Electronic Supplementary Information

Synthesis of Novel Styryl-*N*-isopropyl-9H-carbazoles for Designing *trans*-conjugated Regular Silicon Hybrid Materials

Mariusz Majchrzak[a], Magdalena Grzelak[a], Bogdan Marciniec[a,b]

[a] Faculty of Chemistry, Adam Mickiewicz University in Poznan, Umultowska 89b, 61-614 Poznań, Poland

[b] Wielkopolska Centere of Advanced Technology, Adam Mickiewicz University in Poznań, Umultowska 89c, 61-614 Poznan, Poland

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Synthesis procedures

Syntheses of carbazole derivatives

3-bromo-*9H*-carbazole (**6**)[1] A solution of NBS (4.48 g, 0.02392 mol) in 8 mL DMF was added slowly to a solution of *9H*-carbazole (4 g, 0.02392 mol, which was recrystallized from hot acetone) in dichloromethane (75 mL) in to a two-necked round bottom flask. The reaction mixture was stirred at room temperature and the progress of the reaction was controlled by GCMS analysis. The mixture was extracted with H_2O and dried over anhydrous $MgSO_4$ for 12h and filtered. The organic part was isolated by very quick 'flash' column system (glass filter G3, silica gel, Celite®) connected with membrane pump. The excess of solvent was evaporated and dried under vacuum. The isolated yield was 98% (5.76 g) as a white solid. The final product was confirmed by spectroscopic methods.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (m, 1H, (G), 7.31 (d, 1H, (B), J_{HH} = 8.4Hz), 7.43 (m, 1H, (F)), 7.5 (d, 1H, (C), J_{HH} = 6.6 Hz), 8.0 (d, 1H, (H), J_{HH} = 7.8 Hz), 8.08 (s, 1H, (D)), 8.1 (s, 1H, (A)), 8.18 (d, 1H, (E), J_{HH} = 4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.9, 138.1, 128.6, 126.7, 125.2, 123.4, 122.5, 120.6, 120.0, 112.3, 112.1, 110.9. MS (m/z (relat. int. %)): 246.3 (73.4) ($M^{+\cdot}$), 244.9 (82.3), 166 (100), 164 (19.8), 140 (70), 122.3 (12.8), 87.2 (15), 82.5 (23.6), 69.3 (27.6). mp. 188.2-188.5°C.

3,6-dibromo-*9H*-carbazole (**7**)[2] was synthesized by the same method as **6** using 2 eq. of NBS (4.96 g, 0.04784 mol) in 12 mL DMF, *9H*-carbazole (4 g, 0.02392 mol) in dichloromethane (120 mL). The isolated yield was 97% (7.54 g) as a white solid. The final product was confirmed by spectroscopic methods.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.3 (d, 2H, (C), J_{HH} = 8.4 Hz), 7.51 (d, 2H, (B), J_{HH} = 8.1 Hz), 8.12 (s, 2H, (D)), 8.12 (s, 1H, (A)). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.5, 129.4, 124.2, 123.4, 112.76, 29.7. MS (m/z (relat. int. %)): 324.7 (100) ($M^{+\cdot}$), 322.7 (51.9), 245.8 (36.5), 243.9 (41.4), 165.1 (82.7), 164 (74.4), 138 (37.5), 137 (29.4), 111.1 (14.5), 97.9 (10.6), 87 (25.7), 86 (27), 82.4 (46.6), 74 (27.7). mp. 200.0-200.3°C.

***N*-isopropylcarbazole** (**8**)[26] A two-necked round bottom flask equipped with a condenser and magnetic stirring bar was charged with carbazole (15 g, 0.09 mol) and acetone (300 mL). The solution was stirred and heated at boiling point. Isopropyl bromide (14 mL, 0.153 mol), tetrabutylammonium bromide (1.6 g, 0.005 mol) and potassium hydroxide (8 g, 0.144 mol) were added to a solution. The reaction mixture was stirred for 4 hours. The mixture was cooled to the room temperature and the solvent was evaporated. The residue was dissolved in dichloromethane and extracted with H_2O. The organic part was dried over anhydrous $MgSO_4$ for 24 hours and filtered. The solution was isolated by very quick 'flash' column system (glass filter G3, silica gel, Celite®) connected with membrane pump. The excess of solvent was evaporated under vacuum. The residue was stirred with cold petroleum ether, filtered and dried under high vacuum pump. *N*-isopropylcarbazole was obtained with 96% yield (18 g) as a white solid. The reaction progress was monitored by TLC and GCMS analysis. The final product was confirmed by spectroscopic methods.
^{1}H NMR (300 MHz, $CDCl_3$; δ(ppm)): 1.75 (d, 6H, (F), J_{HH} = 6.9 Hz), 5.03 (m, 1H, (E)), 7.24 (d, 2H, (D), J_{HH} = 7.5 Hz), 7.28 (t, 2H, (C)), 7.57 (d, 2H (B), J_{HH} = 9 Hz), 8.16 (d, 2H, (A), J_{HH} = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$; δ(ppm)): 139.5, 125.4, 123.3, 120.4, 118.6, 110.0, 46.7, 20.8. MS (EI) (m/z (relat. int. %)): 209.2 (100) ($M^{+\cdot}$), 208.2 (11.9), 207.3 (5.9), 194.4 (36), 193.5 (11.6). mp. 120.5-120.7°C.

3-bromo-*N*-isopropylcarbazole (**9**)[26] A solution of NBS (3.4 g, 0.019 mol) in 8 mL DMF was added slowly to a solution of *N*-isopropyl-carbazole (4 g, 0.019 mol) in dichloromethane (50 mL). The reaction mixture was stirred at room temperature and the progress of the reaction was controlled by GCMS analysis. The mixture was extracted with H_2O and dried over anhydrous $MgSO_4$ for 24h and filtered. The organic part was isolated by very quick 'flash' column system (glass filter G3, silica gel, Celite®) connected with membrane pump. The excess of solvent was evaporated and dried under vacuum. The isolated yield was over 98% (5.4 g).
^{1}H NMR (300 MHz, $CDCl_3$; δ(ppm)): 1.72 (d, 6H, (A), J_{HH} = 7.2 Hz), 4.98 (m, 1H, (B)), 7.23-7.57 (5H, (I, C, H, D, G), 8.08 (d, 1H, (F), J_{HH} = 7.8 Hz), 8.24 (s, 1H, (E)). ^{13}C NMR (75 MHz, $CDCl_3$; δ(ppm)):139.9, 138.2, 128.1, 126.2, 125.2, 123.2,

122.4, 120.6, 119.1, 111.5, 110.3, 47.0, 20.9. MS (EI) (m/z (relat. int. %)): 289.1 (37.5) ($M^{+\cdot}$), 288.2 (8.4), 287.1 (37), 275.2 (17.5), 274.1 (100), 273.2 (18), 272.2 (90), 193.2 (34.5), 192.3 (8.9), 166.2 (14.9). MS (FAB, m/z (%) (M^+,100): 288. mp. 87.6-87.8°C.

3,6-dibromo-*N*-isopropylcarbazole (**10**)[26] was synthesized by the same method as (**9**) using 2 eq. of NBS (2.55 g, 0.01413 mol) in 5 mL DMF, *N*-isopropylcarbazole (1.5 g, 0.00717 mol) in dichloromethane (90 mL). The isolated yield was 98% (2.58 g) as a white solid. The final product was confirmed by spectroscopic methods.
^{1}H NMR (300 MHz, $CDCl_3$; δ(ppm)): 1.68 (d, 6H (A), J_{HH} = 7.2 Hz), 4.91 (m, 1H, (B)), 7.39 (d, 2H, (D), J_{HH} = 8.7 Hz), 7.52 (d, 2H, (C), J_{HH} = 8.7 Hz), 8.14 (s, 2H, (E)). ^{13}C NMR (75 MHz, $CDCl_3$; δ(ppm)): 179.6, 169.9, 165.2, 164.4, 153.1, 118.3, 88.4, 62.0. MS (EI) (m/z (relat. int. %)): 369.1 (28.2) ($M^{+\cdot}$), 368.1 (10.1), 367.2 (59.2), 366.2 (5.9), 365.2 (27.8), 355.2 (8.2), 354.2 (55.5), 353.2 (17.2), 352.2 (100), 351.4 (8.5), 350.3 (46.5) 273.3 (30.3), 271.4 (28.7), 164.3 (15.3). MS (FAB, m/z (%) (M^+,100): 367. mp. 126.6-126.8°C.

2,7-dibromo-*N*-isopropylcarbazole (**11**) A two-neck round bottom flask equipped with a condenser and magnetic stirring bar was charged with 2,7-dibromocarbazole (1.038 g, 0.0032 mol) and acetone (30 mL). The solution was stirred and heated at boiling point. Isopropyl bromide (0.51 mL, 0.00544 mol), tetra-n-butylammonium bromide (0.057 g, 0.000176 mol) and potassium hydroxide (0.287 g, 0.00512 mol) were added to the solution. The reaction mixture was stirred for 4 hours. The reaction progress was monitored by TLC and GCMS analysis.The mixture was cooled to the room temperature and the solvent was evaporated. The residue was dissolved in dichloromethane and extracted with H_2O. The organic part was dried over anhydrous $MgSO_4$ for 24 hours and filtered. The organic part was isolated by very quick 'flash' column system (glass filter G3, silica gel, Celite®) connected to membrane pump. The excess of solvent was evaporated under high vacuum. The residue was stirred with petroleum ether, filtered and dried. Product was obtained with 99% yield (1.15 g) as a white solid.
^{1}H NMR (300 MHz, $CDCl_3$; δ(ppm)): 1.69 (d, 6H, (A), J_{HH} = 7.2 Hz), 4.87 (m, 1H, (B)), 7.34 (d, 2H, (D), J_{HH} = 6.9 Hz), 7.66 (s, 2H, (C)), 7.89 (d, 2H, (E), J_{HH} = 8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$; δ(ppm)): 140.5, 122.5, 121.9, 121.5, 119.6, 113.4, 47.3, 20.9. MS (EI) (m/z (relat. int. %)): 368.4 (22.9) ($M^{+\cdot}$), 367.5 (8.6), 366.3 (47.4), 364.4 (23.7), 353.4 (29.5), 351.3 (60.5), 324.5 (19.7), 323.5 (11.4), 272.6 (44.8), 270.8 (52.2), 245.9 (15.5), 243.9 (19), 192.1 (28.2), 191 (37.1), 165.1 (61.7), 163.9 (100)). MS (FAB, m/z (%) (M^+,100): 367. HRMS (m/z) calcd. for $C_{15}H_{13}Br_2N$: 364.94147, found 364.94143. mp. 147.1-147.2°C.

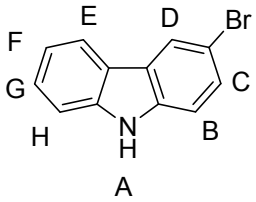
Reference

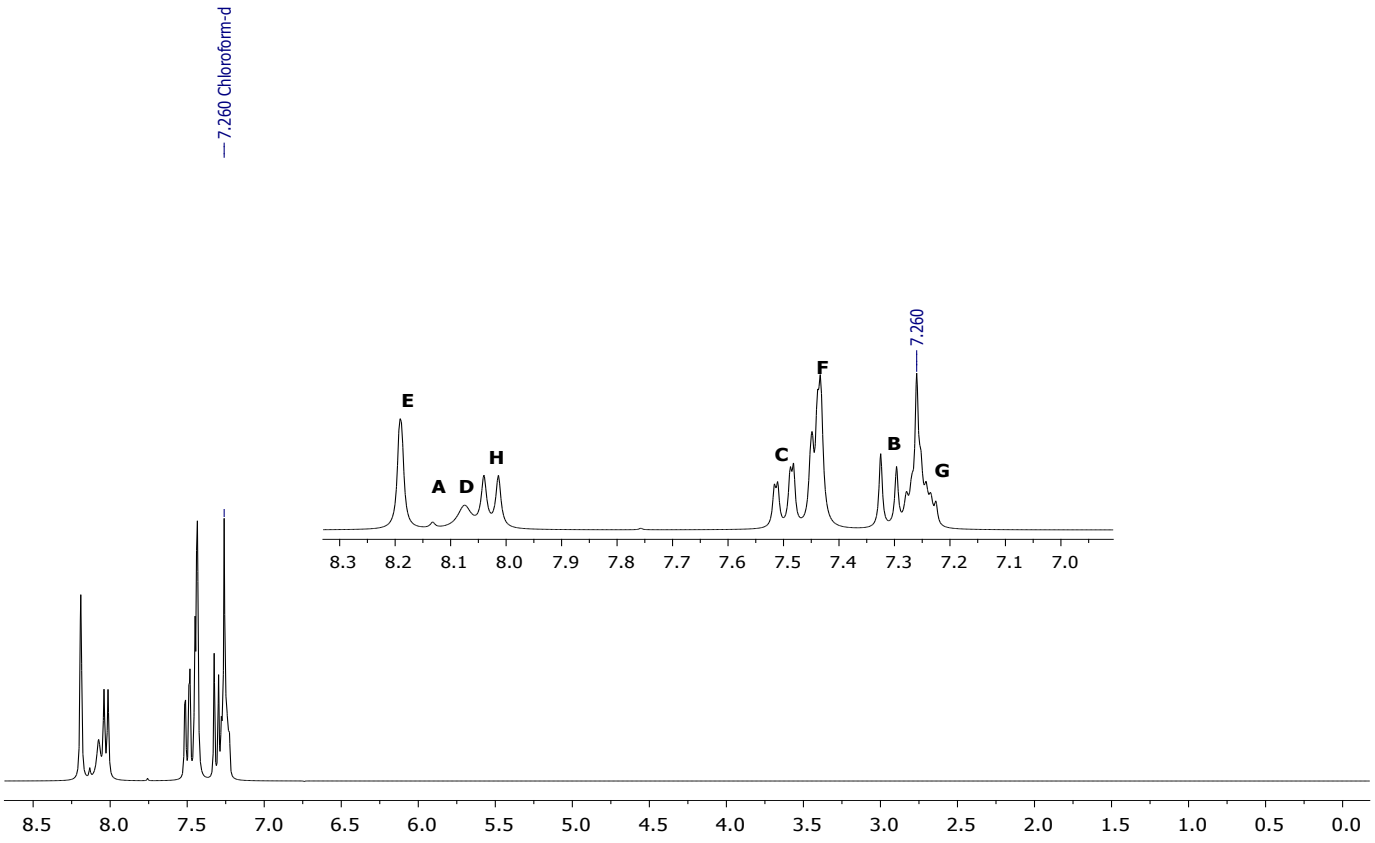
1. Xiaoqi Chen at all, *Bioorganic & Medicinal Chemistry Letters,* 2012, **22**, 363–366
2. Y. Yang, M. M. Xue, , J. L. Marshall, J. De Mendoza, *Organic Letters*, 2011, vol. 13, **12**, 3186-3189

NMR Spectra

Compound 6

3-Bromo-*9H*-carbazole





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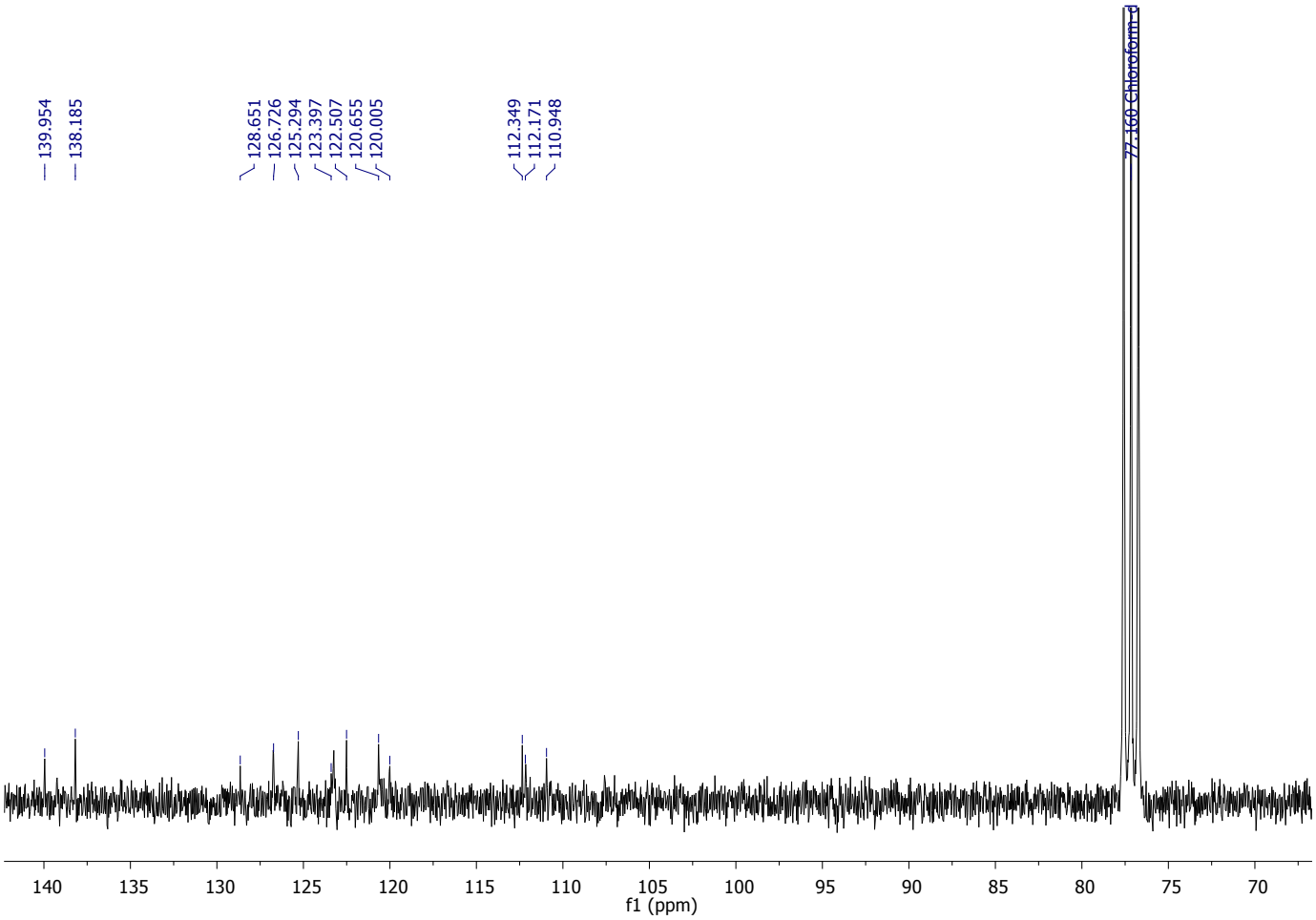
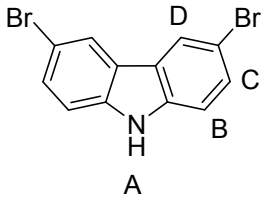
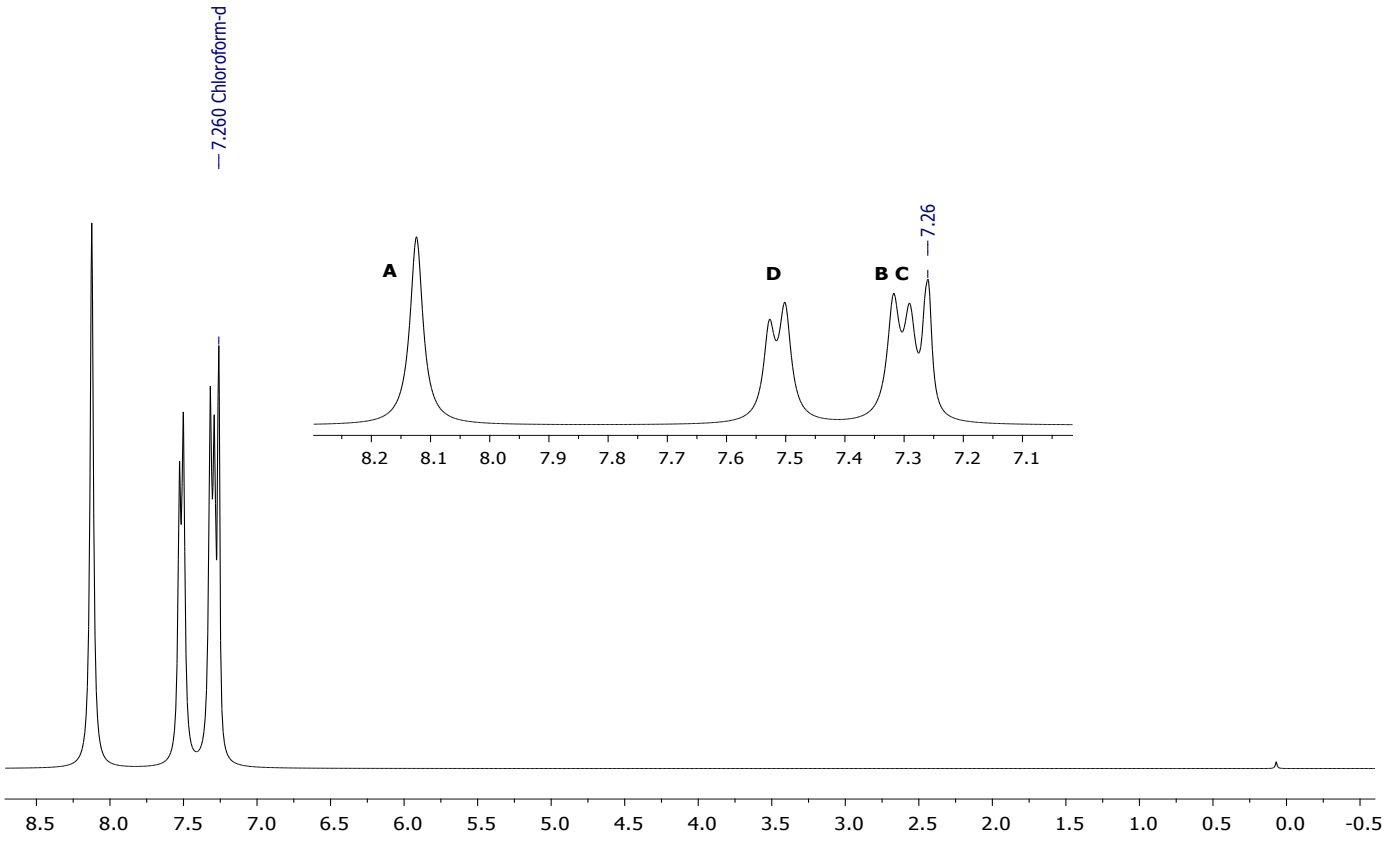


Compound 6 - ^{13}C NMR in $CDCl_3$

Compound 7

3,6-Dibromo-*9H*-carbazole





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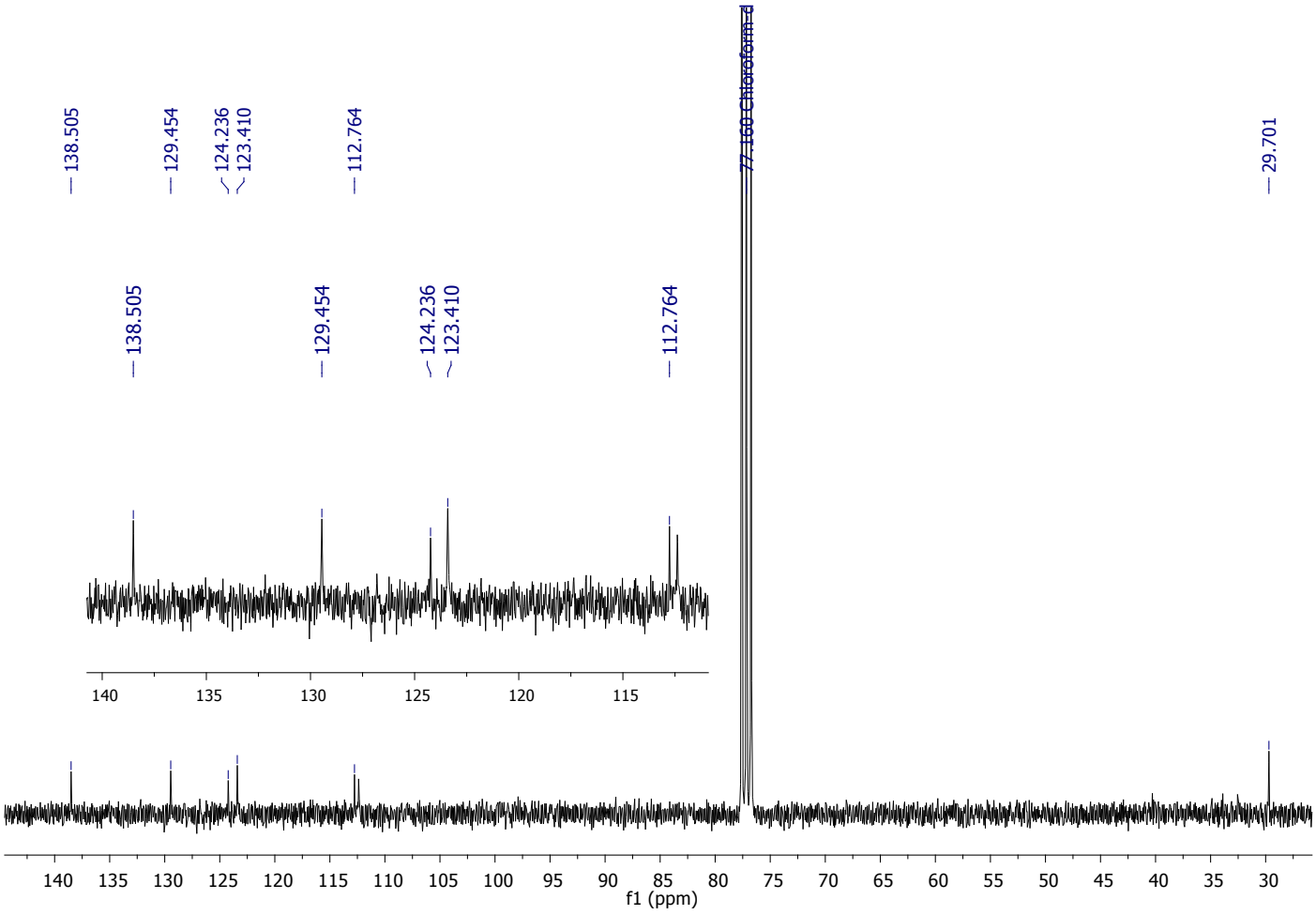
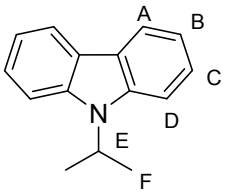
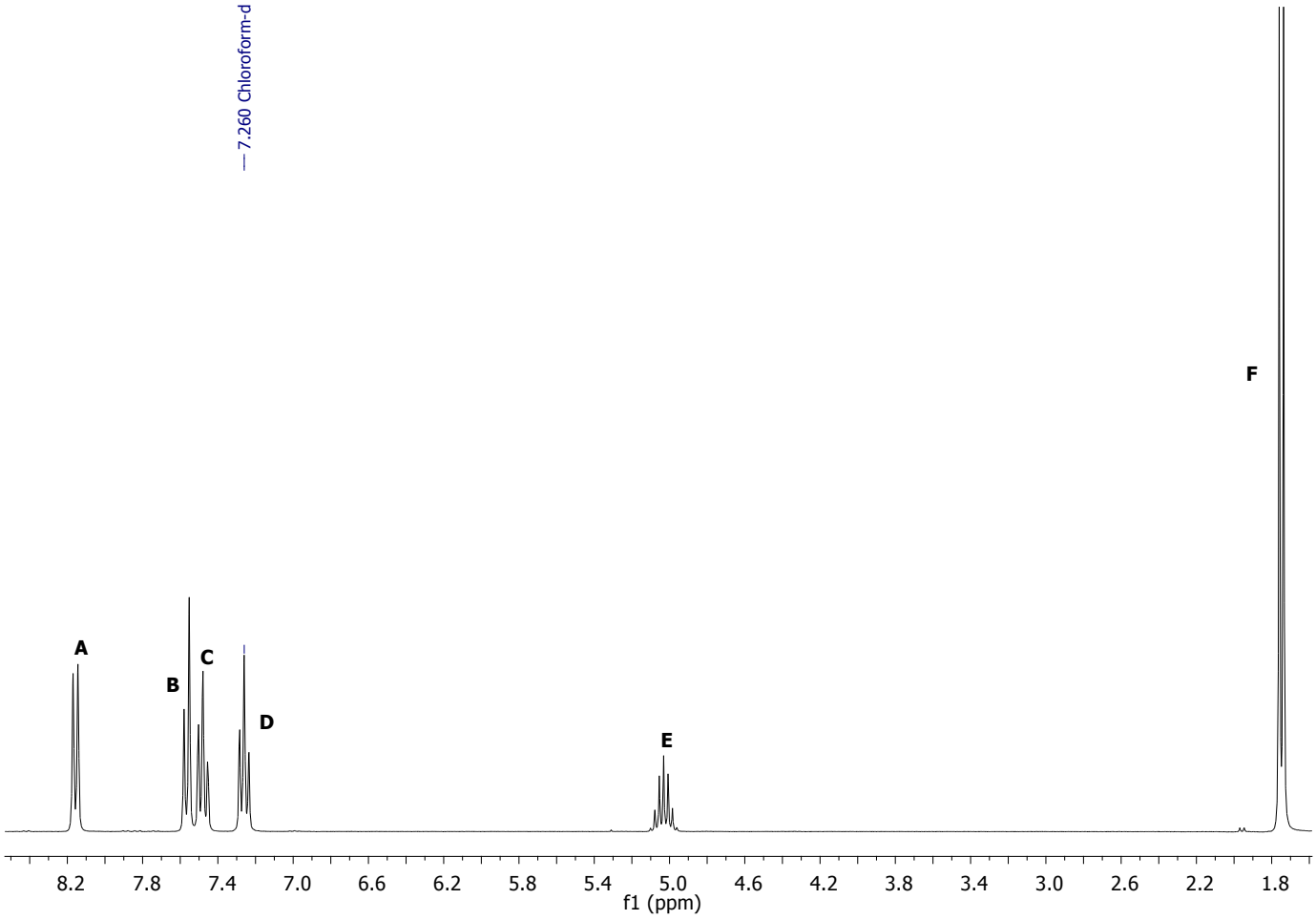


