Supplementary Information

Oxidative homodimerization of substituted olefins by DDQ visible light photocatalysis

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Table of Contents:

Experimental Section

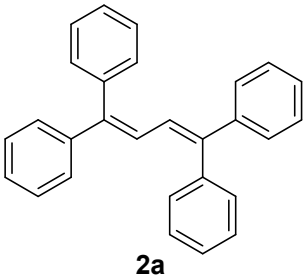
General Aspects

Unless otherwise noted, all the reactions were performed at 30 °C. All commercial chemicals, reagents and precursors were used as received. All reactions were carried out under nitrogen gas atmosphere. All solvents were dried over 4Å molecular sieves and distilled prior to use. Reactions were monitored by analytical thin layer chromatography on silica gel and visualization was accomplished by irradiation with short wave UV light at 254 nm and near UV 366 nm lights. Column chromatography was carried out on silica gel using 60-120 mesh powder. All NMR spectra were recorded on a Bruker Avance (300 MHz) spectrometer in deuterated solvents such as CD_2Cl_2, CD_3CN or DMSO-d_6. Chemical shifts are expressed in parts per million (ppm) and were calibrated using the residual protonated solvent peak. High resolution mass spectra were collected on Waters-Q-TOF-Premier. IR spectra were recorded on a Perkin Elmer Spectrum 1000 FT-IR spectrometer. Photochemical reactions were performed with 455 nm (OSRAM Oslon SSL 80 royal-blue LEDs (λ = 455 nm (± 15 nm), 3.5 V, 700 mA).

General procedure for the synthesis of substituted buta-1,4-dienes

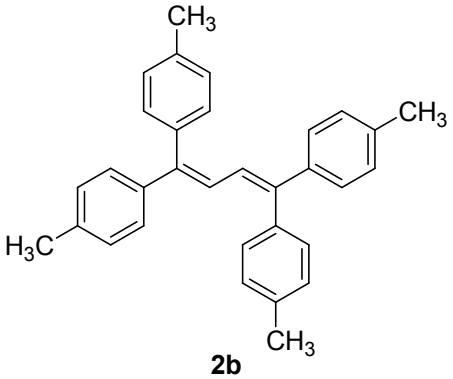
A crimp vial equipped with a magnetic stir bar was charged with DDQ (0.2 mmol, 20 mol%) and $ClCH_2CH_2Cl$. To this solution, the olefins (1.0 mmol), and TBN (1.0 mmol) were added. The vial was sealed with a rubber cork and inlet/outlet for N_2 gas was provided by needles. The mixture was stirred few minutes to mix well and then the vial was irradiated through the plane bottom side of the crimp vial using a 5W 455 nm LED at a distance of 2 cm. After stirring at 30 °C for 12-15 h, the solvent was removed under reduced pressure to get the crude product that was purified by column chromatography using hexane-ethyl acetate-$CHCl_3$ mixtures as an eluent. The purity of the compound was confirmed by IR, ^1H and ^{13}C NMR and HRMS measurements, vide infra.

Experimental characterization data for products



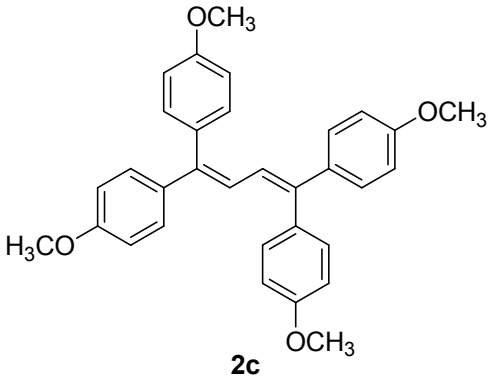
2a

1,1,4,4-tetraphenylbuta-1,3-diene (2a)[1]: 308 mg, 86% yield; R_f 0.31 in pet. ether; IR (KBr, cm^{-1}): *v* 3054, 2923, 2852, 1484, 1449, 756; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 7.47-7.37 (m, 6H), 7.34-7.29 (m, 4H), 7.26-7.19 (m, 6H), 7.18-7.11 (m, 4H), 6.76 (s, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 144.5, 142.9, 140.3, 131.1, 128.7, 128.5, 128.0, 127.9, 127.8, 126.4 . HRMS (EI) *m/z* calcd for $C_{28}H_{22}$: 358.1722, found: 358.1726.



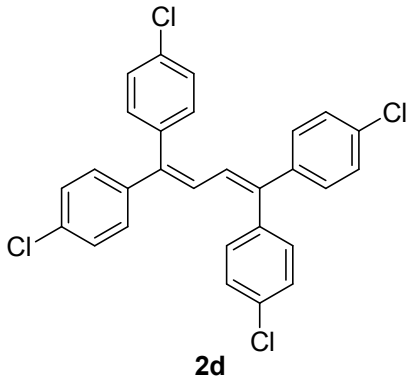
2b

1,1,4,4-tetra-*p*-tolylbuta-1,3-diene (2b): 356 mg, 86% yield; R_f 0.28 in pet. ether; IR (KBr, cm^{-1}): *v* 3073, 3064, 1481, 1316, 733, 689; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.32 (d, J = 8.2 Hz, 4H), 7.29-7.18 (m, 8H), 7.12 (d, J = 8.2 Hz, 4H), 6.76 (s, 2H), 2.33 (s, 6H), 2.32 (s, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 144.5, 141.3, 139.1, 136.8, 136.7, 130.6, 129.2, 128.9, 127.7, 126.1, 21.0, 20.9. HRMS (EI) *m/z* calcd for $C_{32}H_{30}$: 414.2348, found: 414.2346.



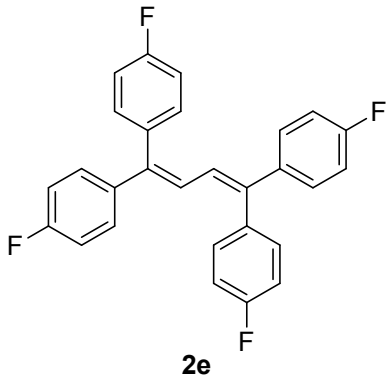
2c

1,1,4,4-tetrakis(4-methoxyphenyl)buta-1,3-diene (2c)[2]: 430 mg, 90% yield; R_f 0.30 in $CHCl_3$-pet. ether (20:80); IR (KBr, cm^{-1}): *v* 2926, 2856, 1451, 1433, 833; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.29 (d, J = 9.4 Hz, 4H), 7.13 (d, J = 8.6 Hz, 4H), 6.96 (d, J = 8.6 Hz, 4H), 6.81 (d, J = 9.4 Hz, 4H), 6.67 (s, 2H), 3.86 (s, 6H), 3.81 (s, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 158.9, 158.5, 142.0, 135.6, 132.4, 131.8, 128.7, 124.7, 113.4, 113.3, 55.38, 55.36. HRMS (EI) *m/z* calcd for $C_{32}H_{30}O_4$: 478.2144, found: 478.2143.



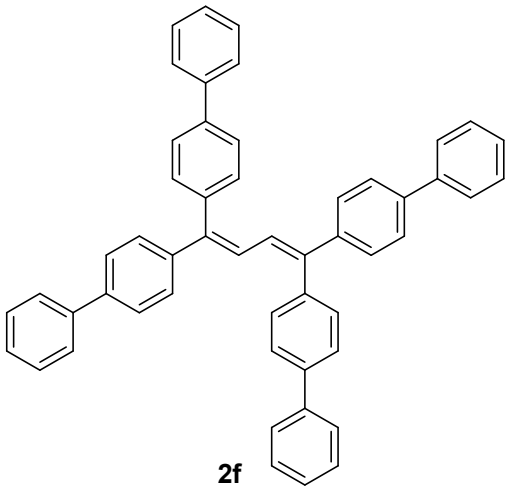
2d

1,1,4,4-tetrakis(4-chlorophenyl)buta-1,3-diene (2d): 366 mg, 74% yield, R_f 0.80 in $CHCl_3$-pet. ether (20:80); IR (KBr, cm^{-1}): *v* 2922, 2853, 2384, 1453, 1432, 836; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.34 (d, J = 8.8 Hz, 4H), 7.27-7.20 (m, 8H), 7.18 (d, J = 8.8 Hz, 4H), 6.69 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 144.4, 140.6, 137.7, 135.9, 135.6, 132.4, 130.2, 128.8, 128.6, 126.3. HRMS (EI) *m/z* calcd for $C_{28}H_{18}Cl_4$: 494.0163, found: 494.0167.



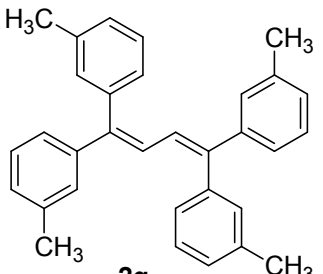
2e

1,1,4,4-tetrakis(4-fluorophenyl)buta-1,3-diene (2e)[3]: 285 mg, 66% yield; R_f 0.81 in $CHCl_3$-pet. ether (20:80); IR (KBr, cm^{-1}): *v* 3044, 2932, 2854, 1458, 753; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.31-7.27 (m, 4H), 7.19-7.11 (m, 8H), 7.03-6.97 (m, 4H), 6.64 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 162.5 (d, J = 246 Hz), 162.2 (d, J = 246 Hz), 142.4, 138.5 (d, J = 4 Hz), 135.6 (d, J = 4 Hz), 132.1 (d, J = 8 Hz), 129.5 (d, J = 8 Hz), 125.8, 115.6 (d, J = 22 Hz), 115.1 (d, J = 22 Hz). HRMS (EI) *m/z* calcd for $C_{28}H_{18}F_4$: 430.1345, found: 430.1347.



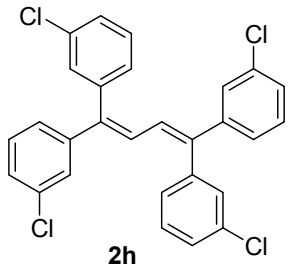
2f

1,1,4,4-tetrakis([1,1'-biphenyl]-4-yl)buta-1,3-diene (2f): 510 mg, 77% yield; R_f 0.71 in $CHCl_3$-pet. ether (20:80); IR (KBr, cm^{-1}): *v* 3046, 2927, 2855, 1457, 759; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.55 (d, J = 8.2 Hz, 4H), 7.48-7.41 (m, 16H), 7.39-7.32 (m, 12H), 7.28-7.24 (d, J = 8.4 Hz, 4H), 6.75 (s, 2H). Anal. calcd for $C_{52}H_{38}$: C, 94.22; H, 5.78; found: C, 94.19; H, 5.76. In common organic solvents **2f** was sparingly soluble that precluded collection of ^{13}C NMR spectra.



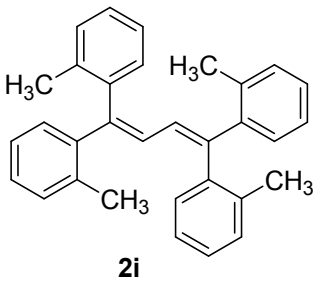
2g

1,1,4,4-tetra-*m*-tolylbuta-1,3-diene (2g): 369 mg, 89% yield; R_f 0.24 in pet. ether; IR (KBr, cm^{-1}): *v* 3053, 2928, 2854, 1457, 1082, 835; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.48-7.44 (m, 4H), 7.31-7.20 (m, 8H), 7.11-7.02 (m, 4H), 6.78 (s, 2H), 1.57 (s, 6H), 1.56 (s, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 144.1, 143.0, 140.6, 139.6, 138.2, 130.7, 130.3, 129.0, 128.2, 128.1, 127.2, 126.3, 126.1, 125.6, 21.4, 21.3. HRMS (EI) *m/z* calcd for $C_{32}H_{30}$: 414.2348, found: 414.2344.



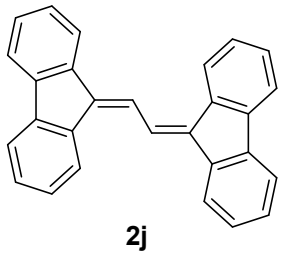
2h

1,1,4,4-tetrakis(3-chlorophenyl)buta-1,3-diene (2h): 356 mg, 72% yield; R_f 0.26 in pet. ether; IR (KBr, cm^{-1}): *v* 2926, 2856, 1455, 1429, 1074, 1025, 968; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.37 (d, J = 8.8 Hz, 2H), 7.31-7.27 (m, 4H), 7.25-7.21 (m, 2H), 7.19-7.13 (m, 8H), 6.76 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 144.2, 143.1, 140.7, 134.2, 134.1, 132.1, 130.7, 129.2, 128.7, 128.6, 127.1, 126.3, 126.2. HRMS (EI) *m/z* calcd for $C_{28}H_{18}Cl_4$: 494.0163, found: 494.0167.



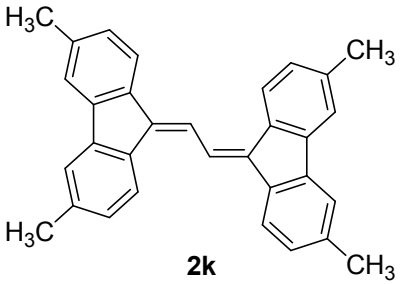
2i

1,1,4,4-tetra-*o*-tolylbuta-1,3-diene (2i): 365 mg, 88% yield; R_f 0.24 in pet. ether; IR (KBr, cm^{-1}): *v* 2926, 2855, 1476, 1458, 1076, 829, 757; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.46 (d, J = 7.4 Hz, 2H), 7.23-7.14 (m, 12H), 7.06 (d, J = 7.4 Hz, 2H), 6.77 (s, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 149.7, 148.2, 144.1, 136.6, 135.3, 130.2, 129.6, 129.3, 128.8, 127.7, 127.6, 126.4, 125.9, 20.0, 19.9. HRMS (EI) *m/z* calcd for $C_{32}H_{30}$: 414.2348, found: 414.2347.



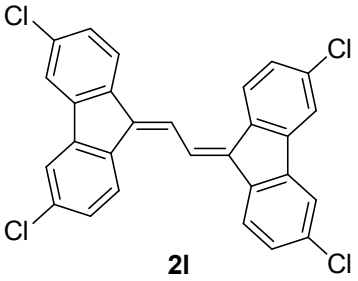
2j

1,2-di(9H-fluoren-9-ylidene)ethane (2j): 308 mg, 87% yield; R_f 0.64 in $CHCl_3$-pet. ether (20:80); IR (KBr, cm^{-1}): *v* 2932, 2856, 1458, 1079, 832; ^1H NMR (DMSO-d_6, 300 MHz) δ 8.06-7.89 (m, 4H), 7.44-7.26 (m, 12H), 6.64 (s, 2H). Anal. calcd. for $C_{28}H_{18}$: C, 94.88; H, 5.12; found: C, 94.82; H, 5.16. In common organic solvents **2j** was sparingly soluble that precluded collection of ^{13}C NMR spectra.



