Supporting Information for:

"Anion Radical [2+2]Cycloaddition as a Mechanistic Probe: Stoichiometry and Concentration Dependent Partitioning of Electron-Transfer (ET) and Alkylation Pathways in the Reaction of the Gilman Reagent Me_2CuLi•LiI with *bis*(Enones)"

Jingkui Yang, David F. Cauble, Adam J. Berro, Nathan L. Bauld,* and Michael J. Krische*
University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX 78712.

Contents

I. Materials and Instrumentation

Commercial reagents were used without further purification, unless otherwise stated. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately prior to use. All reactions were conducted in oven-dried glassware, under an inert atmosphere of Nitrogen or Argon.

High-resolution mass spectra (HRMS) are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+1) or a suitable fragment ion. Proton NMR spectra were recorded with a 300 MHz spectrometer. Carbon NMR spectra were recorded with a 75 MHz MHz spectrometer.

II. Experimental Procedures

Dimethyllithium cuprate-Lithium Iodide (Me_2CuLi-LiI) reagent was prepared by adding 200 mol% MeLi (1.6 M in Et_2O) to a suspension of 100 mol% CuI in 0 °C THF. Stirring for approximately 30 minutes at 0°C resulted in a homogeneous solution.

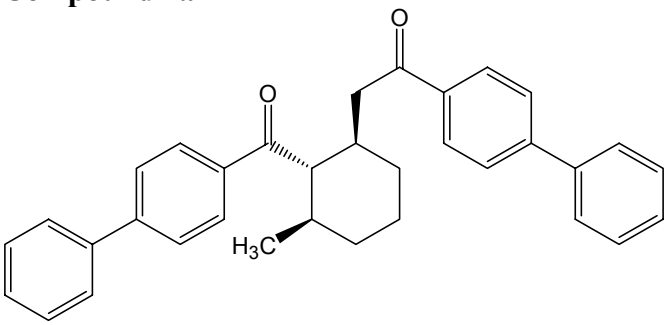
Table I data was obtained using the following procedure: Me_2CuLi-LI reagent solution (0.5 M in Et_2O/THF) was added at the indicated rate to a solution of bis-enone substrate (0.25 mmol) in 25 mL 0 °C THF. The reaction was stirred at 0 °C for 25 minutes, and then quenched with several drops of saturated aqueous NH_4Cl solution. The residue was concentrated and purified via silica gel chromatography, eluting with a mixture of ethyl acetate and hexane.

Table II data was obtained using the following representative procedures:
A. Me_2CuLi-LiI (15.7 mL; 0.0032 M in Et_2O/THF; 200 mol%) was added over 5s to a solution of substrate (0.26 mmol; 100 mol%) in 5 mL 0 °C THF. Stirring was maintained for 25 minutes and then was worked up and purified as described above.
B. Me_2CuLi-LiI (1.0 mL; 0.5 M in Et_2O/THF; 25 mol%) was added over 60s to a solution of substrate (0.25 mmol; 100 mol%) in 25 mL 0 °C THF. Stirring was maintained for 25 minutes and then was worked up and purified as described above.

Table III data represents measurements from separate, parallel reactions, conducted using the following procedure: Me_2CuLi-LiI (0.98 mL; 0.034 M in Et_2O/THF; 25 mol%) was added over 5s to a solution of substrate (0.1316 mmol; 100 mol%) in 3.5 mL 0 °C THF. Stirring was maintained for the indicated time before work up and purification as described above.

III. Product Characterization

Compound 2a

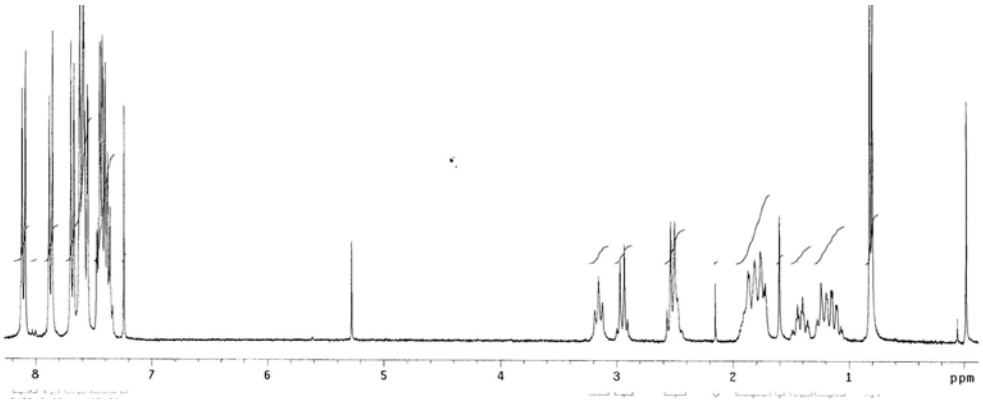


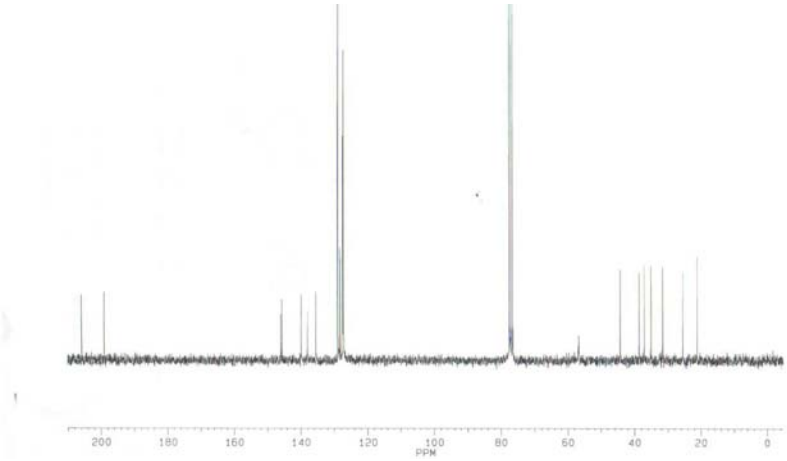
[1]HNMR (300 MHz, $CDCl_3$): δ 8.1-8.12 (d, J = 8.4 Hz, 2H), 7.89-7.86 (d, J = 8.4 Hz, 2H), 7.66-7.67 (d, J = 8.4 Hz, 2H), 7.55-7.63 (m, 6H), 7.36-7.47 (m, 6H), 3.12-3.19 (t, J = 9.9 Hz, 1H), 2.90-3.0 (q, J = 8.7 Hz, 1H), 2.42-2.57 (m, 2H), 1.72-1.87 (m, 4H), 1.36-1.49 (m, 1H), 1.06-1.27 (m, 2H), 0.80-0.82 (d, J = 6.3 Hz, 3H).