Compound 7 - ^{13}C NMR in $CDCl_3$

Compound 8

***N*-isopropylcarbazole**





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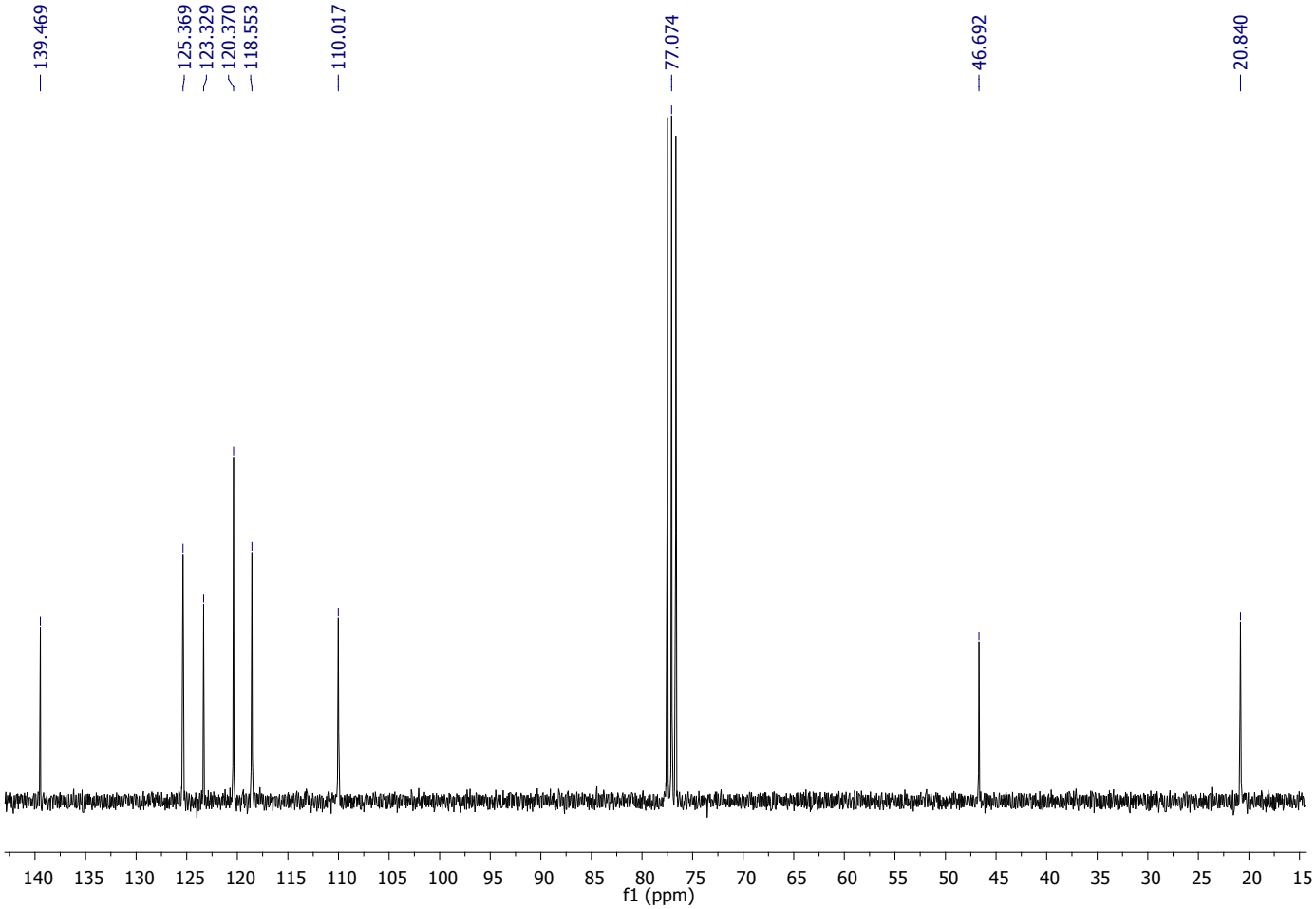
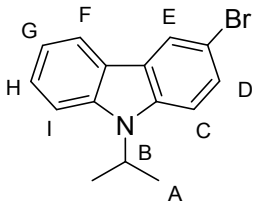
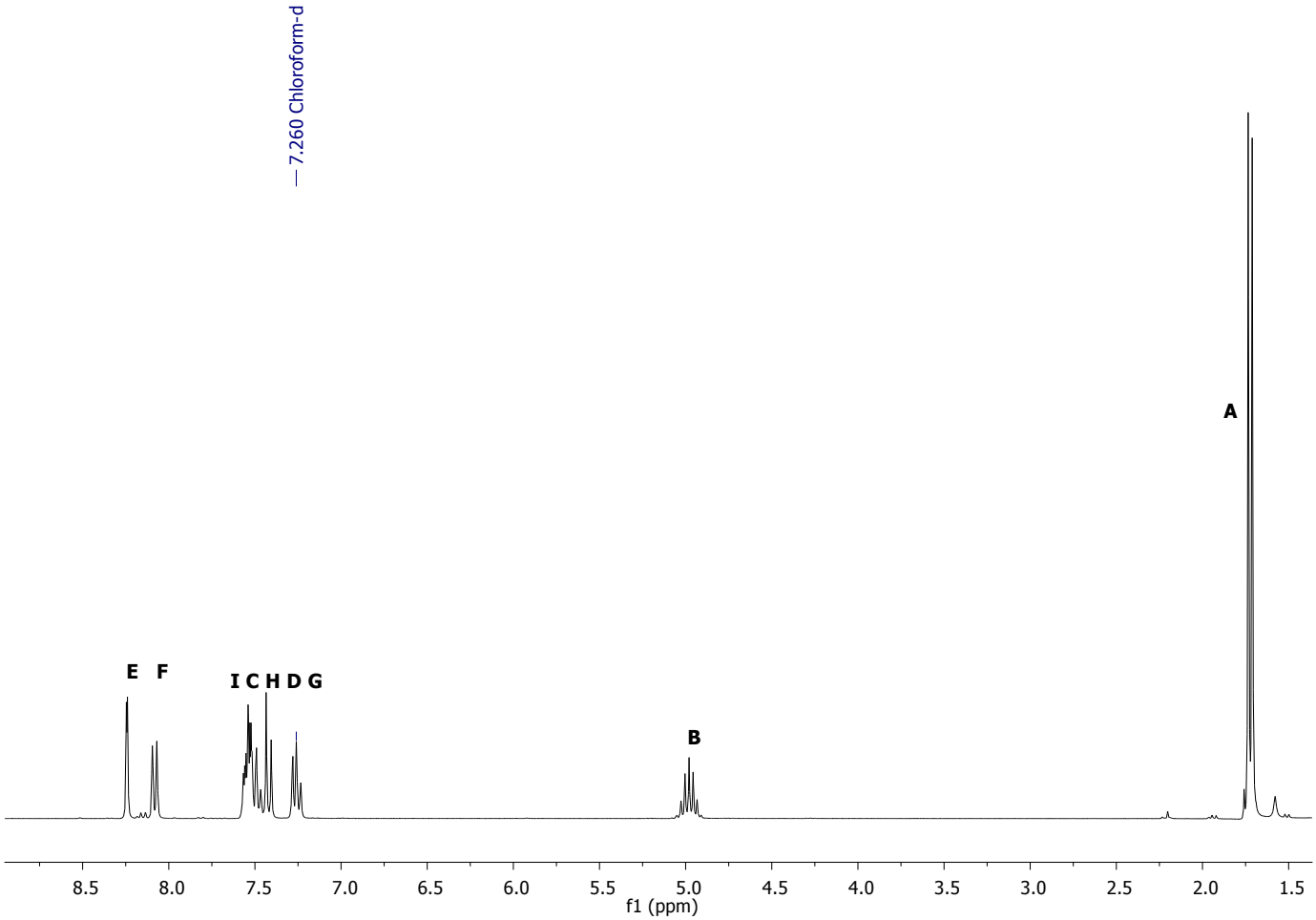


Compound 8 - ^{13}C NMR in $CDCl_3$

Compound 9

3-Bromo-*N*-isopropylcarbazole





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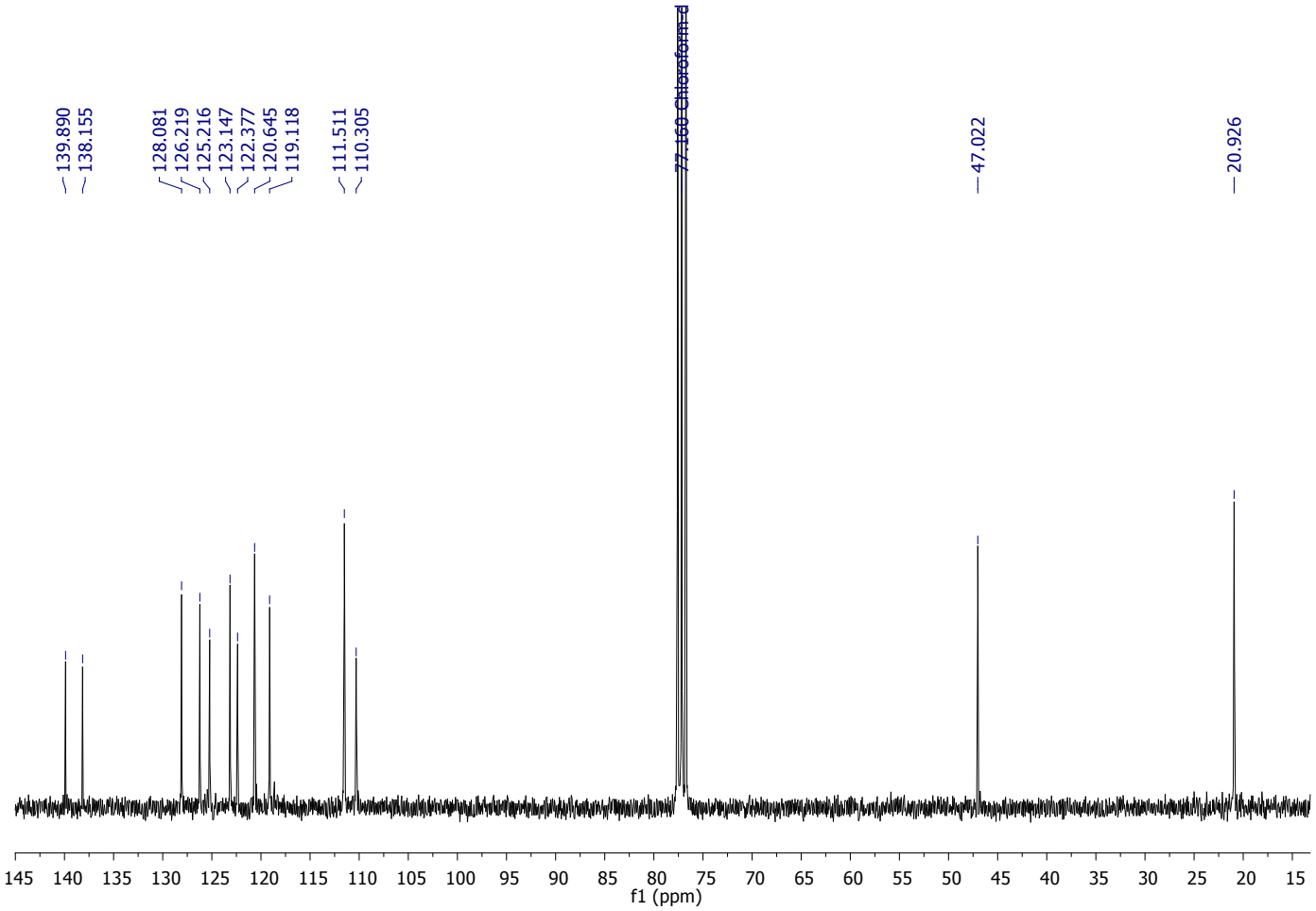
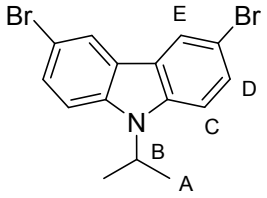
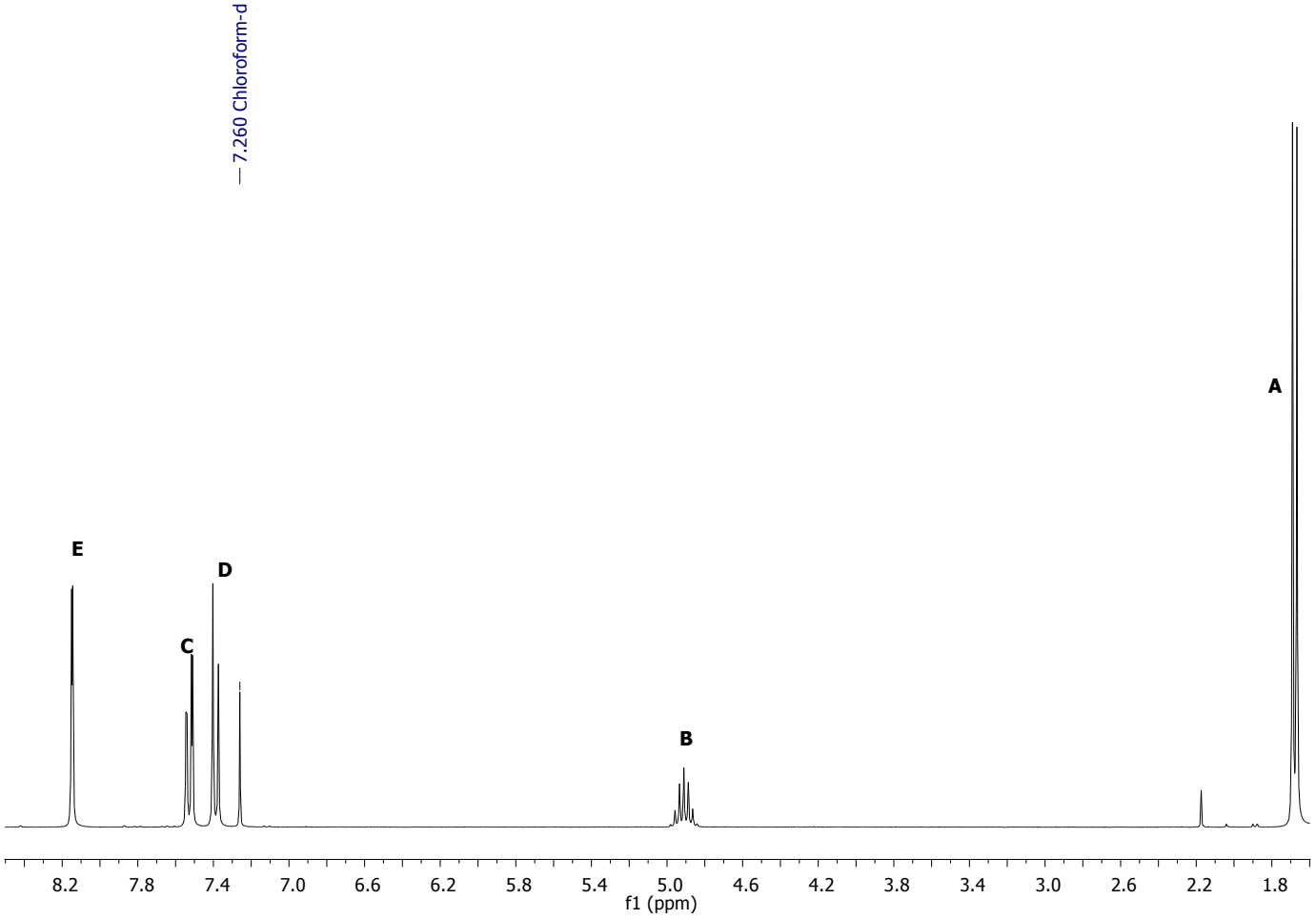


Compound 9 – ^{13}C NMR in $CDCl_3$

Compound 10

3,6-Dibromo-*N*-isopropylcarbazole





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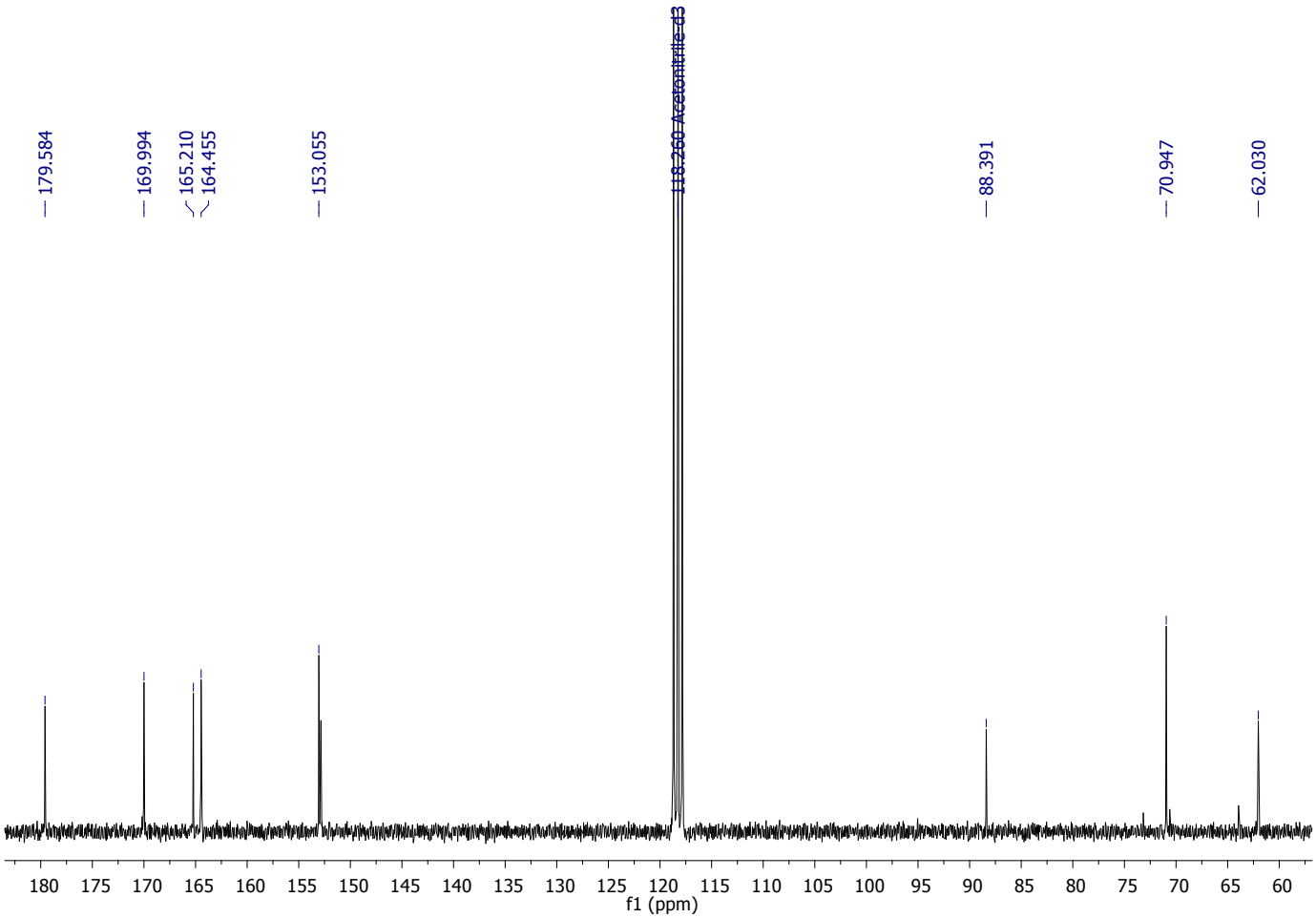
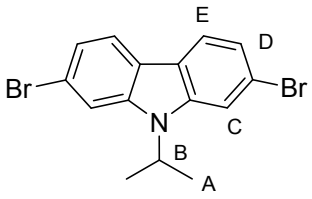
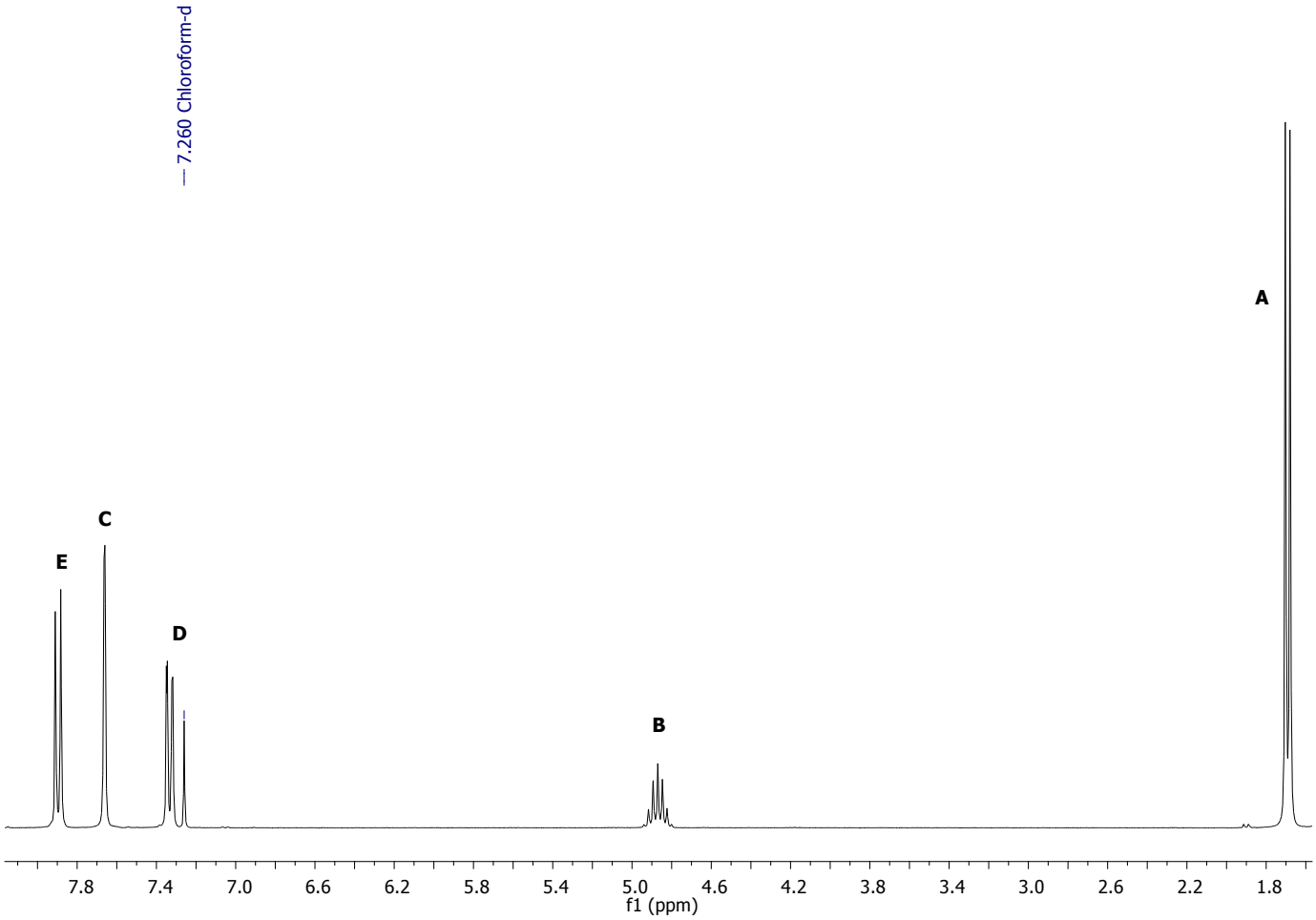