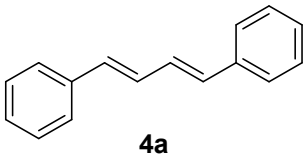
2k

1,2-bis(3,6-dimethyl-9H-fluoren-9-ylidene)ethane (2k): 353 mg, 86% yield; R_f 0.59 in $CHCl_3$-pet. ether (20:80); IR (KBr, cm^{-1}): *v* 3053, 2935, 2854, 1455, 1076, 839, 754; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.71 (s, 2H), 7.53 (s, 2H), 7.32-7.15 (m, 6H), 7.03-6.99 (m, 2H), 6.68 (s, 2H), 2.34 (s, 6H), 2.33 (s, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 142.8, 142.1, 141.2, 140.2, 139.3, 138.6, 137.4, 136.4, 135.6, 128.3, 127.8, 127.2, 126.8, 126.2, 21.2, 21.1. HRMS (EI) *m/z* calcd for $C_{32}H_{26}$: 410.2035, found: 410.2039.



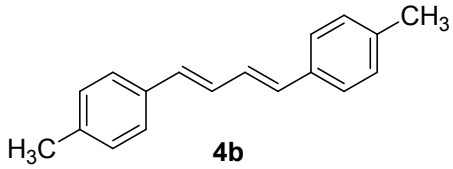
2l

1,2-bis(3,6-dichloro-9H-fluoren-9-ylidene)ethane (2l): 353 mg, 72% yield; R_f 0.60 in $CHCl_3$-pet. ether (20:80); IR (KBr, cm^{-1}): *v* 3072, 2967, 2856, 1441, 1377, 1131, 721; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.85 (s, 2H), 7.67 (s, 2H), 7.40-7.28 (m, 8H), 6.71 (s, 2H). Anal. calcd. for $C_{28}H_{14}Cl_4$: C, 68.32; H, 2.87; found: C, 68.29; H, 2.91. In common organic solvents **2l** was sparingly soluble that precluded collection of ^{13}C NMR spectra.



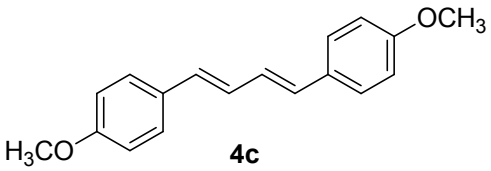
4a

(1E,3E)-1,4-diphenylbuta-1,3-diene (4a)[4]: 118 mg, 57% yield; R_f 0.53 in pet. ether; IR (KBr, cm^{-1}): *v* 3066, 2939, 1464, 1349, 1108, 757; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.47-7.43 (m, 4H), 7.36-7.29 (m, 4H), 7.26-7.21 (m, 2H), 6.98 (AA' of AA'BB' pattern, 2H), 6.67 (BB' of AA'BB' pattern, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 137.4, 132.9, 129.4, 128.6, 127.7, 126.4. HRMS (EI) *m/z* calcd for $C_{16}H_{14}$: 206.1096, found: 206.1092.



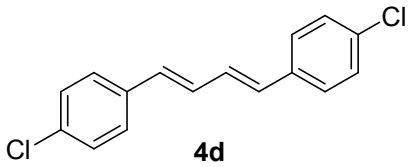
4b

(1E,3E)-1,4-di-*p*-tolylbuta-1,3-diene (4b)[5]: 139 mg, 59% yield; R_f 0.49 in pet. ether; IR (KBr, cm^{-1}): *v* 3064, 3035, 2997, 1458, 1374, 1313, 1168, 759; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.36 (d, *J* = 8.4 Hz, 4H), 7.16 (d, *J* = 8.4 Hz, 4H), 6.91 (AA' of AA'BB' pattern, 2H), 6.65 (BB' of AA'BB' pattern, 2H), 2.37(s, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 137.4, 134.7, 132.3, 129.2, 128.6, 126.3, 21.2. HRMS (EI) *m/z* calcd for $C_{18}H_{18}$: 234.1409, found: 234.1406.



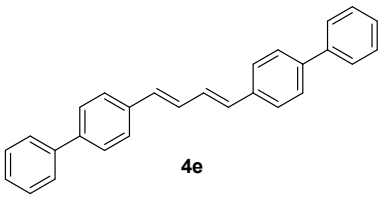
4c

(1E,3E)-1,4-bis(4-methoxyphenyl)buta-1,3-diene (4c)[5]: 136 mg, 51% yield; R_f 0.36 in pet. ether; IR (KBr, cm^{-1}): *v* 2957, 2925, 2856, 1468, 797, 614; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.41-7.34 (m, 4H), 6.89-6.83 (m, 4H), 6.82 (AA' of AA'BB' pattern, 2H), 6.58 (BB' of AA'BB' pattern, 2H), 3.83 (s, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 159.1, 131.4, 130.4, 127.5, 127.4, 114.1, 55.3. HRMS (EI) *m/z* calcd for $C_{18}H_{18}O_2$: 266.1307, found: 266.1309.



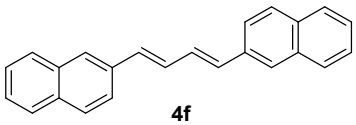
4d

(1E,3E)-1,4-bis(4-chlorophenyl)buta-1,3-diene (4d)[6]: 135 mg, 49% yield; R_f 0.50 in pet. ether; IR (KBr, cm^{-1}): *v* 3037, 2994, 2967, 1457, 1433, 1377, 1167, 731, 648; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.36 (d, *J* = 7.8 Hz, 4H) 7.31 (d, *J* = 7.8 Hz, 4H) 6.93 (AA' of AA'BB' pattern, 2H), 6.63 (BB' of AA'BB' pattern, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 135.8, 133.4, 132.0, 130.1, 128.9, 127.7. HRMS (EI) *m/z* calcd for $C_{16}H_{12}Cl_2$: 274.0316, found: 274.0318.



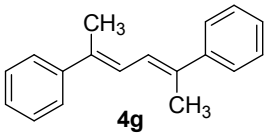
4e

(1E,3E)-1,4-di([1,1'-biphenyl]-4-yl)buta-1,3-diene (4e)[7]: 240 mg, 67% yield; R_f 0.45 in pet. ether; IR (KBr, cm^{-1}): *v* 3080, 3067, 1464, 1448, 1433, 786, 734, 689; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.59-7.55 (m, 4H), 7.51-7.40 (m, 10H) 7.39-7.30 (m, 4H) 6.76 (AA' of AA'BB' pattern, 2H), 5.81 (BB' of AA'BB' pattern, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 141.1, 140.9, 136.9, 133.1, 129.7, 129.1, 128.7, 127.9, 127.7, 126.9. HRMS (EI) *m/z* calcd for $C_{28}H_{22}$: 358.1722, found: 358.1727.



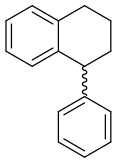
4f

(1E,3E)-1,4-di(naphthalen-2-yl)buta-1,3-diene (4f)[5]: 211 mg, 61% yield; R_f 0.41 in pet. ether; IR (KBr, cm^{-1}): *v* 3084, 3068, 1466, 1454, 1431, 786, 735, 686; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.86-7.80 (m, 8H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.50-7.43 (m, 4H), 7.20 (AA' of AA'BB', 2H), 6.91 (BB' of AA'BB', 2H). Anal. calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92; found: C, 94.06; H, 5.87. In common organic solvents **4f** was sparingly soluble that precluded collection of ^{13}C NMR spectra.



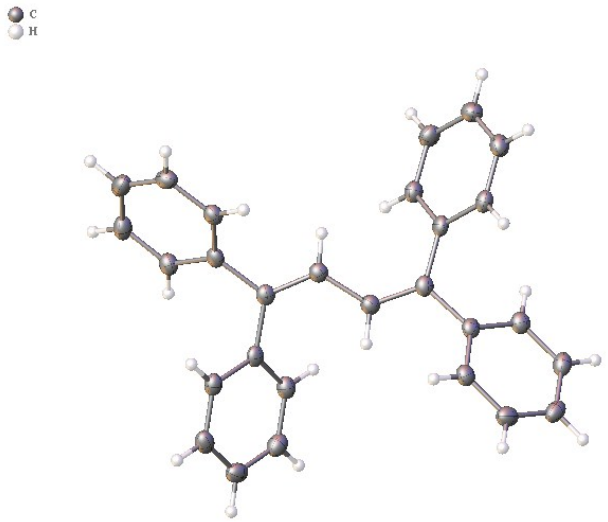
4g

(2E,4E)-hexa-2,4-diene-2,5-diyldibenzene (4g): 165 mg, 70% yield; R_f 0.49 in pet. ether; IR (KBr, cm^{-1}): *v* 3045, 2932, 2854, 1454, 1072, 827, 749; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.38-7.35 (m, 10H), 6.72 (s, 2H), 2.22 (s, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 141.1, 133.2, 129.5, 128.6, 127.8, 126.3, 21.8. HRMS (EI) *m/z* calcd for $C_{18}H_{18}$: 234.1409, found: 234.1408.



1-phenyl-1,2,3,4-tetrahydronaphthalene (5): R_f 0.61 in pet. ether; IR (KBr, cm^{-1}): *v* 3042, 2936, 2855, 829, 751; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.31-6.98 (m, 9H), 4.12 (t, *J* = 6.2 Hz, 1H), 2.91-2.83 (m, 2H), 2.22-2.13 (m, 1H), 1.93-1.71 (m, 3H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 147.5, 139.4, 137.7, 130.3, 129.0, 128.8, 128.3, 125.9, 125.5, 45.6, 33.4, 29.8, 21.1. HRMS (EI) *m/z* calcd for $C_{16}H_{16}$: 208.1252, found: 208.1257.

Crystal Data of compound 2a



Experimental. Single clear colourless plate-shaped crystals of (**Q119**) were obtained by recrystallisation from .... A suitable crystal (0.21×0.17×0.09) mm^3 was selected and mounted on a MITIGEN holder oil on a SuperNova, Single source at offset, Atlas diffractometer. The crystal was kept at T = 122.98(13) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2016/6 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{28}H_{22}$, M_r = 358.45, triclinic, P-1 (No. 2), a = 9.7638(5) Å, b = 10.0633(5) Å, c = 10.6246(5) Å, α = 100.341(4)°, β = 103.170(4)°, γ = 95.285(4)°, V = 990.28(9) $Å^3$, T = 122.98(13) K, Z = 2, Z' = 1, μ(CuK_α) = 0.511, 21623 reflections measured, 3440 unique (R_{int} = 0.0470) which were used in all calculations. The final wR_2 was 0.0934 (all data) and R_1 was 0.0358 (I > 2(I)).

Compound	**Q119**
Formula	$C_{28}H_{22}$
$D_{calc.}$/ g cm^{-3}	1.202
μ/mm^{-1}	0.511
Formula Weight	358.45
Colour	clear colourless
Shape	plate
Size/mm^3	0.21×0.17×0.09
T/K	122.98(13)
Crystal System	triclinic
Space Group	P-1
a/Å	9.7638(5)
b/Å	10.0633(5)
c/Å	10.6246(5)
α/°	100.341(4)
β/°	103.170(4)
γ/°	95.285(4)
V/$Å^3$	990.28(9)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	CuK_α
Θ_{min}/°	4.368
Θ_{max}/°	66.631
Measured Refl.	21623
Independent Refl.	3440
Reflections Used	2950
R_{int}	0.0470
Parameters	253
Restraints	0
Largest Peak	0.148
Deepest Hole	-0.223
GooF	1.036
wR_2 (all data)	0.0934
wR_2	0.0881
R_1 (all data)	0.0434
R_1	0.0358

Structure Quality Indicators

Reflections:	d min (Cu) 0.84	I/σ 22.3	Rint 4.70%	complete at 2θ=125° 98%
Refinement:	Shift 0.000	Max Peak 0.1	Min Peak -0.2	GooF 1.036

A clear colourless plate-shaped crystal with dimensions 0.21×0.17×0.09 mm^3 was mounted on a MITIGEN holder oil.X-ray diffraction data were collected using a SuperNova, Single source at offset, Atlas diffractometer equipped with a n/a low-temperature device, operating at T = 122.98(13) K.

Data were measured using ω scans scans of 1.0 ° per frame for 1.0 s using CuK_α radiation (micro-focus sealed X-ray tube, n/a kV, n/a mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Agilent).The maximum resolution achieved was Θ = 66.631. °

Cell parameters were retrieved using the CrysAlisPro (Agilent) software and refined using CrysAlisPro (Agilent) on 9100 reflections, 42 % of the observed reflections. Data reduction was performed using the CrysAlisPro (Agilent) software which corrects for Lorentz polarisation. The final completeness is 98.50 out to 66.631 in Θ. The absorption coefficient μ of this material is 0.511 at this wavelength (λ = 1.54184) and the minimum and maximum transmissions are 0.958 and 0.983.

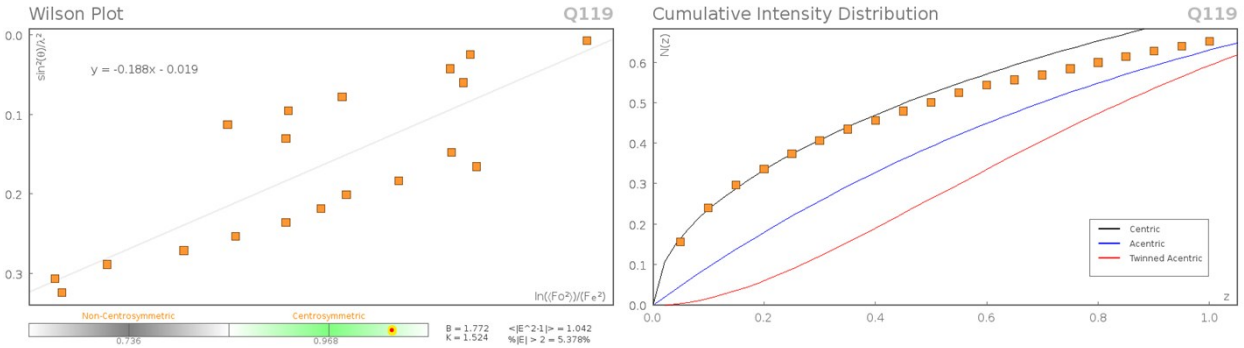
The structure was solved in the space group P-1 (# 2) by Intrinsic Phasing using the **ShelXT** (Sheldrick, 2015) structure solution program and refined by Least Squares using version 2016/6 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

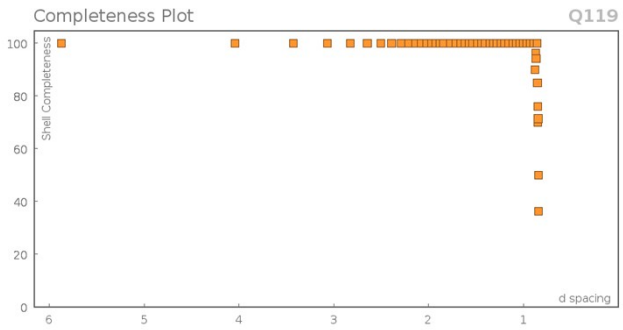
_refine_special_details: ?

