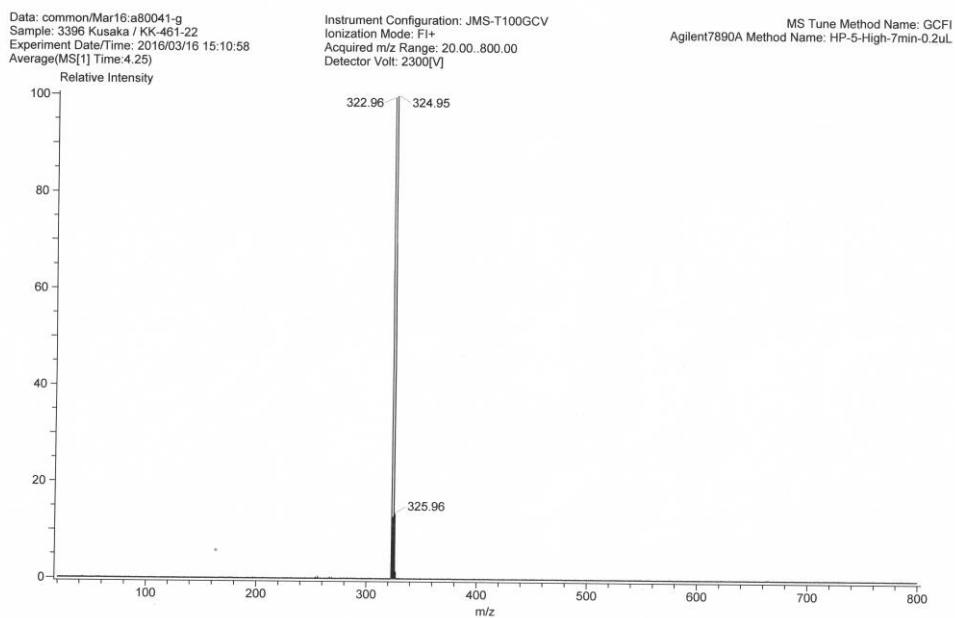


^{13}C NMR (100 MHz) spectrum of **29**, measured in chloroform-*d* at room temperature.

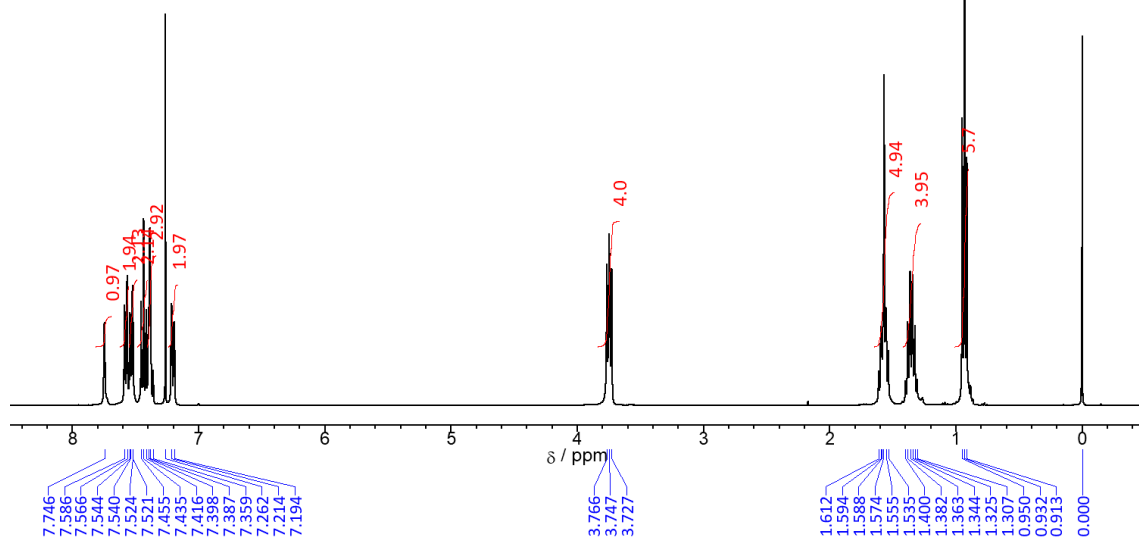
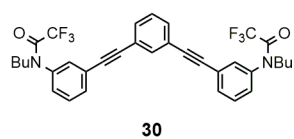