Compound 10 – ^{13}C NMR in $CDCl_3$

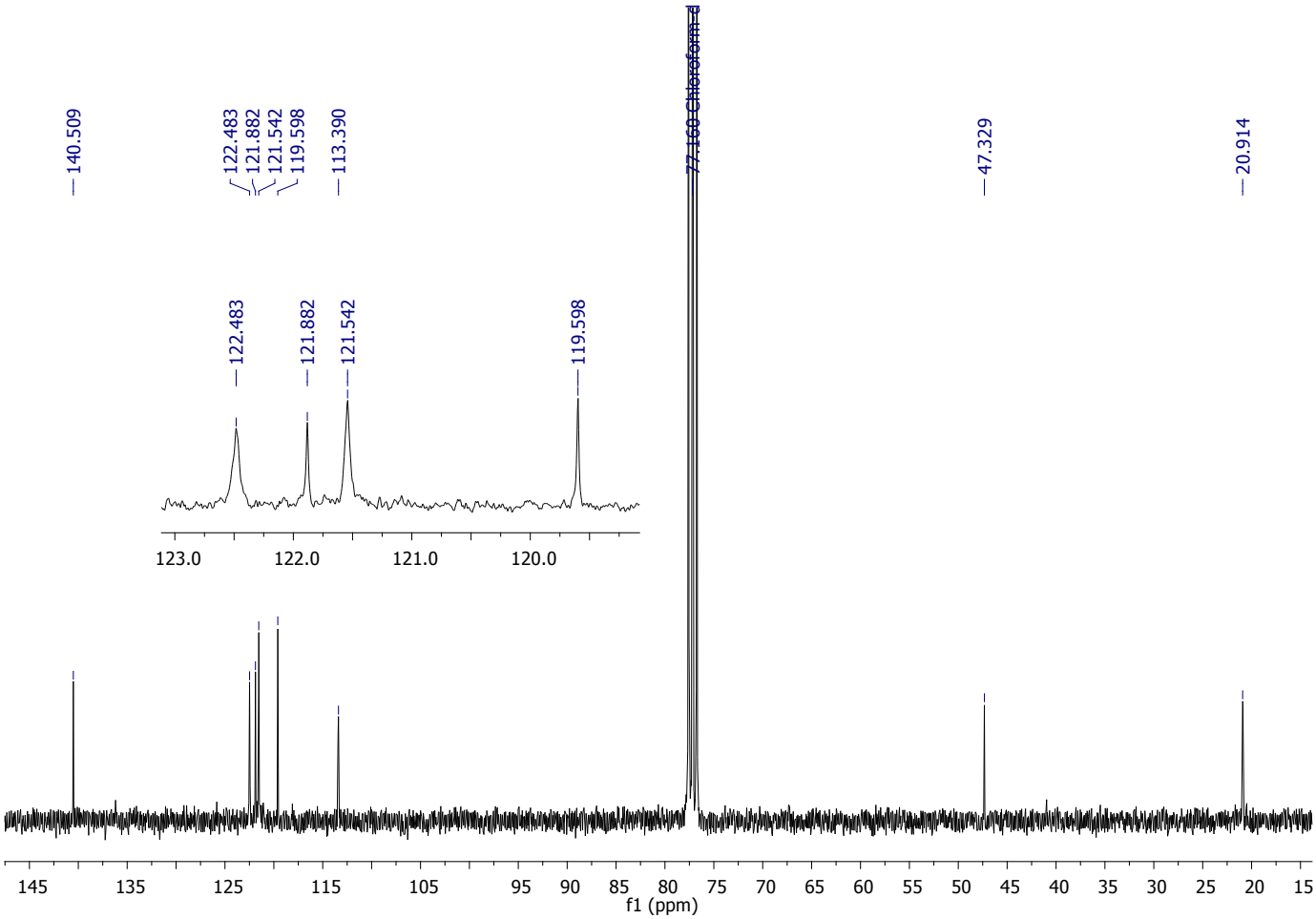
Compound 11

2,7-dibromo-*N*-isopropylcarbazole





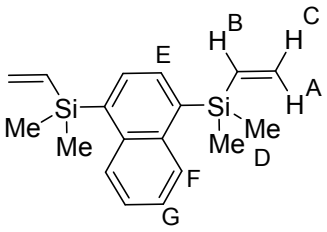
Compound 11 - ^{1}H NMR in $CDCl_3$

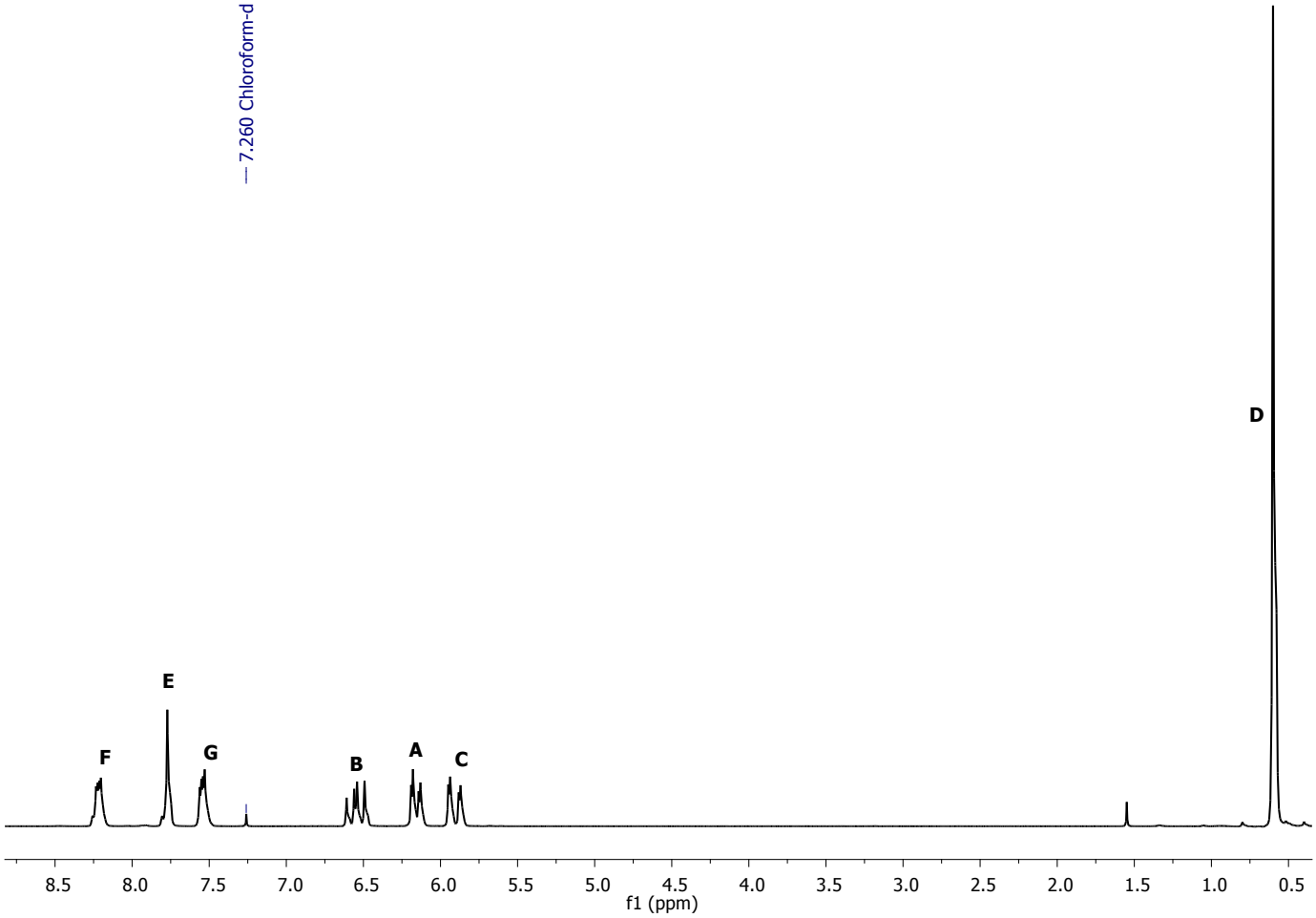


Compound 11 – ^{13}C NMR in $CDCl_3$

Compound 12

1,4-Bis(dimethylvinylsilyl)naphthalene





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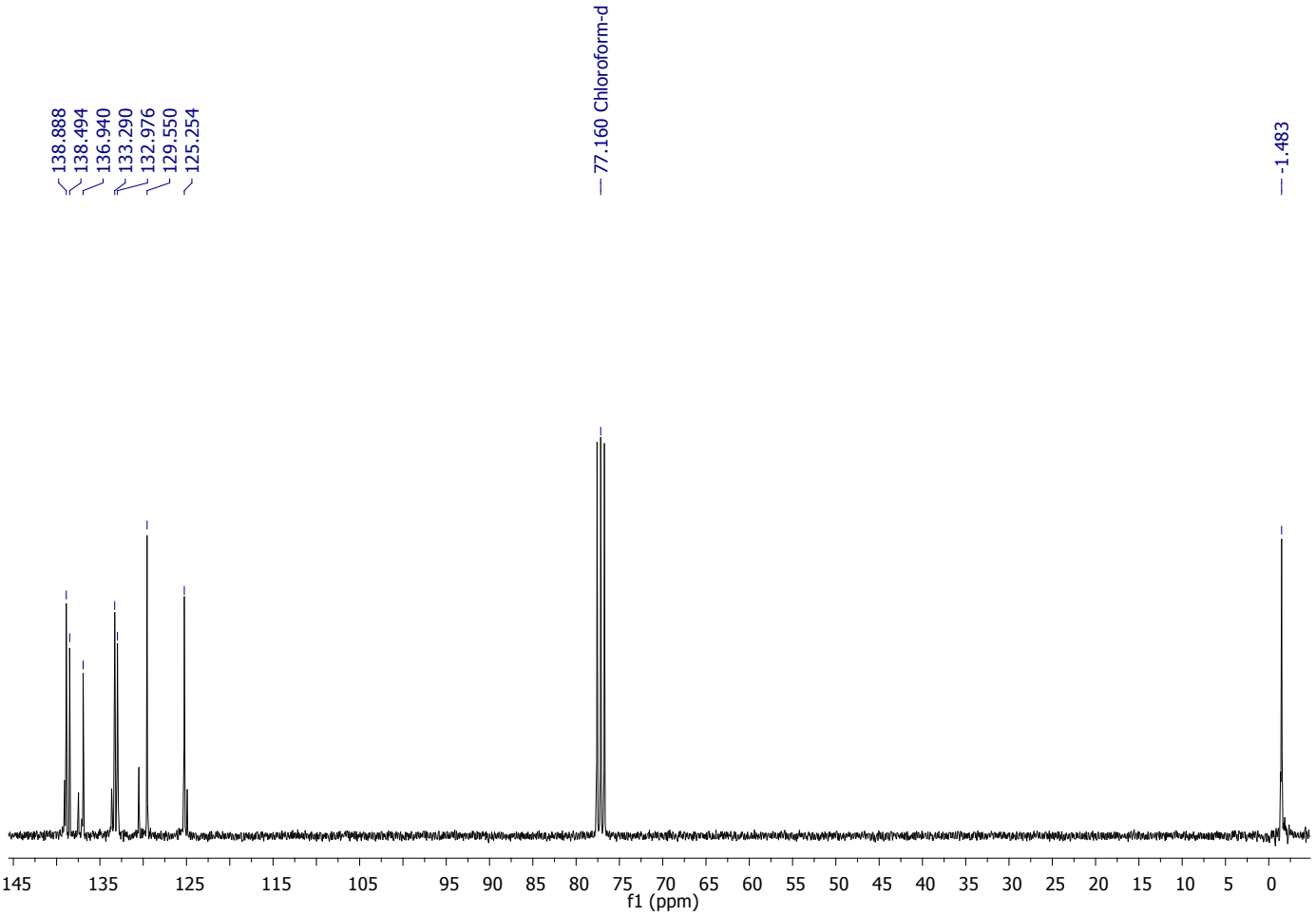
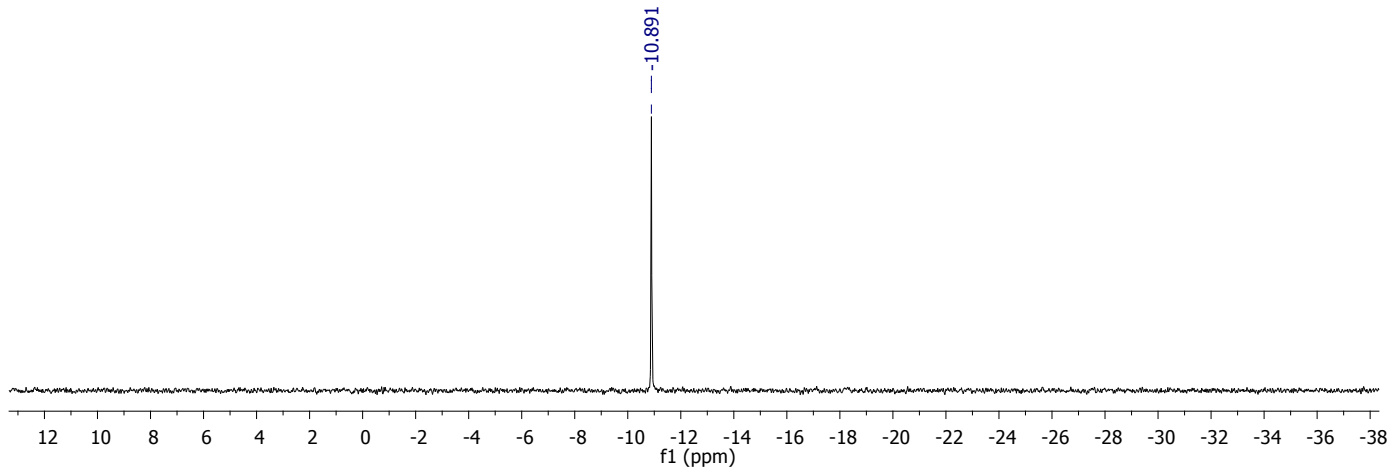


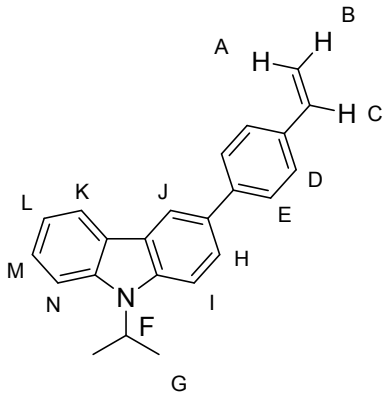
Compound 12 – ^{13}C NMR in $CDCl_3$

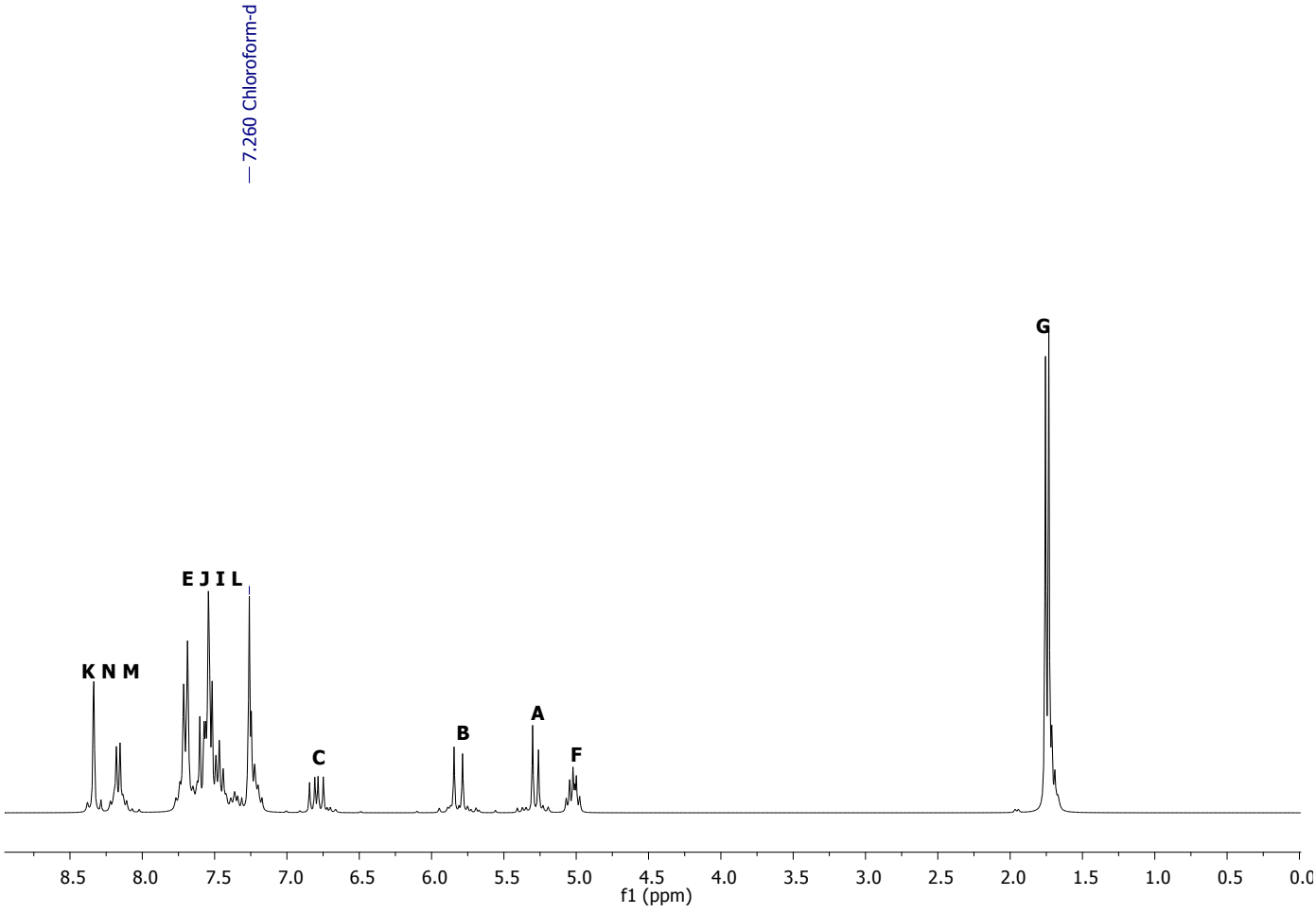


Compound 12 – ^{29}Si NMR in $CDCl_3$

Compound 13

3-(4-Vinylphenyl)-*N*-isopropylcarbazole





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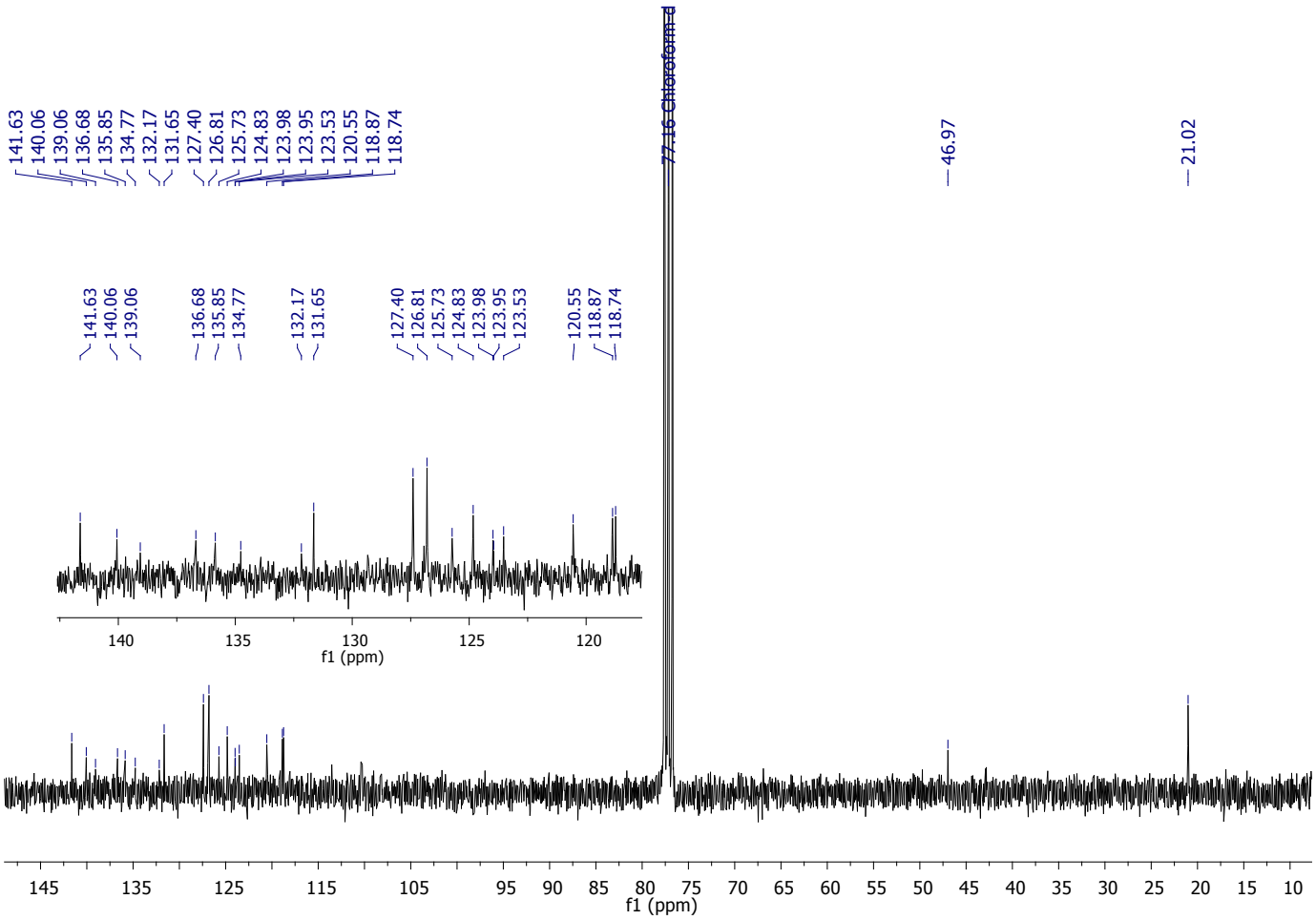
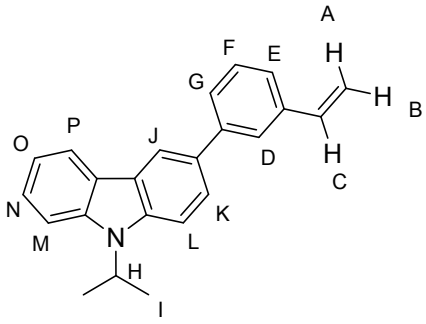
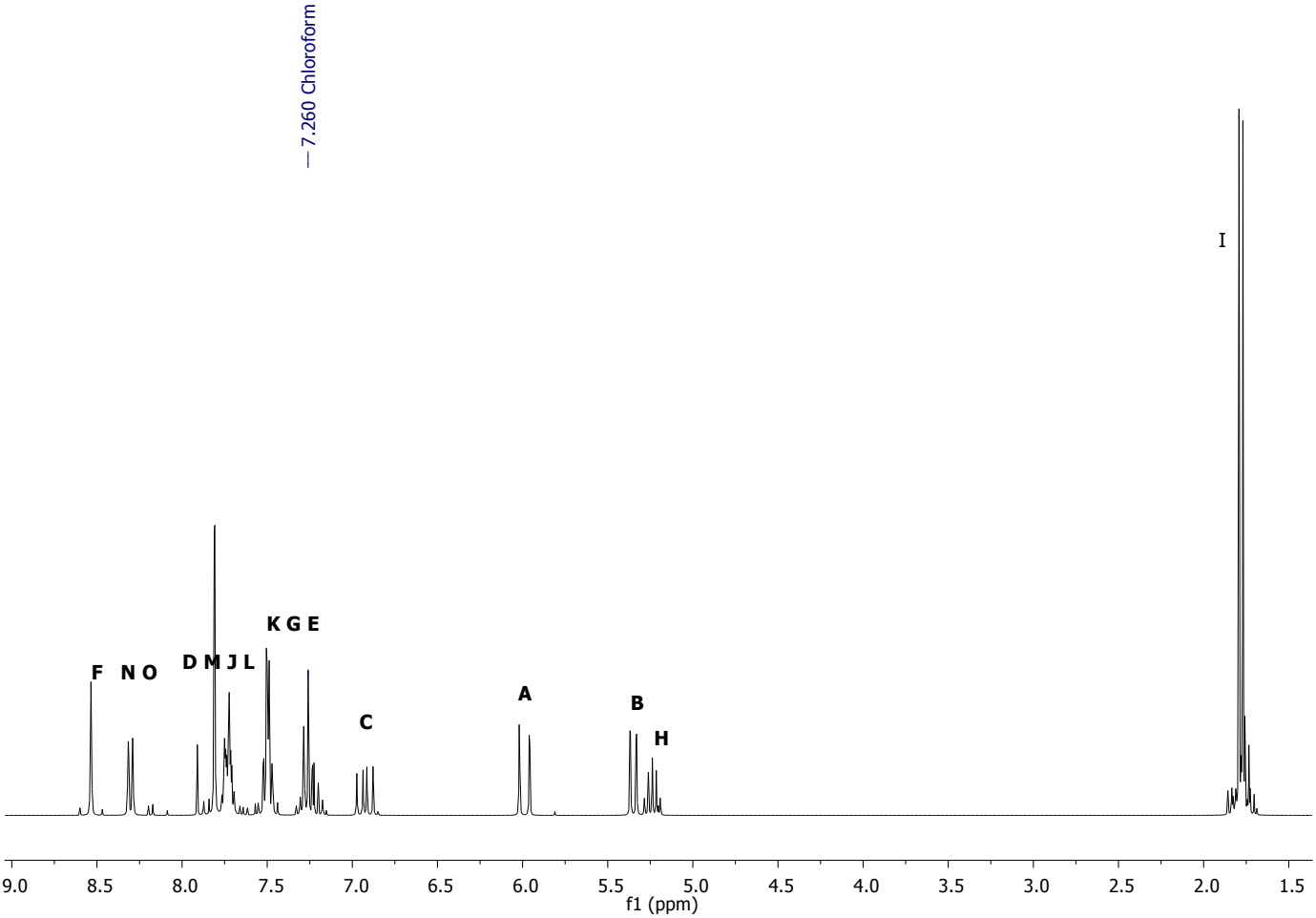


Compound 13 – ^{13}C NMR in $CDCl_3$

Compound 14

3-(3-Vinylphenyl)-*N*-isopropylcarbazole





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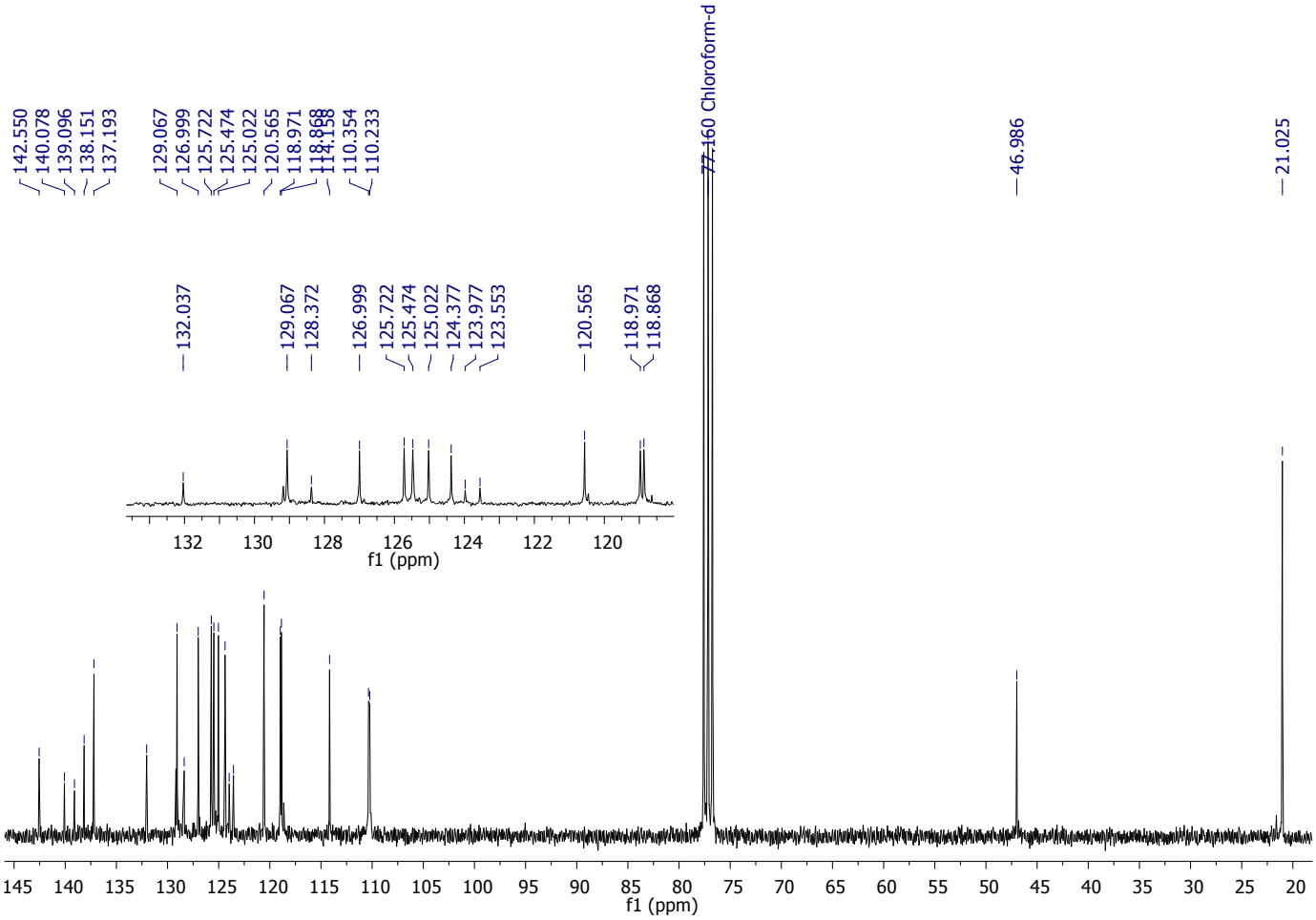
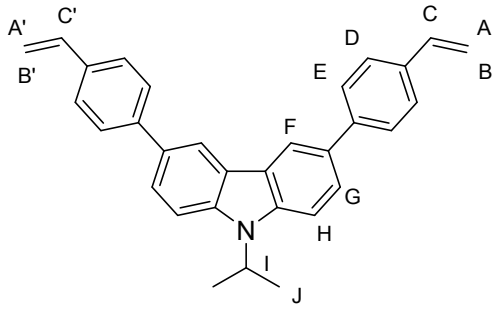
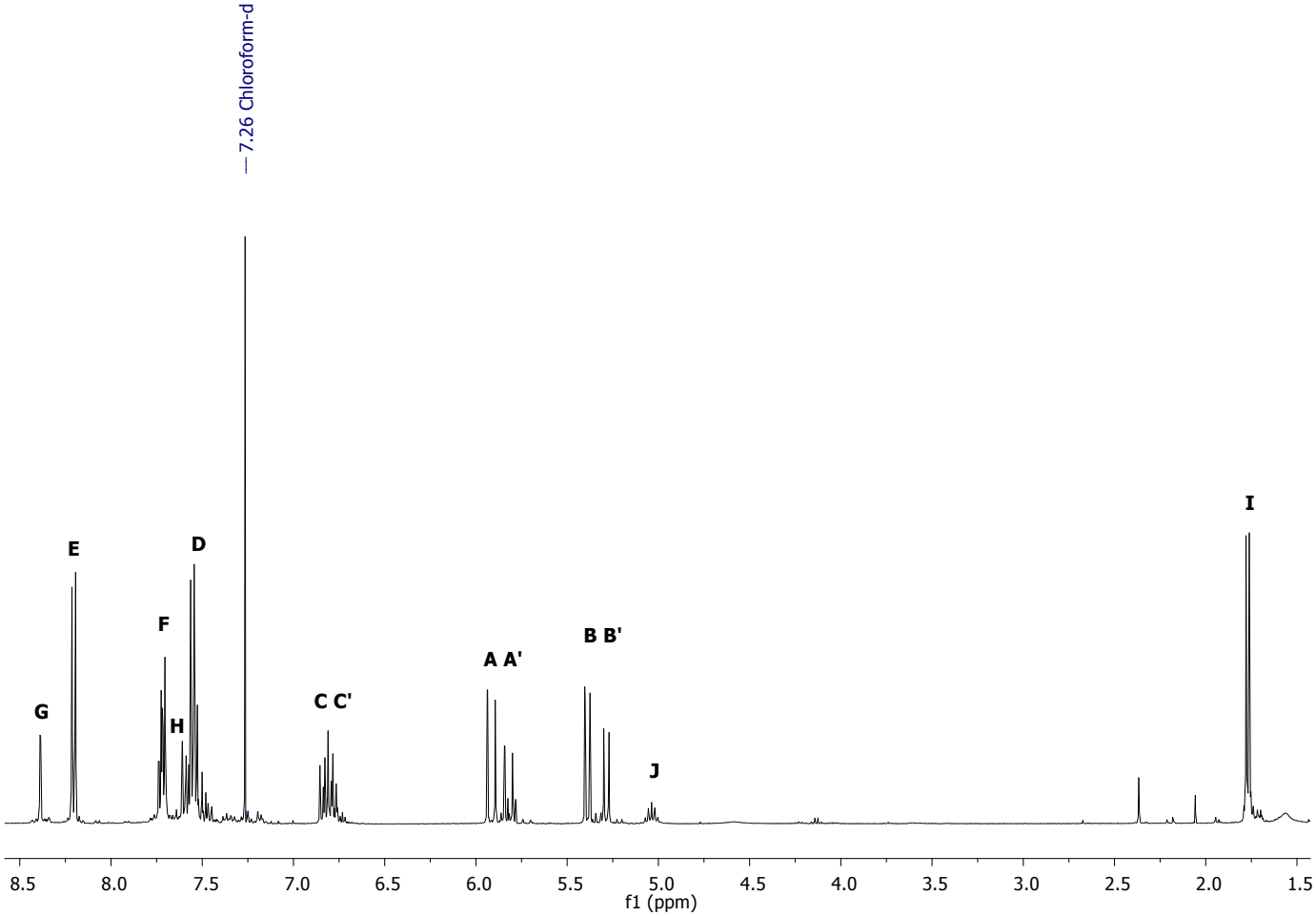


