Supplementary information

Synthesis, Rotational Dynamics, and Photophysical Characterization of a Crystalline Linearly Conjugated Phenyleneethynylene Molecular Dirotor

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PAGES	CONTENT
3 –5	^{1}H-NMR, ^{13}C-NMR, ATR-FTIR spectra of (3-(4-iodophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (**3**)
6 –8	^{1}H-NMR, ^{13}C-NMR, ATR-FTIR spectra of (3-(*d4*-4-bromophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (**3-*d*$_4$**).
9 –11	^{1}H-NMR, ^{13}C-NMR, ATR-FTIR spectra of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1**)
12 –14	^{1}H-NMR, ^{13}C-NMR, ATR-FTIR spectra of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1-*d*$_8$**)

15 –17 ^{1}H-NMR, ^{13}C-NMR, ATR-FTIR spectra of 6-ethynyl-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**7**)

18 –20 ^{1}H-NMR, ^{13}C-NMR, ATR-FTIR spectra of 6-((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**8**)

21 Arrhenius plot of phenylene flipping rate verses temperature, as determined by line-shape analysis.

21 Powder x-ray diffraction pattern of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1**), 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1-*d*$_8$**), and simulated powder x-ray diffraction pattern from single crystal structure of **1-*d*$_8$**.

22 TGA and DSC of TGA of crystals of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1**).

23 Emission spectra of solid samples of **1** obtained upon excitation at 380 nm and 405 nm.

23 –28 Computation details

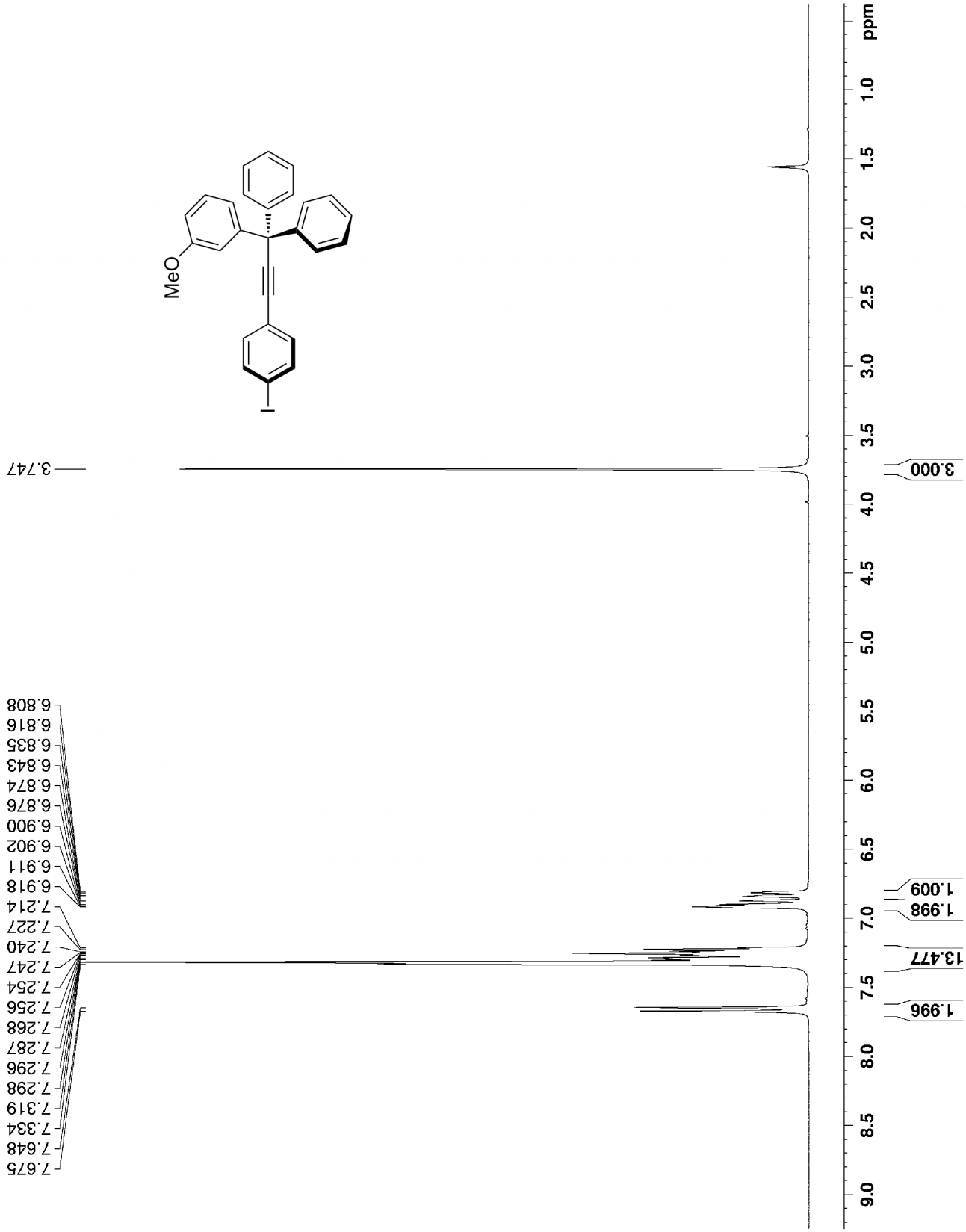


Figure S1. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (3-(4-iodophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (**3**)

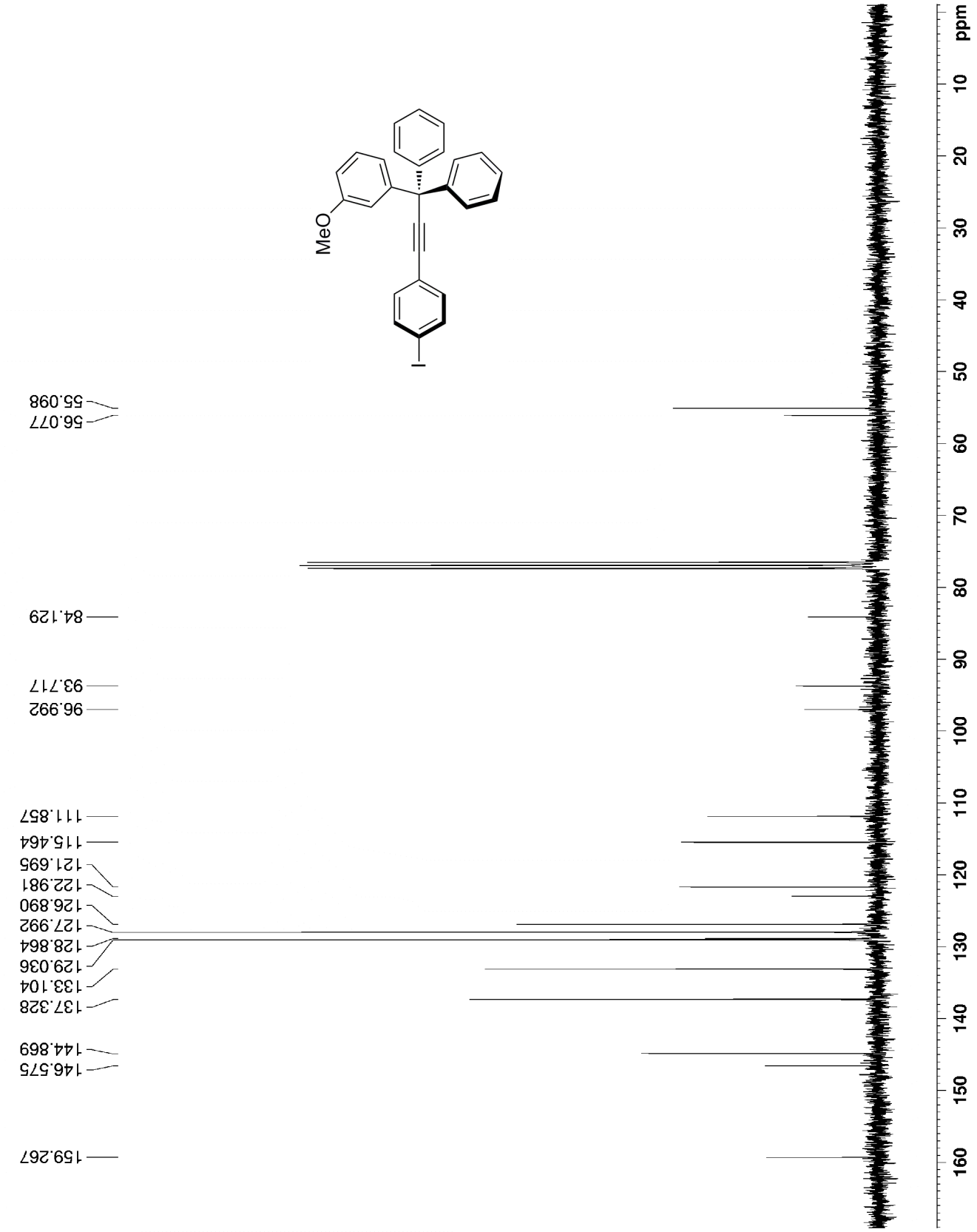


Figure S2. ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of (3-(4-iodophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (**3**)

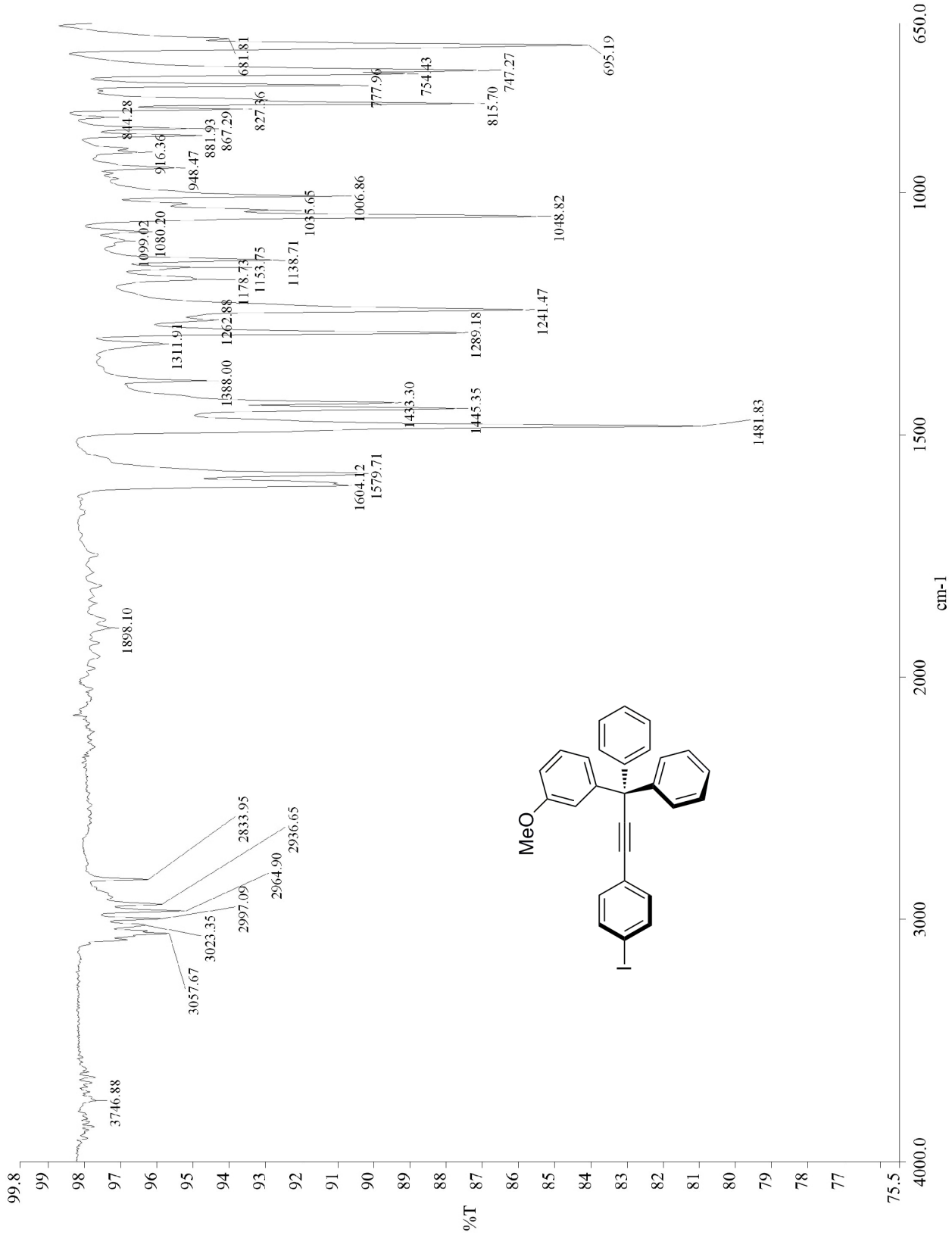


Figure S3. ATR-FTIR spectrum of (3-(4-iodophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (**3**)

