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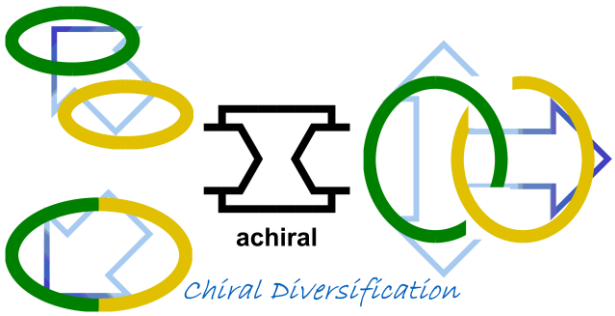
Supplementary Information 2

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



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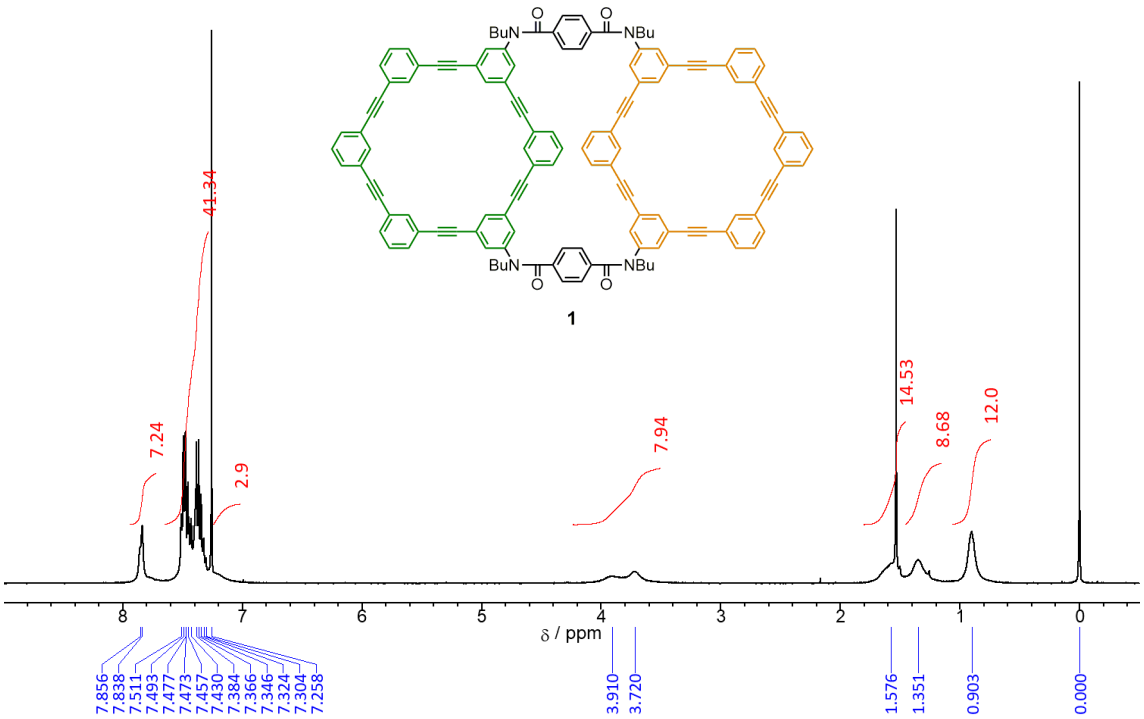
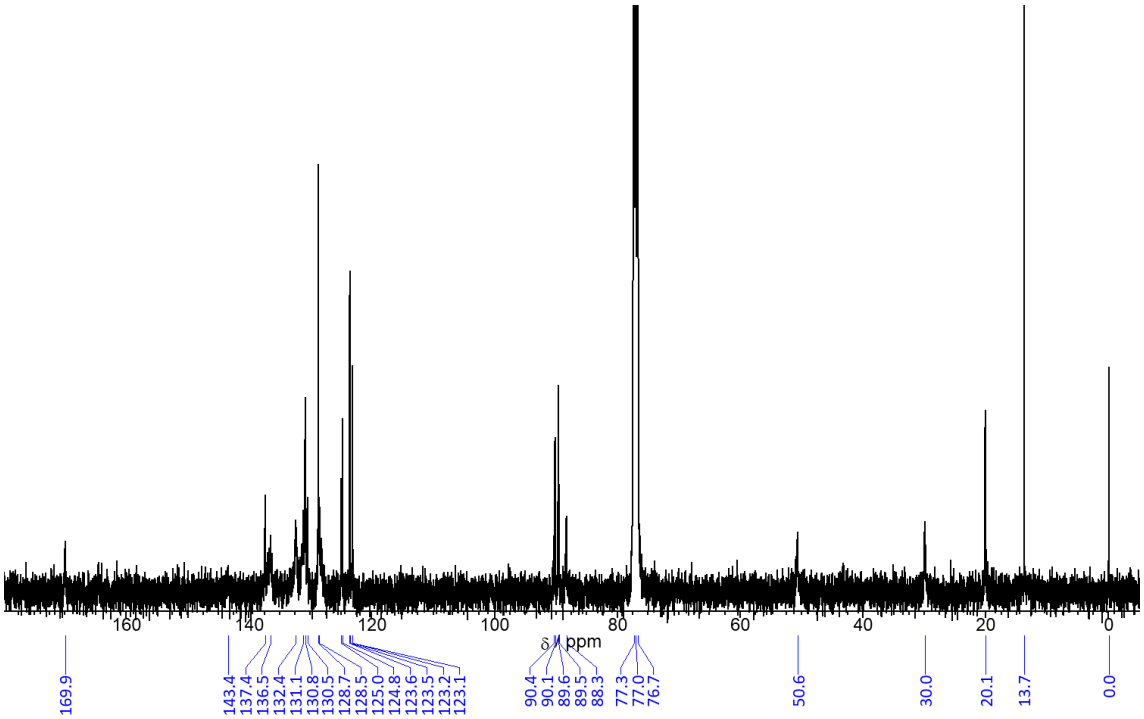
Copies of chiral HPLC traces	S81

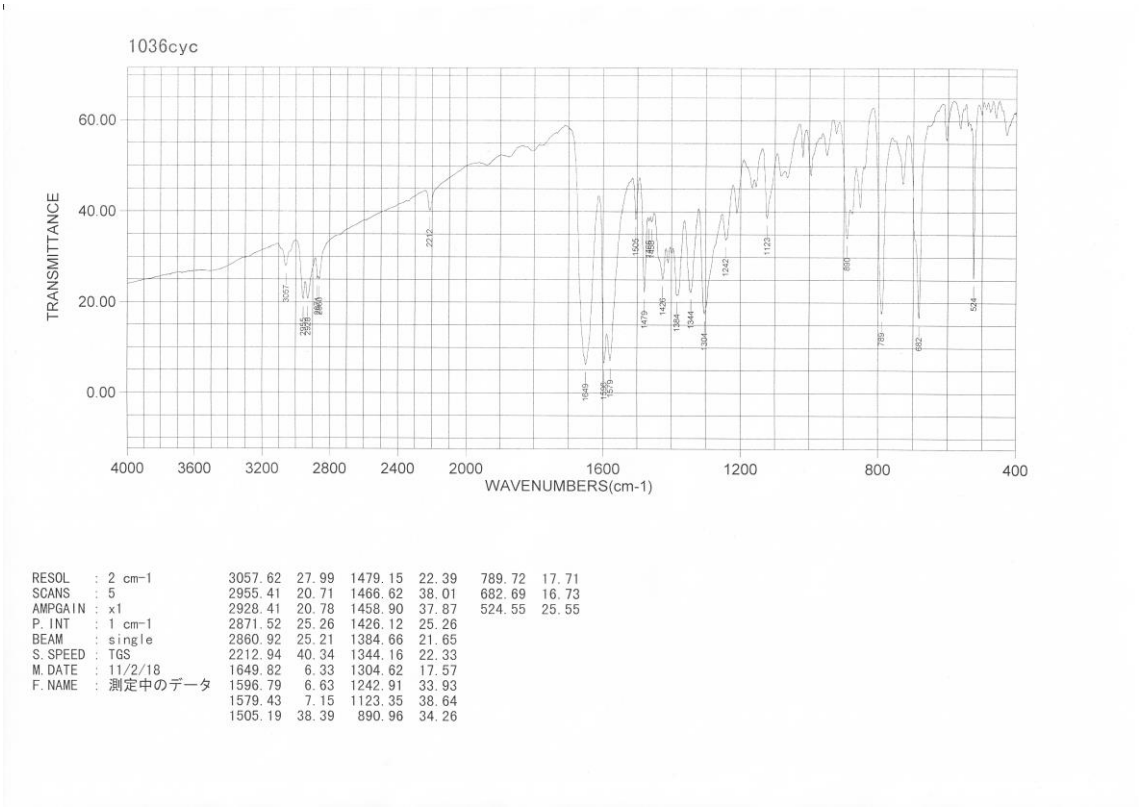
^{1}H and ^{13}C NMR spectra of new compounds



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

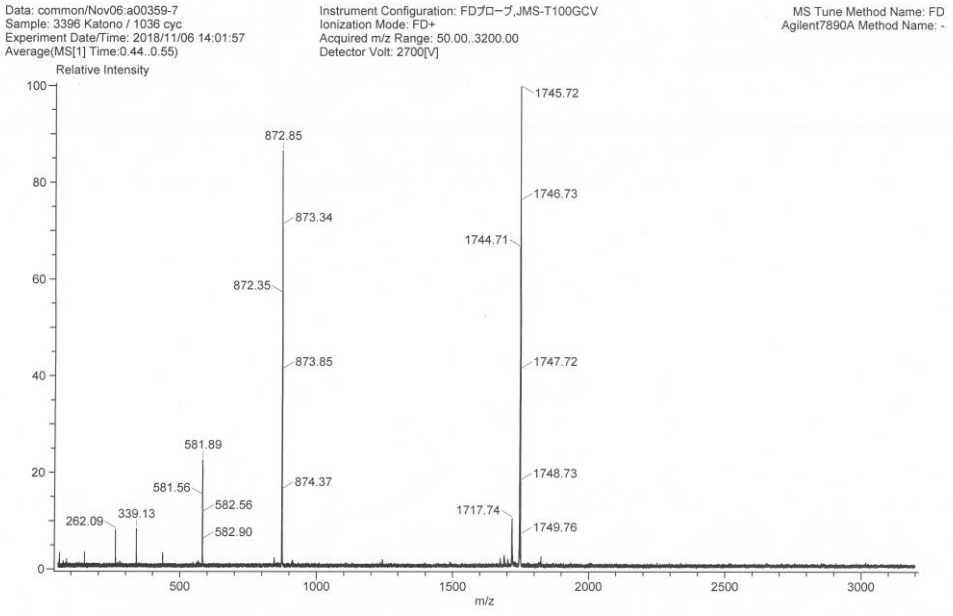


^{13}C NMR (100 MHz) spectrum of **1**, measured in chloroform-*d* at 313 K.

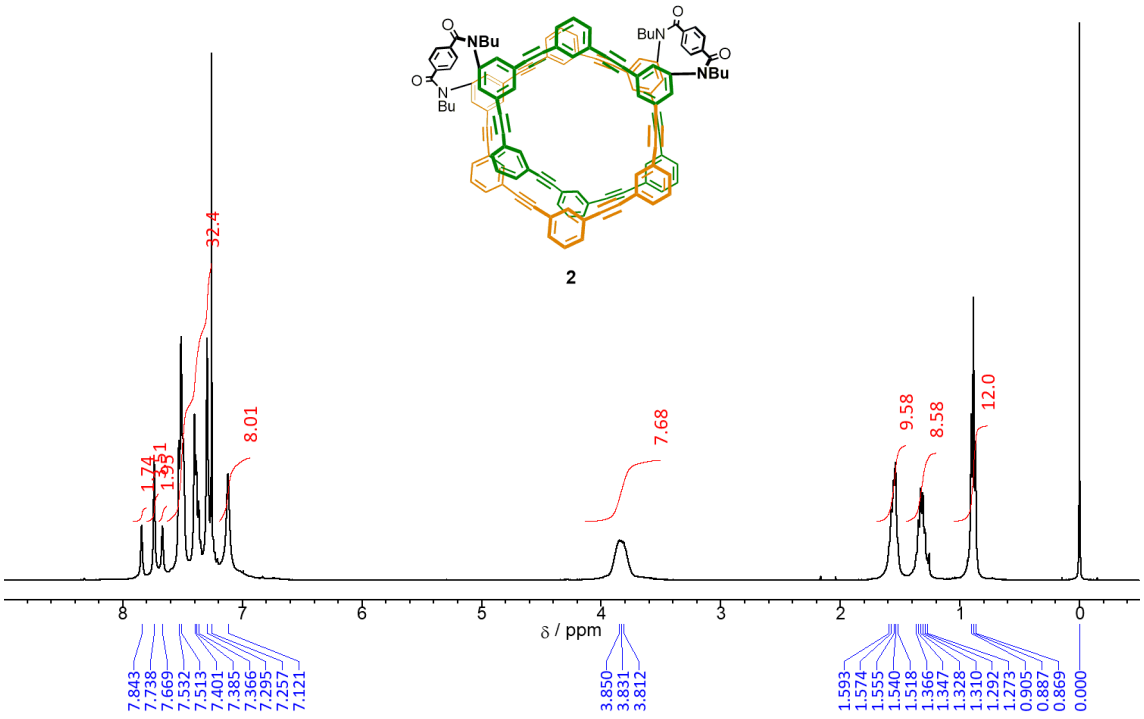


RESOL	: 2 cm-1	3057.62	27.99	1479.15	22.39	789.72	17.71
SCANS	: 5	2955.41	20.71	1466.62	38.01	682.69	16.73
AMPGAIN	: x1	2928.41	20.78	1458.90	37.87	524.55	25.55
P.INT	: 1 cm-1	2871.52	25.26	1426.12	25.26		
BEAM	: single	2860.92	25.21	1384.66	21.65		
S.SPEED	: TGS	2212.94	40.34	1344.16	22.33		
M.DATE	: 11/2/18	1649.82	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		

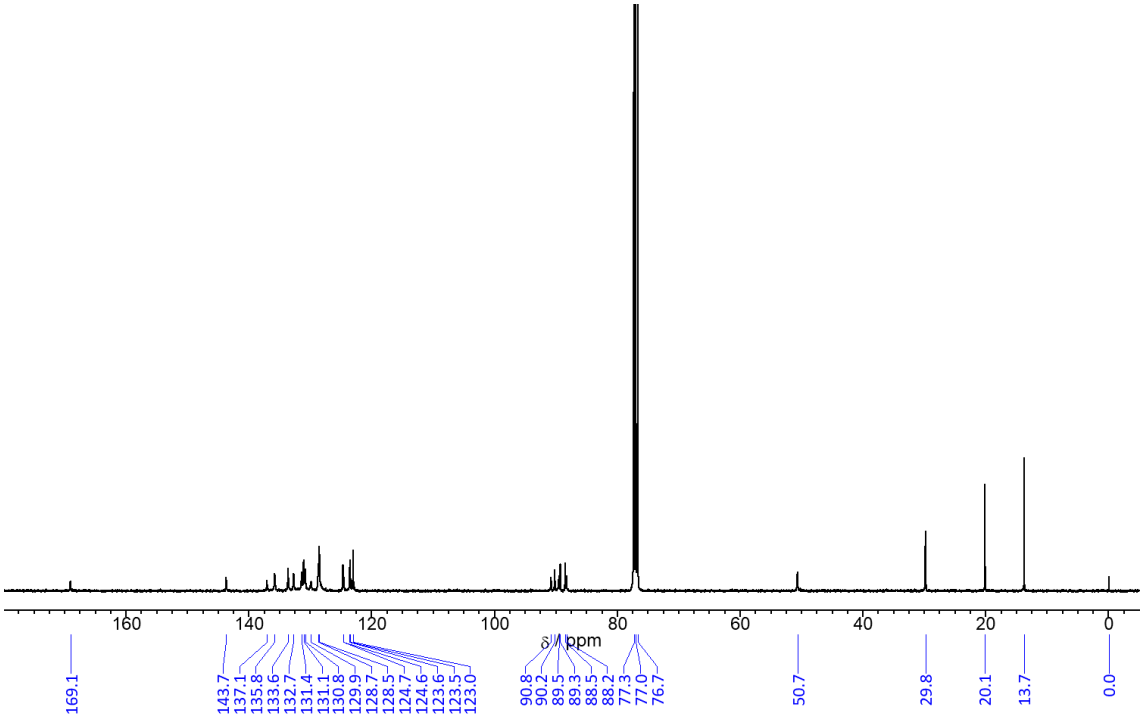
IR spectrum of **1**.



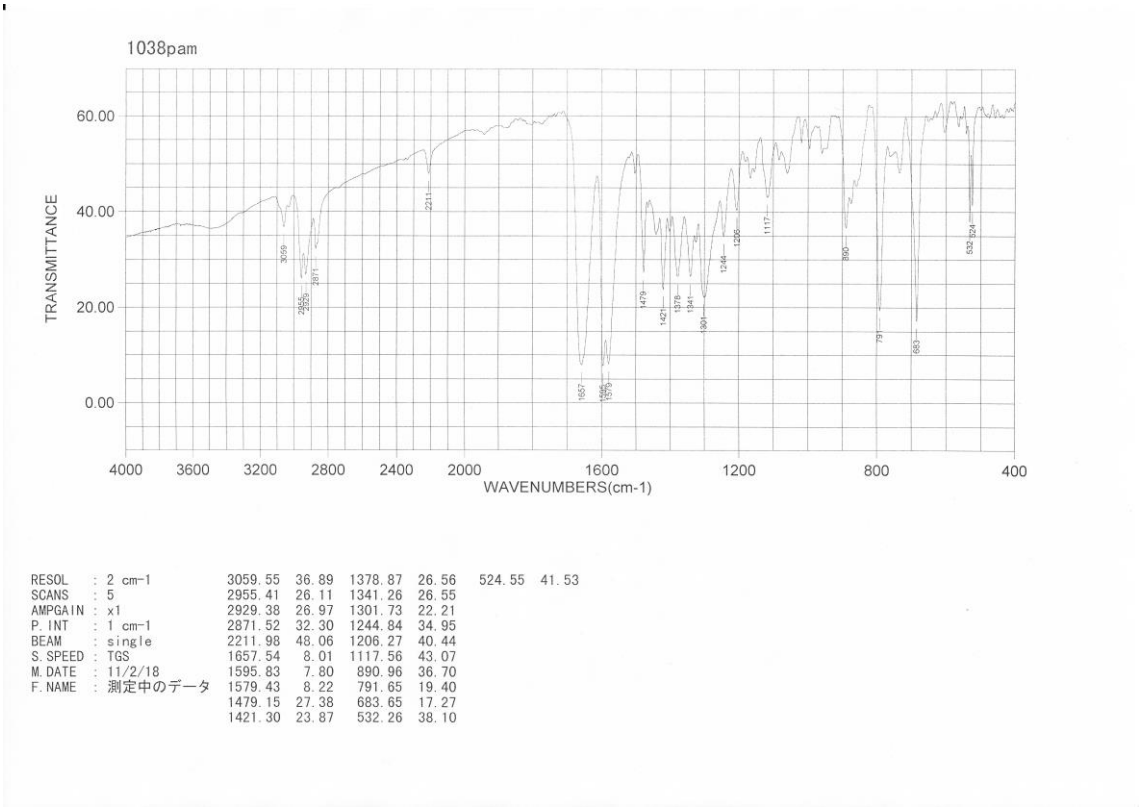
Mass spectrum (FD) of **1**.



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

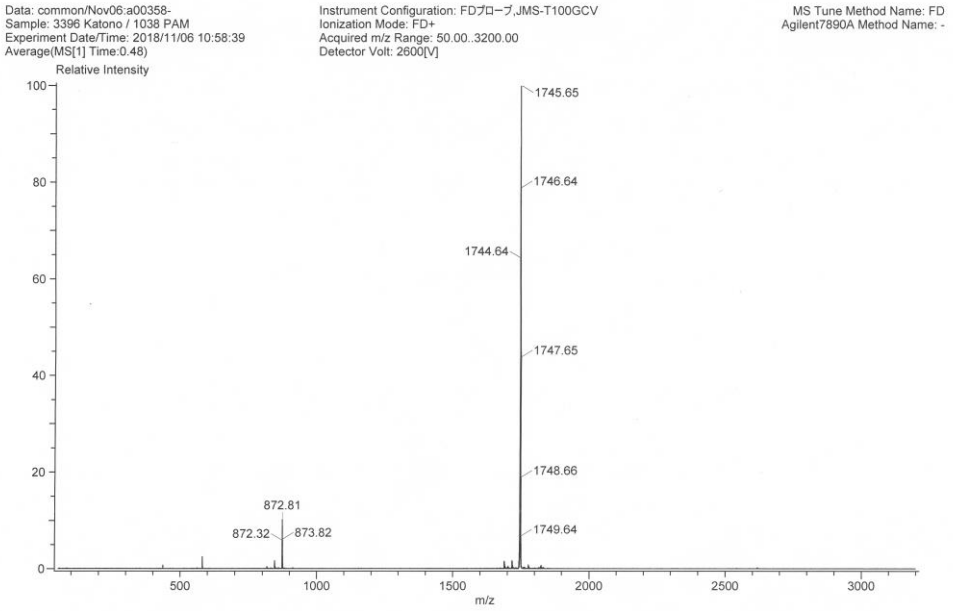


^{13}C NMR (100 MHz) spectrum of **2**, measured in chloroform-*d* at 313 K.

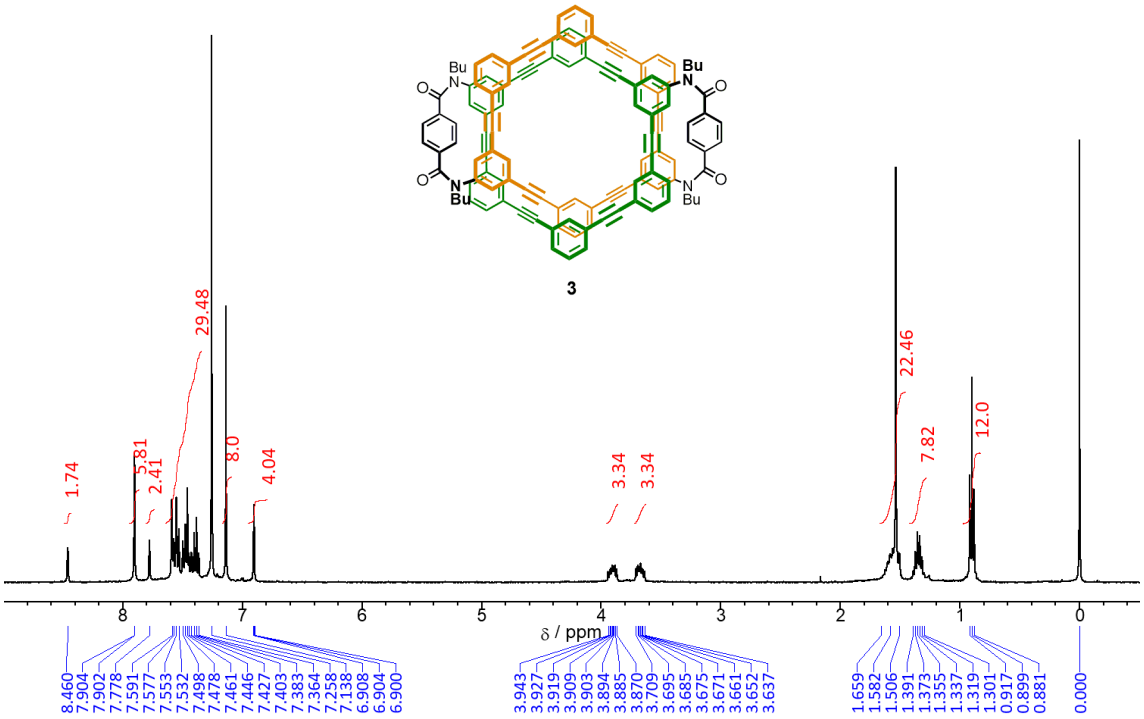


RESOL	: 2 cm-1	3059.55	36.89	1378.87	26.56	524.55	41.53
SCANS	: 5	2955.41	26.11	1341.26	26.55		
AMPGAIN	: x1	2929.38	26.97	1301.73	22.21		
P.INT	: 1 cm-1	2871.52	32.30	1244.84	34.95		
BEAM	: single	2211.98	48.06	1206.27	40.44		
S.SPEED	: TGS	1657.54	8.01	1117.56	43.07		
M.DATE	: 11/2/18	1595.83	7.80	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		

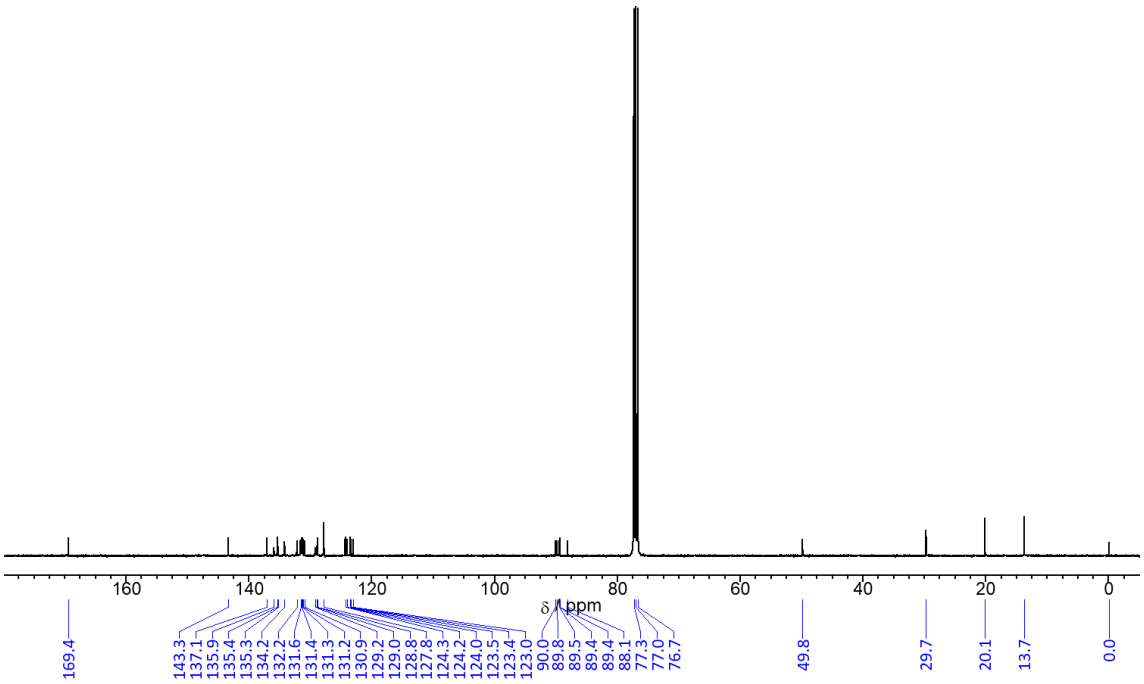
IR spectrum of **2**.



