Supporting Information

for

Synthesis and Characterization of Novel Chiral Derivatizing Agents Containing *β*-Keto–Anthracene Adducts (KAAs) by ^{1}H-NMR: Aromatic influence and chiral alcohol absolute configuration determination

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Crystal structures of (–)-(1'*S*,1''*R*,11*R*)-16a and (–)-(1'*S*,1''*S*,11*R*)-18a

Absolute Configurations Determination by X-ray Crystallography

Single crystals of (–)-(1'*S*,1"*R*,11*R*)-**16a** and (–)-(1'*S*,1"*S*,11*R*)-**18a** were perfectly recrystallized in 20% CH_2Cl_2 in hexane. Suitable crystals were selected and subjected to X-ray diffraction on a Bruker APEX-II CCD diffractometer with Mo Kα radiation (λ = 0.71073). The crystals were kept at ambient condition during data collection. Using Olex,4 the structure was solved with the Using Olex,[1] the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimization.[1,2] Asymmetric unit of (–)-(1'*S*,1"*R*,11*R*)-**16a** and (–)-(1'*S*,1"*S*,11*R*)-**18a** are illustrated in Fig 1S and 2S, respectively.

The enantiomerically pure compounds **13** as starting materials and their absolute stereochemistry at the C11 stereogenic center was determined by X-ray crystallographic analysis which have already been reported by Kongsaeree *et. al* in 2001.[3] Therefore, the absolute configurations of the rest of the molecules are then relatively determined using the configuration at C11 as an internal reference.[4] Crystallographic information for the two crystals are shown in Table 1S. Hydrogen bonds in (–)-(1'*S*,1"*R*,11*R*)-**16a** are listed in Table 2S.

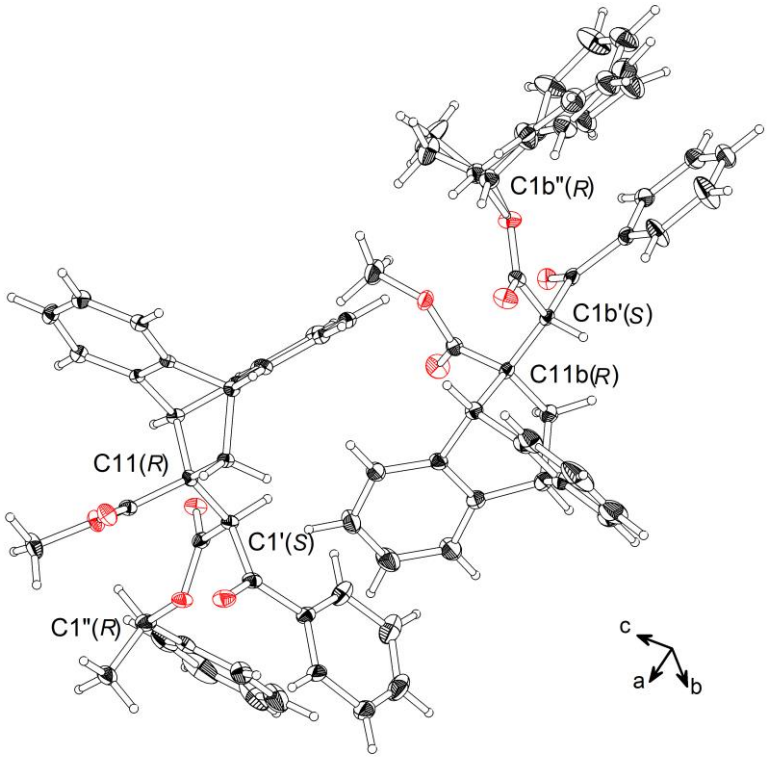


Fig. 1S Asymmetric unit of (–)-(1'*S*,1"*R*,11*R*)-**16a**; thermal ellipsoids are drawn at the 10% probability level.

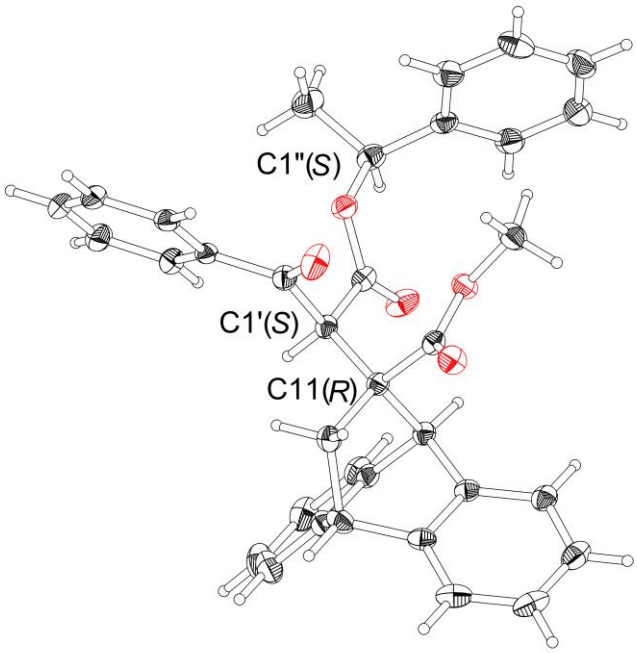


Fig. 2S Crystal structures of (–)-(1'*S*,1"*S*,11*R*)-**18a**; thermal ellipsoids are drawn at the 10% probability level.

Table 1S Crystallographic information for (–)-(1'*S*,1"*R*,11*R*)-**16a** and (–)-(1'*S*,1"*S*,11*R*)-**18a**

Compound	(–)-(1'*S*,1"*R*,11*R*)-**16a**	(–)-(1'*S*,1"*S*,11*R*)-**18a**
CCDC Number	CCDC 1873118	CCDC 1881998
Identification code	(–)-(1'*S*,1"*R*,11*R*)-**16a**	(–)-(1'*S*,1"*S*,11*R*)-**18a**
Empirical formula	$C_{140}H_{120}O_{20}$	$C_7H_6O_5$
Formula weight	2122.35	530.59
Temperature/K	273.15	273.15
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a/Å	13.391(17)	11.3620(4)
b/Å	10.239(13)	15.3627(7)
c/Å	21.40(3)	16.0741(7)
α/°	90	90.00
β/°	106.18(3)	90.00
γ/°	90	90.00
Volume/Å^3	2817(6)	2805.8(2)
Z	1	4
ρ_{calc}g/cm^3	1.251	1.256
μ/mm^{-1}	0.083	0.083
F(000)	1120.0	1120.0
Crystal size/mm^3	0.42 × 0.20 × 0.17	0.5 × 0.42 × 0.38
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.178 to 42.356	4.39 to 50.16
Reflections collected	32630	20316
Independent reflections	6020 R_{int} = 0.0900, R_{sigma} = 0.1026	4982 R_{int} = 0.0386, R_{sigma} = 0.0374
Data/restraints/parameters	6020/144/799	4982/0/363
Goodness-of-fit on F^2	0.802	1.027

Compound	(–)-(1'*S*,1"*R*,11*R*)-**16a**	(–)-(1'*S*,1"*S*,11*R*)-**18a**
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.0633	R_1 = 0.0377, wR_2 = 0.0862
Final R indexes [all data]	R_1 = 0.0839, wR_2 = 0.0717	R_1 = 0.0557, wR_2 = 0.0945
Largest diff. peak/hole / e Å^{-3}	0.10/-0.17	0.25/-0.15
Flack parameter	0.0(8)	-0.1(5)
Absolute structure determination	Reference molecule	Reference molecule

Table 2S Weak hydrogen bond in crystal structure of (–)-(1'*S*,1"*R*,11*R*)-**16a**.

D-H…A	***d* D-H (Å)**	***d* D…A (Å)**	***d* D-H…A (Å)**	**∠ D-H…A (°)**
C2B-H2B…O4A	0.93(1)	3.658(1)	2.780(1)	157.8(7)
C3B-H3B…O1A	0.93(1)	3.577(1)	2.759(8)	147.2(3)
C4"B-H4"B…π	0.93(1)	3.847(5)	2.994(3)	153.3(7)

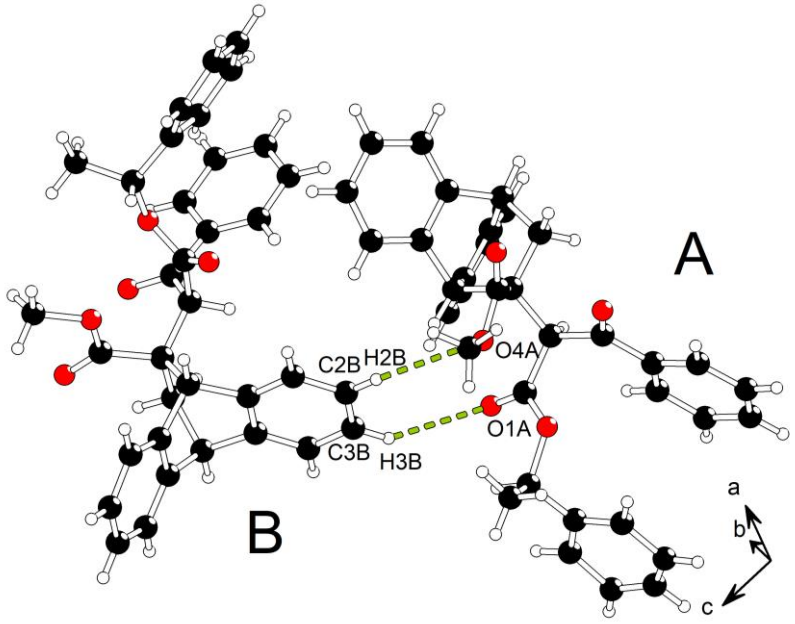
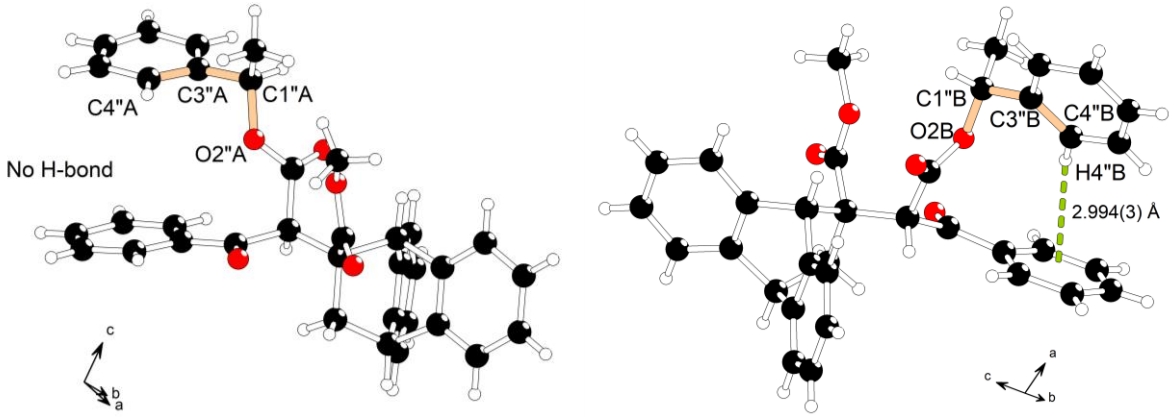


Fig. 3S Intermolecular C-H…O hydrogen bond between the two conformers (**A** and **B**) in asymmetric unit of (–)-(1'*S*,1"*R*,11*R*)-**16a** represented by green dashed lines.



(a) (b)

Fig. 4S Graphical representative of (–)-(1'*S*,1"*R*,11*R*)-**16a** (a) conformer A with torsion angle O2"A-C1"A-C3"A-C4"A of 62.14°, and (a) conformer B with torsion angle O2"B-C1"B-C3"B-C4"B of 33.62°. There is a C-H…π bond (2.994 Å) observed in confermer B (green dashed line), but no C-H…π bond in A.

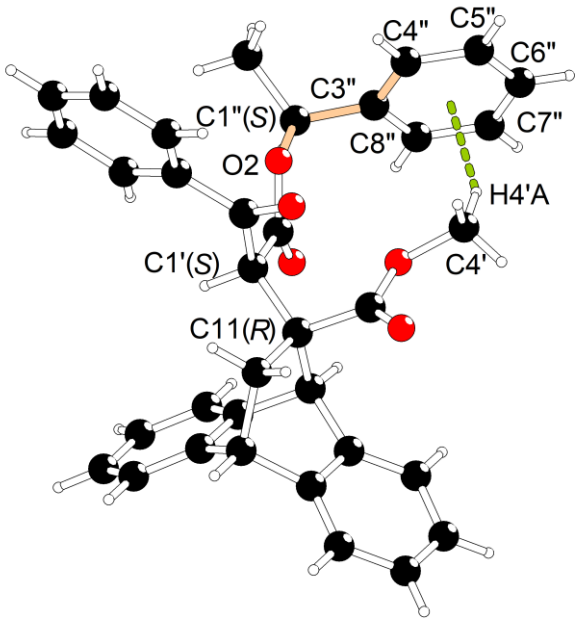


Fig. 5S Graphical representative of (–)-(1'*S*,1"*S*,11*R*)-**18a** showing C-H…π bond (2.942 Å). Tortion angle of O2"-C1"-C3"-C4" is 65.94°.

Comments on CHECKCIF:

1. Crystal structure of (–)-(1'*S*,1''*R*,11*R*)-16a

Alert level A

1. THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
   Calculated sin(theta_max)/wavelength = 0.5083

Author Response: This alert is due to low quality crystal that weakly diffracted. We have tried several times to get a good crystal for better diffraction data but unable to get it.

2. PLAT023_ALERT_3_A Resolution (too) Low [sin(theta)/Lambda < 0.6].. 21.18 Degree

Author Response: A full set of data was collected, however the very high angle data was poor and was omitted. This alert is due to low quality crystal that weakly diffracted. We have tried several times to get a good crystal for better diffraction data but unable to get it.

Alert level B

1. PLAT089_ALERT_3_B Poor Data / Parameter Ratio (Zmax < 18) ..... 4.05 Note

Author Response: A full set of data was collected, however the very high angle data was poor and was omitted. This is due to low quality crystal that weakly diffracted. We have tried several times to get a good crystal for better diffraction data but unable to get it.

2. PLAT234_ALERT_4_B Large Hirshfeld Difference C3A --C3BA . 0.30 Ang

Author Response: This alert is generated due to severe disorder in the crystal.

3. PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01343 Ang.

Author Response: This alert is also generated due to severe disorder in the crystal.

2. Crystal structure of (–)-(1'*S*,1''*S*,11*R*)-18a

There is no serious alert.

Solvent effect of diastereomers KAA esters (16a-b and 18a-b)

We tested the influence of the NMR spectroscopic solvents by changing the solvent such as less polar or more polarity than $CDCl_3$, it will affect the $\Delta\delta^{RS}$ values.[5] Unfortunately, some compounds are not soluble in methanol-d_4 so we used acetone-d_6 (ε 20.7)[6] instead because for the diastereomers KAAs (**16a-b** and **18a-b**) dissolve very well. The chemical shift difference ($\Delta\delta^{RS}$) of each substituent can be calculated explicitly from $\Delta\delta^{RS}(L_1/L_2) = \delta L_1/L_2(11R)_{KAA} – \delta L_1/L_2(11S)_{KAA}$. As summarized below, the $\Delta\delta^{RS}$ values of KAA ester (**16a-b**, **18a-b**) in acetone-d_6 were greater, especially H-1" position and also have the same pattern as those obtained in $CDCl_3$ as depicted in Fig. 6s and 7S.

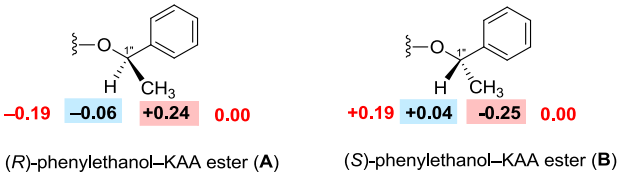


Fig. 6S Comparison of the selected $\Delta\delta^{RS}$ values of (*R*)- and (*S*)-phenylethanol KAA esters obtained in both NMR solvents: $CDCl_3$ (**bold black colour**) and acetone-d_6 (**bold red colour**).

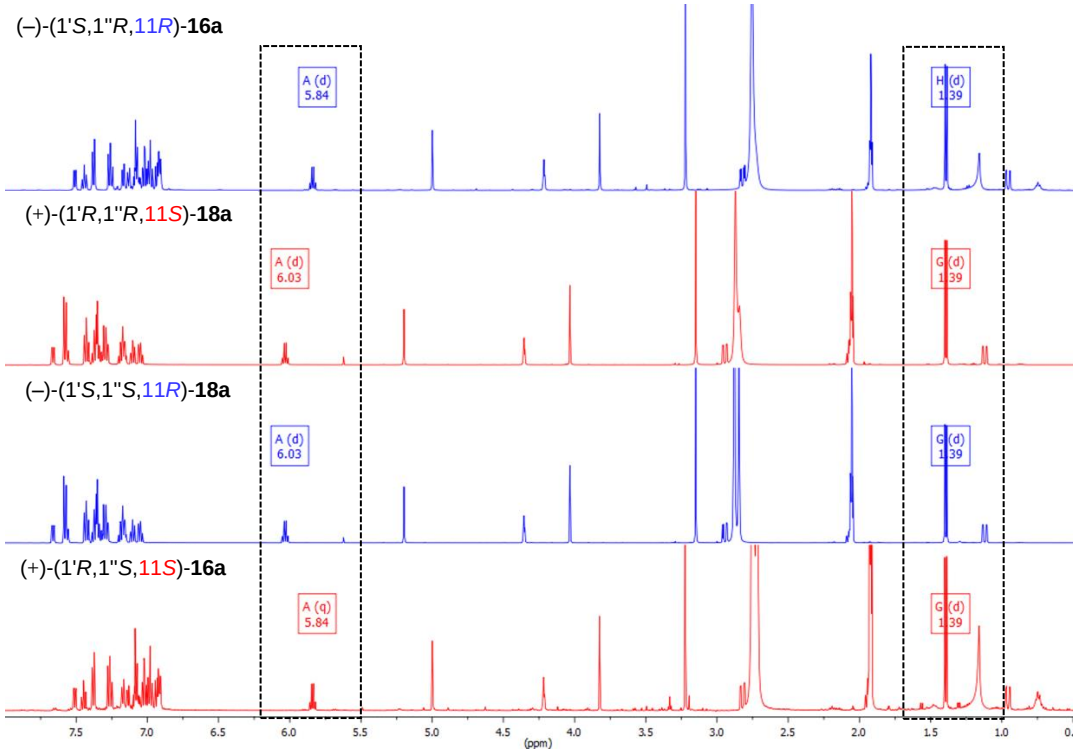


Fig. 7S Comparison of the ^{1}H-NMR spectra of (*R*)- and (*S*)-phenylethanol KAA esters in acetone-d_6.

Racemization study of all diastereomers KAA esters [(16a-b, 18a-b) and (21a–24a)]

The solution of all diastereomers KAA esters (**16a-b**, **18a-b**) and (**21a**–**24a**) (5-7 mg) in $CDCl_3$ (0.8 mL) were characterized by ^{1}H-NMR (500 MHz) technique in different period of times (first attempt and second attempt (24 hours later) and then the ^{1}H NMR data were collected, so we achieved the same spectra for each compound even in the different dates. The results obviously revealed that all ^{1}H-NMR spectra have exhibited the same signals as found in the beginning and the racemization of KAA esters was not occurred.