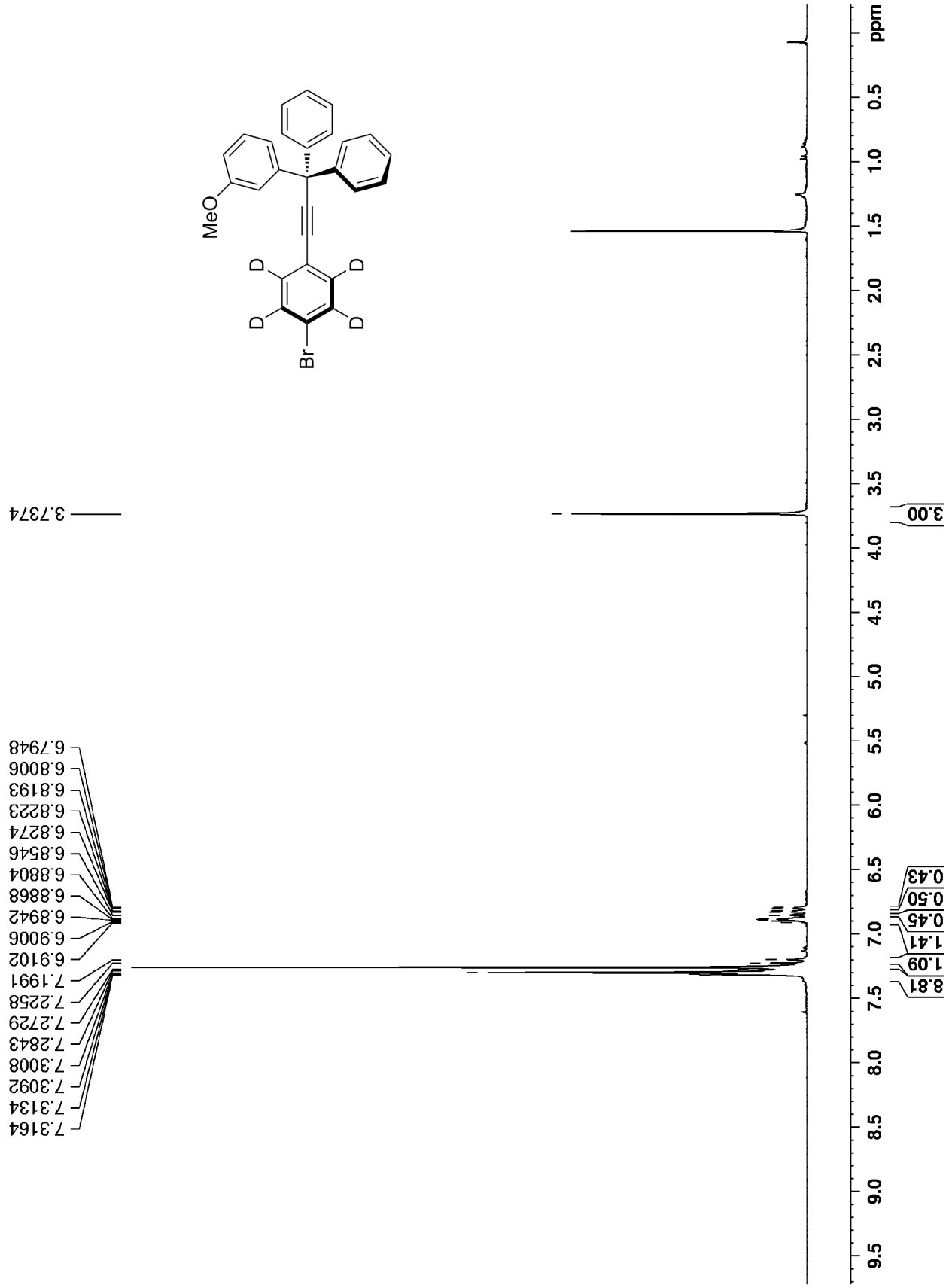


Figure S4. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of (3-(*d4*-4-bromophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (**3-*d*$_4$**)

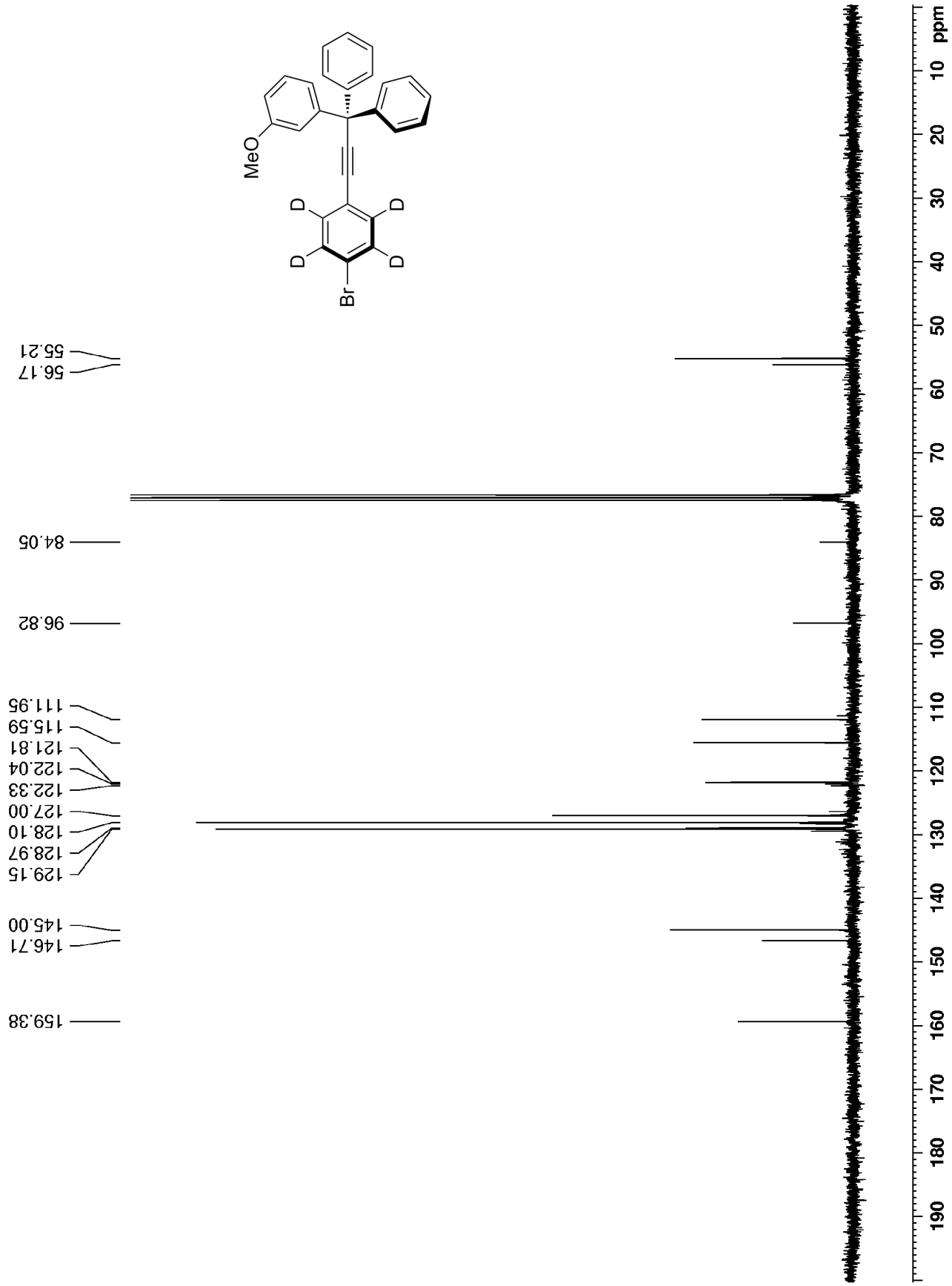


Figure S5. ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of (3-(*d4*-4-bromophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (**3-*d*$_4$**)

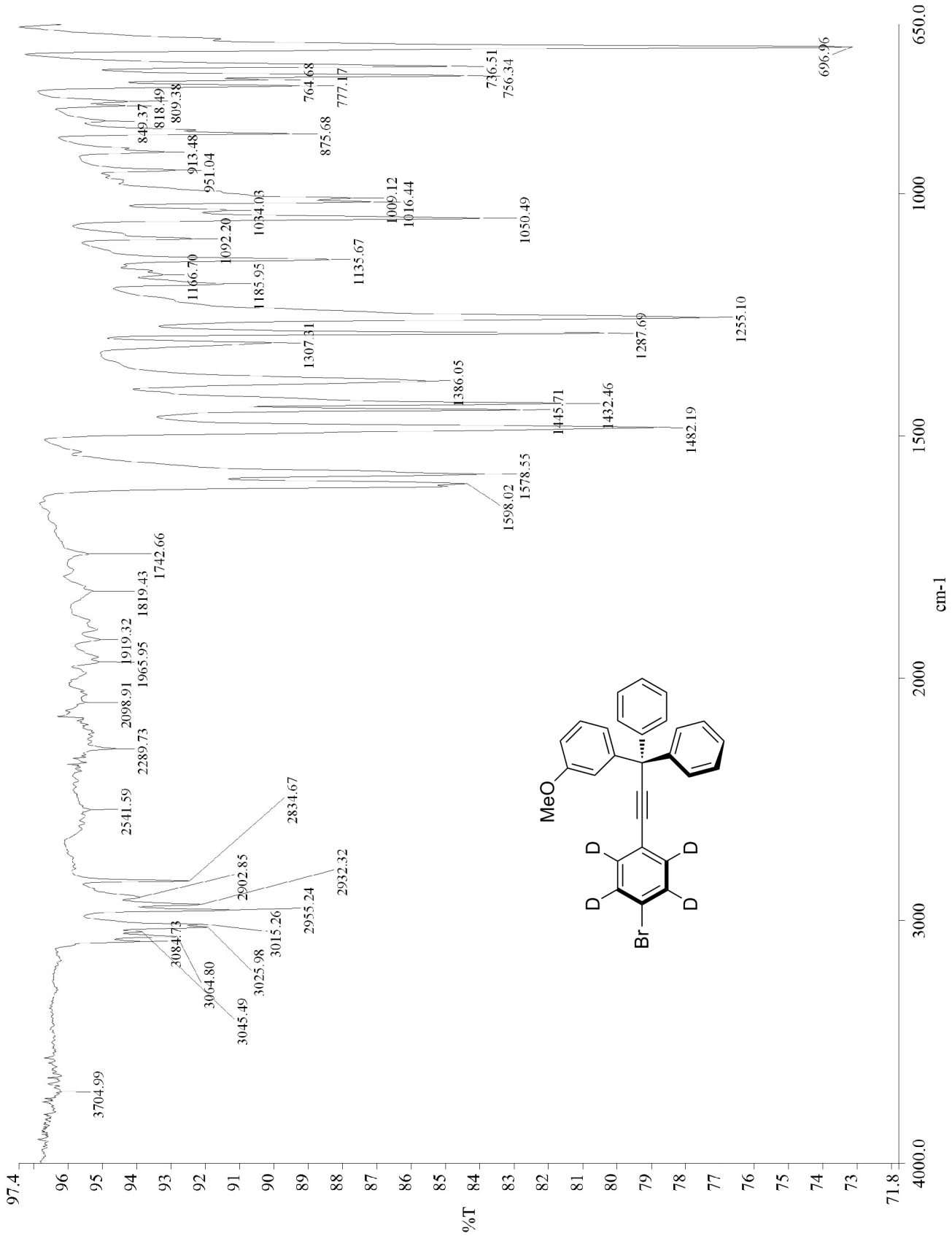


Figure S6. ATR-FTIR spectrum of (3-(*d4*-4-bromophenyl)-1-(3-methoxyphenyl)prop-2-yne-1,1-diyl)dibenzene (**3-*d*$_4$**)