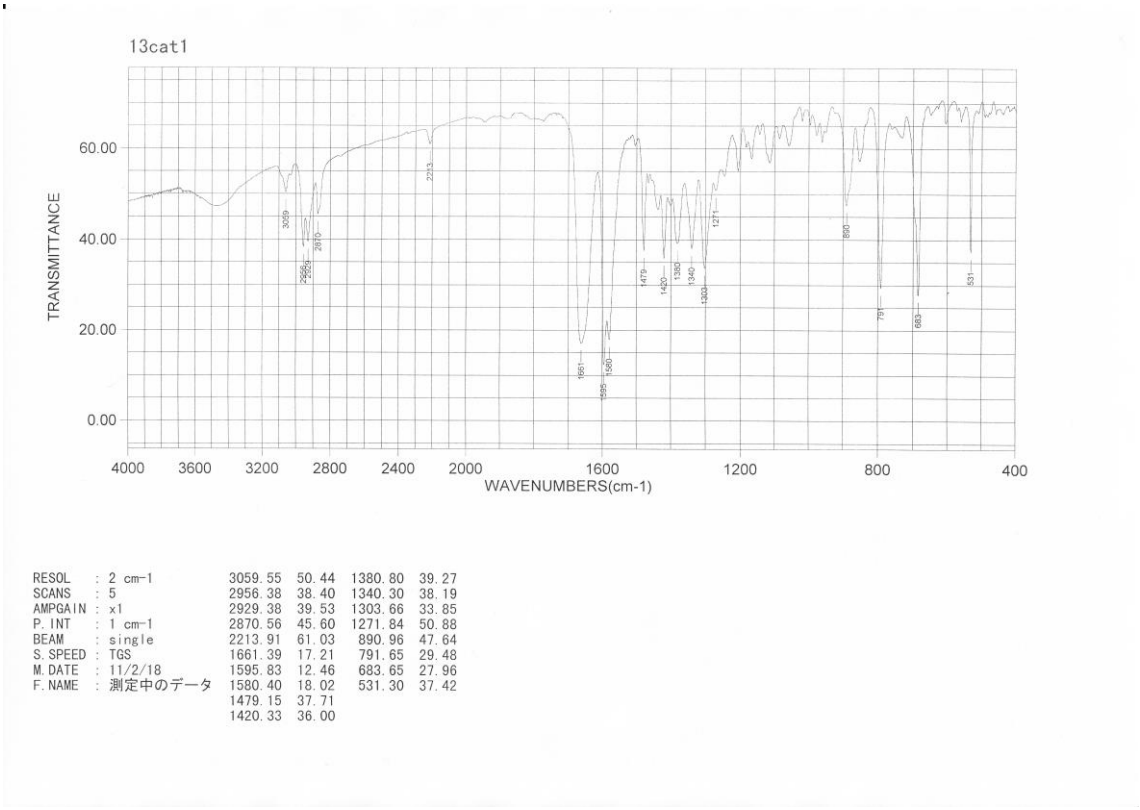
Mass spectrum (FD) of **2**.



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

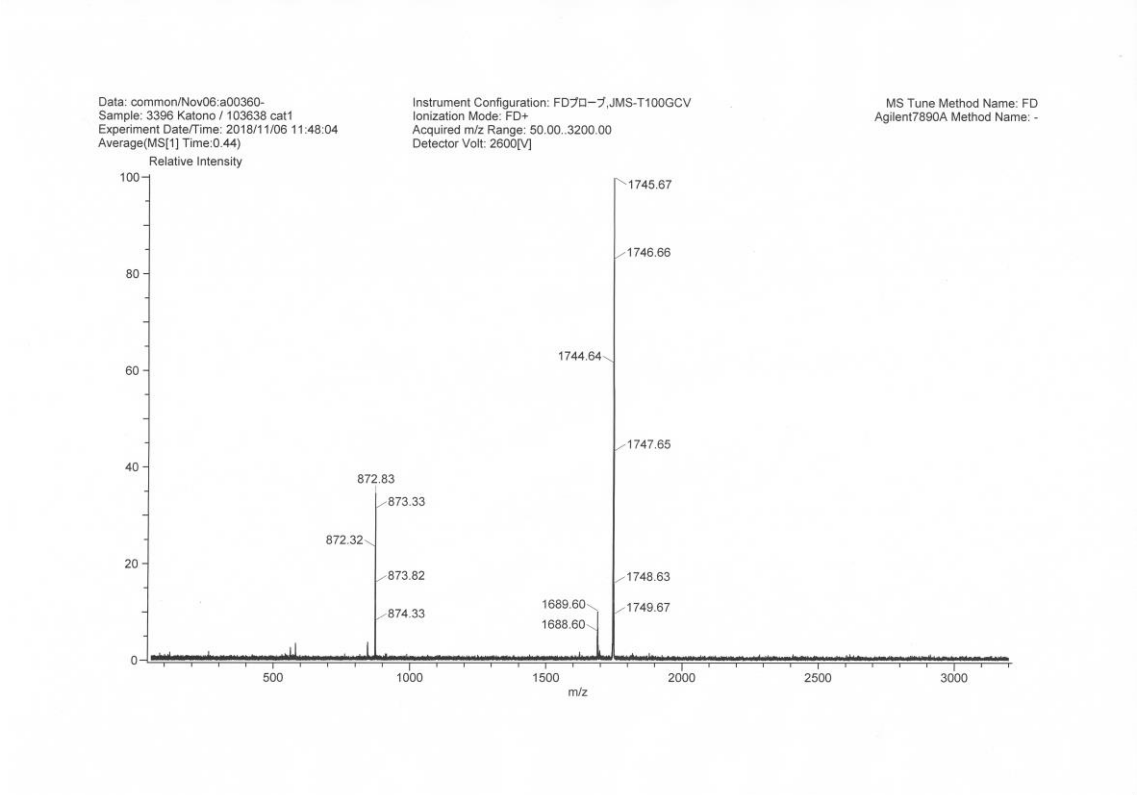


^{13}C NMR (100 MHz) spectrum of (±)-**3**, measured in chloroform-*d* at 313 K.

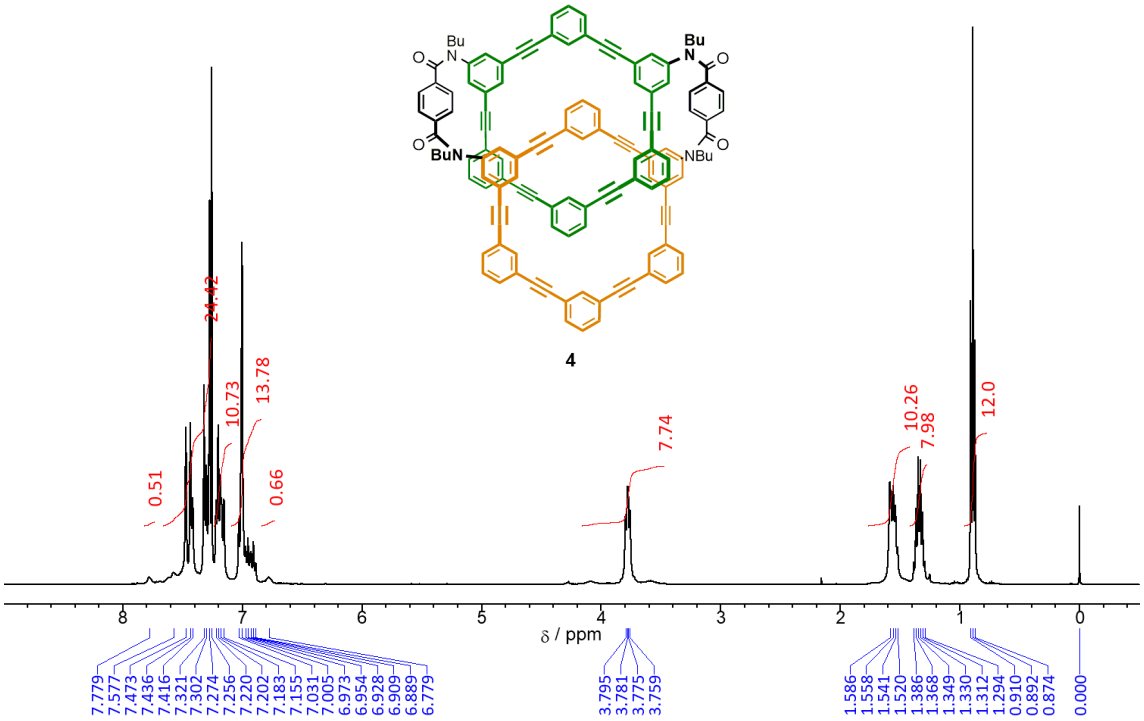


RESOL	: 2 cm-1	3059.55	50.44	1380.80	39.27
SCANS	: 5	2956.38	38.40	1340.30	38.19
AMPGAIN	: x1	2929.38	39.53	1303.66	33.85
P.INT	: 1 cm-1	2870.56	45.60	1271.84	50.88
BEAM	: single	2213.91	61.03	890.96	47.64
S.SPEED	: TGS	1661.39	17.21	791.65	29.48
M.DATE	: 11/2/18	1595.83	12.46	683.65	27.96
F.NAME	: 測定中のデータ	1580.40	18.02	531.30	37.42
		1479.15	37.71		
		1420.33	36.00		

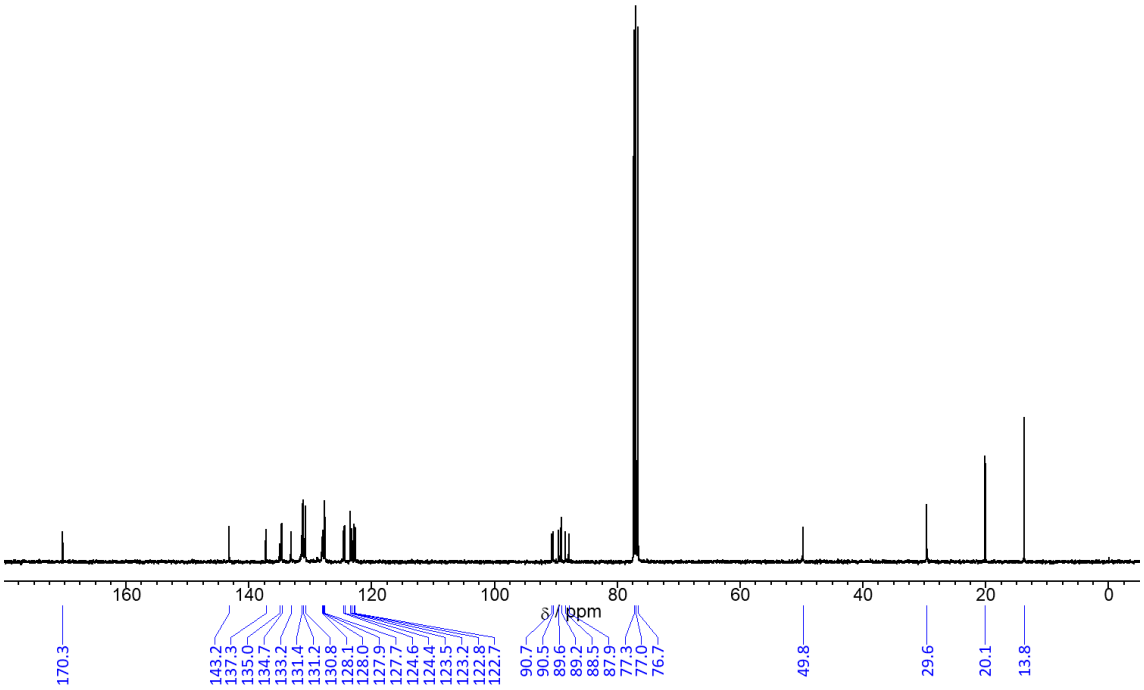
IR spectrum of (±)-**3**.



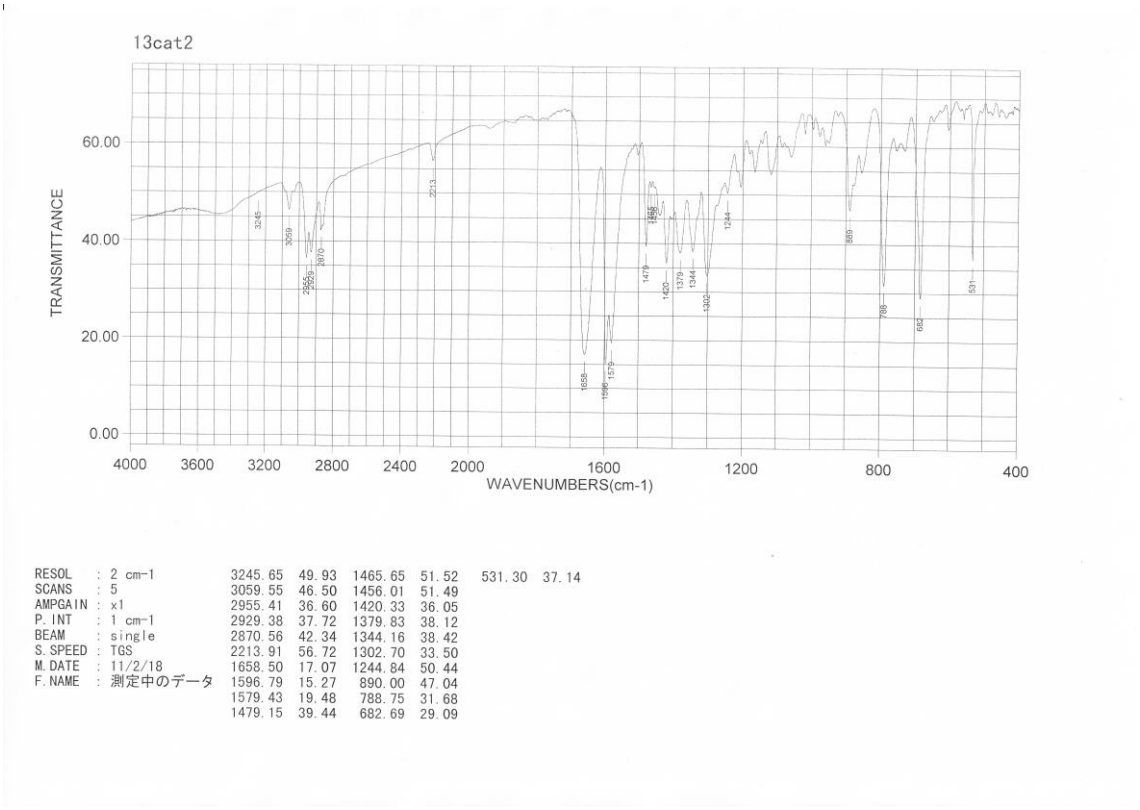
Mass spectrum (FD) of (±)-**3**.



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

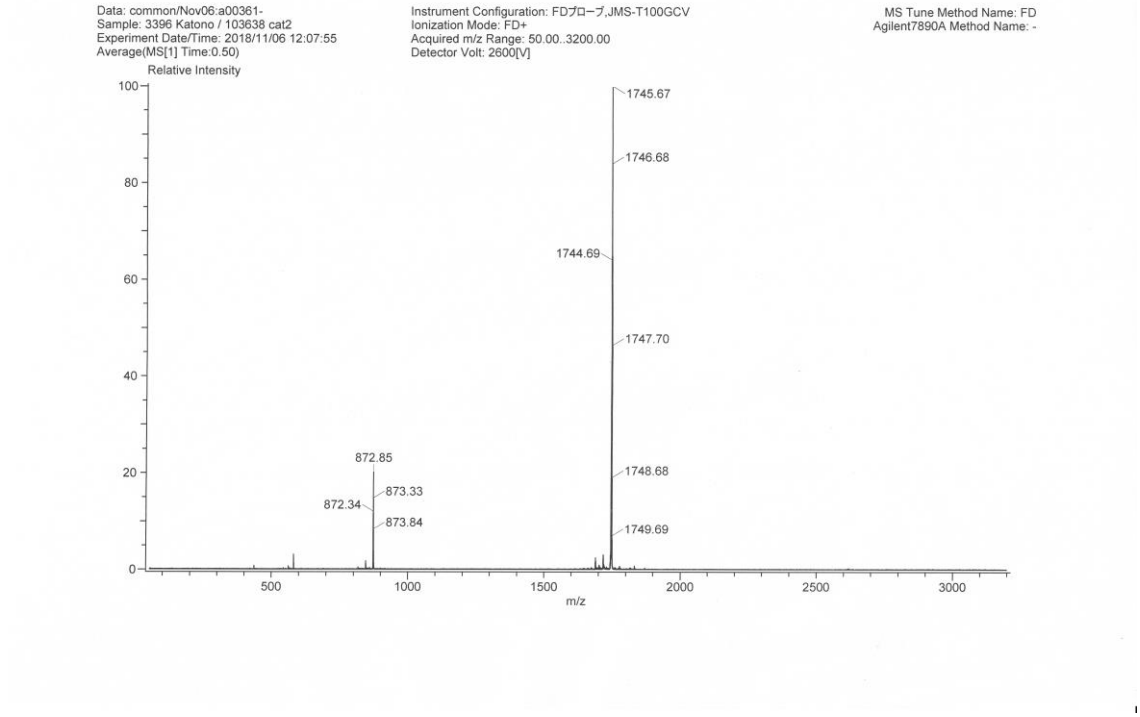


^{13}C NMR (100 MHz) spectrum of (±)-**4**, measured in chloroform-*d* at room temperature.

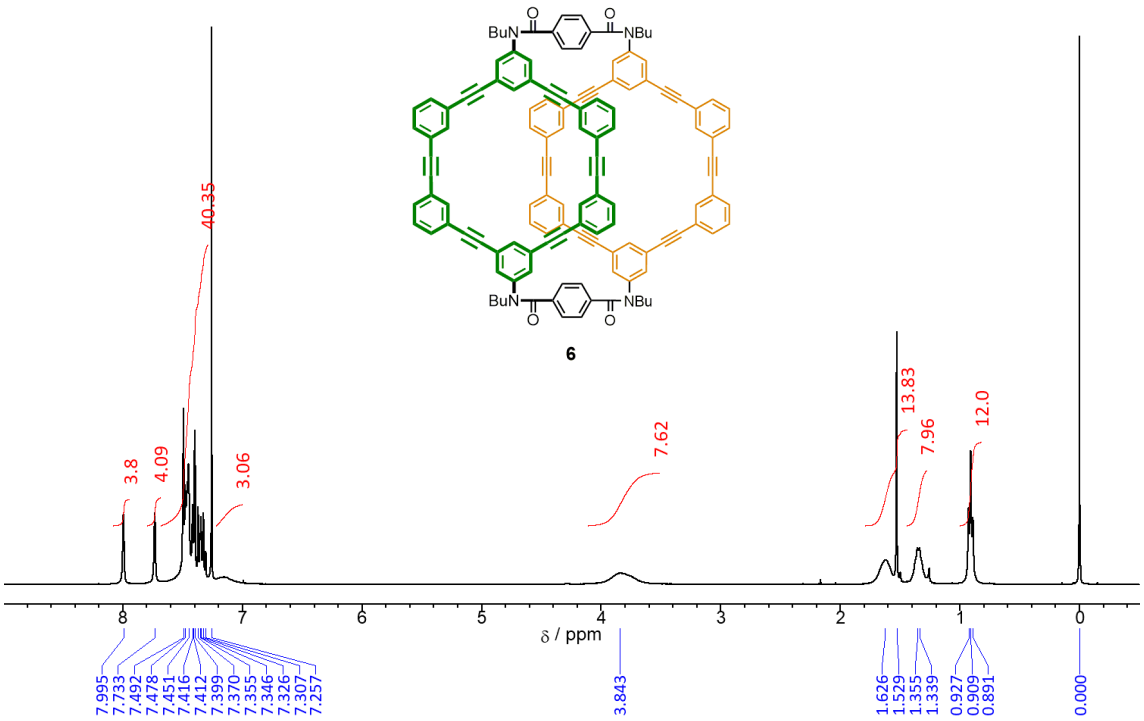


RESOL	: 2 cm-1	3245.65	49.93	1465.65	51.52	531.30	37.14
SCANS	: 5	3059.55	46.50	1456.01	51.49		
AMPGAIN	: x1	2955.41	36.60	1420.33	36.05		
P.INT	: 1 cm-1	2929.38	37.72	1379.83	38.12		
BEAM	: single	2870.56	42.34	1344.16	38.42		
S.SPEED	: TGS	2213.91	56.72	1302.70	33.50		
M.DATE	: 11/2/18	1658.50	17.07	1244.84	50.44		
F.NAME	: 測定中のデータ	1596.79	15.27	890.00	47.04		
		1579.43	19.48	788.75	31.68		
		1479.15	39.44	682.69	29.09		

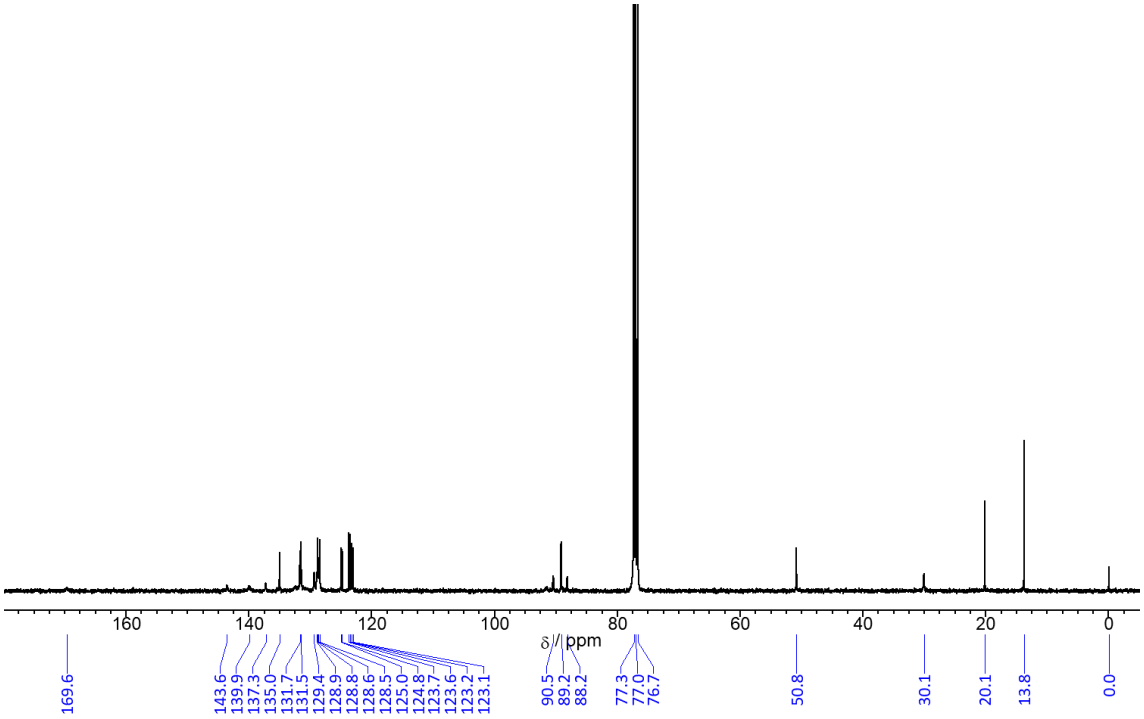
IR spectrum of (±)-**4**.



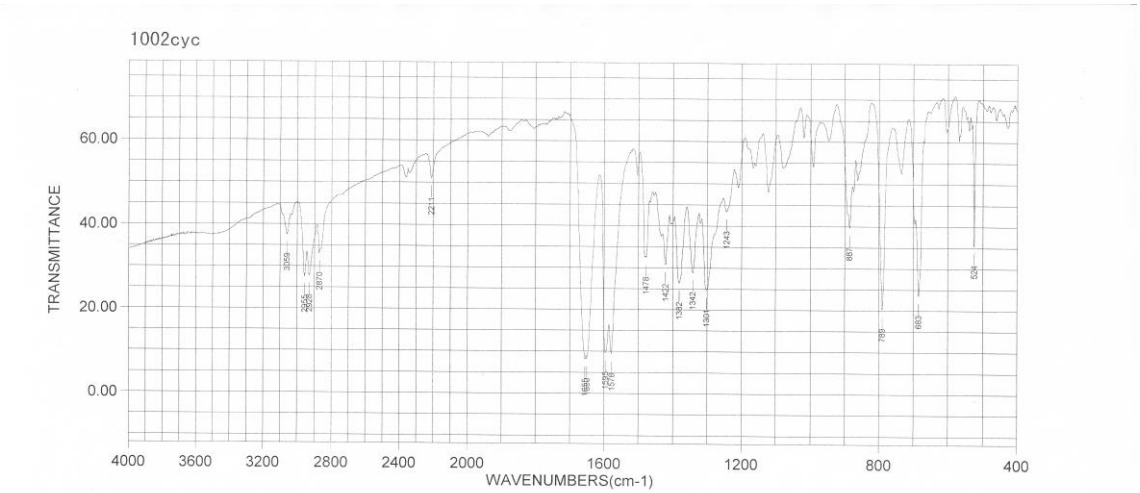
Mass spectrum (FD) of (±)-**4**.



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

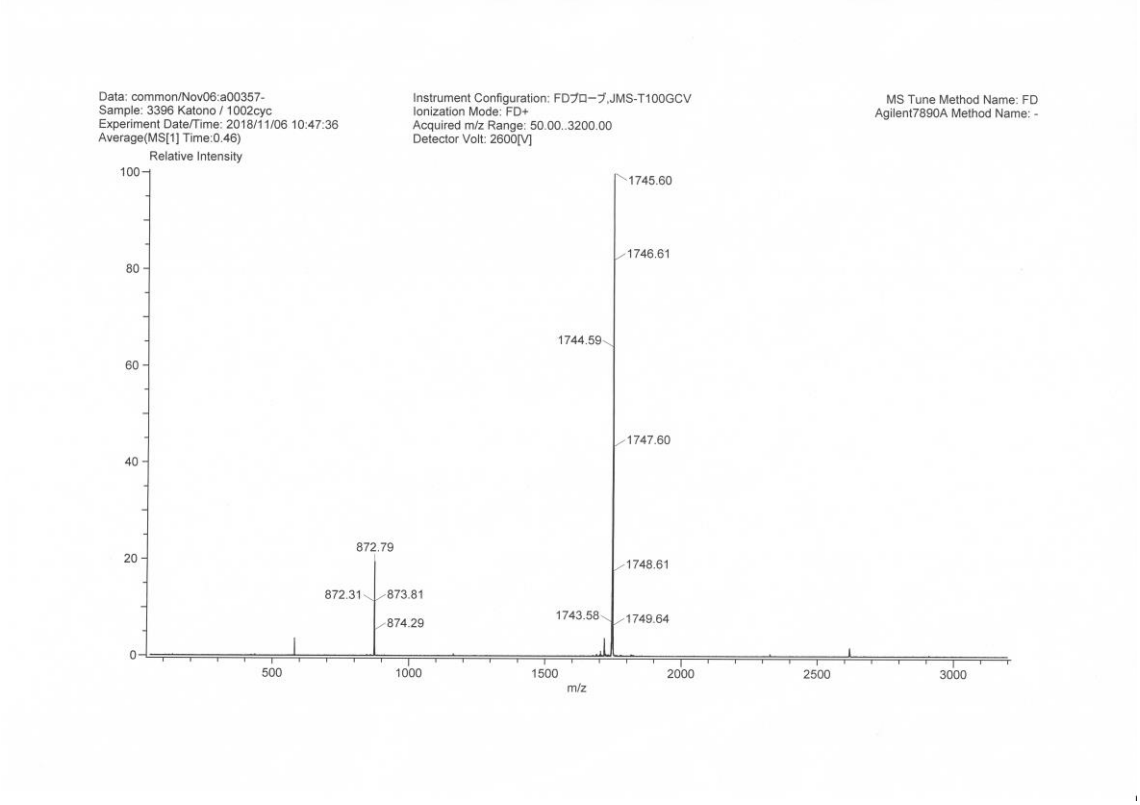


^{13}C NMR (100 MHz) spectrum of **6**, measured in chloroform-*d* at 313 K.