RESOL	: 2 cm ⁻¹	3070.16	73.28	1209.16	8.27	710.65	34.60
SCANS	: 5	2962.16	37.71	1152.27	10.67	699.08	22.79
AMP GAIN	: x1	2935.16	40.47	1094.42	57.48	665.33	57.25
P. INT	: 1 cm ⁻¹	2875.38	52.46	1070.31	52.87	654.72	53.54
BEAM	: single	1701.89	6.80	1033.67	65.43		
S. SPEED	: TGS	1589.08	22.89	999.92	60.86		
M. DATE	: 3/23/16	1573.65	30.24	953.64	64.29		
F. NAME	: 測定中のデータ	1477.22	16.87	787.79	49.16		
		1430.94	44.08	755.97	45.00		
		1381.76	64.52	735.72	58.68		

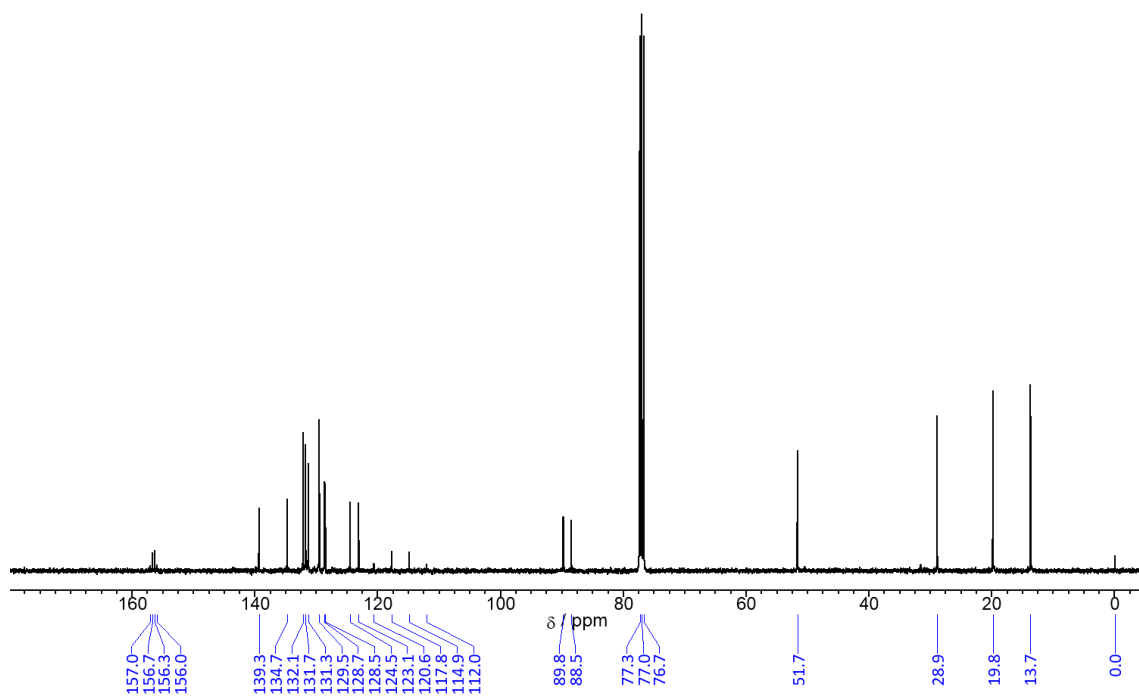
IR spectrum of **29**.



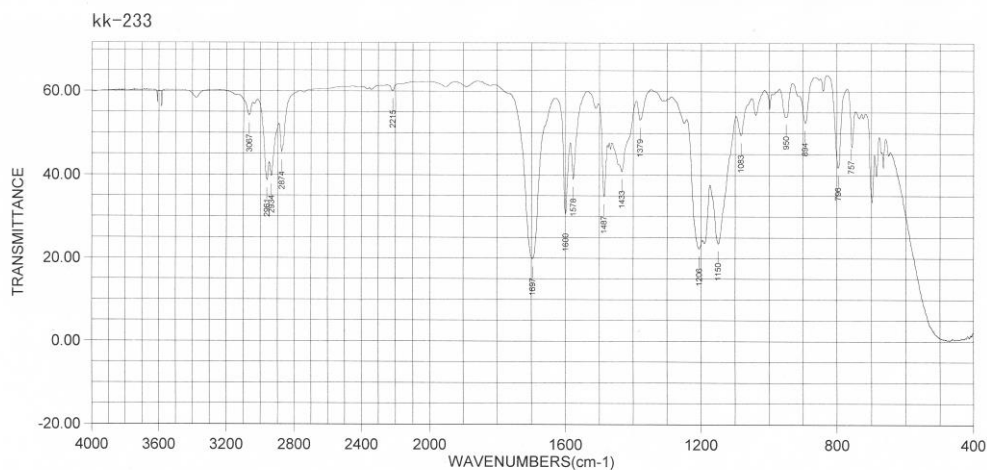
Mass spectrum (FD) of **29**.