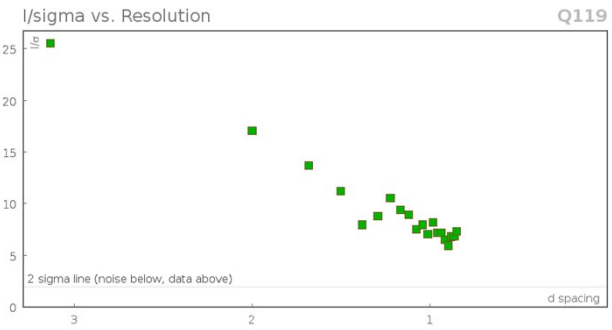
_exptl_absorpt_special_details: ?

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

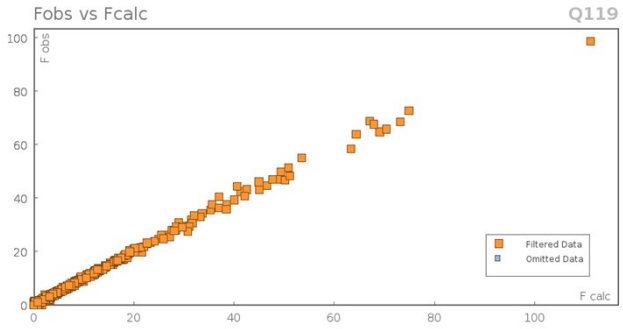
Data Plots: Diffraction Data

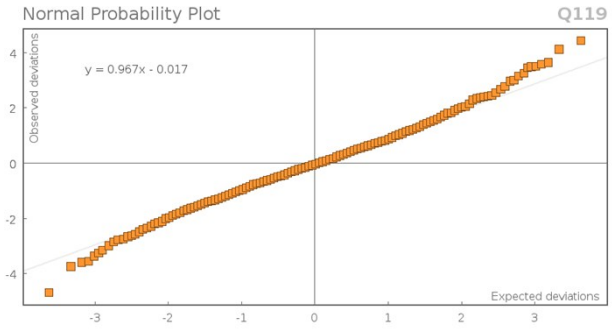






Data Plots: Refinement and Data





Reflection Statistics

Total reflections (after filtering)	21623	Unique reflections	3440
Completeness	0.985	Mean I/σ	22.28
hkl_{max} collected	(11, 11, 12)	hkl_{min} collected	(-11, -11, -12)
hkl_{max} used	(11, 11, 12)	hkl_{min} used	(-11, -11, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	10.12	d_{min} used	0.84
Friedel pairs	3194	Friedel pairs merged	1
Inconsistent equivalents	7	R_{int}	0.047
R_{sigma}	0.0261	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(1228, 1449, 1285, 1061, 756, 500, 245, 93, 12, 4, 1)	Maximum multiplicity	19
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Images of the Crystal on the Diffractometer

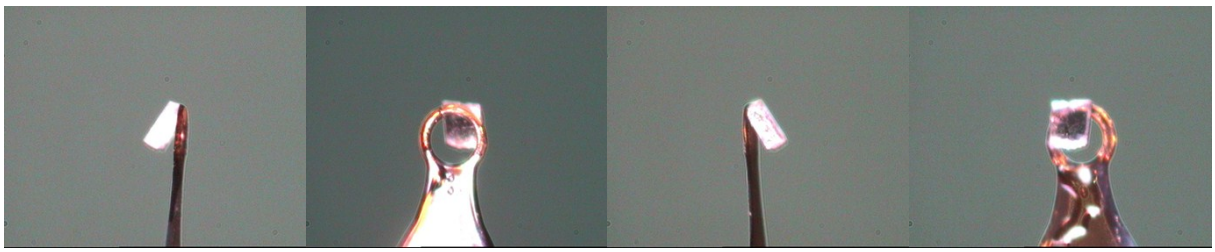


Table 1: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **Q119**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
C(17)	3313.0(13)	3322.8(12)	8409.8(11)	22.1(3)
C(7)	5013.9(13)	6406.5(12)	6577.2(11)	22.0(3)
C(2)	6541.3(13)	6884.0(12)	6733.8(11)	21.6(3)
C(8)	3954.6(13)	7190.0(12)	5901.2(11)	22.1(3)
C(16)	4781.7(12)	3409.6(12)	8223.5(11)	21.9(3)
C(18)	2734.3(13)	4481.6(13)	8861.2(11)	24.8(3)
C(9)	4238.6(13)	8605.2(13)	6073.9(11)	25.2(3)
C(23)	5667.9(12)	2386.2(12)	8694.3(11)	21.9(3)
C(22)	2464.3(13)	2056.7(13)	8127.7(11)	24.3(3)
C(3)	6996.6(13)	7258.8(12)	5671.1(11)	23.8(3)
C(24)	6529.3(13)	1765.9(13)	7948.4(12)	24.7(3)
C(15)	5321.4(13)	4367.2(12)	7643.8(11)	23.0(3)
C(21)	1075.6(13)	1959.9(14)	8243.1(12)	28.1(3)
C(19)	1347.1(14)	4381.9(14)	8973.4(12)	29.4(3)
C(1)	7566.8(13)	6987.3(12)	7921.0(12)	25.1(3)
C(28)	5670.9(13)	2025.3(12)	9909.4(12)	25.2(3)
C(12)	1601.9(14)	7287.3(14)	4581.9(12)	28.6(3)
C(6)	8983.5(14)	7420.3(13)	8024.4(12)	29.0(3)
C(14)	4527.8(13)	5325.5(12)	7033.5(11)	23.1(3)
C(25)	7372.1(13)	830.3(13)	8401.5(13)	28.4(3)
C(4)	8411.1(14)	7676.8(13)	5772.9(12)	27.8(3)
C(20)	505.6(13)	3123.2(14)	8657.8(12)	29.5(3)
C(11)	1892.2(14)	8695.2(14)	4792.6(12)	29.2(3)
C(10)	3218.1(14)	9350.9(13)	5525.9(12)	28.0(3)
C(13)	2619.1(13)	6539.9(13)	5120.9(11)	24.7(3)
C(27)	6544.4(14)	1121.7(13)	10377.2(13)	29.7(3)
C(5)	9417.6(14)	7758.7(14)	6952.8(13)	30.3(3)
C(26)	7393.3(13)	515.8(13)	9624.1(13)	30.6(3)

Table 2: Anisotropic Displacement Parameters (×10⁴) **Q119**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(17)	27.1(6)	23.1(6)	15.2(5)	6.5(4)	2.3(4)	2.4(5)
C(7)	27.3(6)	21.4(6)	17.2(5)	3.8(5)	5.7(5)	3.3(5)
C(2)	27.3(6)	15.9(6)	22.2(6)	5.0(5)	6.1(5)	5.0(5)
C(8)	26.3(6)	24.7(7)	18.1(6)	6.9(5)	8.7(5)	4.7(5)
C(16)	25.1(6)	21.4(6)	16.4(5)	2.4(5)	2.0(5)	0.3(5)
C(18)	30.5(7)	22.5(7)	20.6(6)	5.0(5)	5.1(5)	1.5(5)
C(9)	29.4(7)	25.7(7)	21.2(6)	5.4(5)	7.4(5)	2.9(5)
C(23)	22.4(6)	18.4(6)	21.5(6)	3.5(5)	1.7(5)	-3.2(5)
C(22)	28.7(7)	22.5(6)	20.6(6)	6.1(5)	2.8(5)	3.0(5)
C(3)	30.1(7)	20.1(6)	21.0(6)	5.2(5)	4.3(5)	5.4(5)
C(24)	24.5(6)	24.8(7)	24.0(6)	6.0(5)	5.5(5)	-1.3(5)
C(15)	23.8(6)	23.2(6)	21.3(6)	4.7(5)	5.0(5)	1.6(5)
C(21)	28.6(7)	28.6(7)	24.4(6)	8.9(5)	0.8(5)	-1.9(5)
C(19)	34.3(7)	31.2(7)	25.3(6)	8.1(5)	8.2(5)	11.2(6)
C(1)	29.6(7)	24.9(7)	22.2(6)	7.9(5)	6.5(5)	5.0(5)
C(28)	29.1(7)	22.6(7)	23.1(6)	4.7(5)	6.5(5)	0.3(5)
C(12)	25.3(6)	38.8(8)	23.5(6)	10.0(5)	6.5(5)	5.1(6)
C(6)	28.3(7)	30.4(7)	26.7(6)	7.9(5)	1.9(5)	5.2(6)
C(14)	23.4(6)	24.9(7)	20.5(6)	5.3(5)	4.5(5)	2.3(5)
C(25)	23.1(6)	26.3(7)	35.3(7)	4.6(5)	7.8(5)	2.5(5)
C(4)	33.1(7)	26.8(7)	27.7(6)	9.2(5)	12.5(5)	5.9(6)
C(20)	24.1(6)	40.9(8)	24.8(6)	11.9(6)	4.5(5)	5.1(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(11)	32.5(7)	36.4(8)	25.2(6)	12.7(5)	10.7(5)	15.4(6)
C(10)	37.8(7)	24.8(7)	25.8(6)	8.2(5)	12.1(5)	9.5(6)
C(13)	28.0(7)	25.1(7)	22.3(6)	6.6(5)	8.1(5)	1.9(5)
C(27)	33.9(7)	27.6(7)	26.0(6)	10.3(5)	2.2(5)	0.5(6)
C(5)	24.5(7)	31.5(7)	36.1(7)	9.3(6)	8.6(5)	3.7(6)
C(26)	26.8(7)	25.4(7)	37.6(7)	10.7(6)	1.0(5)	3.2(5)

Table 3: Bond Lengths in Å for **Q119**.

Atom	Atom	Length/Å
C(17)	C(16)	1.4885(17)
C(17)	C(18)	1.3975(17)
C(17)	C(22)	1.3983(18)
C(7)	C(2)	1.4863(17)
C(7)	C(8)	1.4907(16)
C(7)	C(14)	1.3574(17)
C(2)	C(3)	1.4020(17)
C(2)	C(1)	1.4009(16)
C(8)	C(9)	1.3961(18)
C(8)	C(13)	1.4040(17)
C(16)	C(23)	1.4871(16)
C(16)	C(15)	1.3614(17)
C(18)	C(19)	1.3826(18)
C(9)	C(10)	1.3875(17)
C(23)	C(24)	1.3956(17)
C(23)	C(28)	1.4019(17)

Atom	Atom	Length/Å
C(22)	C(21)	1.3851(18)
C(3)	C(4)	1.3801(18)
C(24)	C(25)	1.3857(17)
C(15)	C(14)	1.4436(16)
C(21)	C(20)	1.3860(19)
C(19)	C(20)	1.386(2)
C(1)	C(6)	1.3849(18)
C(28)	C(27)	1.3833(17)
C(12)	C(11)	1.386(2)
C(12)	C(13)	1.3832(18)
C(6)	C(5)	1.3872(19)
C(25)	C(26)	1.3874(19)
C(4)	C(5)	1.3895(18)
C(11)	C(10)	1.3845(19)
C(27)	C(26)	1.3853(19)

Table 4: Bond Angles in ° for **Q119**.

Atom	Atom	Atom	Angle/°
C(18)	C(17)	C(16)	121.96(11)
C(18)	C(17)	C(22)	117.89(11)
C(22)	C(17)	C(16)	120.15(11)
C(2)	C(7)	C(8)	117.53(10)
C(14)	C(7)	C(2)	124.25(10)
C(14)	C(7)	C(8)	118.21(11)
C(3)	C(2)	C(7)	119.87(10)
C(1)	C(2)	C(7)	122.41(11)
C(1)	C(2)	C(3)	117.71(11)
C(9)	C(8)	C(7)	120.81(11)
C(9)	C(8)	C(13)	117.91(11)
C(13)	C(8)	C(7)	121.22(11)
C(23)	C(16)	C(17)	117.21(10)
C(15)	C(16)	C(17)	122.85(11)
C(15)	C(16)	C(23)	119.94(11)
C(19)	C(18)	C(17)	120.92(12)
C(10)	C(9)	C(8)	121.07(12)
C(24)	C(23)	C(16)	121.15(10)
C(24)	C(23)	C(28)	118.04(11)
C(28)	C(23)	C(16)	120.81(11)
C(21)	C(22)	C(17)	121.00(12)
C(4)	C(3)	C(2)	121.38(11)
C(25)	C(24)	C(23)	120.96(11)
C(16)	C(15)	C(14)	125.11(11)
C(22)	C(21)	C(20)	120.33(12)
C(18)	C(19)	C(20)	120.54(12)

Atom	Atom	Atom	Angle/°
C(6)	C(1)	C(2)	120.76(11)
C(27)	C(28)	C(23)	120.87(12)
C(13)	C(12)	C(11)	120.36(12)
C(1)	C(6)	C(5)	120.66(11)
C(7)	C(14)	C(15)	128.74(11)
C(24)	C(25)	C(26)	120.20(12)
C(3)	C(4)	C(5)	120.18(12)
C(21)	C(20)	C(19)	119.26(12)
C(10)	C(11)	C(12)	119.65(11)
C(11)	C(10)	C(9)	120.14(12)
C(12)	C(13)	C(8)	120.83(12)
C(28)	C(27)	C(26)	120.29(12)
C(6)	C(5)	C(4)	119.28(12)
C(27)	C(26)	C(25)	119.58(12)

Table 5: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Q119**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H(18)	3290.03	5331.52	9089.34	30
H(9)	5126.22	9055.46	6564.19	30
H(22)	2837.93	1267.48	7858.6	29
H(3)	6331.52	7224.91	4880.92	29
H(24)	6537.83	1983.72	7135.53	30
H(15)	6276.03	4407.2	7640.6	28
H(21)	522.97	1110.16	8041.19	34
H(19)	975.37	5165.65	9262.91	35
H(1)	7292.98	6762.63	8647.98	30
H(28)	5077.7	2398.47	10407.56	30
H(12)	718.32	6842.75	4075.35	34
H(6)	9650.56	7484.74	8820.24	35
H(14)	3552	5183.05	6940.35	28
H(25)	7925.26	412.01	7884.29	34
H(4)	8691.39	7904.36	5049.82	33
H(20)	-430.8	3060.19	8723.57	35
H(11)	1200.08	9196.71	4443.36	35
H(10)	3425.18	10293.22	5651.37	34
H(13)	2415.86	5594.84	4964.47	30
H(27)	6561.85	919.96	11200.88	36
H(5)	10371.86	8037.32	7023.33	36
H(26)	7973.65	-97.98	9936.18	37

References:

1. Cheng, J. S.; Tang, L. H.; Xu, J. Y. *Adv. Synth. Catal.* **2010**, 352, 3275.

2. Volger, H. C. *Wiley* **1967**, 86, 677-686.

3. Itami, K.; Ushiogi, Y.; Nokami, T.; Ohashi, Y.; Yoshida, J.-I. *Org. Lett.*, **2004**, 6, 3695–3698.

Wang, Z.; Zhang, G.; Guzei, I.; Verkade, J. G. *J. Org. Chem.* **2001**, *66*, 3521.