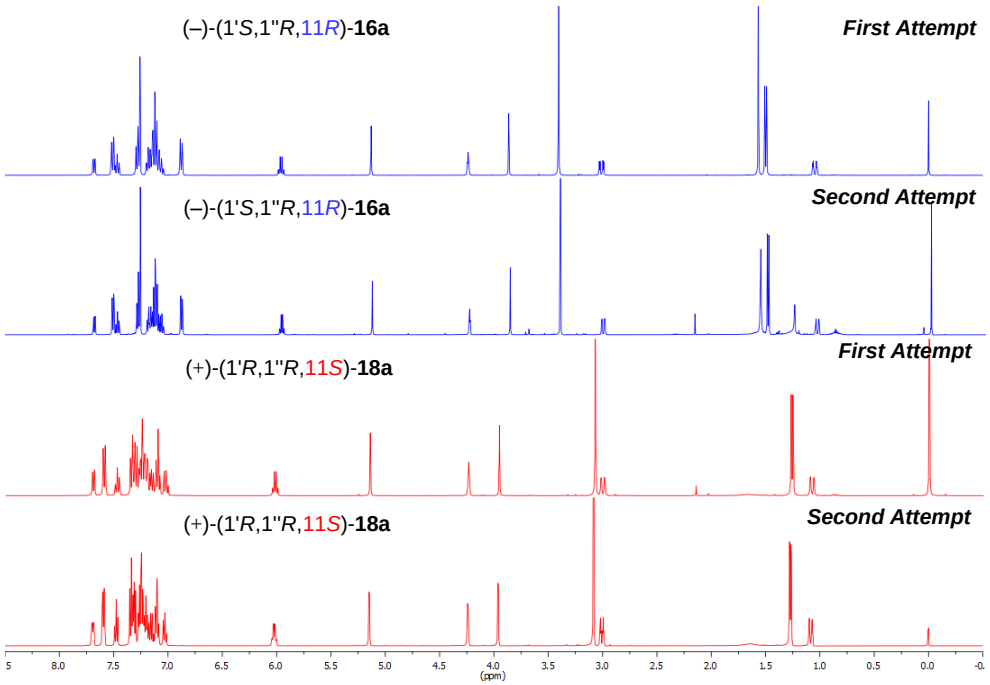


Fig. 8S Comparison of the ^{1}H-NMR spectra of (*R*)-phenylethanol KAA esters in different time periods.

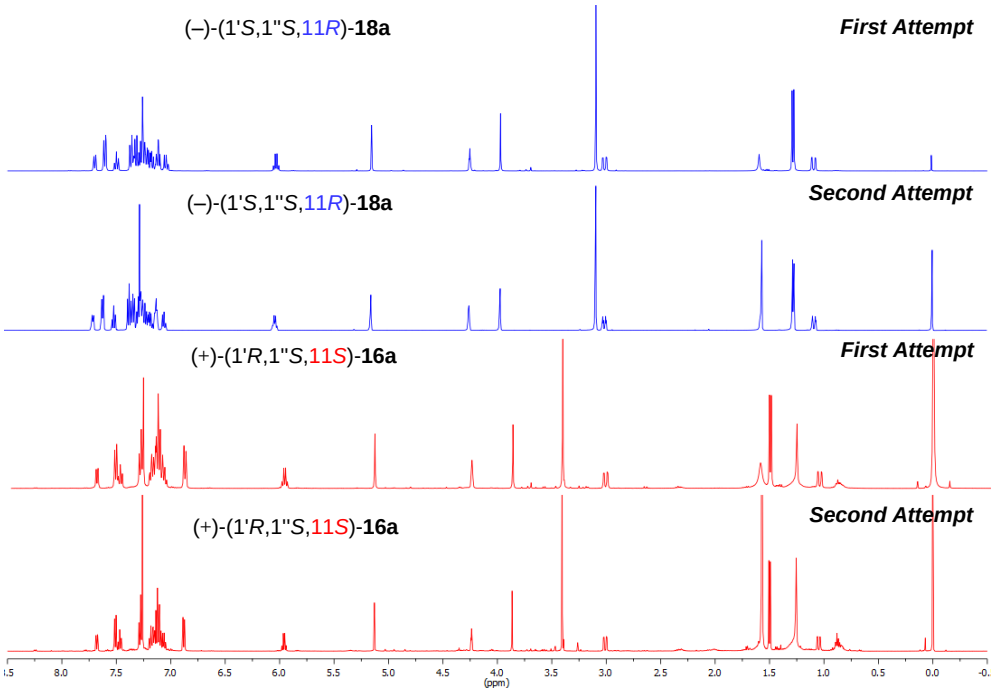


Fig. 9S Comparison of the ^{1}H-NMR spectra of (*S*)-phenylethanol KAA esters in different time periods.

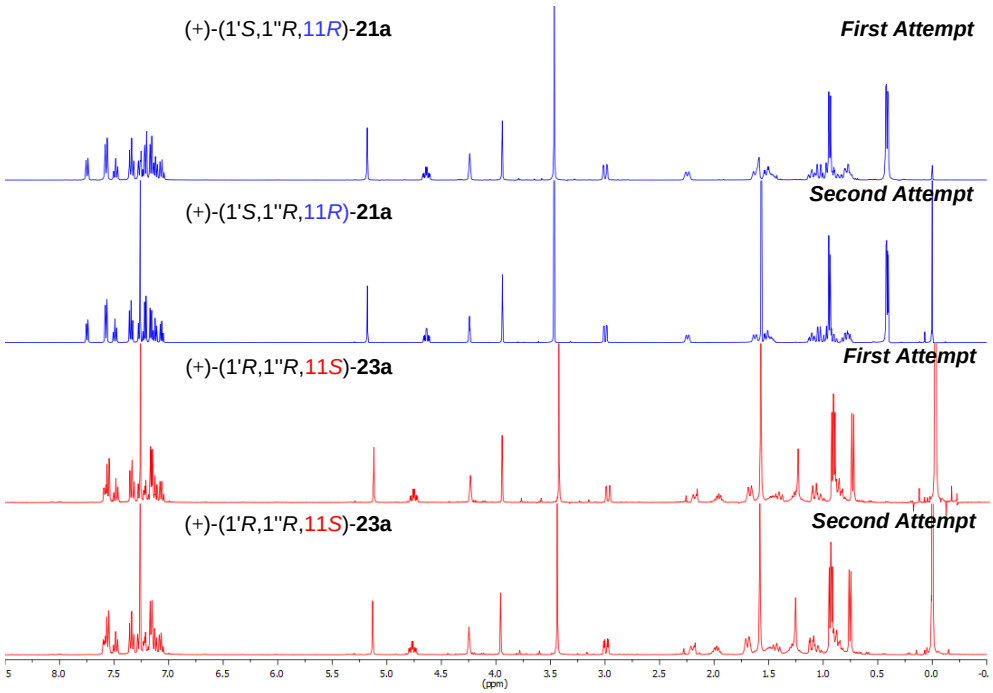


Fig. 10S Comparison of the ^{1}H-NMR spectra of (–)-menthol KAA esters in different time periods.

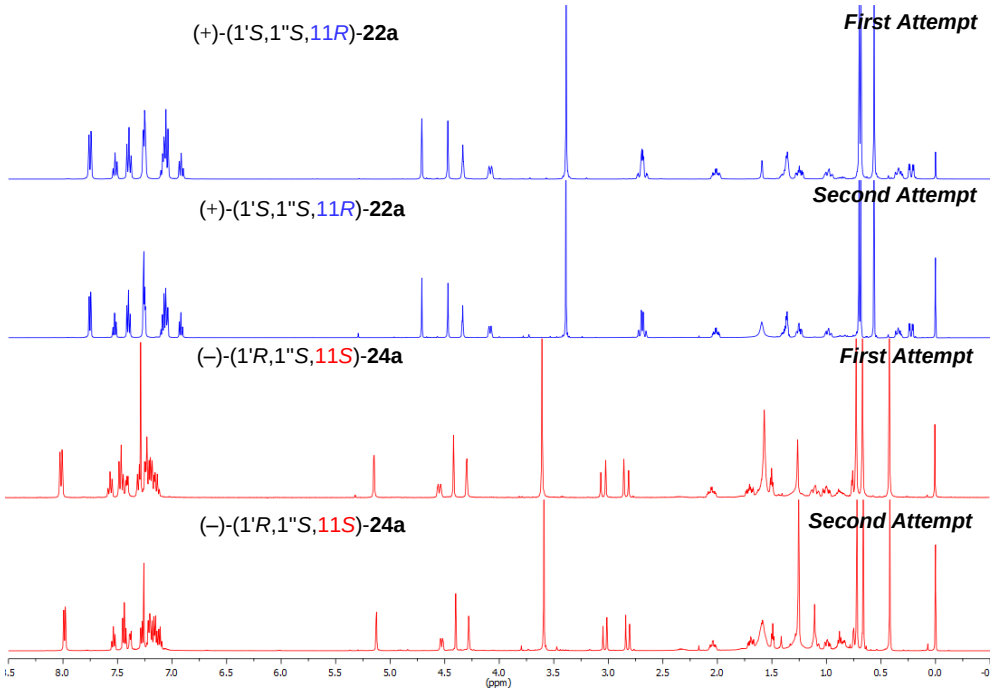
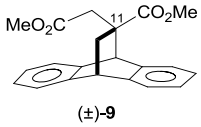


Fig. 11S Comparison of the ^{1}H-NMR spectra of (–)-borneol KAA esters in different time periods.

References

1. G. Sheldrick, *Acta. Cryst,. Section A* 2015, **71**, 3–8.
2. (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*., 2009, **42**, 339–341., 2009, **42**, 339–341; (b) G. Sheldrick, *Acta. Cryst,. Section C*, 2015, **71**, 3–8.
3. P. Kongsaeree, P. Meepowpan and Y. Thebtaranonth, *Tetrahedron: Asymmetry*, 2001, **12**, 1913–1922.
4. H. D. Flack and G. Bernardinelli, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 1999, **55**, 908–915.
5. S.-Y. Han and K. Choi, *Euro. J. Org. Chem.* **2011**, 2920–2923.
6. NMR Solvent Data Chart, Cambridge Isotope Laboratories, Inc., Andover, MA.

^{1}H-NMR and ^{13}C-NMR spectra of compounds 9–24



(±)-**9**

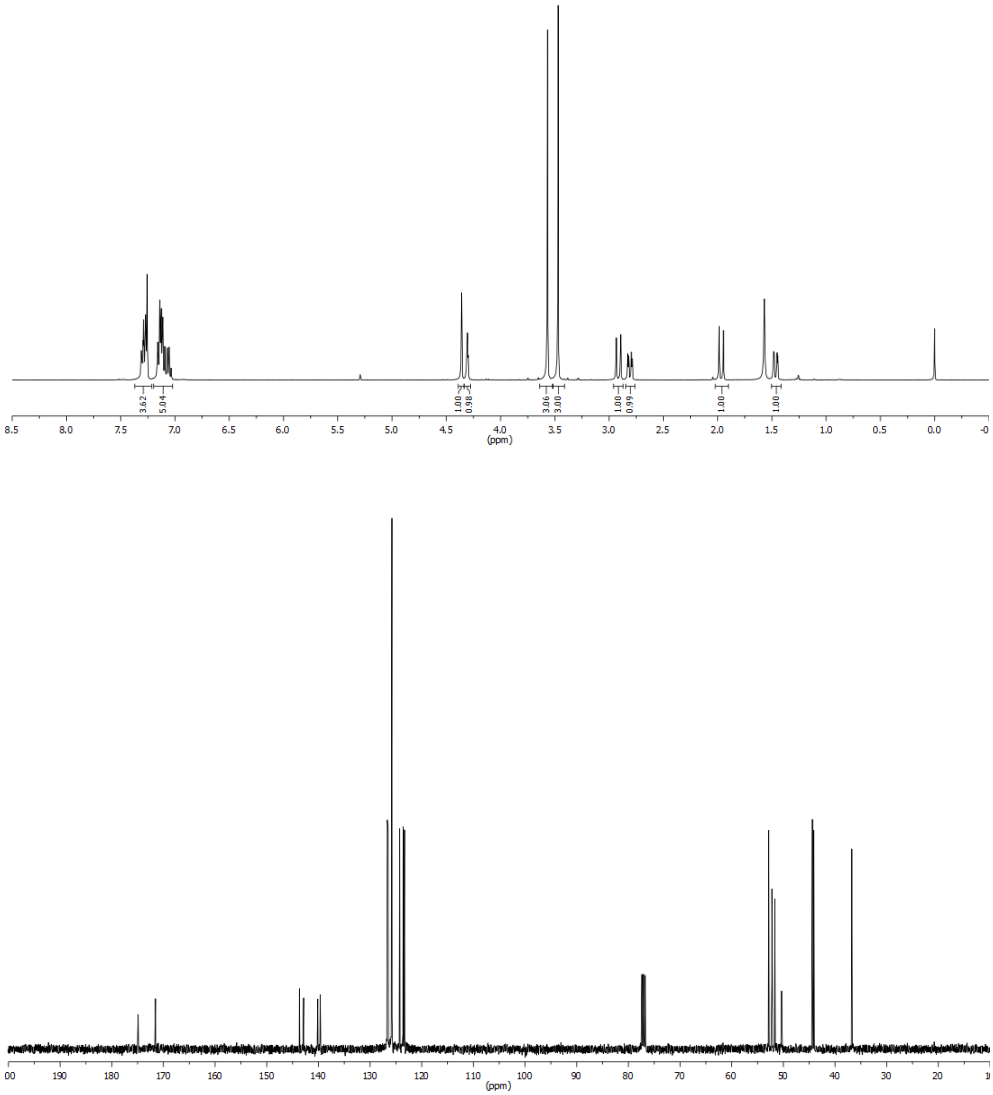
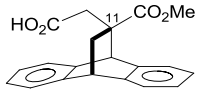
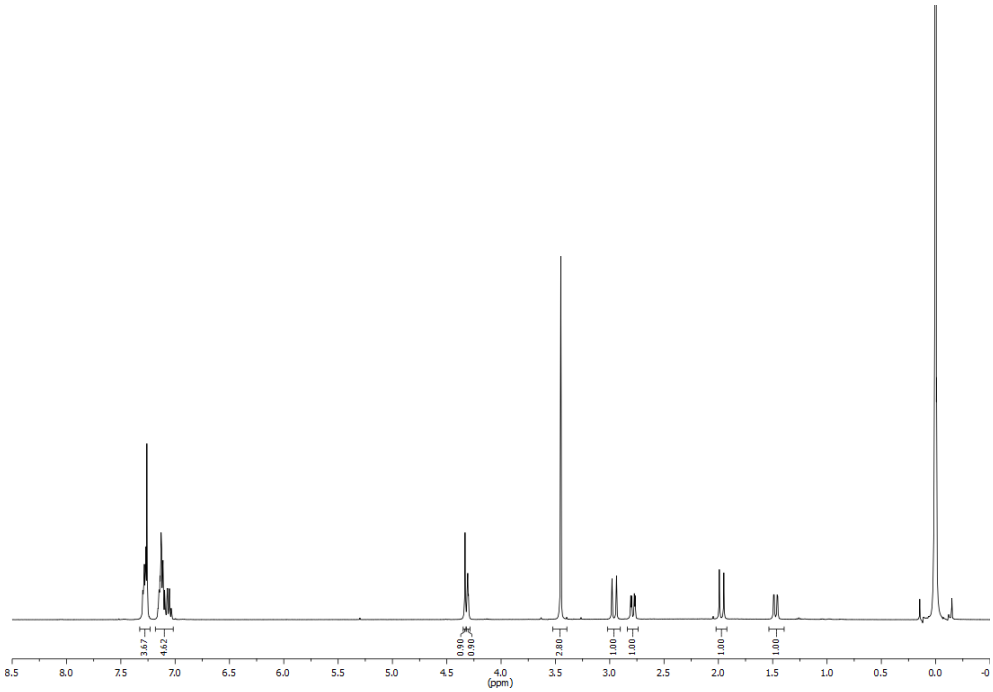


Fig. 12S 11-Carbomethoxy-11-(1'-carbomethoxymethyl)-9,10-dihydro-9,10-ethanoanthracene ((±)-**9**).



(±)-**13**



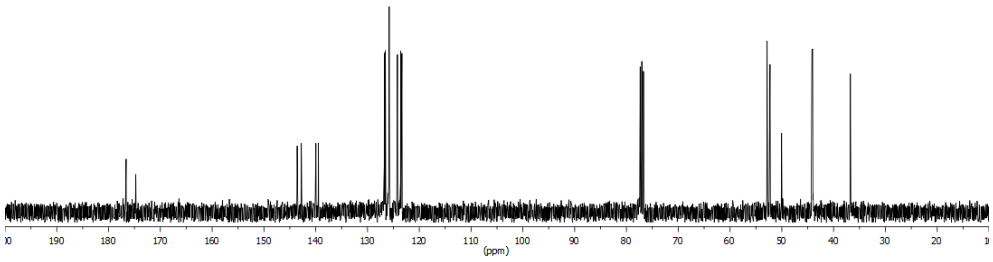
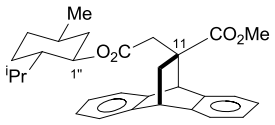


Fig. 13S 11-Carbomethoxy-11-(1'-carboxymethyl)-9,10-dihydro-9,10-ethanoanthracene ((±)-**13**).