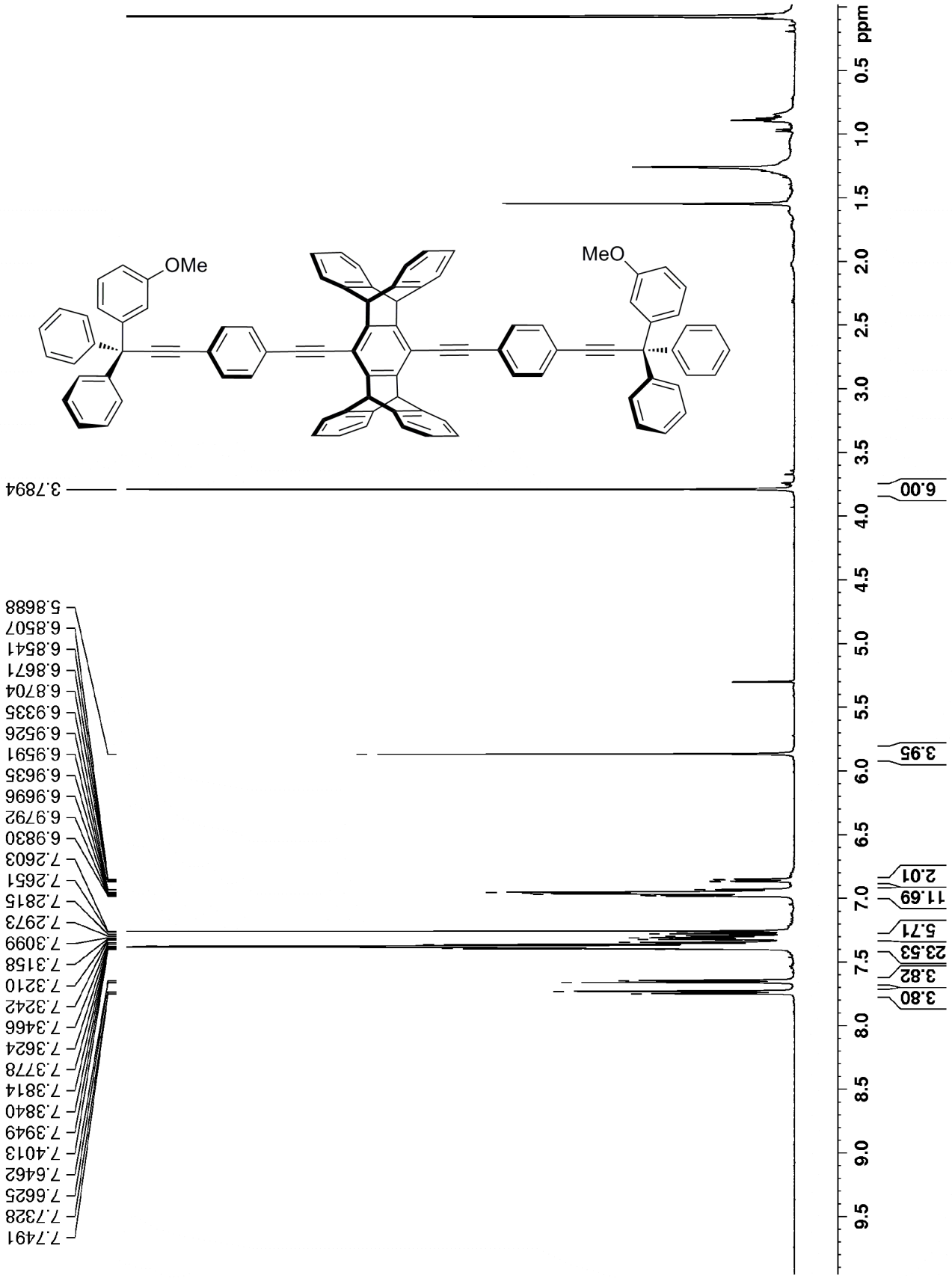


Figure S7. ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1**)

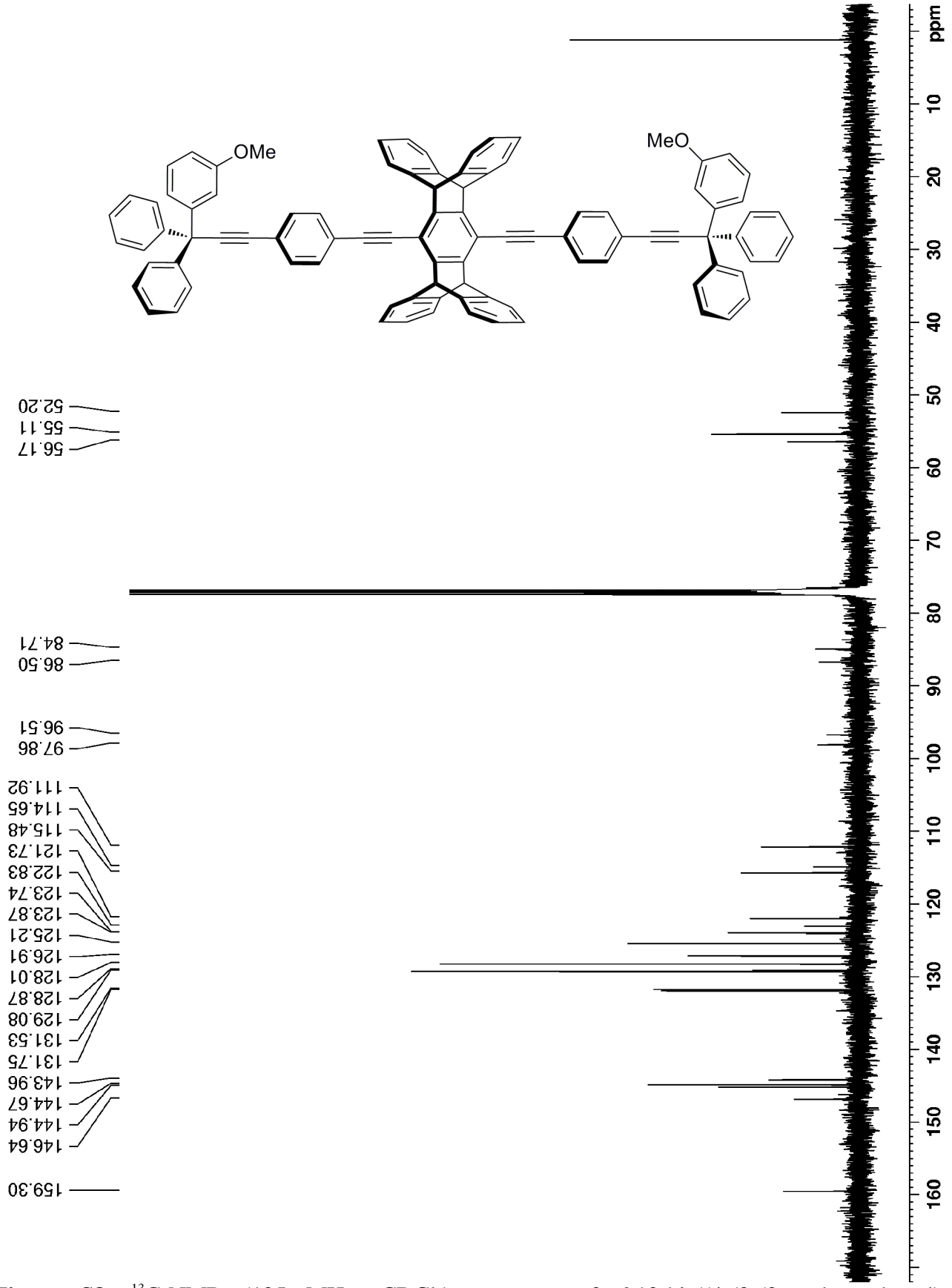


Figure S8. ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1**)