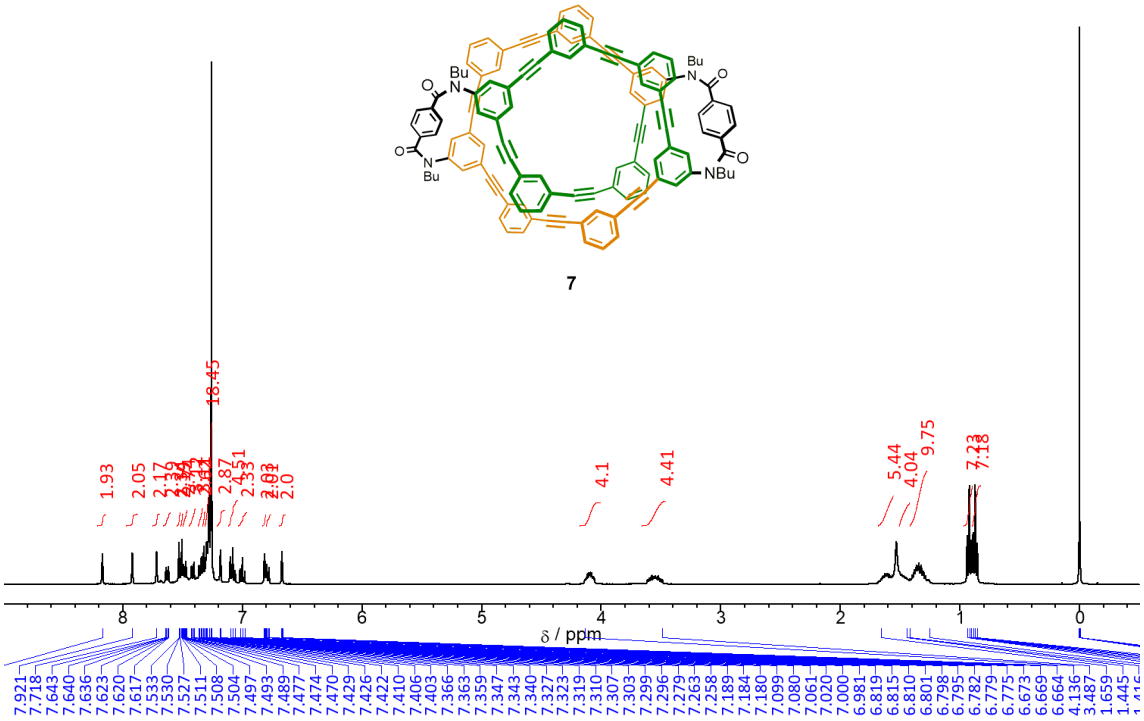


RESOL	: 2 cm-1	3059.55	37.59	1422.26	30.82
SCANS	: 5	2955.41	27.62	1382.73	26.47
AMPGAIN	: x1	2928.41	27.80	1342.23	28.88
P.INT	: 1 cm-1	2870.56	33.07	1301.73	24.77
BEAM	: single	2211.98	51.06	1243.88	43.43
S.SPEED	: TGS	1655.61	8.20	887.11	39.74
M.DATE	: 11/2/18	1650.79	8.31	789.72	20.39
F.NAME	: 測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

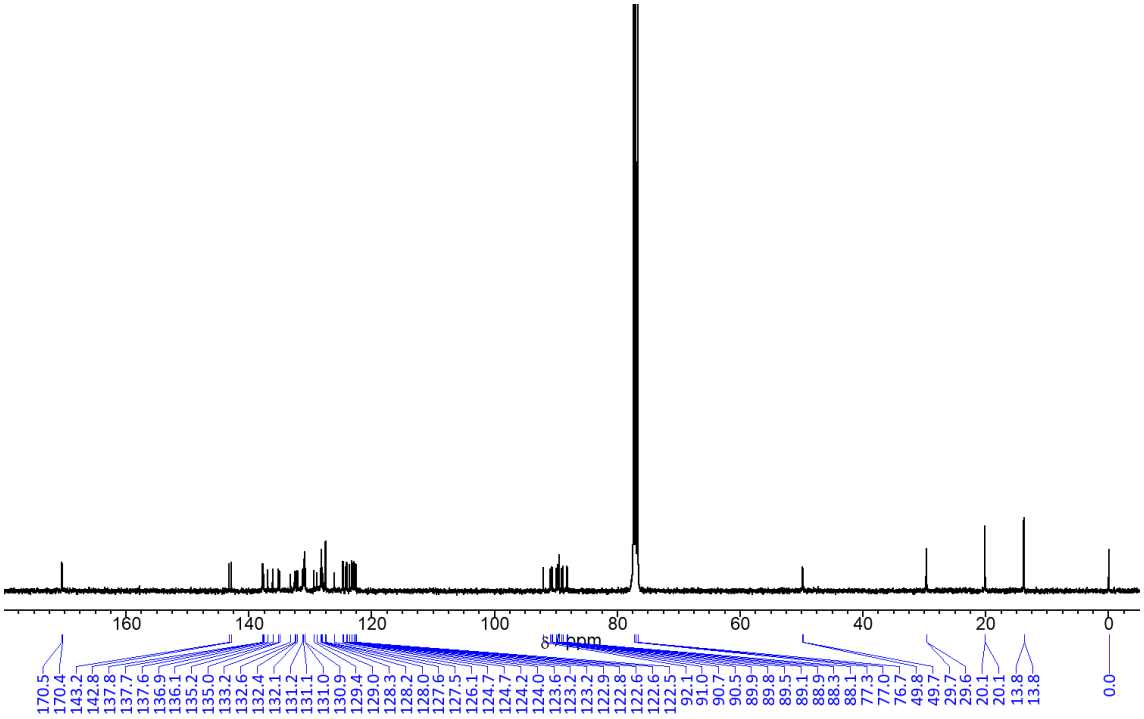
IR spectrum of **6**.



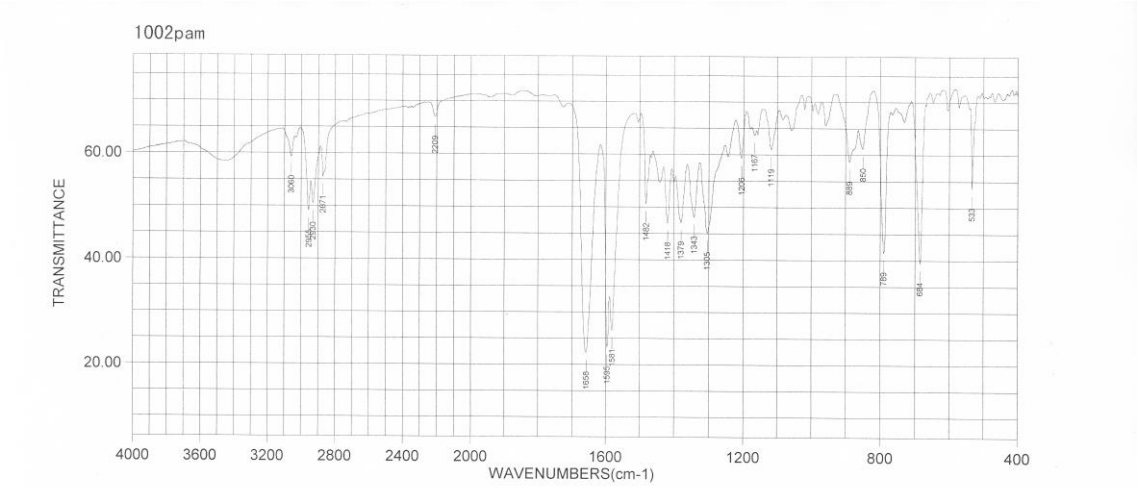
Mass spectrum (FD) of **6**.



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

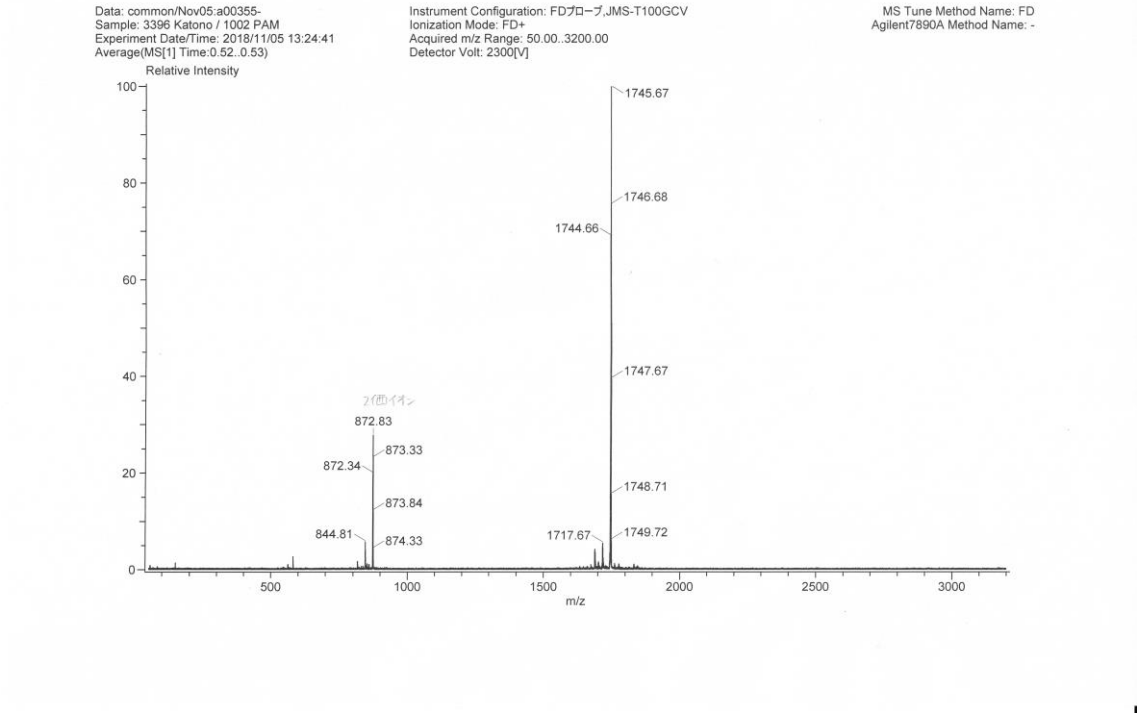


^{13}C NMR (100 MHz) spectrum of **7**, measured in chloroform-*d* at room temperature.

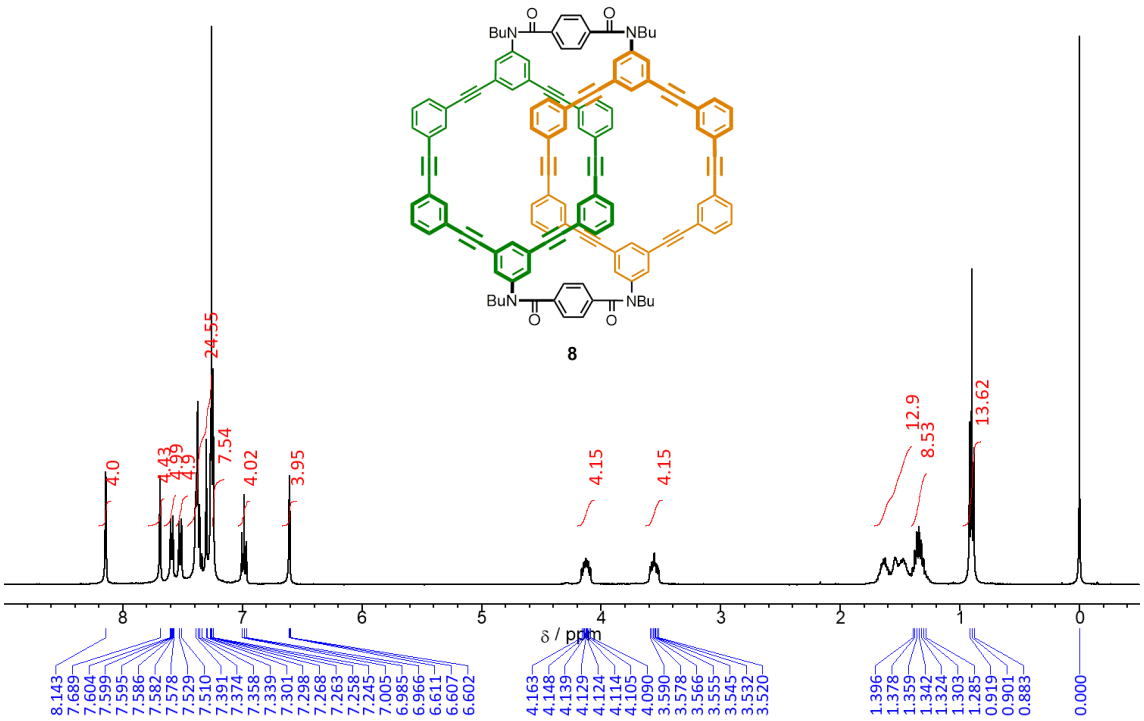


RESOL	: 2 cm-1	3060.51	59.30	1379.83	47.11	533.23	53.77
SCANS	: 5	2955.41	49.06	1343.19	48.12		
AMPGAIN	: x1	2930.34	50.44	1305.59	45.14		
P.INT	: 1 cm-1	2871.52	55.52	1206.27	59.32		
BEAM	: single	2209.09	66.94	1167.70	63.71		
S.SPEED	: TGS	1658.50	22.31	1119.49	60.97		
M.DATE	: 11/2/18	1595.83	23.34	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		

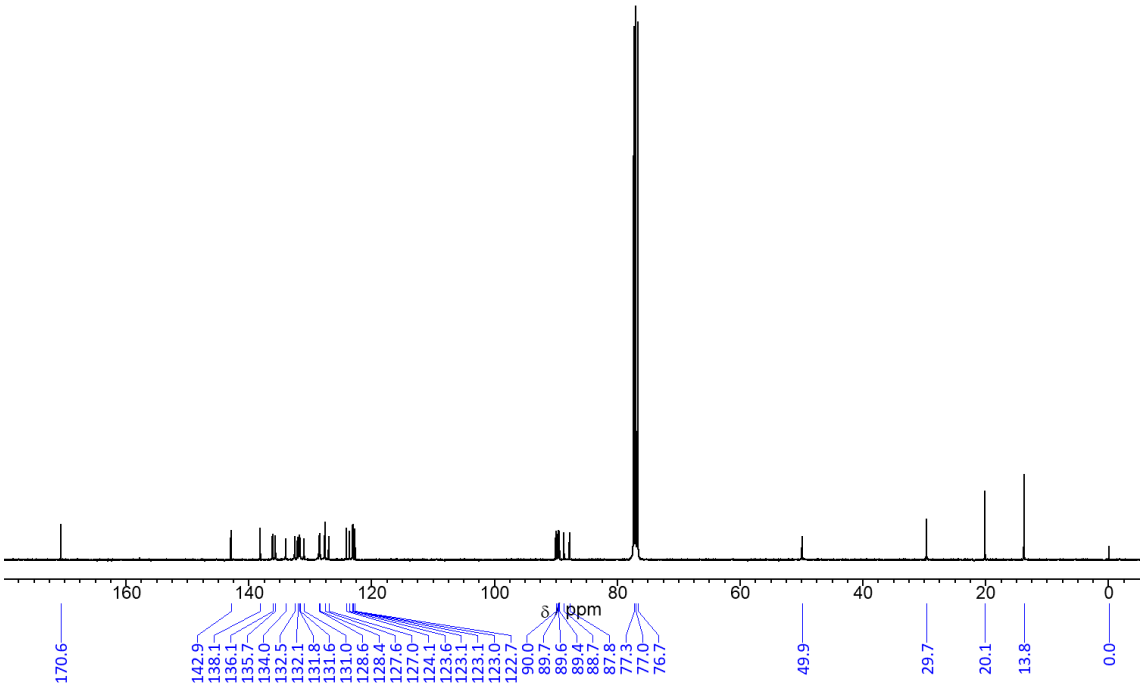
IR spectrum of **7**.



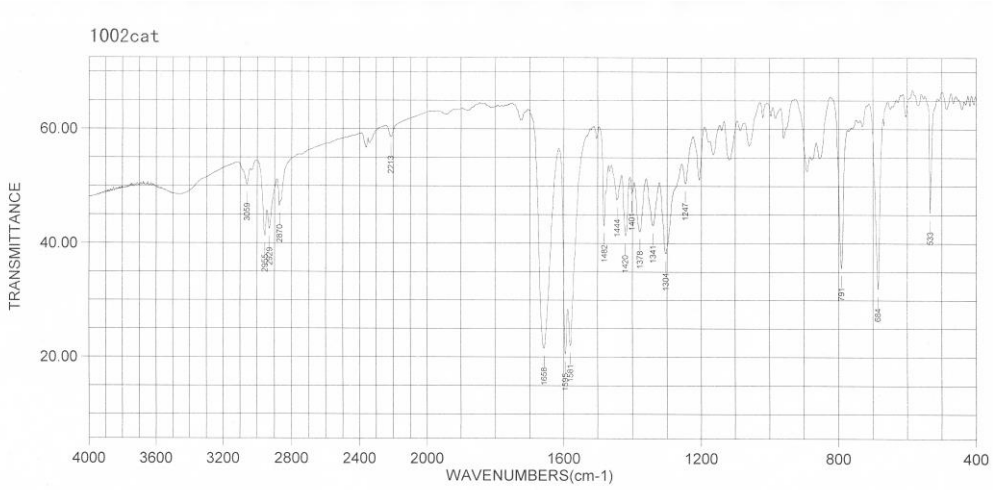
Mass spectrum (FD) of **7**.



^{1}H NMR (400 MHz) spectrum of (±)-**8**, measured in chloroform-*d* at 303 K.

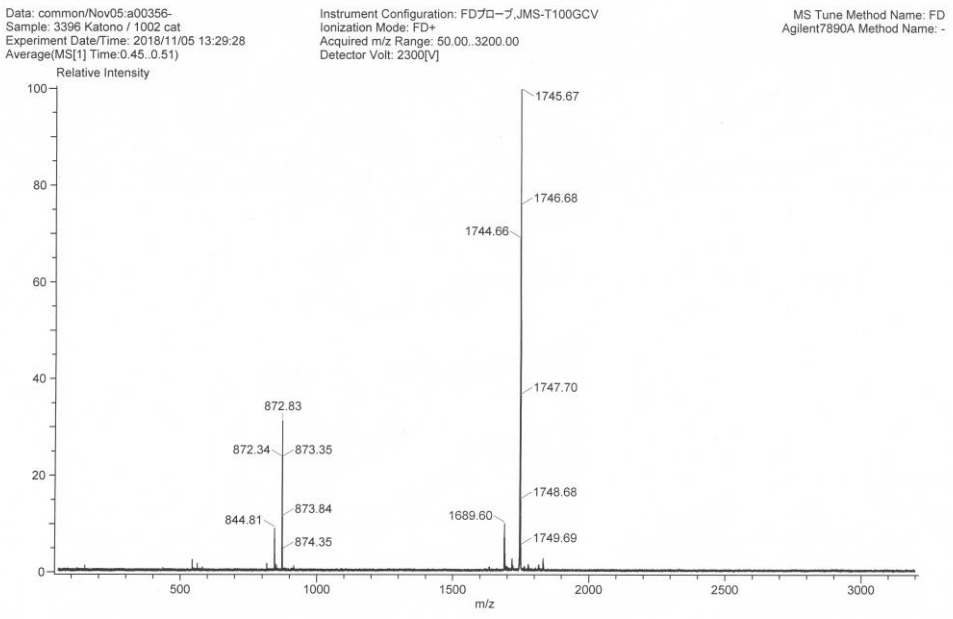


^{13}C NMR (100 MHz) spectrum of (±)-**8**, measured in chloroform-*d* at room temperature.

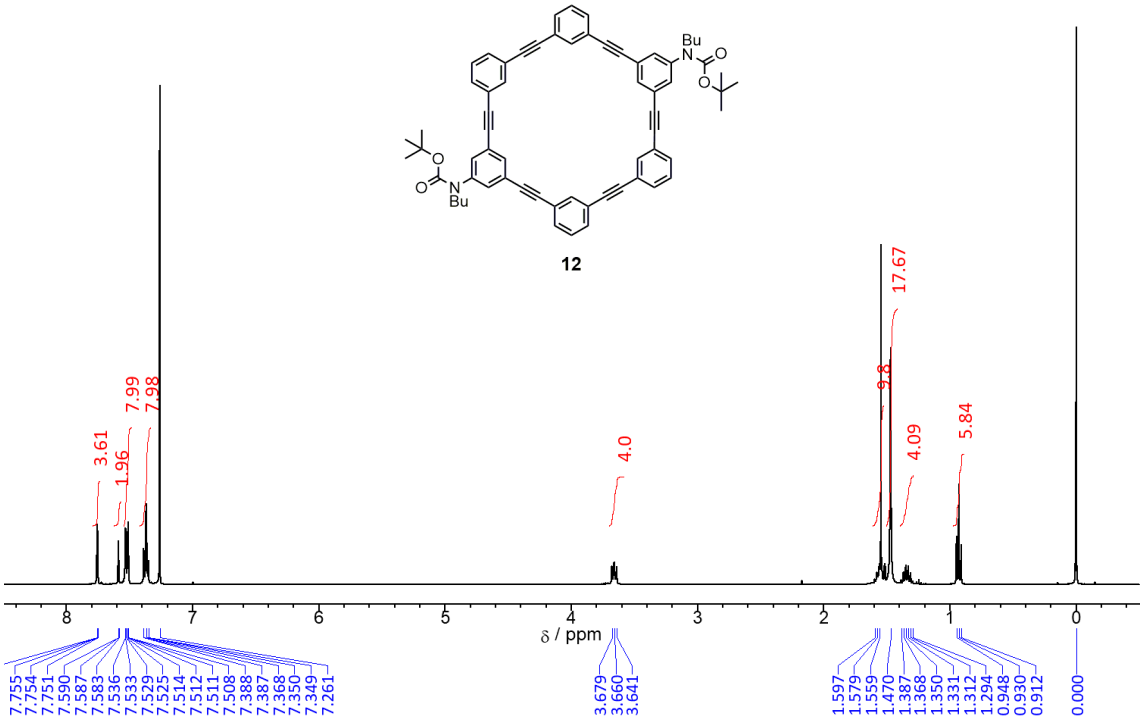


RESOL	: 2 cm-1	3059.55	50.29	1420.33	41.31
SCANS	: 5	2955.41	41.31	1401.05	48.78
AMPGAIN	: x1	2929.38	42.53	1378.87	42.06
P.INT	: 1 cm-1	2870.56	46.54	1341.26	43.09
BEAM	: single	2213.91	58.66	1304.62	38.20
S.SPEED	: TGS	1658.50	21.54	1247.73	50.51
M.DATE	: 11/2/18	1595.83	20.55	791.65	35.69
F.NAME	: 測定中のデータ	1581.36	22.06	684.61	32.06
		1482.04	43.11	533.23	45.47
		1444.44	47.59		

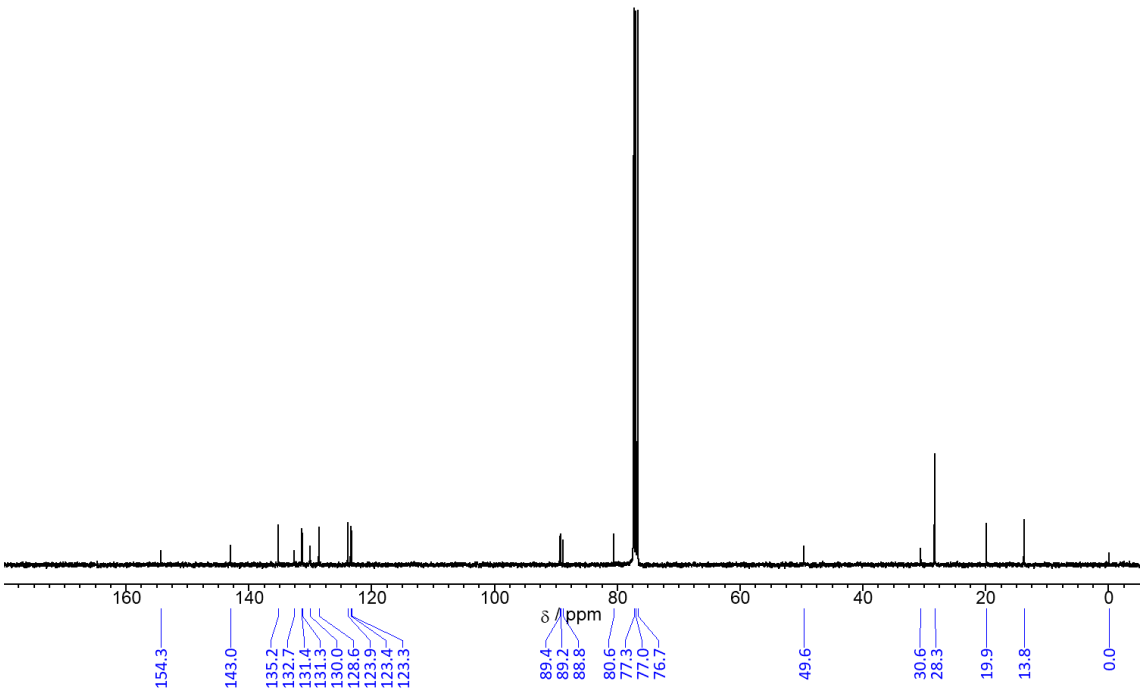
IR spectrum of (±)-**8**.