(–)-(1"*R*,11*S*)-**11**

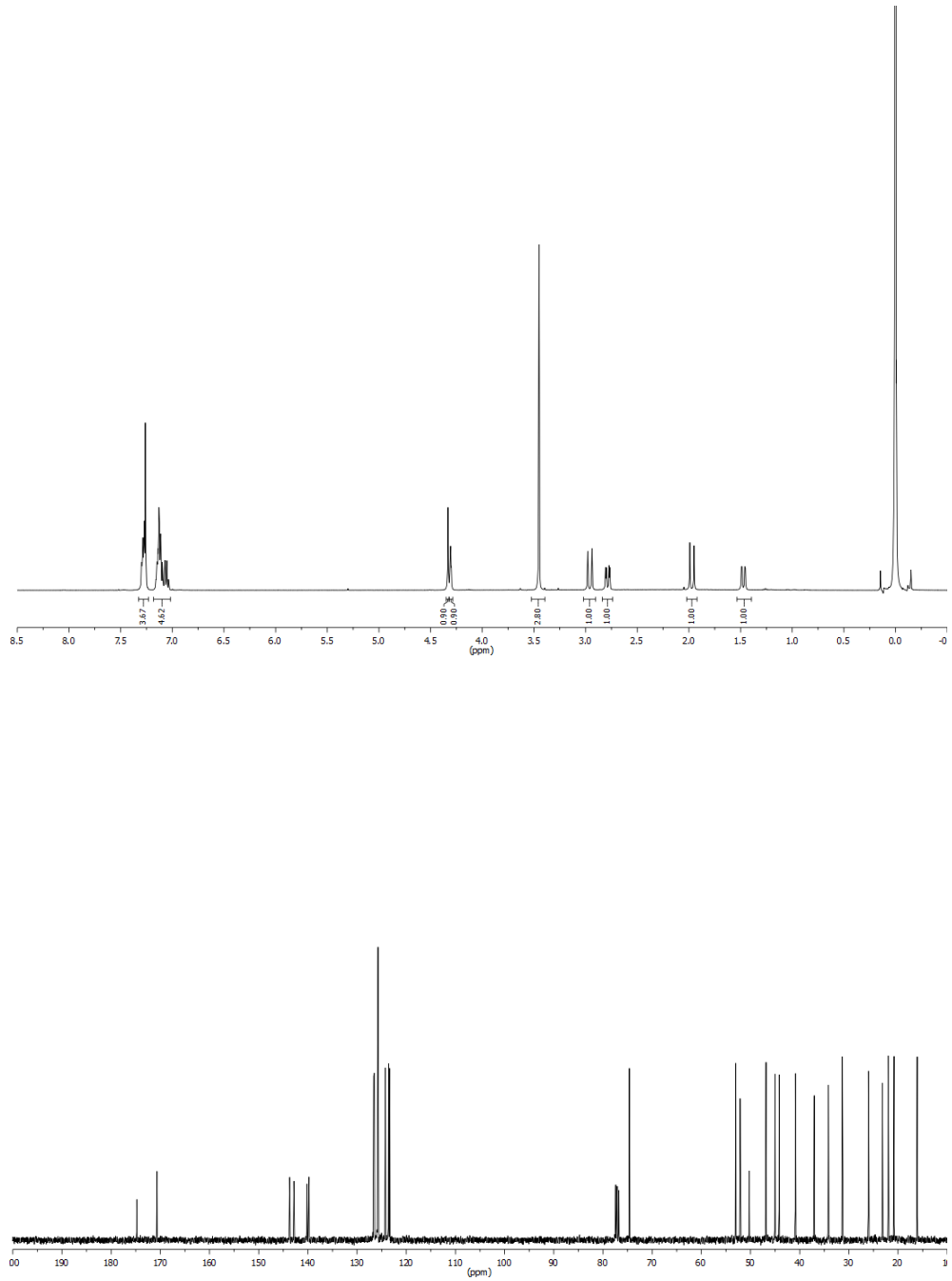
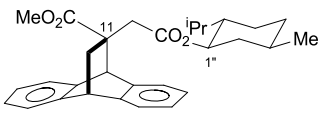
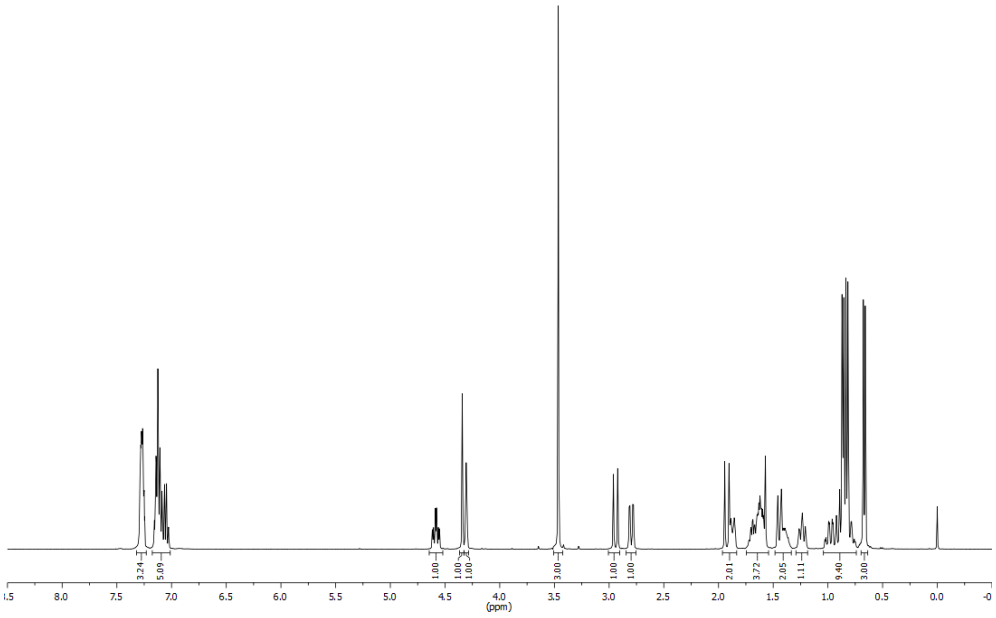


Fig. 14S 11-Carbomethoxy-11-[(–)-menthoxyacetyl]-9,10-dihydro-9,10-ethanoanthracene ((–)-(1",11*S*)-**11**).



(–)-(1"*R*,11*R*)-**12**



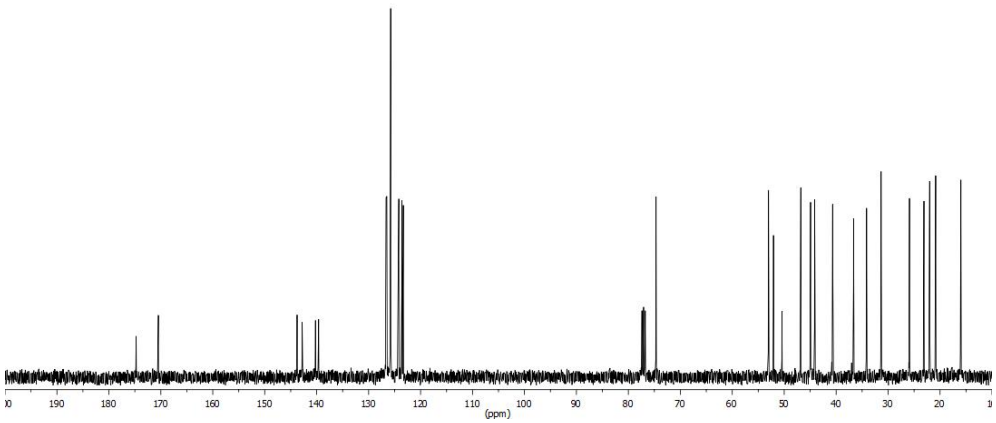
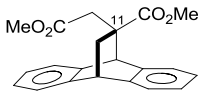


Fig. 15S 11-Carbomethoxy-11-[(–)-menthoxyacetyl]-9,10-dihydro-9,10-ethanoanthracene ((–)-(1",11*R*)-**12**).



(+)-(11*S*)-**9**

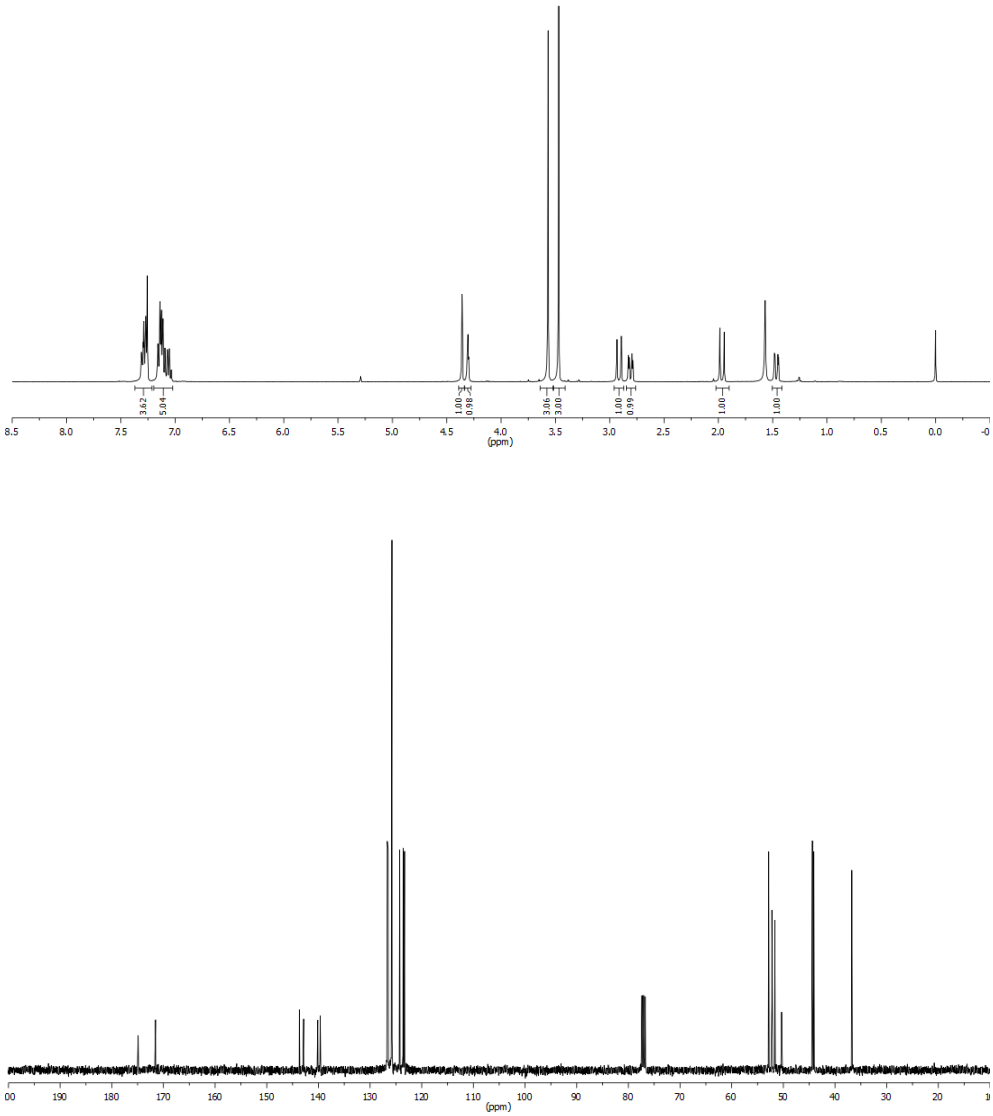
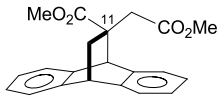


Fig. 16S 11-Carbomethoxy-11-(1'-carbomethoxymethyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(11*S*)-**9**).



(–)-(11*R*)-**9**

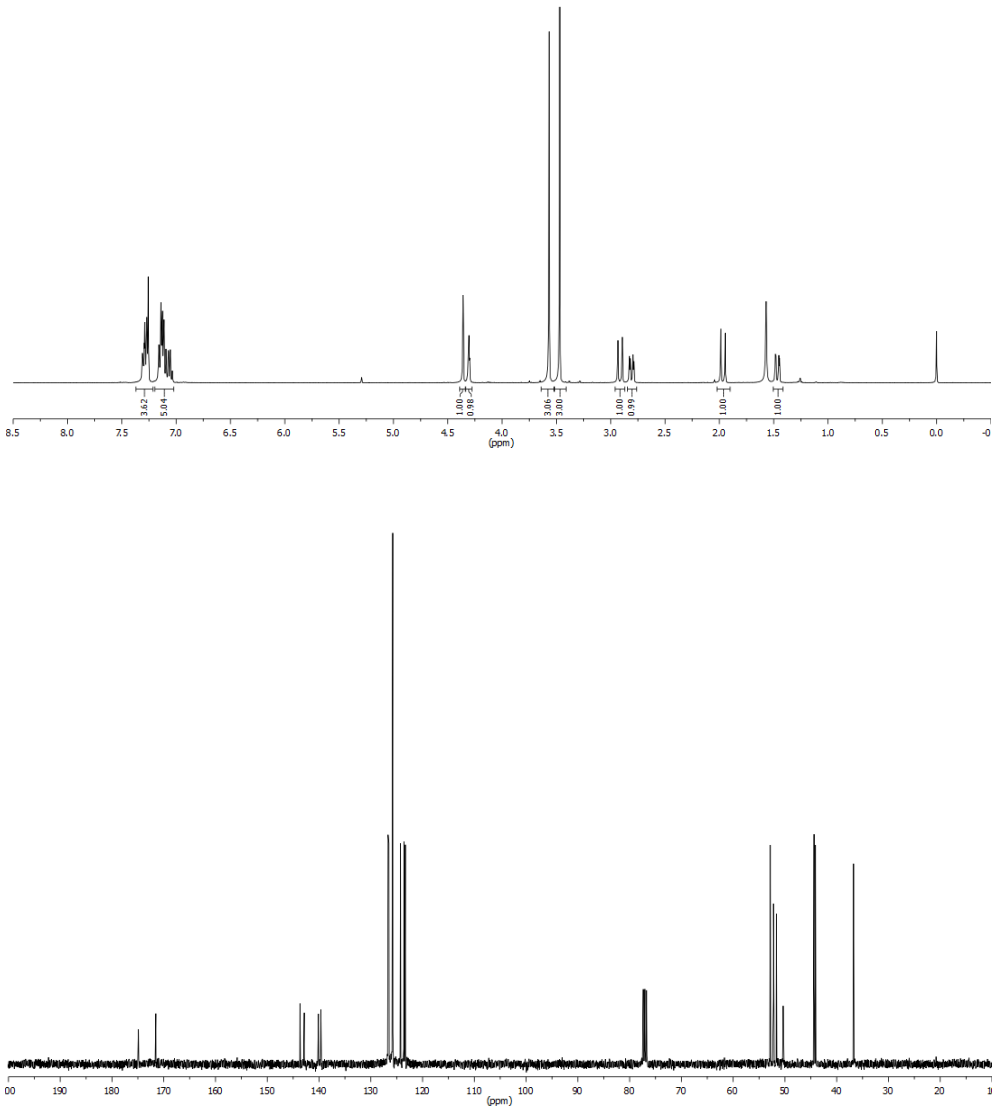
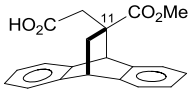
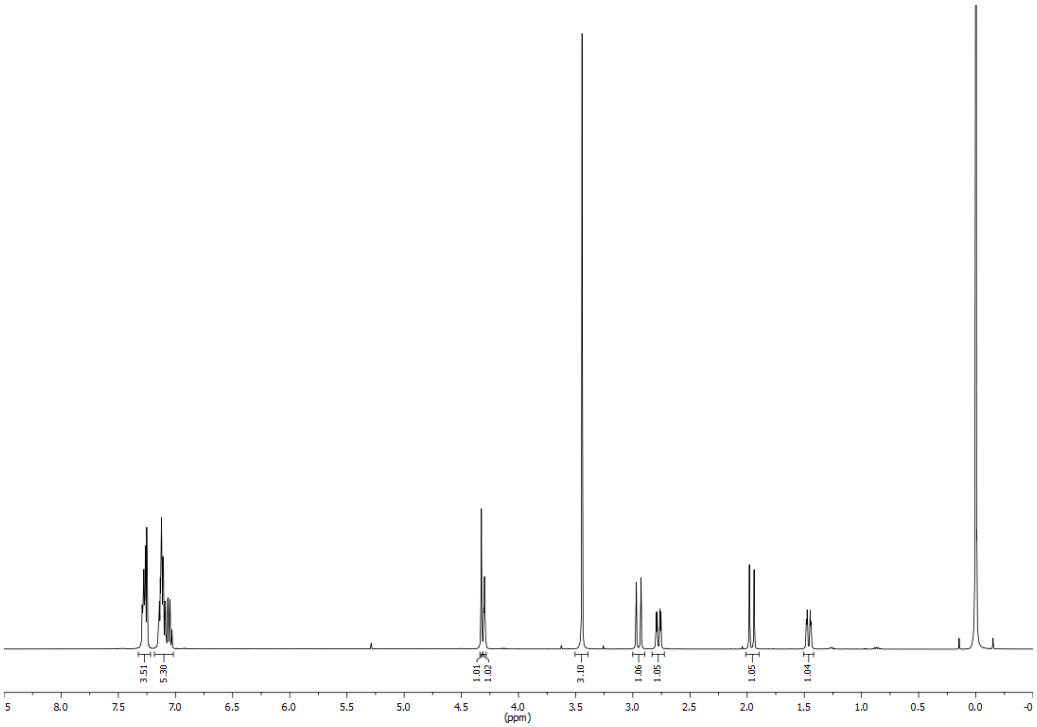


Fig. 17S 11-Carbomethoxy-11-(1'-carbomethoxymethyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(11*R*)-**9**).



(+)-(11*S*)-**13**



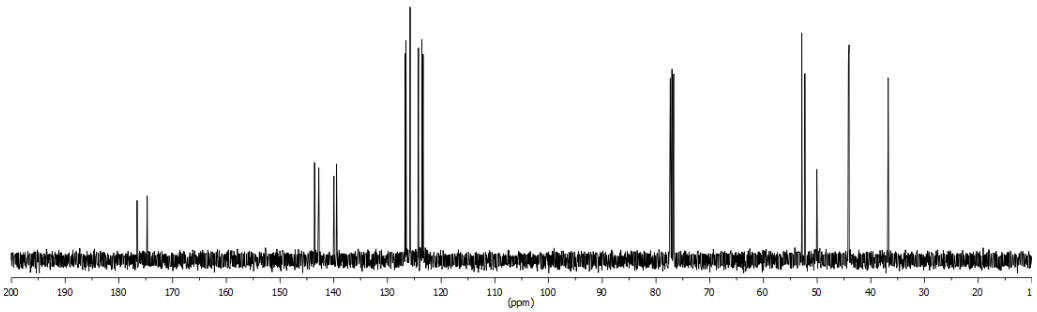
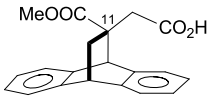


Fig. 18S 11-Carbomethoxy-11-(1'-carboxymethyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(11*S*)-**13**).



(–)-(11*R*)-**13**

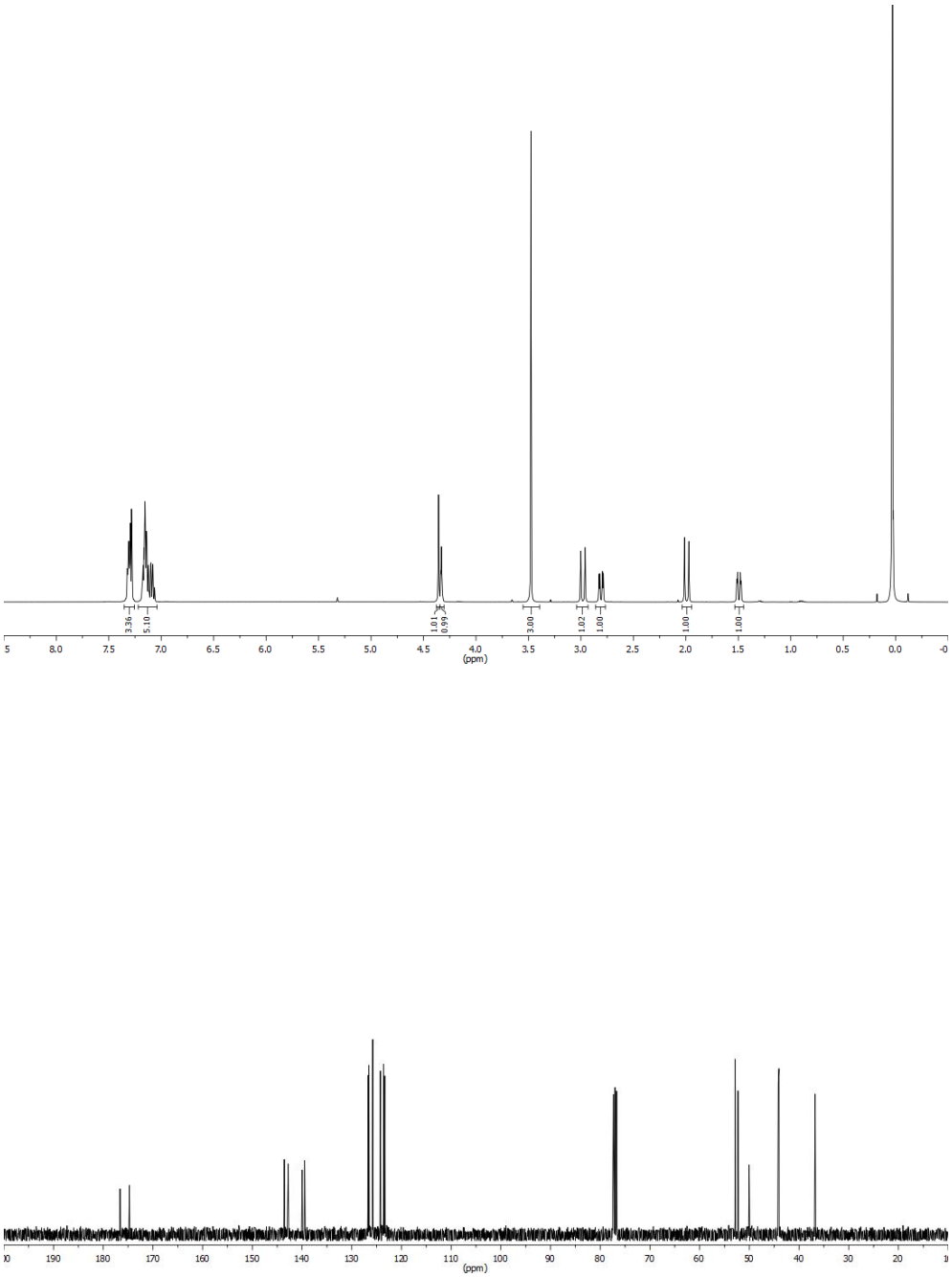
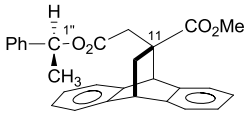


Fig. 19S 11-Carbomethoxy-11-(1'-carboxymethyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(11*R*)-**13**).