[13]CNMR (75 MHz, $CDCl_3$): δ 205.7, 198.9, 145.9, 145.5, 139.9, 139.7, 137.9, 135.4, 128.9, 128.8, 128.2, 128.1, 127.4, 127.3, 127.2, 127.2, 56.6, 44.1, 38.5, 36.9, 34.9, 31.5, 25.4, 21.1

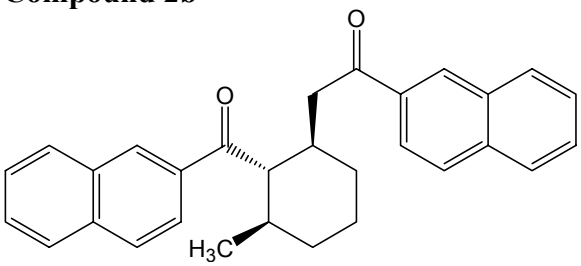
HRMS: Calc. [M+1] for $C_{34}H_{32}O_2$: 473.2481; Found: 473.2460.

IR (KBr): 3060, 3031, 2950, 2921, 2848, 1674, 1601, 1601, 1553, 1403, 1212, 1193, 1003, 761, 746, 695 cm^{-1}.





Compound 2b

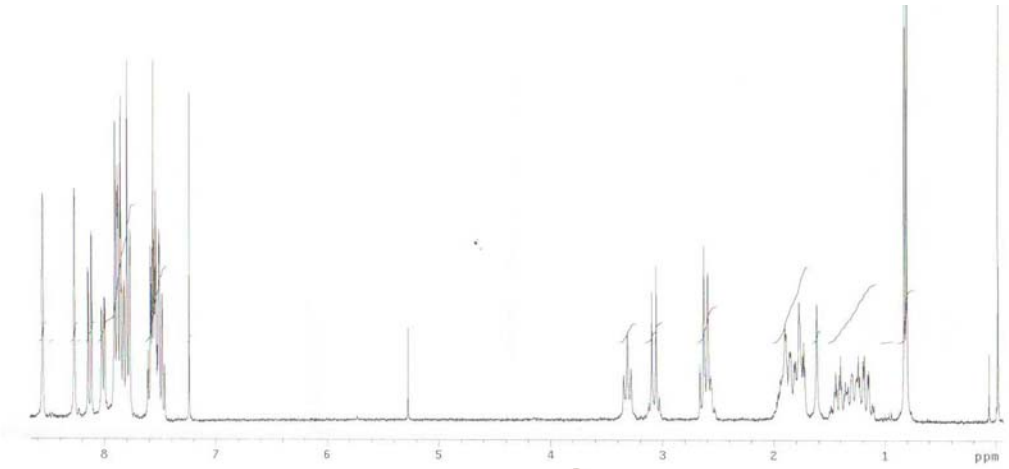


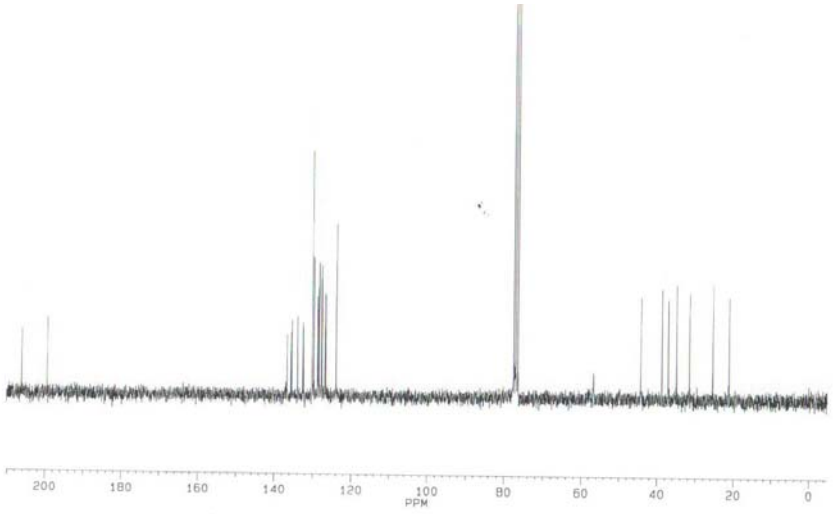
[1]HNMR (300 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.27 (s, 1H), 8.12-8.15 (dd, J1 = 8.7 Hz, J2 = 1.8 Hz, 1H), 7.99-8.03 (m, 1H), 7.77-7.91 (m, 6H), 7.46-7.61 (m, 4H), 3.28-3.34 (t, J = 9.9 Hz, 1H), 3.02-3.09 (q, J = 9 Hz, 1H), 2.52-2.66 (m, 2H), 1.72-1.97 (m, 4H), 1.14-1.45 (m, 3H), 0.80-0.83 (d, J = 6.9 Hz, 3H).

[13]CNMR (75 MHz, $CDCl_3$): δ 206.1, 199.4, 136.6, 135.6, 135.4, 133.9, 132.6, 132.4, 130.1, 129.7, 129.7, 128.7, 128.6, 128.3, 128.3, 127.7, 127.6, 126.8, 126.5, 123.9, 56.6, 44.2, 38.7, 37.1, 34.9, 31.5, 25.4, 21.1.

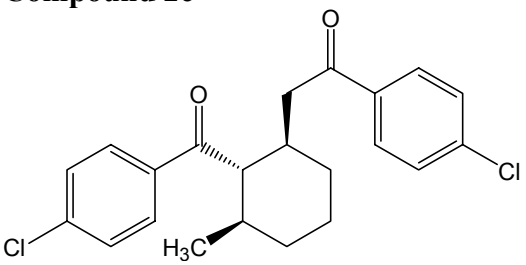
HRMS: Calc. [M+1] for $C_{30}H_{28}O_2$: 421.2168; Found: 421.2168.

IR (KBr): 3453, 3057, 2950, 2925, 2848, 1674, 1626, 1461, 1373, 1270, 1179, 1120, 819, 753 cm^{-1}.