Compound 14 – ^{13}C NMR in $CDCl_3$

Compound 15

3,6-di(4-vinylphenyl)-*N*-isopropylcarbazole





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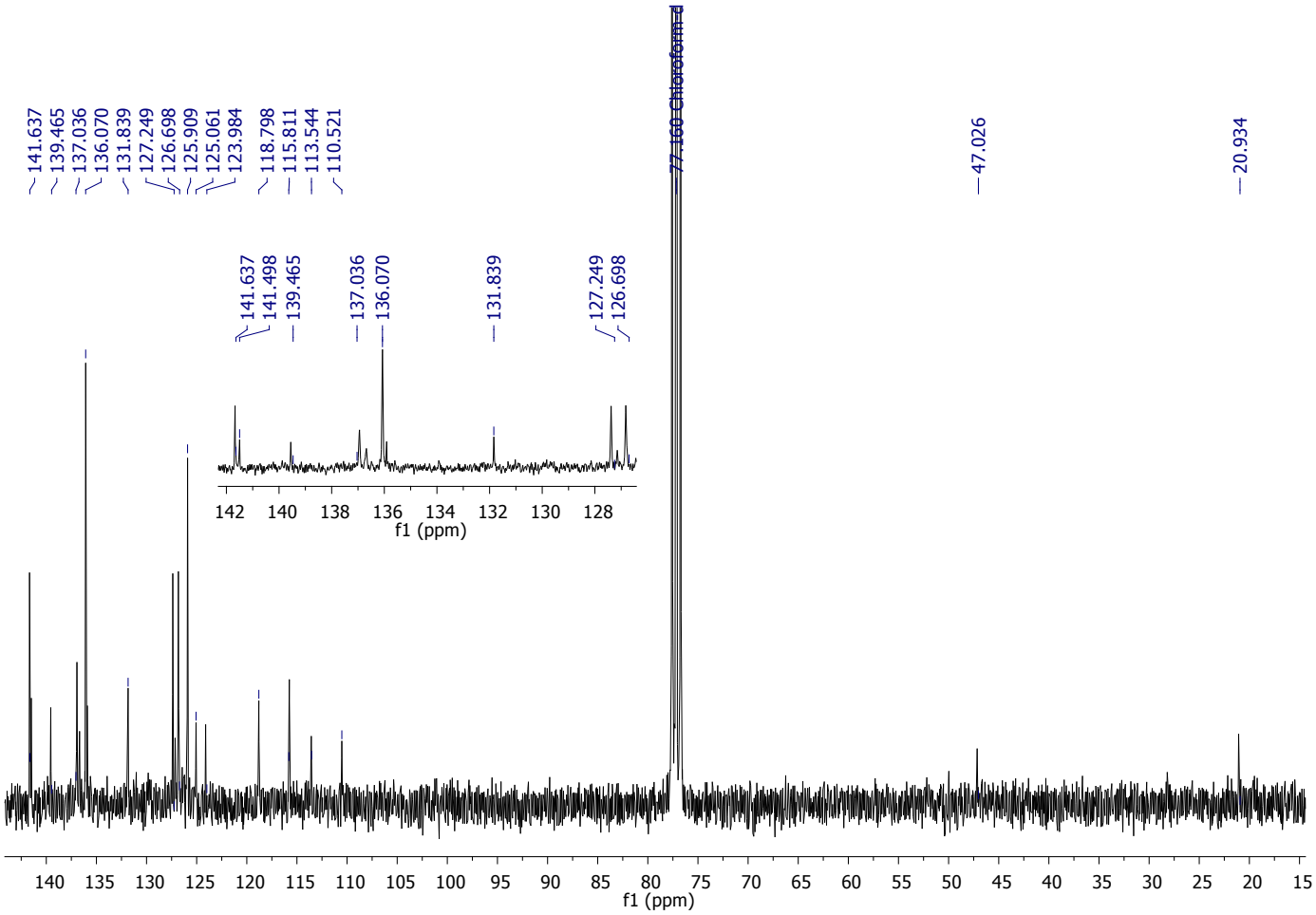
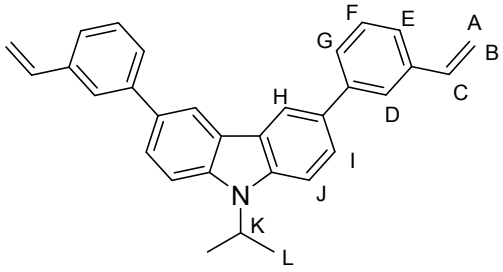
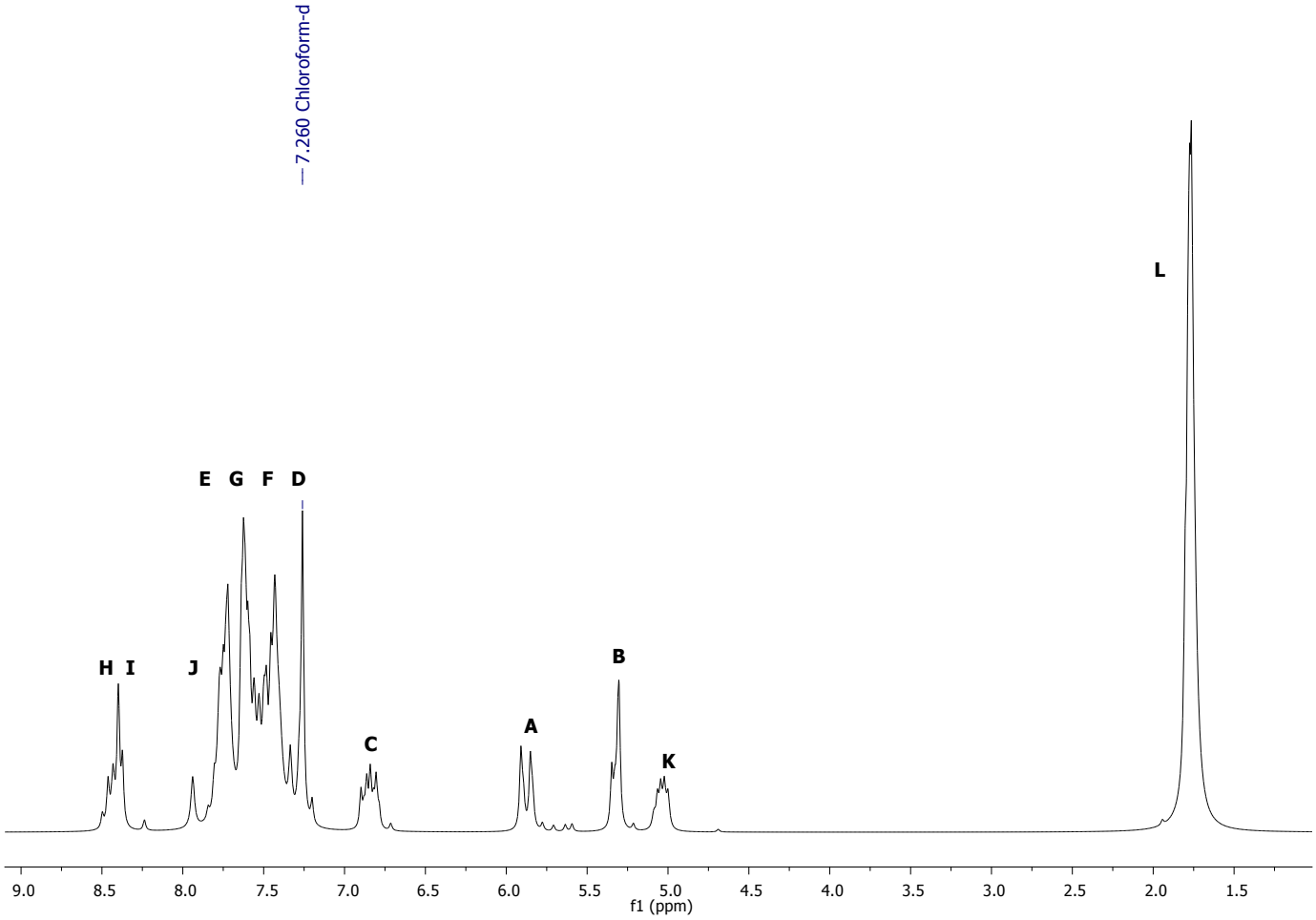


Compound 15 – ^{13}C NMR in $CDCl_3$

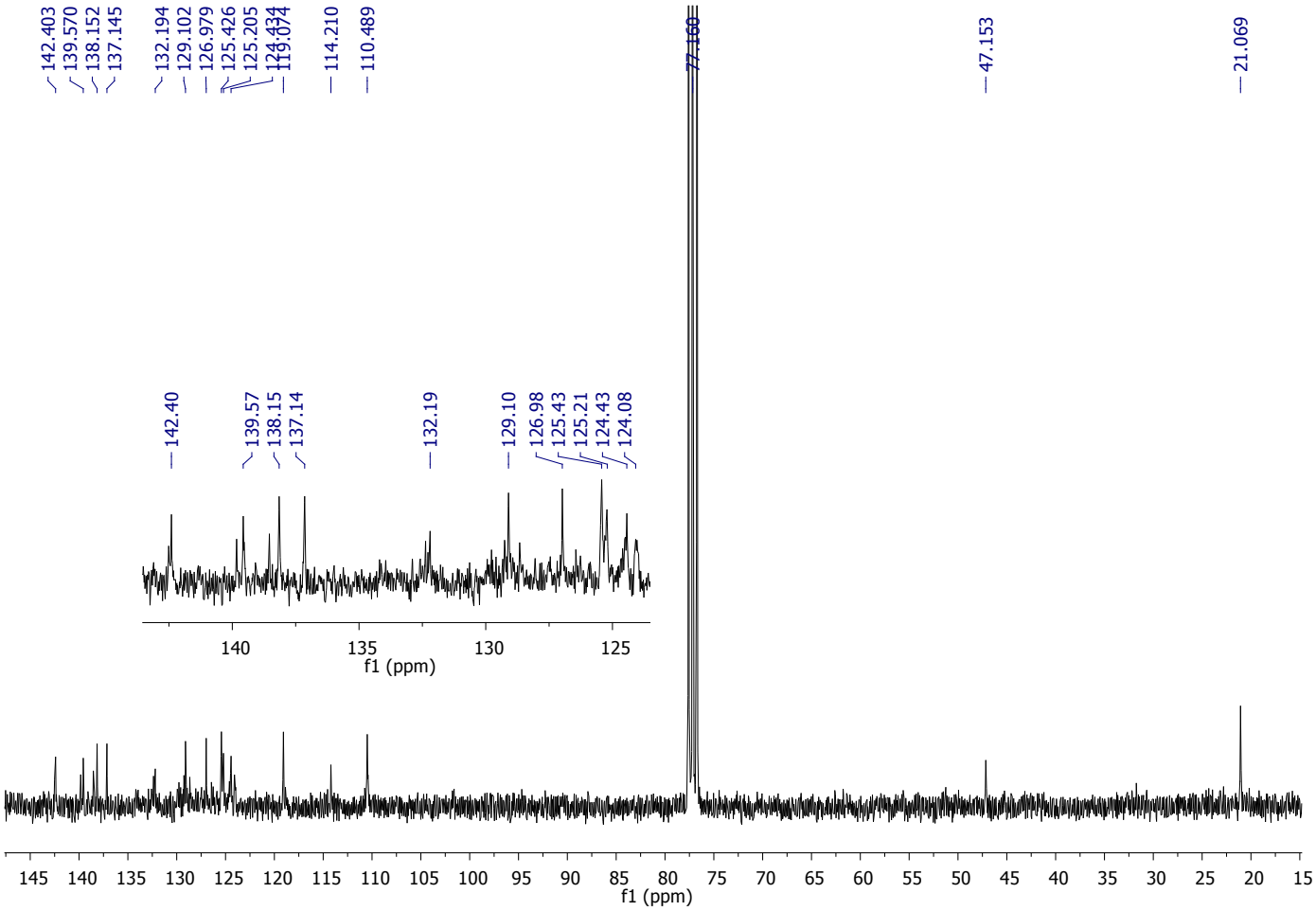
Compound 16

3,6-di(3-vinylphenyl)-*N*-isopropylcarbazole





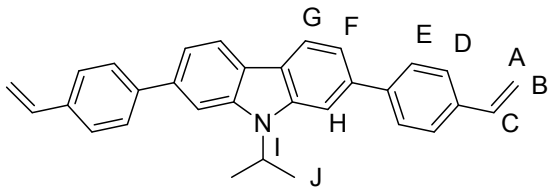
Compound 16 - ^{1}H NMR in $CDCl_3$

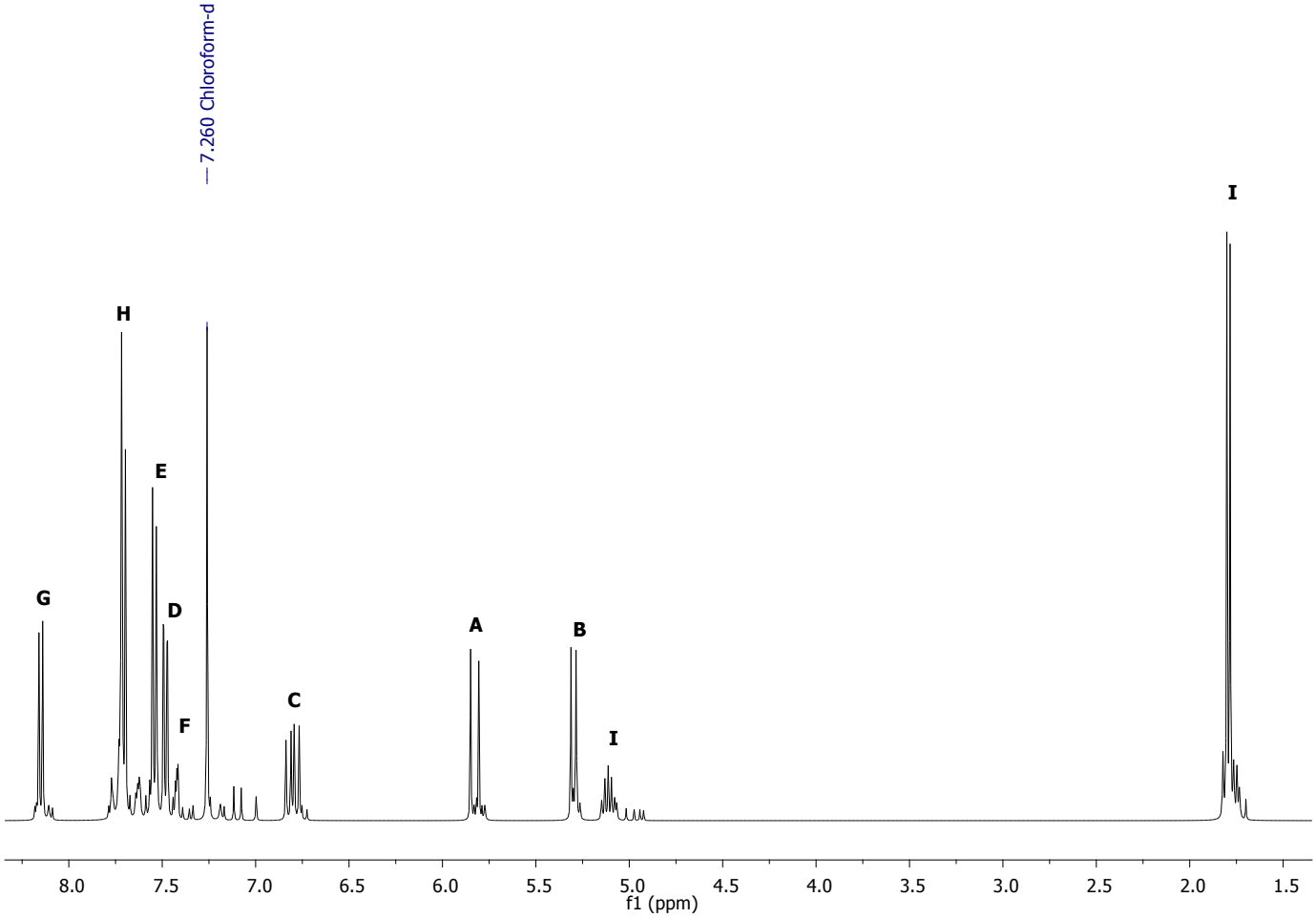


Compound 16 – ^{13}C NMR in $CDCl_3$

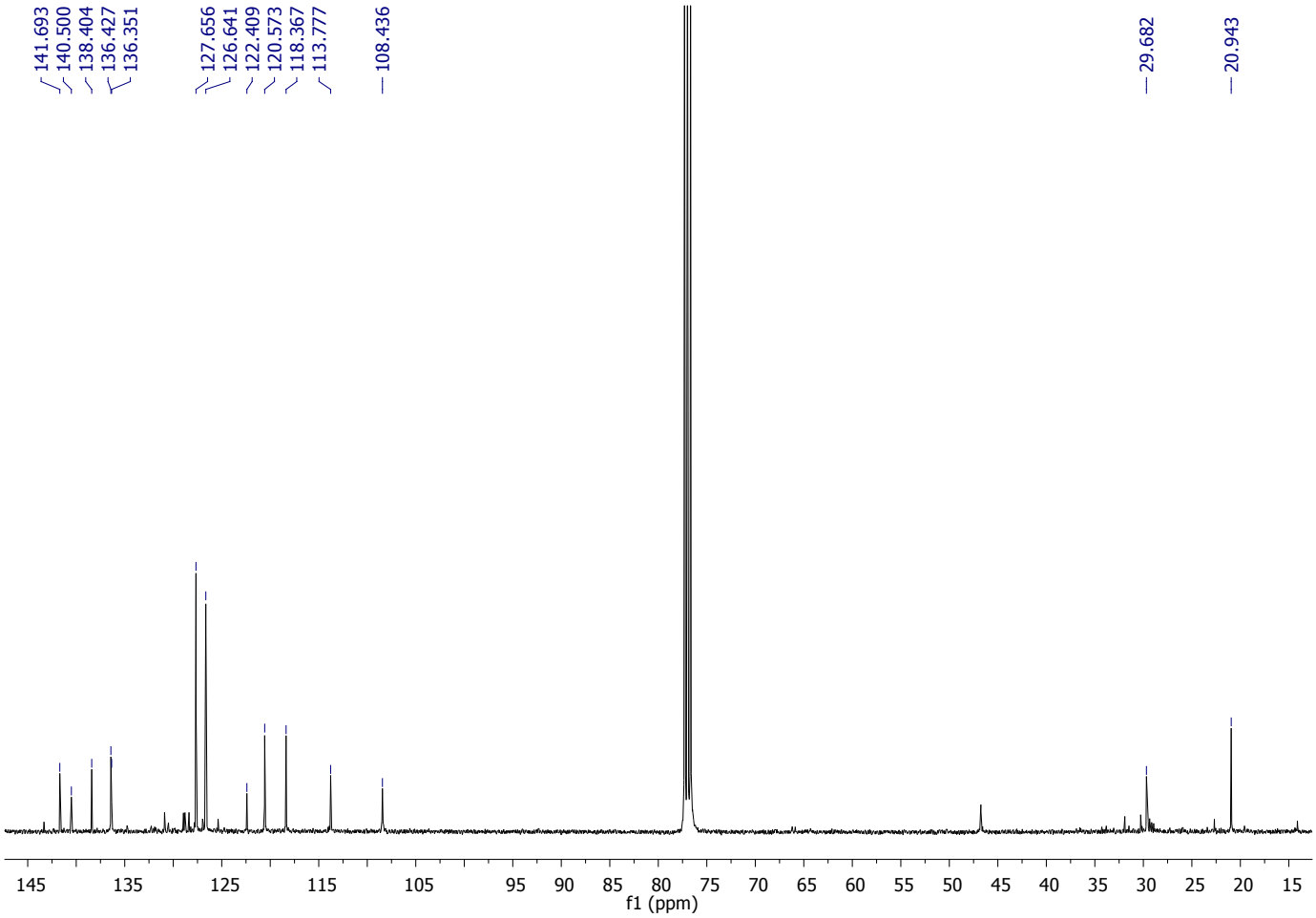
Compound 17

2,7-di(4-vinylphenyl)-*N*-isopropylcarbazole





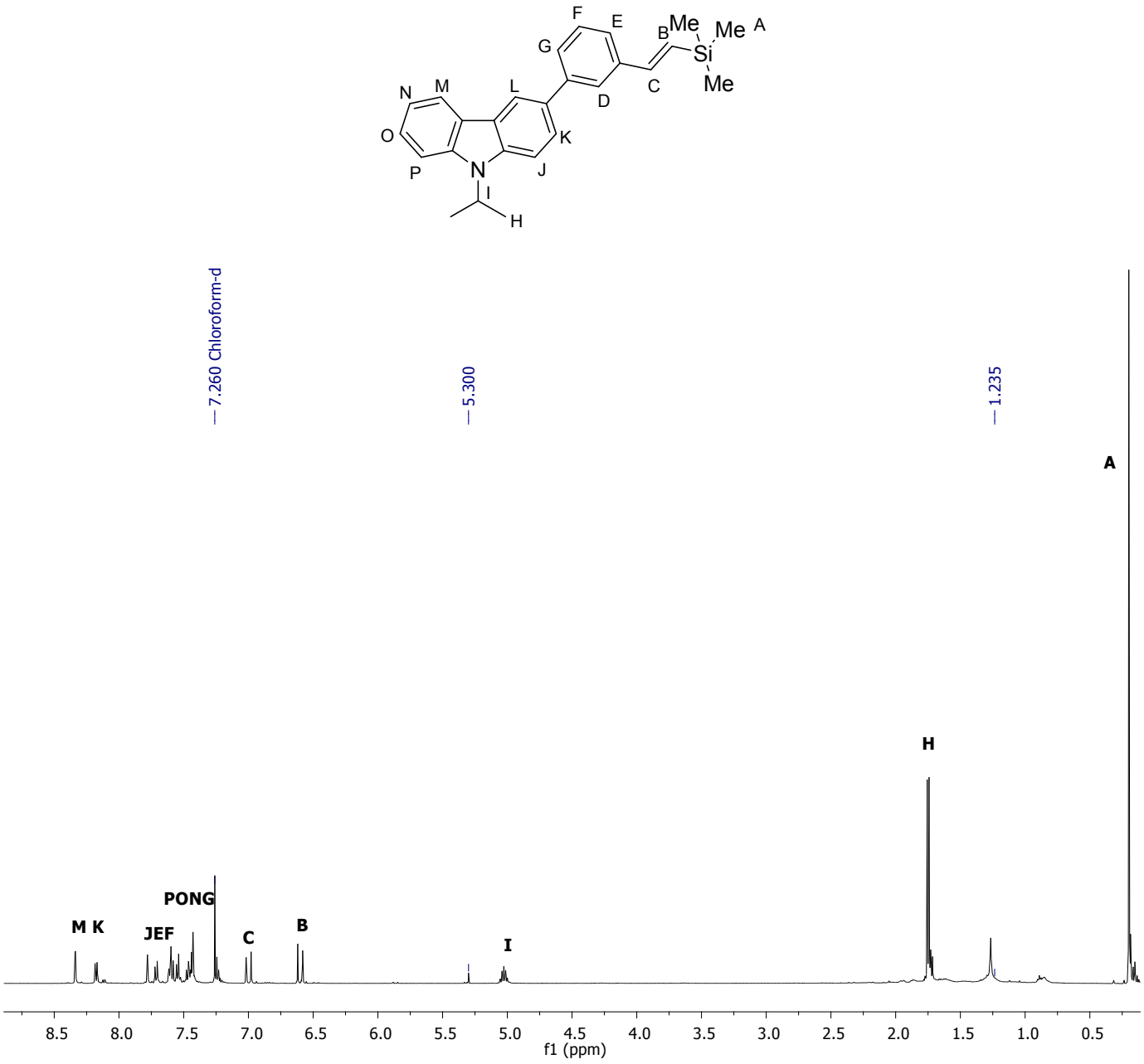
Compound 17 - ^{1}H NMR in $CDCl_3$



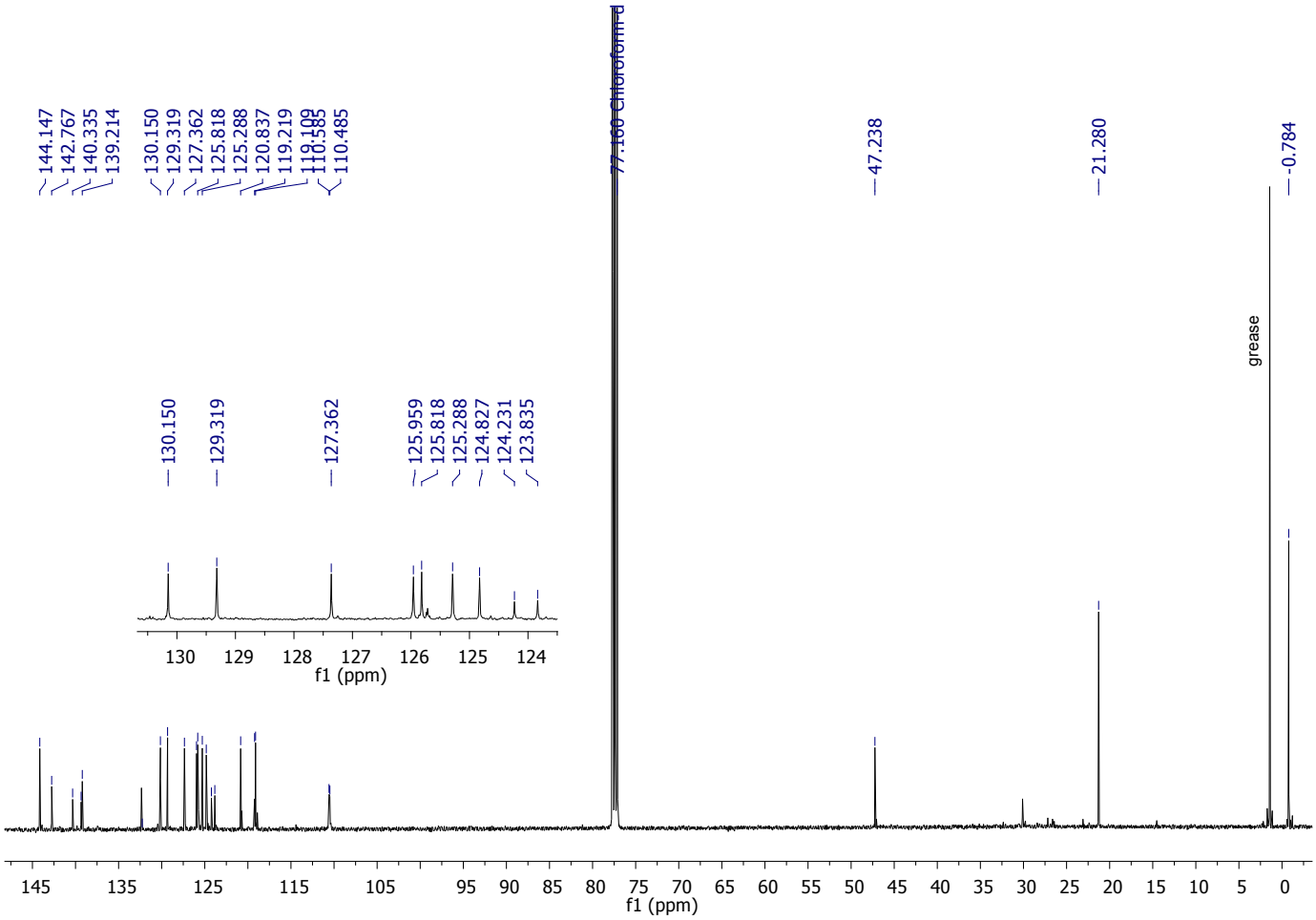
Compound 17 – ^{13}C NMR in $CDCl_3$

Compound 18

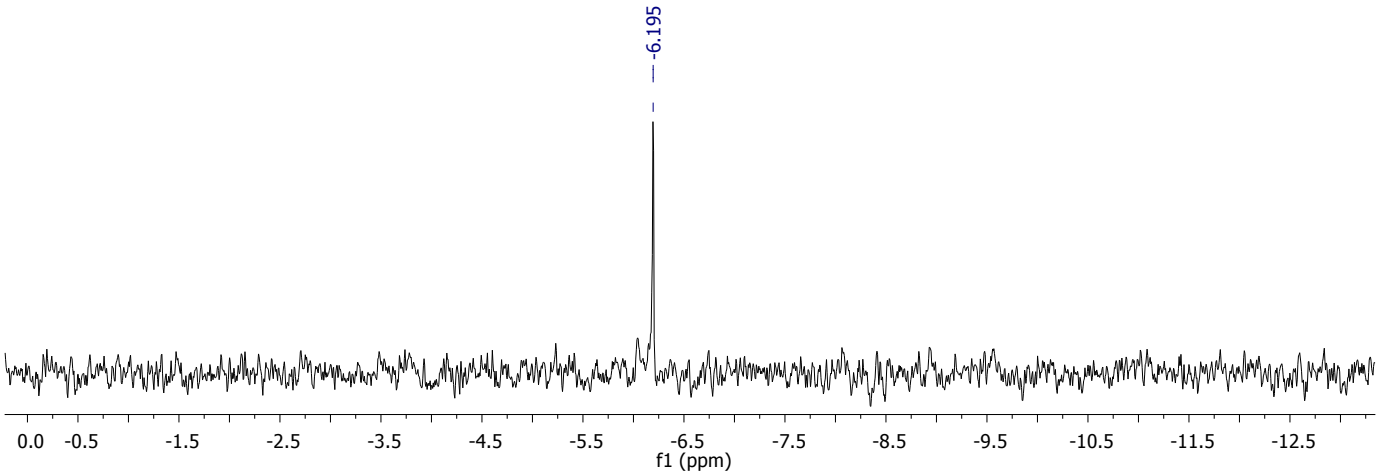
3-(3-((*E*)-2(trimethylsilyl)vinyl)phenyl)-*N*-isopropylcarbazole