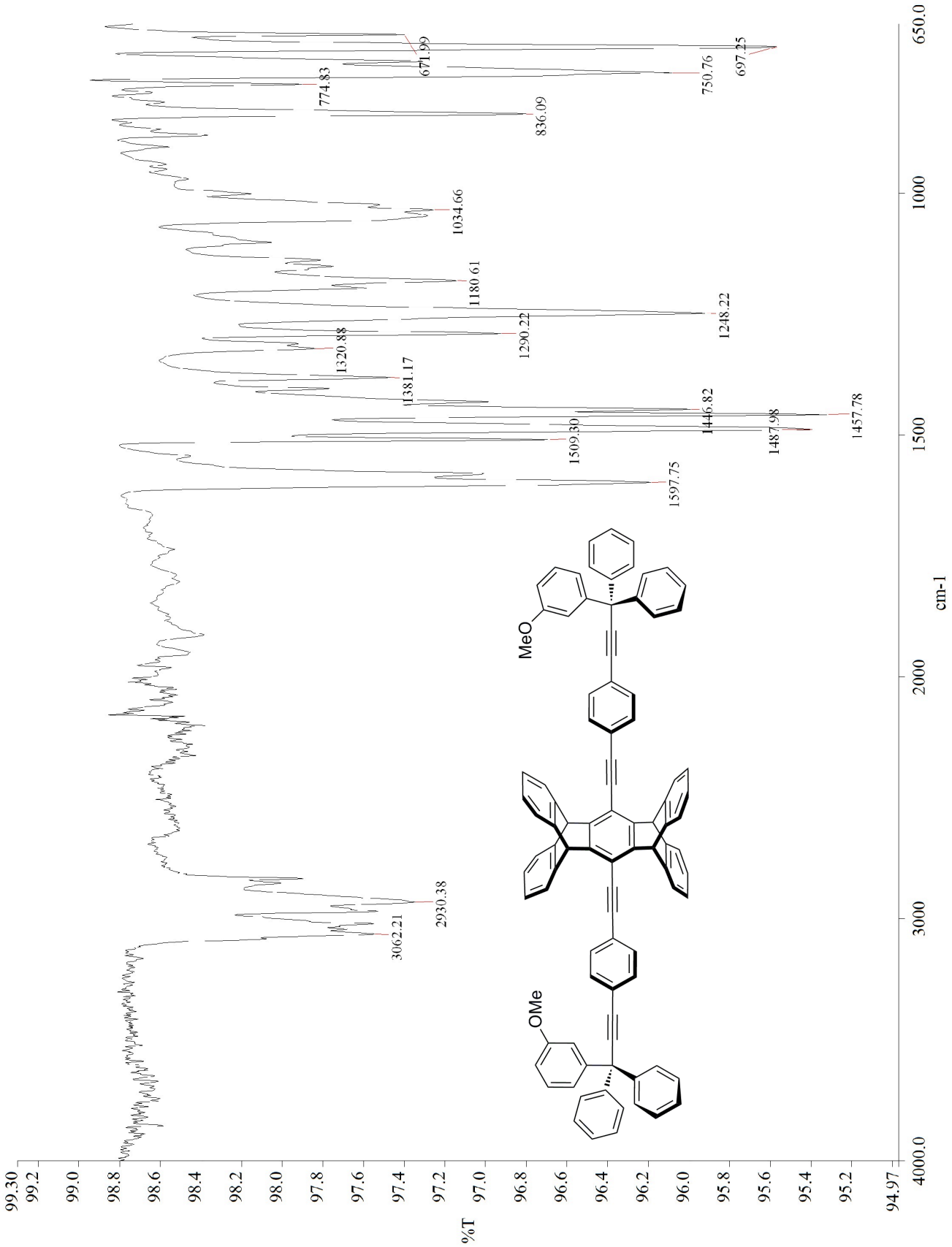
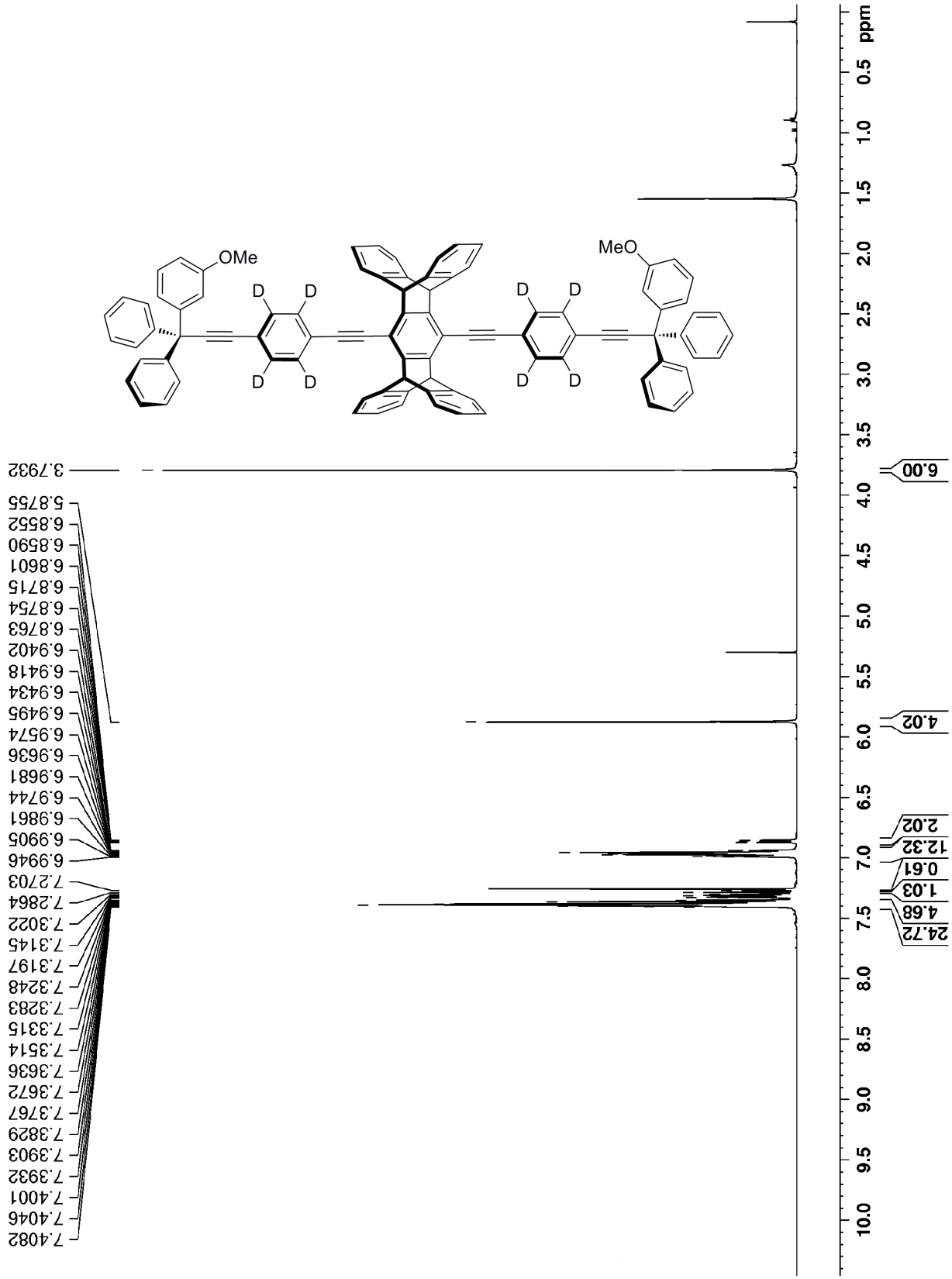


Figure S9. ATR-FTIR spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1**)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MeO
D
ppm
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1.03
0.61
12.32
2.02
4.02
6.00
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6.8715
6.8754
6.8763
6.9402
6.9418
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6.9495
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7.3636
7.3672
7.3767
7.3829
7.3903
7.3932
7.4001
7.4046
7.4082

Figure S10. ^{1}H-NMR (500 MHz, CDCl3) spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1-*d*$_8$**)

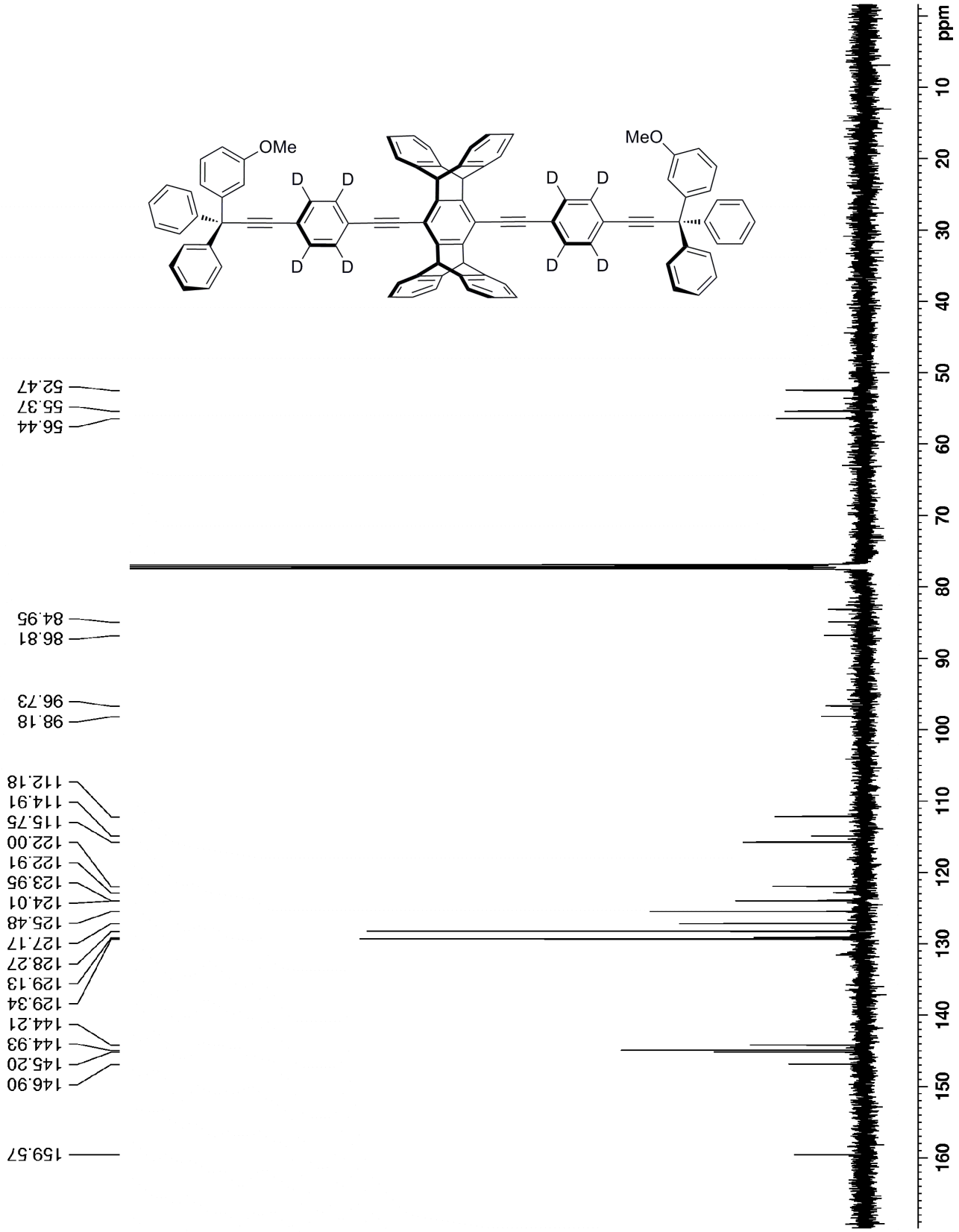

Figure S11. ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1-*d*$_8$**)

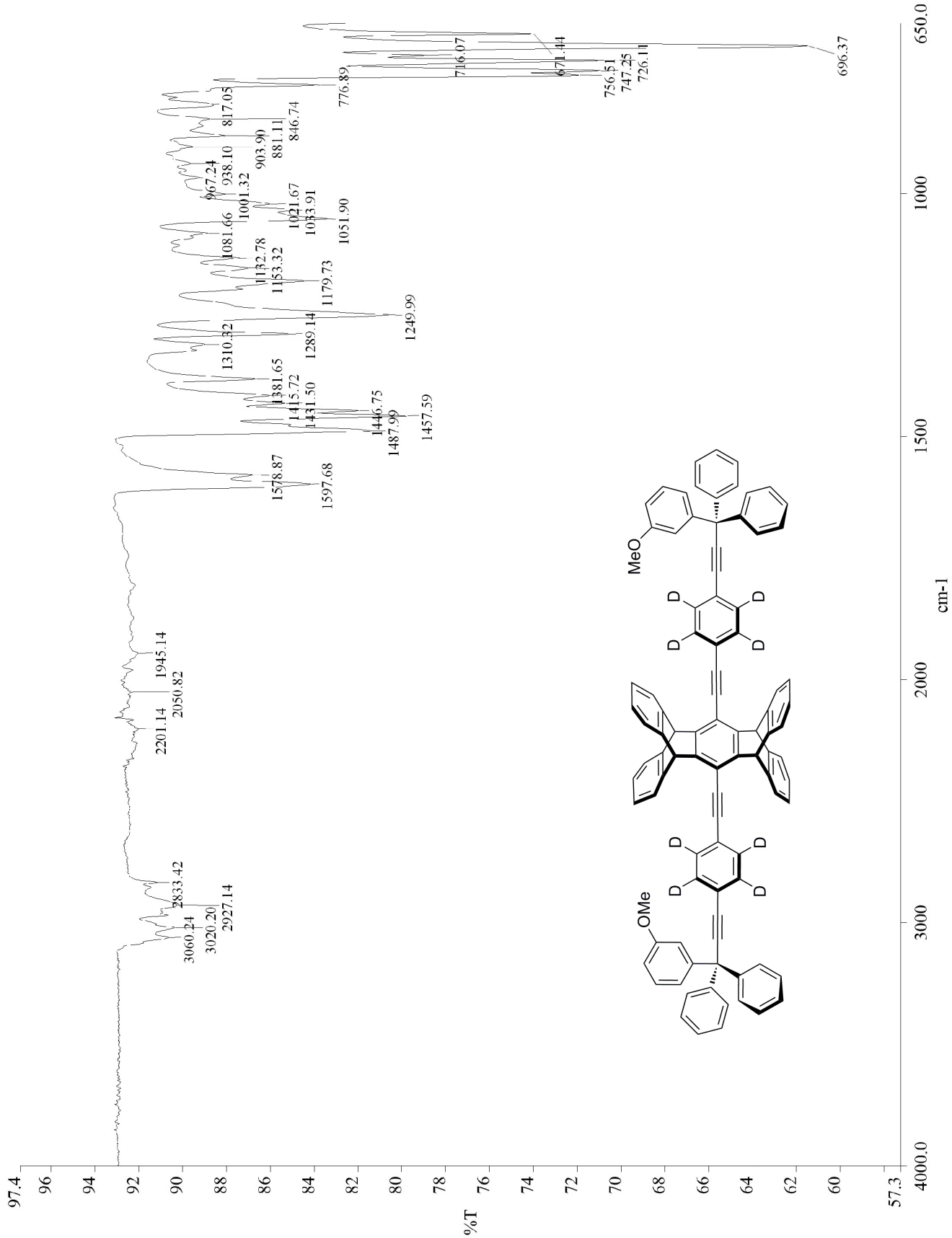

Figure S12. ATR-FTIR spectrum of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1-*d*$_8$**)