Compound 2c

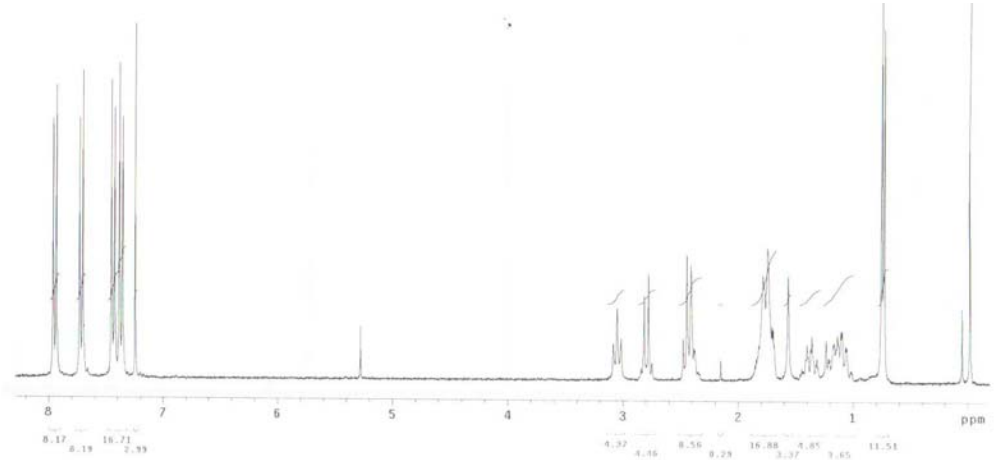


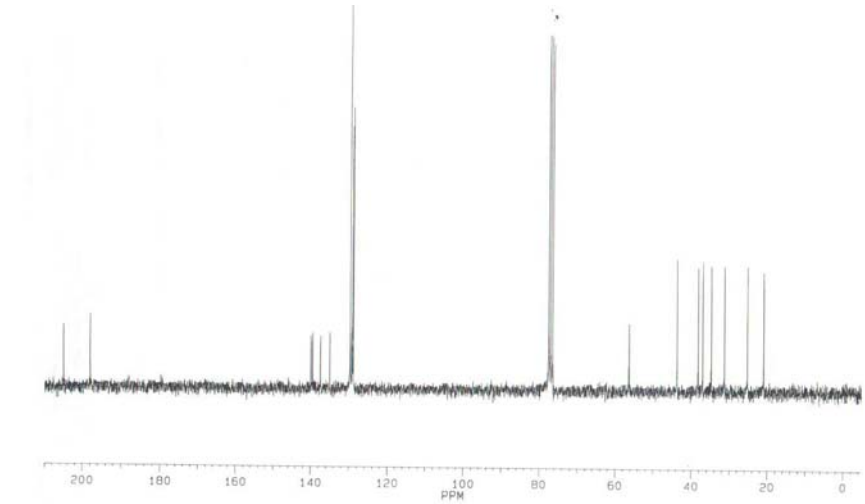
[1]HNMR (300 MHz, $CDCl_3$): δ 7.96-7.93 (d, J = 8.7 Hz, 2H), 7.70-7.73 (d, J = 8.7 Hz, 2H), 7.42-7.45 (d, J = 8.7 Hz, 2H), 7.35-7.38 (d, J = 8.7 Hz, 2H), 3.10-3.08 (t, J = 9.9 Hz, 1H), 2.75-2.82 (q, J = 11.1Hz, 1H), 2.38-2.45 (m, 2H), 1.70-1.84 (m, 4H), 1.31-1.40 (m, 1H), 1.10-1.23 (m, 2H), 0.73-0.75 (d, J = 6.6 Hz, 3H).

[13]CNMR (75 MHz, $CDCl_3$): δ 204.9, 197.9, 139.8, 139.4, 137.4, 134.9, 129.6, 129.1, 128.8, 56.3, 43.8, 38.2, 37.0, 34.8, 31.3, 25.3, 21.0.

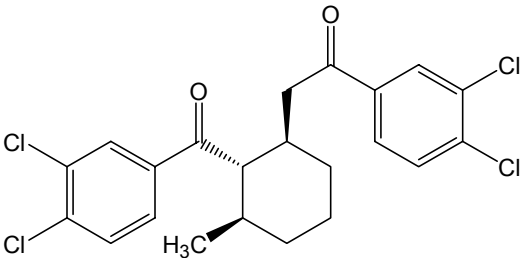
HRMS: Calc. [M+1] for $C_{22}H_{22}O_2Cl_2$: 389.1075; Found: 389.1081.

IR (KBr): 3071, 2955, 1932, 2850, 1877, 1850, 1685, 1662, 1588, 1565, 1401, 1211, 1087, 982, 898, 815 cm^{-1}.





Compound 2d

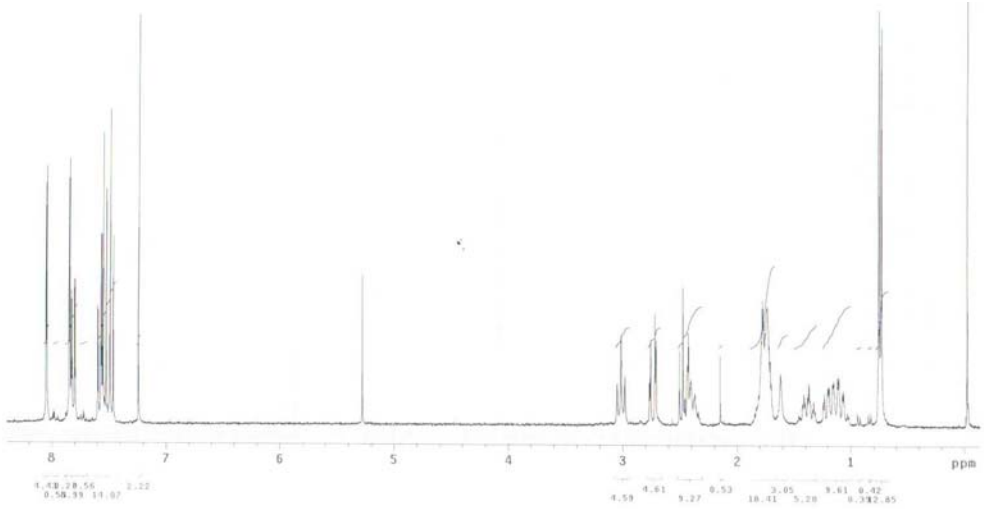


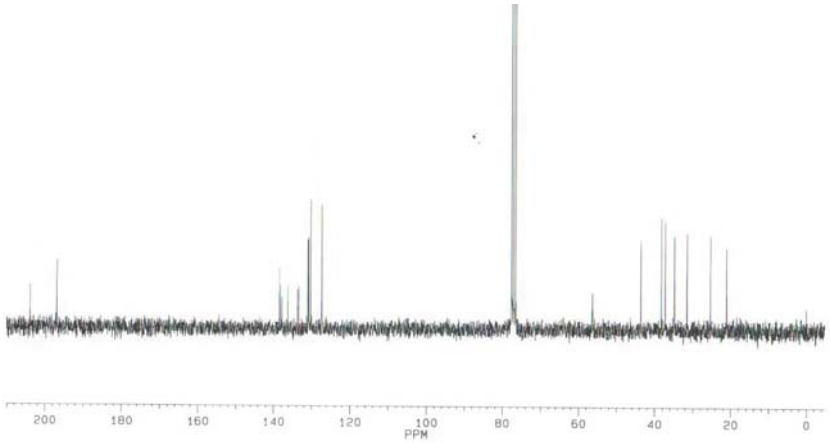
[1]HNMR (300 MHz, $CDCl_3$): δ 8.05-8.05 (d, J = 2.1 Hz, 1H), 7.84-7.85 (d, J = 2.1 Hz, 1H), 7.79-7.83 (dd, J1 = 8.4 Hz, J2 = 2.1 Hz, 1H), 7.46-7.60 (m, 3H), 2.98-3.05 (t, J = 10.2 Hz, 1H), 2.71-2.77 (dd, J1 = 14.1 Hz, J2 = 2 Hz, 1H), 2.34-2.51 (m, 2H), 1.70-1.78 (m, 4H), 1.33-1.46 (m, 1H), 1.03-1.24 (m, 2H), 0.73-0.76 (d, J = 6.3 Hz, 3H).

[13]CNMR (75 MHz, $CDCl_3$): δ 203.8, 196.8, 138.4, 138.1, 137.6, 136.2, 133.6, 133.3, 130.9, 130.7, 130.2, 130.1, 127.2, 127.2, 56.3, 43.5, 38.1, 37.2, 34.8, 31.4, 25.3, 21.0.