¹H NMR (400 MHz) spectrum of **30**, measured in chloroform-*d* at room temperature.

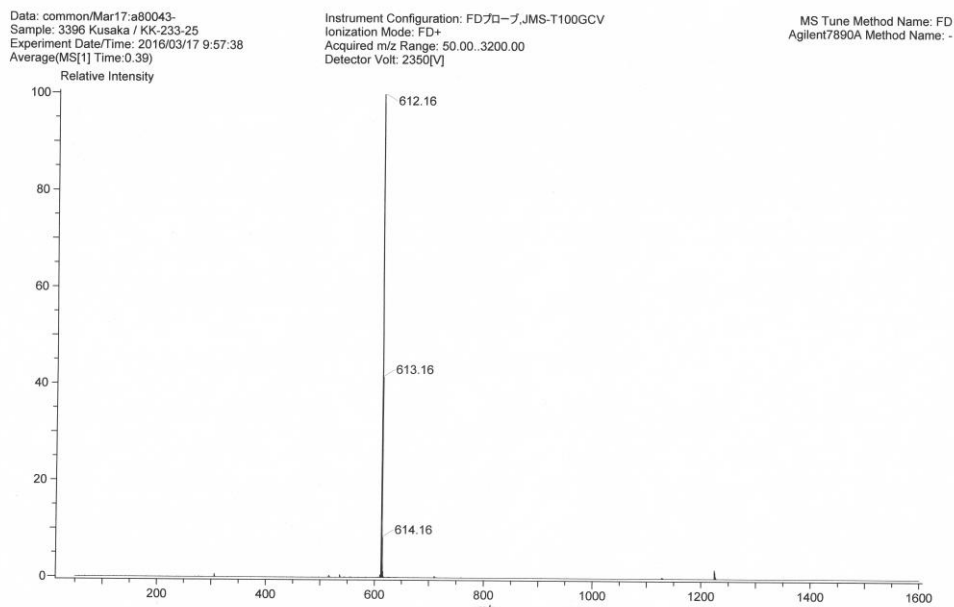


¹³C NMR (100 MHz) spectrum of **30**, measured in chloroform-*d* at room temperature.



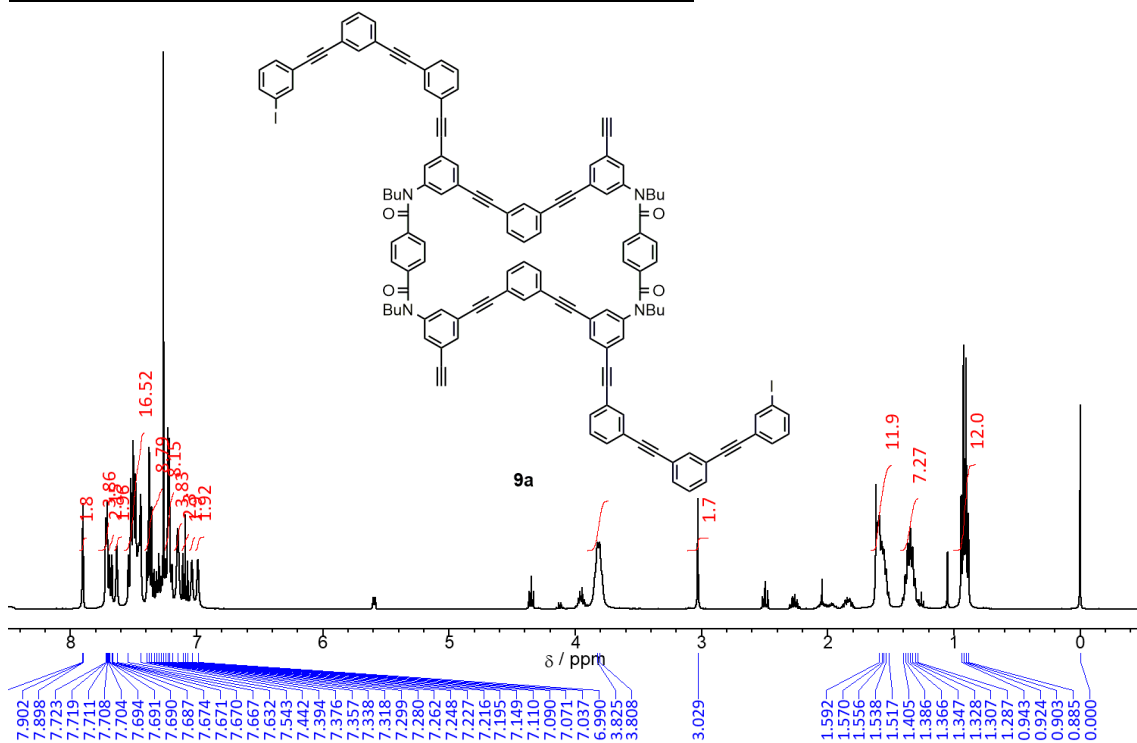
RESOL	: 2	cm-1	3067.26	54.15	1379.83	53.19
SCANS	: 5		2961.20	38.66	1206.27	22.34
AMPGAIN	: x1		2934.20	39.61	1150.34	23.59
P. INT	: 1	cm-1	2874.41	45.30	1083.81	49.51
BEAM	: single		2215.84	60.07	950.75	54.01
S. SPEED	: TGS		1697.07	19.87	894.82	52.48
M. DATE	: 3/27/16		1600.65	30.56	796.47	41.82
F. NAME	: 測定中のデータ		1578.47	38.97	757.90	48.17
			1487.83	34.83		
			1433.83	40.86		