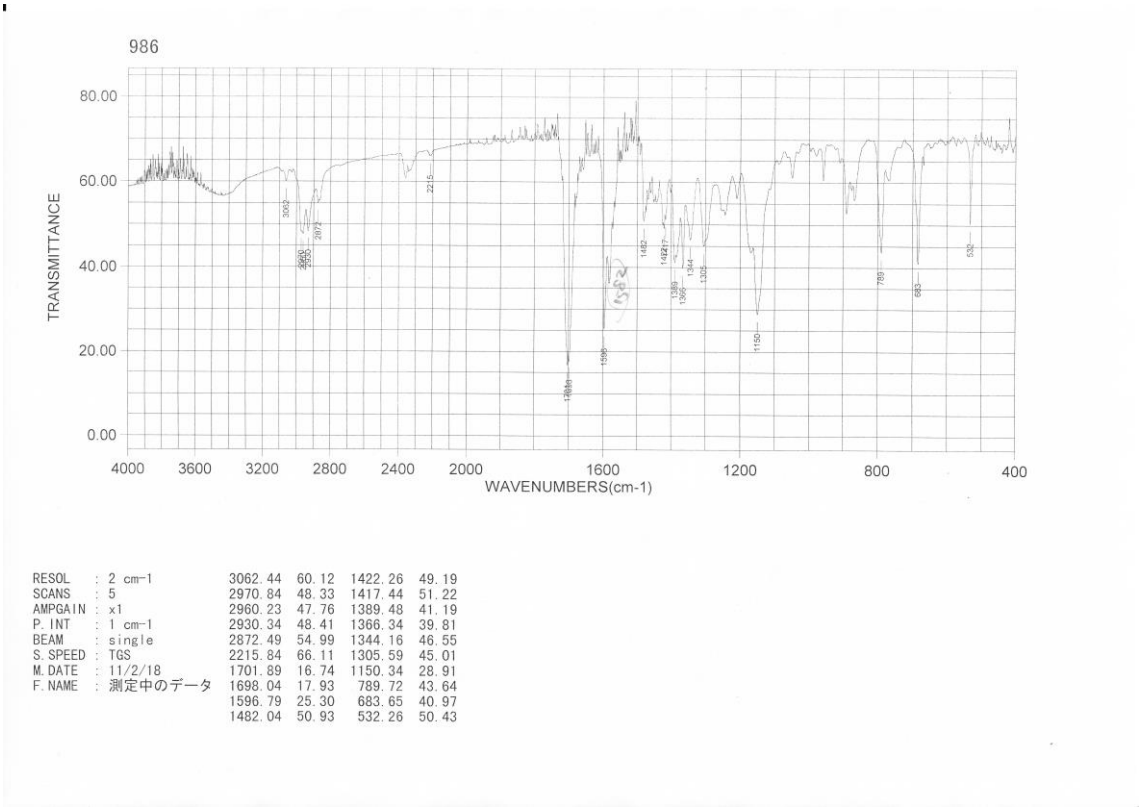
Mass spectrum (FD) of (±)-**8**.



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

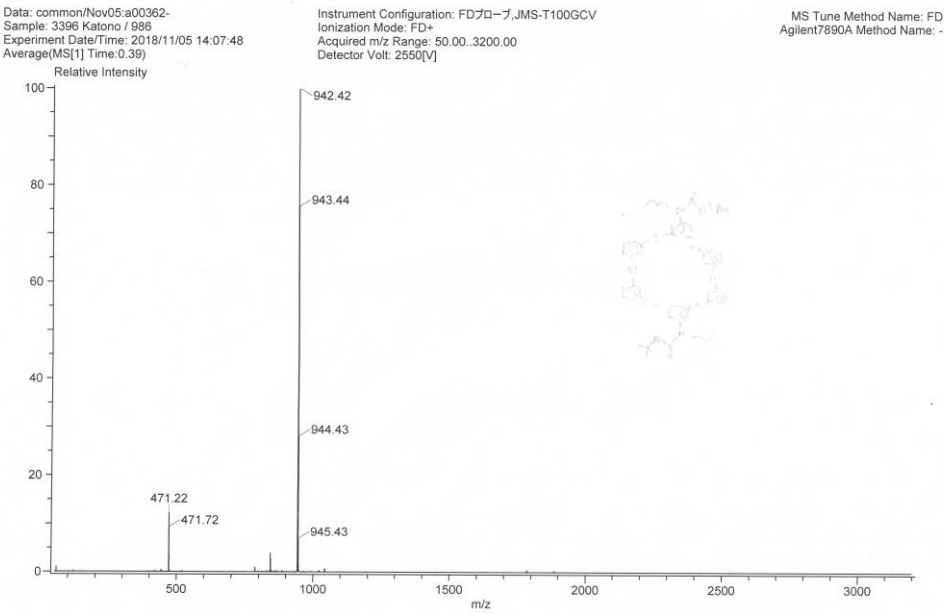


^{13}C NMR (100 MHz) spectrum of **12**, measured in chloroform-*d* at room temperature.

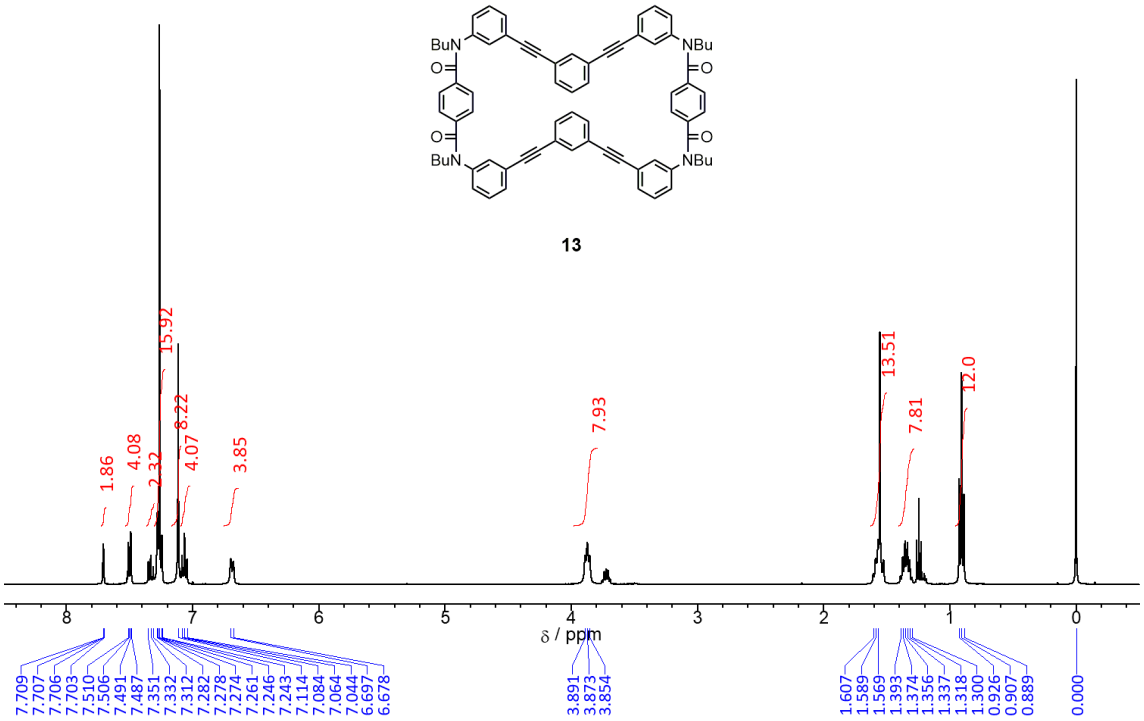


RESOL	: 2 cm-1	3062.44	60.12	1422.26	49.19
SCANS	: 5	2970.84	48.33	1417.44	51.22
AMPGAIN	: x1	2960.23	47.76	1389.48	41.19
P.INT	: 1 cm-1	2930.34	48.41	1366.34	39.81
BEAM	: single	2872.49	54.99	1344.16	46.55
S.SPEED	: TGS	2215.84	66.11	1305.59	45.01
M.DATE	: 11/2/18	1701.89	16.74	1150.34	28.91
F.NAME	: 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

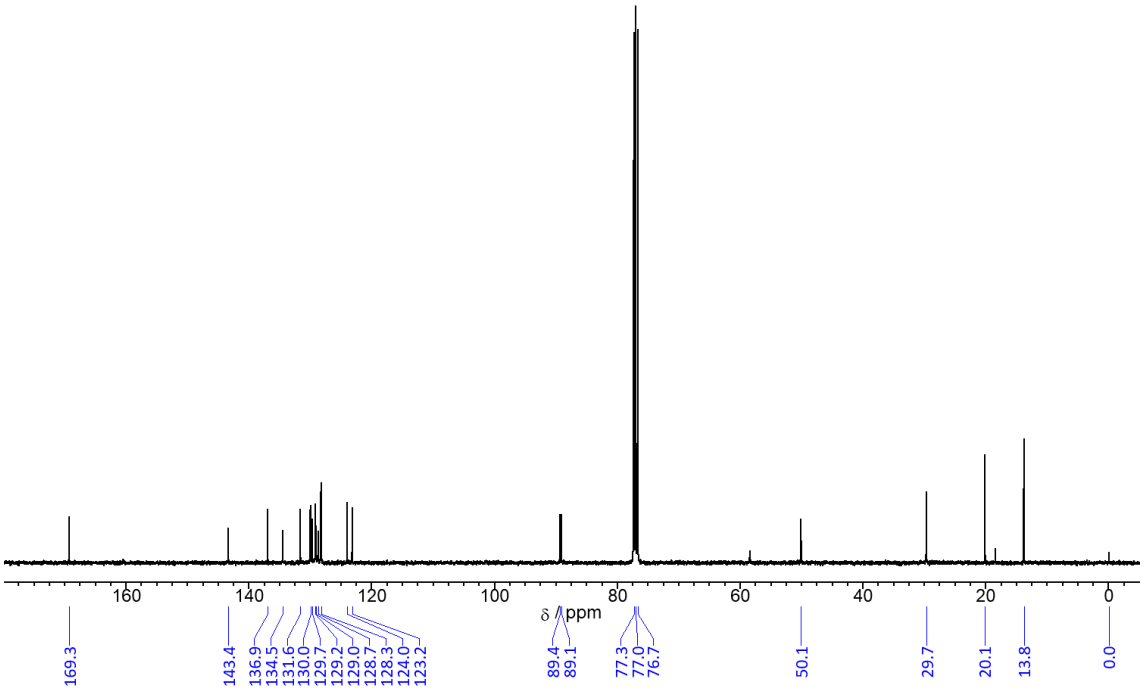
IR spectrum of **12**.



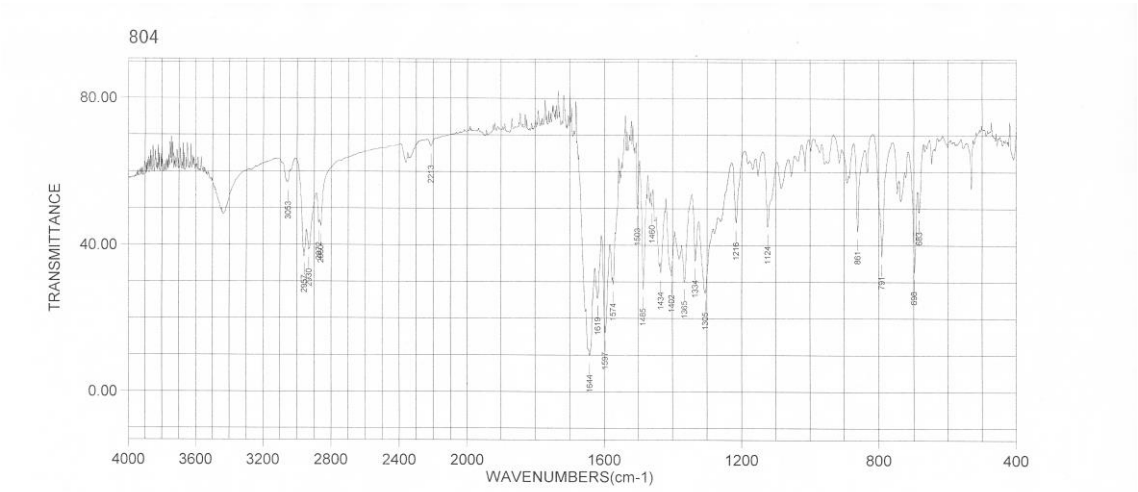
Mass spectrum (FD) of **12**.



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

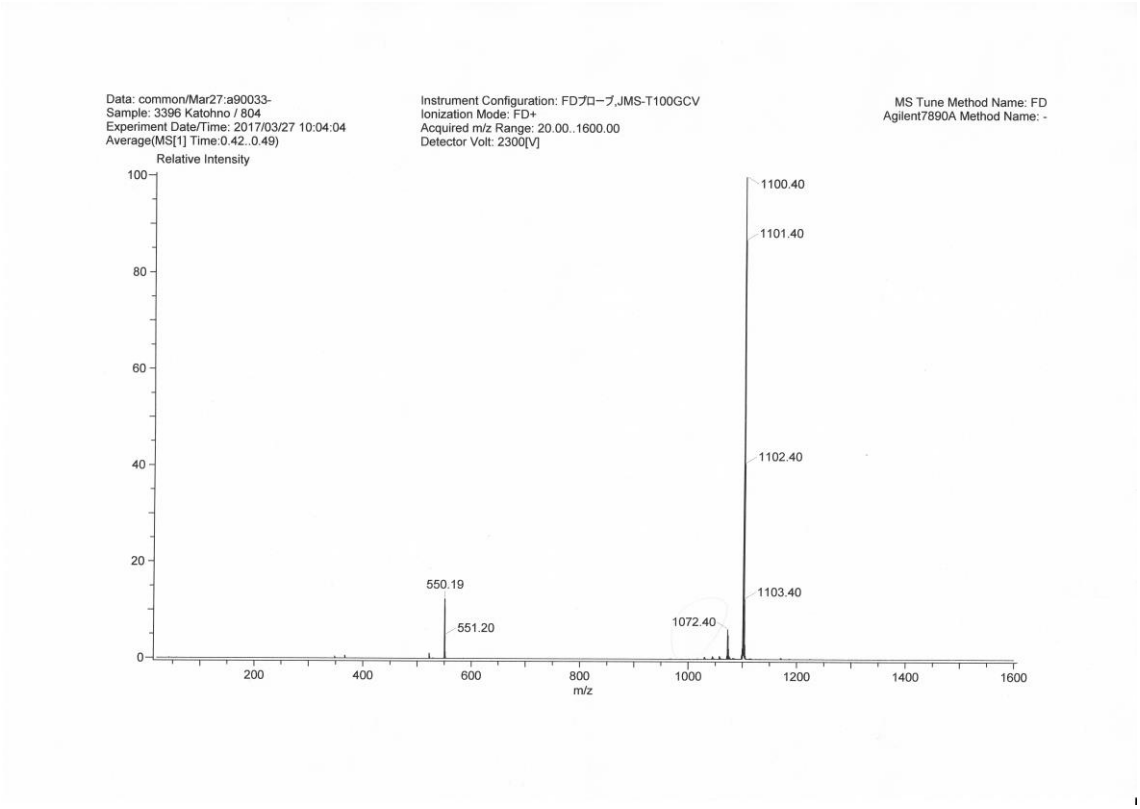


^{13}C NMR (100 MHz) spectrum of **13** cont. ethanol, measured in chloroform-*d* at room temperature.

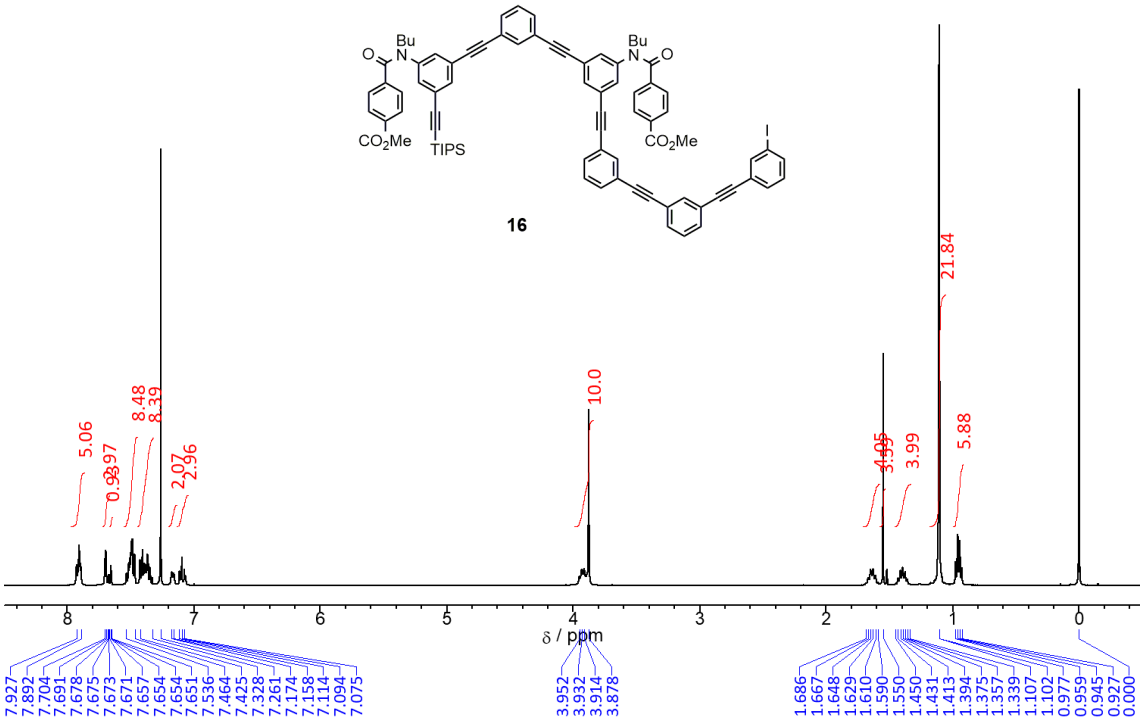


RESOL	: 2 cm-1	3053.76	57.01	1503.26	50.01	861.07	43.90
SCANS	: 5	2957.34	37.01	1485.90	28.10	791.65	37.04
AMPGAIN	: x1	2930.34	38.69	1460.83	50.72	698.11	32.82
P.INT	: 1 cm-1	2872.49	46.00	1434.80	32.57	683.65	49.04
BEAM	: single	2860.92	45.14	1402.98	31.84		
S.SPEED	: TGS	2213.91	66.96	1365.37	30.13		
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		

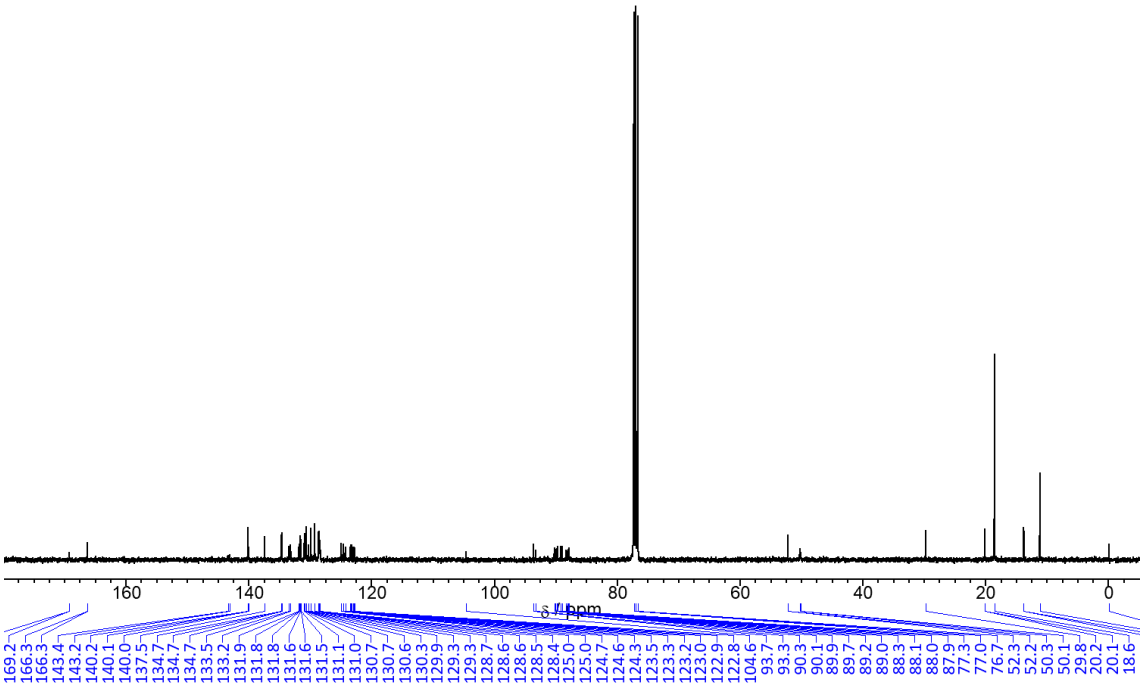
IR spectrum of **13**.



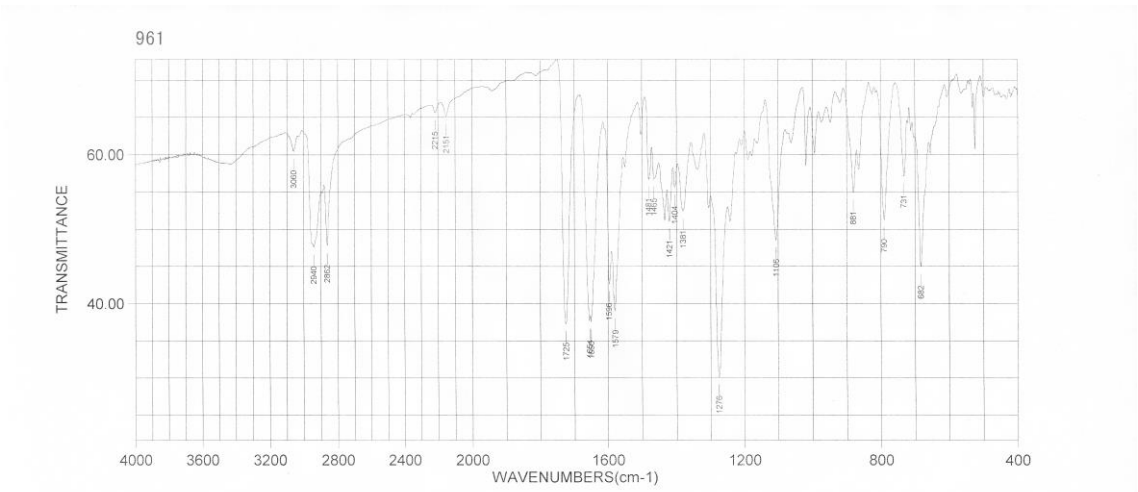
Mass spectrum (FD) of **13**.



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



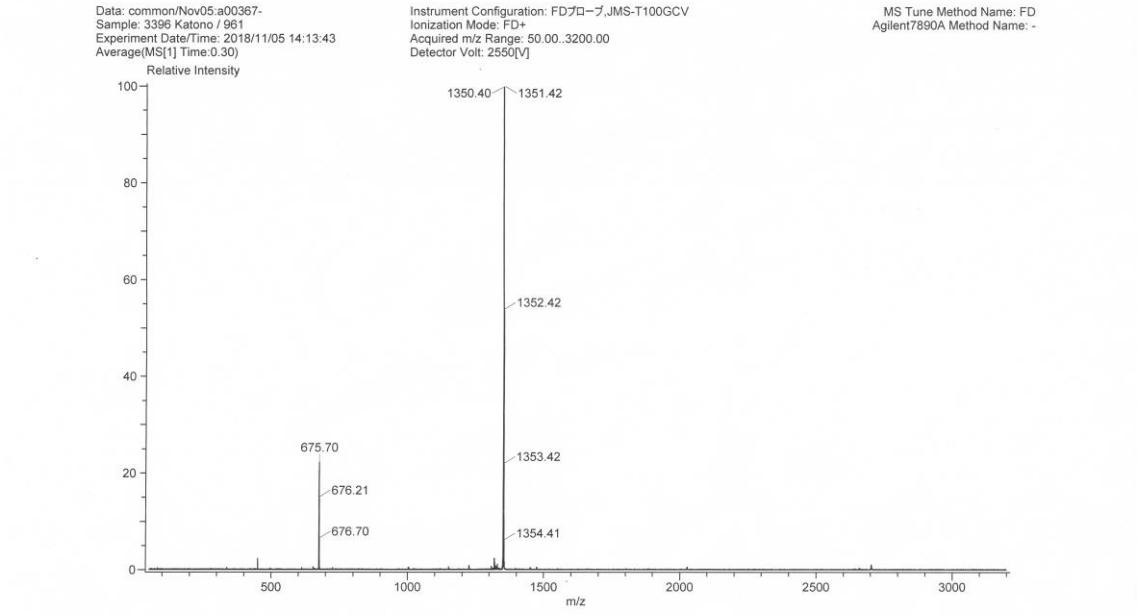
^{13}C NMR (100 MHz) spectrum of **16**, measured in chloroform-*d* at room temperature.



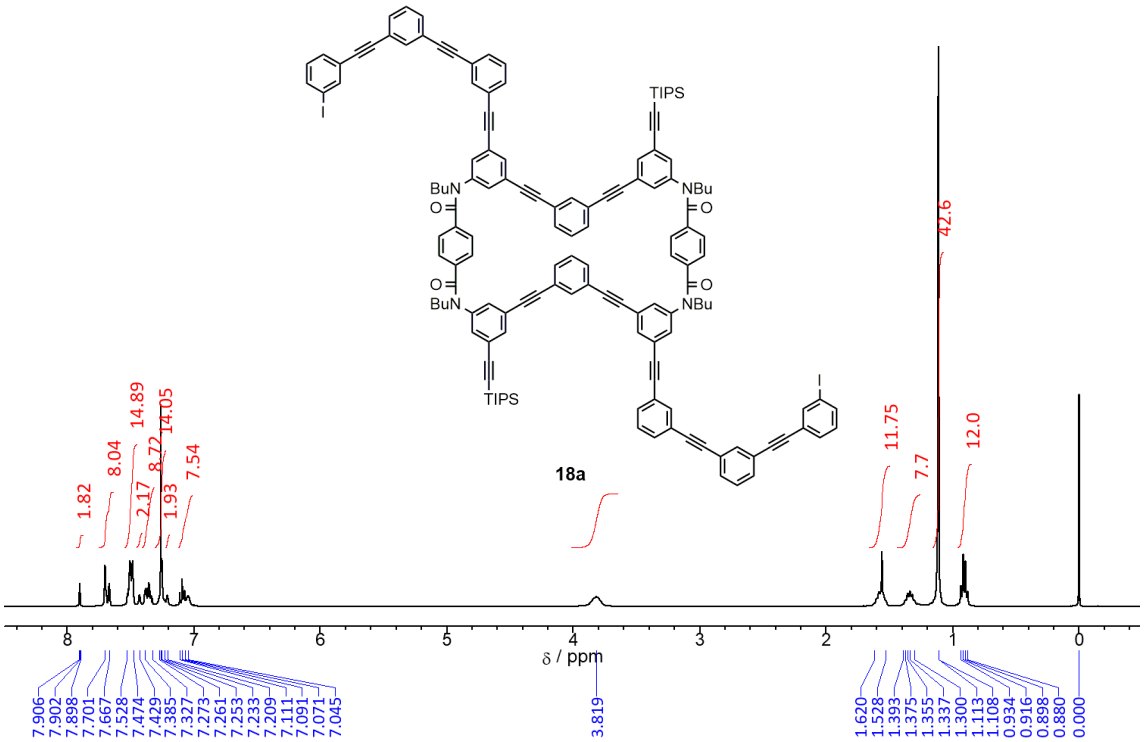
RESOL : 2 cm-1
SCANS : 5
AMPGAIN : x1
P.INT : 1 cm-1
BEAM : single
S.SPEED : TGS
M.DATE : 11/2/18
F.NAME : 測定中のデータ

3060.51	60.52	1481.08	56.78	682.69	45.03
2940.95	47.66	1465.65	56.77		
2862.84	47.87	1421.30	51.13		
2215.84	65.70	1404.91	55.71		
2151.23	65.22	1381.76	52.49		
1725.03	37.33	1276.66	30.14		
1654.64	37.70	1106.95	48.61		
1650.79	37.55	881.32	55.03		
1596.79	42.71	790.68	51.30		
1579.43	39.04	731.86	57.24		

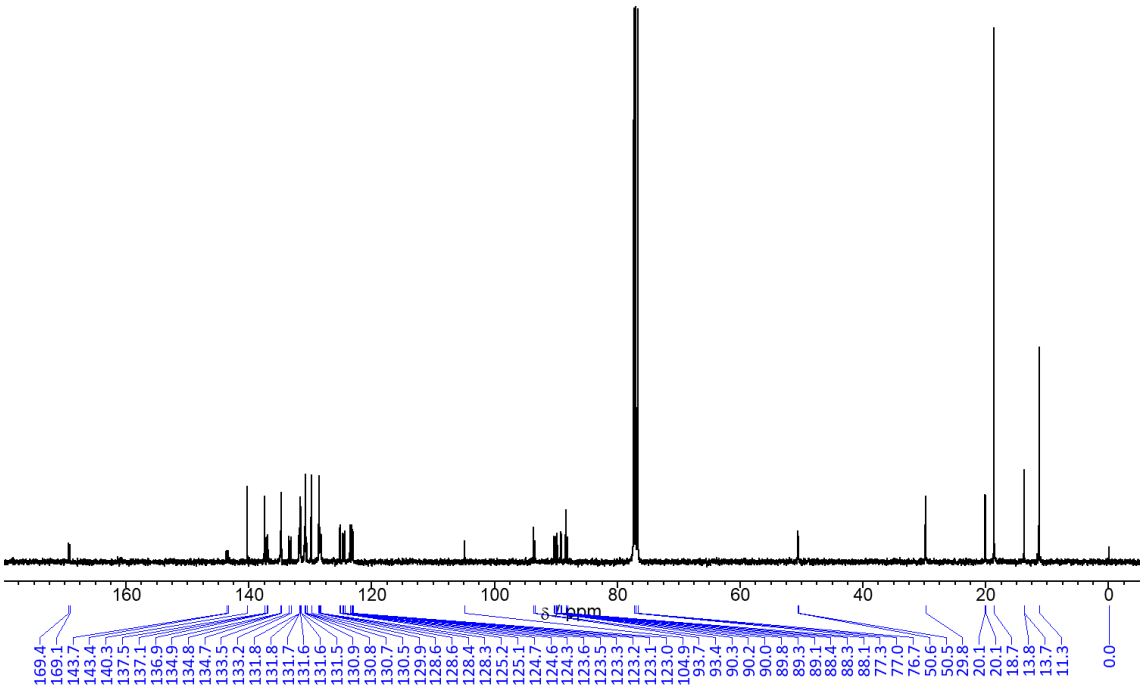
IR spectrum of **16**.