4. Wang, Z.; Zhang, G.; Guzei, I.; Verkade, J. G. *J. Org. Chem.* **2001**, *66*, 3521.

5. Marnell, M. W.; Li, B.; Zhou, T.; Jespersen, K. K.; Brennessel, W. W.; Emge, T. J.; Goldman, A. S.; Jones, W. D. *J. Am. Chem. Soc*. **2017**, 139, 8977-8989.

6. Parrish, J. P.; Jung. Y. C.; Floyd, R. J.; Jung, K. W. *Tetrahedron Lett.* **2002**, 43, 7899-7902.

7. Mulla, S. A. R.; Chavan, S. S.; Pathan, M. Y.; Inamdar, S. M.; Shaikh, T. M. Y. *RSC Adv.* **2015**, 5, 24675-24680.

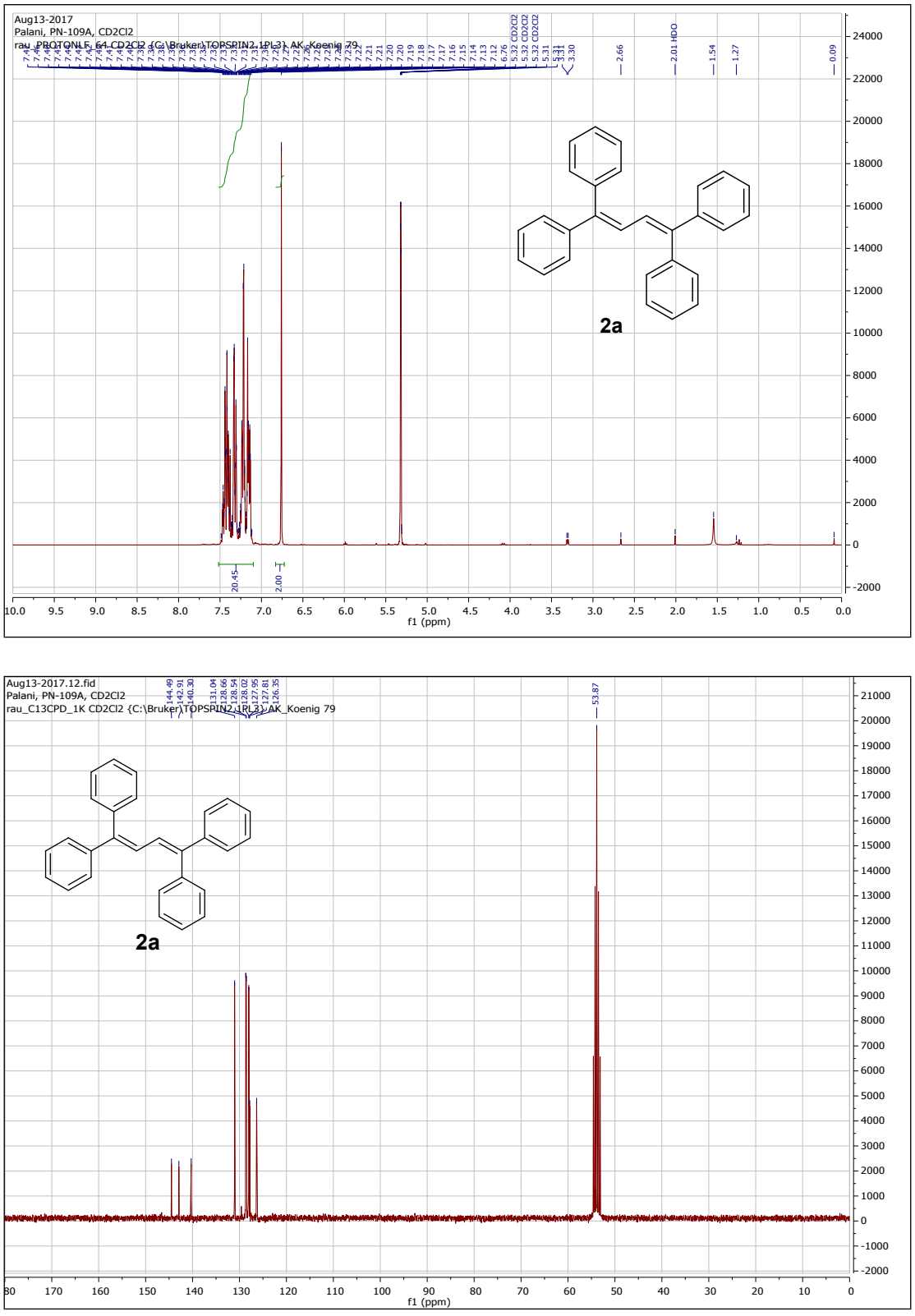


Figure S1. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **2a** in CD_2Cl_2.

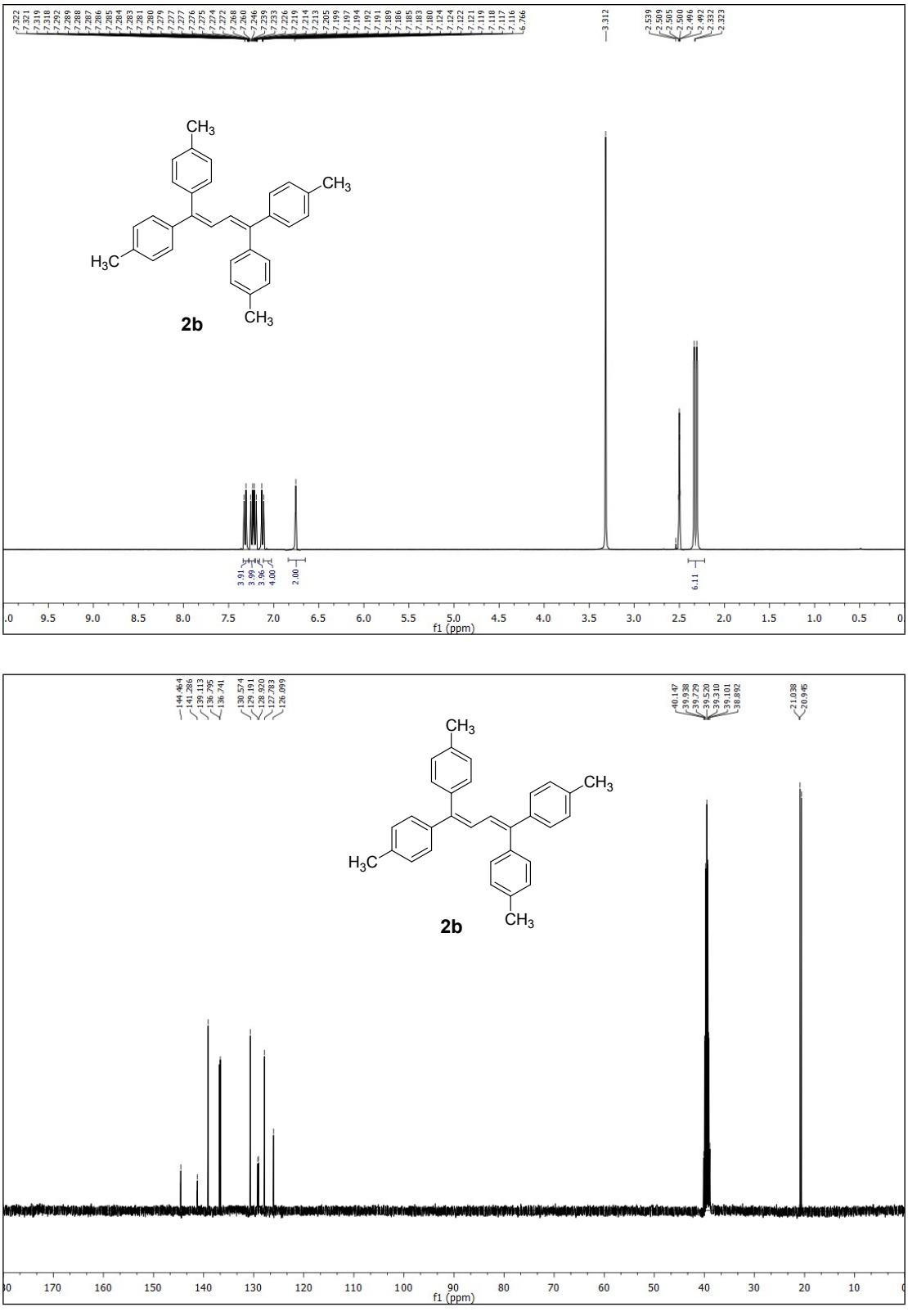


Figure S2. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **2b** in DMSO-d_6.

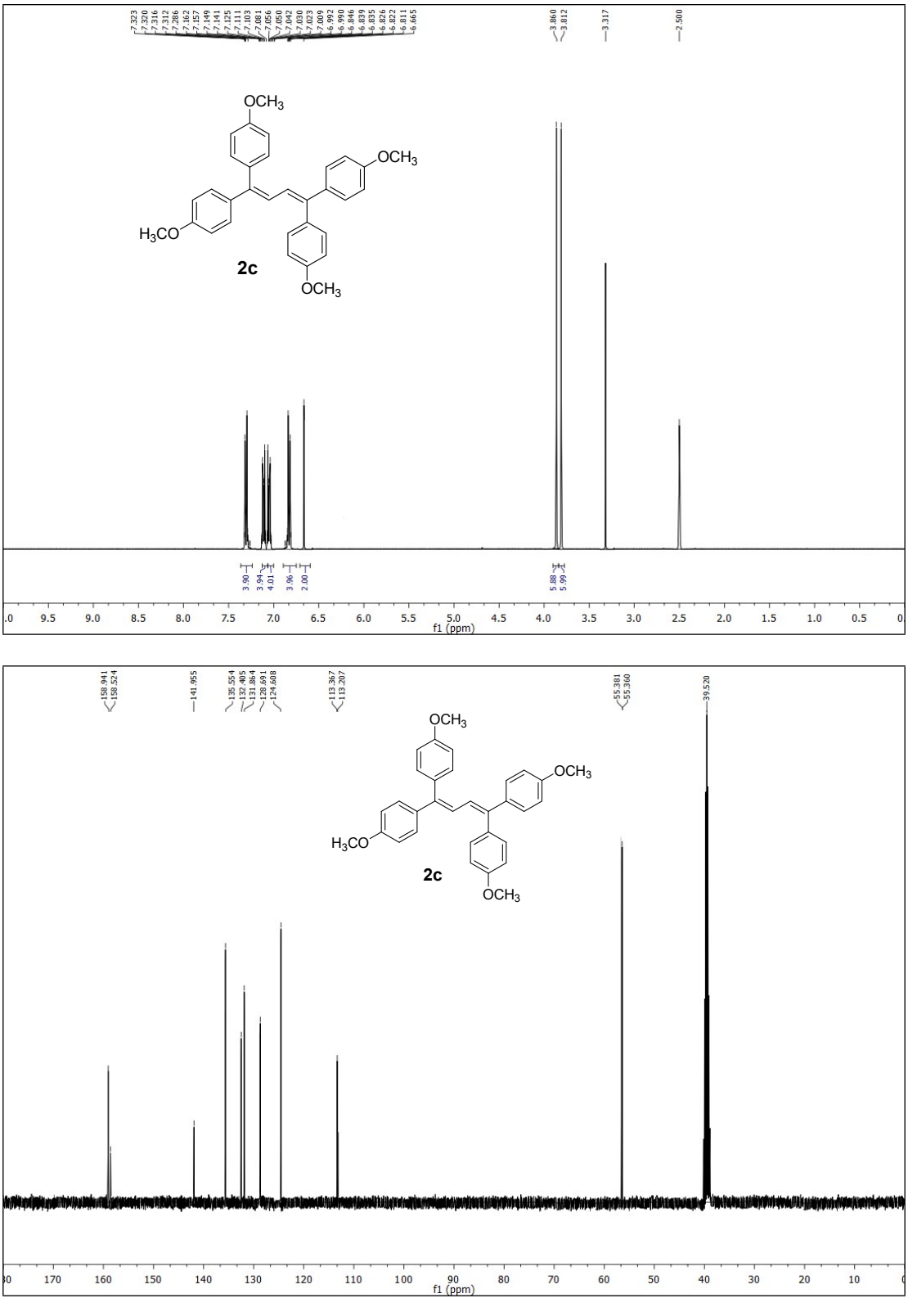
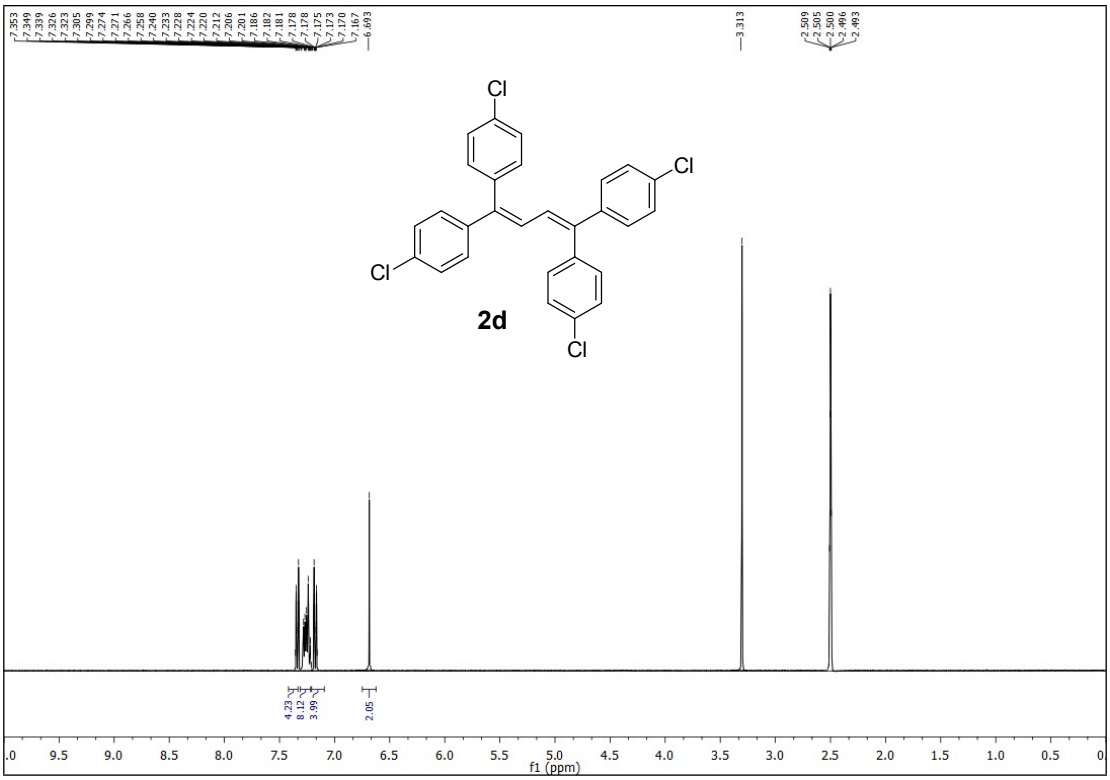


Figure S3. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **2c** in DMSO-d_6.