IR spectrum of 30.

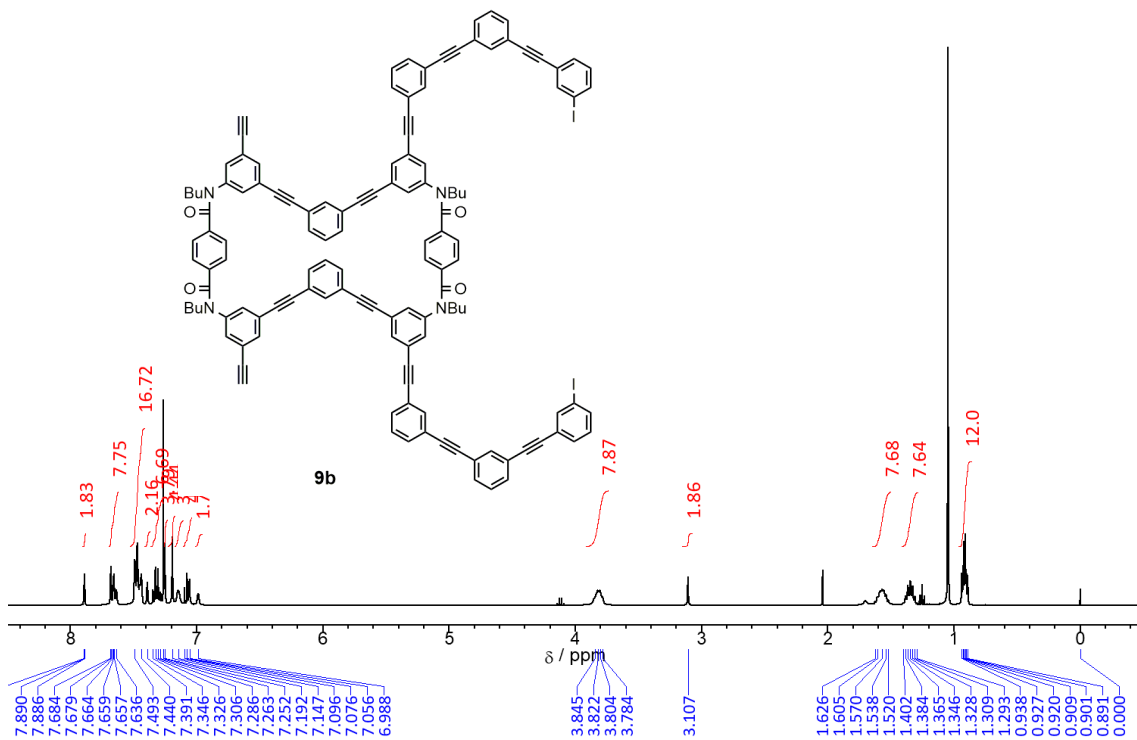


Mass spectrum (FD) of 30.