Compound 18 - ^{1}H NMR in $CDCl_3$



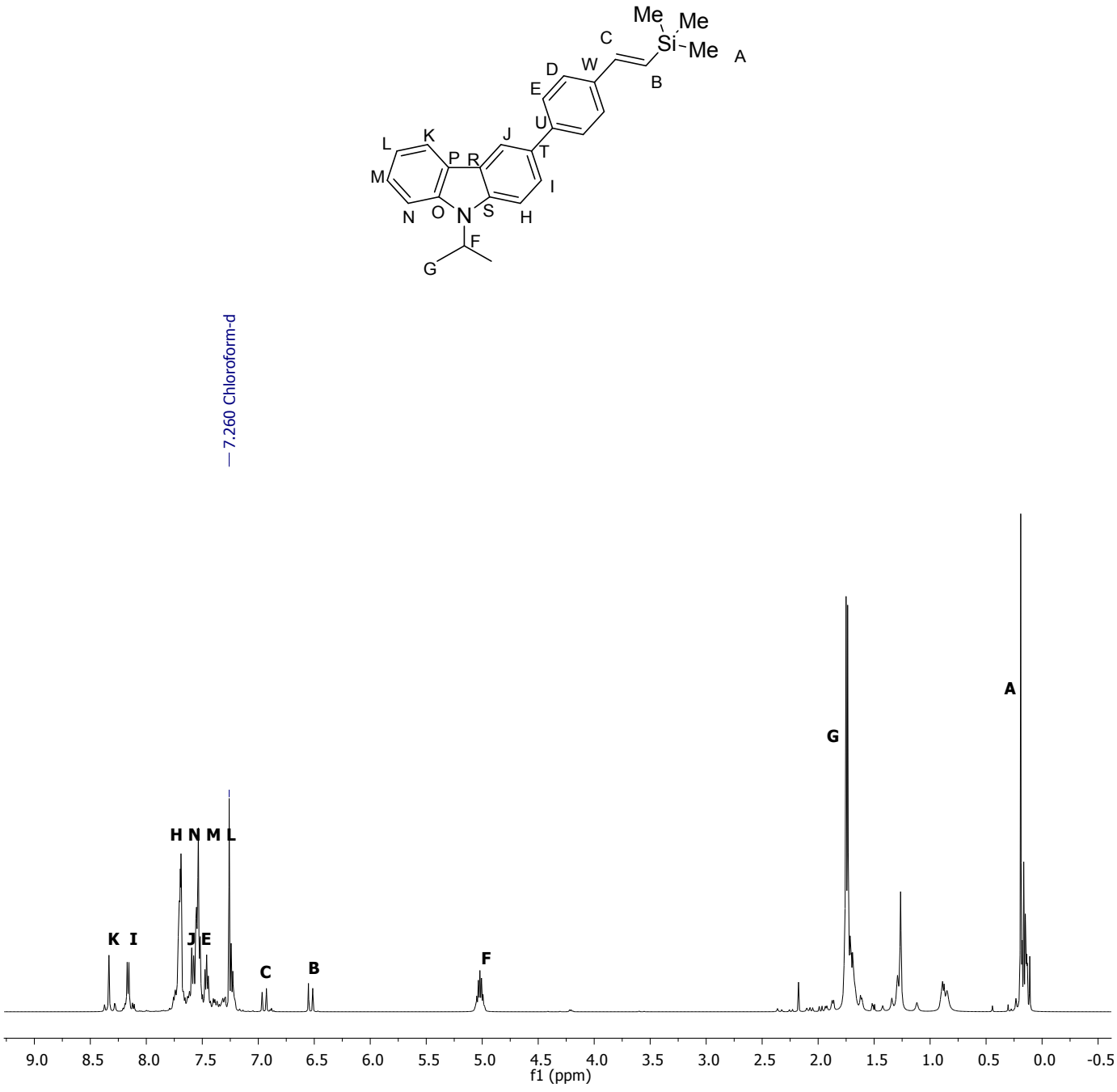
Compound 18 – ^{13}C NMR in $CDCl_3$



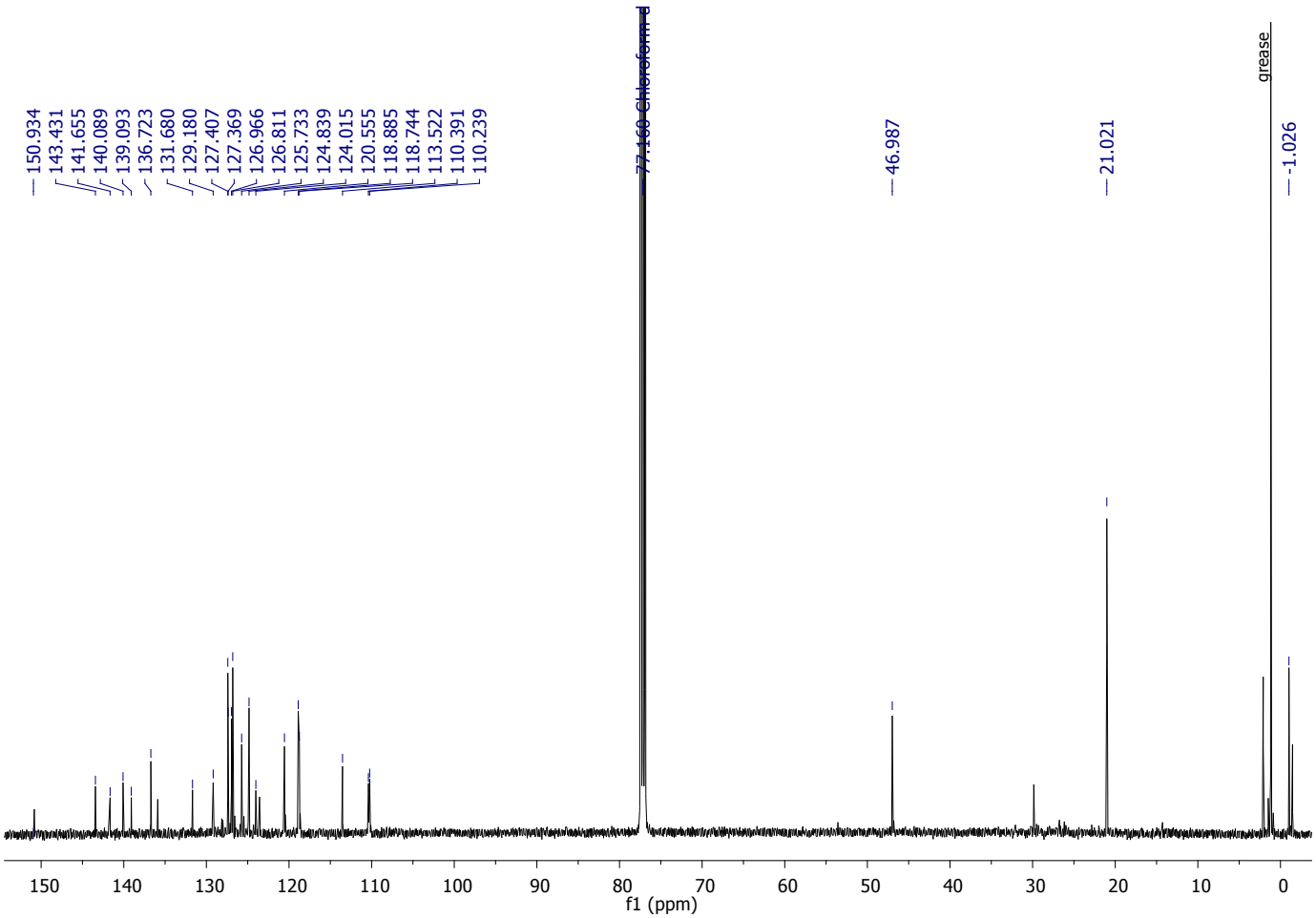
Compound 18 – ^{29}Si NMR in $CDCl_3$

Compound 19

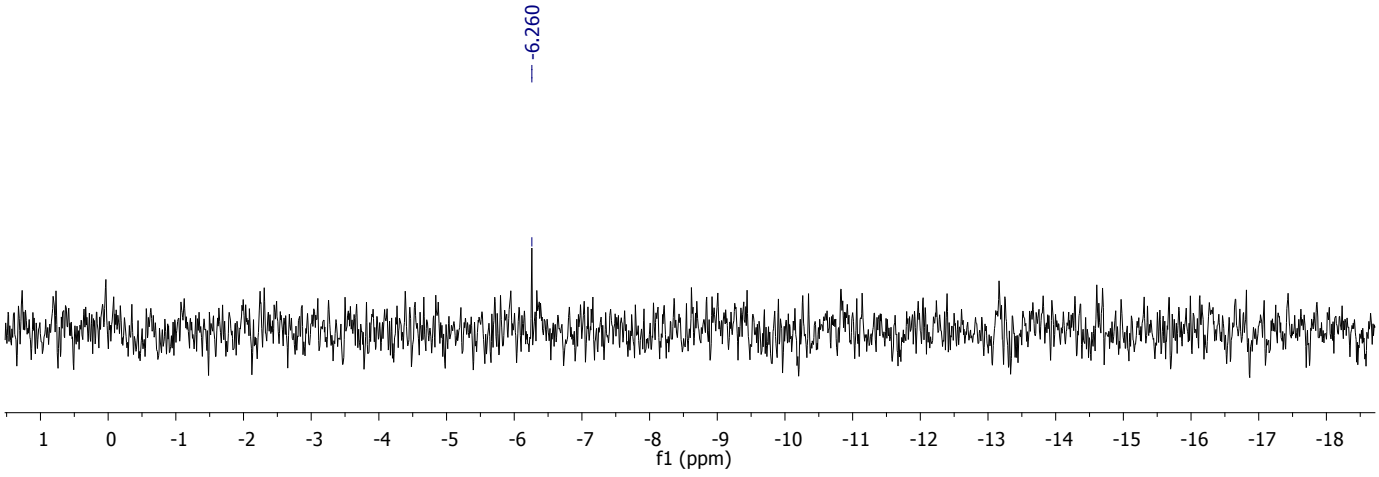
3-(4-((*E*)-2(trimethylsilyl)vinyl)phenyl)-*N*-isopropylcarbazole



Compound 19 - ^{1}H NMR in $CDCl_3$



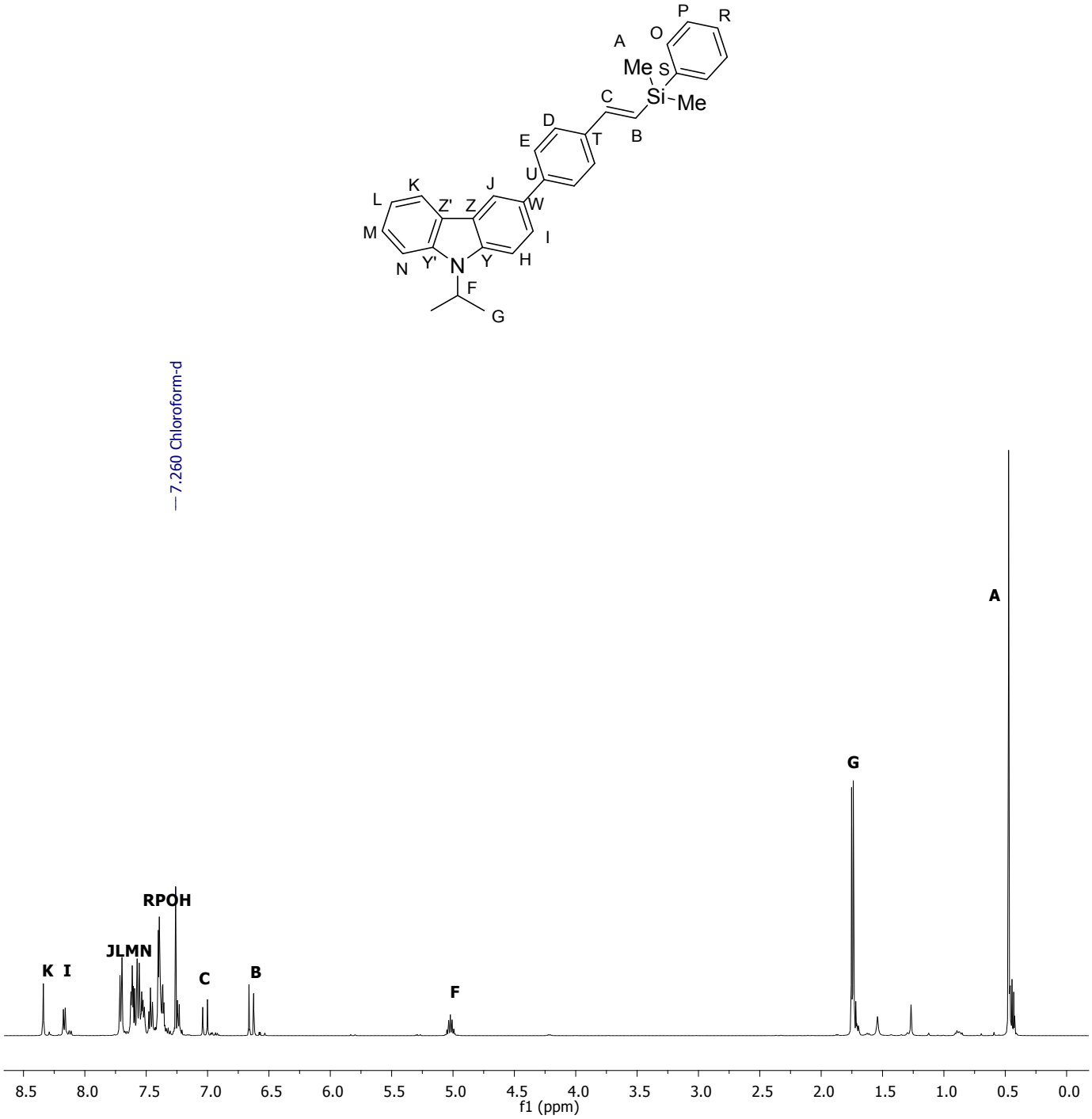
Compound 19 – ^{13}C NMR in $CDCl_3$



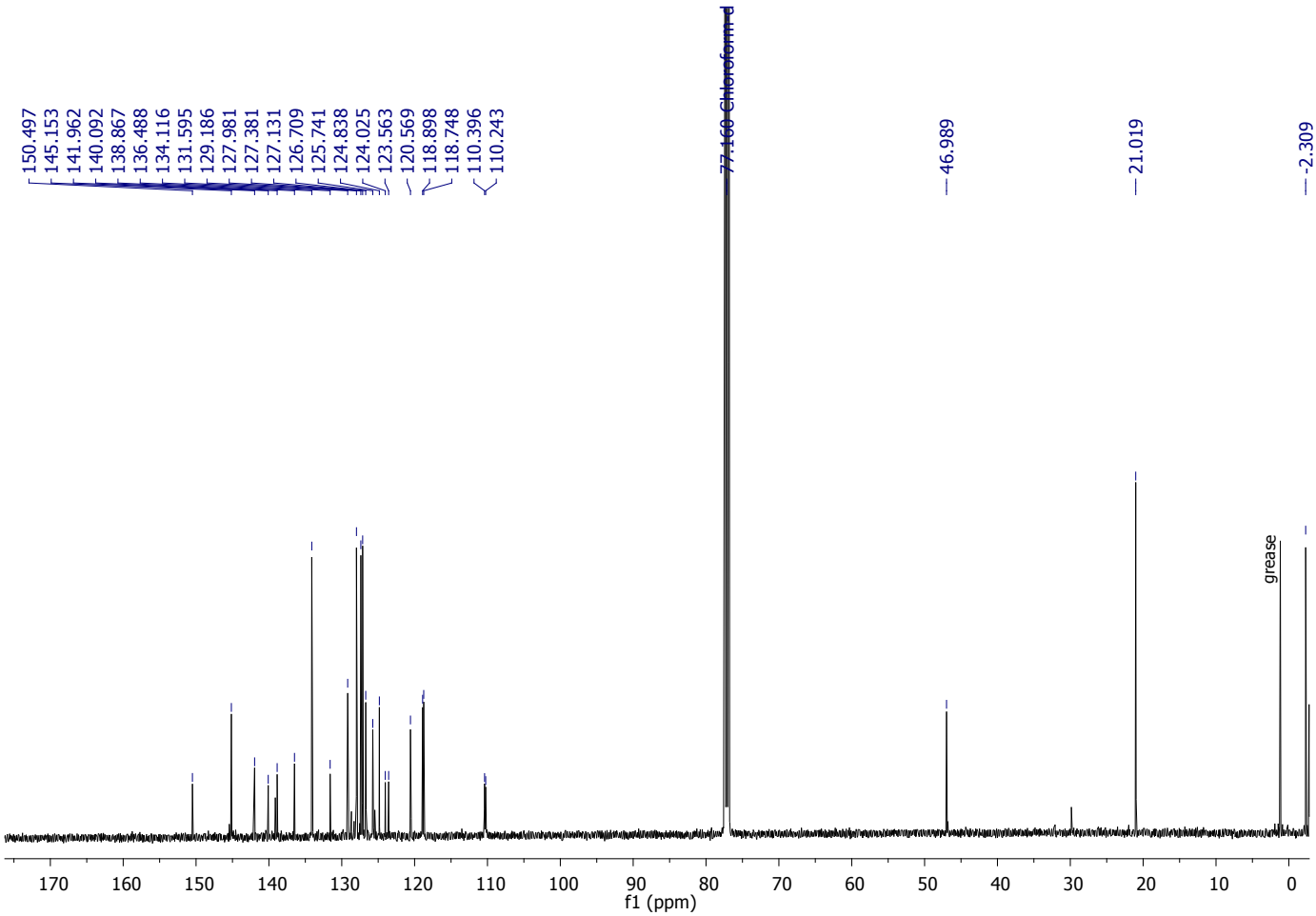
Compound 19 – ^{29}Si NMR in $CDCl_3$

Compound 20

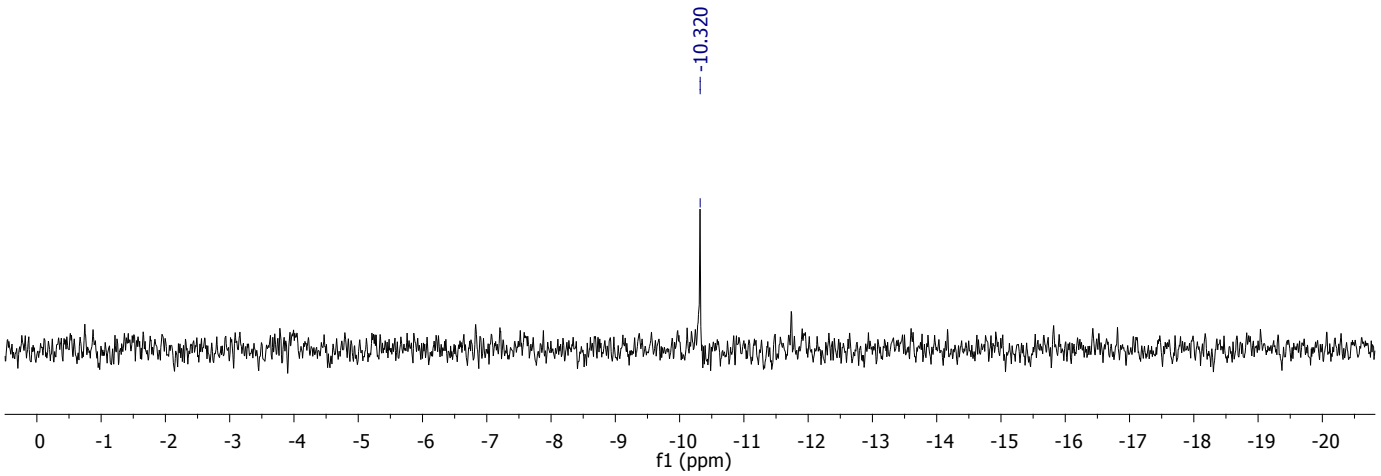
3-(4-((*E*)-2-(phenyldimethylsilyl)vinyl)phenyl)-*N*-isopropylcarbazole