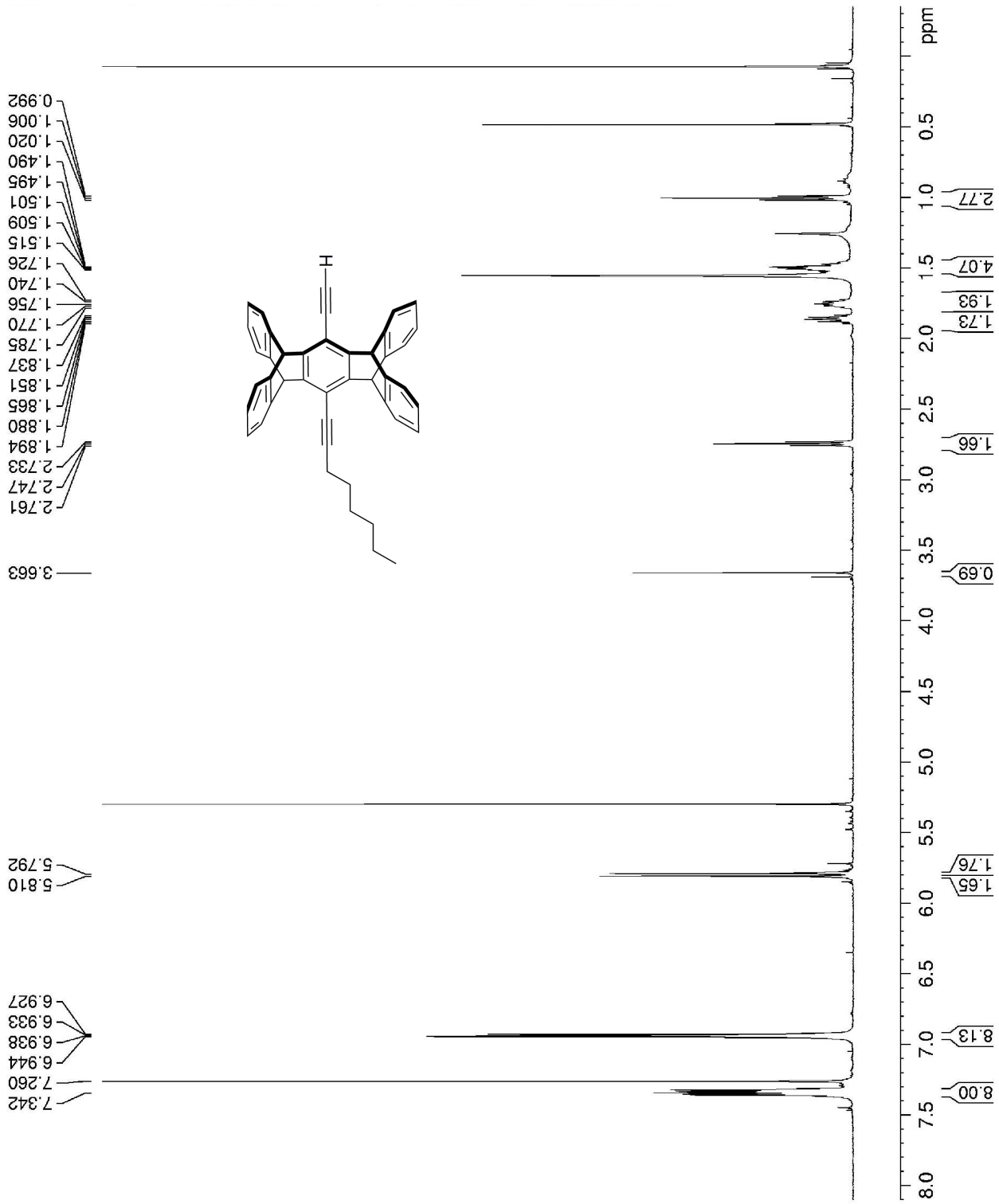

Figure S13. ^{1}H-NMR (500 MHz, CDCl3) spectrum of 6-ethynyl-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**7**)

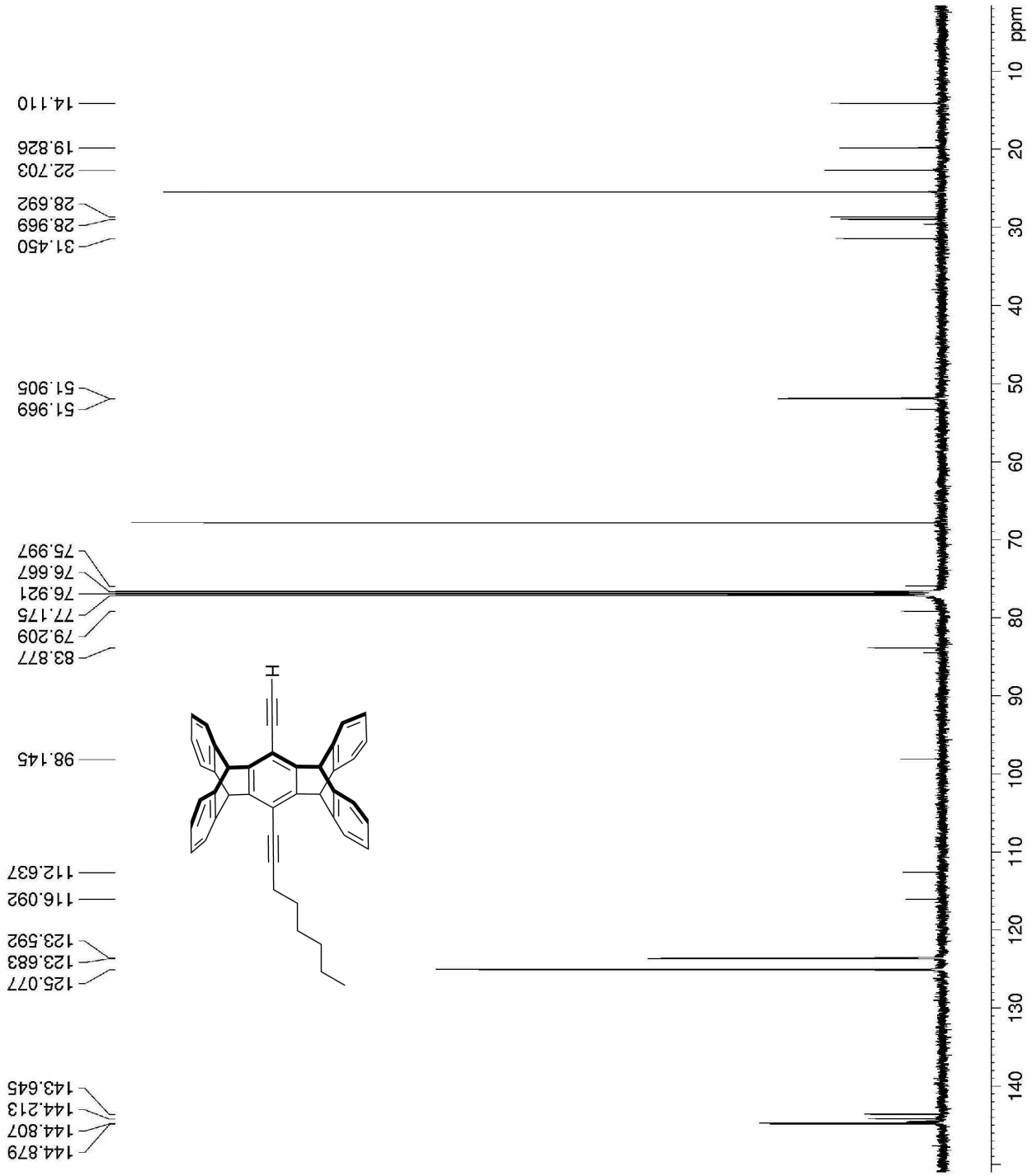

Figure S14. ^{13}C-NMR (125 MHz, CDCl3) spectrum of 6-ethynyl-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**7**)

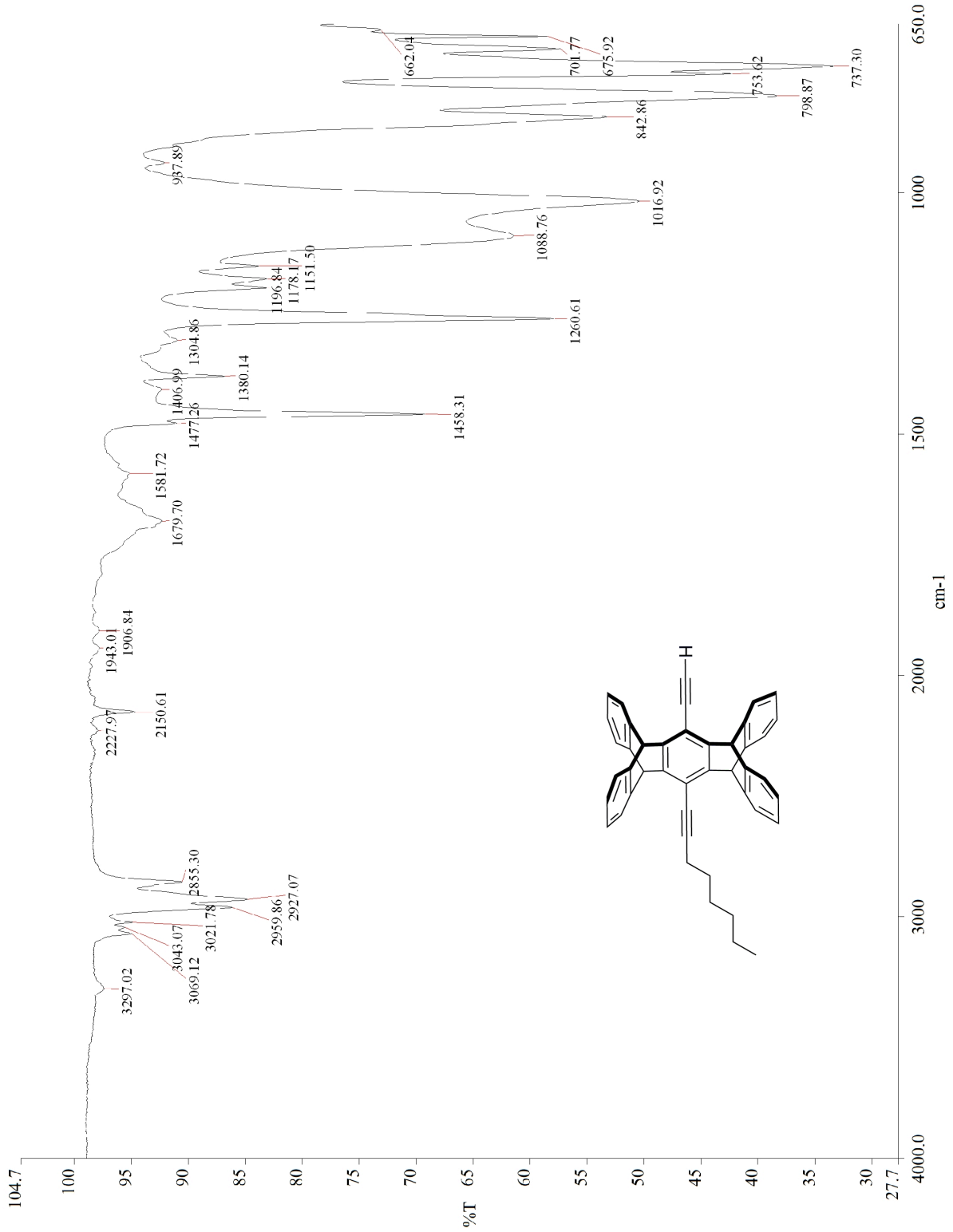

Figure S15. ATR-FTIR spectrum of 6-ethynyl-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**7**)