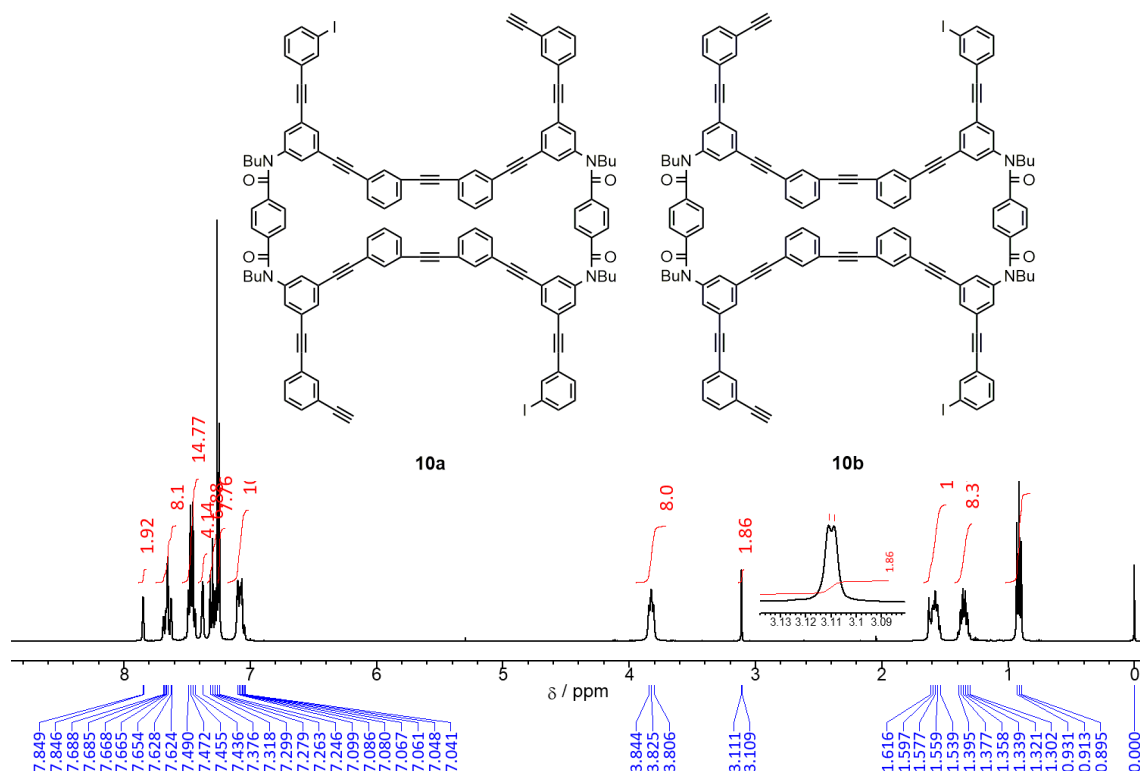
¹H NMR spectra of new compounds (unprotected)



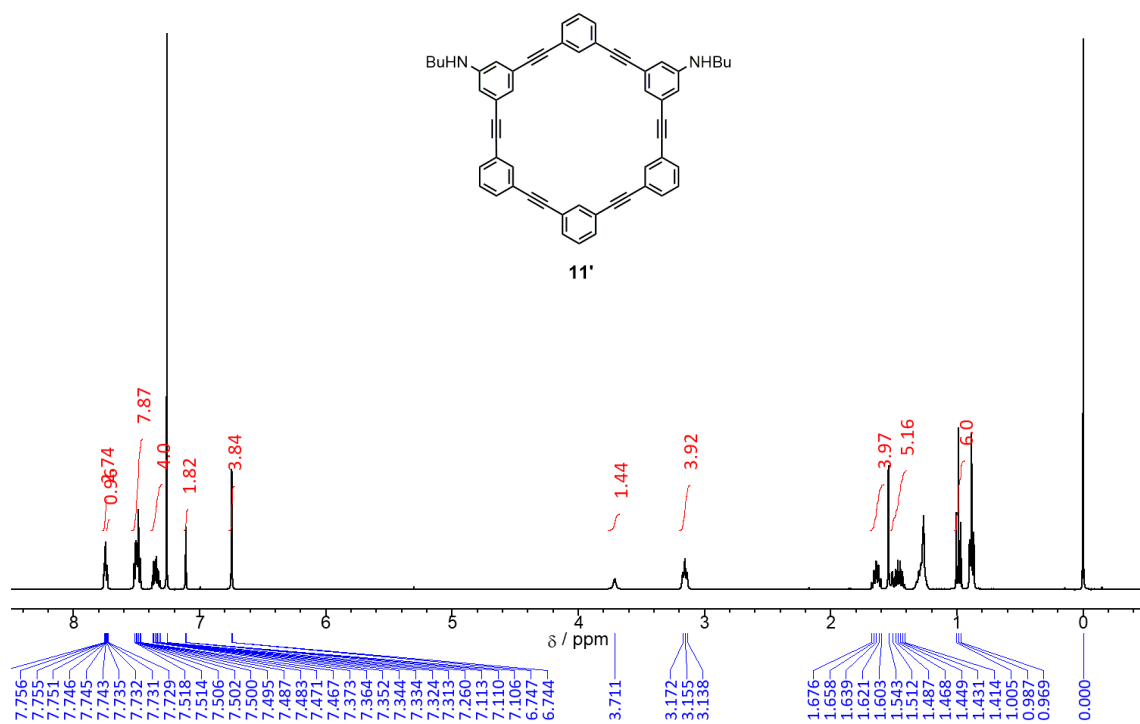
¹H NMR spectrum (400 MHz) of **9a** cont. residual solvents (ethanol and ethyl acetate etc.), measured in chloroform-*d* at room temperature.