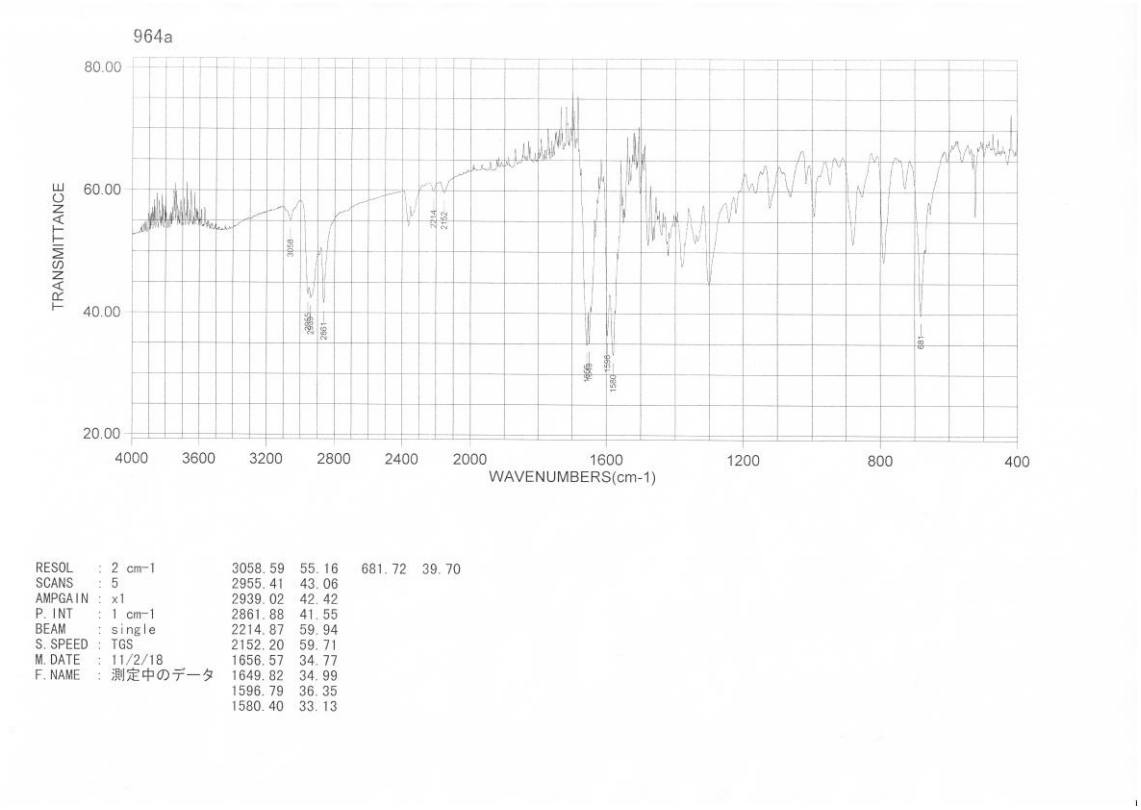
Mass spectrum (FD) of **16**.



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

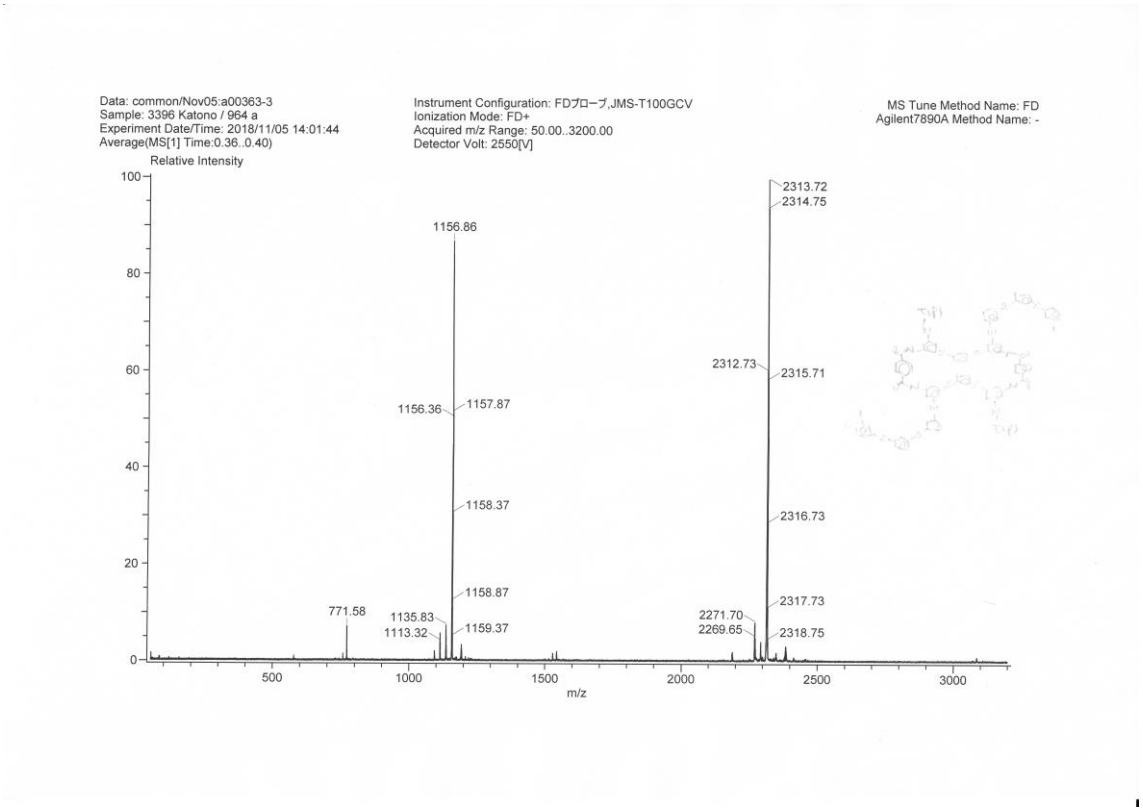


^{13}C NMR (100 MHz) spectrum of **18a**, measured in chloroform-*d* at 313 K.

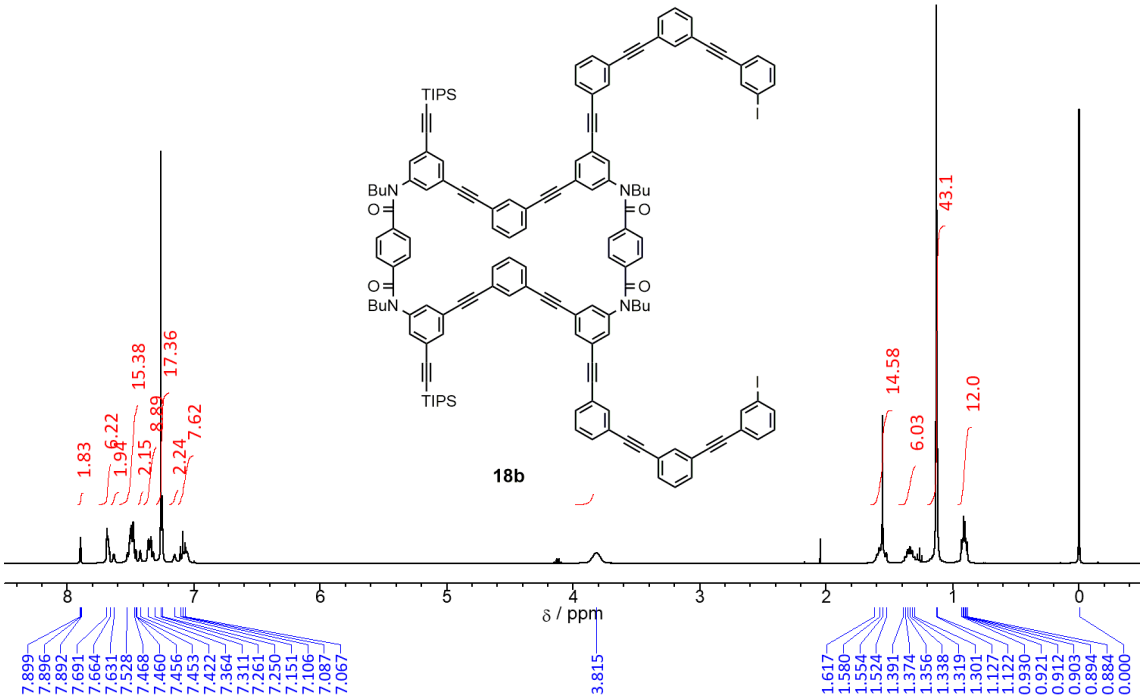


RESOL	: 2 cm-1	3058.59	55.16	681.72	39.70
SCANS	: 5	2955.41	43.06		
AMPGAIN	: x1	2939.02	42.42		
P.INT	: 1 cm-1	2861.88	41.55		
BEAM	: single	2214.87	59.94		
S.SPEED	: TGS	2152.20	59.71		
M.DATE	: 11/2/18	1656.57	34.77		
F.NAME	: 測定中のデータ	1649.82	34.99		
		1596.79	36.35		
		1580.40	33.13		

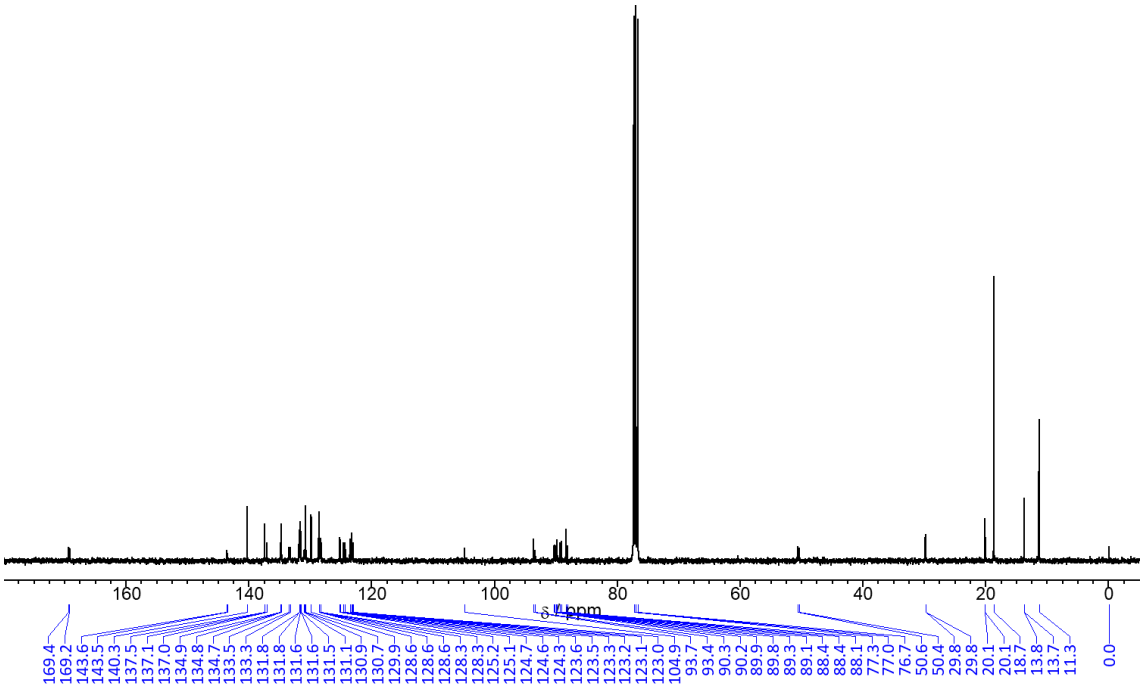
IR spectrum of **18a**.



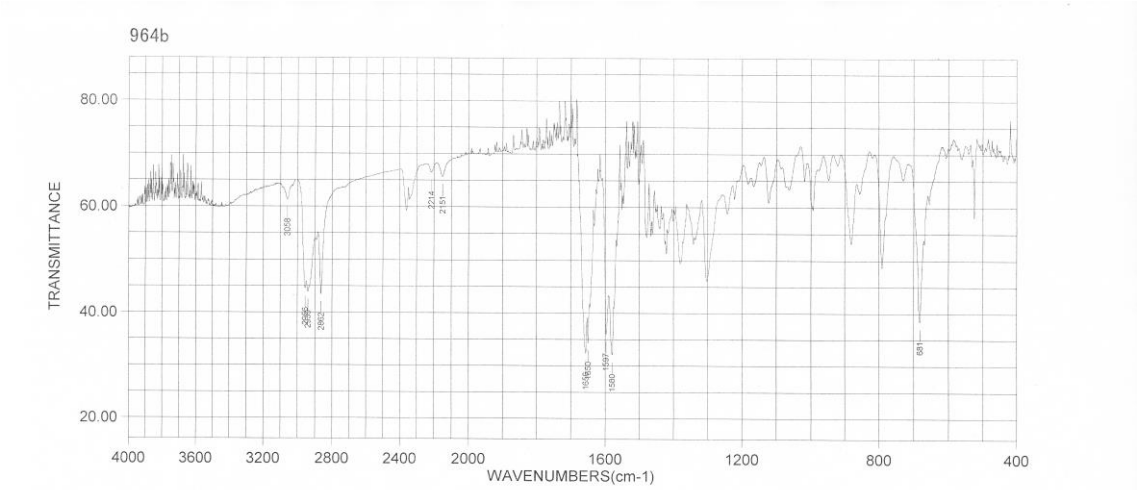
Mass spectrum (FD) of **18a**.



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

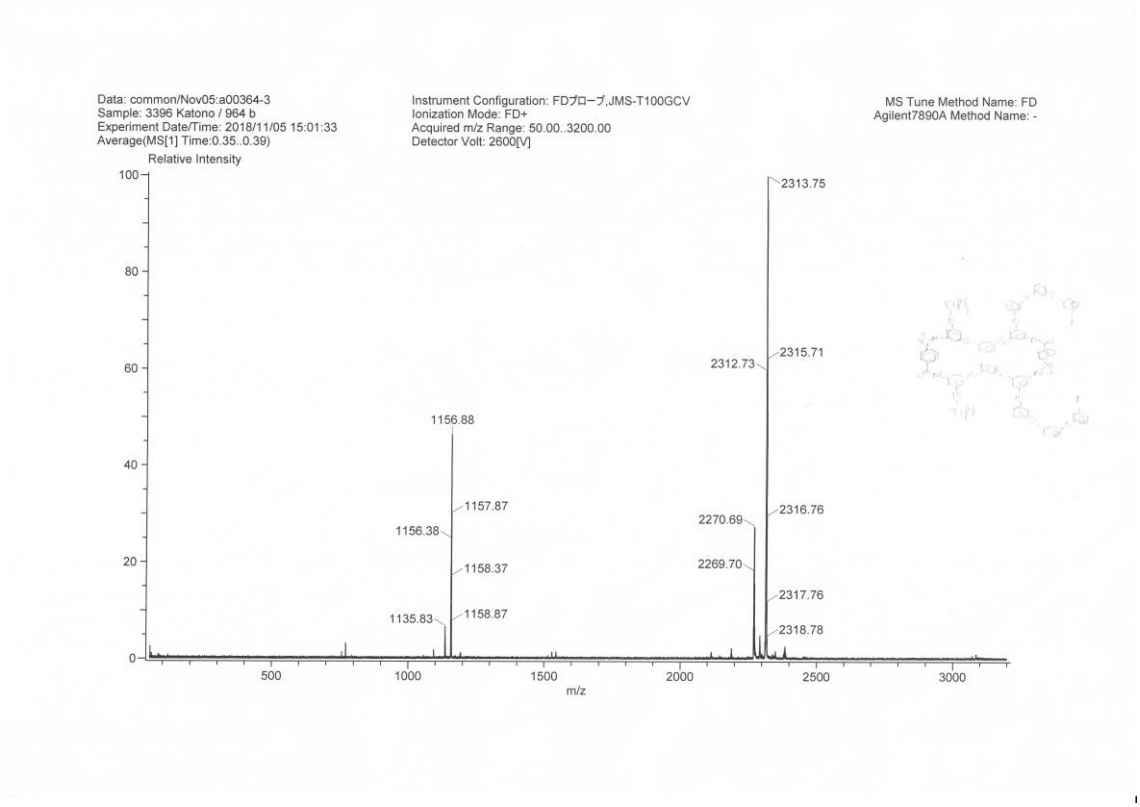


^{13}C NMR (100 MHz) spectrum of **18b**, measured in chloroform-*d* at 313 K.

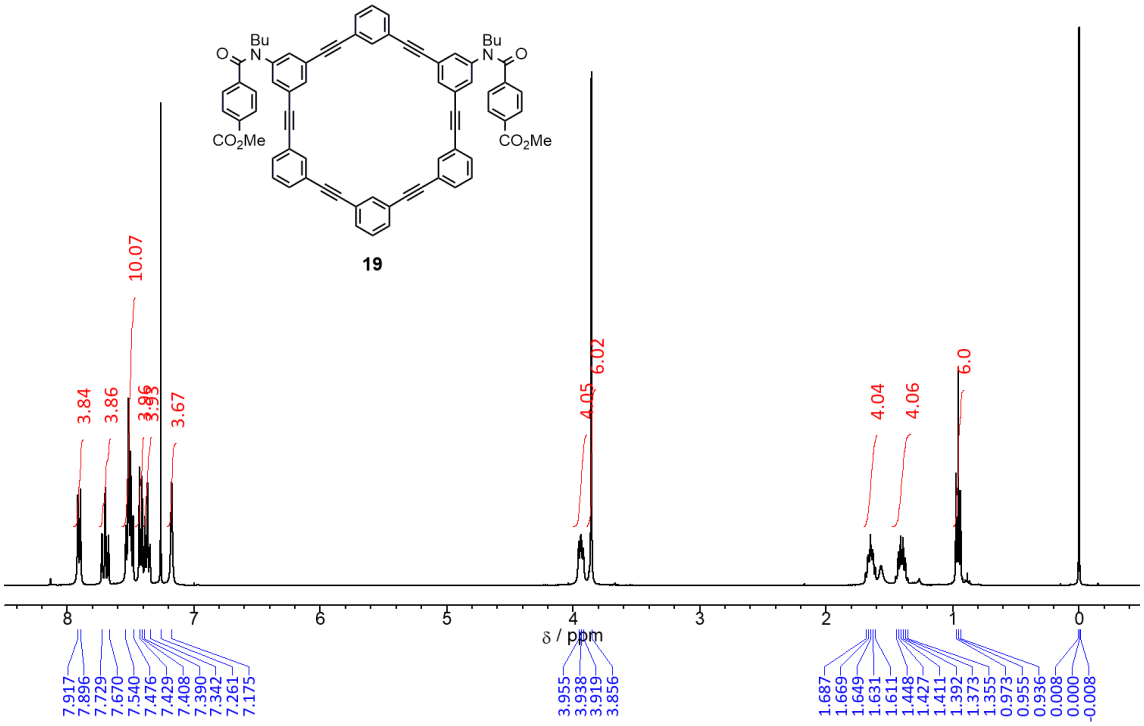


RESOL	: 2 cm-1	3058.59	61.36	681.72	38.48
SCANS	: 5	2956.38	44.51		
AMPGAIN	: x1	2939.98	43.95		
P.INT	: 1 cm-1	2862.84	43.46		
BEAM	: single	2214.87	66.52		
S.SPEED	: TGS	2151.23	65.70		
M.DATE	: 11/2/18	1656.57	32.45		
F.NAME	: 測定中のデータ	1650.79	34.39		
		1597.75	36.08		
		1580.40	32.14		

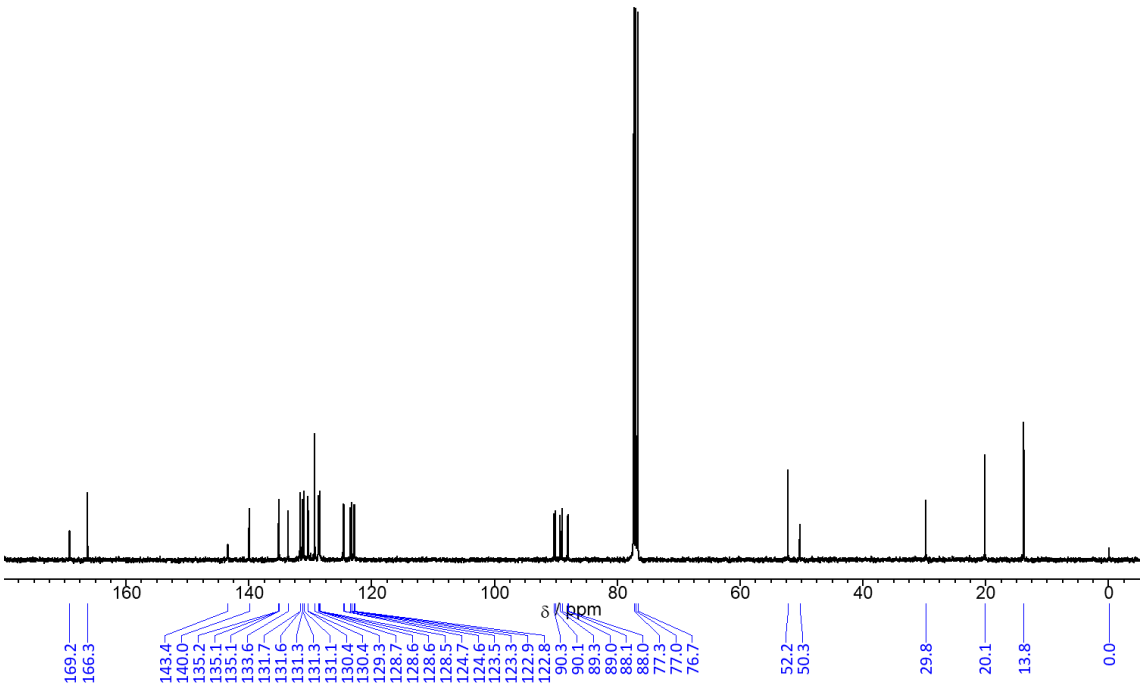
IR spectrum of **18b**.



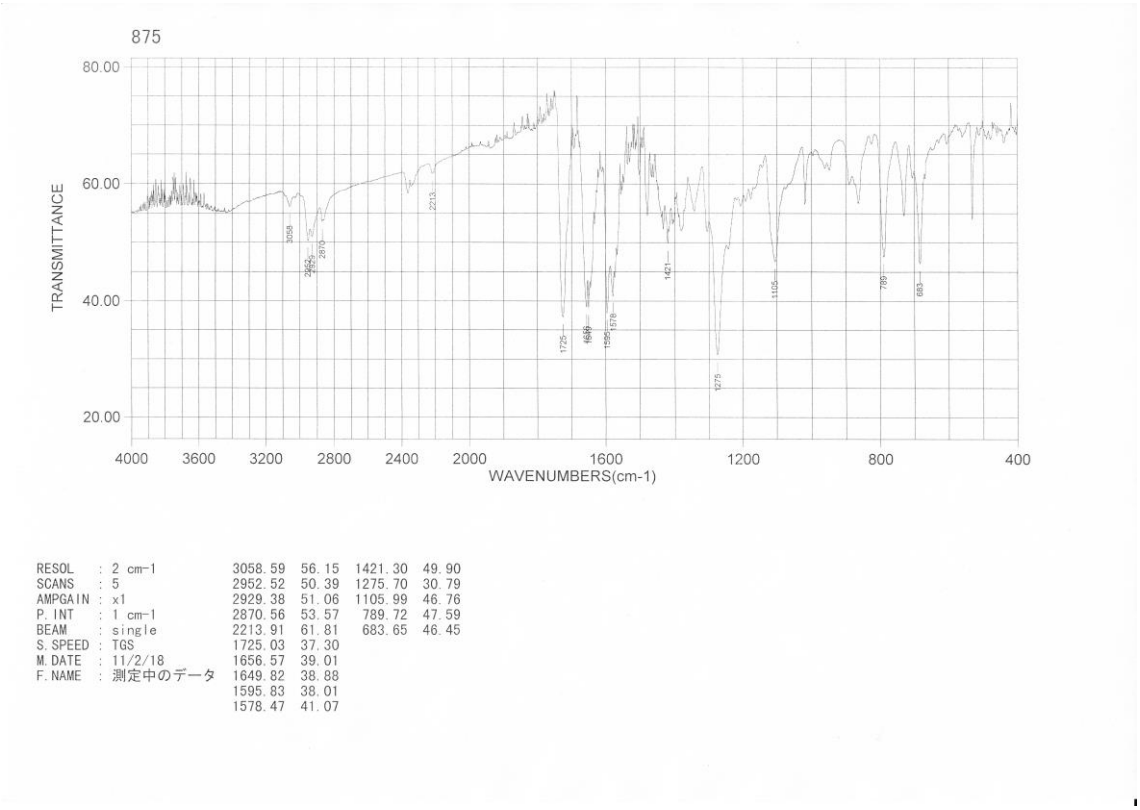
Mass spectrum (FD) of **18b**.