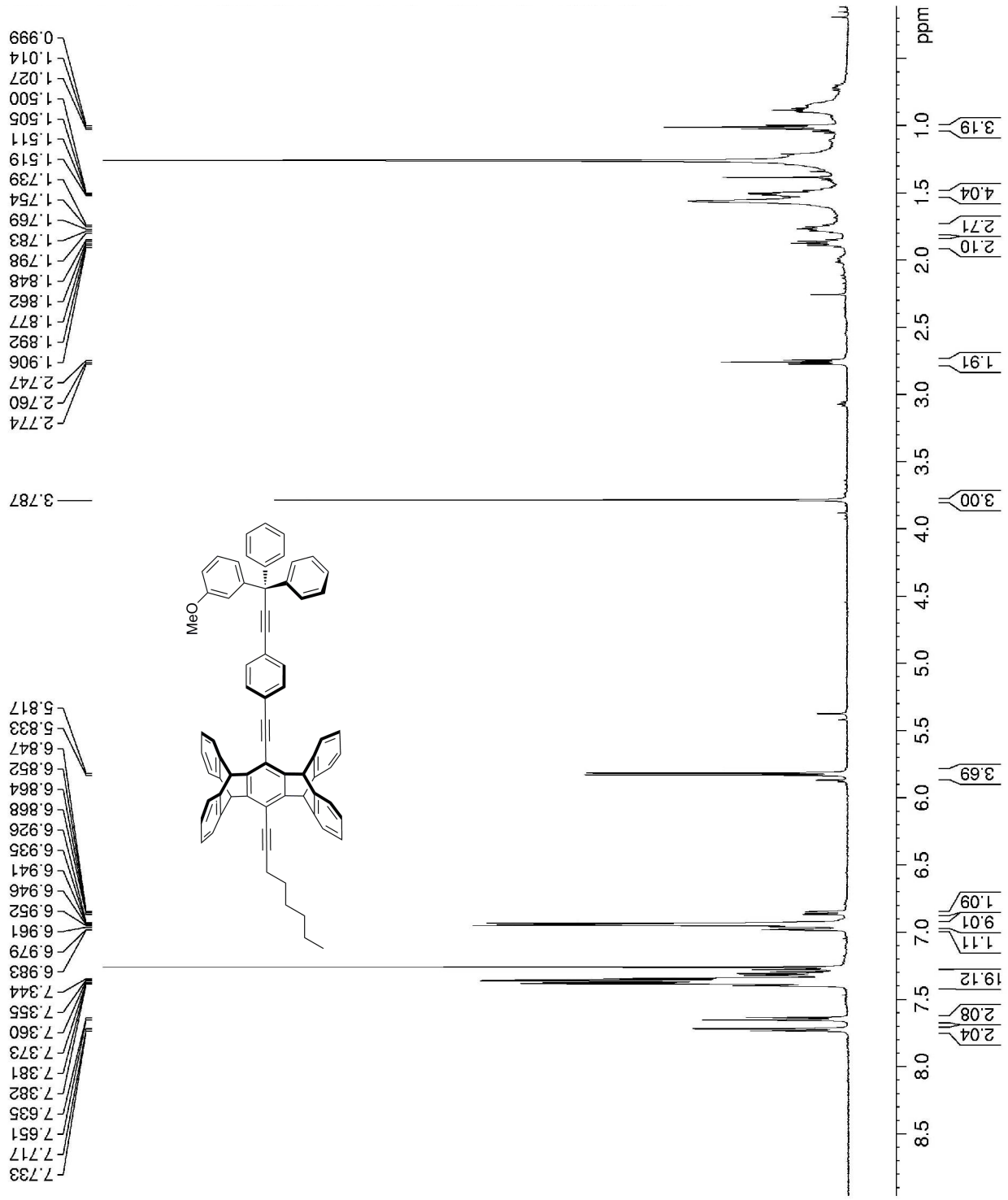

Figure S16. ^{1}H-NMR (500 MHz, CDCl3) spectrum of 6-((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**8**)

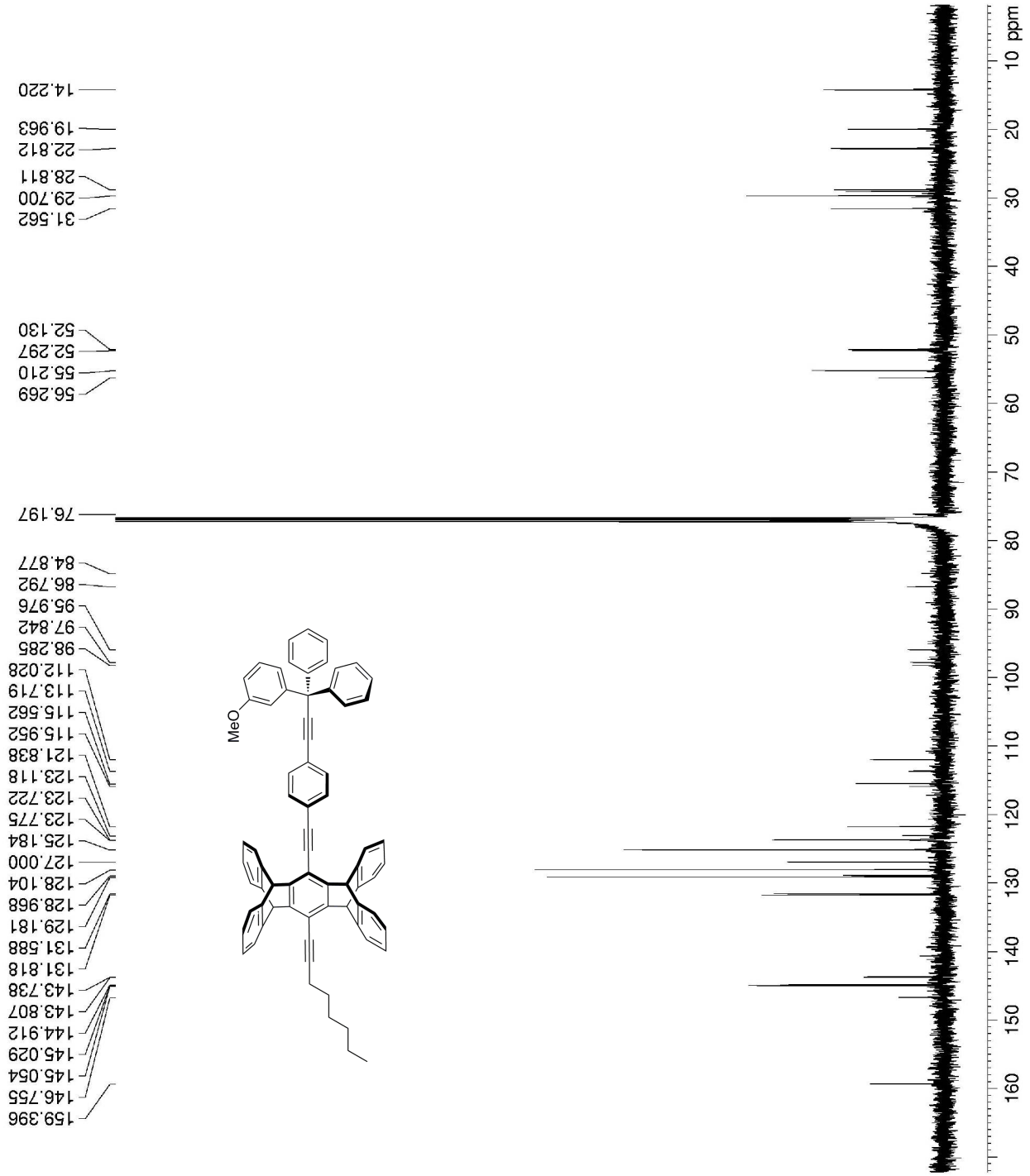

Figure S17. ^{13}C-NMR (125 MHz, CDCl3) spectrum of 6-((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**8**)