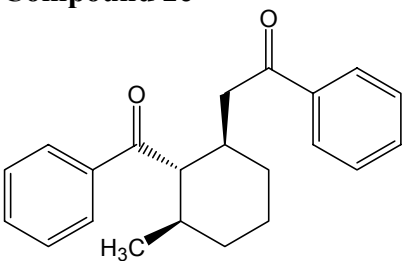
HRMS: Calc. [M+1] for $C_{22}H_{20}O_2Cl_4$: 457.0296; Found: 457.0299.

IR (film): 3423, 3090, 3068, 2950, 2928, 2848, 1681, 1678, 1652, 1582, 1557, 1454, 1381, 1204, 1028 cm^{-1}.





Compound 2e

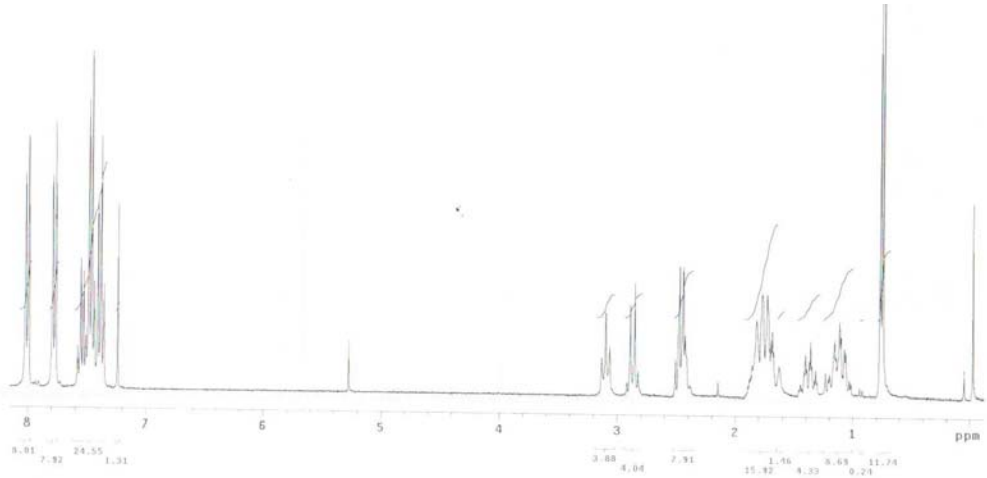


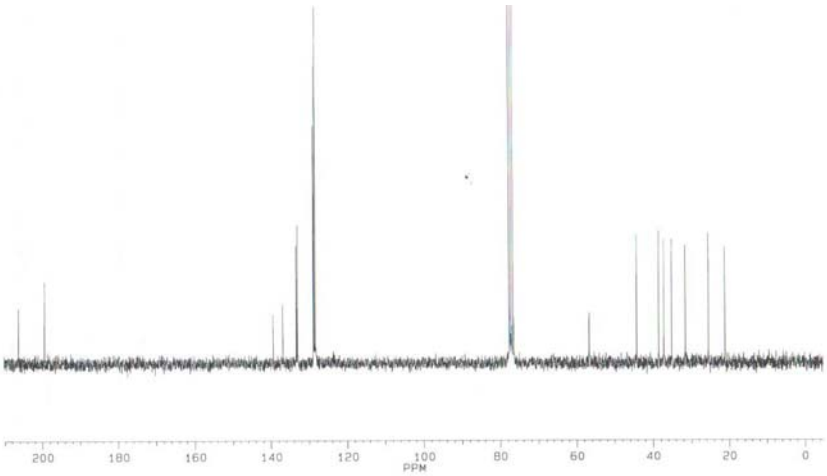
[1]HNMR (300 MHz, $CDCl_3$): δ 7.99-8.03 (d, J = 8.4 Hz, 2H), 7.77-7.79 (d, J = 8.7 Hz, 2H), 7.36-7.58 (m, 6H), 3.06-3.13 (t, J = 9.9 Hz, 1H), 2.82-2.92 (q, J = 11.1 Hz, 1H), 2.38-2.51 (m, 2H), 1.63-1.88 (m, 4H), 1.32-1.42 (m, 1H), 1.02-1.233 (m, 2H), 0.75-0.77 (d, J = 6.6 Hz, 3H).

[13]CNMR (75 MHz, $CDCl_3$): δ 206.2, 199.3, 139.3, 136.7, 133.2, 132.9, 128.7, 128.5, 128.2, 56.5, 44.0, 38.3, 36.9, 34.9, 31.4, 25.3, 21.0.

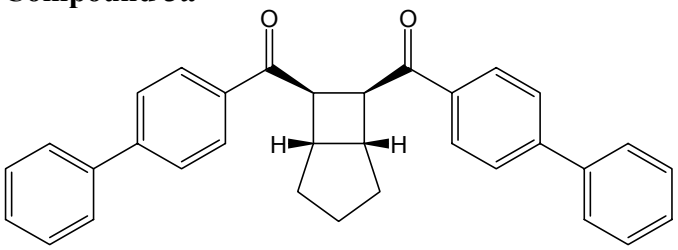
HRMS: Calc. [M+1] for $C_{22}H_{24}O_2$: 321.1855; Found: 321.1853.

IR (KBr): 3082, 3067, 3024, 2958, 2939, 2932, 2914, 2851, 2833, 1678, 1593, 1450, 1362, 1201, 999, 970, 889, 786, 750, 706, 684 cm^{-1}.