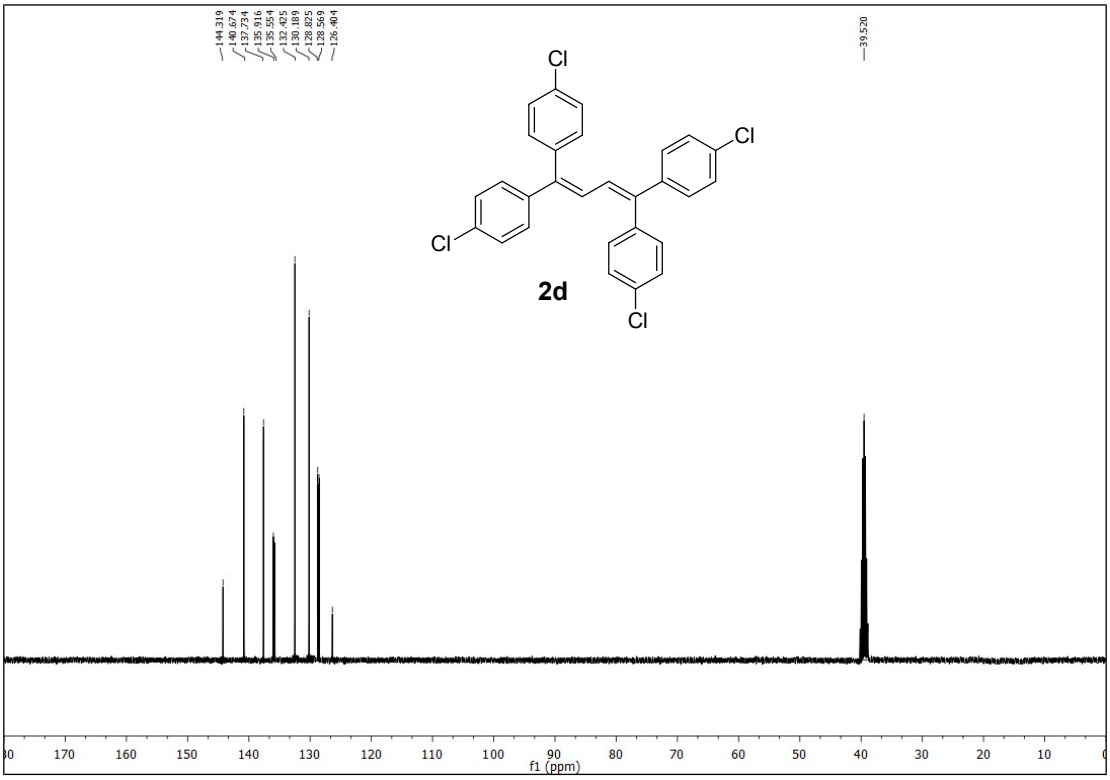


Figure S4. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **2d** in DMSO-d_6.

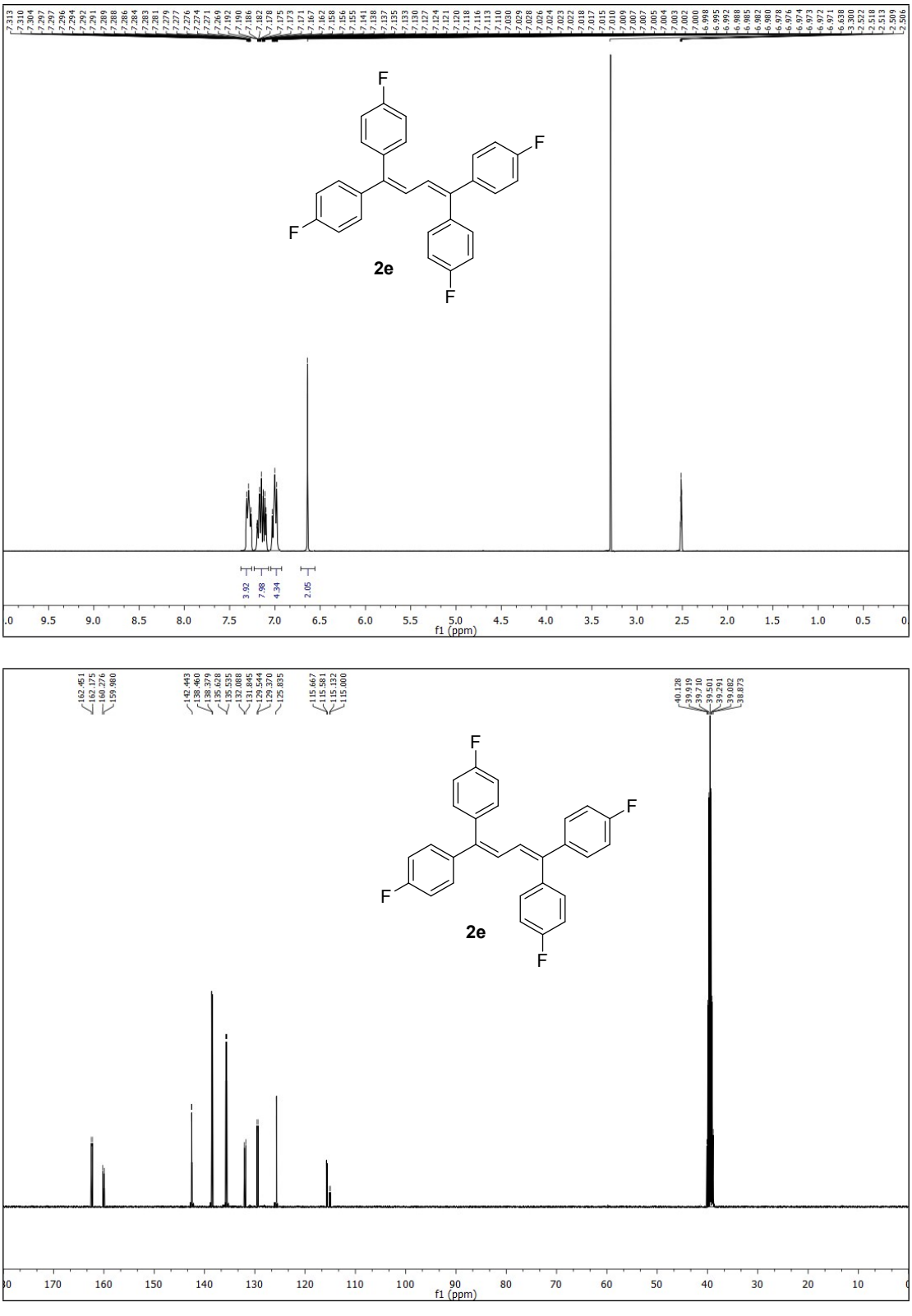


Figure S5. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **2e** in DMSO-d_6.

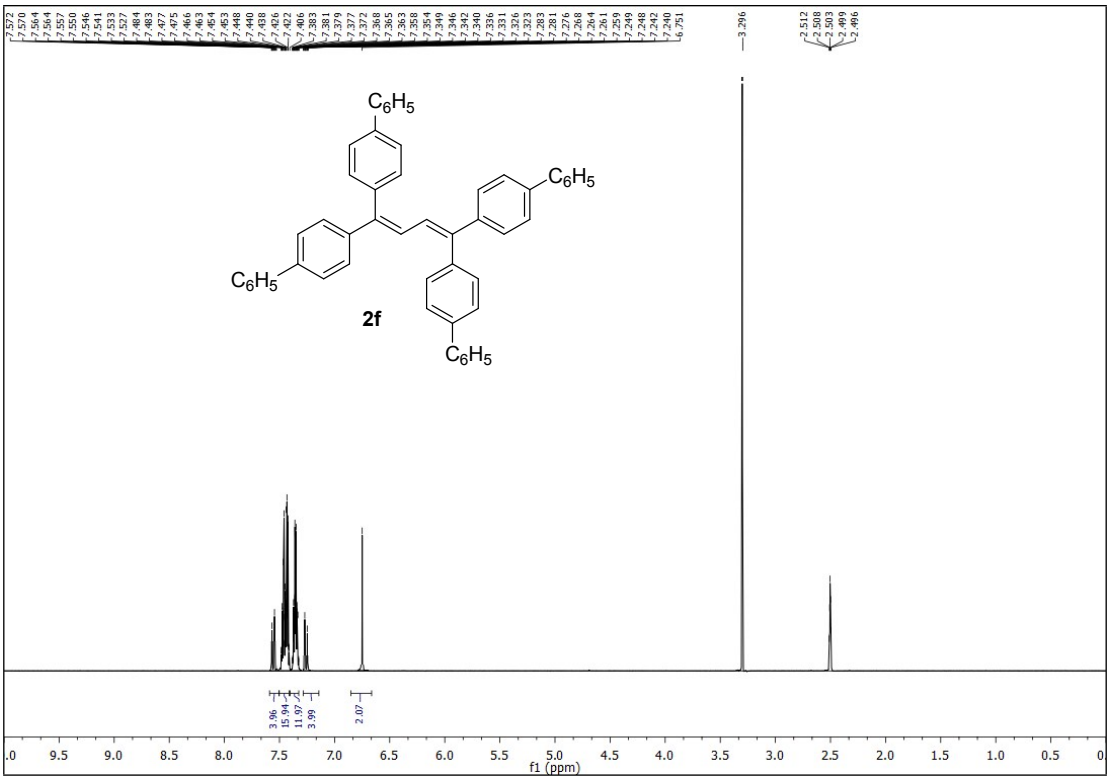


Figure S6. ^{1}H (300 MHz) NMR spectra of **2f** in DMSO-d_6.

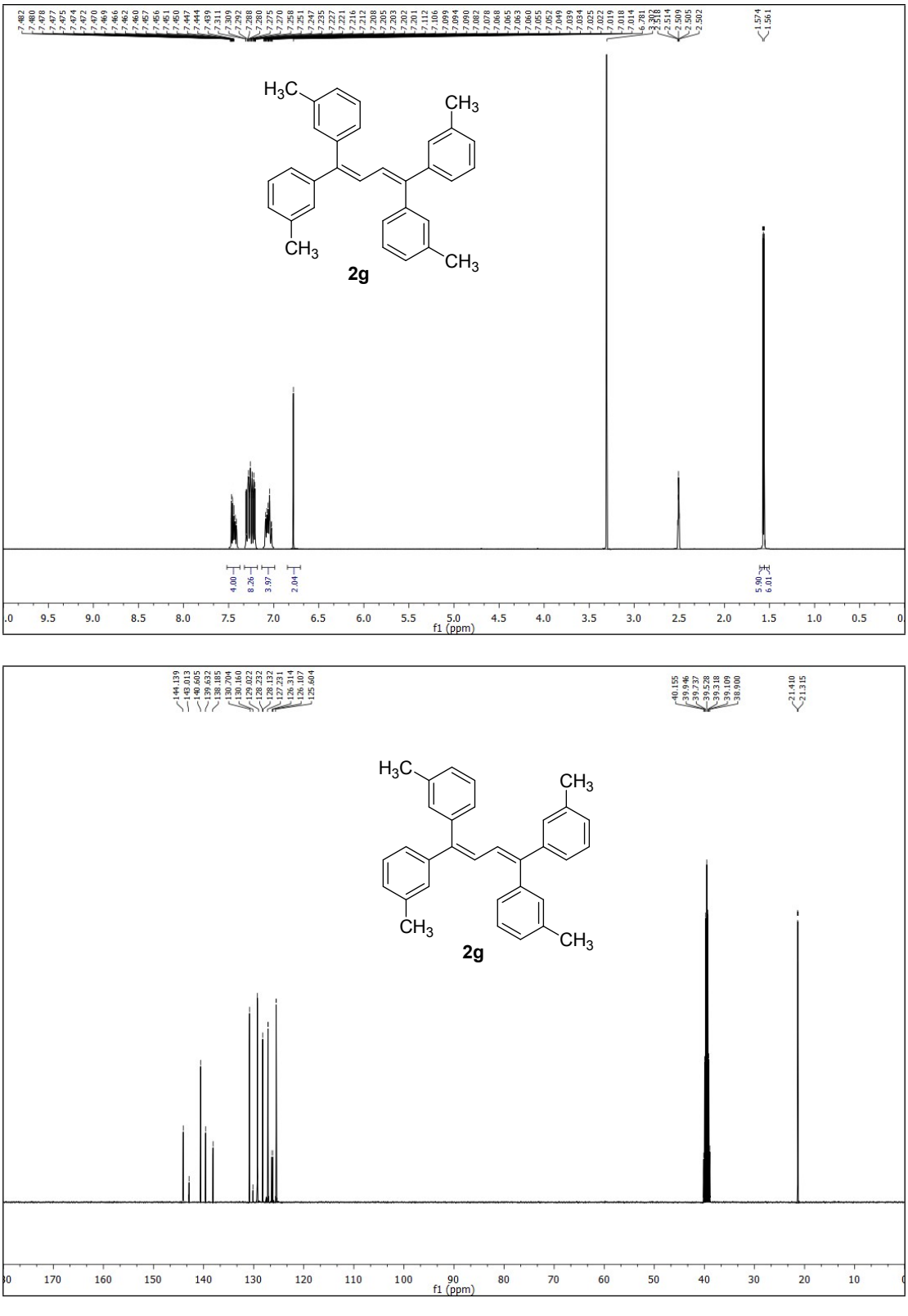


Figure S7. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **2g** in DMSO-d_6.