(+)-(1"*R*,11*S*)-**14**

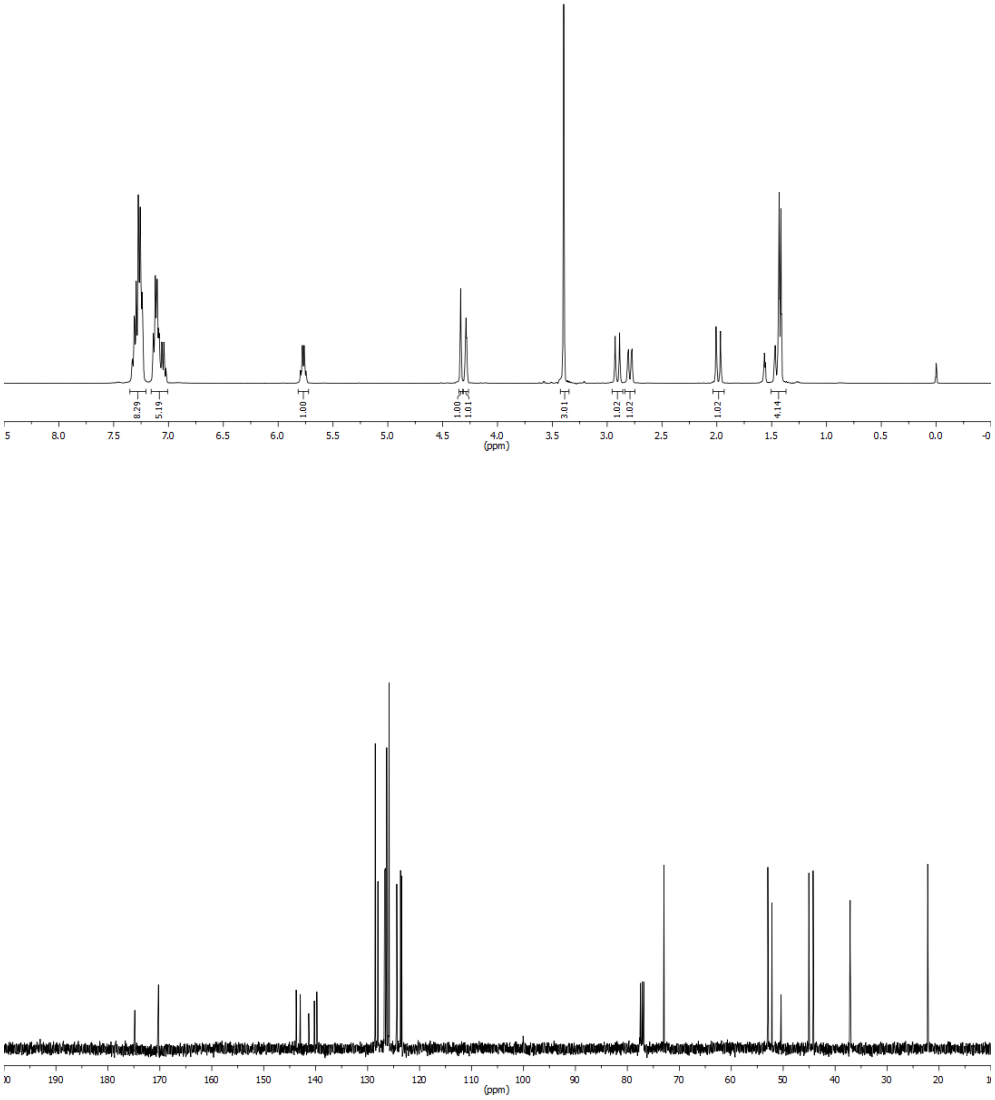
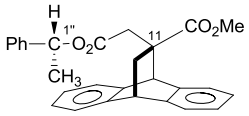


Fig. 20S 11-Carbomethoxy-11-(1'-carboxymethyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1",11*S*)-**14**).



(–)-(1"*S*,11*S*)-**15**

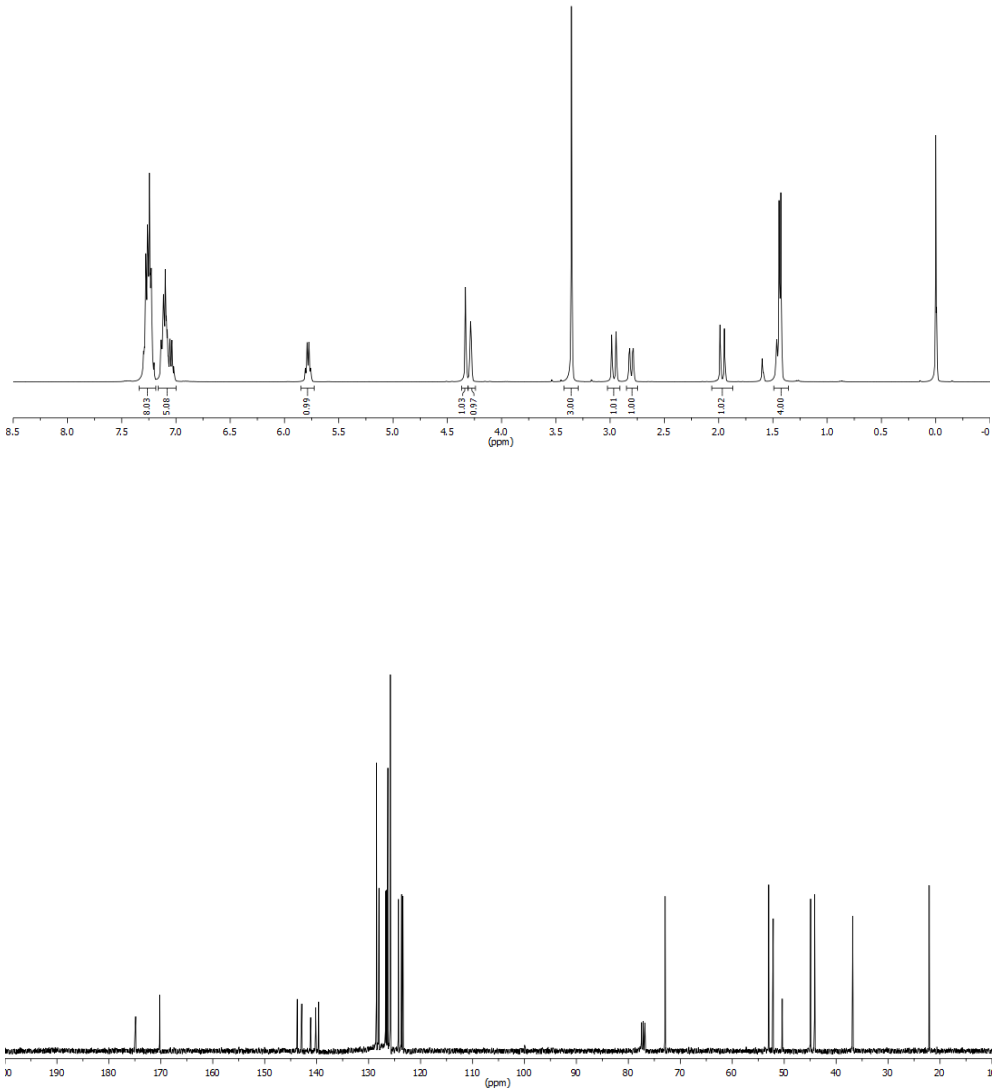
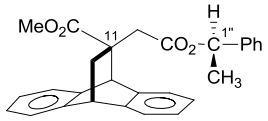
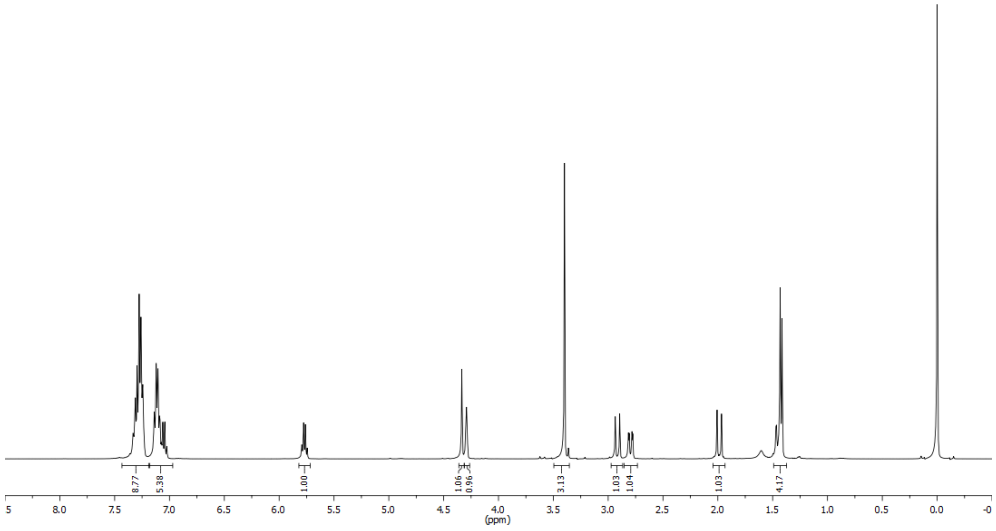


Fig. 21S 11-Carbomethoxy-11-(1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1"*S*,11*S*)-**15**).



(–)-(1"*S*,11*R*)-**14**



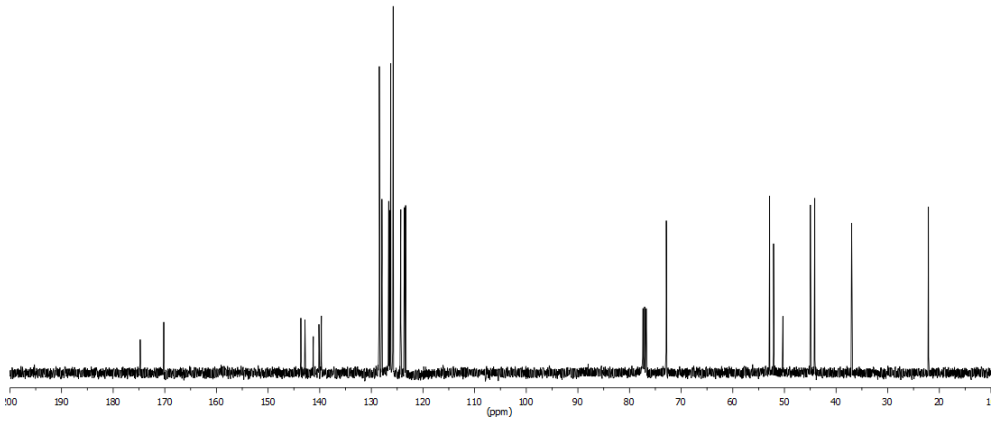
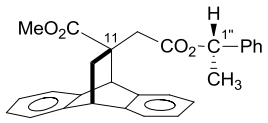
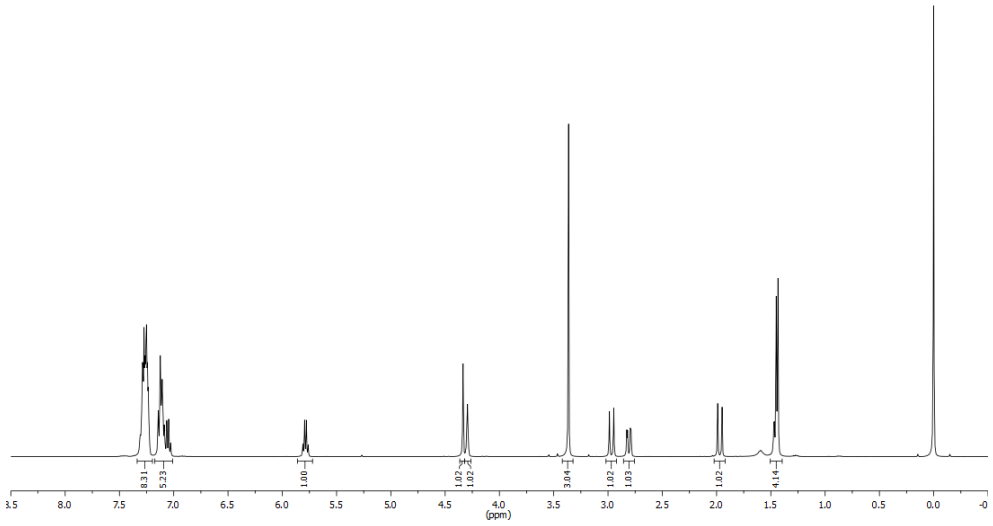


Fig. 22S 11-Carbomethoxy-11-(1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1"*S*,11*R*)-**14**).



(+)-(1"*R*,11*R*)-**15**



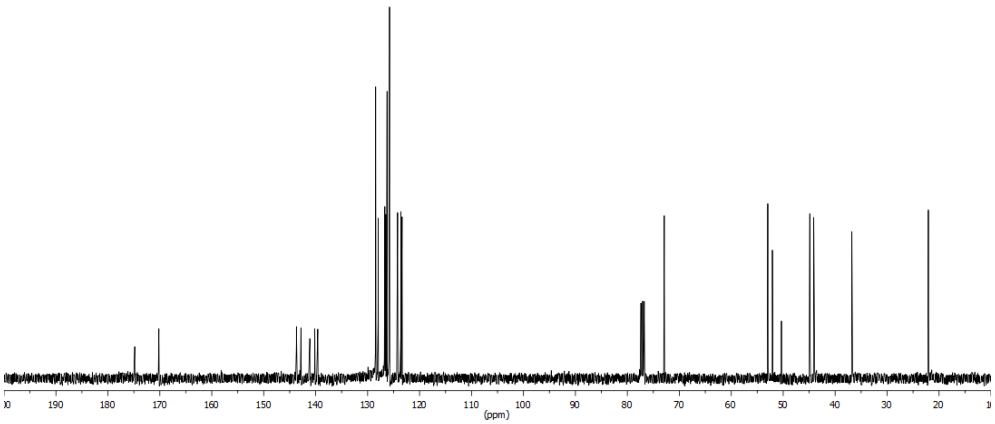
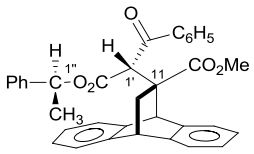
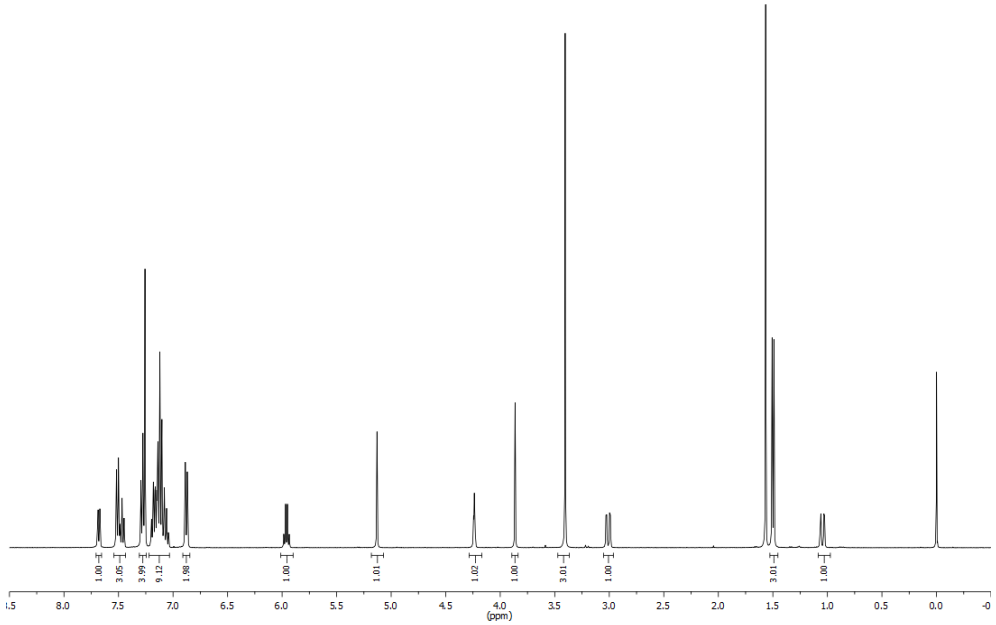


Fig. 23S 11-Carbomethoxy-11-(1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1"*R*,11*R*)-**15**).