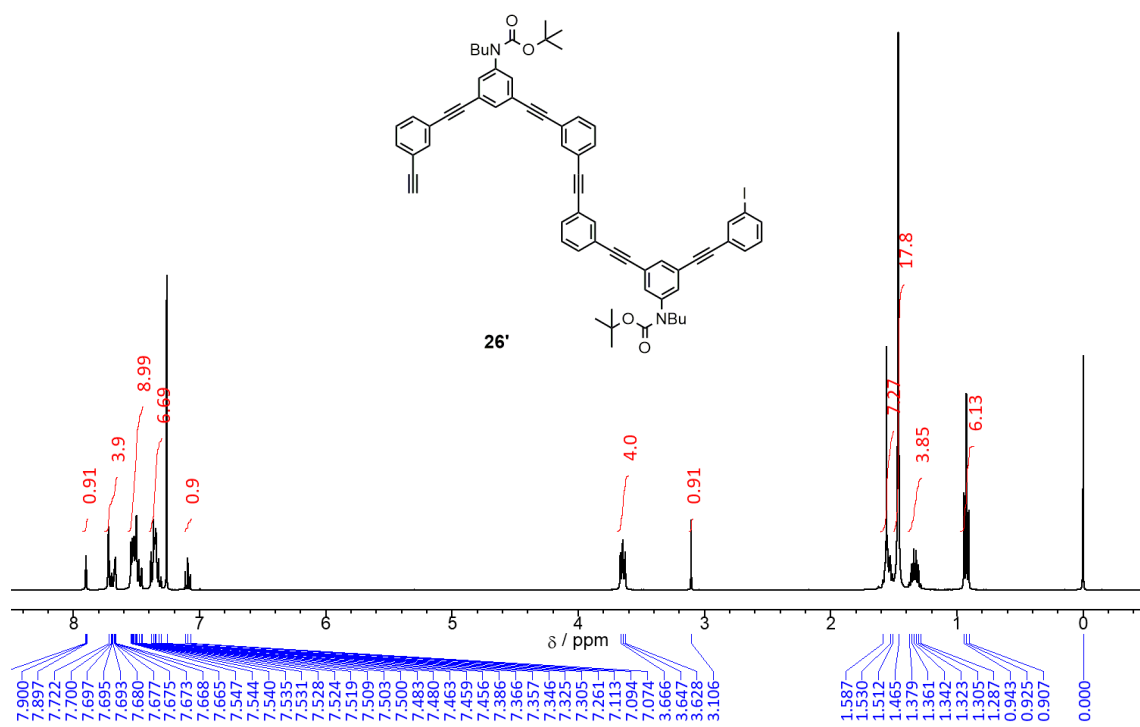
¹H NMR spectrum (400 MHz) of **9b** cont. residual solvents (ethyl acetate etc.), measured in chloroform-*d* at room temperature.