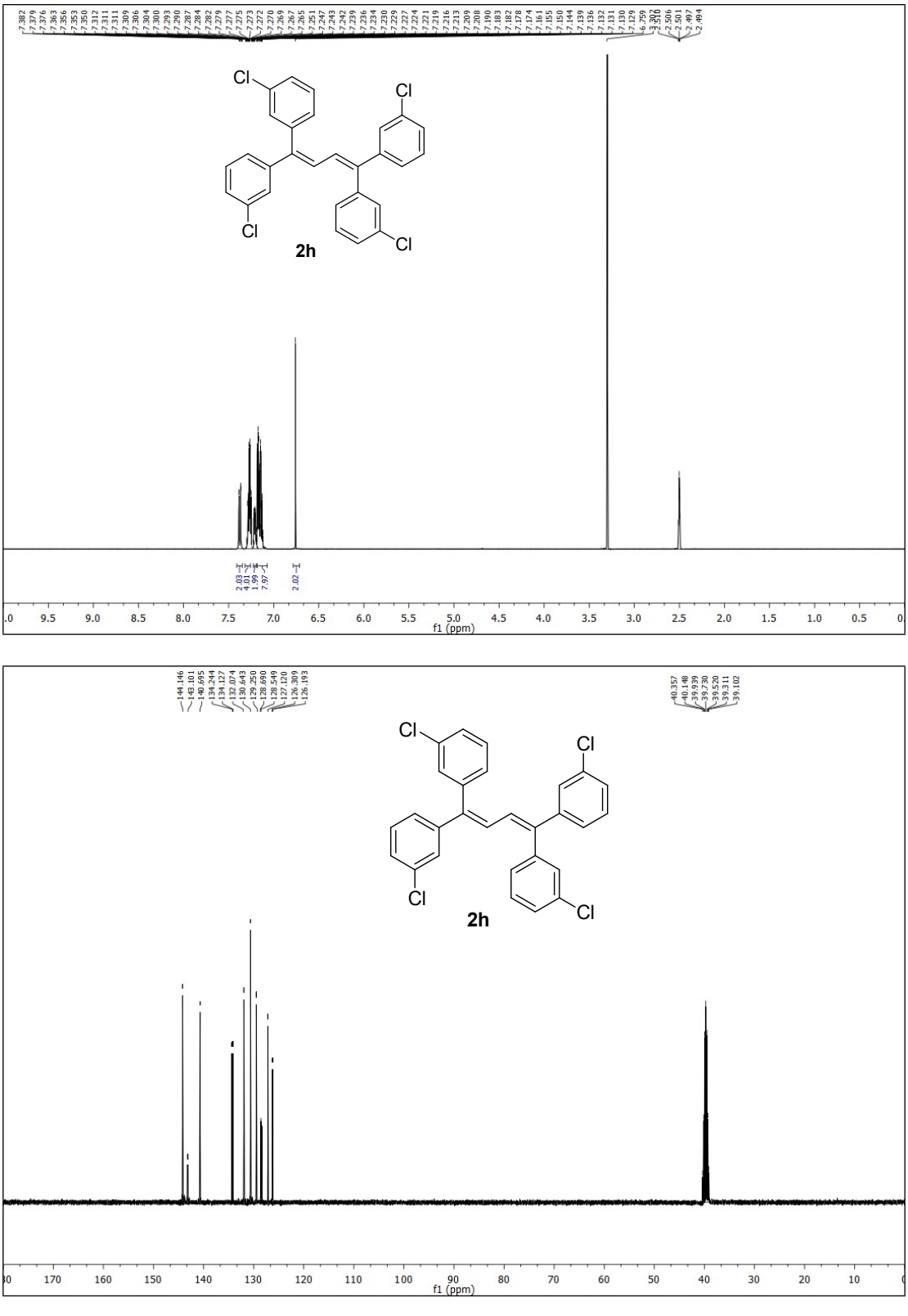


Figure S8. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **2h** in DMSO-d_6.

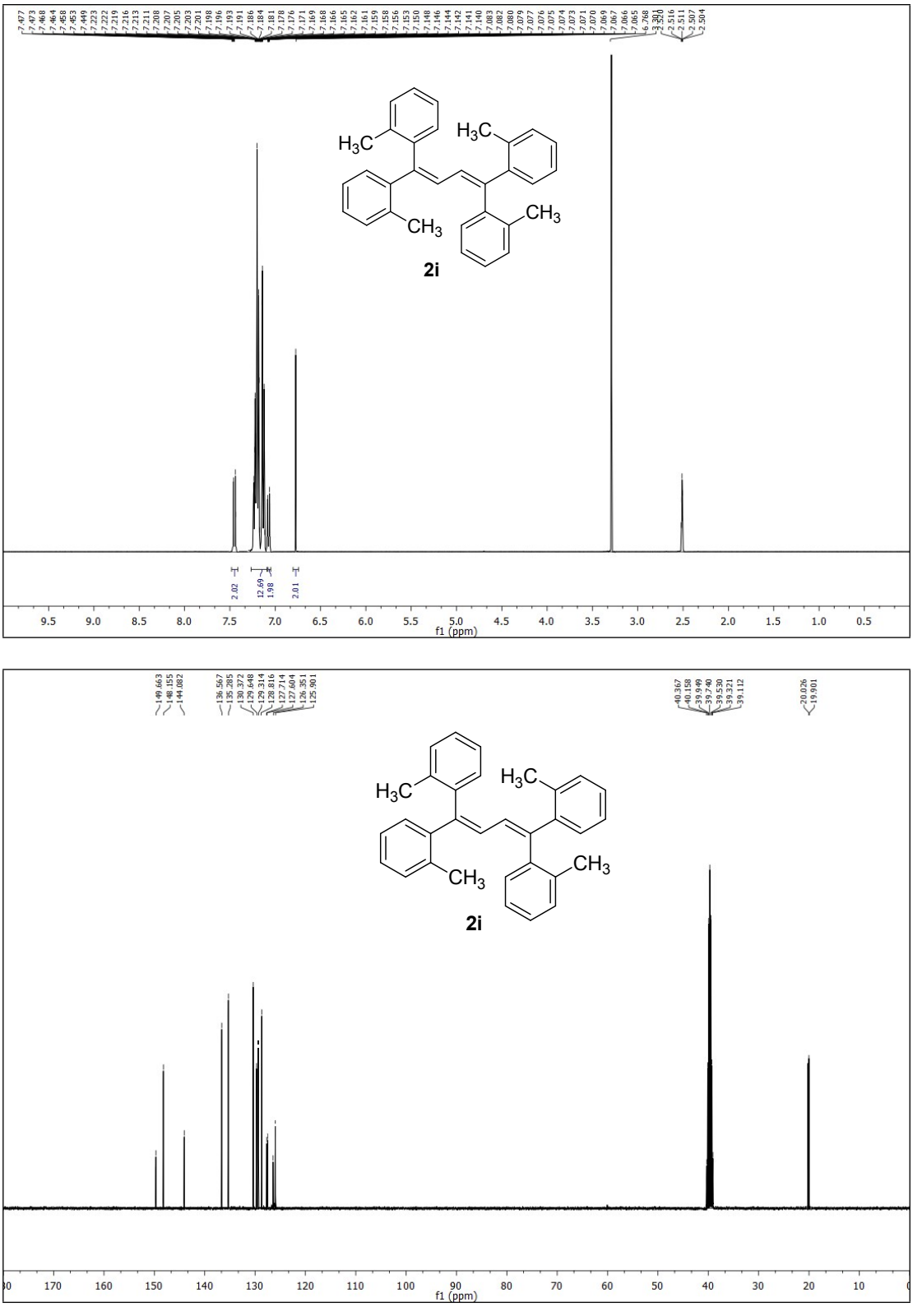


Figure S9. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **2i** in DMSO-d_6.

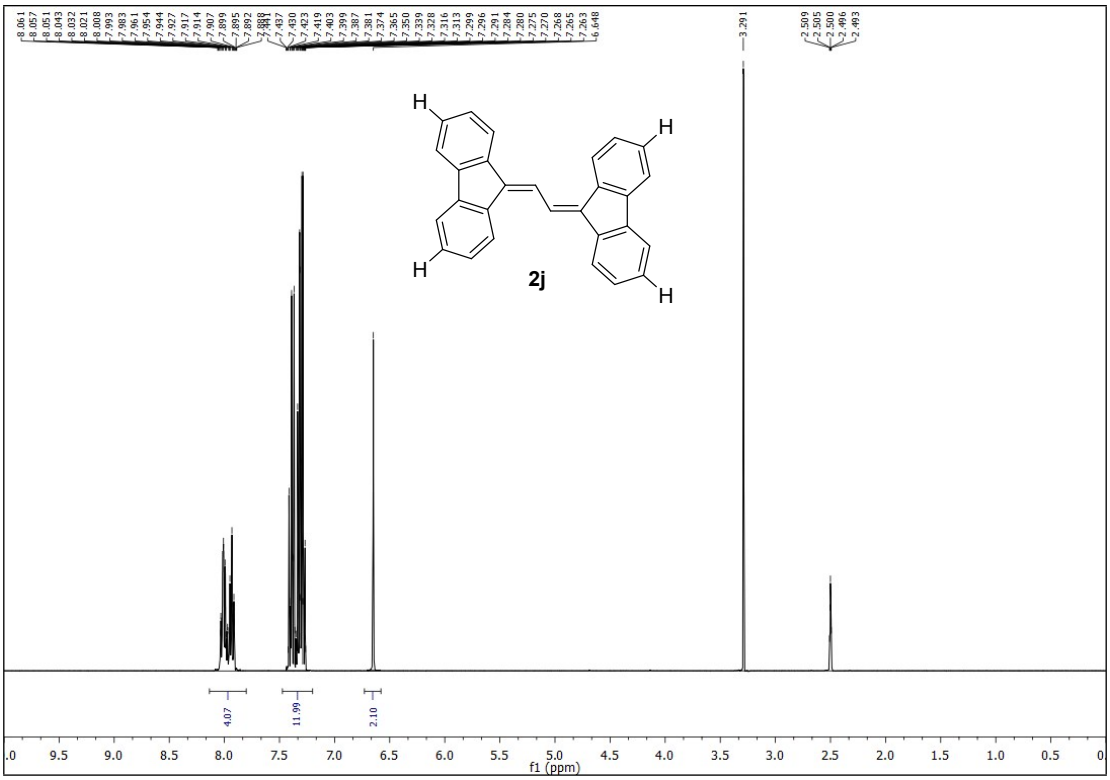


Figure S10. ^{1}H (300 MHz) NMR spectra of **2j** in DMSO-d_6.

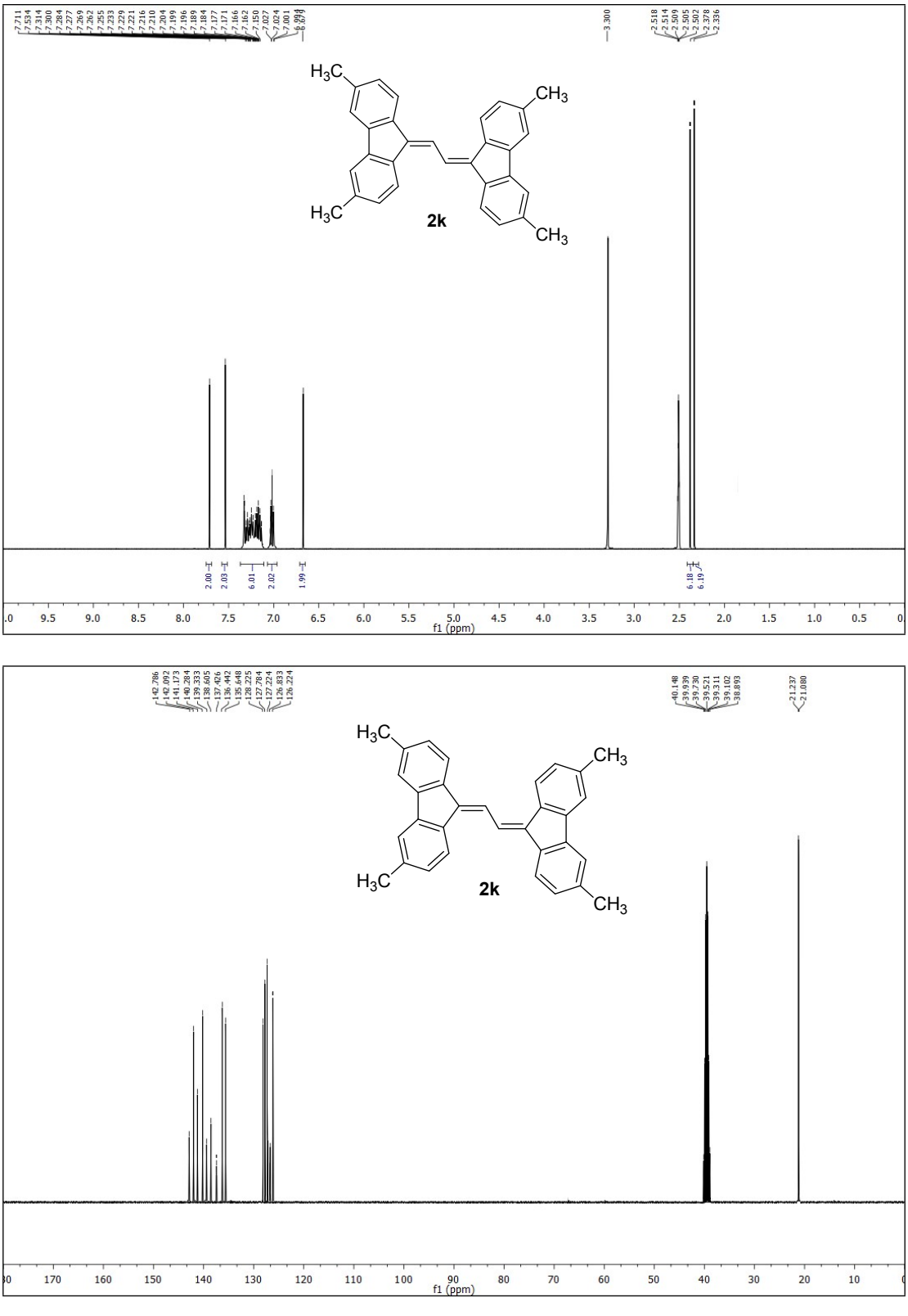


Figure S11. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **2k** in DMSO-d_6.