Compound 20 - ^{1}H NMR in $CDCl_3$



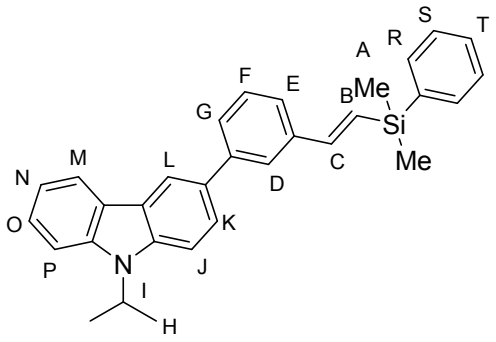
Compound 20 – ^{13}C NMR in $CDCl_3$

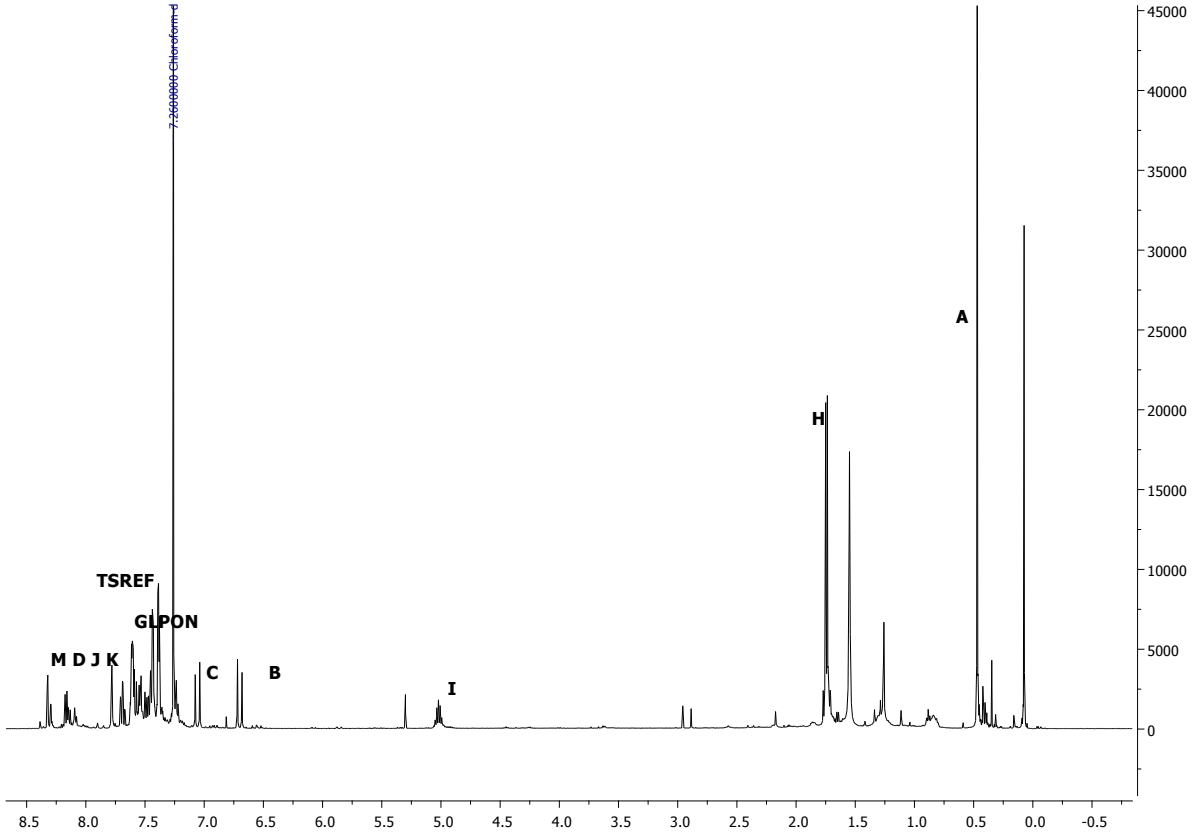


Compound 20 – ^{29}Si NMR in $CDCl_3$

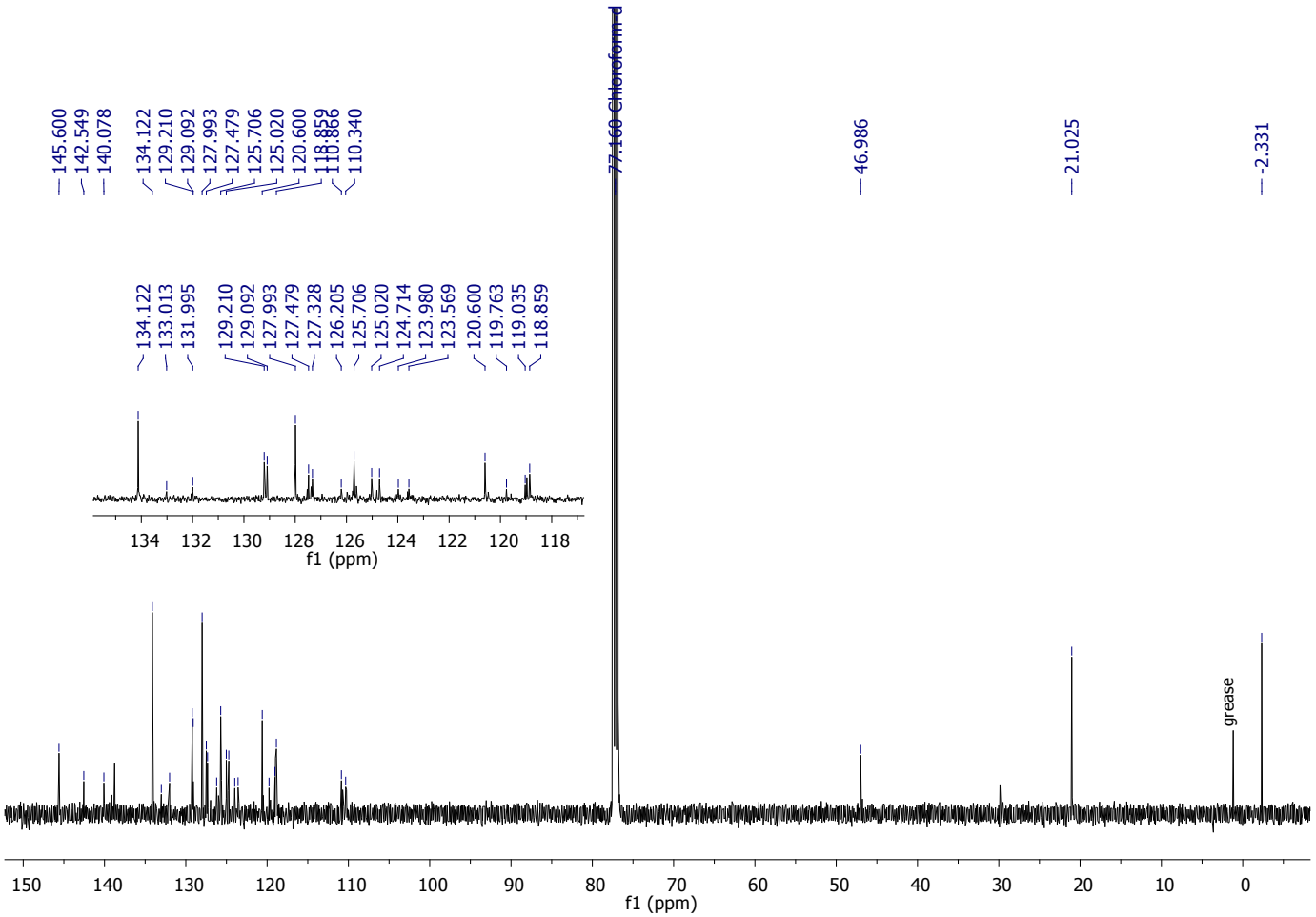
Compound 21

3-(3-((*E*)-2-(phenyldimethylsilyl)vinyl)phenyl)-*N*-isopropylcarbazole

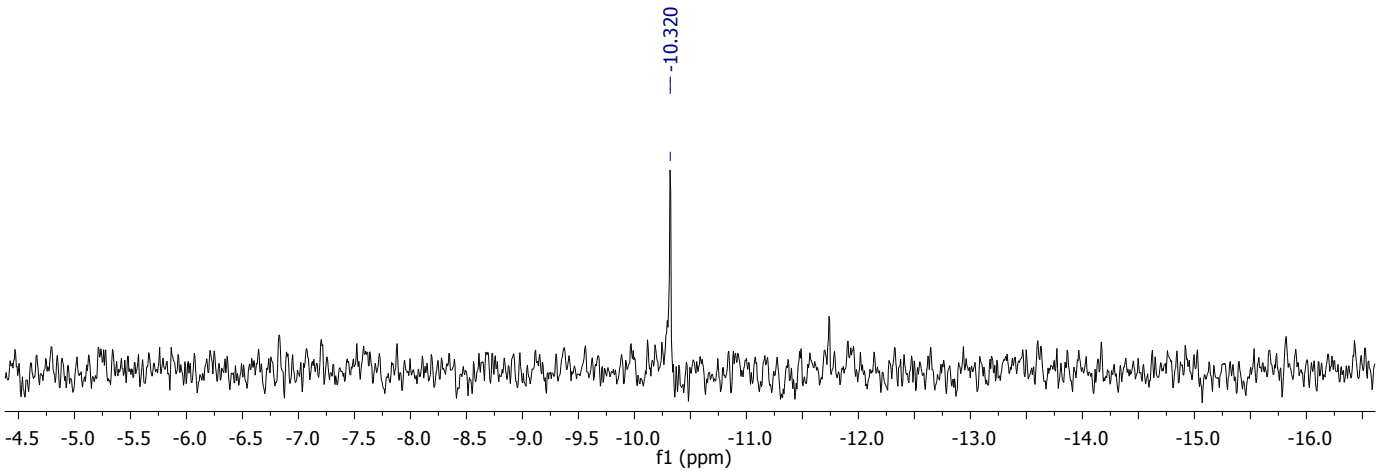




Compound 21 - ^{1}H NMR in $CDCl_3$



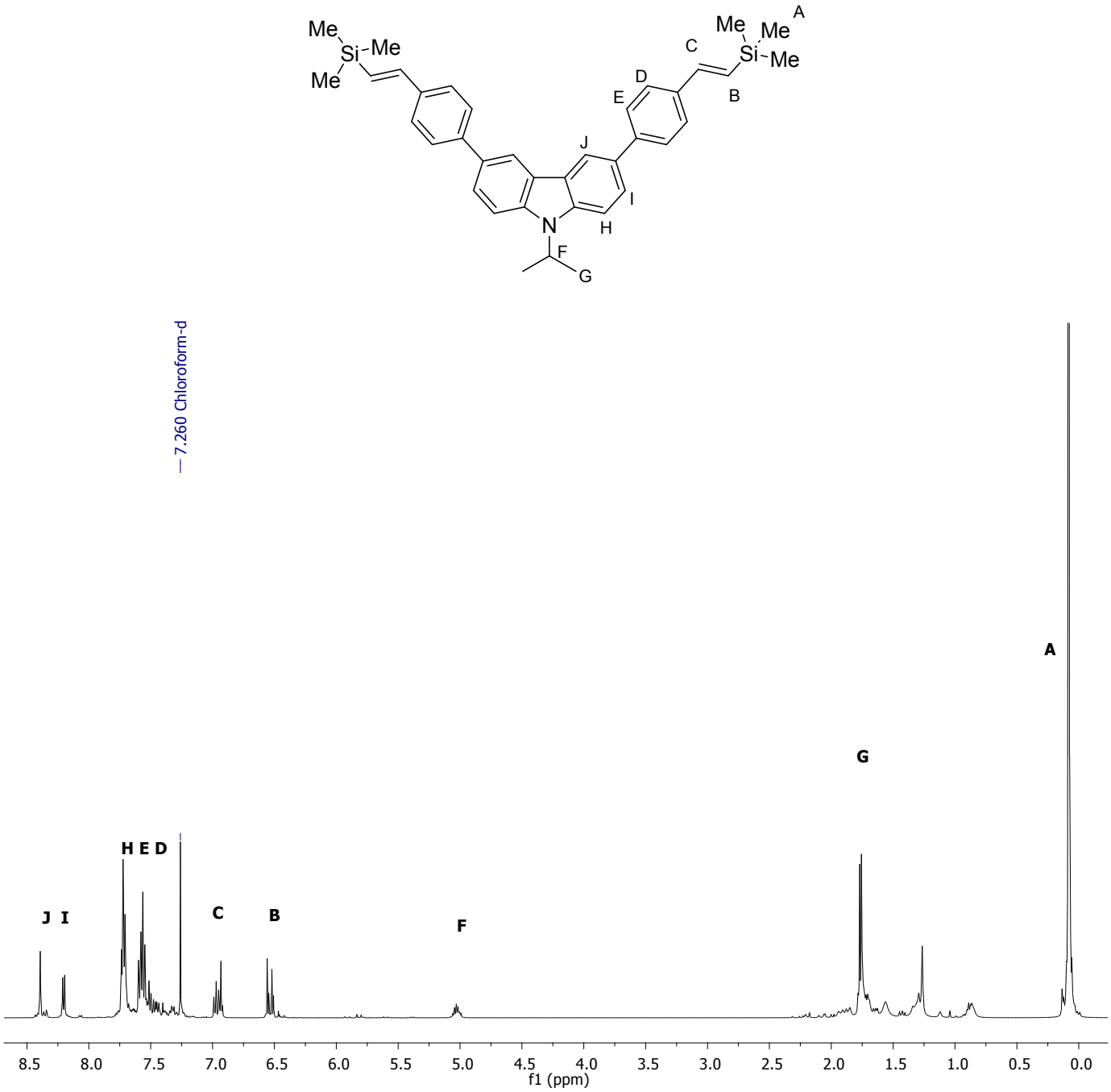
Compound 21 – ^{13}C NMR in $CDCl_3$



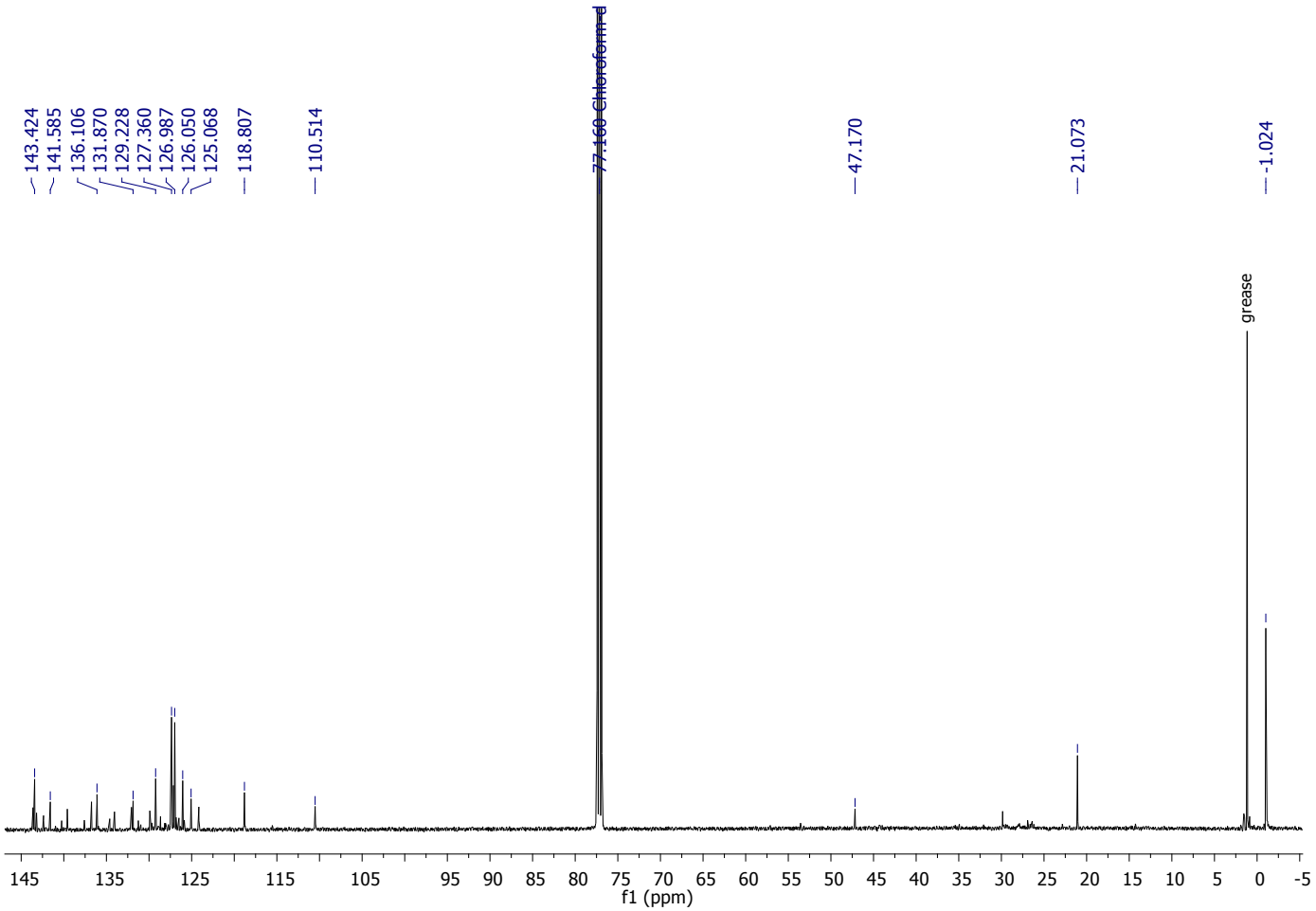
Compound 21 – ^{29}Si NMR in $CDCl_3$

Compound 22

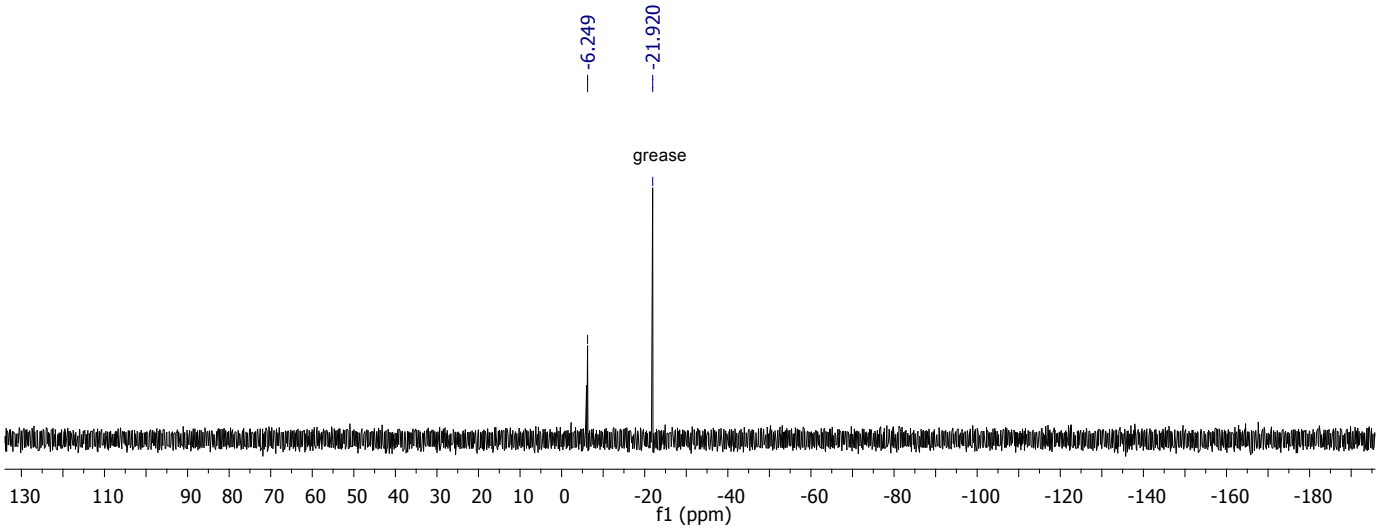
3,6-bis(4-((*E*)-2(trimethylsilyl)vinyl)phenyl)-*N*-isopropylcarbazole