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

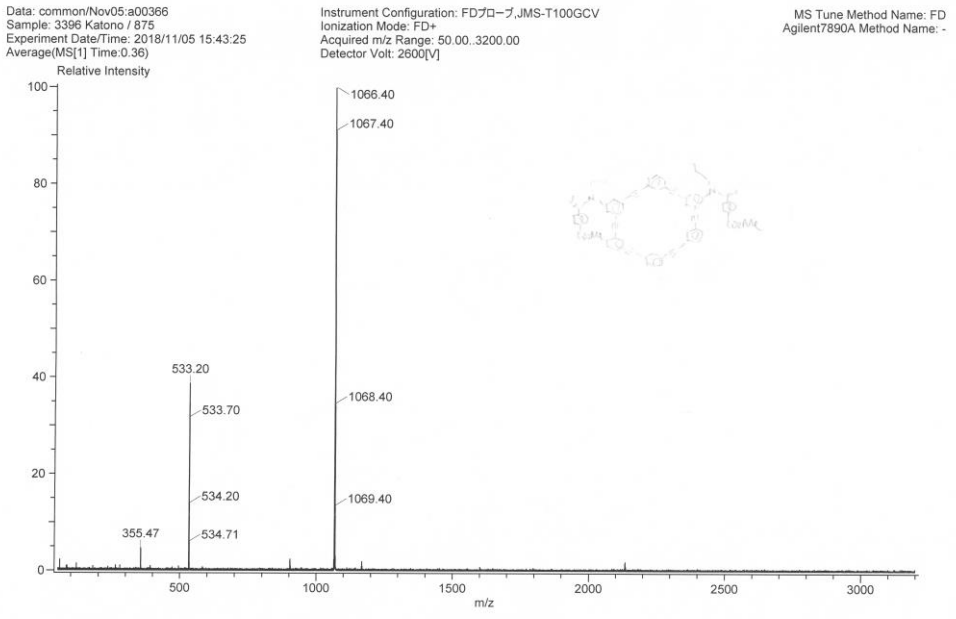


^{13}C NMR (100 MHz) spectrum of **19**, measured in chloroform-*d* at room temperature.

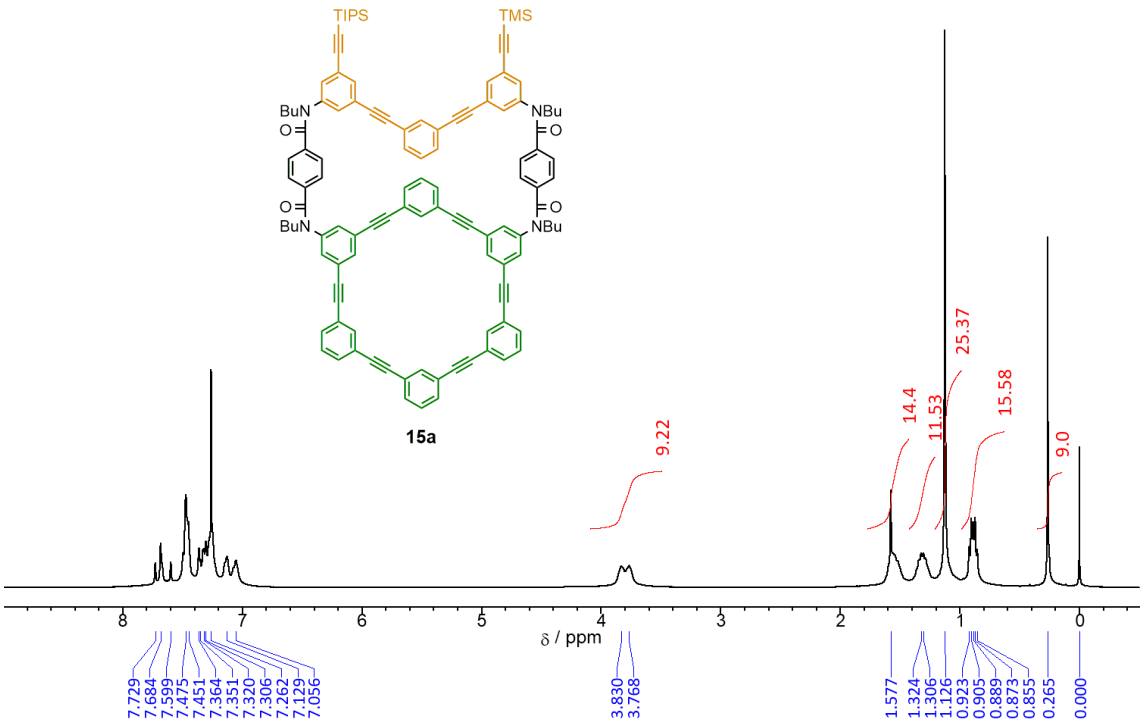


RESOL	: 2 cm-1	3058.59	56.15	1421.30	49.90
SCANS	: 5	2952.52	50.39	1275.70	30.79
AMPGAIN	: x1	2929.38	51.06	1105.99	46.76
P.INT	: 1 cm-1	2870.56	53.57	789.72	47.59
BEAM	: single	2213.91	61.81	683.65	46.45
S.SPEED	: TGS	1725.03	37.30		
M.DATE	: 11/2/18	1656.57	39.01		
F.NAME	: 測定中のデータ	1649.82	38.88		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

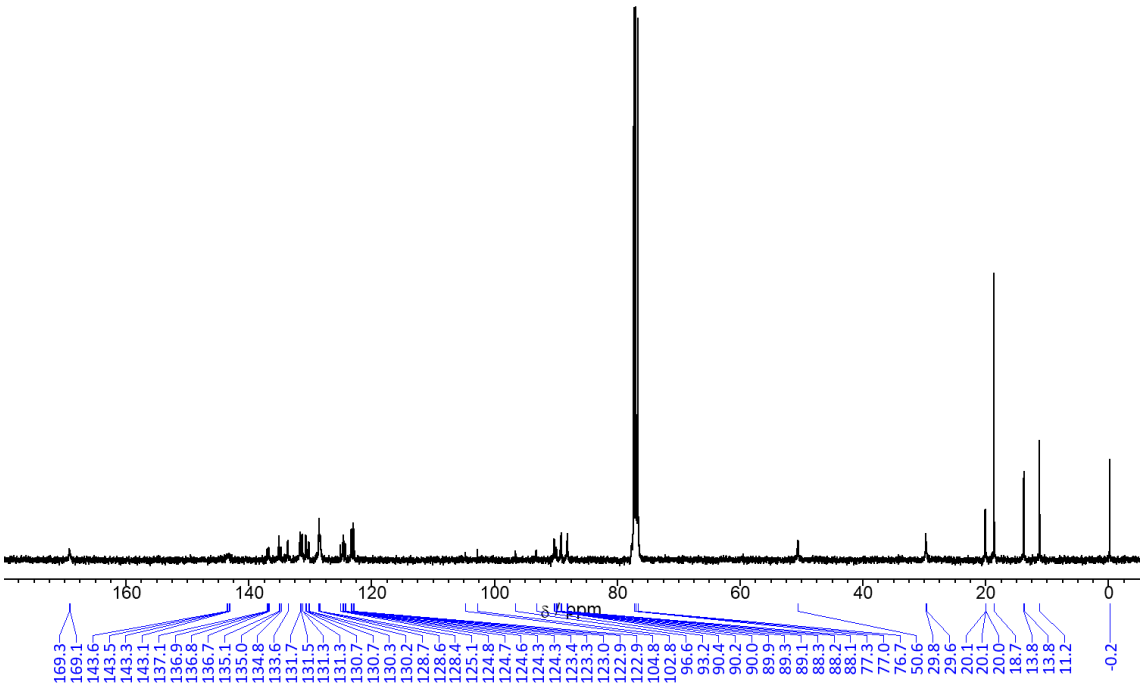
IR spectrum of **19**.



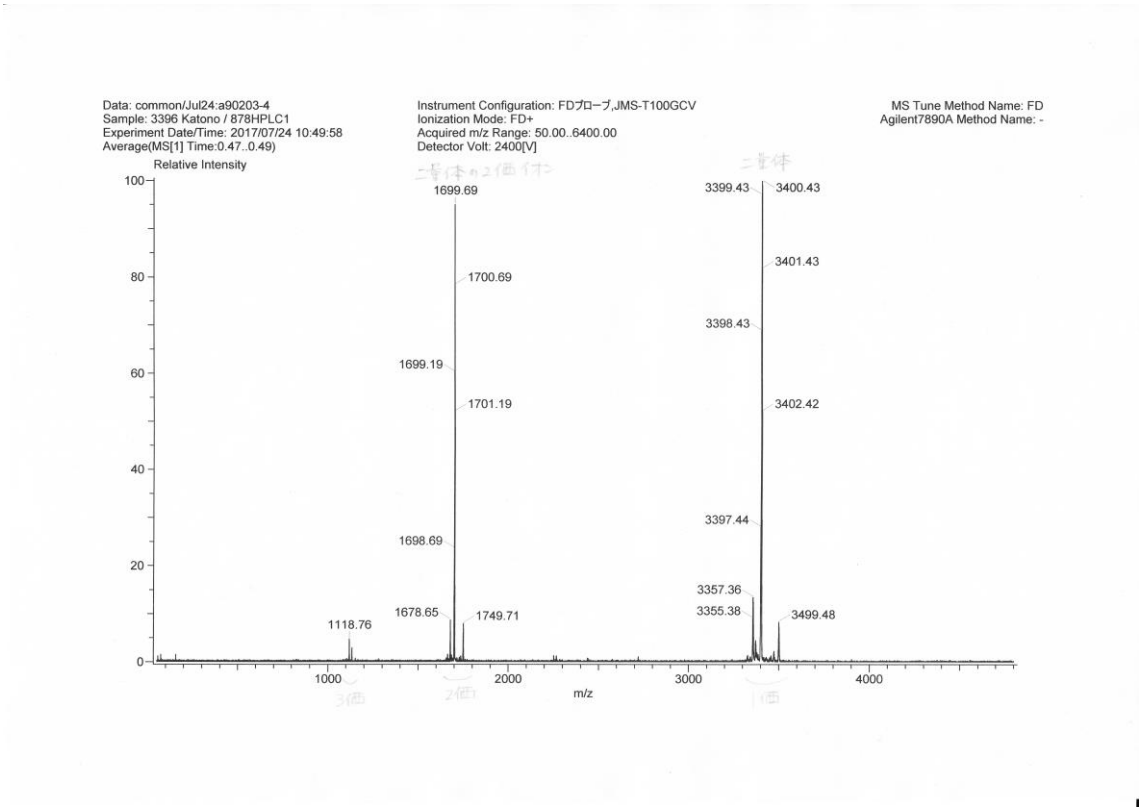
Mass spectrum (FD) of **19**.



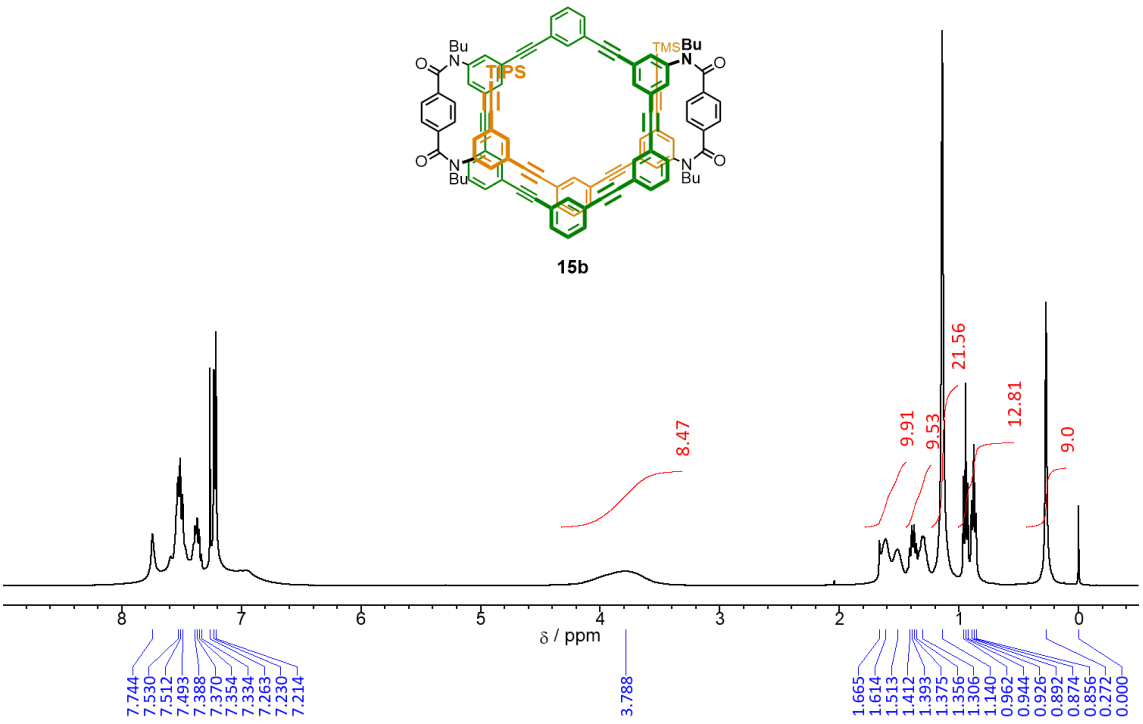
^{1}H NMR (400 MHz) spectrum of **15a**, measured in chloroform-*d* at room temperature.



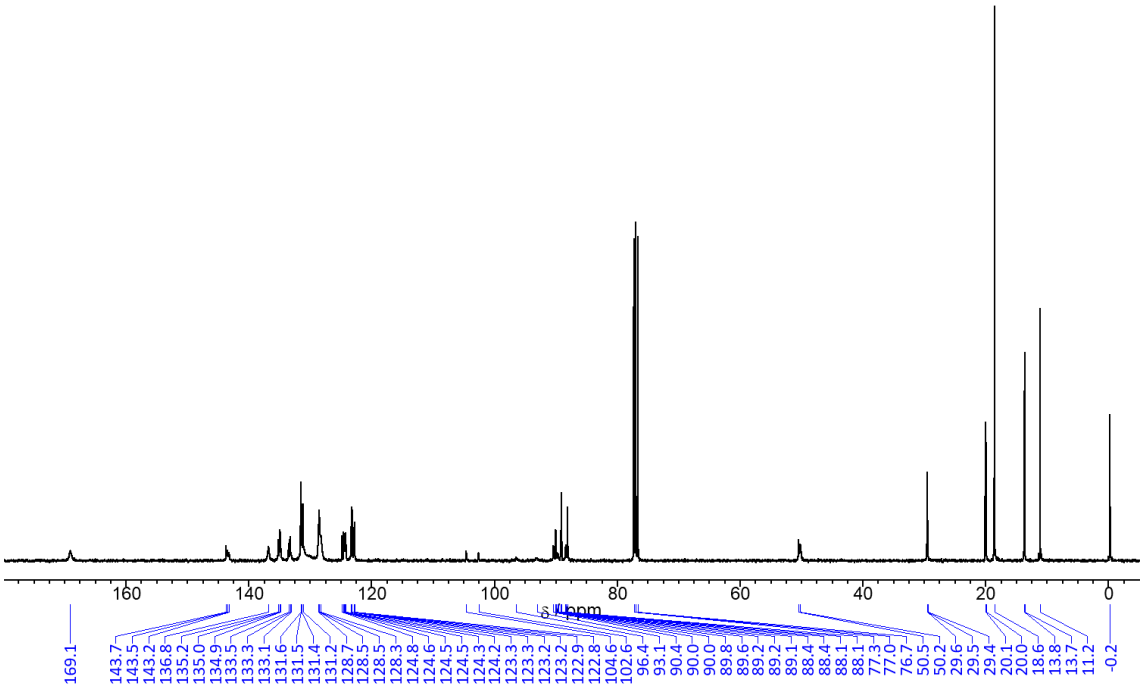
^{13}C NMR (100 MHz) spectrum of **15a**, measured in chloroform-*d* at room temperature.



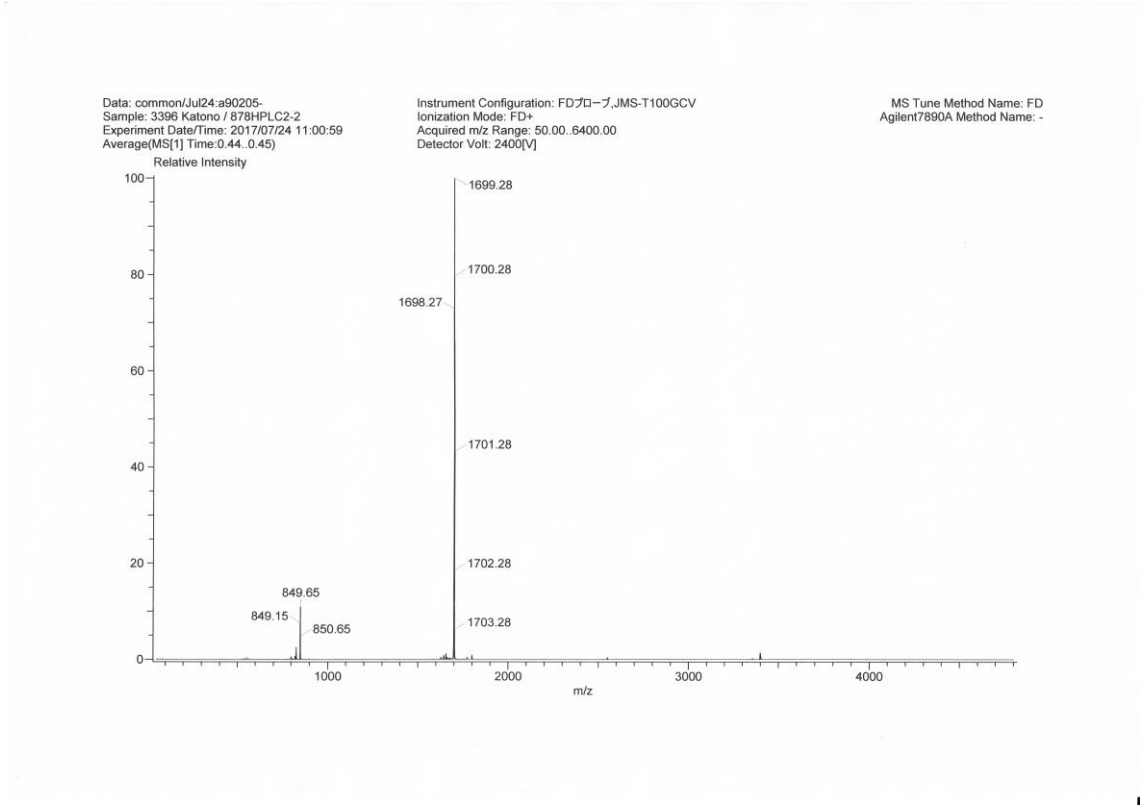
Mass spectrum (FD) of **15a**.



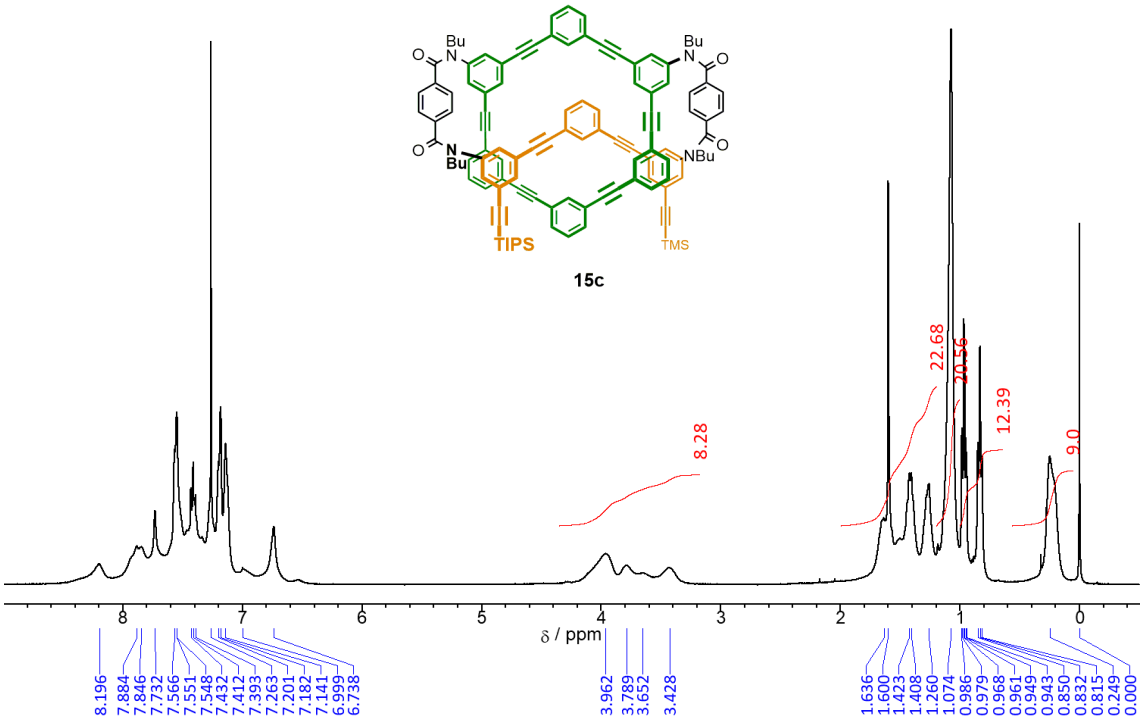
^{1}H NMR (400 MHz) spectrum of **15b**, measured in chloroform-*d* at room temperature.



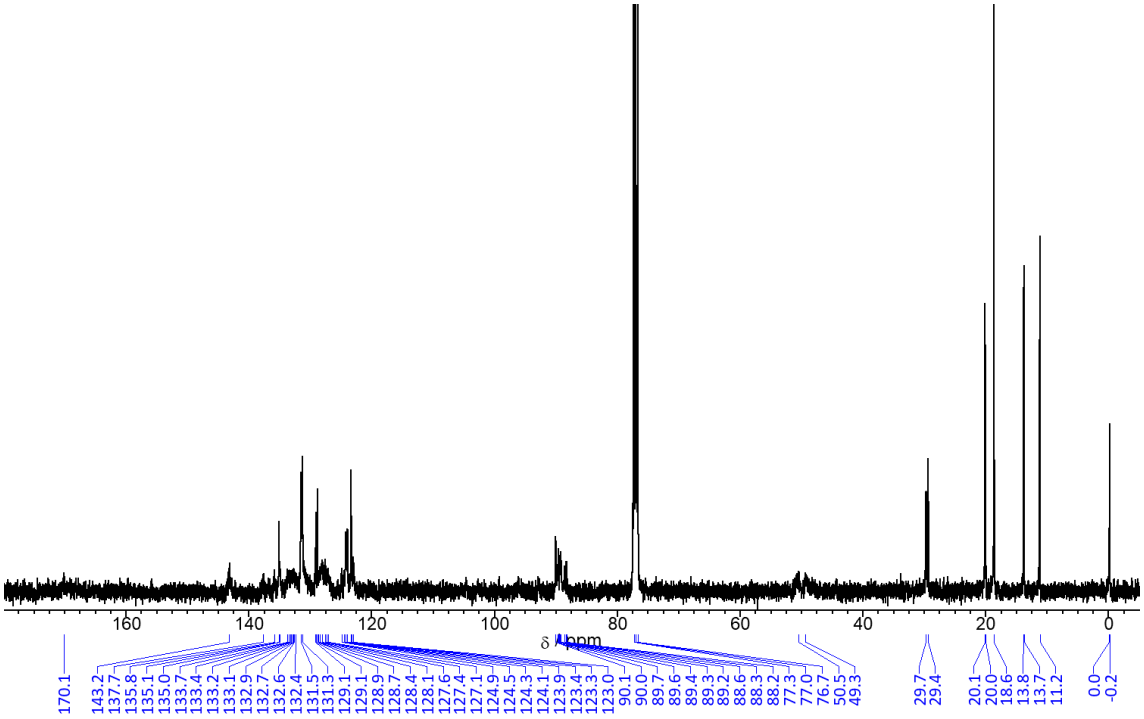
^{13}C NMR (100 MHz) spectrum of **15b**, measured in chloroform-*d* at room temperature.



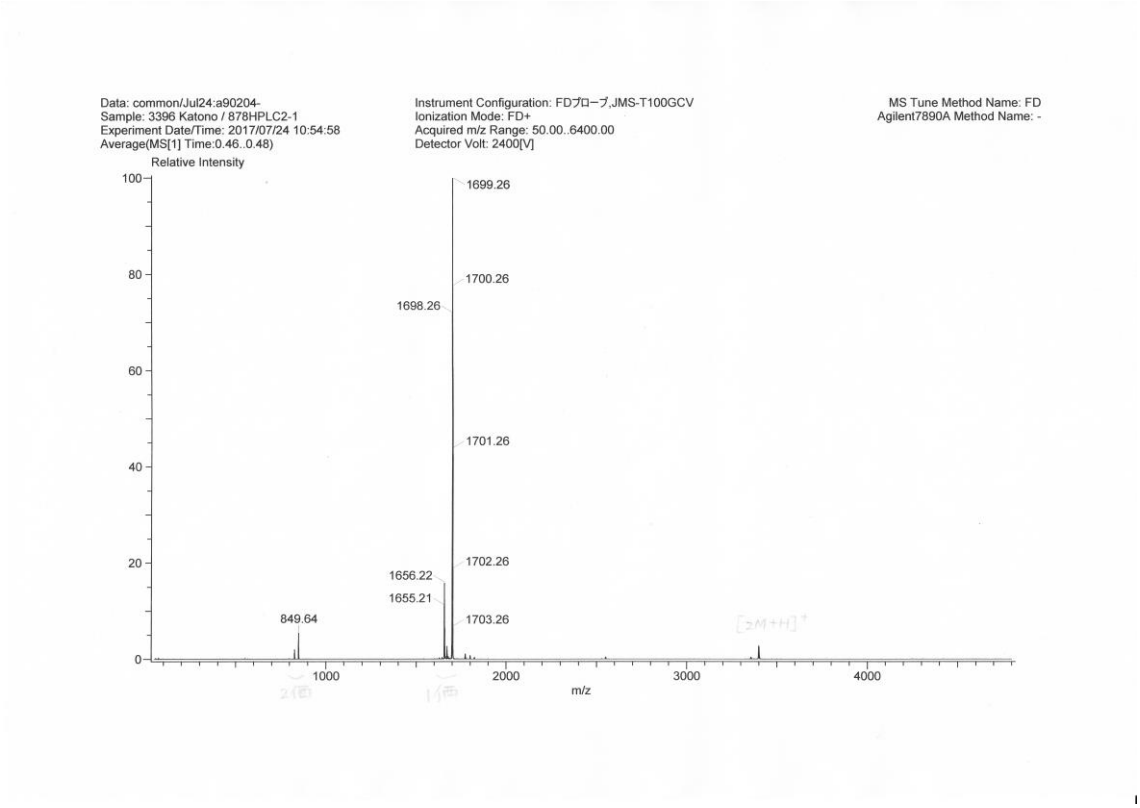
Mass spectrum (FD) of **15b**.