Compound 3a

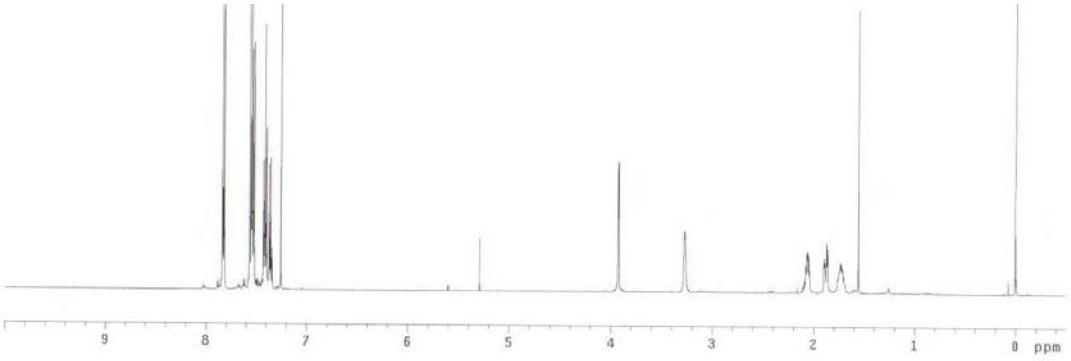


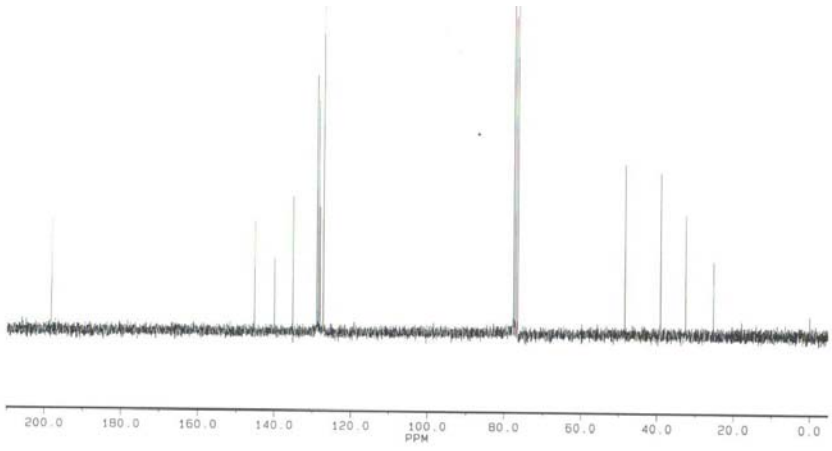
[1]HNMR: (500 MHz, $CDCl_3$): δ 1.69-1.77 (m, 2H), 1.86-1.90 (ddd, J1 = 13 Hz , J2 = 5.5 Hz, J3 = 1.5 Hz, 2H), 2.04-2.11 (m, 2H), 3.26-3.28 (m, 2H), 3.92-3.93 (d, J = 4.2 Hz, 2H), 7.34-7-37 (tt, J1 = 7.5, J2 = 1.0, 2H), 7.39-7.43 ((tt, J1 = 8.0, J2 = 1.5, 4H), 7.82-7.84 (dt, J1 = 9.0, J2 = 2.0, 4H), 8.22 (s, 2H).

[13]CNMR (75 MHz, $CDCl_3$): δ 198.3, 145.2, 139.9, 135.1, 128.8, 128.3, 128.0, 127.2, 127.1, 48.4, 39.0, 32.5, 25.3.

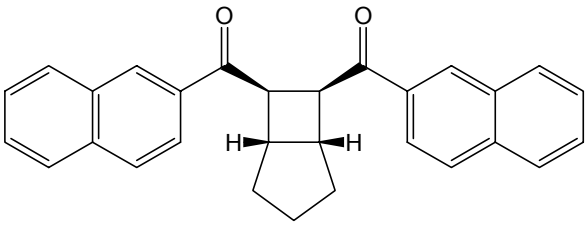
HRMS: Calc. [M+1] for $C_{33}H_{29}O_2$: 457.2168; Found: 457.2174.

IR (KBr): 3025, 2928, 2846, 1681, 1603, 1479, 1401, 1347, 1266, 1219, 1176, 1005, 838, 765, 691 cm^{-1}.





Compound 3b

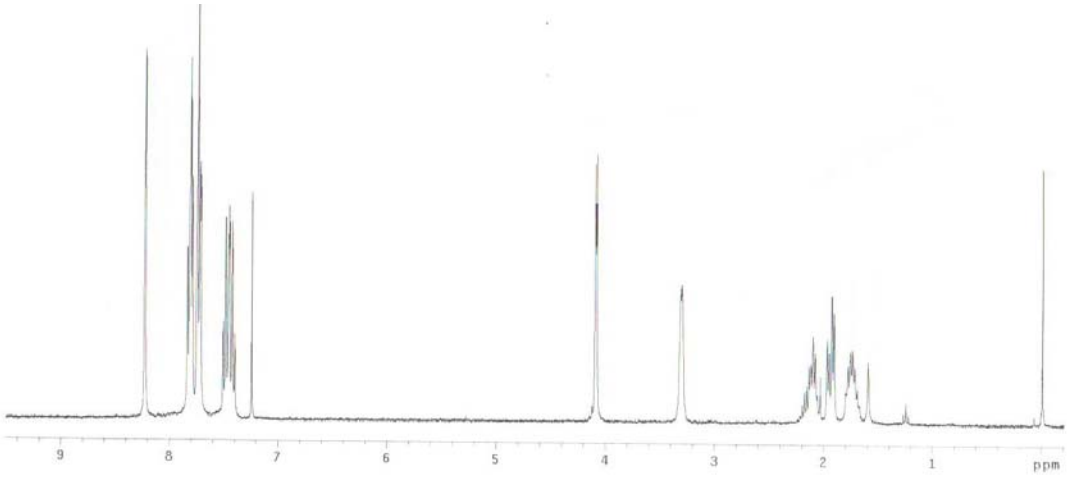


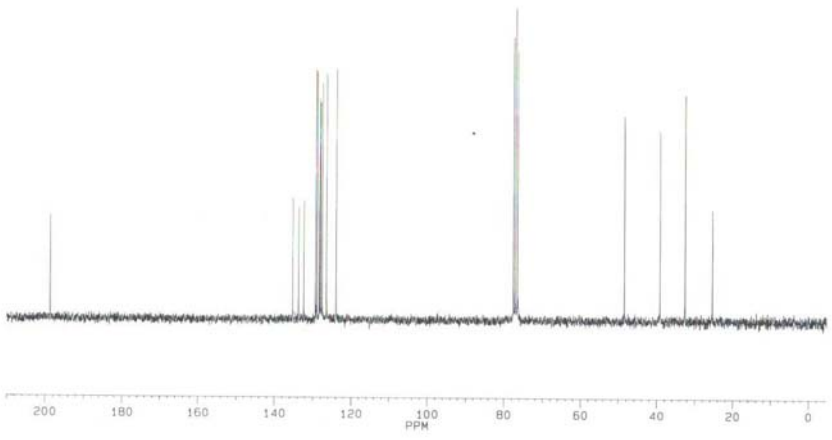
[1]HNMR: (300 MHz, $CDCl_3$): δ 1.69-1.78 (m, 2H), 1.90-1.97 (dd, J1 = 14.1 Hz , J2 = 5.4 Hz, 2H), 2.08-2.22 (m, 2H), 3.29-3.30 (d, J = 2.4 Hz, 2H), 4.07-4.09 (d, J = 4.2 Hz, 2H), 7.40-7-51 (m, 4H), 7.73-7.74 (m, 4H), 7.80-7.83 (m, 4H), 8.22 (s, 2H).

[13]CNMR (75 MHz, $CDCl_3$): δ 198.6, 135.2, 133.7, 132.3, 129.3, 128.9, 128.3, 127.6, 126.4, 123.9, 48.4, 39.1, 32.5, 25.3.

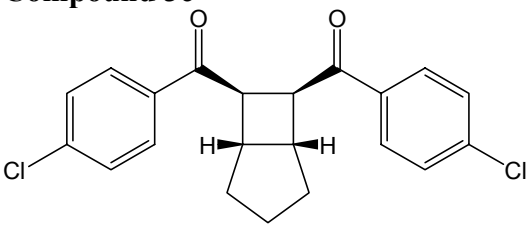
HRMS: Calc. [M+1] for $C_{29}H_{25}O_2$: 485.1855; Found: 405.1858.

IR (KBr): 3053, 2921, 2848, 1678, 1623, 1461, 1362, 1274, 1362, 1274, 1182, 1127, 819, 746 cm^{-1}.