(–)-(1'*S*,1"*R*,11*R*)-**16a**



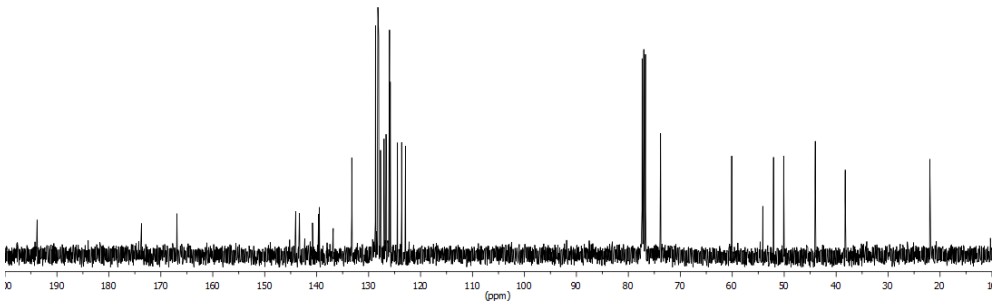
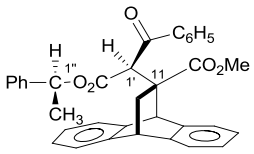
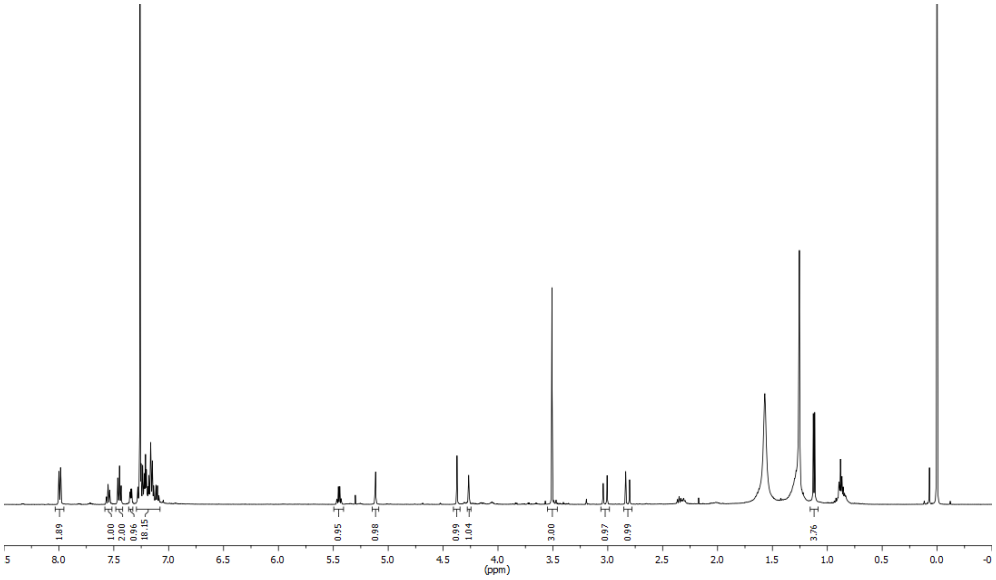
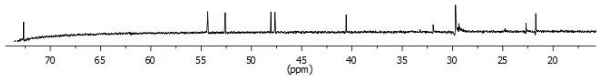


Fig. 24S 11-carbomethoxy-11-(1'-benzoyl or naphthoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1'*S*,1"*R*,11*R*)-**16a**).



(+)-(1'*R*,1"*R*,11*R*)-**19a**





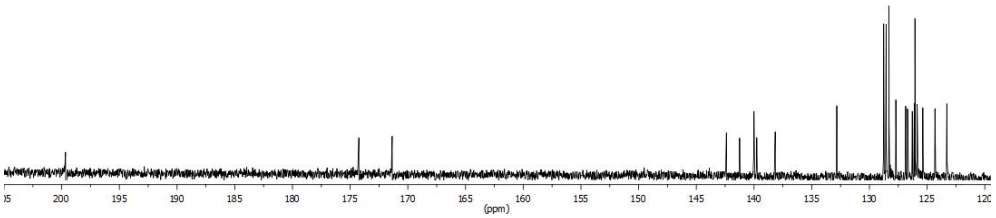
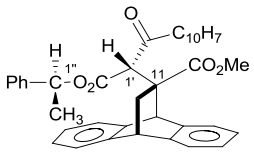


Fig. 25S 11-carbomethoxy-11-(1'-benzoyl or naphthoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*R*,1"*R*,11*R*)-**19a**).



(–)-(1'*S*,1"*R*,11*R*)-**16b**

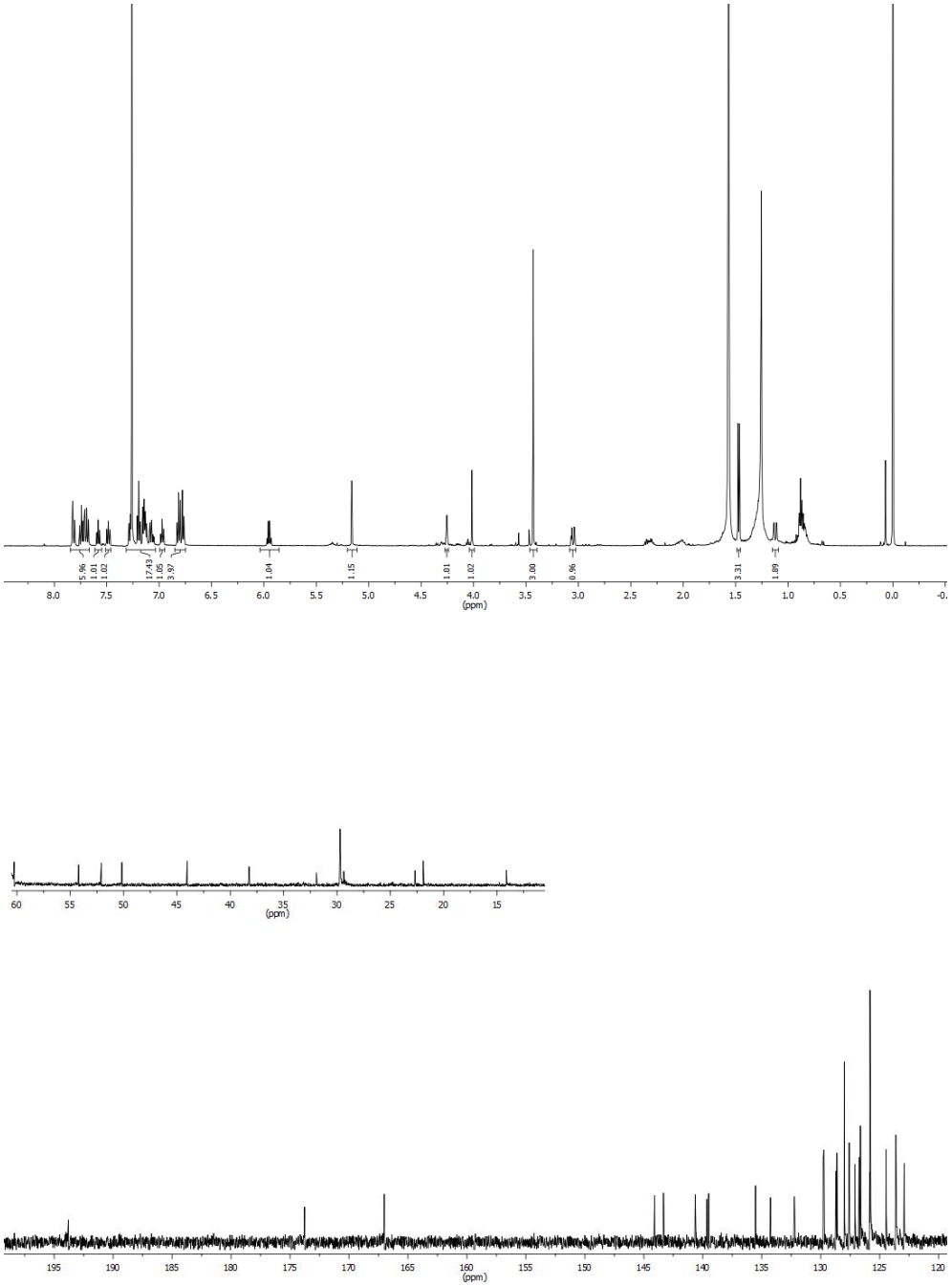
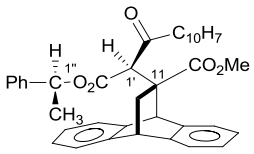


Fig. 26S 11-Carbomethoxy-11-(1'-naphthoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1'*S*,1"*R*,11*R*)-**16b**).



(+)-(1'*R*,1"*R*,11*R*)-**17b**

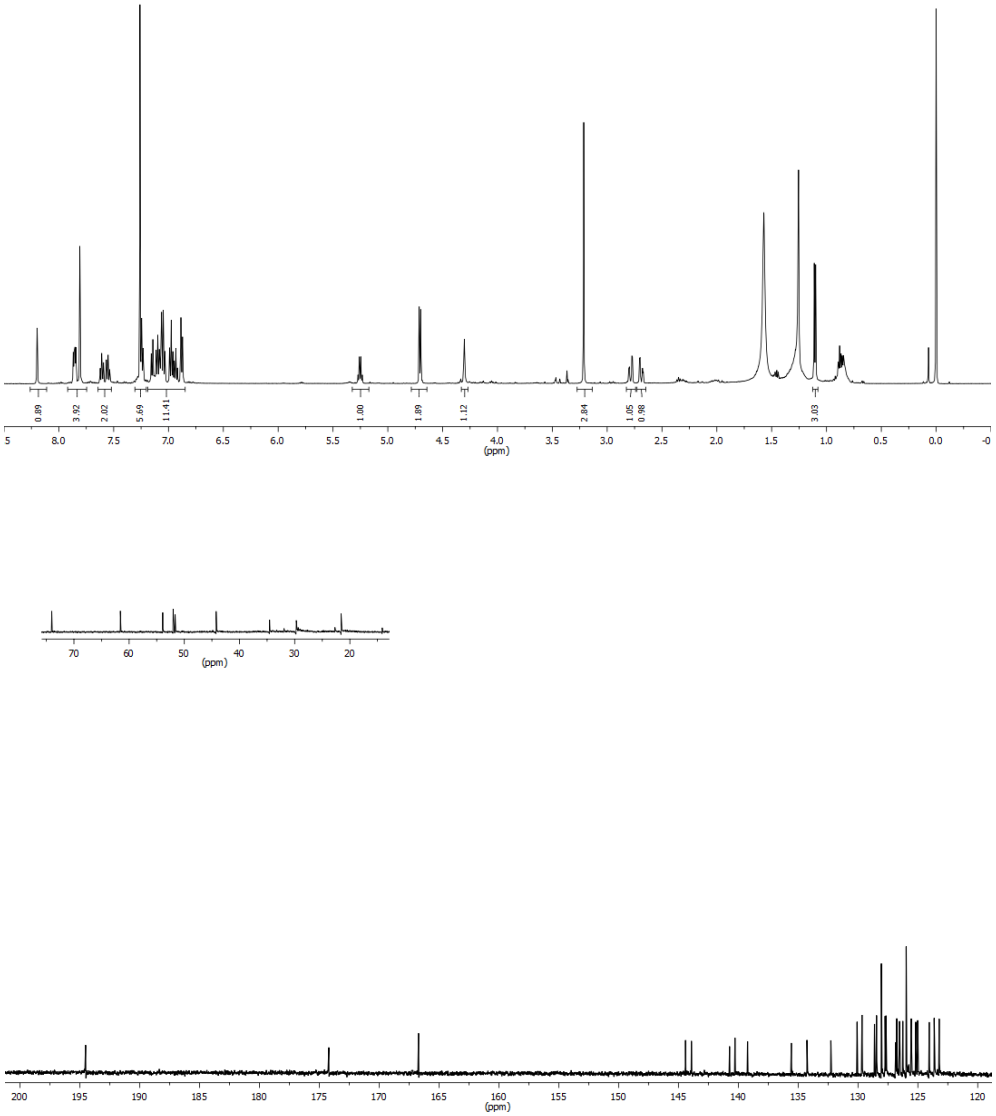
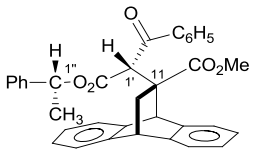
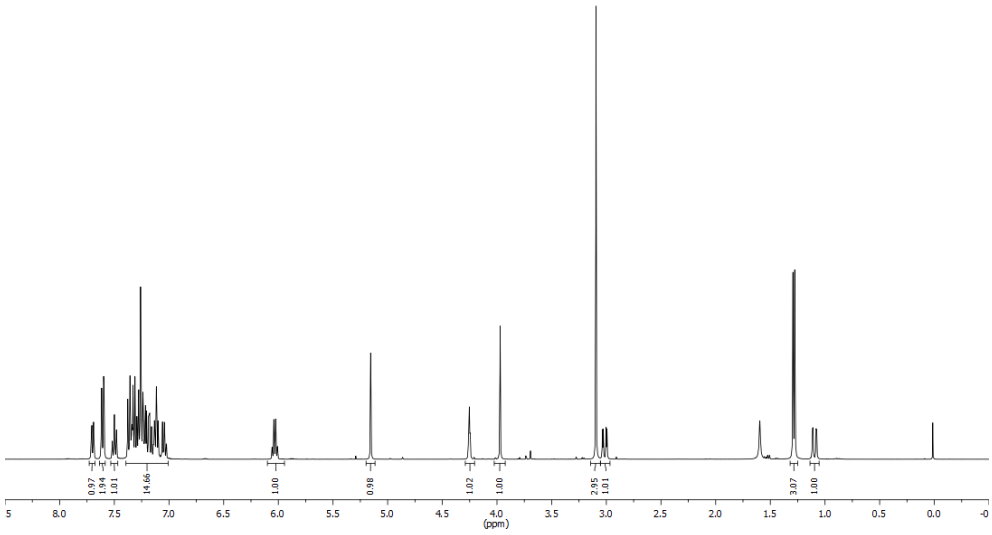


Fig. 27S 11-Carbomethoxy-11-(1'-naphthoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*R*,1"*R*,11*R*)-**17b**).



(–)-(1'*S*,1"*S*,11*R*)-**18a**



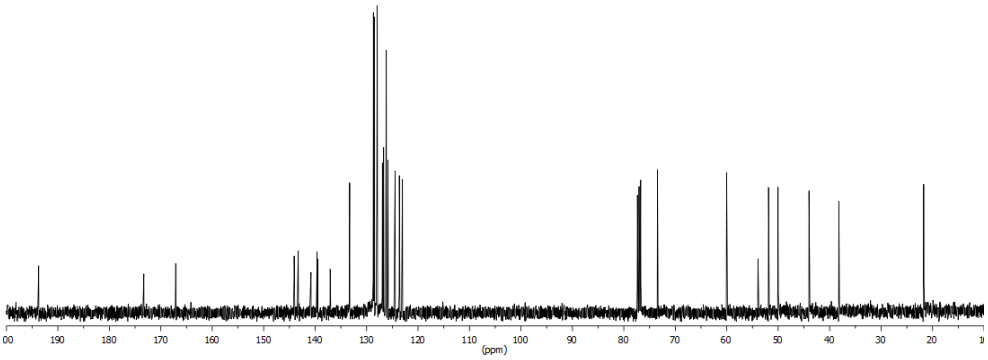
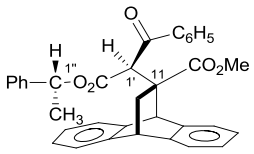


Fig. 28S 11-(Carbomethoxy)-(1'-benzoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1'*S*,1"*S*,11*R*)-**18a**).



(+)-(1'*R*,1"*S*,11*R*)-**19a**

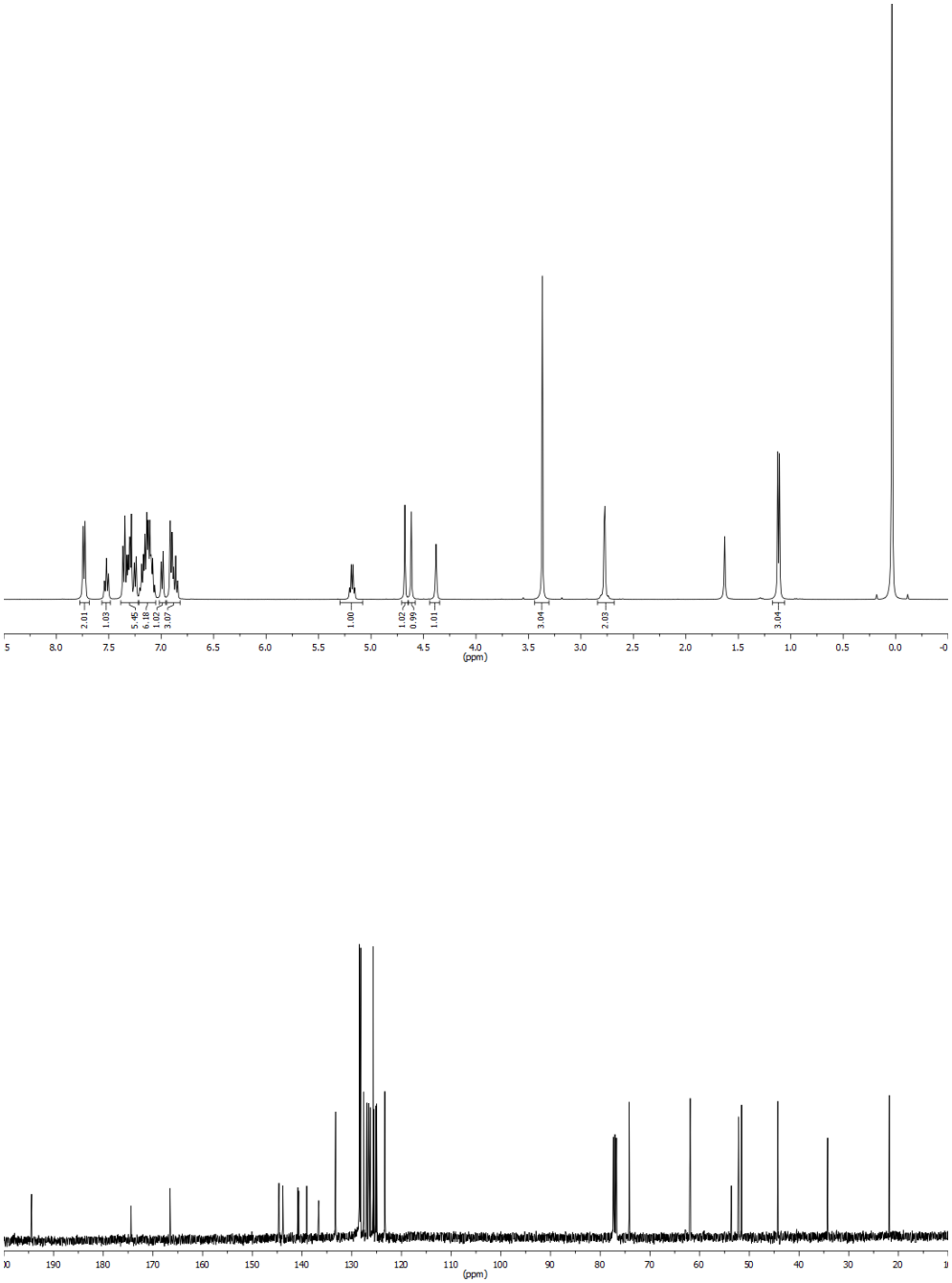
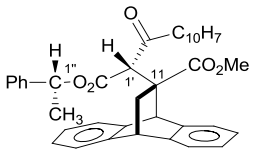


Fig. 29S 11-(Carbomethoxy)-(1'-benzoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*R*,1"*S*,11*R*)-**19a**).