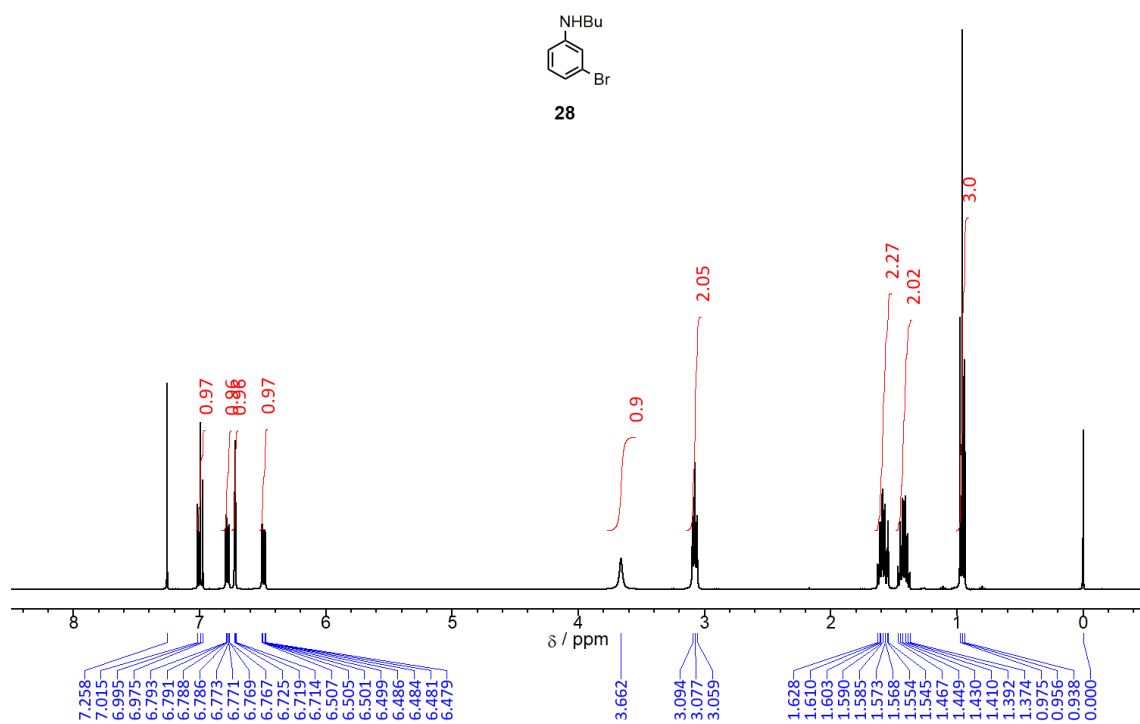
^1H NMR spectrum (400 MHz) of **10a** and **10b**, measured in chloroform-*d* at room temperature.



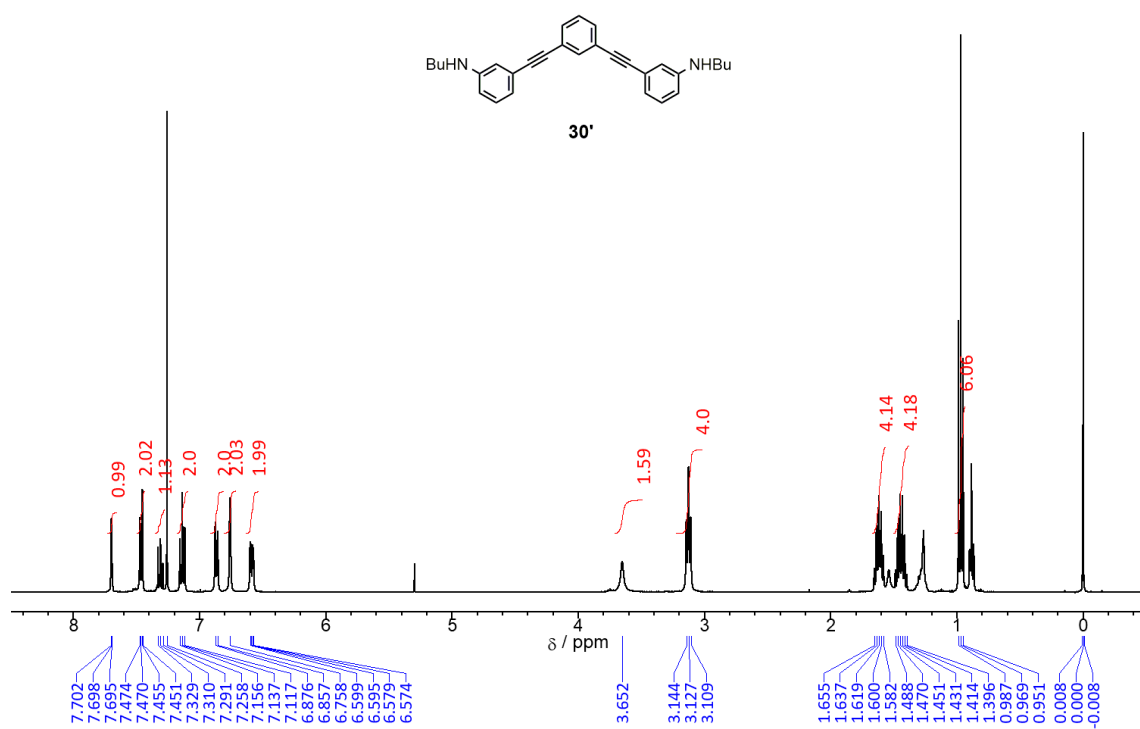
^1H NMR spectrum (400 MHz) of **11'** cont. residual solvents (hexane), measured in chloroform-*d* at room temperature.