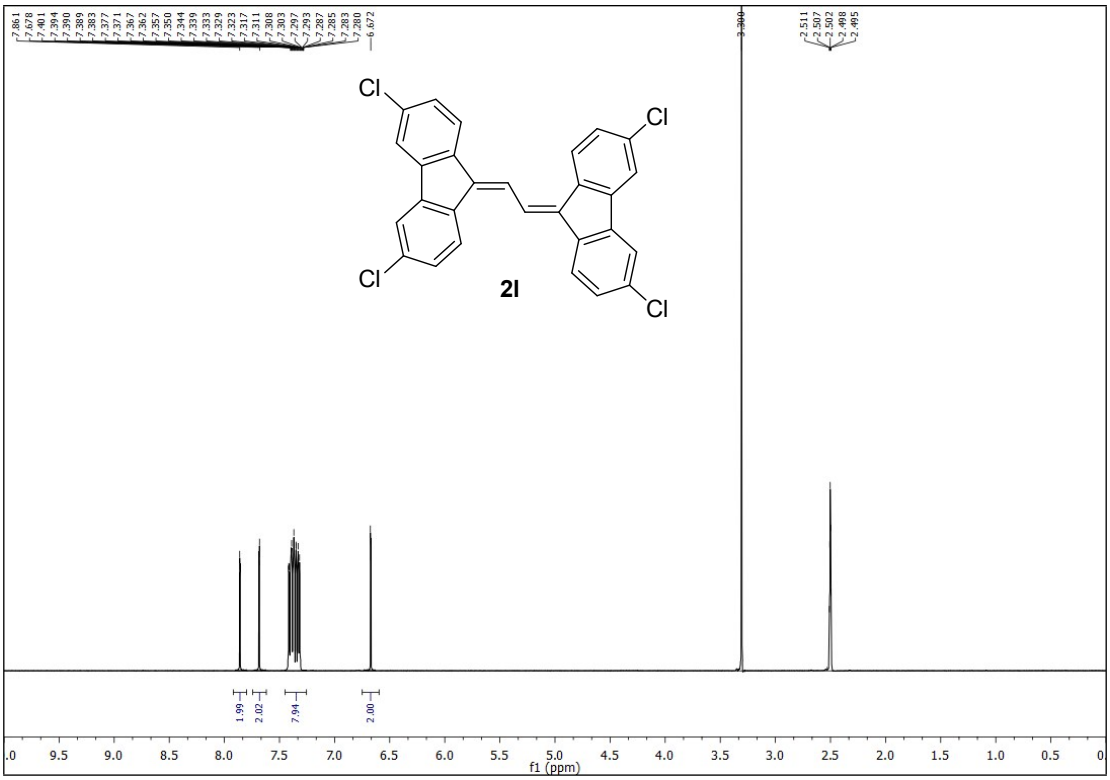


Figure S12. ^{1}H (300 MHz) NMR spectra of **2l** in DMSO-d_6.

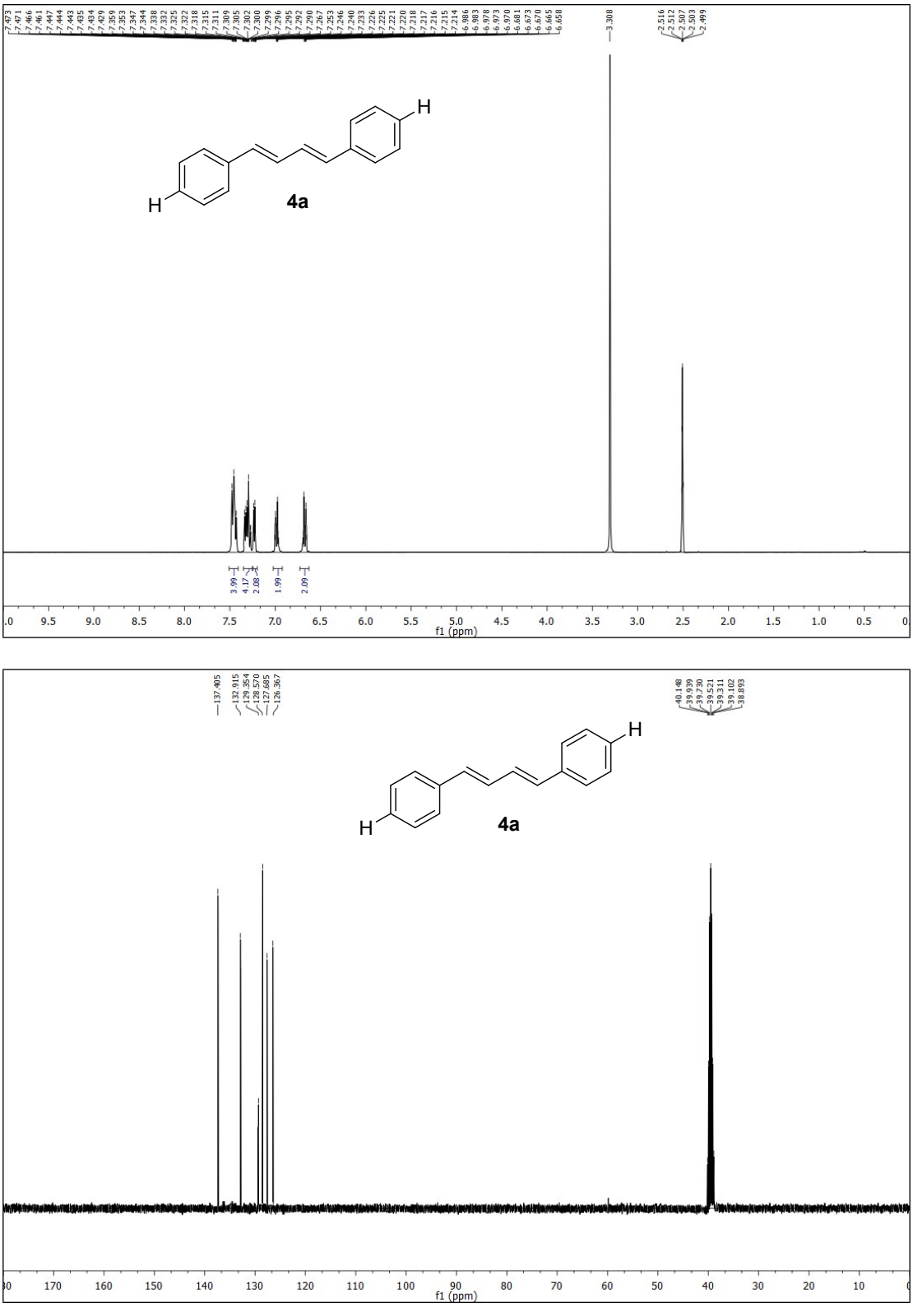


Figure S13. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **4a** in DMSO-d_6.

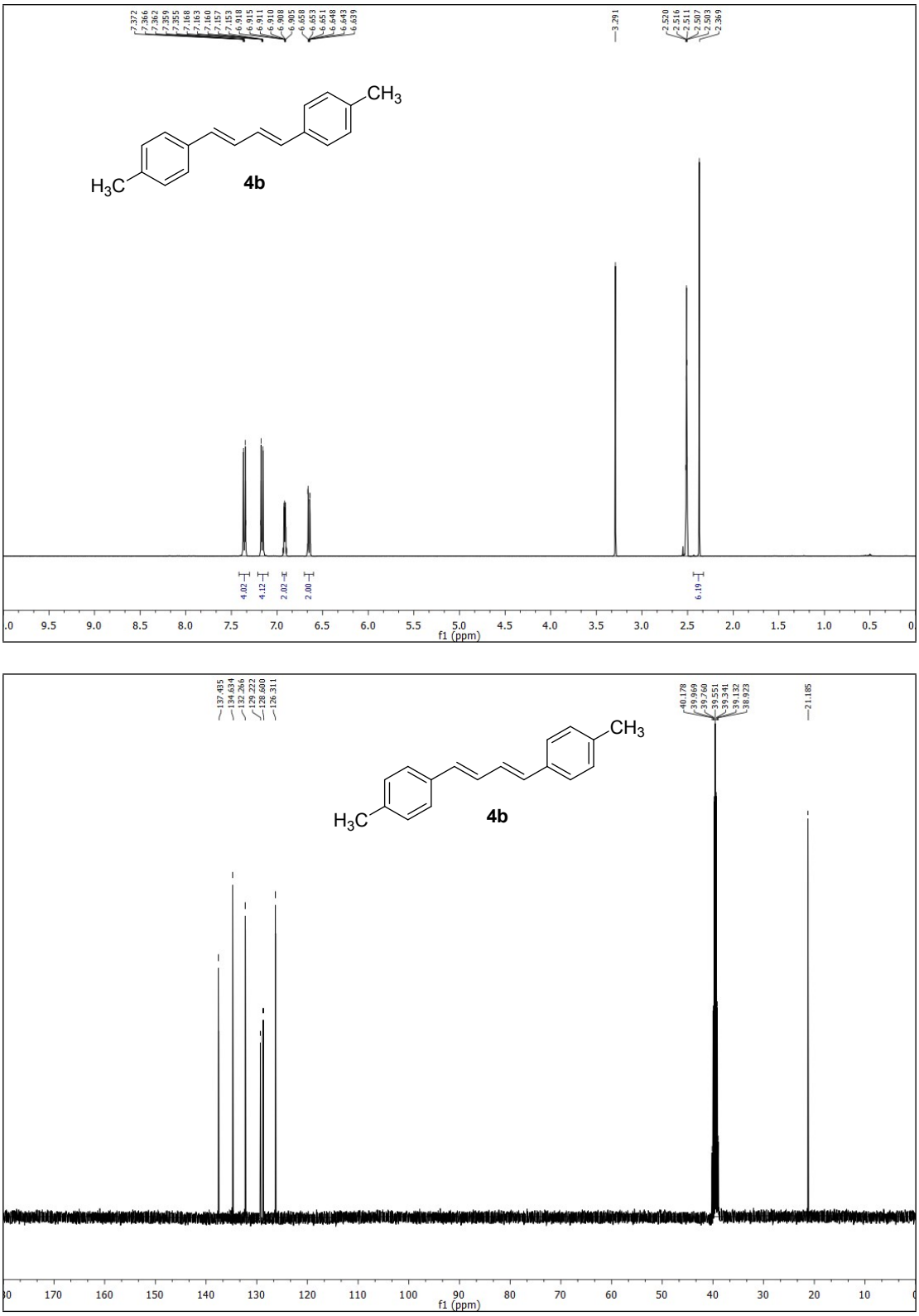


Figure S14. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **4b** in DMSO-d_6.

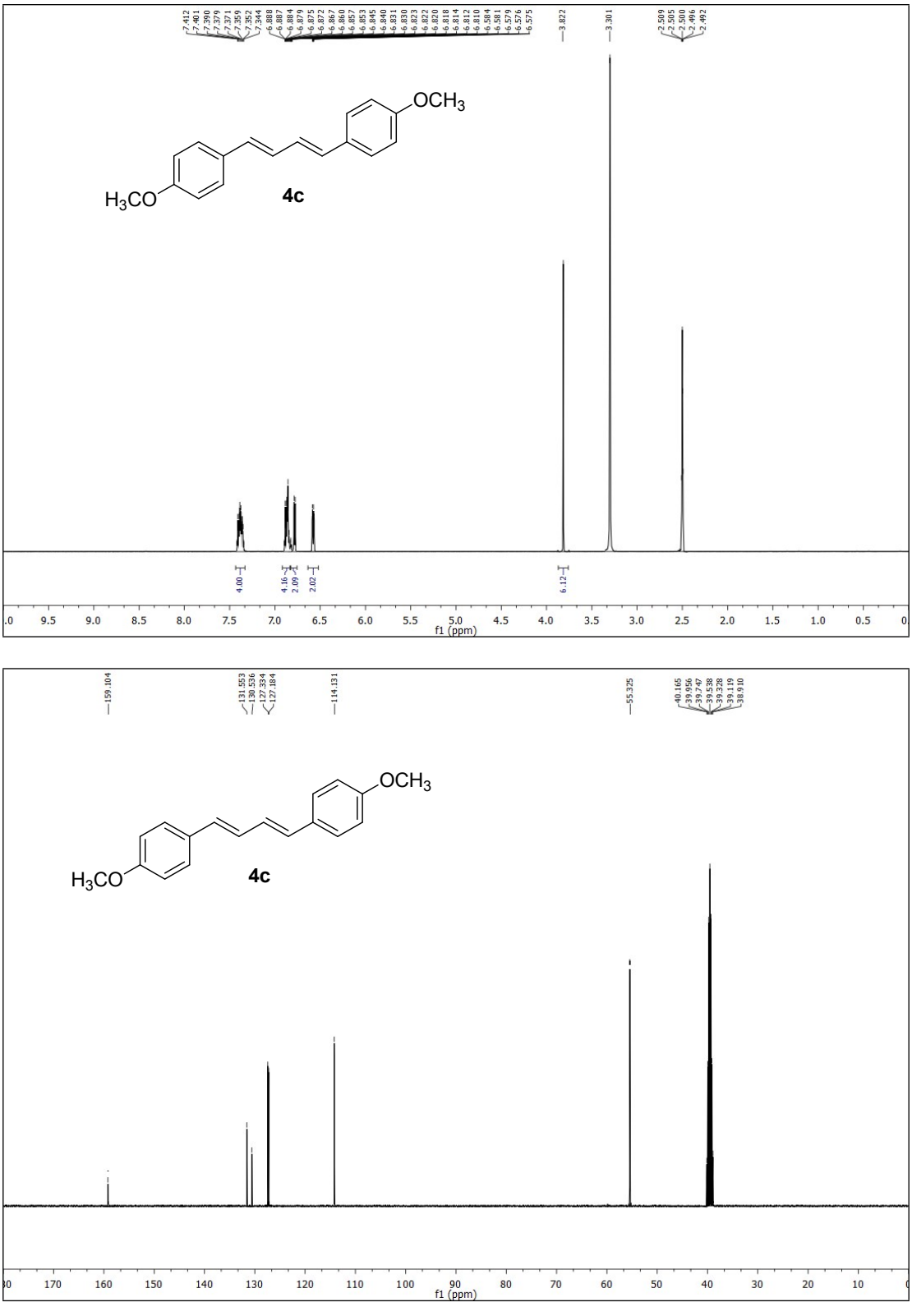


Figure S15. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **4c** in DMSO-d_6.