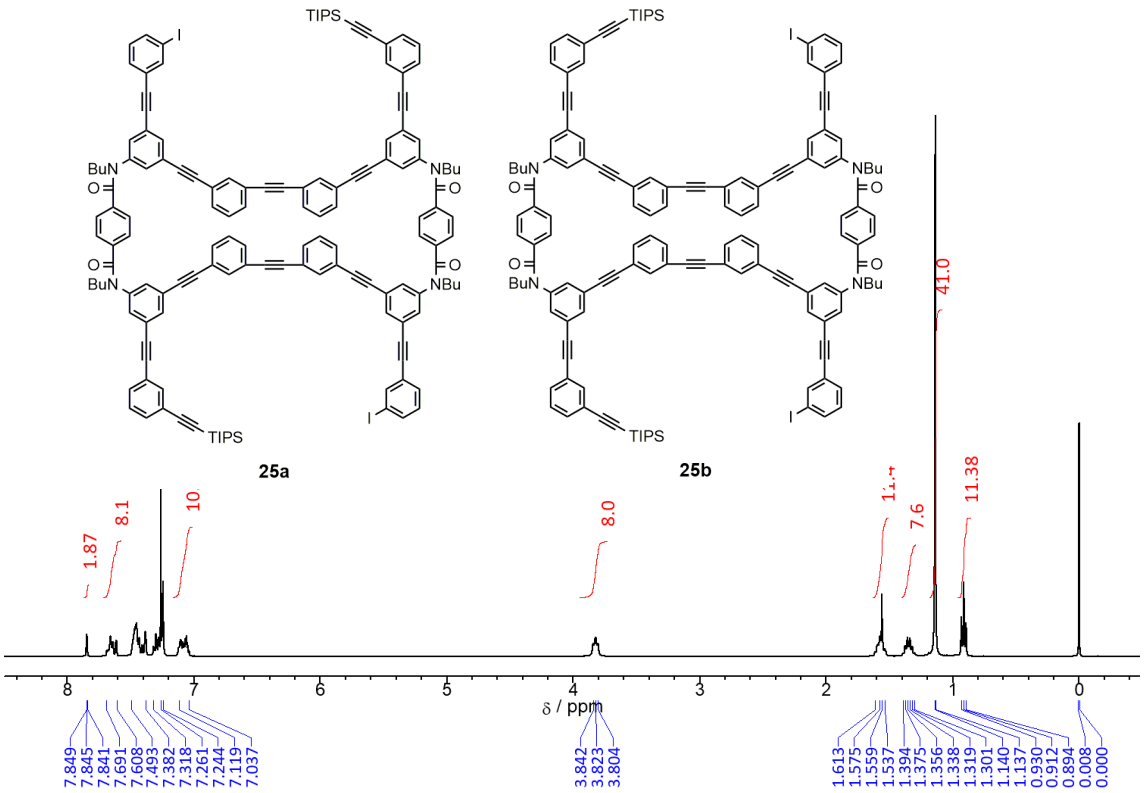
^{1}H NMR (400 MHz) spectrum of **15c**, measured in chloroform-*d* at room temperature.



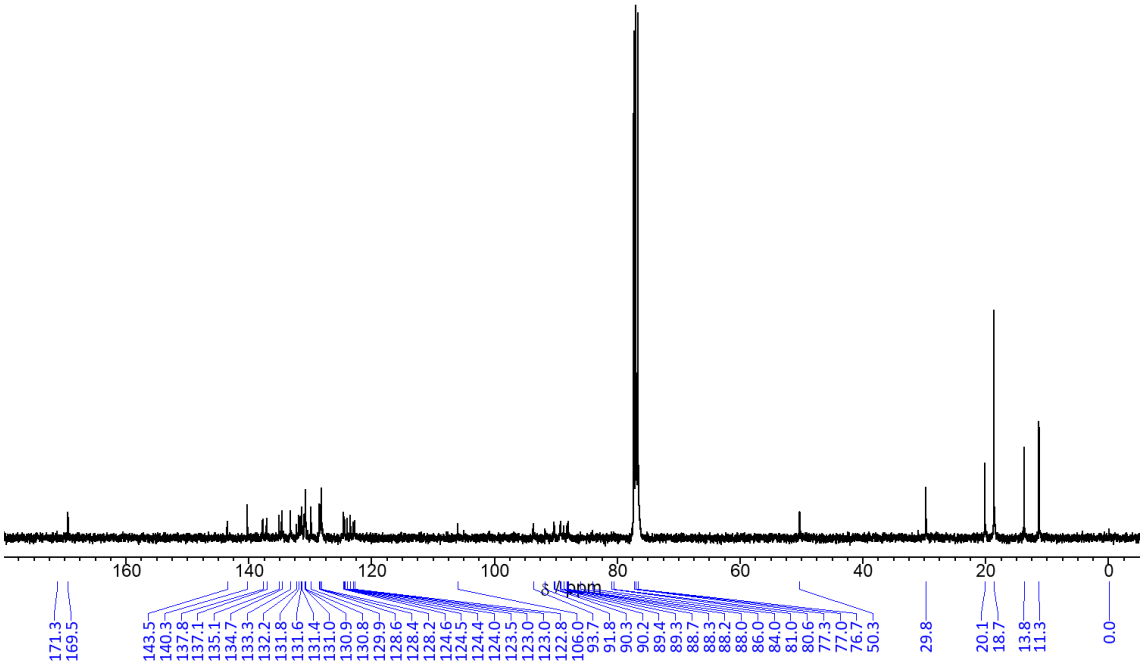
^{13}C NMR (100 MHz) spectrum of **15c**, measured in chloroform-*d* at room temperature.



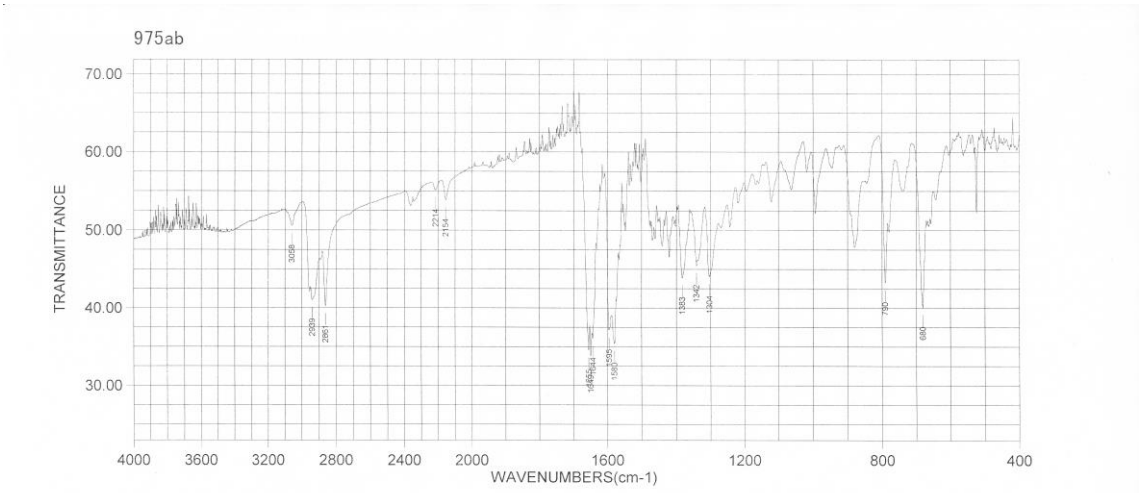
Mass spectrum (FD) of **15c**.



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

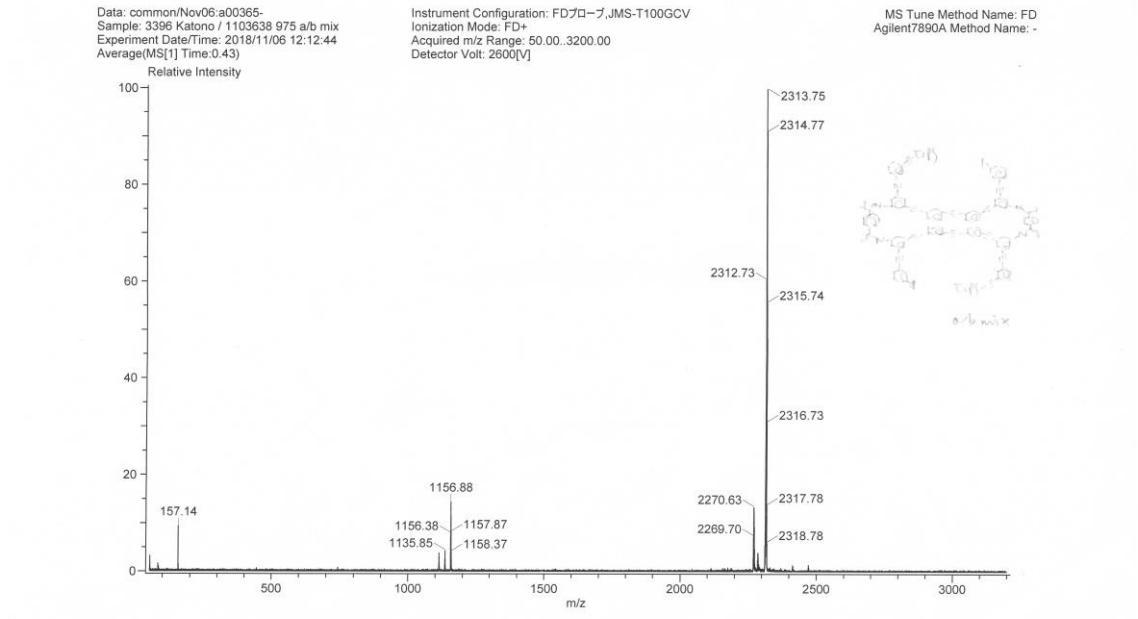


^{13}C NMR (100 MHz) spectrum of a mixture of **25a** and **25b**, measured in chloroform-*d* at 308 K.

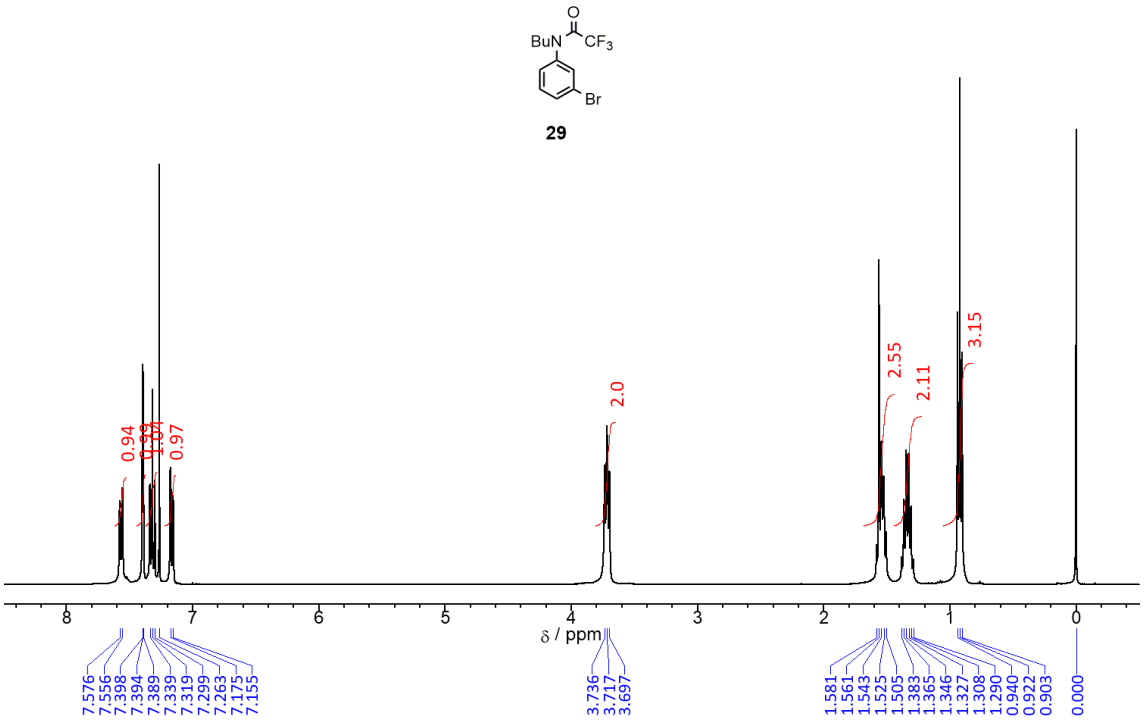


RESOL	: 2 cm-1	3058.59	50.58	1383.69	43.92
SCANS	: 5	2939.02	41.06	1342.23	45.46
AMPGAIN	: x1	2861.88	40.26	1304.62	44.08
P.INT	: 1 cm-1	2214.87	55.15	790.68	43.29
BEAM	: single	2154.12	53.87	680.76	40.09
S.SPEED	: TGS	1655.61	34.58		
M.DATE	: 11/2/18	1649.82	33.84		
F.NAME	: 測定中のデータ	1644.04	36.08		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

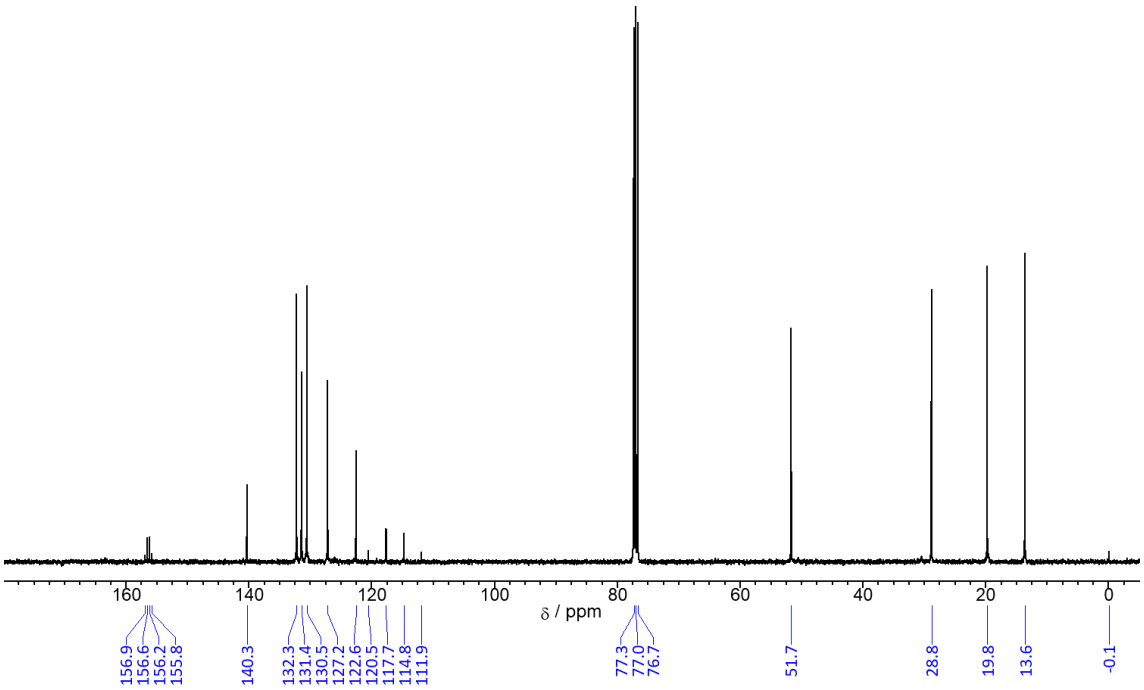
IR spectrum of a mixture of **25a** and **25b**.



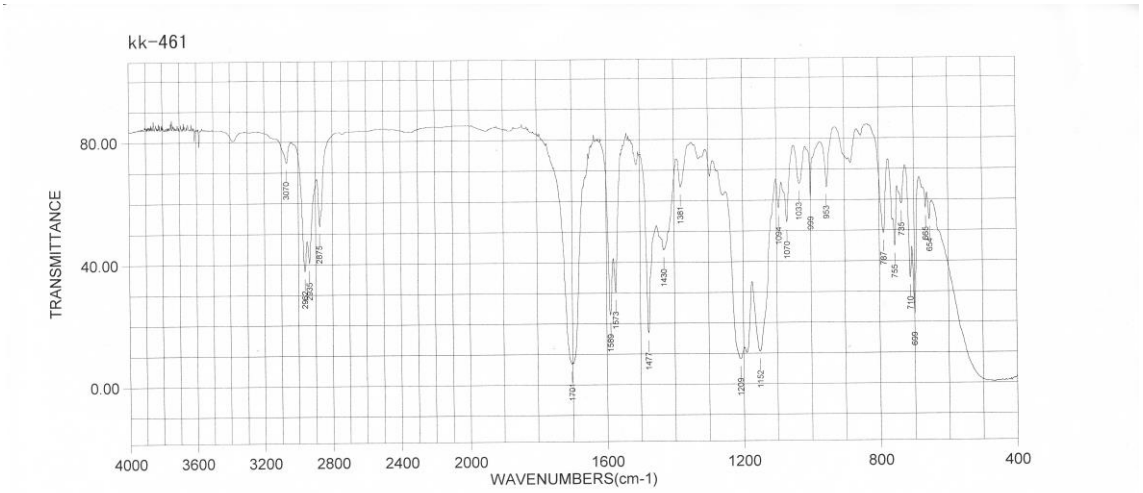
Mass spectrum (FD) of a mixture of **25a** and **25b**.



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

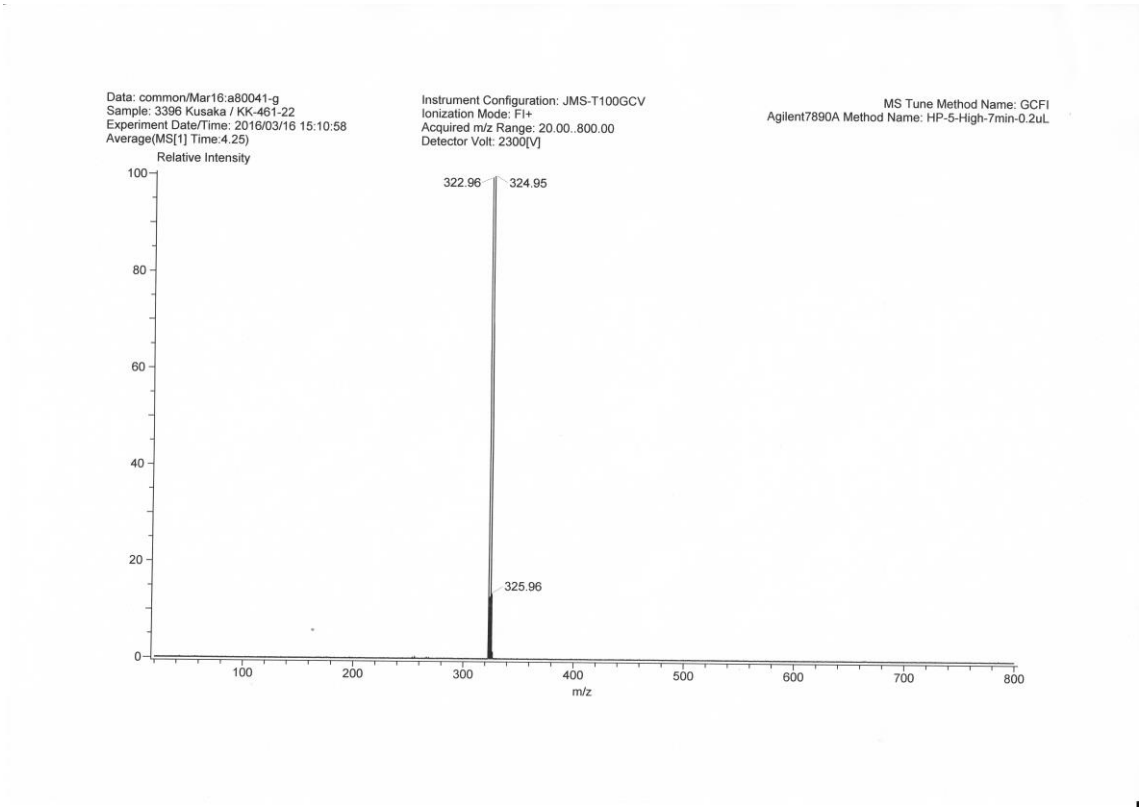


^{13}C NMR (100 MHz) spectrum of **29**, measured in chloroform-*d* at room temperature.

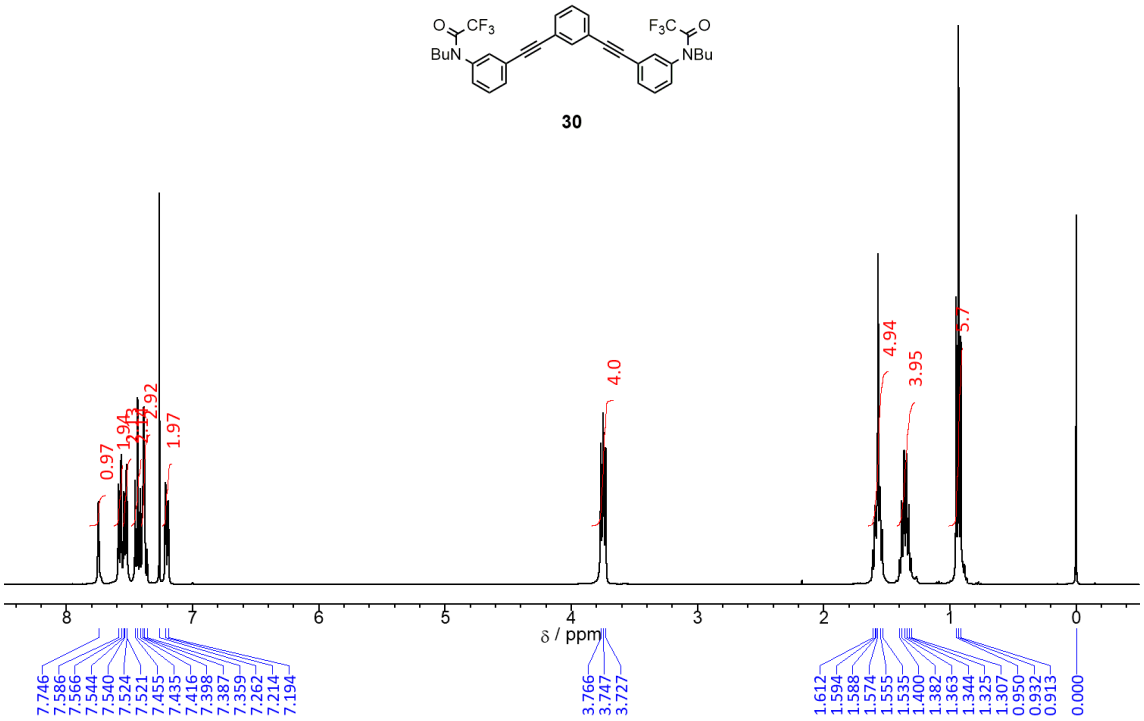


RESOL	: 2 cm-1	3070.16	73.28	1209.16	8.27	710.65	34.60
SCANS	: 5	2962.16	37.71	1152.27	10.67	699.08	22.79
AMPGAIN	: x1	2935.16	40.47	1094.42	57.48	665.33	57.25
P.INT	: 1 cm-1	2875.38	52.46	1070.31	52.87	654.72	53.54
BEAM	: single	1701.89	6.80	1033.67	65.43		
S.SPEED	: TGS	1589.08	22.89	999.92	60.86		
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		

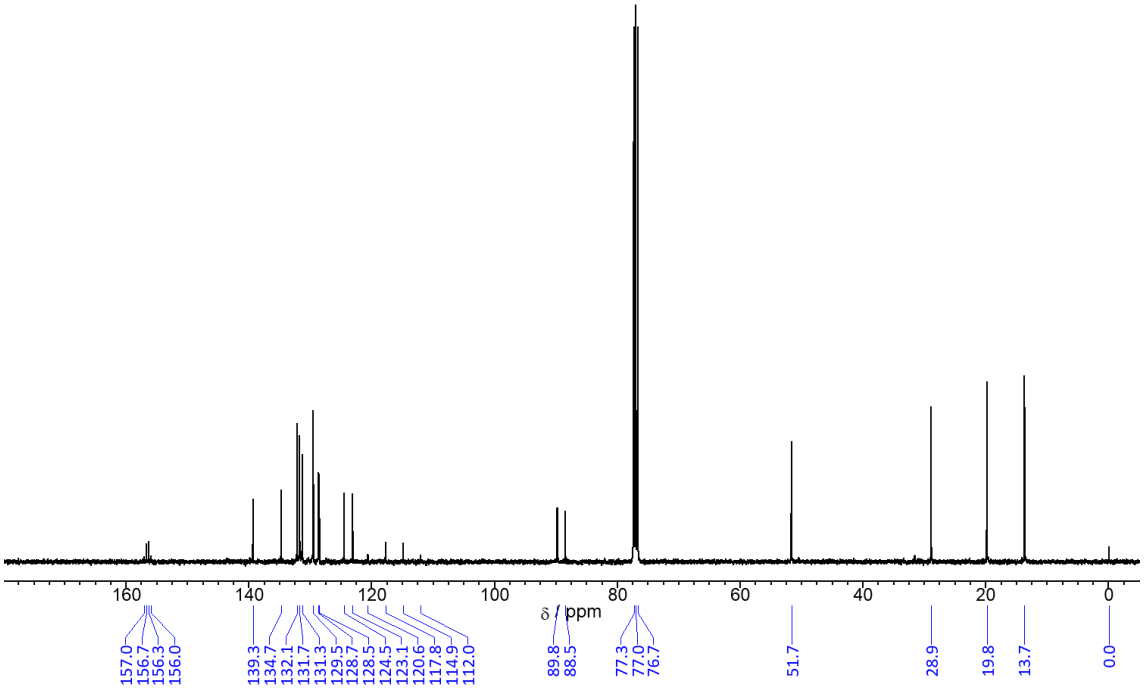
IR spectrum of **29**.