Compound 3c

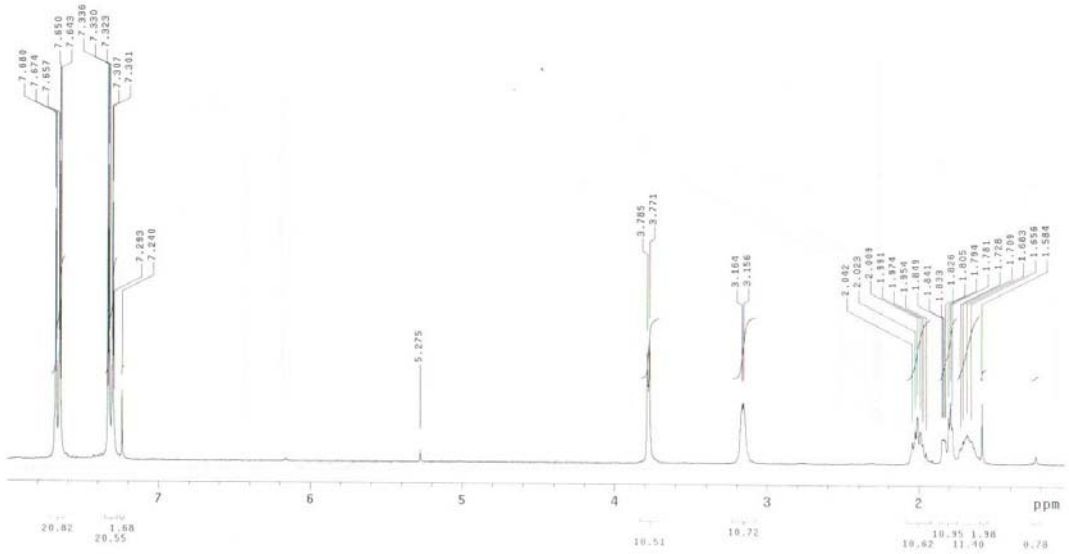


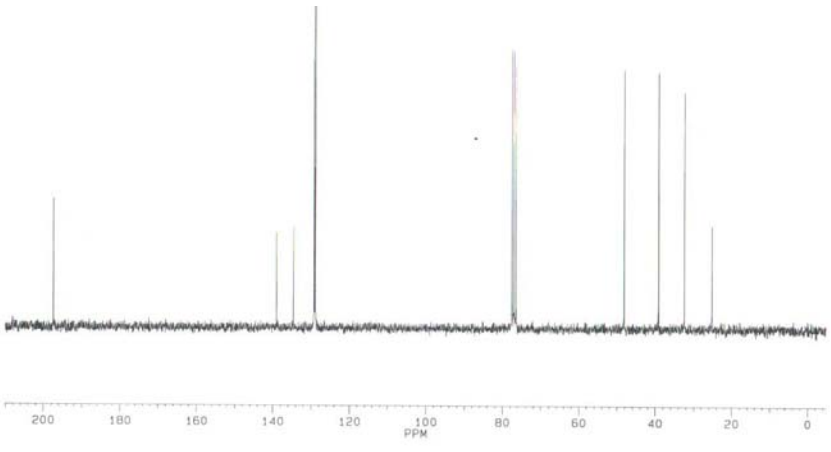
[1]HNMR: (300 MHz, $CDCl_3$): δ 1.66-1.70 (m, 2H), 1.80-1.83 (dd, J1 = 9.9 Hz , J2 = 2.4 Hz, 2H), 1.97-2.04 (m, 2H), 3.15-3.17 (m, 2H), 3.77-3.78 (d, J = 3.9 Hz, 2H), 7.31-7.33 (d, J = 8.4 Hz, 4H), 7.65-7.68 (dd, J = 9 Hz, 4H).

[13]CNMR (75 MHz, $CDCl_3$): δ 197.3, 138.9, 134.5, 129.1, 128.8, 48.1, 39.0, 32.3, 25.1.

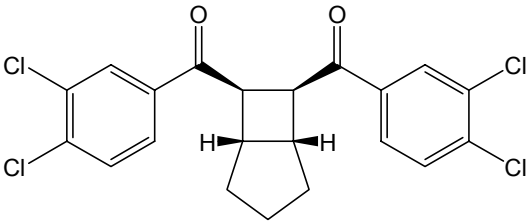
HRMS: Calc. [M+1] for $C_{22}H_{19}O_2Cl_2$: 373.0762; Found: 373.0762.

IR (KBr): 3064, 2961, 2925, 2899, 2859, 1681, 1586, 1487, 1399, 1340, 1234, 1094, 1010, 922, 841, 812 cm^{-1}.