(+)-(1'*S*,1"*S*,11*R*)-**18b**

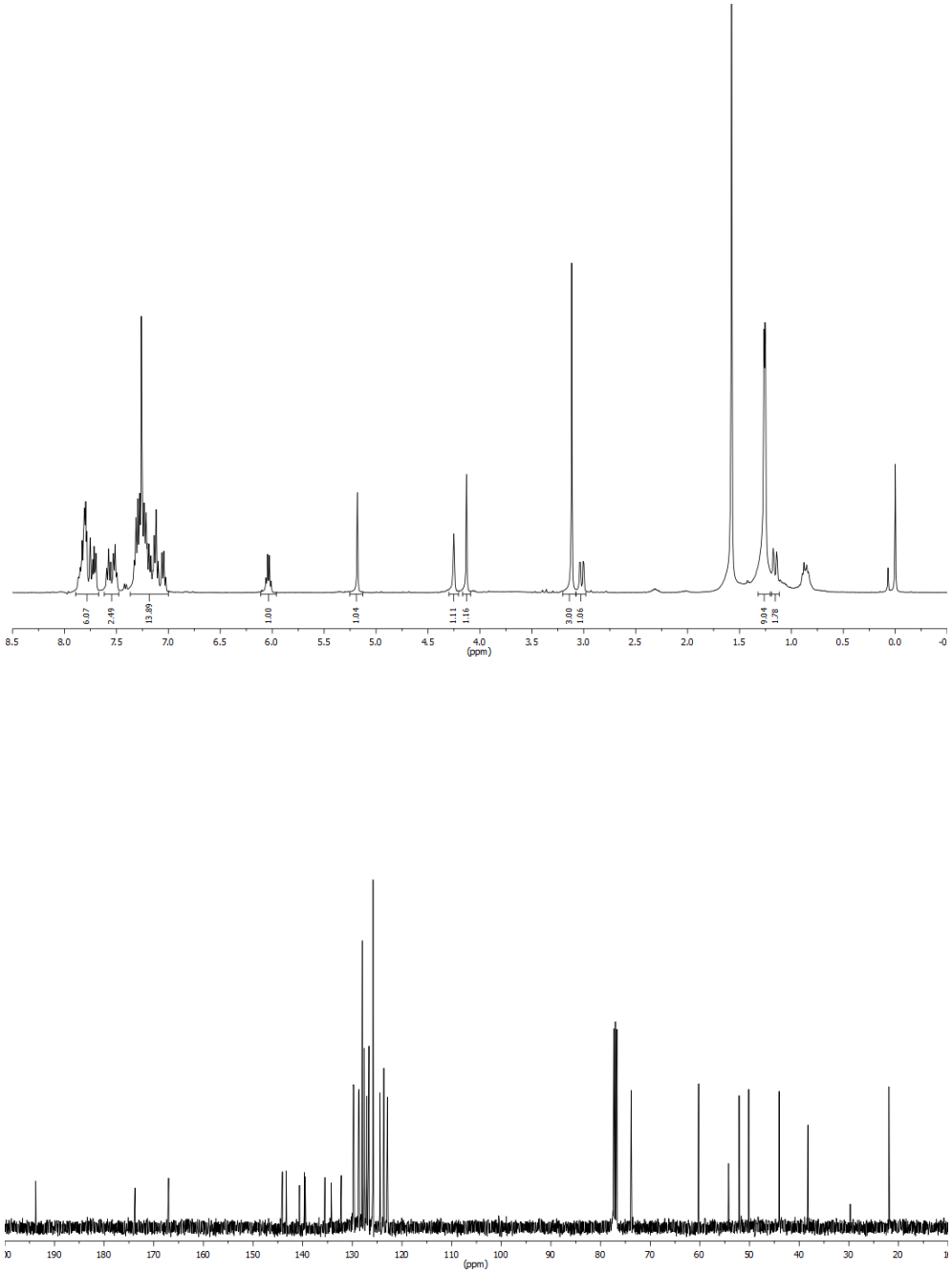
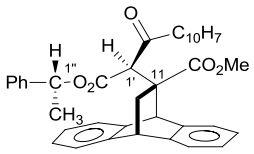


Fig. 30S 11-(Carbomethoxy)-(1'-naphthoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*S*,1"*S*,11*R*)-**18b**).



(–)-(1'*R*,1"*S*,11*R*)-**19b**

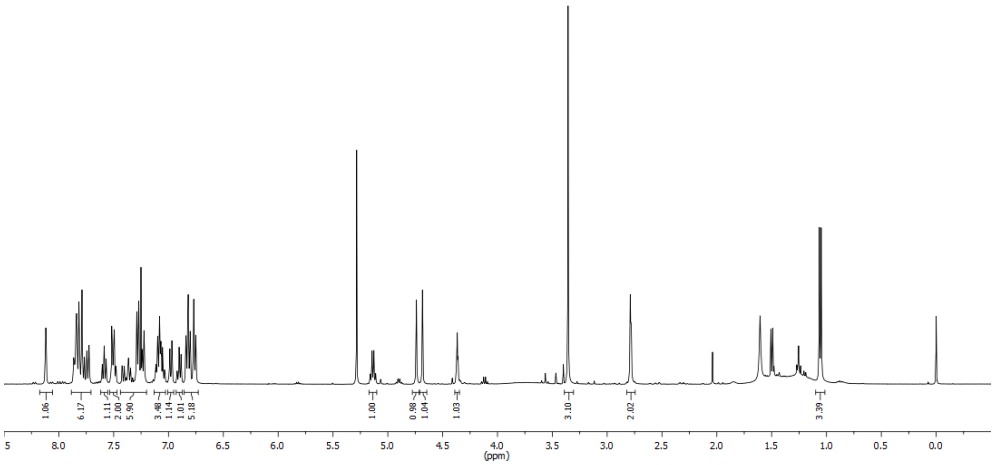
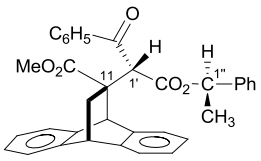
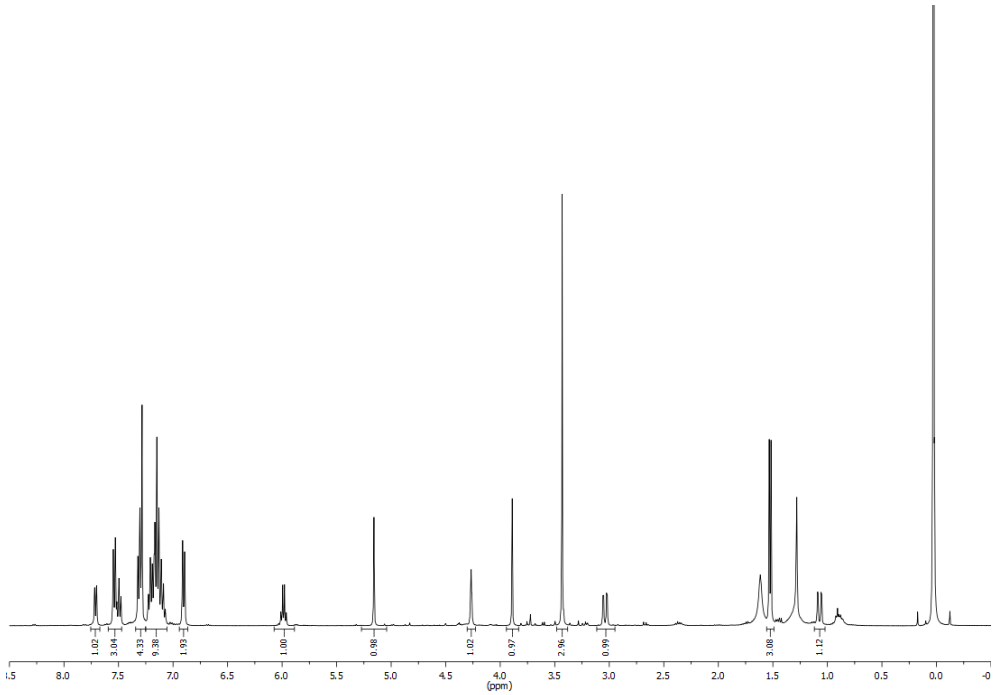


Fig. 31S 11-(Carbomethoxy)-(1'-naphthoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1'*R*,1"*S*,11*R*)-**19b**).



(+)-(1'*R*,1"*S*,11*S*)-**16a**



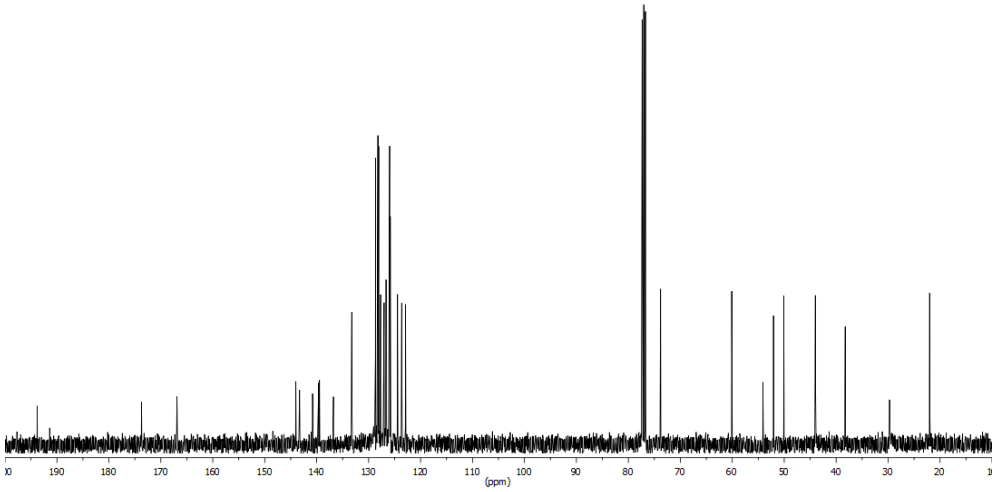
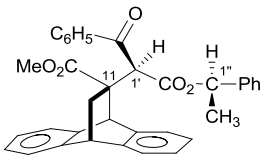


Fig. 32S 11-(Carbomethoxy)-(1'-benzoyl-1'-carbo-(1''-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*R*,1''*S*,11*S*)-**16a**).



(–)-(1'*S*,1"*S*,11*S*)-**17a**

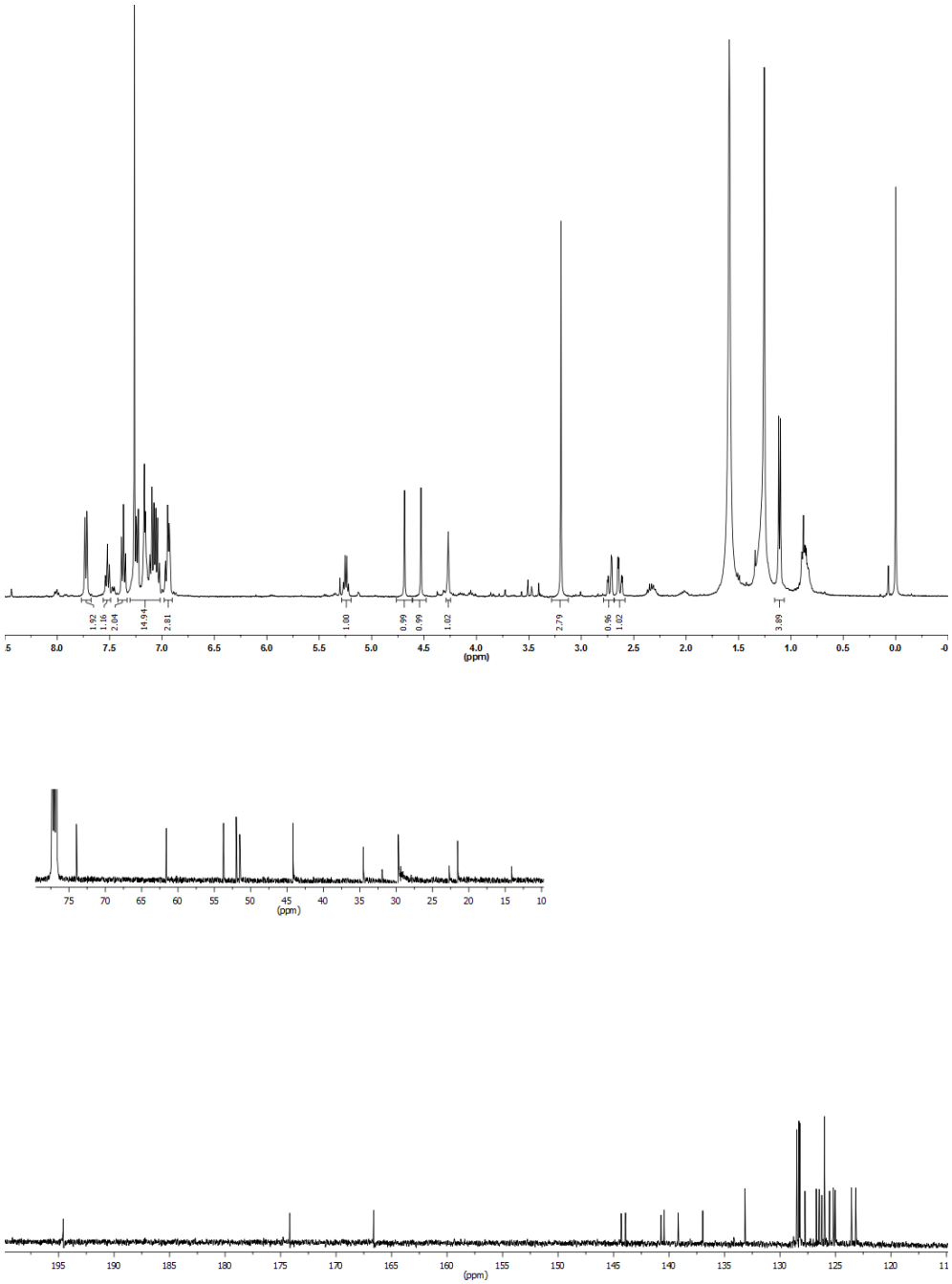
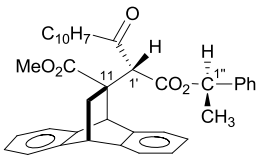
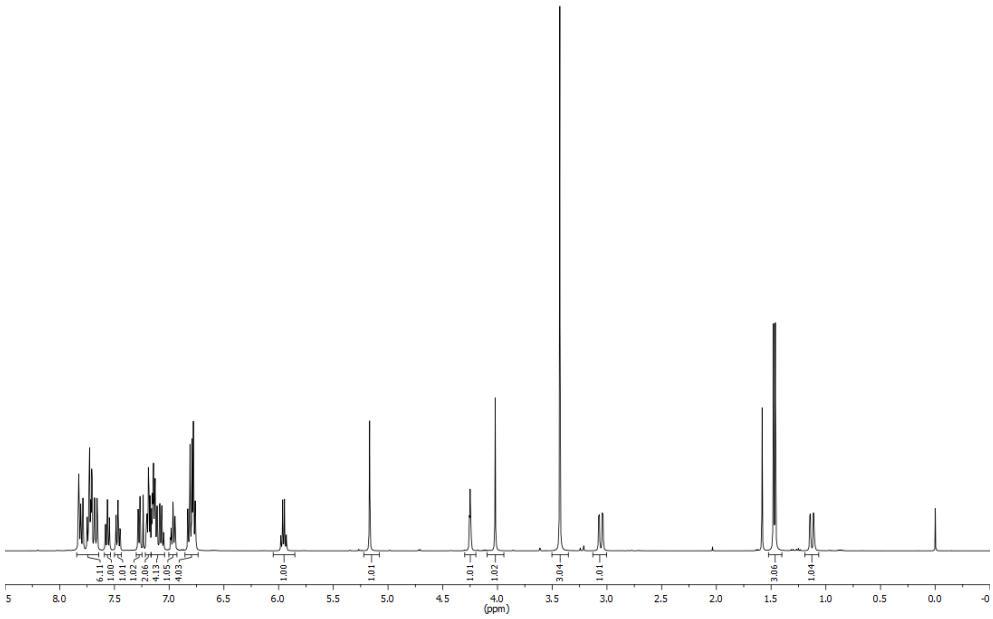


Fig. 33S 11-(Carbomethoxy)-(1'-benzoyl-1'-carbo-(1''-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1'*S*,1"*S*,11*S*)-**17a**).



(+)-(1'*R*,1"*S*,11*S*)-**16b**



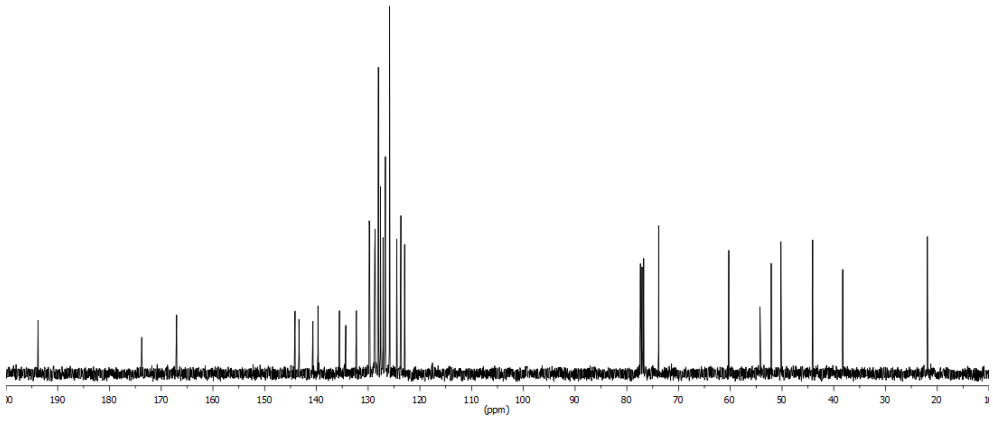
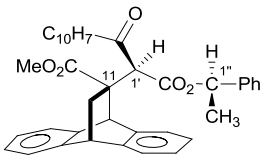


Fig. 34S 11-(Carbomethoxy)-(1'-naphthoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*R*,1"*S*,11*S*)-**16b**).



(–)-(1'*S*,1"*S*,11*S*)-**17b**

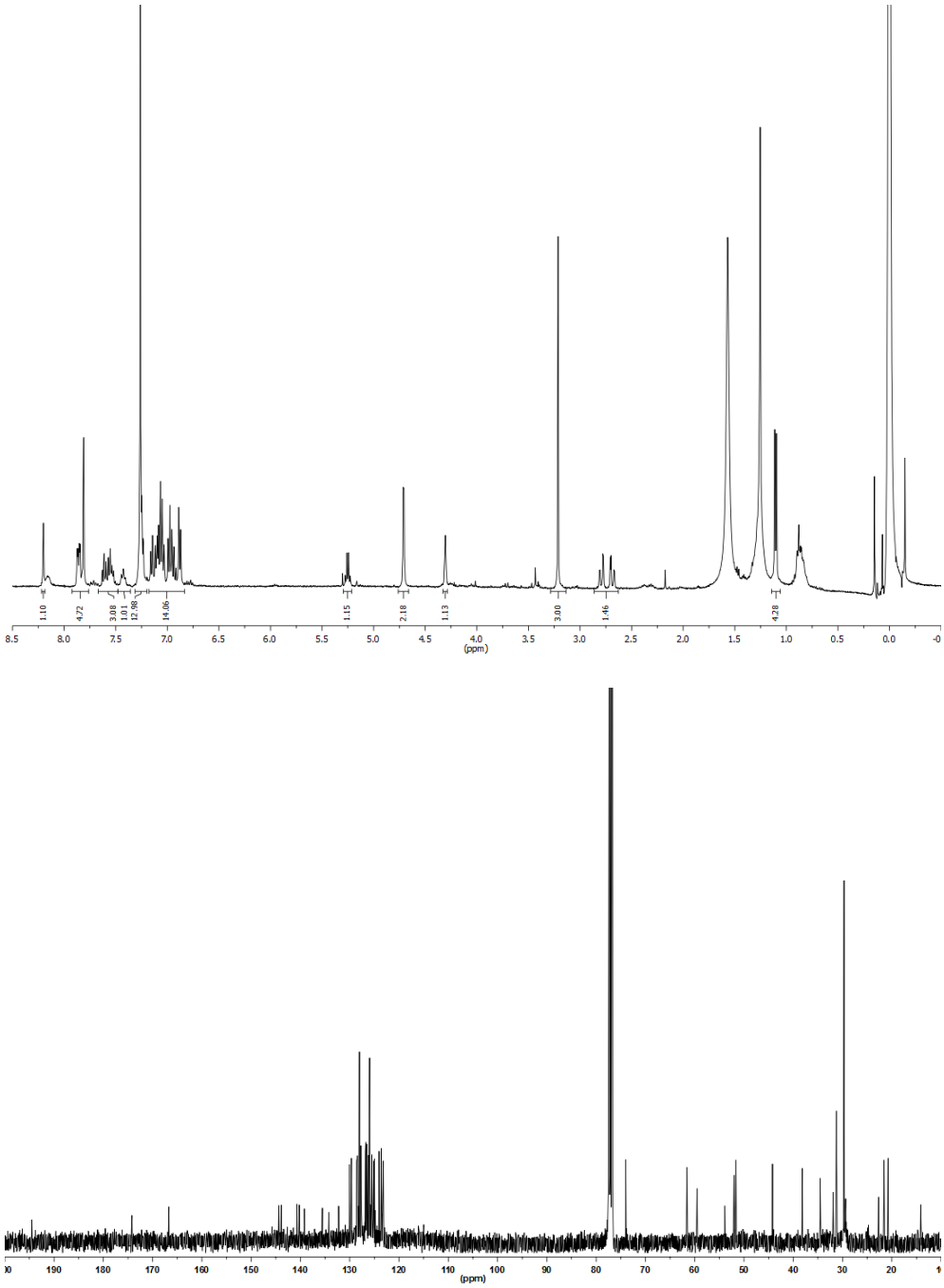
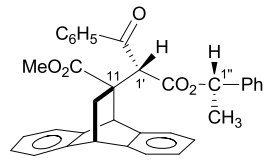


Fig. 35S 11-(Carbomethoxy)-(1'-naphthoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1'*S*,1"*S*,11*S*)-**17b**).