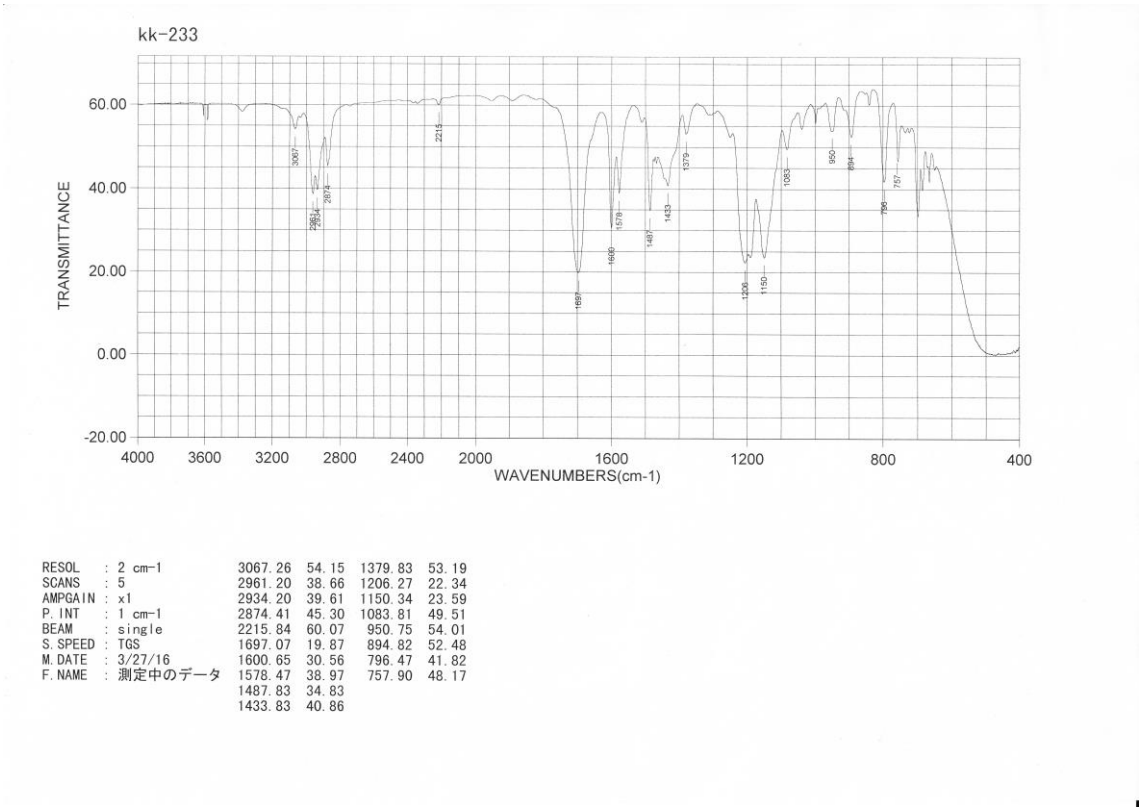
Mass spectrum (FD) of **29**.



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

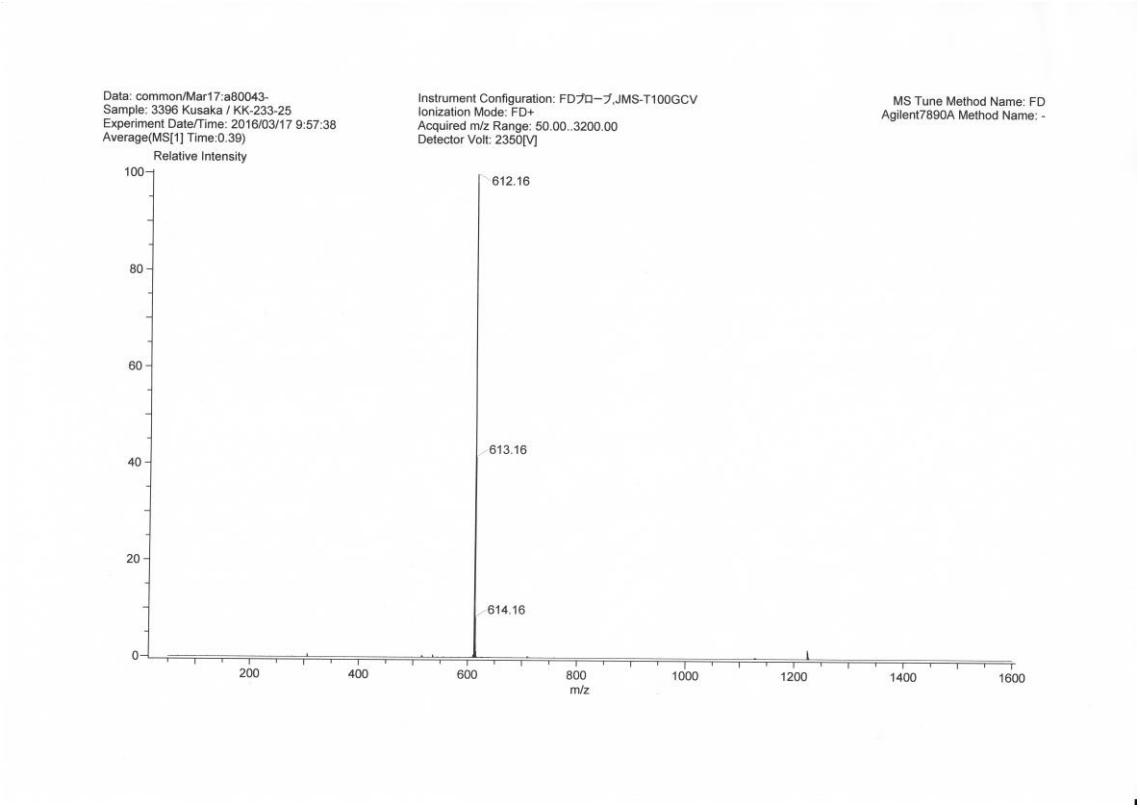


^{13}C NMR (100 MHz) spectrum of **30**, measured in chloroform-*d* at room temperature.



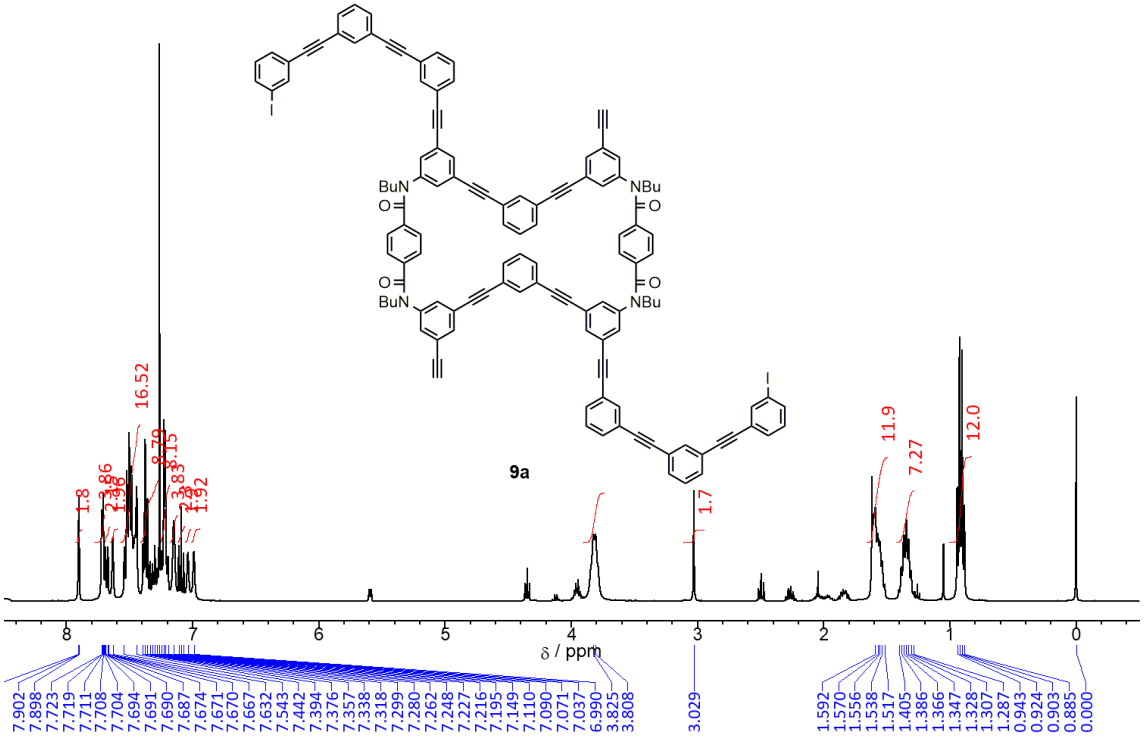
RESOL	: 2 cm-1	3067.26	54.15	1379.83	53.19
SCANS	: 5	2961.20	38.66	1206.27	22.34
AMPGAIN	: x1	2934.20	39.61	1150.34	23.59
P.INT	: 1 cm-1	2874.41	45.30	1083.81	49.51
BEAM	: single	2215.84	60.07	950.75	54.01
S.SPEED	: TGS	1697.07	19.87	894.82	52.48
M.DATE	: 3/27/16	1600.65	30.56	796.47	41.82
F.NAME	: 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**.

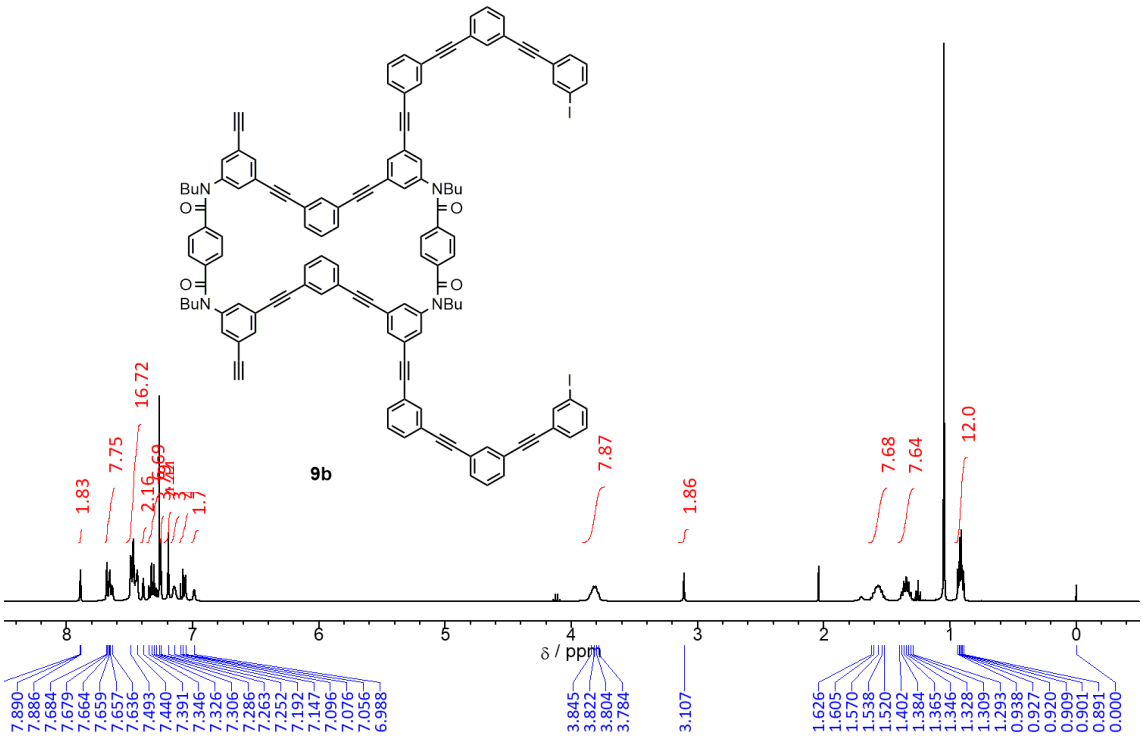


Mass spectrum (FD) of **30**.

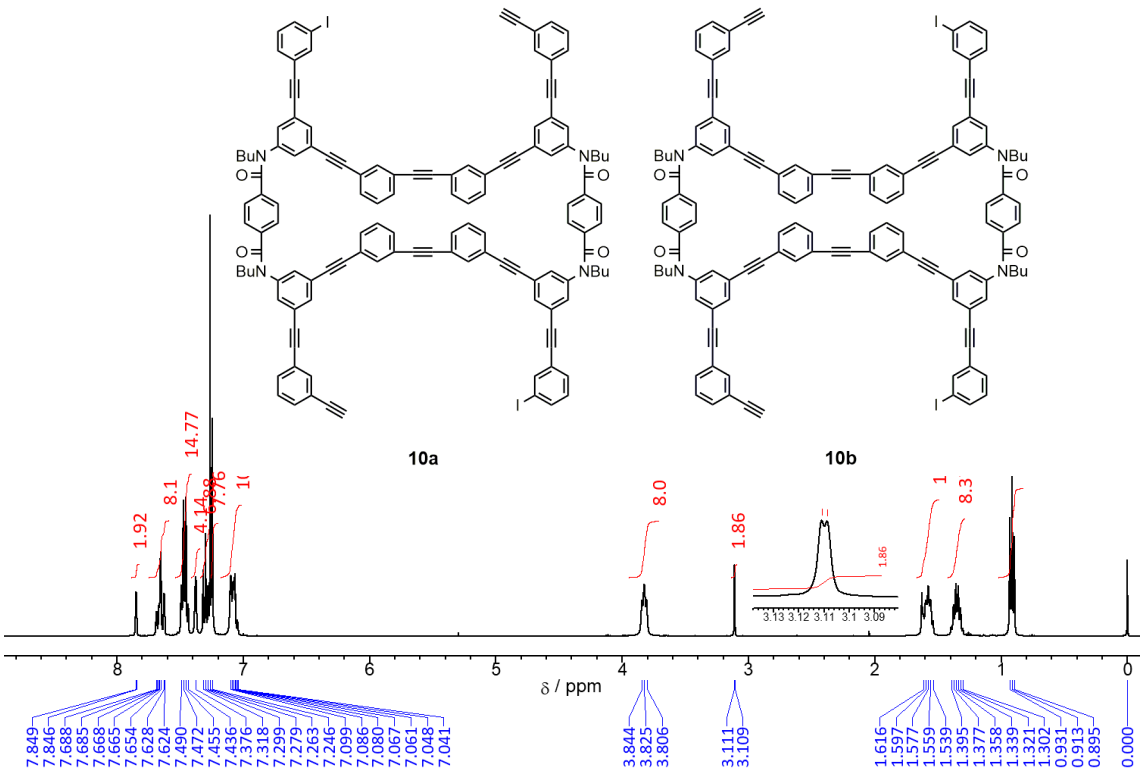
[1]H NMR spectra of new compounds (unprotected)



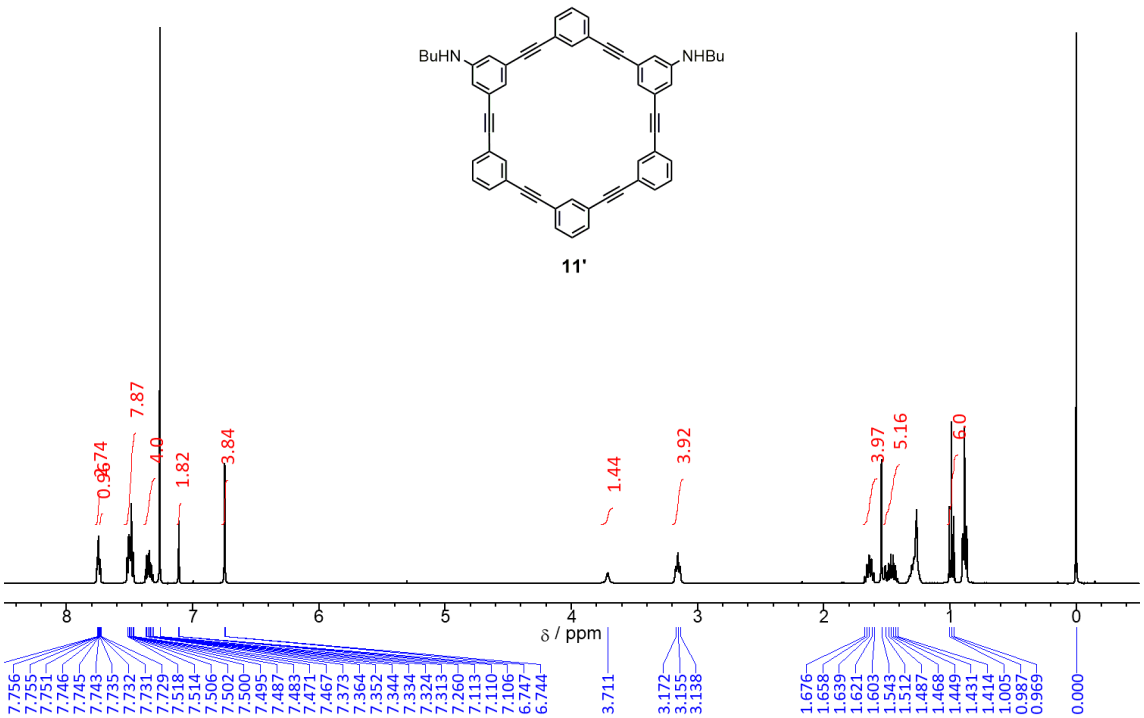
[1]H NMR spectrum (400 MHz) of **9a** cont. residual solvents (ethanol and ethyl acetate etc.), measured in chloroform-*d* at room temperature.



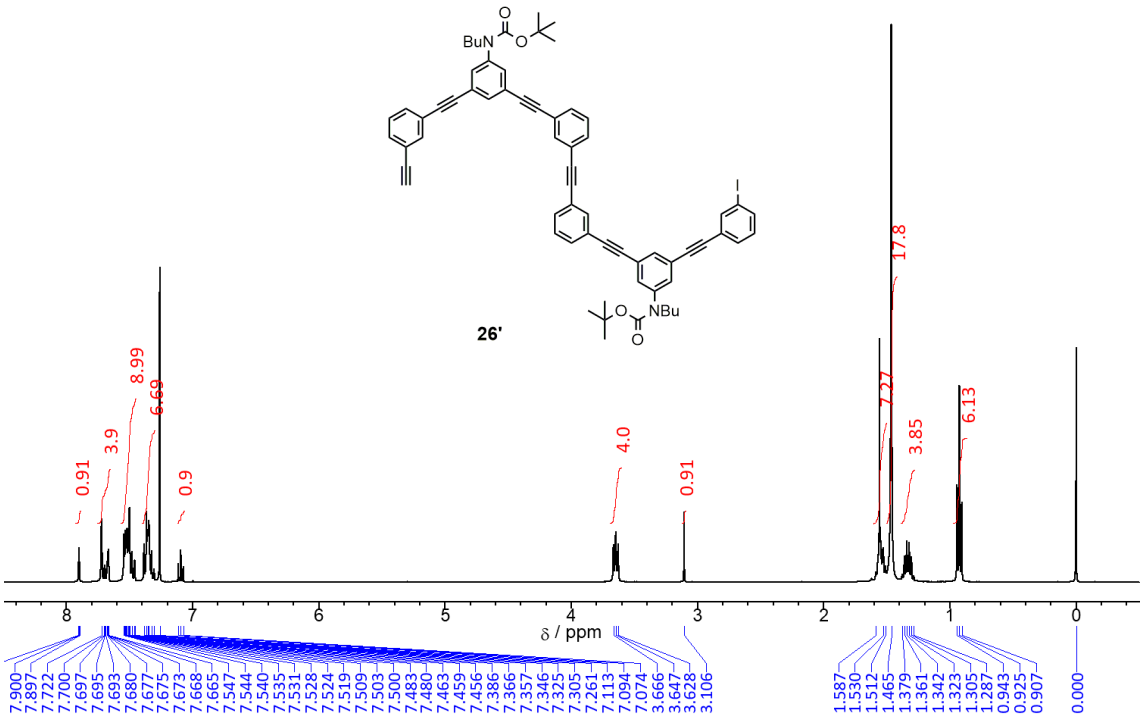
[1]H NMR spectrum (400 MHz) of **9b** cont. residual solvents (ethyl acetate etc.), measured in chloroform-*d* at room temperature.



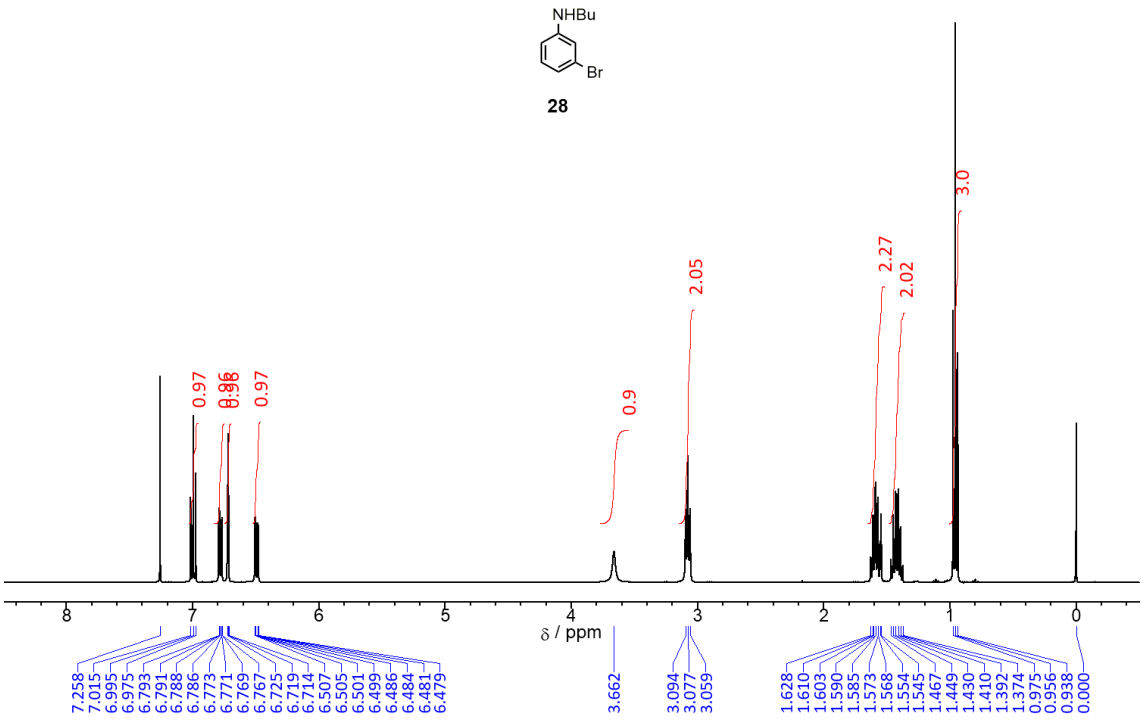
^{1}H NMR spectrum (400 MHz) of **10a** and **10b**, measured in chloroform-*d* at room temperature.



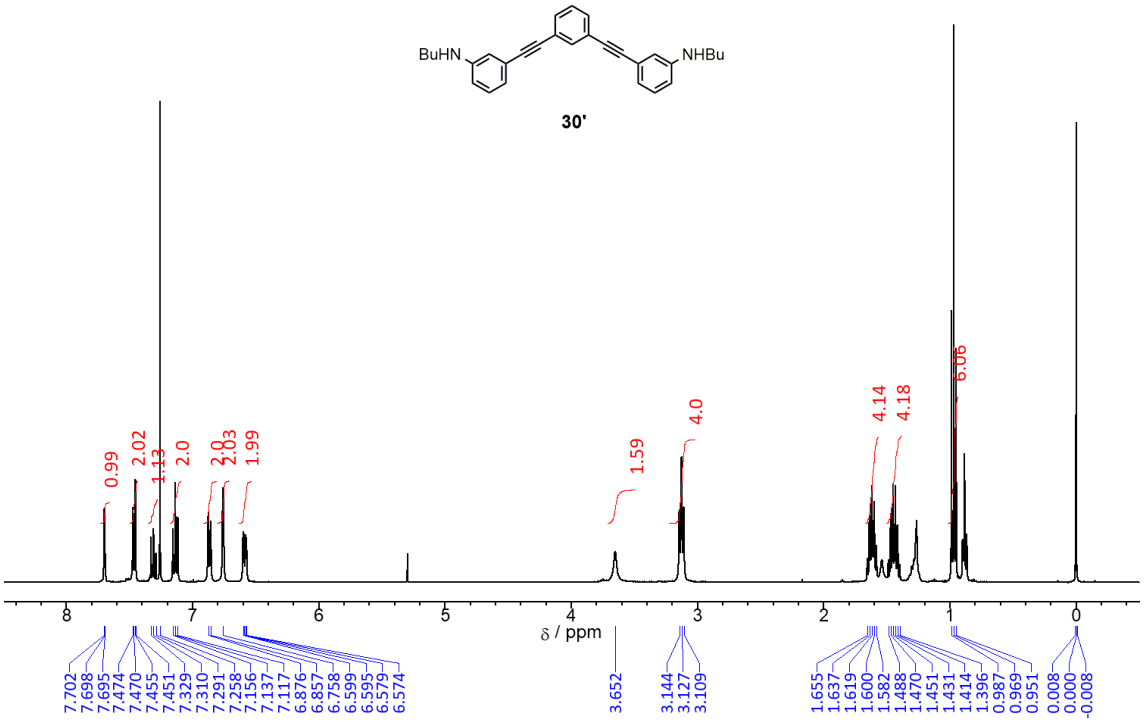
^{1}H NMR spectrum (400 MHz) of **11'** cont. residual solvents (hexane), measured in chloroform-*d* at room temperature.



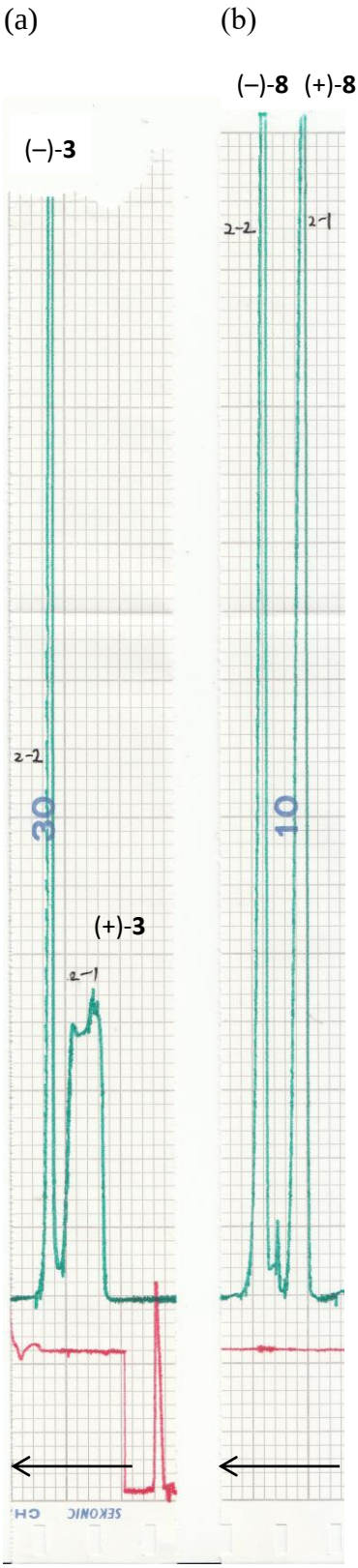
^{1}H NMR spectrum (400 MHz) of **26'**, measured in chloroform-*d* at room temperature.



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



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



(a) (±)-**3**
1:50 ethanol/chloroform; CHIRALPAK IF, DAICEL Co., Japan
first fraction: (+)-**3** ($[\alpha]_D$ = +590.8)
second fraction: (–)-**3** ($[\alpha]_D$ = –572.6)

(b) (±)-**8**
1:200 ethanol/chloroform; CHIRALPAK IF, DAICEL Co., Japan
first fraction: (+)-**8** ($[\alpha]_D$ = +1062)
second fraction: (–)-**8** ($[\alpha]_D$ = –1067)

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