Compound 22 - ^{1}H NMR in $CDCl_3$



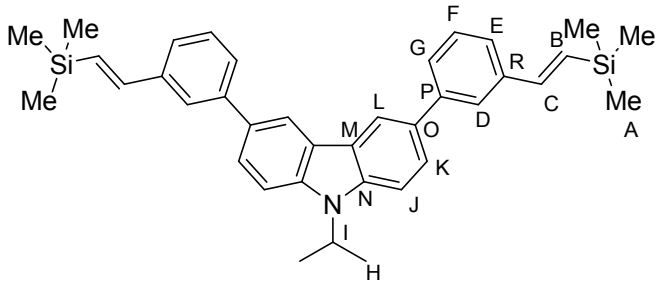
Compound 22 – ^{13}C NMR in $CDCl_3$

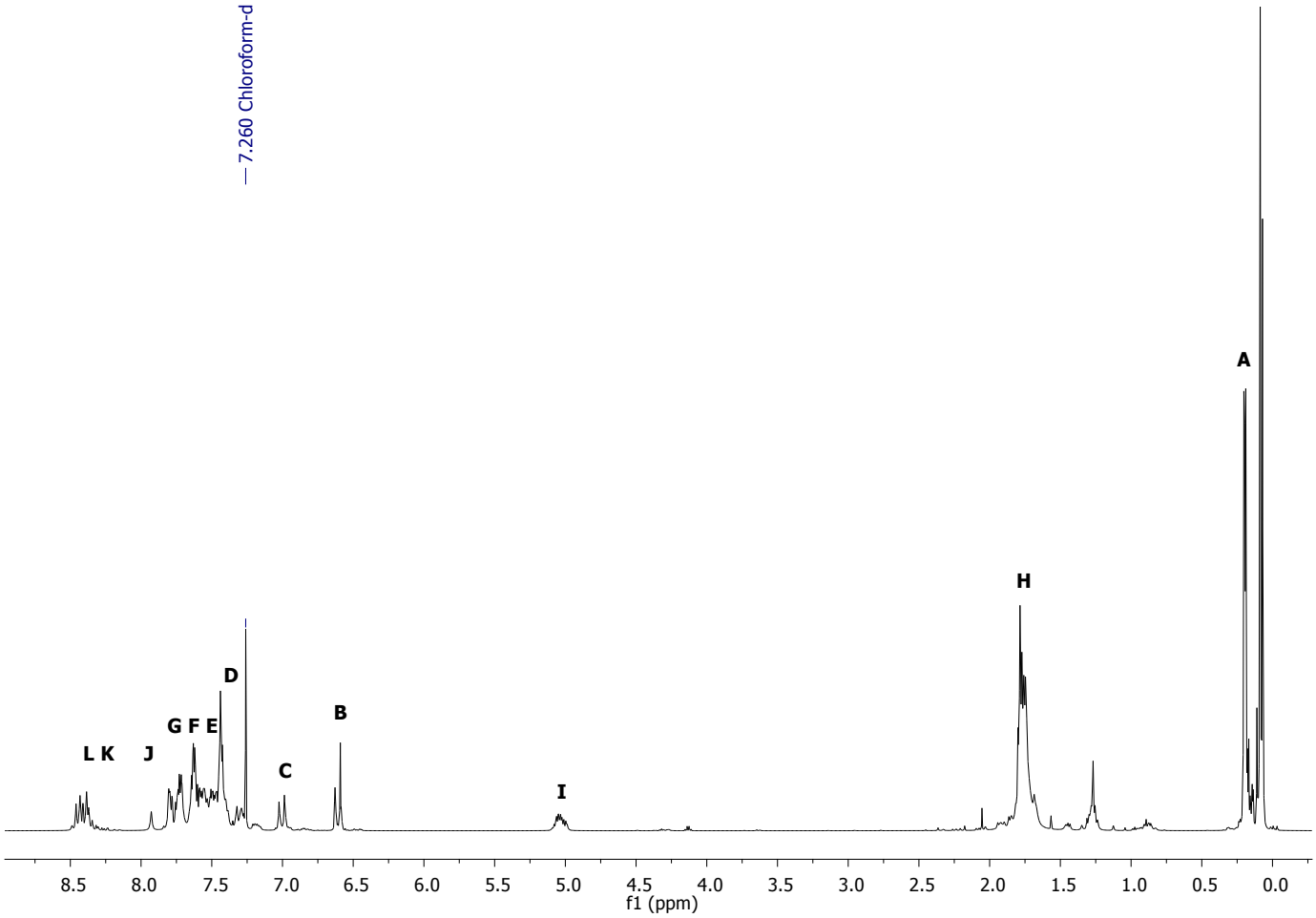


Compound 22 – ^{29}Si NMR in $CDCl_3$

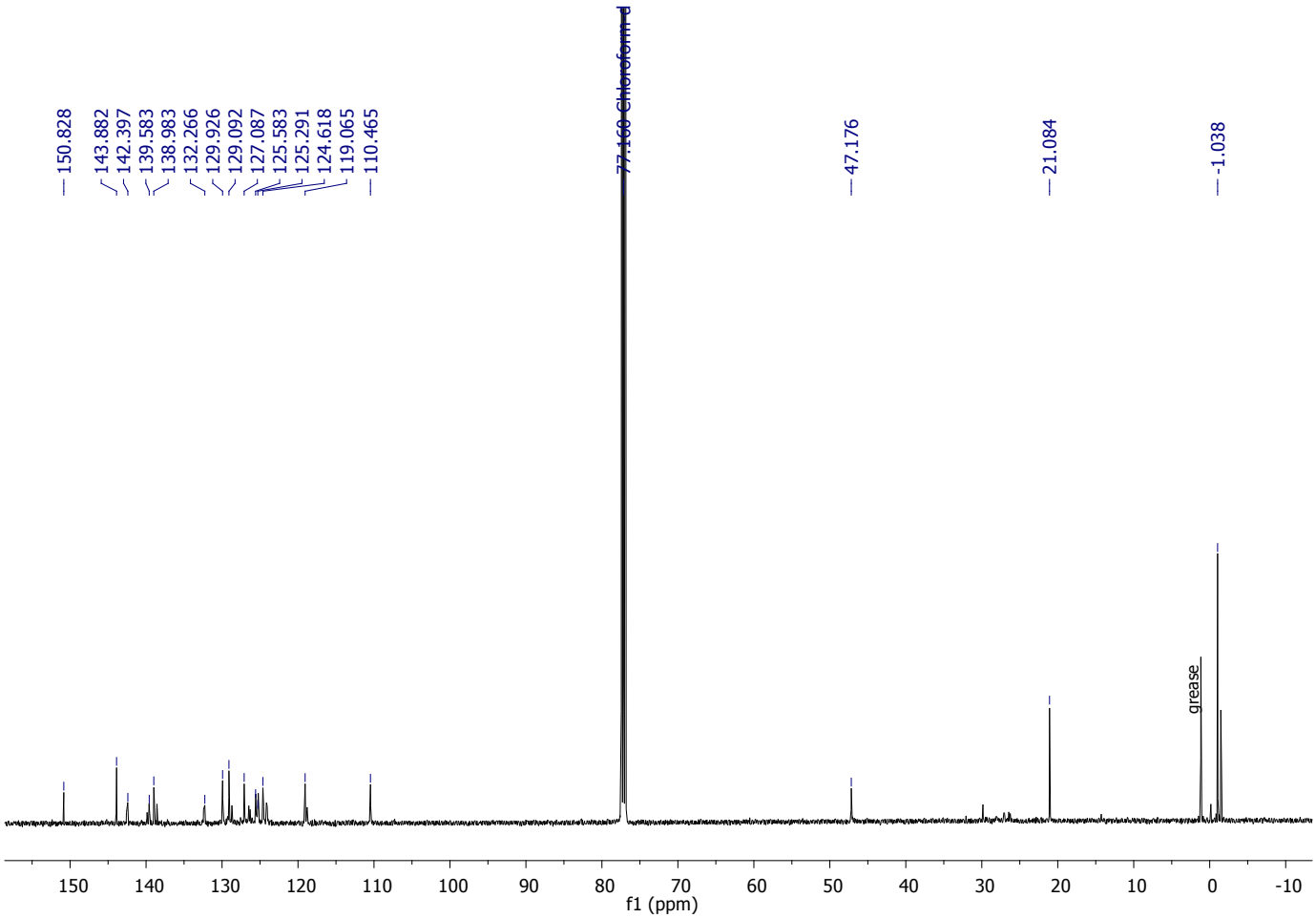
Compound 23

3,6-bis(3-((*E*)-2(trimethylsilyl)vinyl)phenyl)-*N*-isopropylcarbazole

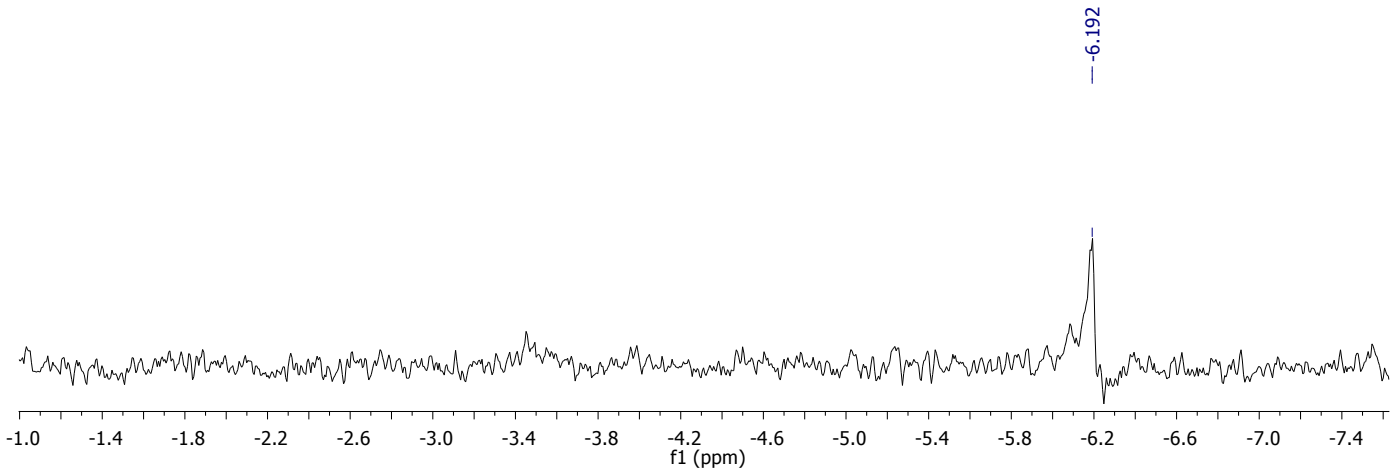




Compound 23 - ^{1}H NMR in $CDCl_3$



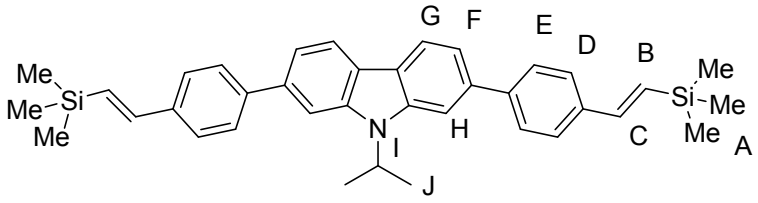
Compound 23 – ^{13}C NMR in $CDCl_3$

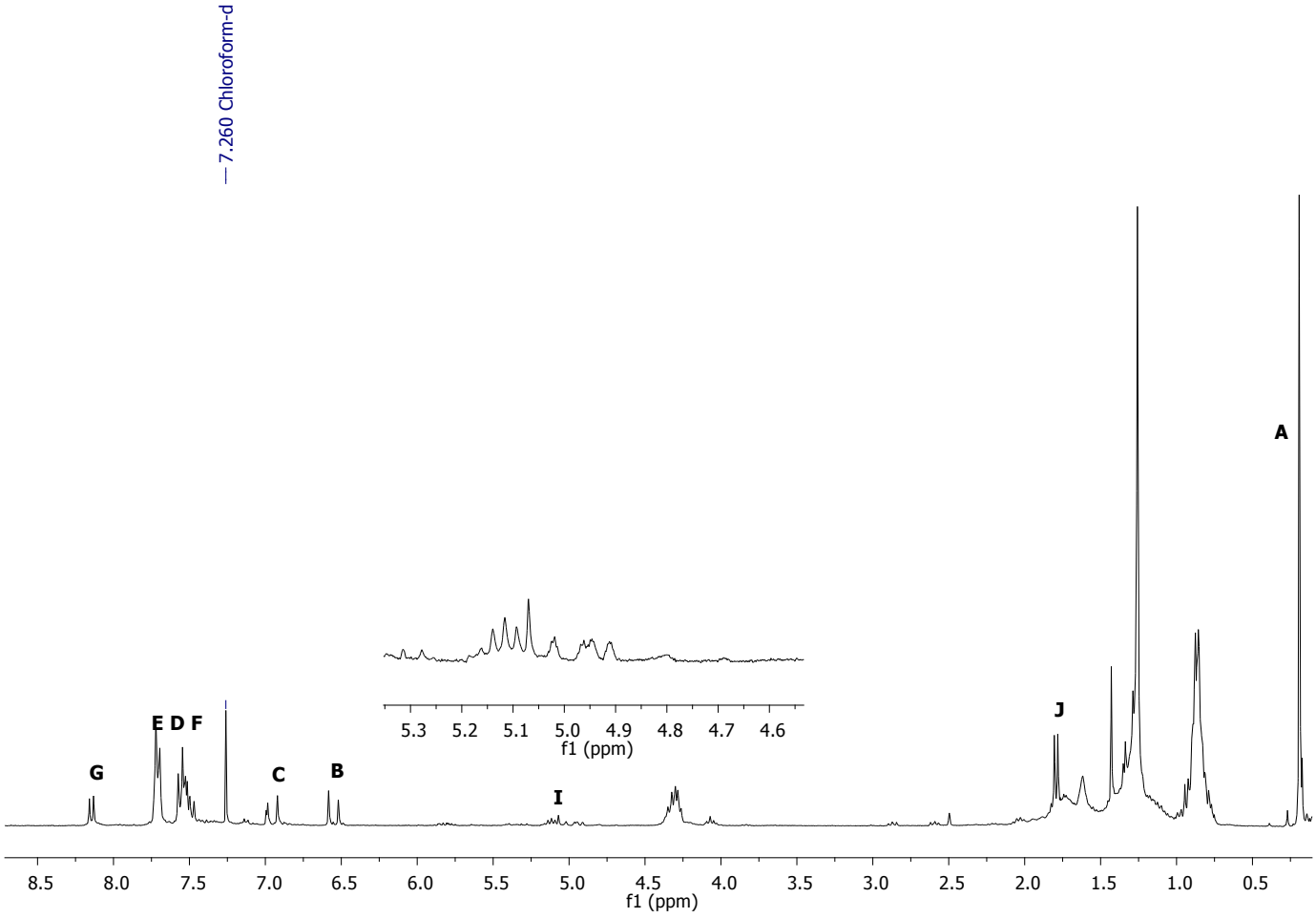


Compound 23 – ^{29}Si NMR in $CDCl_3$

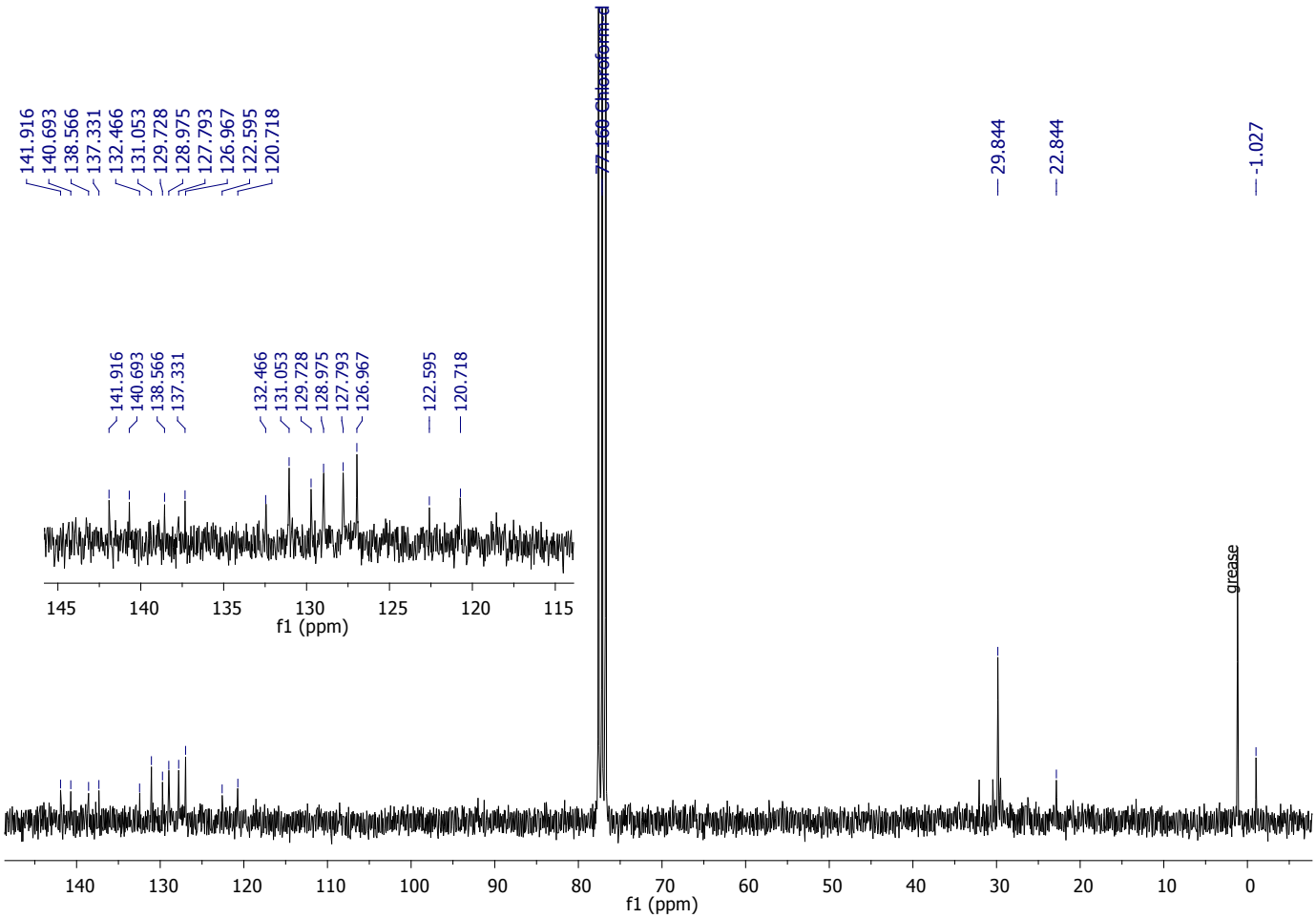
Compound 24

2,7-bis(3-((*E*)-2(trimethylsilyl)vinyl)phenyl)-*N*-isopropylcarbazole

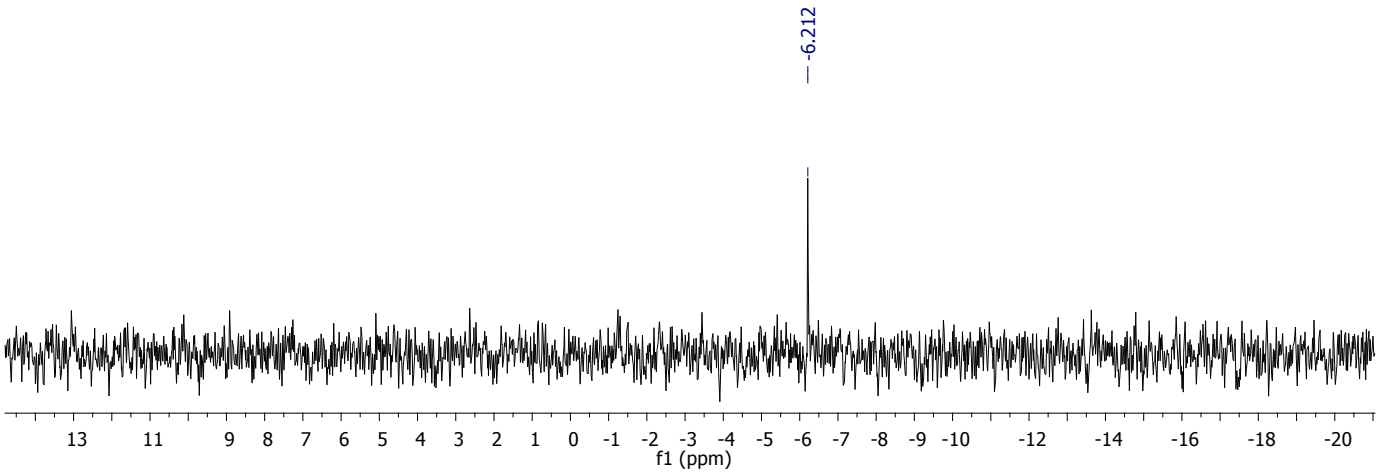




Compound 24 - ^{1}H NMR in $CDCl_3$



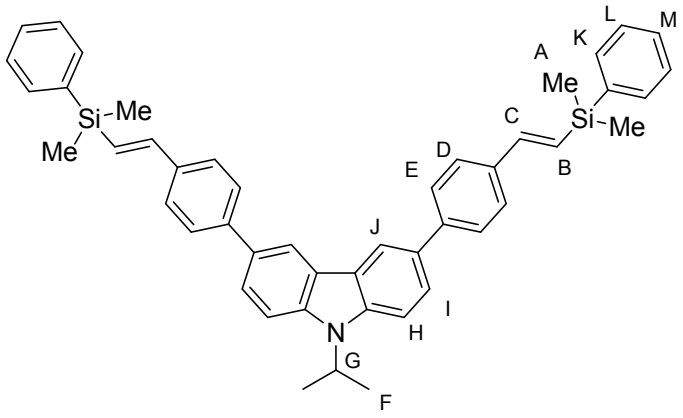
Compound 24 – ^{13}C NMR in $CDCl_3$

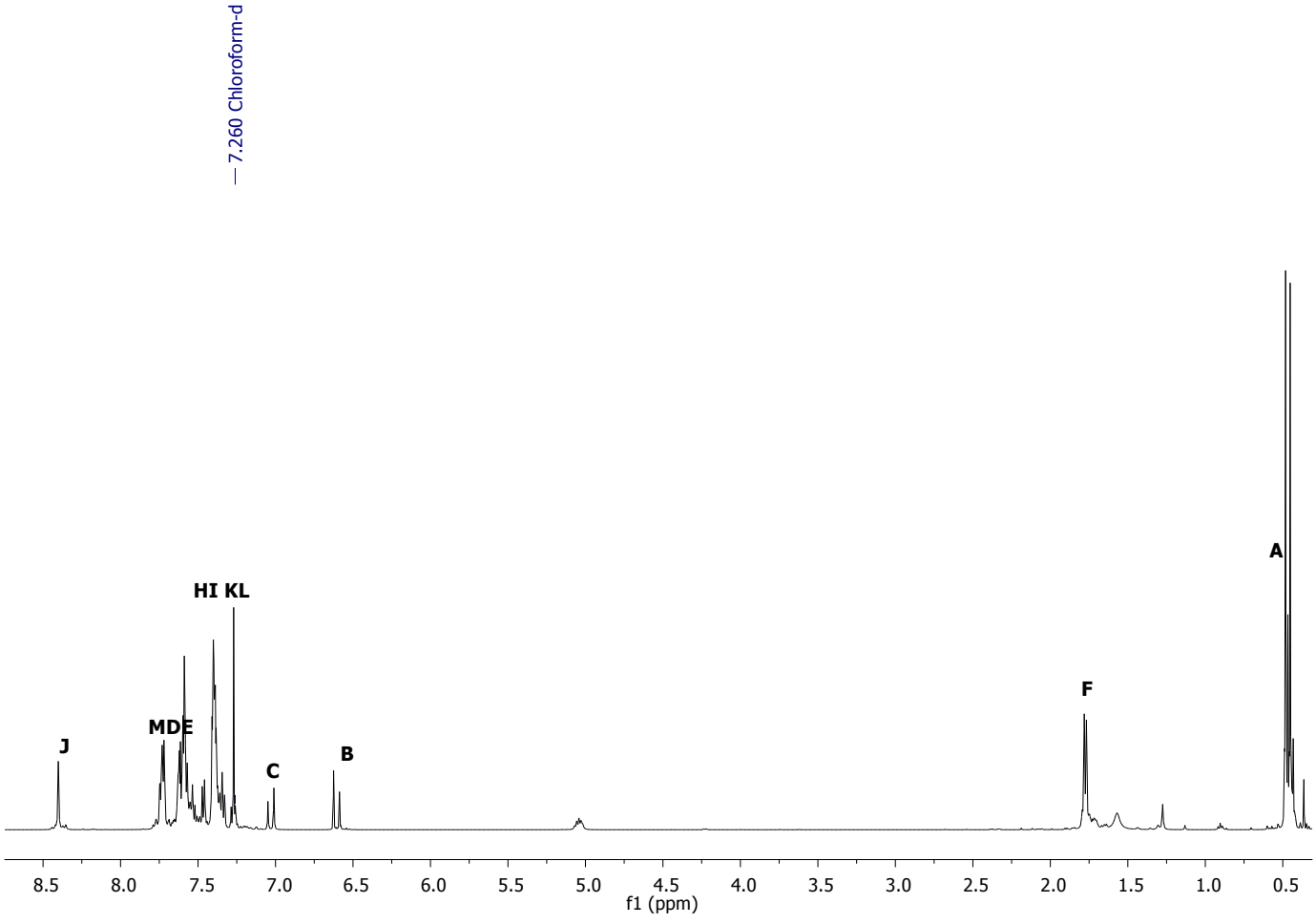


Compound 24 – ^{29}Si NMR in $CDCl_3$

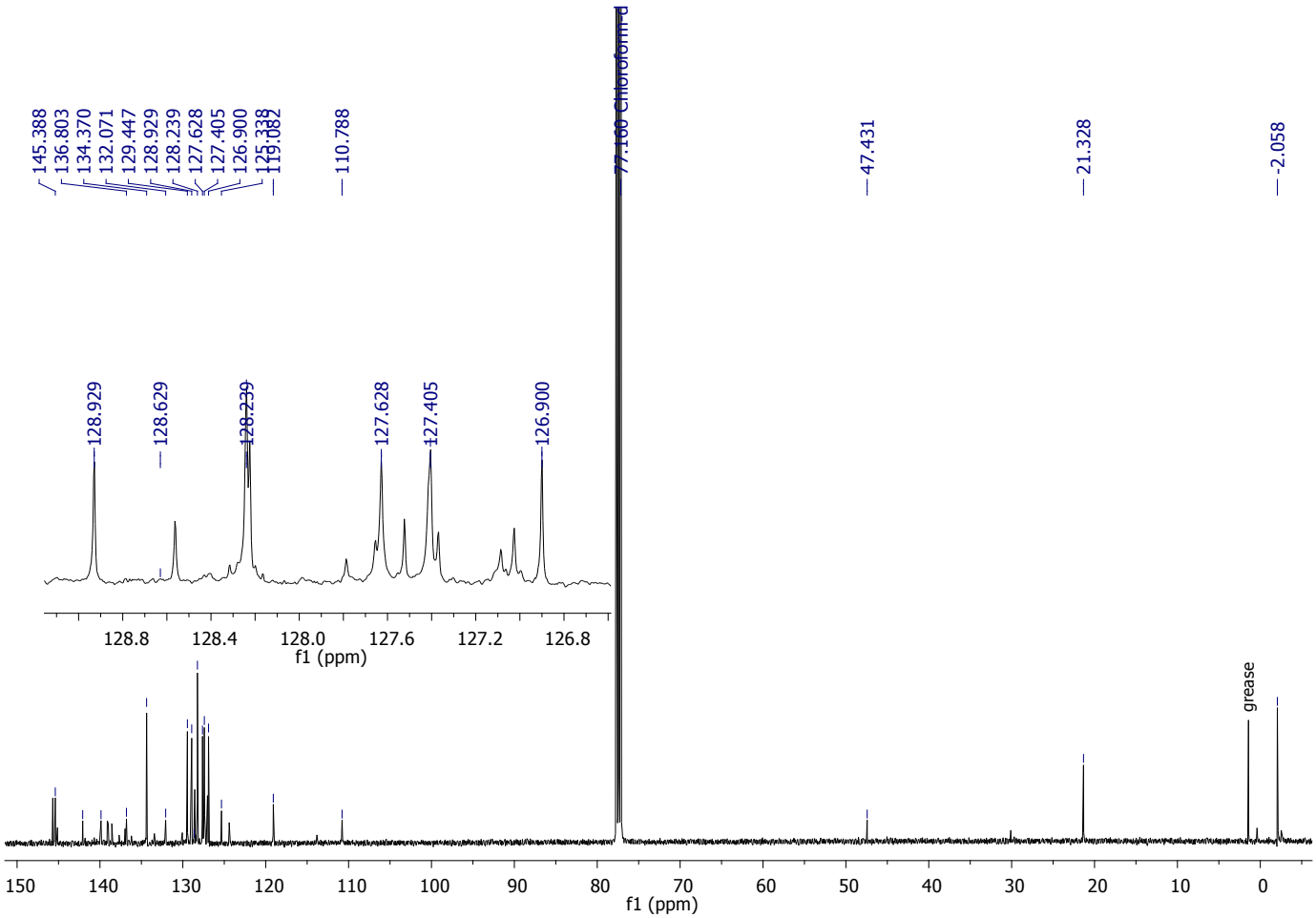
Compound 25

3,6-bis(4-((*E*)-2-(phenyldimethylsilyl)vinyl)phenyl)-*N*-isopropylcarbazole

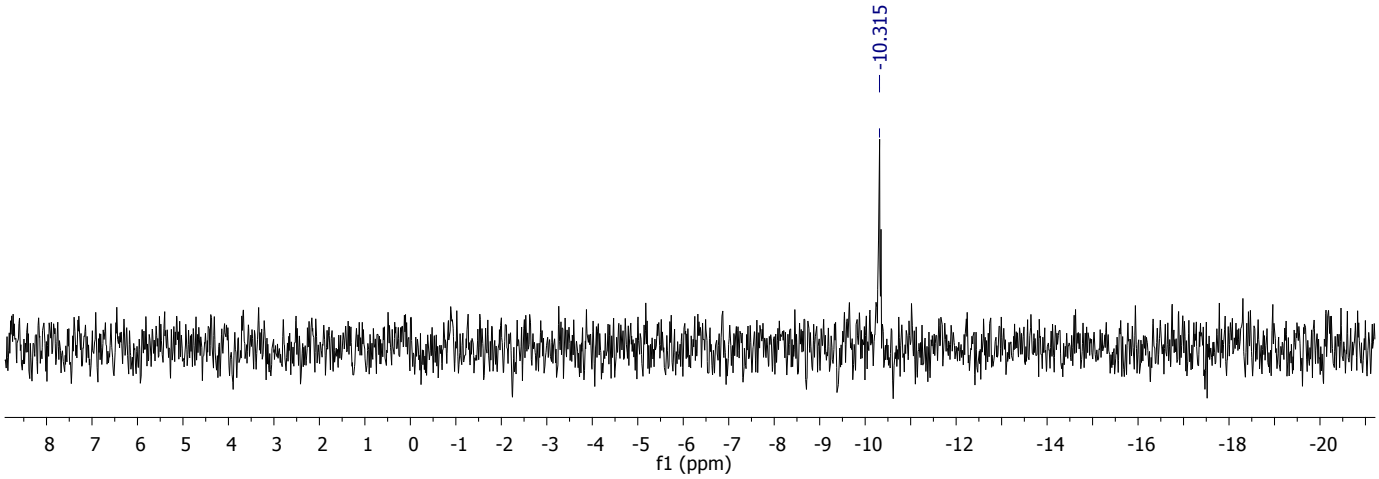




Compound 25 - ^{1}H NMR in $CDCl_3$



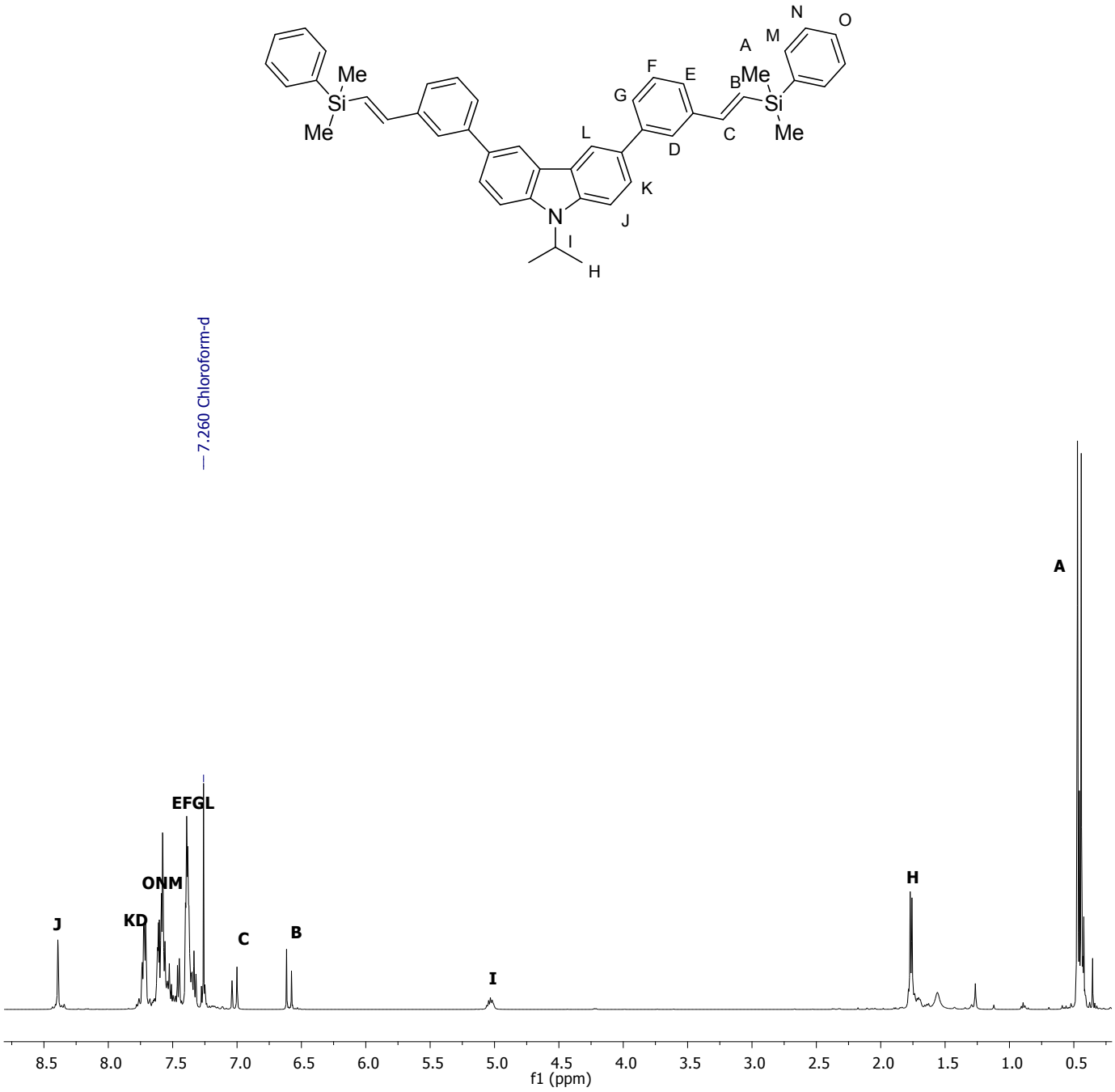
Compound 25 – ^{13}C NMR in $CDCl_3$



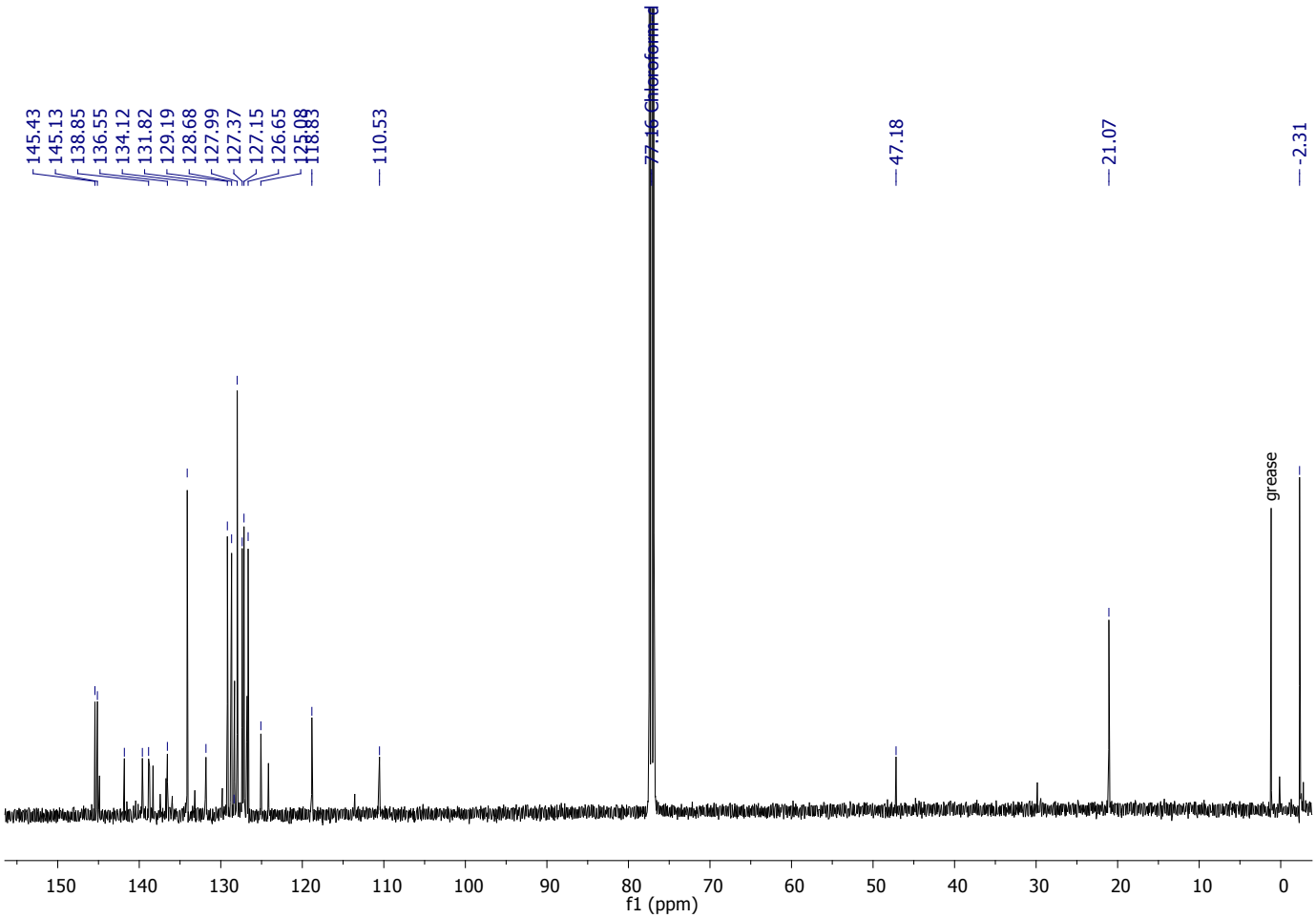
Compound 25 – ^{29}Si NMR in $CDCl_3$

Compound 26

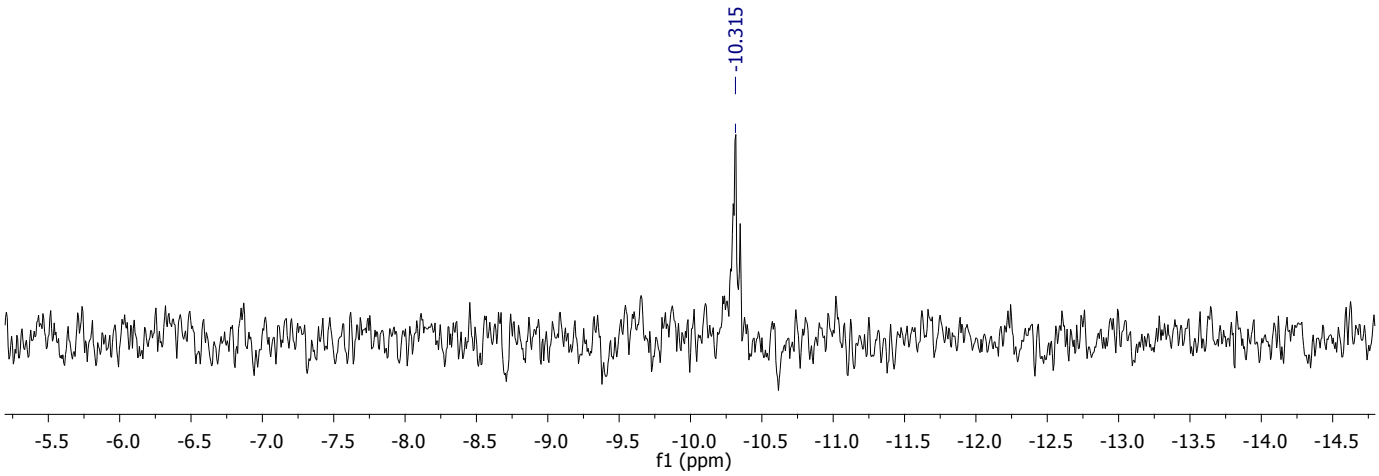
3,6-bis(3-((*E*)-2-(phenyldimethylsilyl)vinyl)phenyl)-*N*-isopropylcarbazole



Compound 26 - ^{1}H NMR in $CDCl_3$



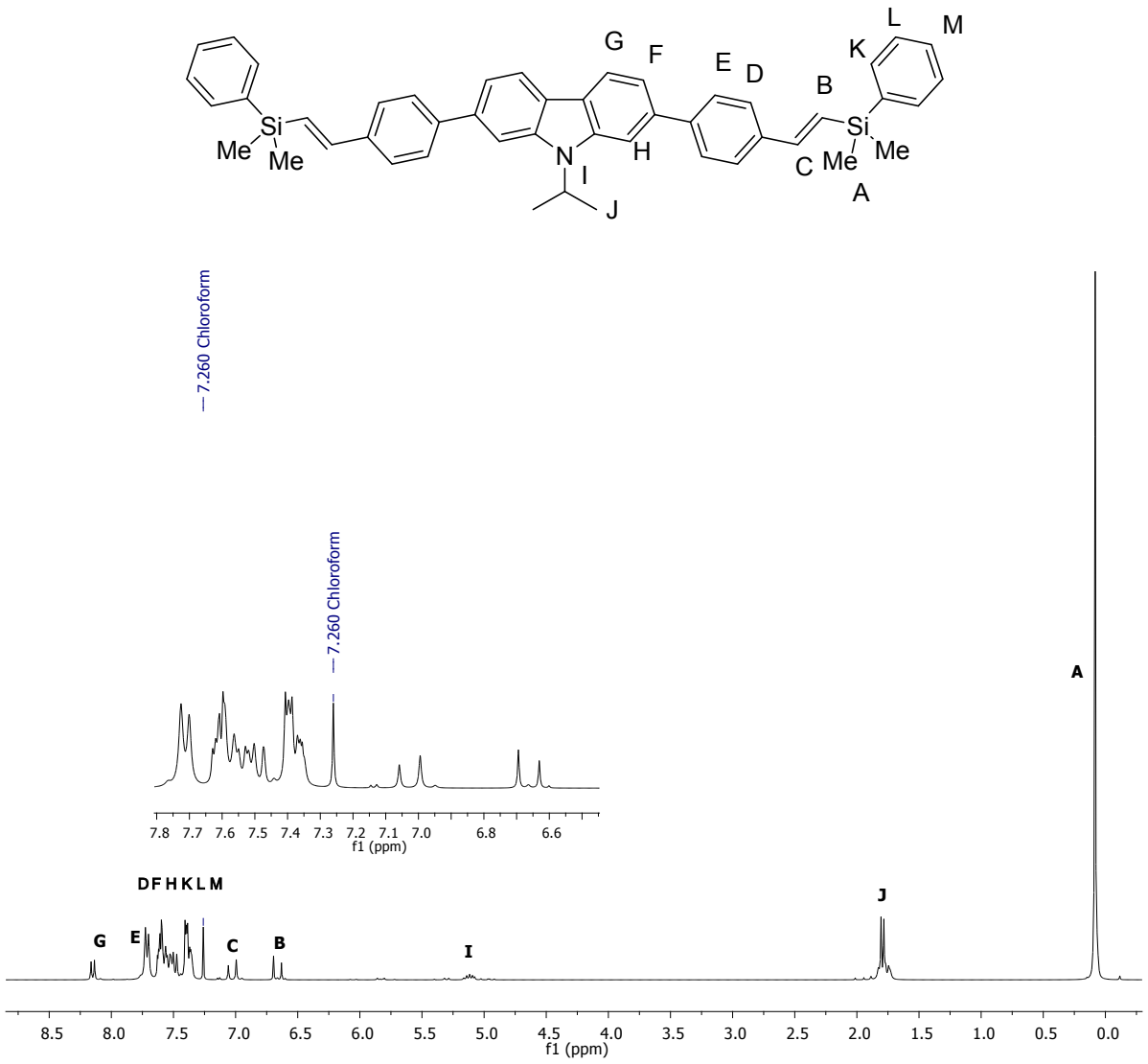
Compound 26 – ^{13}C NMR in $CDCl_3$



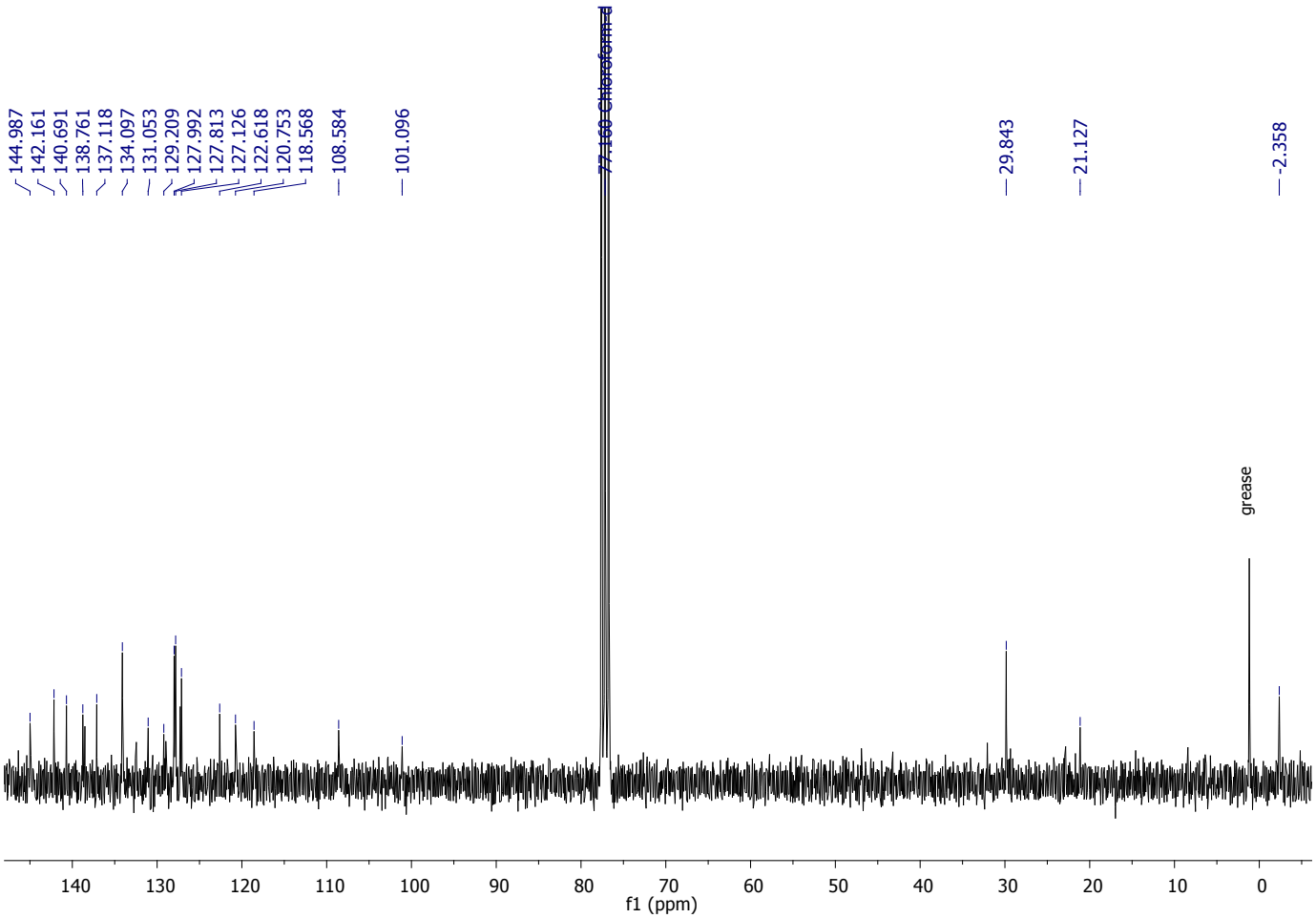
Compound 26 – ^{29}Si NMR in $CDCl_3$

Compound 27

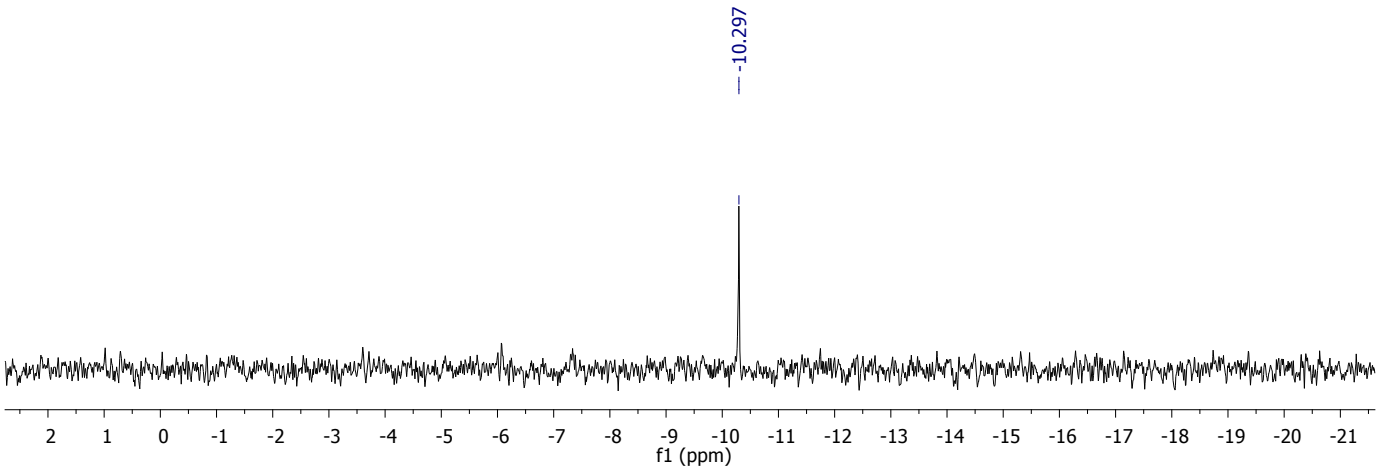
2,7-bis(3-((*E*)-2-(phenyldimethylsilyl)vinyl)phenyl)-*N*-isopropylcarbazole



Compound 27 - ^{1}H NMR in $CDCl_3$



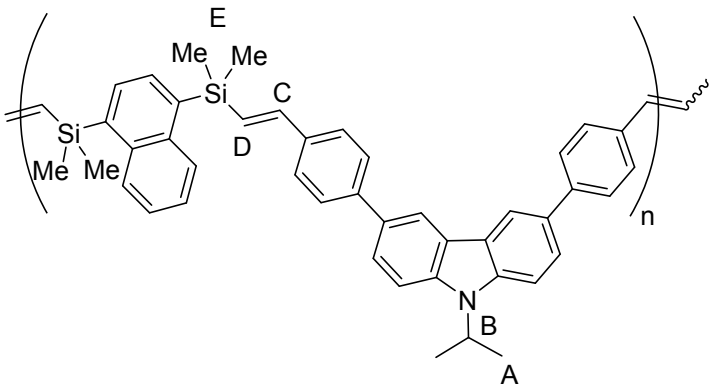
Compound 27 – ^{13}C NMR in $CDCl_3$

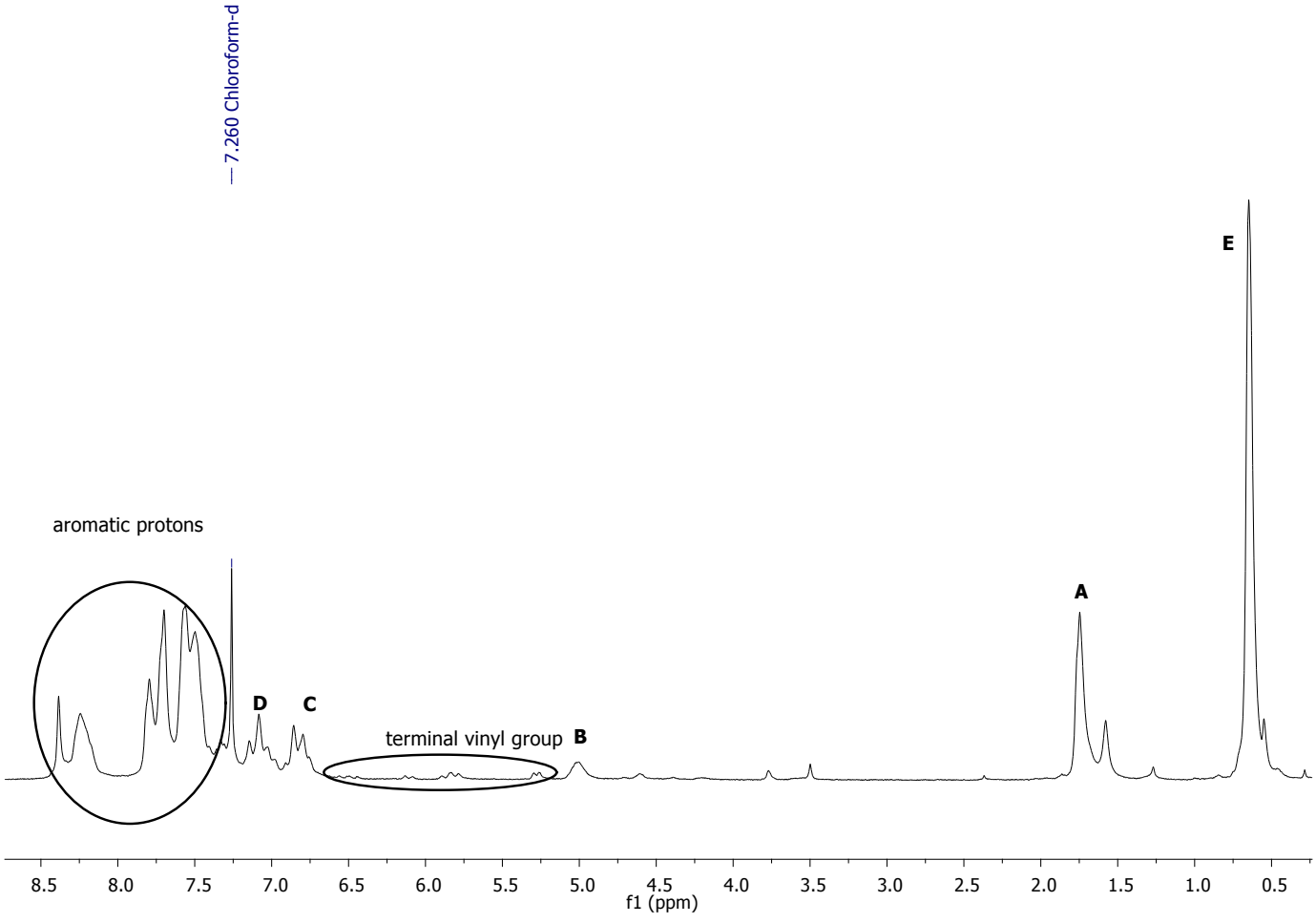


Compound 27 – ^{29}Si NMR in $CDCl_3$

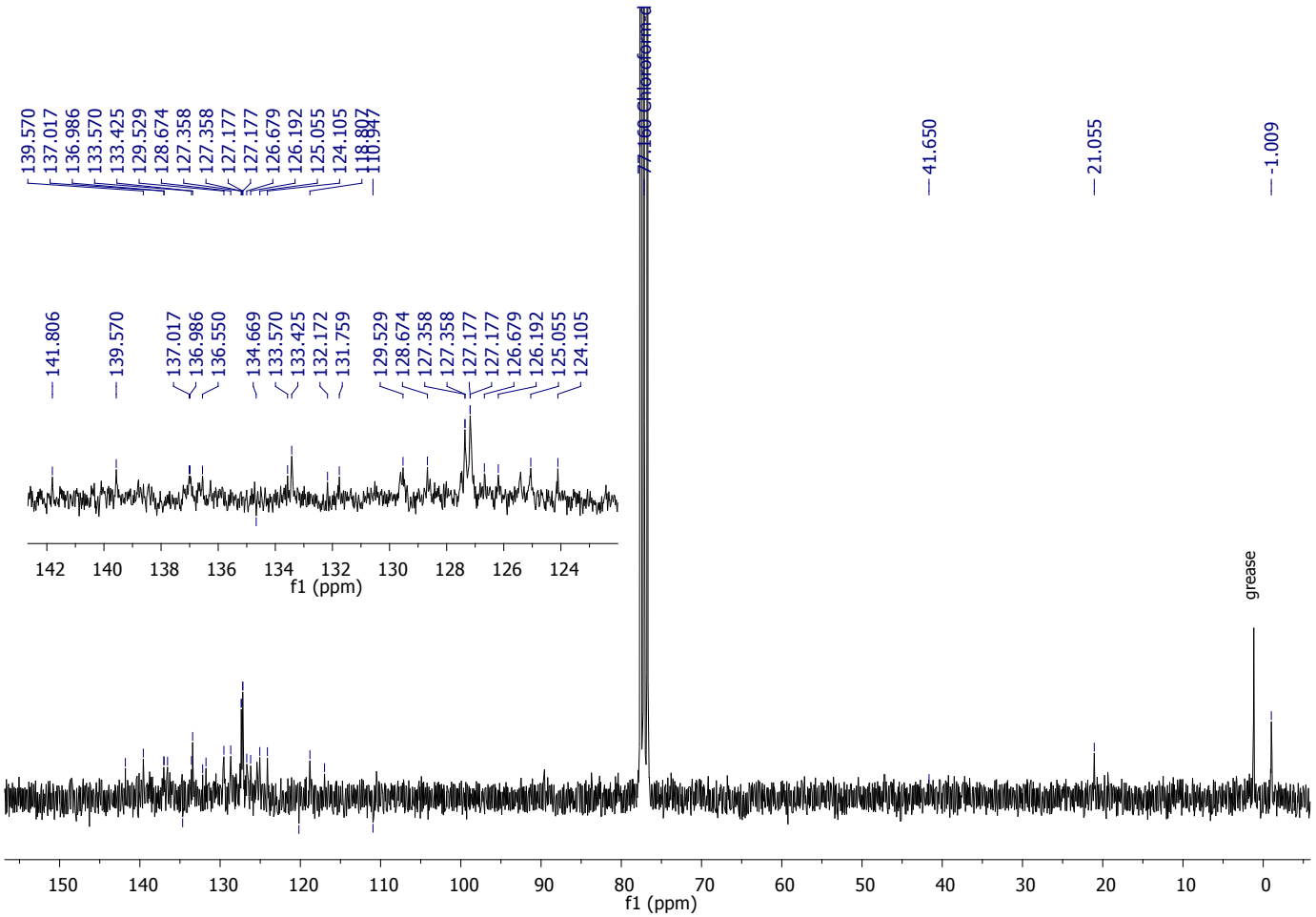
Compound 28-P1

Poly[(3,6-di(4-phenylene)-*N*-isopropylcarbazole-(*E*)-vinylene-(1,4-bis(dimethylsilylene) naphtalene)-(*E*)-vinylene]s