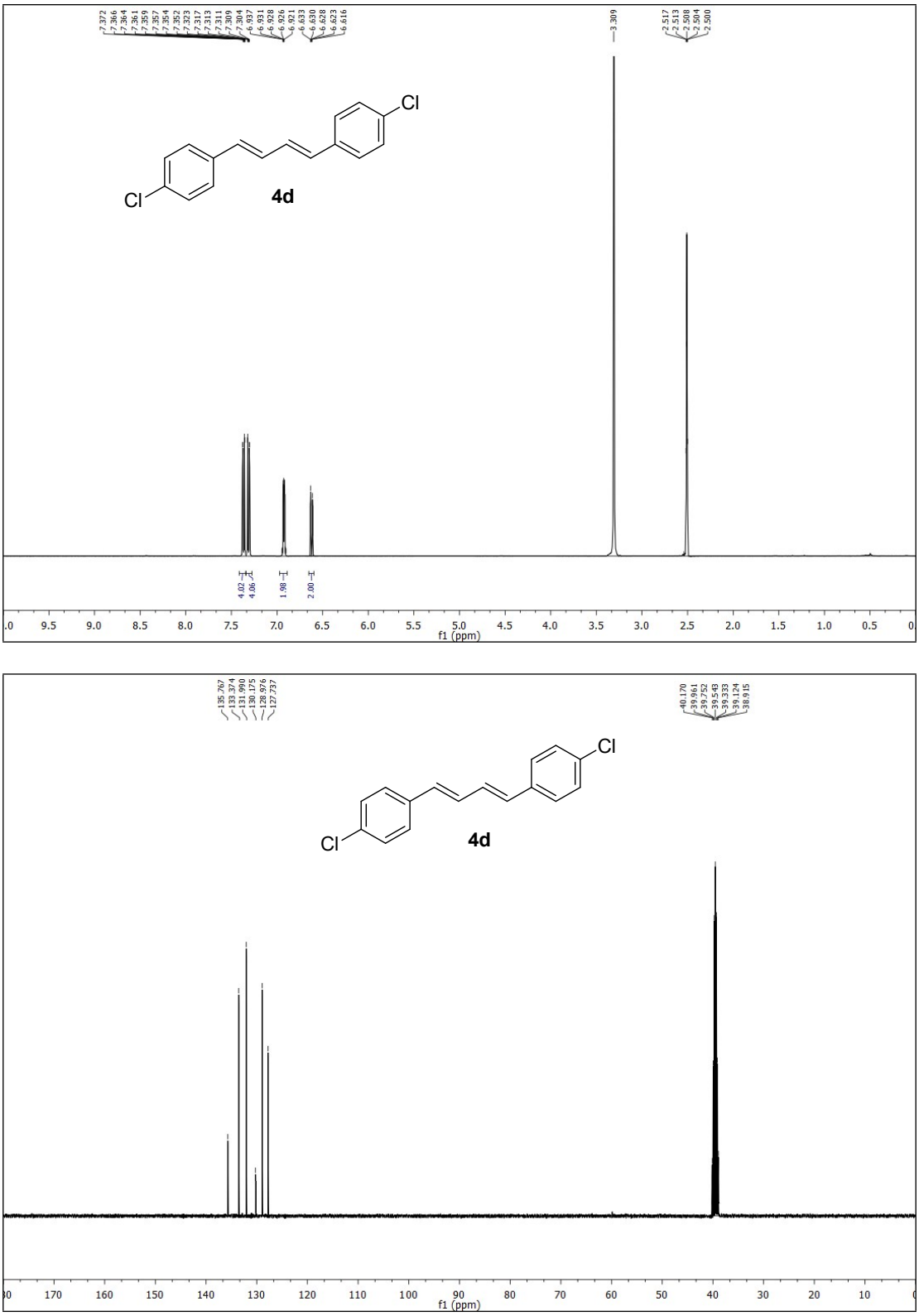


Figure S16. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **4d** in DMSO-d_6.

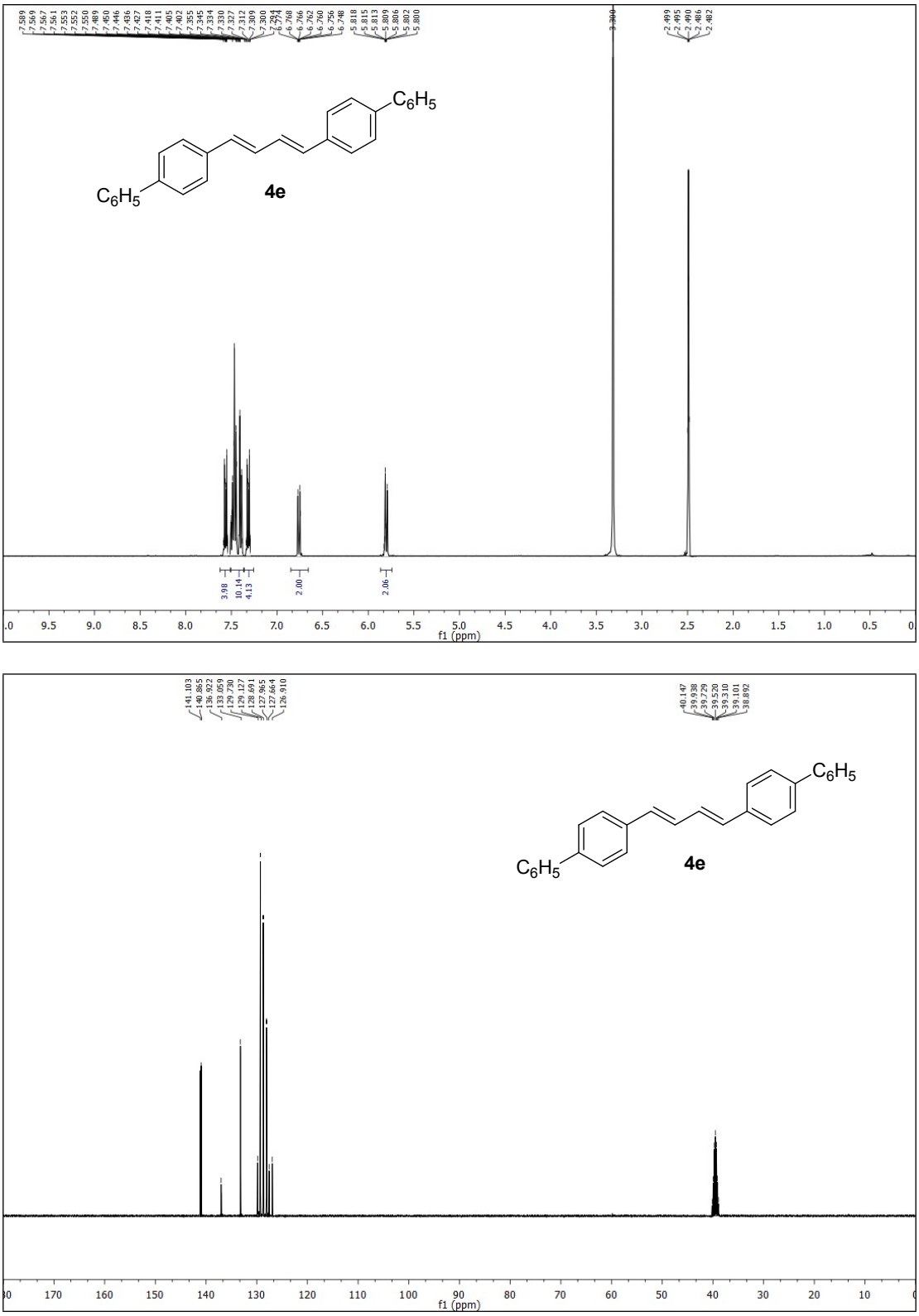


Figure S17. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **4e** in DMSO-d_6.

Figure S18. ^{1}H (300 MHz) NMR spectra of **4f** in DMSO-d_6.

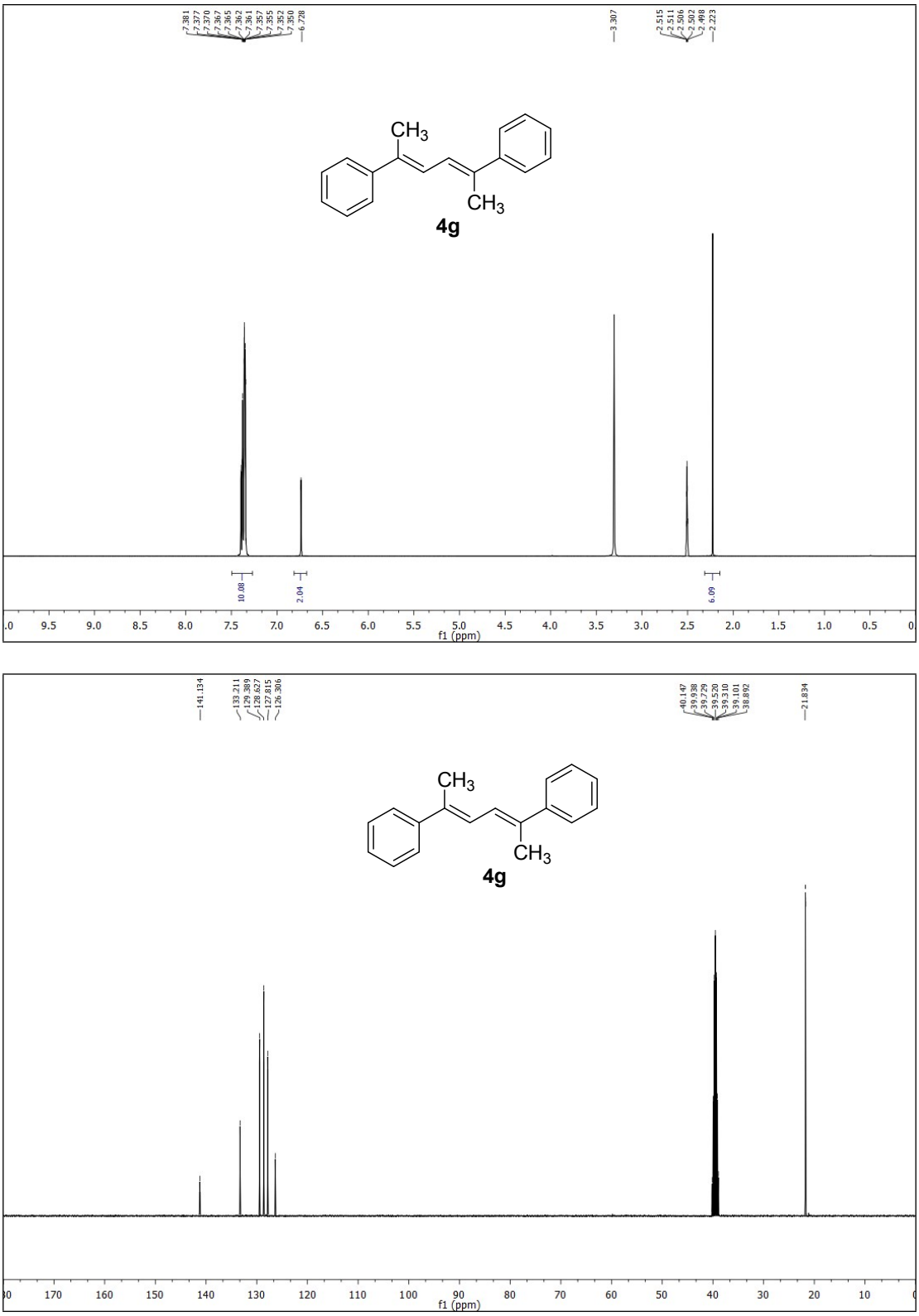


Figure S19. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **4g** in DMSO-d_6.

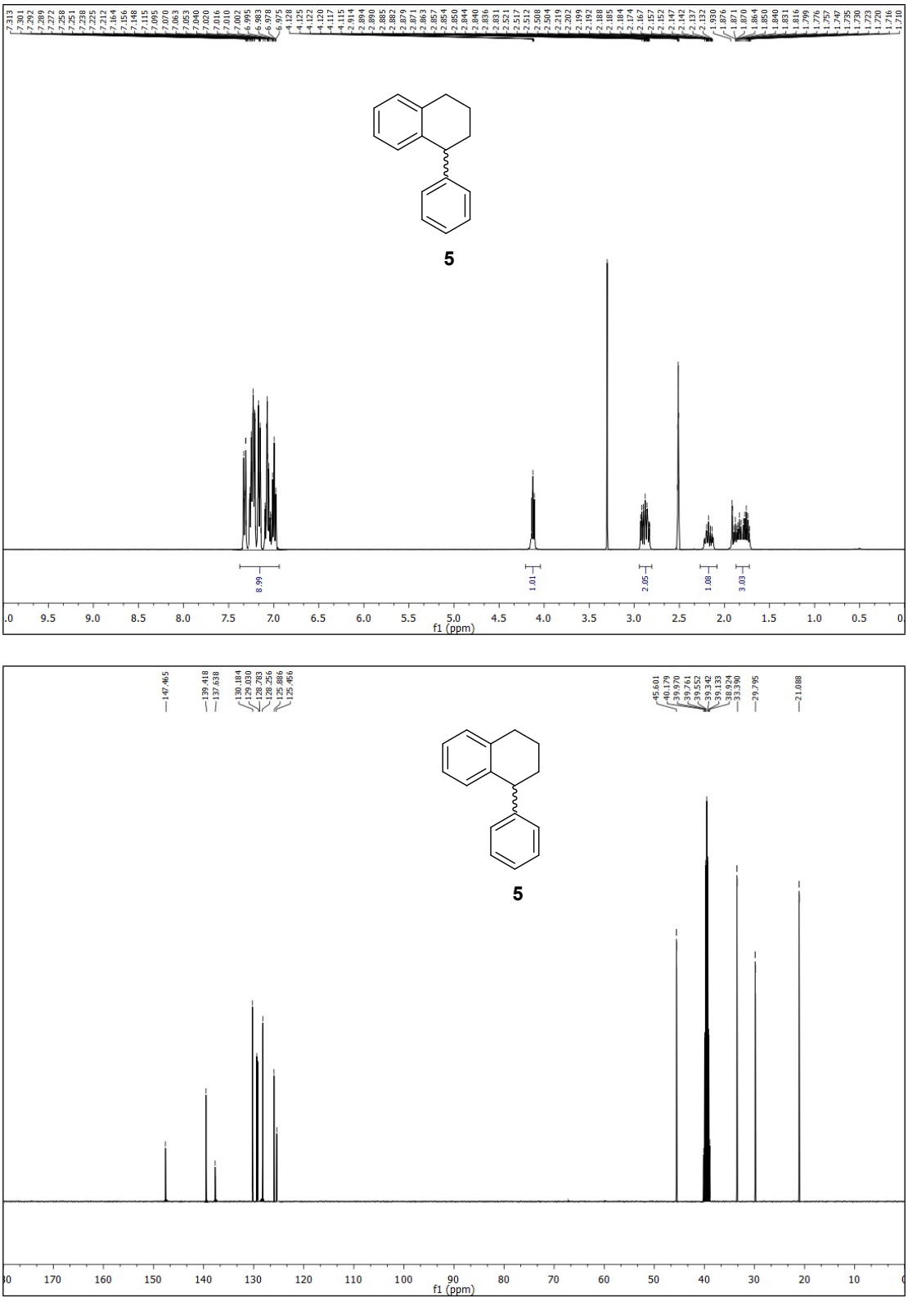


Figure S20. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **5** in DMSO-d_6.