Compound 3d

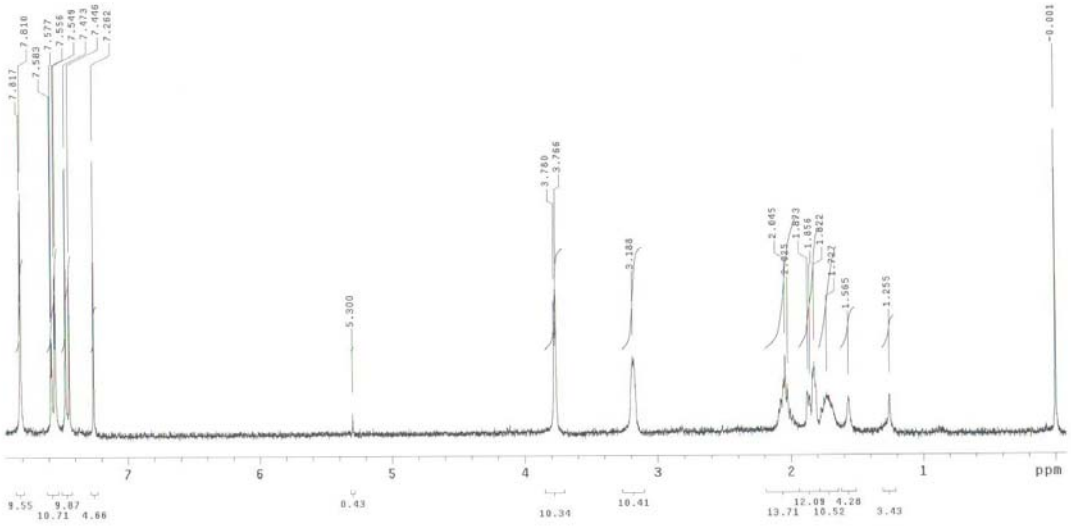


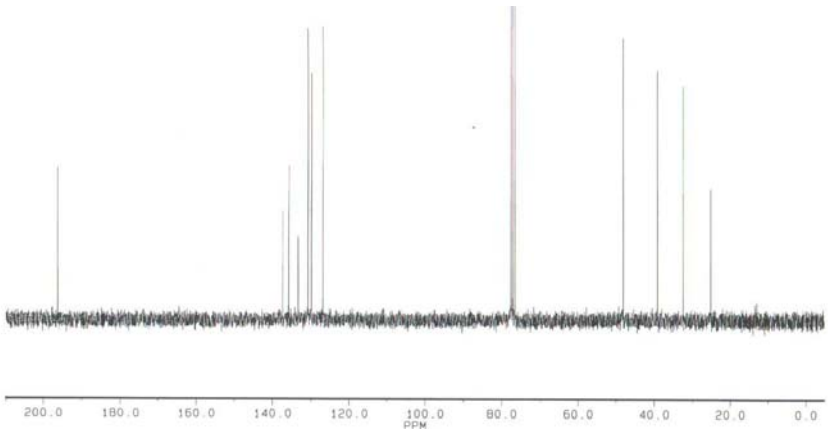
[1]HNMR: (300 MHz, $CDCl_3$): δ 1.65-1.73 (m, 2H), 1.80-1.85 (dd, J1 = 11.7 Hz , J2 = 3.3 Hz, 2H), 2.00-2.06 (m, 2H), 3.15-3.16 (d, J = 2.4 Hz, 2H), 3.74-3.76 (d, J = 3.9 Hz, 2H), 7.42-7.45 (d, J = 8.4 Hz, 2H), 7.53-7.56 (dd, J1 = 8.7 Hz, J2 = 2.2 Hz, 2H), 7.79-7.80 (d, J = 1.8 Hz, 2H).

[13]CNMR (75 MHz, $CDCl_3$): δ 196.3, 137.2, 135.6, 133.2, 130.7, 129.7, 126.7, 48.0, 39.0, 32.3, 25.1.

HRMS: Calc. [M+1] for $C_{22}H_{17}O_2Cl_4$: 440.9983; Found: 440.9979.

IR (KBr): 3086, 2936, 2848, 1681, 1579, 1557, 1465, 1381, 1201, 1028, 827, 680 cm^{-1}.





IV: Crystallographic Data for 2e

Crystallographic Material for **2e**.

X-ray Experimental.

Table 1. Crystallographic Data for **2e**.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for the non-hydrogen atoms of **2e**.

Table 3. Bond Lengths (Å) and Angles (^{o}) for the non-hydrogen atoms of **2e**.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of **2e**.

Table 5. Fractional coordinates and isotropic thermal parameters ($Å^2$) for the hydrogen atoms of **2e**.

Table 6. Torsion Angles (^{o}) for the non-hydrogen atoms of **2e**.

Table 7. Observed and calculated structure factor amplitudes for **2e**. Values for Fo, Fc and σ(Fo) have been multiplied by 10.

Figure 1. View of molecule 1 in **2e** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Figure 2. View of molecule 2 in **2e** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Figure 3. Fit by least-squares of selected atoms of molecule 1 (solid lines) onto the equivalent atoms of molecule 2 (dashed lines). The atoms of molecule 1 used in the fit are labeled.

Figure 4. Unit cell packing diagram for **2e**. The view is approximately down the **b** axis. Molecules 1 are shown in ball-and-stick form while molecules 2 are in wire frame form.

X-ray Experimental for $C_{22}H_{24}O_2$: Crystals grew as long, colorless needles by slow evaporation from CH_3CN: CH_2Cl_2**:** MeOH(4: 1: 0.2). The data crystal was cut from a much longer needle and had approximate dimensions; 0.60 x 0.17 x 0.12 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 327 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 62 seconds per frame. The data were collected at 223 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). There are two crystallographically unique molecules per asymmetric unit. The molecules are nearly identical in conformation (Figure 3). The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0578*P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0**.**132, with R(F) equal to 0.0574 and a goodness of fit, S, = 0.956. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[4] The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (1.17(9)x10^{-5})* F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. The absolute direction of the **c-**axis could not be determined from the X-ray results. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5] All figures were generated using SHELXTL/PC.[6] Tables of positional and thermal parameters, bond lengths and angles, torsion angles, figures and lists of observed and calculated structure factors are located in tables 1 through 7.

References

1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.

2) SIR97. (1999). A program for crystal structure solution. Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C. , Guagliardi A., Moliterni A.G.G., Polidori G.,Spagna R. J. Appl. Cryst. 32, 115-119.

3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

4) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

5) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for 2e.

Empirical formula	C22 H24 O2	
Formula weight	320.41	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pca21	
Unit cell dimensions	a = 16.9116(3) Å	α= 90°.
	b = 5.56190(10) Å	β= 90°.
	c = 36.4494(8) Å	γ = 90°.
Volume	3428.45(11) $Å^3$	
Z	8	
Density (calculated)	1.242 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	1376	
Crystal size	0.60 x 0.17 x 0.12 mm	
Theta range for data collection	2.93 to 27.48°.	
Index ranges	-21<=h<=21, -7<=k<=7, -47<=l<=46	
Reflections collected	7195	
Independent reflections	7195 [R(int) = 0.0000]	
Completeness to theta = 27.48°	99.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7195 / 1 / 434	
Goodness-of-fit on F^2	0.956	
Final R indices [I>2sigma(I)]	R1 = 0.0574, wR2 = 0.1037	
R indices (all data)	R1 = 0.1559, wR2 = 0.1319	
Extinction coefficient	$1.17(9)x10^{-5}$	
Largest diff. peak and hole	0.225 and -0.202 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	7472(2)	2523(5)	3805(1)	23(1)
C2	7504(2)	572(6)	3503(1)	24(1)
C3	8336(2)	281(6)	3339(1)	28(1)
C4	8942(2)	-178(6)	3643(1)	33(1)
C5	8922(2)	1791(6)	3930(1)	33(1)
C6	8100(2)	2037(7)	4096(1)	32(1)
C7	6648(2)	2645(6)	3975(1)	27(1)
C8	6491(2)	4827(6)	4212(1)	26(1)
O9	6963(2)	6497(4)	4224(1)	36(1)
C10	5742(2)	4933(6)	4428(1)	23(1)
C11	5632(2)	6833(7)	4674(1)	30(1)
C12	4940(2)	6967(7)	4879(1)	34(1)
C13	4363(2)	5261(7)	4840(1)	33(1)
C14	4463(2)	3399(7)	4592(1)	36(1)
C15	5146(2)	3218(6)	4389(1)	30(1)
C16	6936(2)	1208(7)	3194(1)	24(1)
O17	7047(1)	3069(4)	3022(1)	34(1)
C18	6246(2)	-369(6)	3099(1)	25(1)
C19	5807(2)	214(7)	2788(1)	32(1)
C20	5169(2)	-1213(7)	2685(1)	33(1)
C21	4968(2)	-3200(7)	2890(1)	31(1)
C22	5400(2)	-3773(6)	3198(1)	33(1)
C23	6033(2)	-2359(6)	3304(1)	29(1)
C24	8362(2)	-1699(6)	3050(1)	34(1)
C1'	4537(2)	7435(6)	6144(1)	24(1)
C2'	4515(2)	5481(6)	6445(1)	24(1)
C3'	3675(2)	5209(6)	6606(1)	29(1)
C4'	3071(2)	4781(6)	6303(1)	31(1)
C5'	3087(2)	6758(6)	6016(1)	33(1)
C6'	3912(2)	6966(6)	5853(1)	29(1)
C7'	5370(2)	7594(6)	5973(1)	25(1)
C8'	5523(2)	9793(6)	5741(1)	25(1)

O9'	5050(2)	11447(4)	5728(1)	36(1)
C10'	6270(2)	9936(6)	5524(1)	25(1)
C11'	6373(2)	11818(6)	5277(1)	29(1)
C12'	7060(2)	11991(6)	5072(1)	34(1)
C13'	7657(2)	10296(6)	5112(1)	35(1)
C14'	7559(2)	8418(7)	5354(1)	35(1)
C15'	6873(2)	8231(7)	5561(1)	32(1)
C16'	5080(2)	6142(6)	6751(1)	26(1)
O17'	4956(1)	8006(4)	6924(1)	35(1)
C18'	5776(2)	4627(6)	6854(1)	25(1)
C19'	6230(2)	5305(6)	7155(1)	31(1)
C20'	6864(2)	3929(7)	7270(1)	36(1)
C21'	7056(2)	1850(7)	7082(1)	39(1)
C22'	6623(2)	1150(6)	6779(1)	35(1)
C23'	5980(2)	2543(6)	6663(1)	32(1)
C24'	3648(2)	3221(6)	6895(1)	38(1)

Table 3. Bond lengths [Å] and angles [°] for 1.