(+)-(1'*R*,1"*R*,11*S*)-**18a**

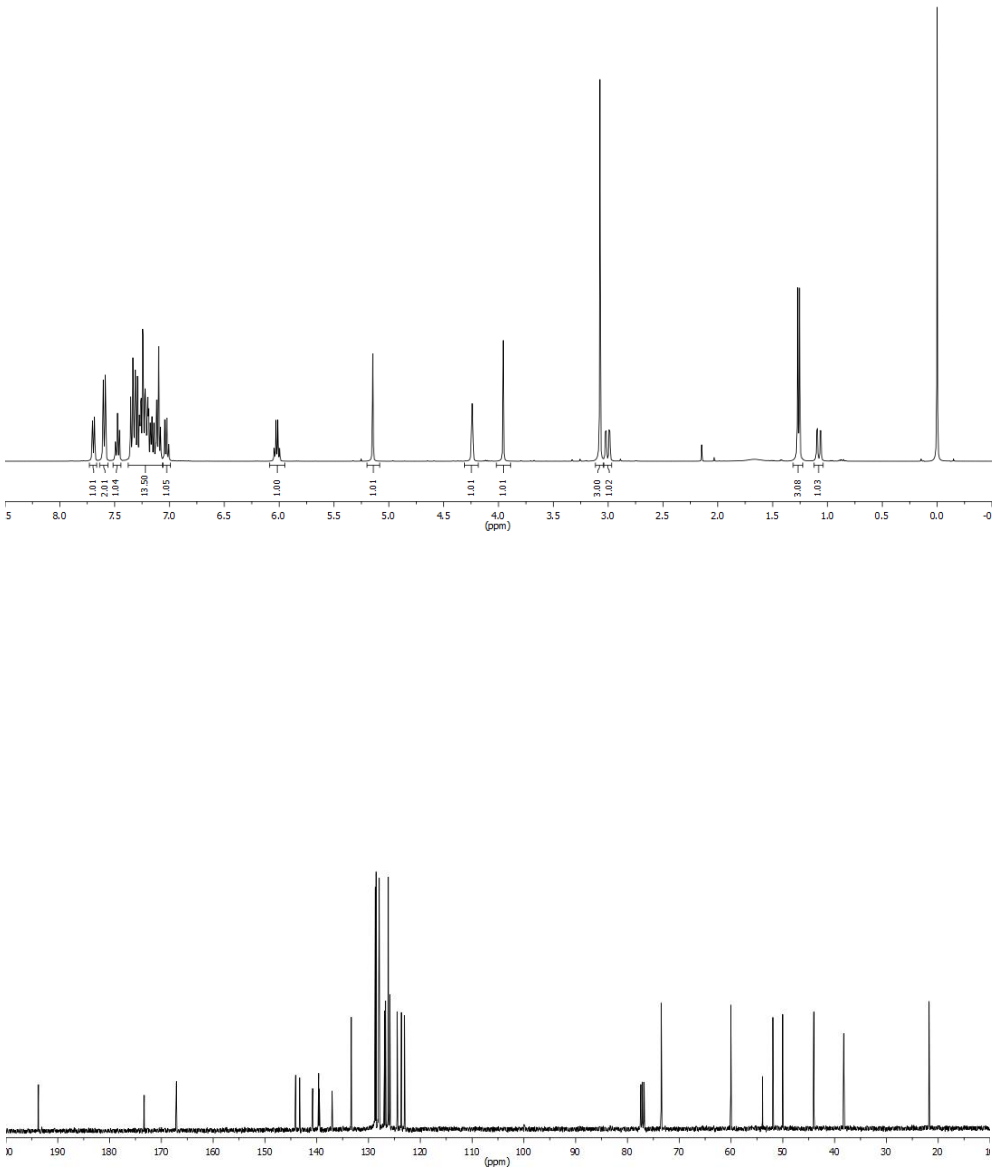
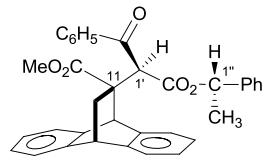
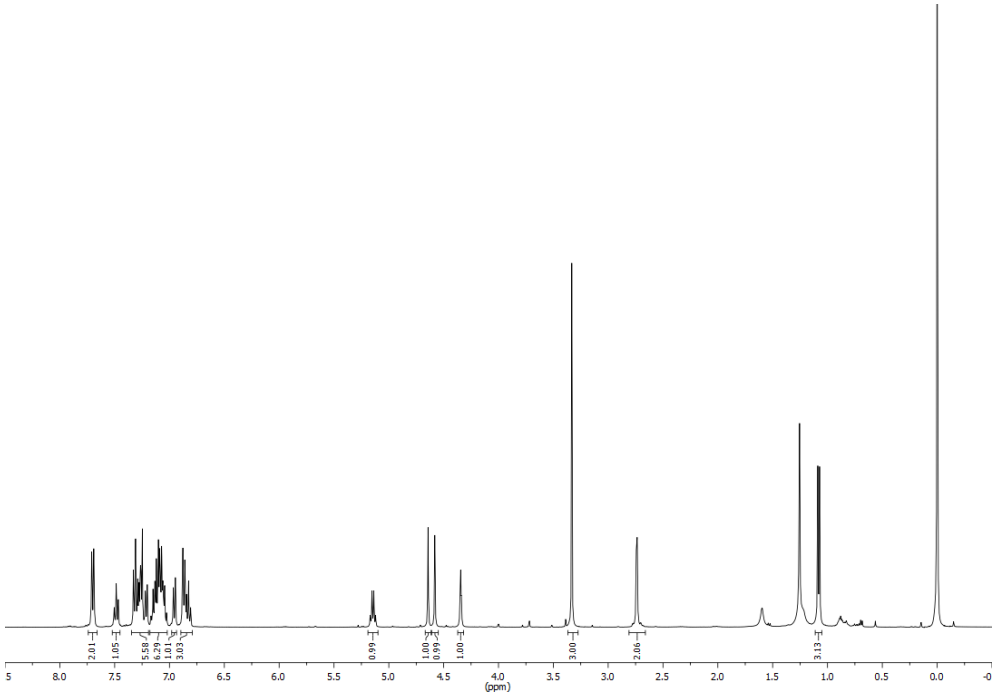


Fig. 36S 11-(Carbomethoxy)-(1'-benzoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*R*,1"*R*,11*S*)-**18a**).



(–)-(1'*S*,1"*R*,11*S*)-**19a**



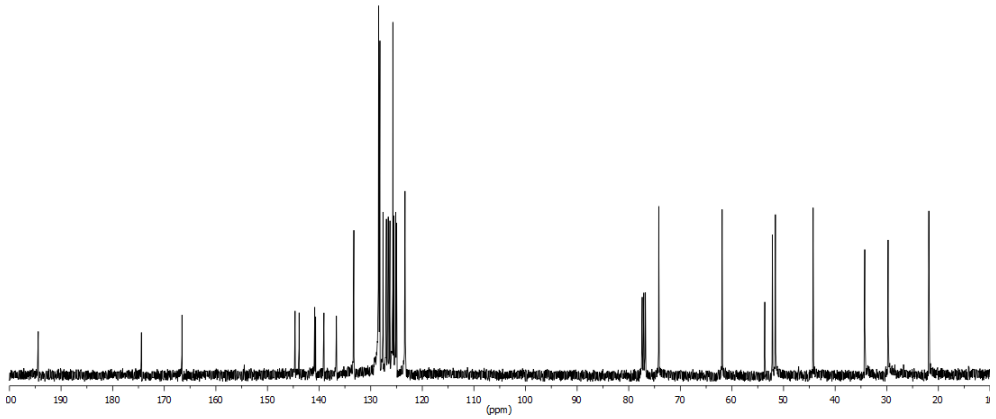
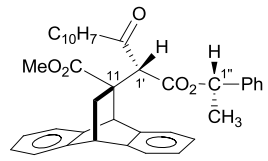


Fig. 37S 11-(Carbomethoxy)-(1'-benzoyl-1'-carbo-(1''-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1'*S*,1"*R*,11*S*)-**19a**).



(–)-(1'*R*,1"*R*,11*S*)-**18b**

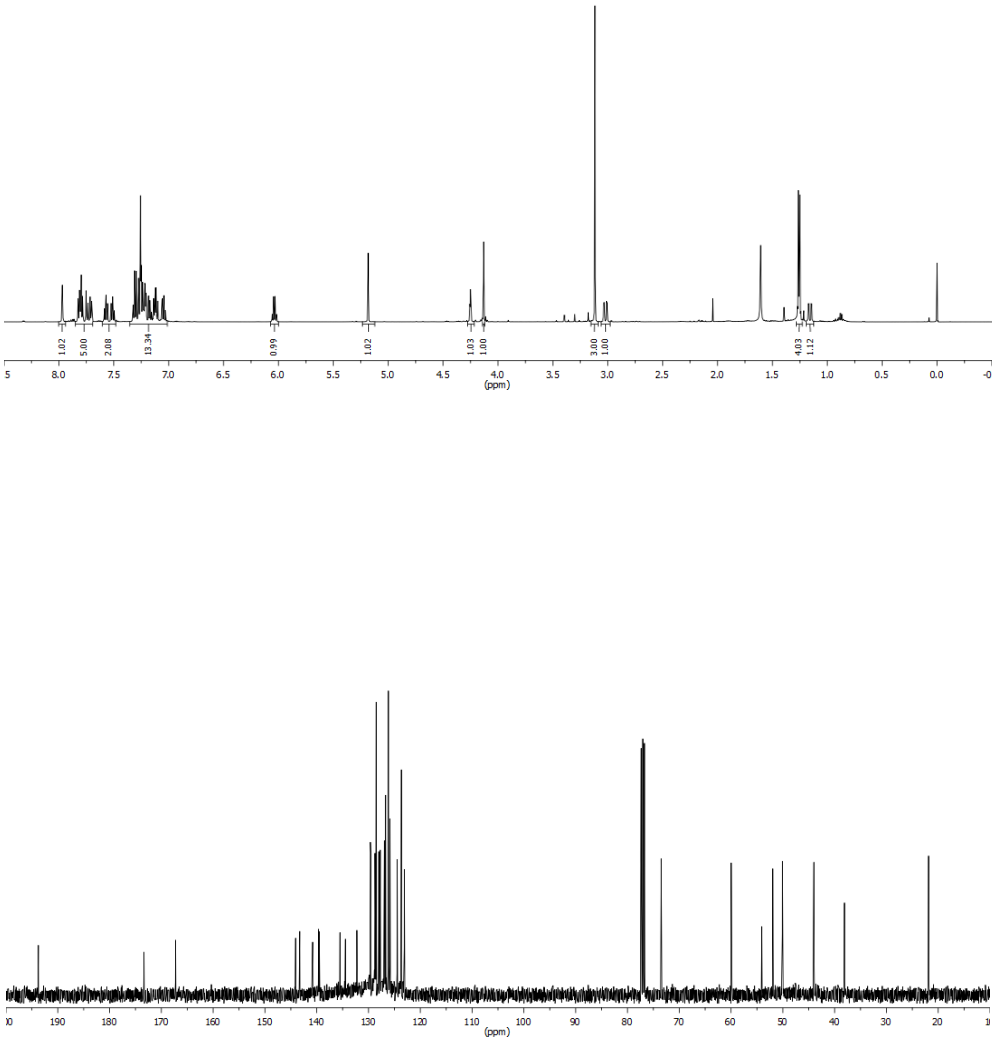
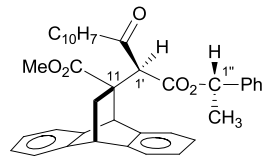


Fig. 38S 11-(Carbomethoxy)-(1'-naphthoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1'*R*,1"*R*,11*S*)-**18b**).



(+)-(1'*S*,1"*R*,11*S*)-**19b**

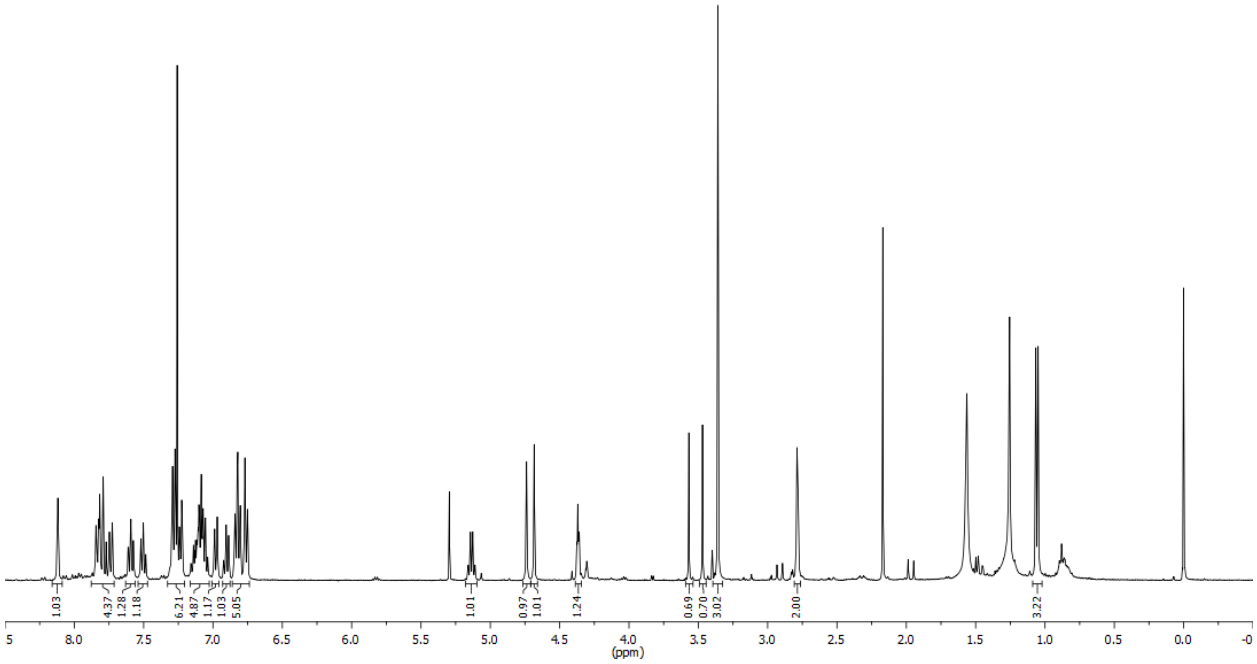
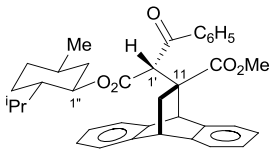
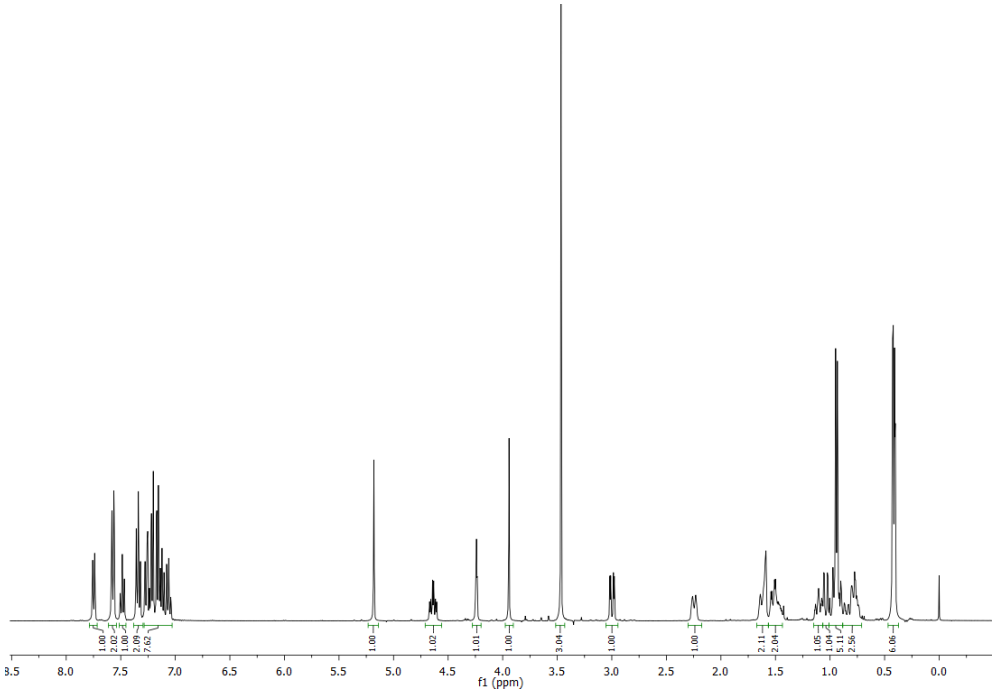


Fig. 39S 11-(Carbomethoxy)-(1'-naphthoyl-1'-carbo-(1"-phenylethoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*S*,1"*R*,11*S*)-**19b**).