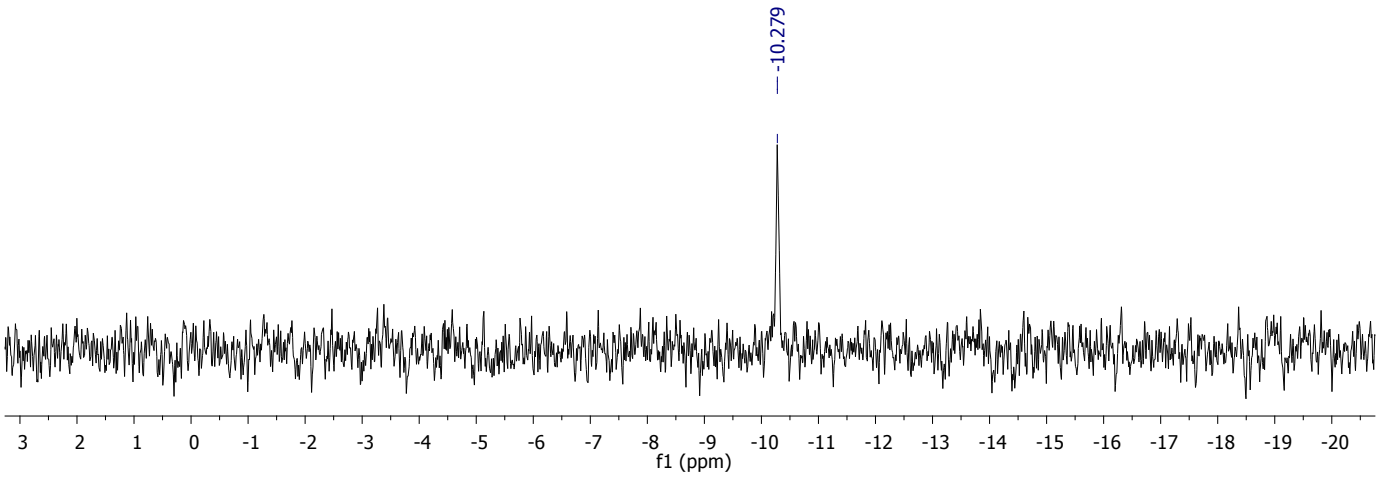




Compound 28 - ^{1}H NMR in $CDCl_3$



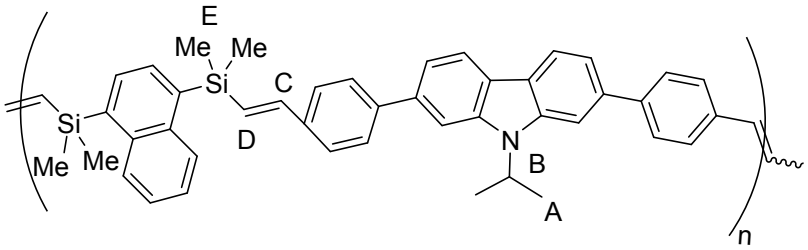
Compound 28 – ^{13}C NMR in $CDCl_3$

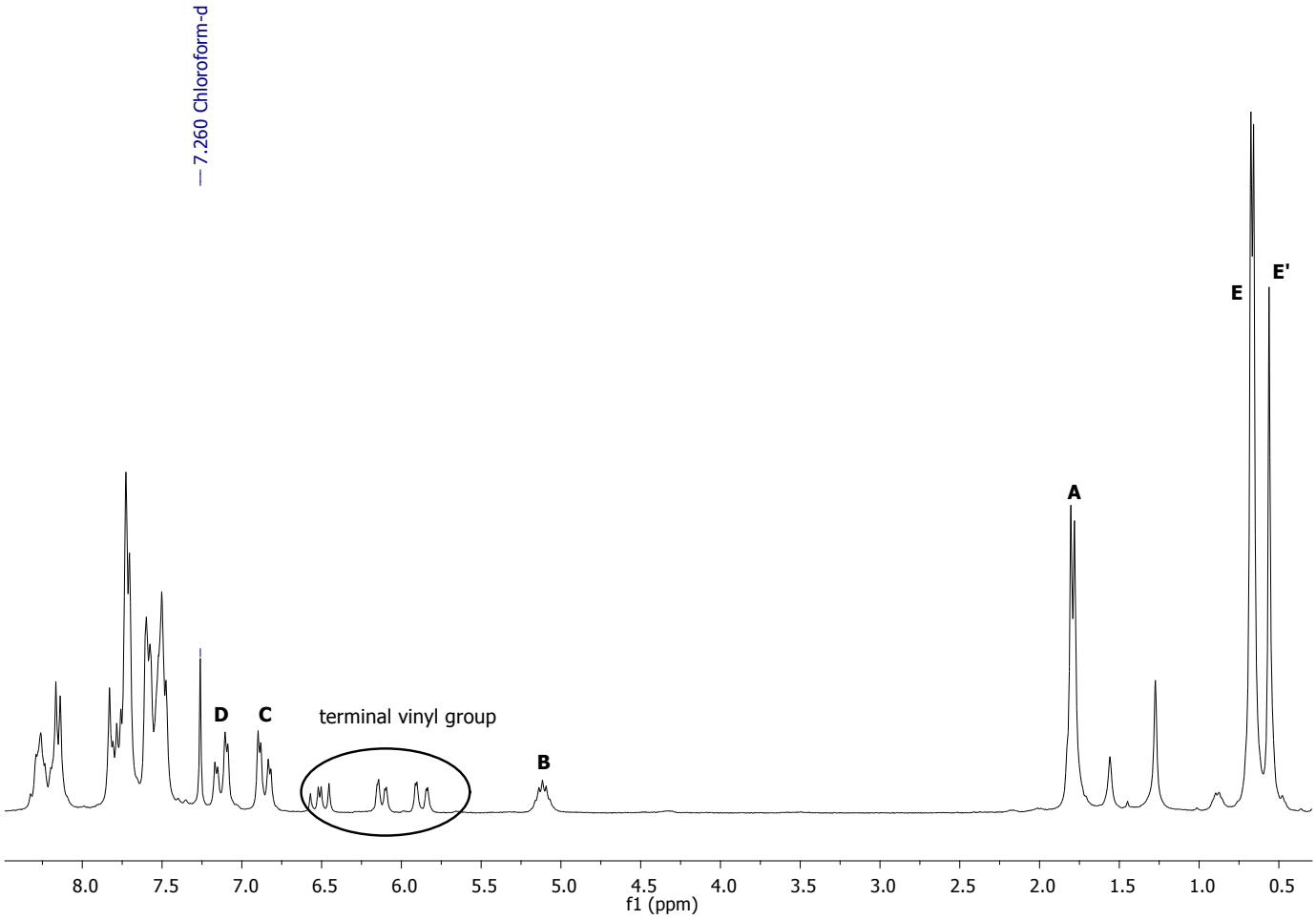


Compound 28 – ^{29}Si NMR in $CDCl_3$

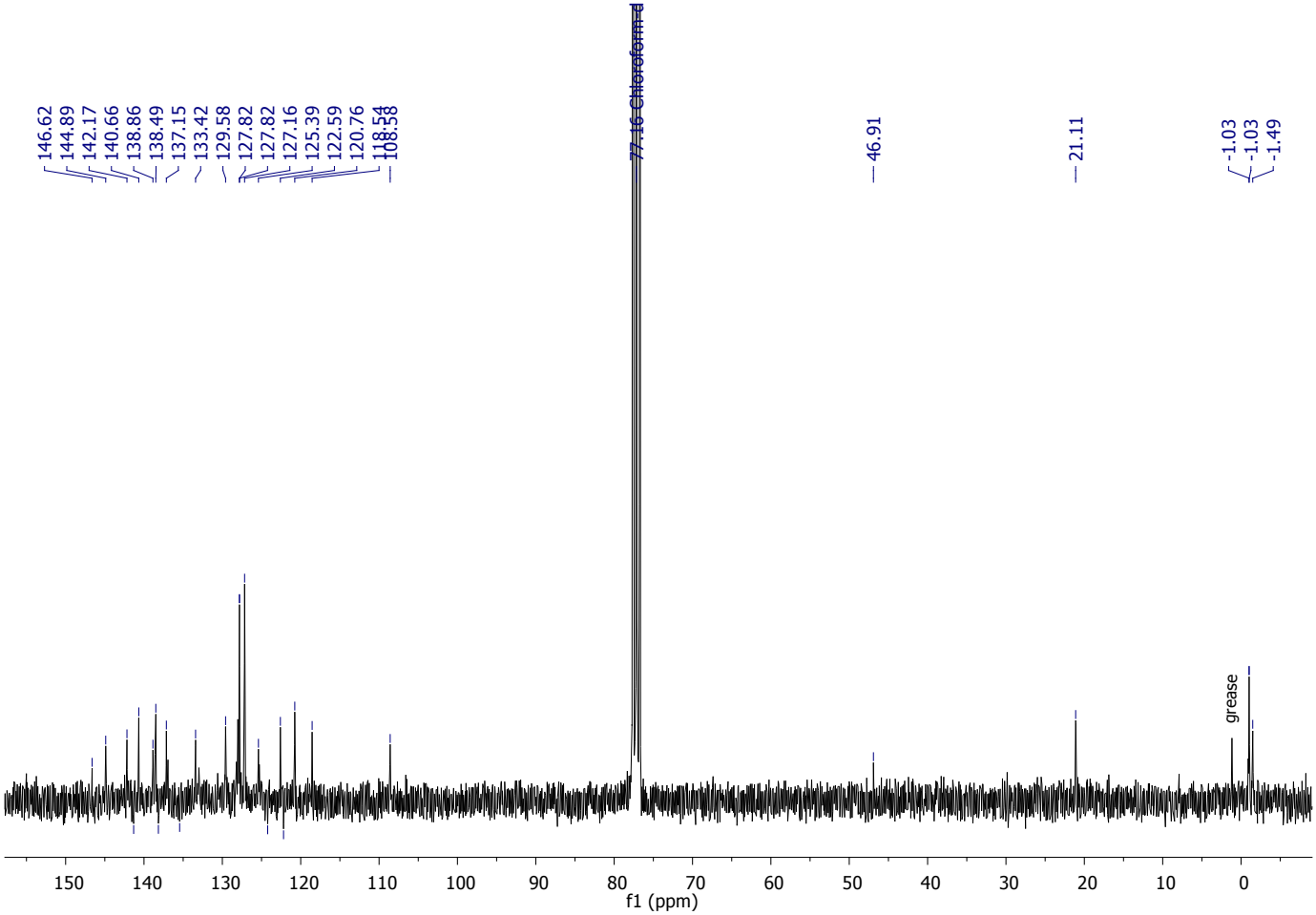
Compound 29-P2

Poly[(2,7-di(4-phenylene)-*N*-isopropylcarbazole-(*E*)-vinylene-(1,4-bis(dimethylsilylene) naphtalene)-(*E*)-vinylene]s

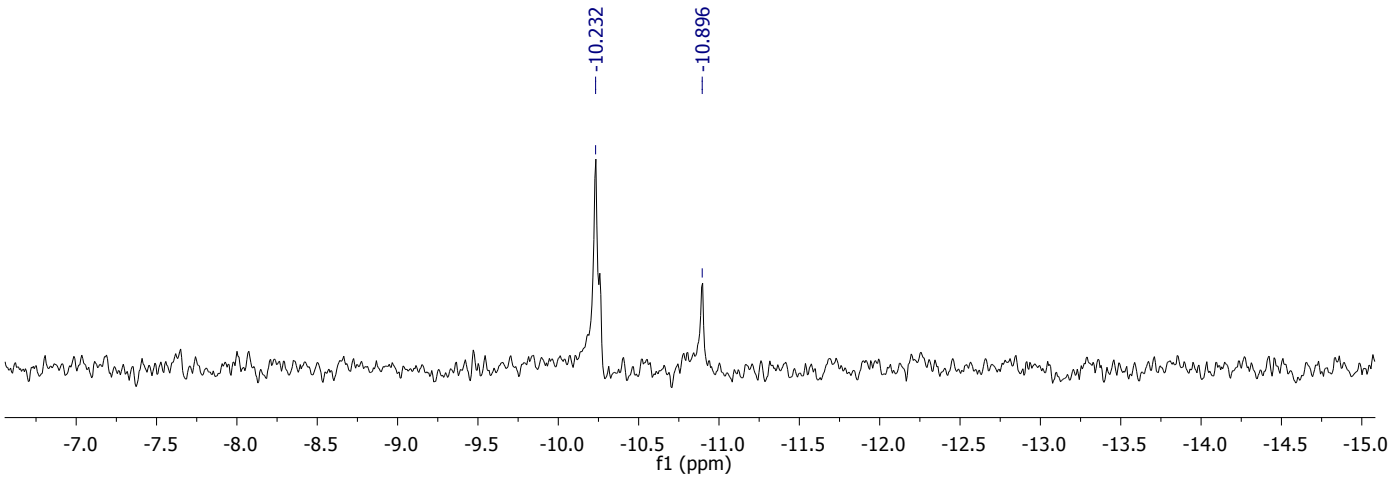




Compound 29 - ^{1}H NMR in $CDCl_3$



Compound 29 – ^{13}C NMR in $CDCl_3$



Compound 29 – ^{29}Si NMR in $CDCl_3$

GPC chromatograms and calculation

The GPC general calculation of **28 - P1**

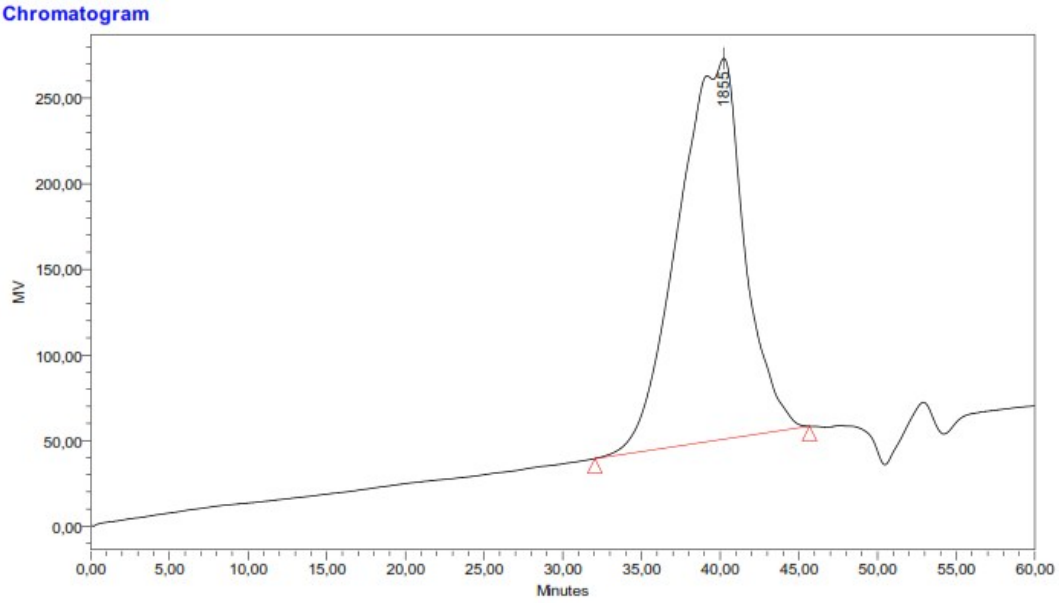


Figure 2. GPC chromatogram of **28 - P1**

GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity	%Area
1	40,235	2073	2930	1855	4225	1,413	100,00

The GPC exact calculation of **28 - P1**

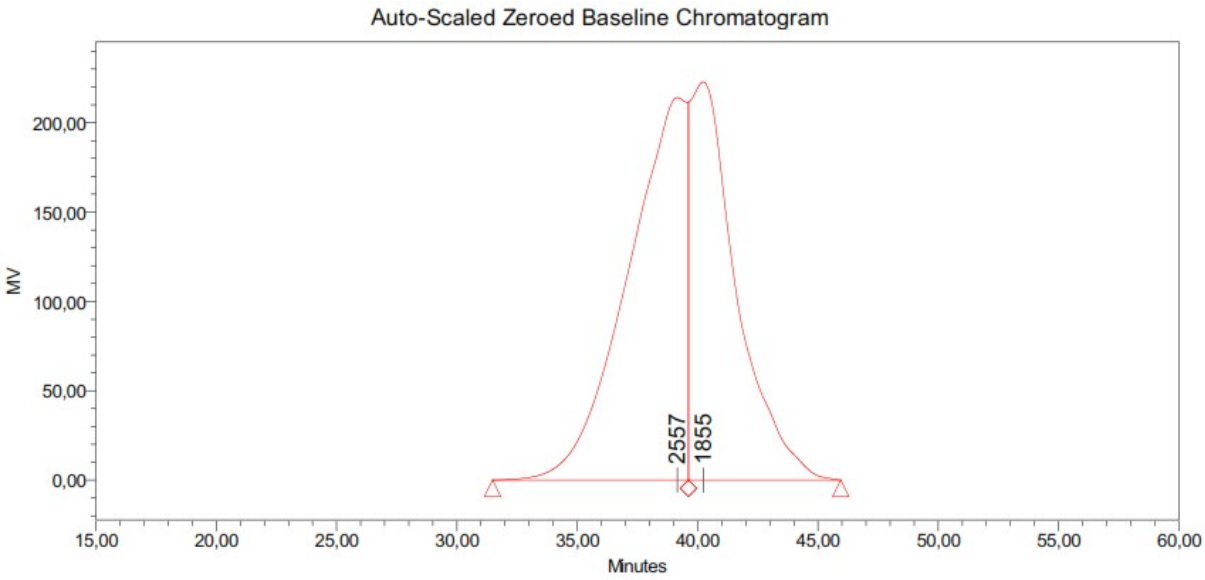


Figure 3. GPC chromatogram of **28- P1**

GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity	%Area
1	39,155	3503	4094	2557	5083	1,169	54,74
2	40,235	1383	1537	1855	1655	1,111	45,26

The GPC general calculation of **29 - P2**

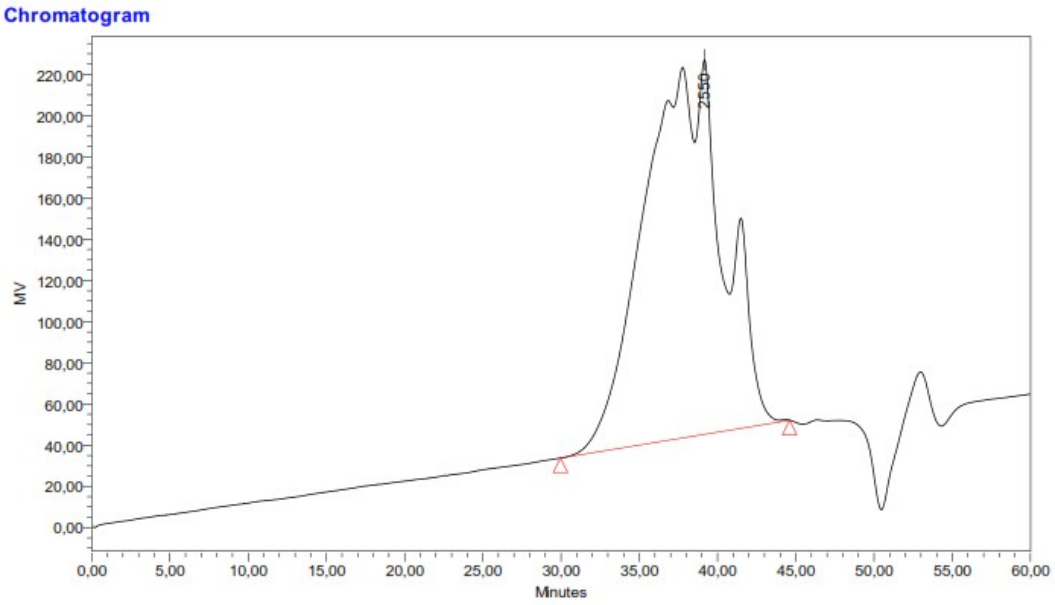


Figure 4. GPC chromatogram of **29 - P2**

GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity	%Area
1	39,164	3089	5120	2550	8257	1,657	100,00

The GPC exact calculation of **29- P2**

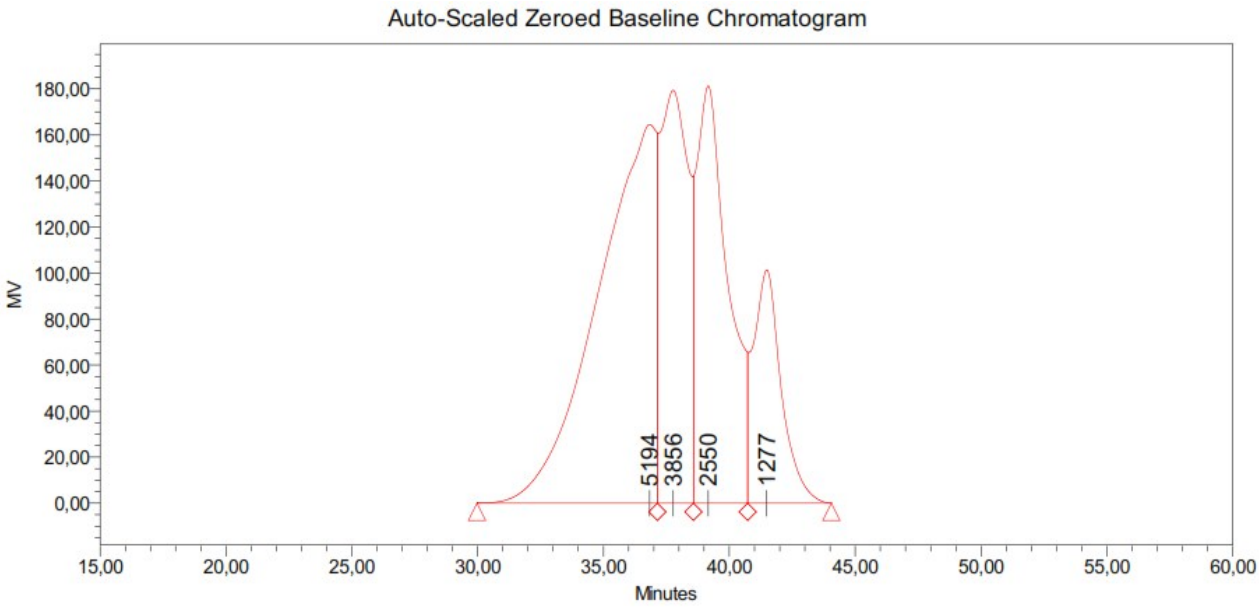


Figure 5. GPC chromatogram of **29 - P2** (exact separation)

GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity	%Area
1	36,837	7470	8658	5194	10522	1,159	40,97
2	37,772	3757	3815	3856	3872	1,015	21,93
3	39,164	2297	2365	2550	2428	1,029	24,81
4	41,492	1221	1254	1277	1284	1,027	12,29

GCMS analysis

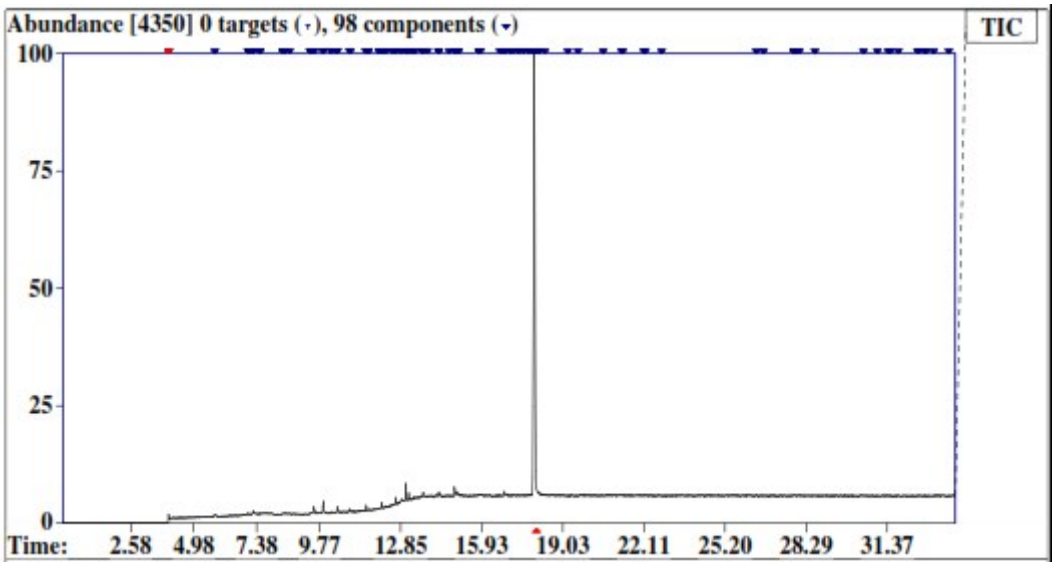


Figure 6. Sample of GCMS chromatogram-spectrum of **19** - catalytic system **5d .**

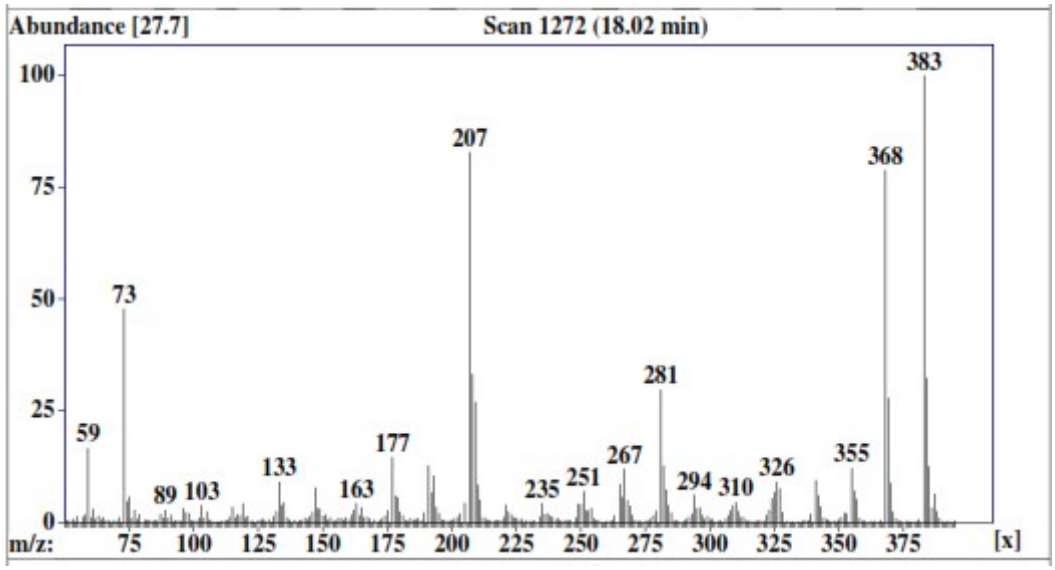


Figure 7. MS spectrum of **19.**