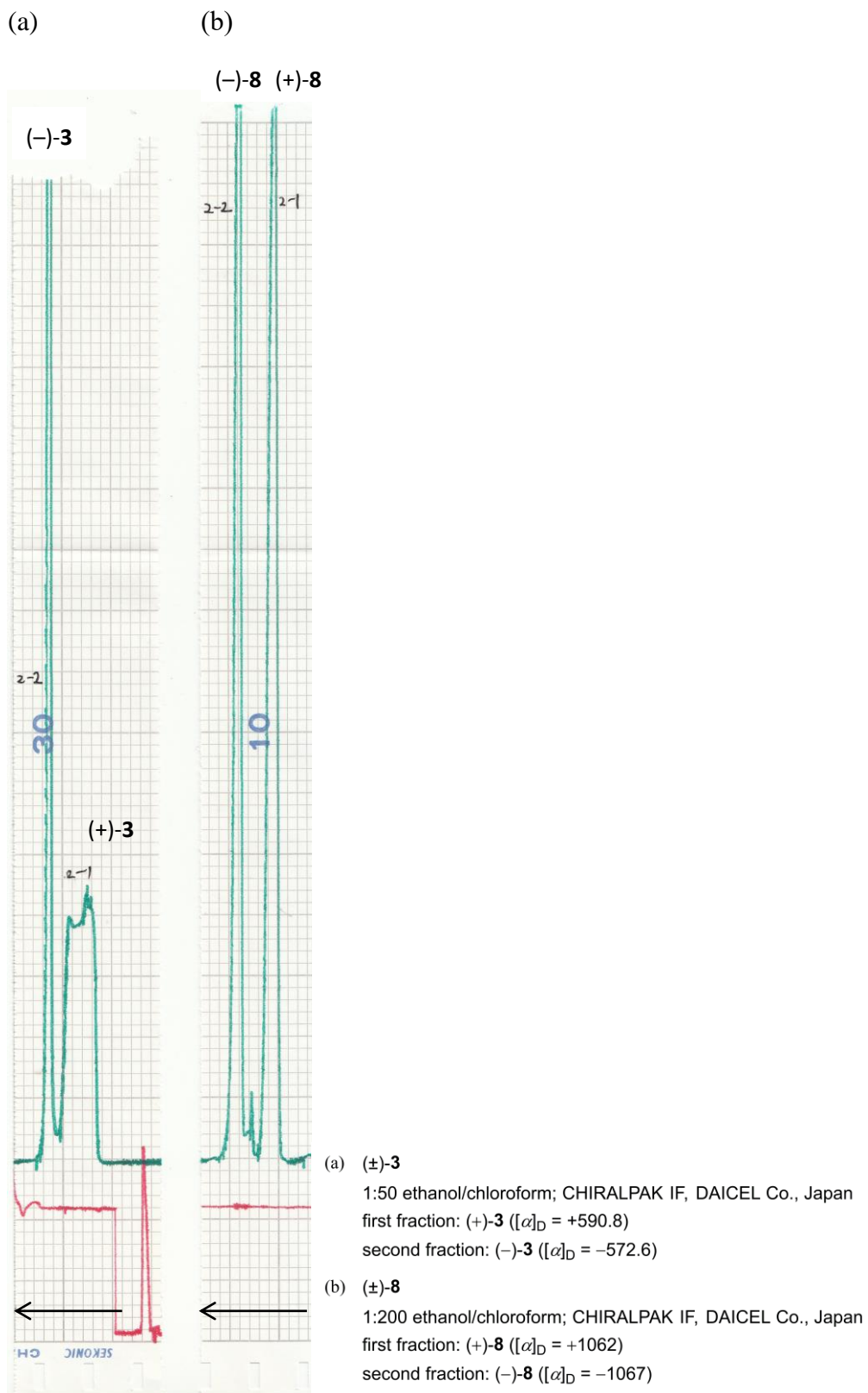
^1H NMR spectrum (400 MHz) of **26'**, measured in chloroform-*d* at room temperature.



^1H NMR spectrum (400 MHz) of **28**, measured in chloroform-*d* at room temperature.



^1H NMR spectrum (400 MHz) of **30'** cont. residual solvents (dichloromethane and hexane), measured in chloroform-*d* at room temperature.



Chiral HPLC traces, detected by UV at 254 nm (green lines).