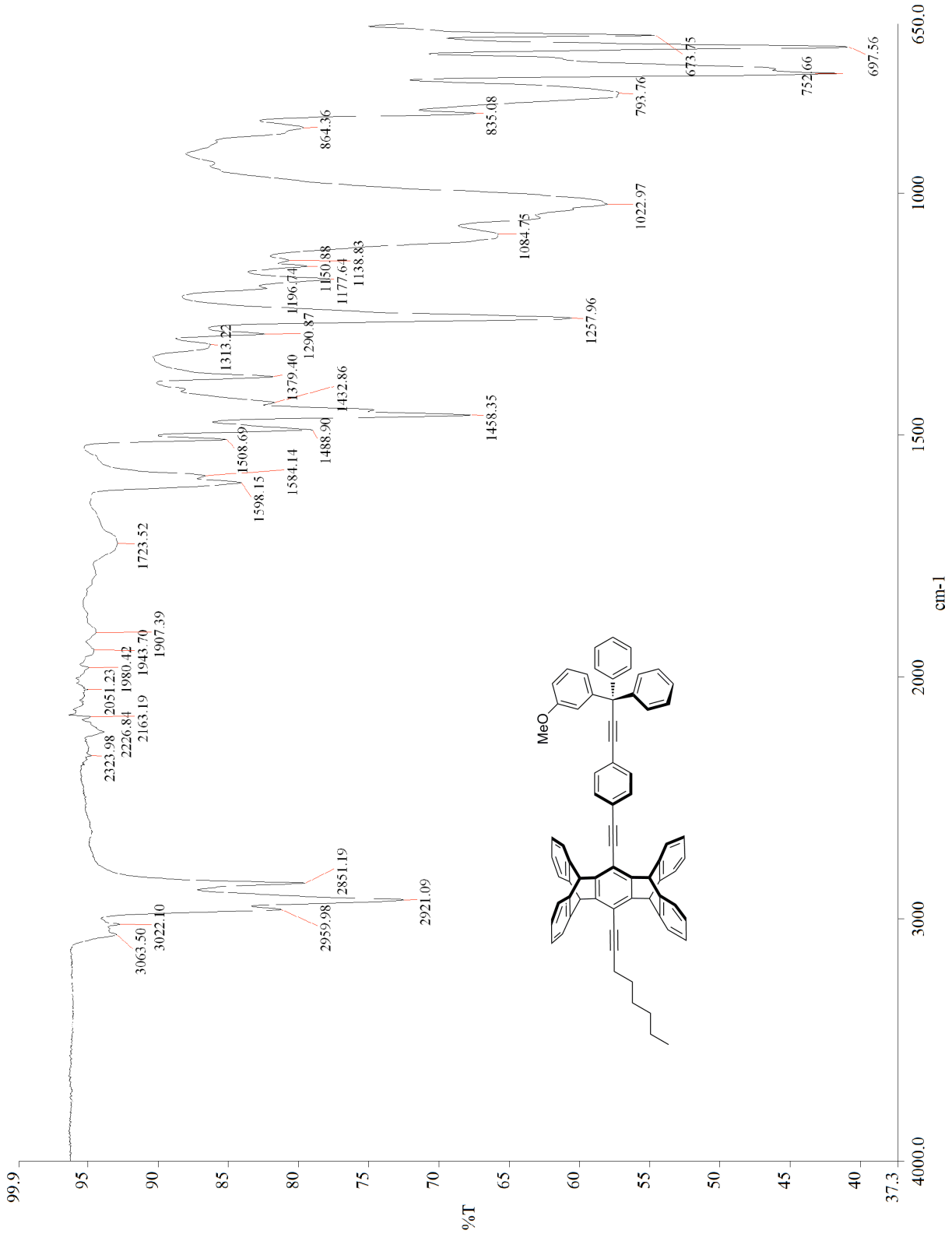

Figure S18. ATR-FTIR spectrum of 6-((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-13-(oct-1-yn-1-yl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**8**)

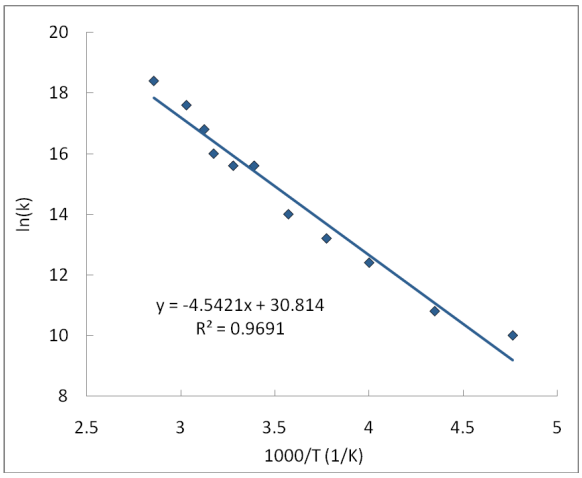

Figure S19: Arrhenius plot of phenylene flipping rate verses temperature, as determined by line-shape analysis.

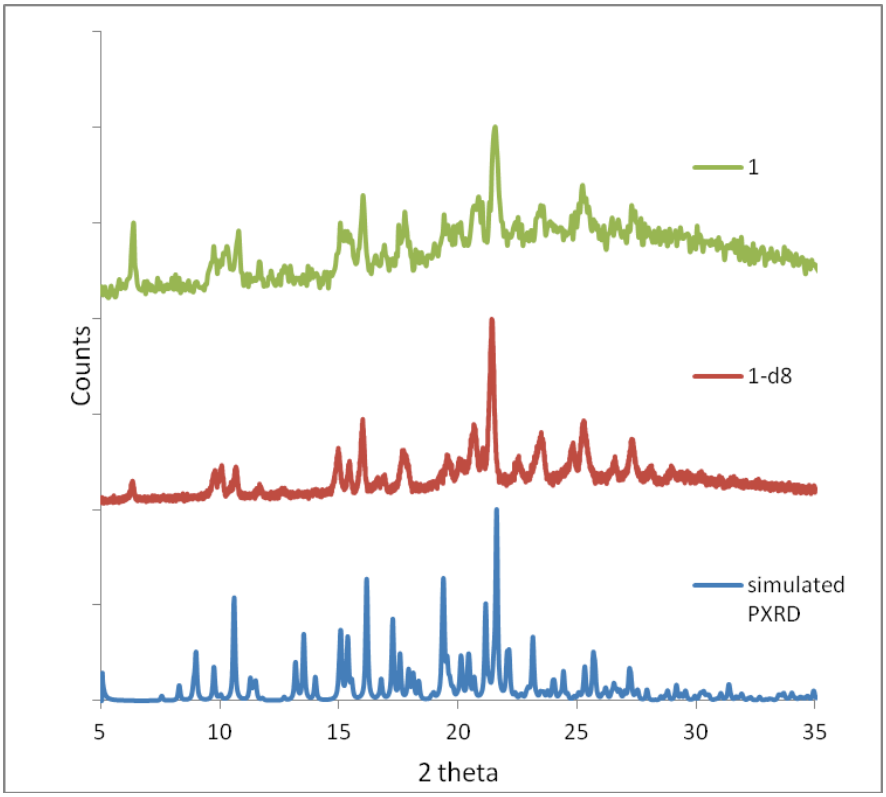

Figure S20: Powder x-ray diffraction pattern of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1**), 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1-*d*$_8$**), and simulated powder x-ray diffraction pattern from single crystal structure of **1-*d*$_8$**.

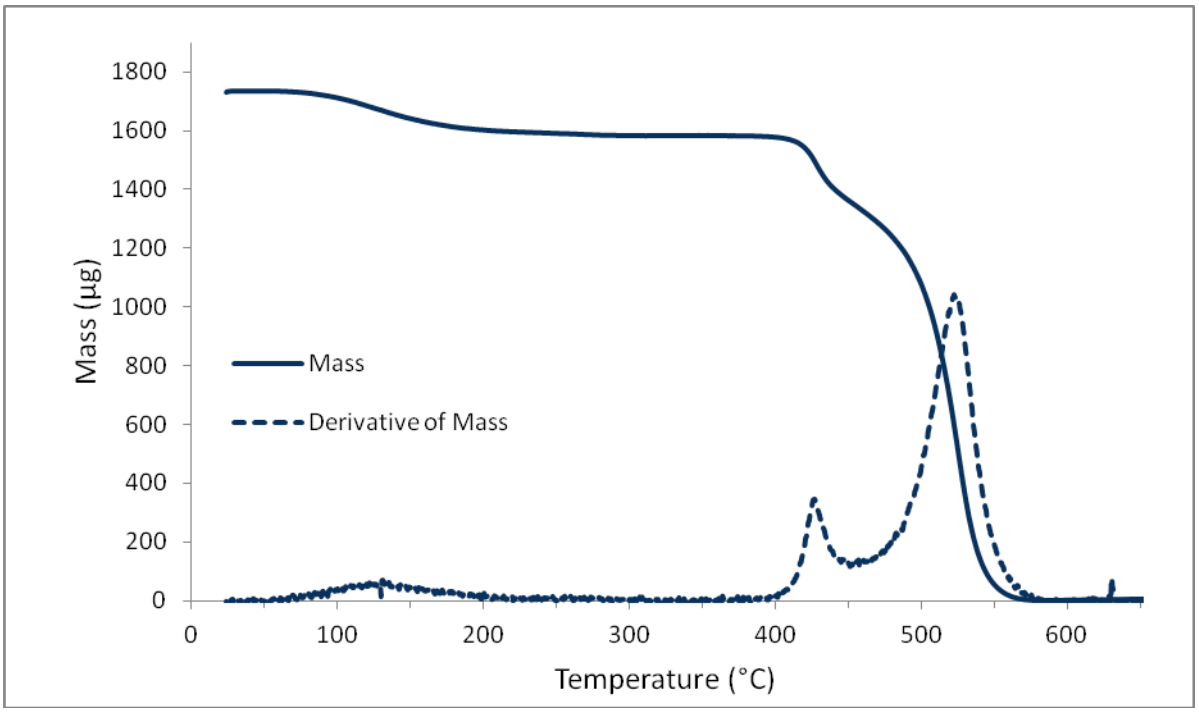

Figure S21: TGA of crystals of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1**). Loss of 23% of mass prior to decomposition is attributed to the loss of toluene from the crystal structure.

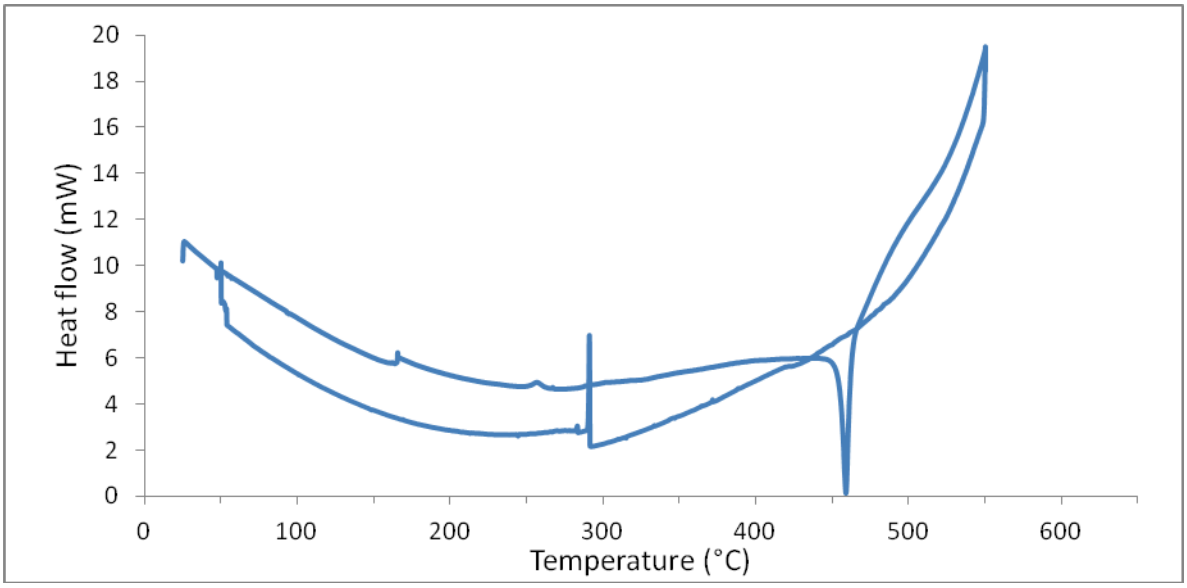

Figure S22: DSC of crystals of 6,13-bis((4-(3-(3-methoxyphenyl)-3,3-diphenylprop-1-yn-1-yl)phenyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene (**1**).

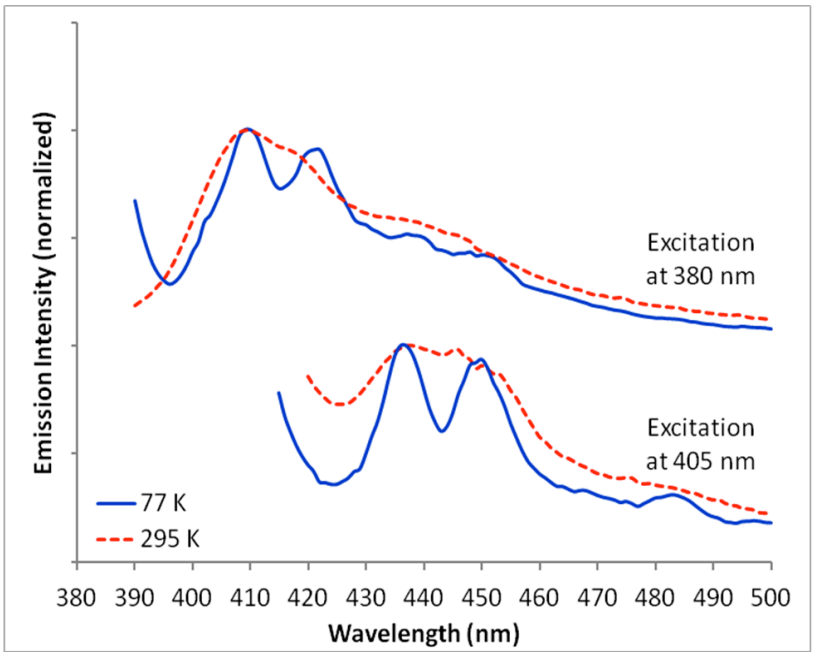

Figure S23: Emission spectra of solid samples of **1** obtained upon excitation at 380 nm and 405 nm.