(+)-(1'*S*,1"*R*,11*R*)-**21a**



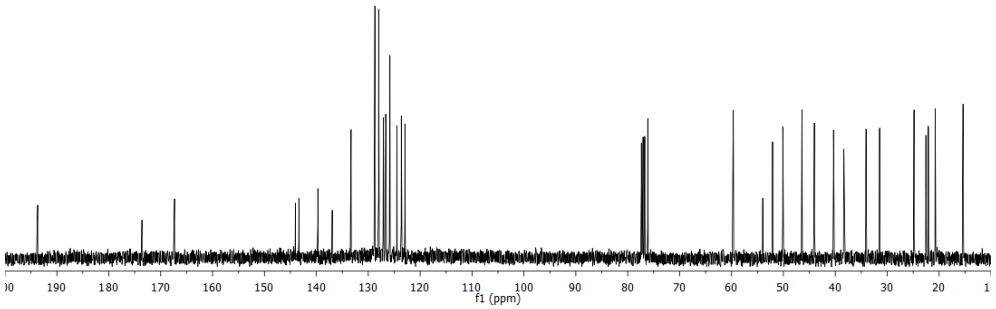
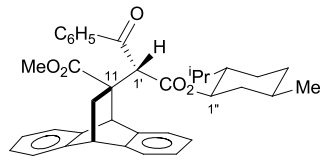


Fig. 40S 11-(Carbomethoxy)-11-(1'-benzoyl-1'-carbo-(1"-alkoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*S*,1"*R*,11*R*)-**21a**).



(+)-(1'*R*,1"*R*,11*S*)-**23a**

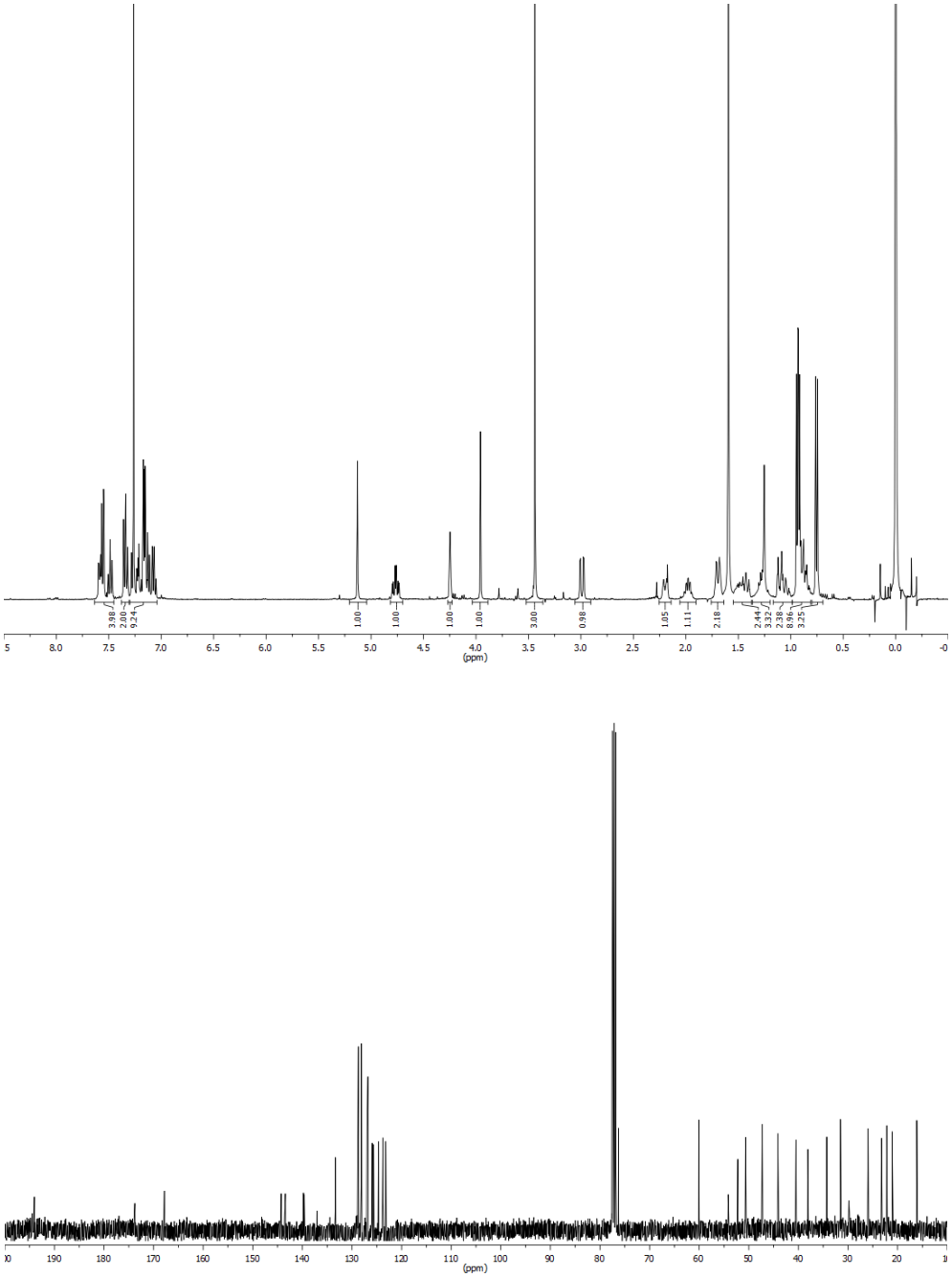
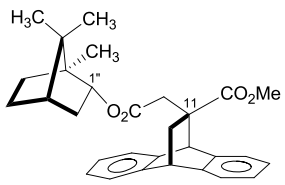
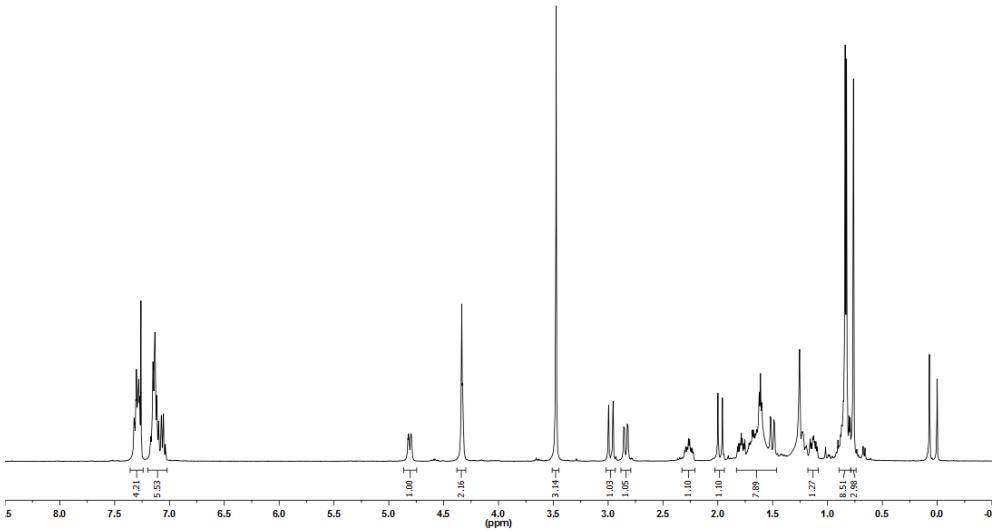
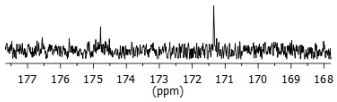


Fig. 41S 11-Carbomethoxy-11-(1'-benzoyl-1'-carbo-(1"-menthoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*R*,1"*R*,11*S*)-**23a**).



(–)-(1"*S*,11*S*)-**19**





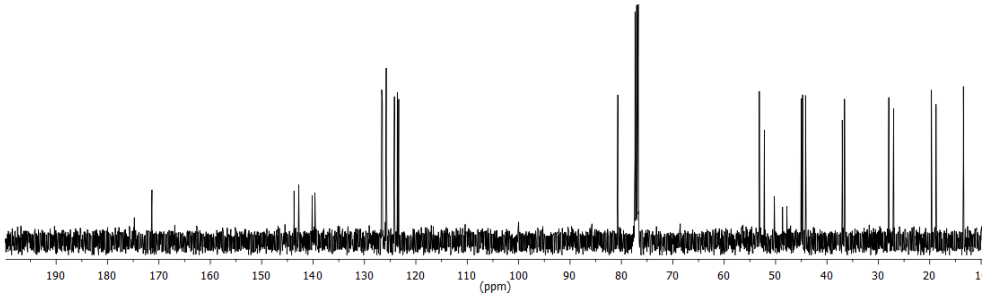
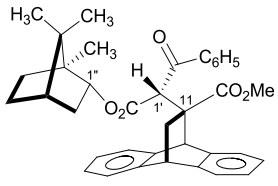
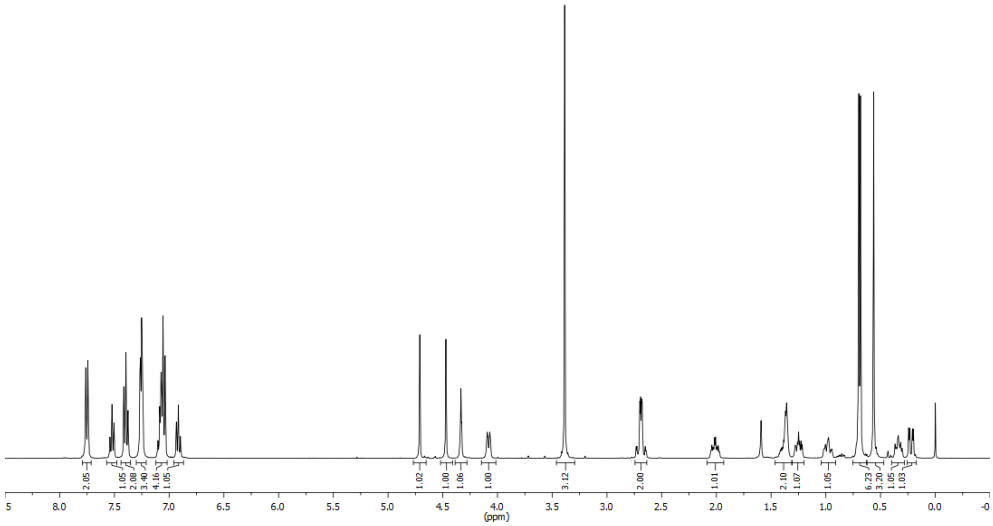


Fig. 42S 11-Carbomethoxy-11-[(–)-borneoxyacetyl]-9,10-dihydro-9,10-ethanoanthracenes ((–)-(1"*S*,11*S*)-**19**).



(+)-(1'*S*,1"*S*,11*R*)-**22a**



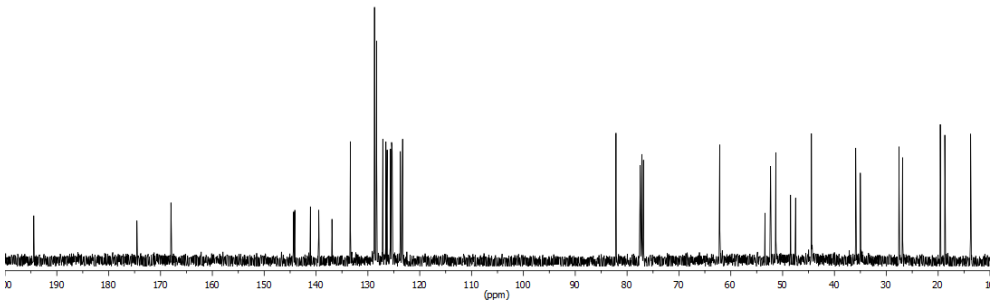
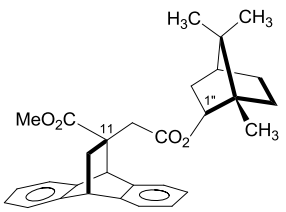
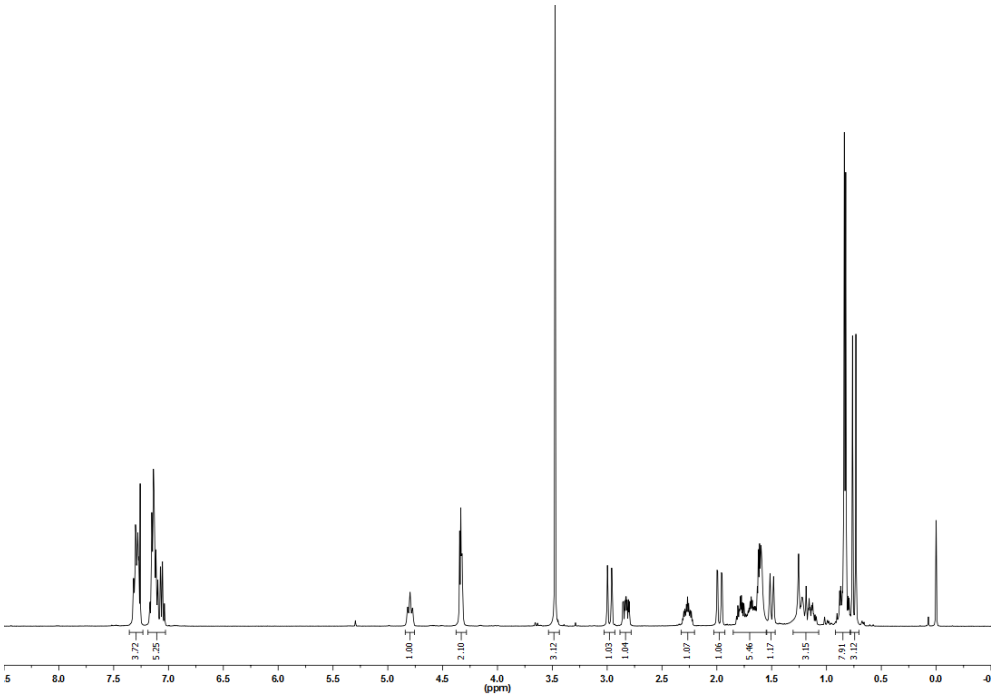


Fig. 43S 11-Carbomethoxy-11-(1'-benzoyl-1'-carbo-(1"-borneoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((+)-(1'*S*,1"*S*,11*R*)-**22a**).



(–)-(1"*S*,11*R*)-**20**



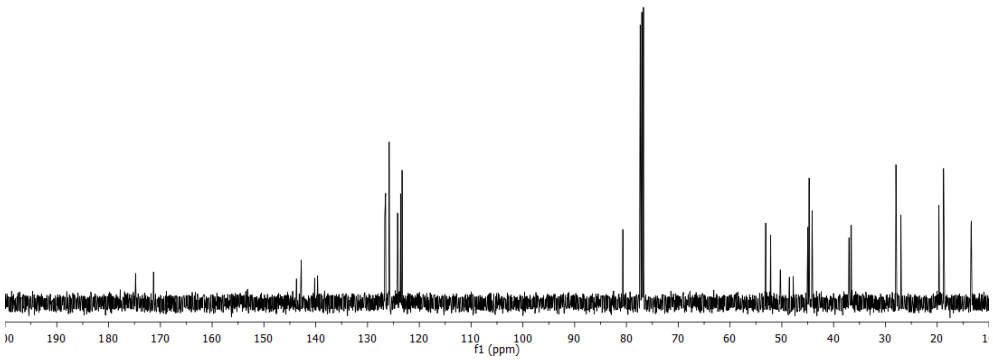
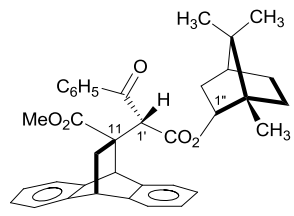


Fig. 44S 11-carbomethoxy-11-[(–)-borneoxyacetyl]-9,10-dihydro-9,10-ethanoanthracene ((–)-(1",11*R*)-**20**).



(–)-(1'*R*,1"*S*,11*S*)-**24a**

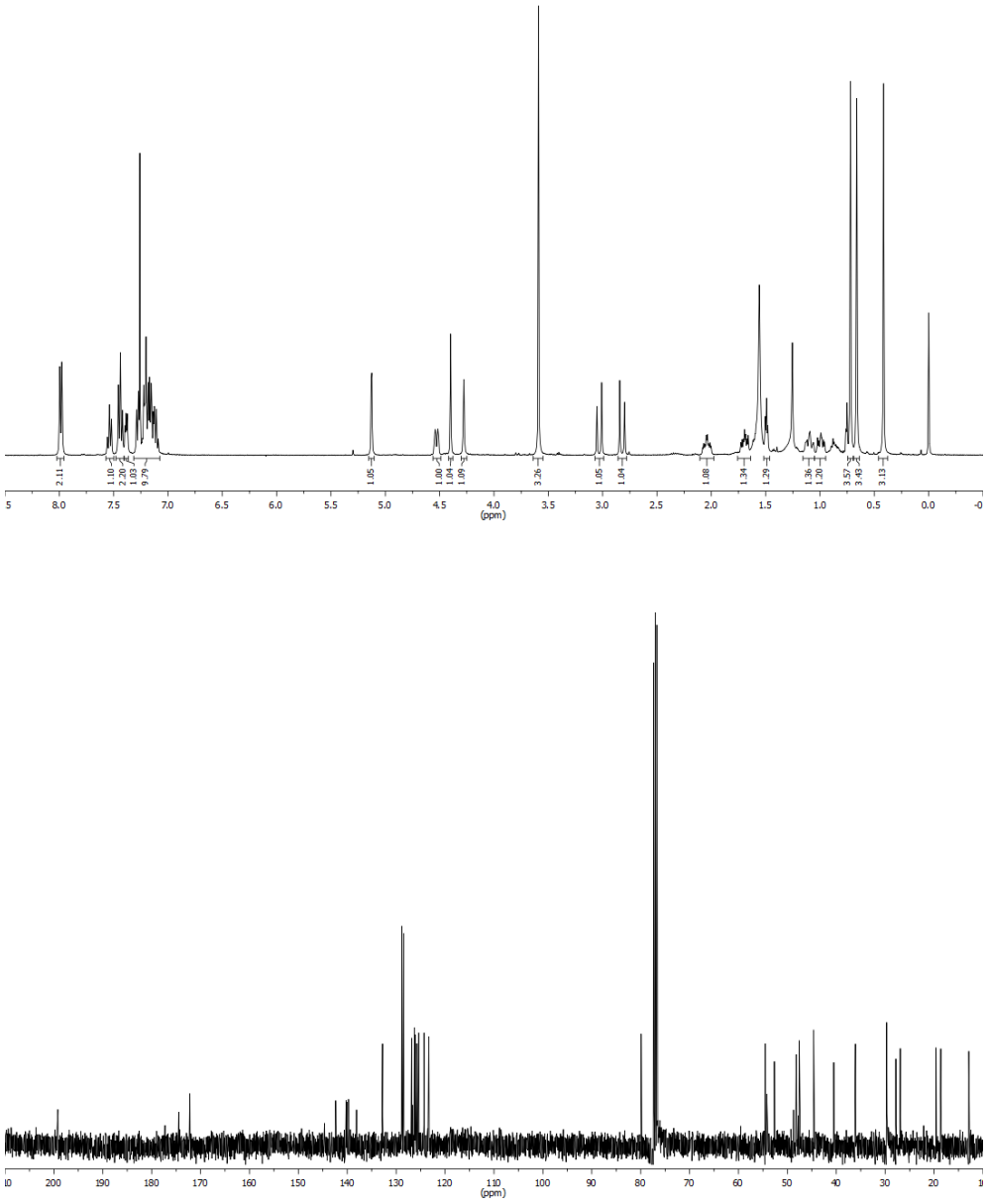


Fig. 45S 11-Carbomethoxy-11-(1'-benzoyl-1'-carbo-(1"-borneoxy)methyl)-9,10-dihydro-9,10-ethanoanthracene ((–)-(1'*R*,1"*S*,11*S*)-**24a**).