Computation details:

Computations of the ground and excited state energies of the model chromophore (see Figure 5) were preformed on the commercially available Spartan '02 program at the B3LYP/6-31G(d) level of theory. The ground and excited state energies are computed for the planar chromophore, for conformations with the central phenylene at torsion angles of 30°, 60°, and 90°, and for a conformation with a terminal phenylene at a 90° torsion angle.

Planar chromophore:

SCF total energy: -998.9218750 hartrees

TDFT Energy: -998.8071096 hartrees First Excited State

1	H	8.269633	-2.149631	0.000000
2	C	7.721632	-1.200467	0.000000
3	C	6.335450	1.200467	0.000000
4	C	6.335450	-1.200467	0.000000
5	C	8.414721	0.000000	0.000000
6	C	7.721632	1.200467	0.000000
7	C	5.642361	0.000000	0.000000
8	H	5.787452	-2.149632	0.000000
9	H	8.269633	2.149631	0.000000
10	H	5.787452	2.149632	0.000000
11	C	9.945721	0.000000	0.000000

12	H	12.235901	0.000000	0.000000
13	C	11.139901	0.000000	0.000000
14	C	4.111361	0.000000	0.000000
15	C	2.917181	0.000000	0.000000
16	C	1.386181	0.000000	0.000000
17	C	-1.386181	0.000000	0.000000
18	C	0.693090	-1.200469	0.000000
19	C	0.693090	1.200469	0.000000
20	C	-0.693090	1.200469	0.000000
21	C	-0.693090	-1.200469	0.000000
22	H	1.241090	-2.149632	0.000000
23	H	1.241090	2.149632	0.000000
24	H	-1.241090	2.149632	0.000000
25	H	-1.241090	-2.149632	0.000000
26	C	-2.917181	0.000000	0.000000
27	C	-4.111361	0.000000	0.000000
28	C	-5.642361	0.000000	0.000000
29	C	-8.414721	0.000000	0.000000
30	C	-6.335450	-1.200467	0.000000
31	C	-6.335450	1.200467	0.000000
32	C	-7.721632	1.200467	0.000000
33	C	-7.721632	-1.200467	0.000000
34	H	-5.787452	-2.149632	0.000000
35	H	-5.787452	2.149632	0.000000
36	H	-8.269633	2.149631	0.000000
37	H	-8.269633	-2.149631	0.000000
38	C	-9.945721	0.000000	0.000000
39	H	-12.235901	0.000000	0.000000
40	C	-11.139901	0.000000	0.000000

Central phenylene at 30° torsion angle:

SCF total energy: -998.9215750 hartrees

TDFT Energy: -998.8036165 hartrees First Excited State

1	H	0.356764	-2.119818	8.269629
2	C	0.199236	-1.183818	7.721628
3	C	-0.199236	1.183817	6.335447
4	C	0.199236	-1.183817	6.335447
5	C	0.000000	0.000000	8.414717
6	C	-0.199236	1.183818	7.721628
7	C	0.000000	0.000000	5.642358
8	H	0.356764	-2.119819	5.787449
9	H	-0.356764	2.119818	8.269629
10	H	-0.356764	2.119819	5.787449
11	C	0.000000	0.000000	9.945716
12	H	0.000000	0.000000	12.235895
13	C	0.000000	0.000000	11.139896
14	C	0.000000	0.000000	4.111359
15	C	0.000000	0.000000	2.917179

16	C	0.000000	0.000000	1.386180
17	C	0.000000	0.000000	-1.386180
18	C	-0.419366	-1.124836	0.693089
19	C	0.419366	1.124836	0.693089
20	C	0.419366	1.124836	-0.693089
21	C	-0.419366	-1.124836	-0.693089
22	H	-0.750943	-2.014200	1.241089
23	H	0.750943	2.014200	1.241089
24	H	0.750943	2.014200	-1.241089
25	H	-0.750943	-2.014200	-1.241089
26	C	0.000000	0.000000	-2.917179
27	C	0.000000	0.000000	-4.111359
28	C	0.000000	0.000000	-5.642358
29	C	0.000000	0.000000	-8.414717
30	C	0.199236	-1.183817	-6.335447
31	C	-0.199236	1.183817	-6.335447
32	C	-0.199236	1.183818	-7.721628
33	C	0.199236	-1.183818	-7.721628
34	H	0.356764	-2.119819	-5.787449
35	H	-0.356764	2.119819	-5.787449
36	H	-0.356764	2.119818	-8.269629
37	H	0.356764	-2.119818	-8.269629
38	C	0.000000	0.000000	-9.945716
39	H	0.000000	0.000000	-12.235895
40	C	0.000000	0.000000	-11.139896

Central phenylene at 60° torsion angle:

SCF total energy: -998.9209969 hartrees

TDFT Energy: -998.7948989 harrtees First Excited State

1	H	0.556366	-2.076383	8.269629
2	C	0.310704	-1.159562	7.721628
3	C	-0.310704	1.159561	6.335447
4	C	0.310704	-1.159561	6.335447
5	C	0.000000	0.000000	8.414717
6	C	-0.310704	1.159562	7.721628
7	C	0.000000	0.000000	5.642358
8	H	0.556366	-2.076384	5.787449
9	H	-0.556366	2.076383	8.269629
10	H	-0.556366	2.076384	5.787449
11	C	0.000000	0.000000	9.945716
12	H	0.000000	0.000000	12.235895
13	C	0.000000	0.000000	11.139896
14	C	0.000000	0.000000	4.111359
15	C	0.000000	0.000000	2.917179
16	C	0.000000	0.000000	1.386180
17	C	0.000000	0.000000	-1.386180
18	C	-0.848858	-0.848859	0.693089
19	C	0.848858	0.848859	0.693089

20	C	0.848858	0.848859	-0.693089
21	C	-0.848858	-0.848859	-0.693089
22	H	-1.520018	-1.520020	1.241089
23	H	1.520018	1.520020	1.241089
24	H	1.520018	1.520020	-1.241089
25	H	-1.520018	-1.520020	-1.241089
26	C	0.000000	0.000000	-2.917179
27	C	0.000000	0.000000	-4.111359
28	C	0.000000	0.000000	-5.642358
29	C	0.000000	0.000000	-8.414717
30	C	0.310704	-1.159561	-6.335447
31	C	-0.310704	1.159561	-6.335447
32	C	-0.310704	1.159562	-7.721628
33	C	0.310704	-1.159562	-7.721628
34	H	0.556366	-2.076384	-5.787449
35	H	-0.556366	2.076384	-5.787449
36	H	-0.556366	2.076383	-8.269629
37	H	0.556366	-2.076383	-8.269629
38	C	0.000000	0.000000	-9.945716
39	H	0.000000	0.000000	-12.235895
40	C	0.000000	0.000000	-11.139896

Central phenylene at 90° torsion angle:

SCF total energy: -998.9206070 hartrees

TDFT Energy: -998.7887699 hartrees First Excited State

1	H	8.269629	-2.149630	0.000000
2	C	7.721628	-1.200467	0.000000
3	C	6.335447	1.200466	0.000000
4	C	6.335447	-1.200466	0.000000
5	C	8.414717	0.000000	0.000000
6	C	7.721628	1.200467	0.000000
7	C	5.642358	0.000000	0.000000
8	H	5.787449	-2.149631	0.000000
9	H	8.269629	2.149630	0.000000
10	H	5.787449	2.149631	0.000000
11	C	9.945716	0.000000	0.000000
12	H	12.235895	0.000000	0.000000
13	C	11.139896	0.000000	0.000000
14	C	4.111359	0.000000	0.000000
15	C	2.917179	0.000000	0.000000
16	C	1.386180	0.000000	0.000000
17	C	-1.386180	0.000000	0.000000
18	C	0.693089	0.000000	1.200467
19	C	0.693089	0.000000	-1.200467
20	C	-0.693089	0.000000	-1.200467
21	C	-0.693089	0.000000	1.200467
22	H	1.241089	0.000000	2.149631
23	H	1.241089	0.000000	-2.149631

24	H	-1.241089	0.000000	-2.149631
25	H	-1.241089	0.000000	2.149631
26	C	-2.917179	0.000000	0.000000
27	C	-4.111359	0.000000	0.000000
28	C	-5.642358	0.000000	0.000000
29	C	-8.414717	0.000000	0.000000
30	C	-6.335447	-1.200466	0.000000
31	C	-6.335447	1.200466	0.000000
32	C	-7.721628	1.200467	0.000000
33	C	-7.721628	-1.200467	0.000000
34	H	-5.787449	-2.149631	0.000000
35	H	-5.787449	2.149631	0.000000
36	H	-8.269629	2.149630	0.000000
37	H	-8.269629	-2.149630	0.000000
38	C	-9.945716	0.000000	0.000000
39	H	-12.235895	0.000000	0.000000
40	C	-11.139896	0.000000	0.000000

Terminal phenylene at a 90° torsion angle:

SCF total energy: -998.9212523 hartrees

TDFT Energy: -998.8015362 hartrees First Excited State

1	H	-2.149629	0.000000	8.269626
2	C	-1.200466	0.000000	7.721626
3	C	1.200465	0.000000	6.335445
4	C	-1.200465	0.000000	6.335445
5	C	0.000000	0.000000	8.414714
6	C	1.200466	0.000000	7.721626
7	C	0.000000	0.000000	5.642357
8	H	-2.149630	0.000000	5.787447
9	H	2.149629	0.000000	8.269626
10	H	2.149630	0.000000	5.787447
11	C	0.000000	0.000000	9.945713
12	H	0.000000	0.000000	12.235891
13	C	0.000000	0.000000	11.139892
14	C	0.000000	0.000000	4.111358
15	C	0.000000	0.000000	2.917179
16	C	0.000000	0.000000	1.386181
17	C	0.000000	0.000000	-1.386178
18	C	-1.200467	0.000000	0.693090
19	C	1.200467	0.000000	0.693090
20	C	1.200467	0.000000	-0.693088
21	C	-1.200467	0.000000	-0.693088
22	H	-2.149630	0.000000	1.241090
23	H	2.149630	0.000000	1.241090
24	H	2.149630	0.000000	-1.241087
25	H	-2.149630	0.000000	-1.241087
26	C	0.000000	0.000000	-2.917177
27	C	0.000000	0.000000	-4.111356

28	C	0.000000	0.000000	-5.642356
29	C	0.000000	0.000000	-8.414717
30	C	0.000000	-1.200468	-6.335447
31	C	0.000000	1.200468	-6.335447
32	C	0.000000	1.200468	-7.721627
33	C	0.000000	-1.200468	-7.721627
34	H	0.000000	-2.149632	-5.787447
35	H	0.000000	2.149632	-5.787447
36	H	0.000000	2.149632	-8.269627
37	H	0.000000	-2.149632	-8.269627
38	C	0.000000	0.000000	-9.945717
39	H	0.000000	0.000000	-12.235897
40	C	0.000000	0.000000	-11.139897