C1-C6	1.525(5)	C16-C18	1.501(5)
C1-C7	1.526(5)	C18-C23	1.383(5)
C1-C2	1.548(5)	C18-C19	1.395(5)
C1-H1	0.96	C19-C20	1.390(5)
C2-C16	1.521(5)	C19-H19	0.96
C2-C3	1.537(5)	C20-C21	1.376(5)
C2-H2	0.96	C20-H20	0.96
C3-C24	1.525(5)	C21-C22	1.377(5)
C3-C4	1.531(5)	C21-H21	0.96
C3-H3	0.96	C22-C23	1.383(5)
C4-C5	1.515(5)	C22-H22	0.96
C4-H4A	0.96	C23-H23	0.96
C4-H4B	0.96	C24-H24A	0.96
C5-C6	1.523(5)	C24-H24B	0.96
C5-H5A	0.96	C24-H24C	0.96
C5-H5B	0.96	C1'-C6'	1.520(5)
C6-H6A	0.96	C1'-C7'	1.544(5)
C6-H6B	0.96	C1'-C2'	1.544(5)
C7-C8	1.514(5)	C1'-H1'	0.96
C7-H7A	0.96	C2'-C16'	1.514(5)
C7-H7B	0.96	C2'-C3'	1.544(4)
C8-O9	1.225(4)	C2'-H2'	0.96
C8-C10	1.492(5)	C3'-C4'	1.524(5)
C10-C15	1.395(5)	C3'-C24'	1.528(5)
C10-C11	1.400(5)	C3'-H3'	0.96
C11-C12	1.389(5)	C4'-C5'	1.518(5)
C11-H11	0.96	C4'-H4'A	0.96
C12-C13	1.368(5)	C4'-H4'B	0.96
C12-H12	0.96	C5'-C6'	1.521(5)
C13-C14	1.387(5)	C5'-H5'A	0.96
C13-H13	0.96	C5'-H5'B	0.96
C14-C15	1.375(5)	C6'-H6'A	0.96
C14-H14	0.96	C6'-H6'B	0.96
C15-H15	0.96	C7'-C8'	1.510(5)
C16-O17	1.225(4)	C7'-H7'A	0.96

C7'-H7'B	0.96	C16'-C18'	1.495(5)
C8'-O9'	1.220(4)	C18'-C19'	1.390(5)
C8'-C10'	1.492(5)	C18'-C23'	1.396(5)
C10'-C11'	1.392(5)	C19'-C20'	1.383(5)
C10'-C15'	1.398(5)	C19'-H19'	0.96
C11'-C12'	1.384(5)	C20'-C21'	1.384(5)
C11'-H11'	0.96	C20'-H20'	0.96
C12'-C13'	1.388(5)	C21'-C22'	1.381(6)
C12'-H12'	0.96	C21'-H21'	0.96
C13'-C14'	1.377(5)	C22'-C23'	1.401(5)
C13'-H13'	0.96	C22'-H22'	0.96
C14'-C15'	1.389(5)	C23'-H23'	0.96
C14'-H14'	0.96	C24'-H24D	0.96
C15'-H15'	0.96	C24'-H24E	0.96
C16'-O17'	1.232(4)	C24'-H24F	0.96

C6-C1-C7	111.3(3)	C3-C4-H4A	109.6
C6-C1-C2	110.3(3)	C5-C4-H4B	108.1
C7-C1-C2	110.6(3)	C3-C4-H4B	108.7
C6-C1-H1	108.1	H4A-C4-H4B	108.4
C7-C1-H1	108.0	C4-C5-C6	111.0(3)
C2-C1-H1	108.4	C4-C5-H5A	107.6
C16-C2-C3	108.4(3)	C6-C5-H5A	108.8
C16-C2-C1	110.0(3)	C4-C5-H5B	110.7
C3-C2-C1	112.5(3)	C6-C5-H5B	110.6
C16-C2-H2	108.9	H5A-C5-H5B	108.1
C3-C2-H2	108.2	C5-C6-C1	112.1(3)
C1-C2-H2	108.7	C5-C6-H6A	109.0
C24-C3-C4	111.2(3)	C1-C6-H6A	107.6
C24-C3-C2	111.7(3)	C5-C6-H6B	109.4
C4-C3-C2	110.5(3)	C1-C6-H6B	110.5
C24-C3-H3	108.5	H6A-C6-H6B	108.2
C4-C3-H3	107.9	C8-C7-C1	115.3(3)
C2-C3-H3	107.0	C8-C7-H7A	108.3
C5-C4-C3	111.4(3)	C1-C7-H7A	106.9
C5-C4-H4A	110.7	C8-C7-H7B	109.4

C1-C7-H7B	109.0	C20-C21-H21	120.8
H7A-C7-H7B	107.8	C22-C21-H21	119.4
O9-C8-C10	120.3(3)	C21-C22-C23	120.5(3)
O9-C8-C7	120.9(3)	C21-C22-H22	121.3
C10-C8-C7	118.8(3)	C23-C22-H22	118.2
C15-C10-C11	119.0(3)	C22-C23-C18	120.4(3)
C15-C10-C8	122.2(3)	C22-C23-H23	120.9
C11-C10-C8	118.7(3)	C18-C23-H23	118.7
C12-C11-C10	119.8(3)	C3-C24-H24A	111.3
C12-C11-H11	120.3	C3-C24-H24B	108.4
C10-C11-H11	119.9	H24A-C24-H24B	109.5
C13-C12-C11	120.5(4)	C3-C24-H24C	108.7
C13-C12-H12	119.4	H24A-C24-H24C	109.5
C11-C12-H12	120.0	H24B-C24-H24C	109.5
C12-C13-C14	119.9(3)	C6'-C1'-C7'	111.2(3)
C12-C13-H13	120.5	C6'-C1'-C2'	111.0(3)
C14-C13-H13	119.6	C7'-C1'-C2'	110.5(3)
C15-C14-C13	120.5(3)	C6'-C1'-H1'	107.8
C15-C14-H14	119.0	C7'-C1'-H1'	108.7
C13-C14-H14	120.4	C2'-C1'-H1'	107.5
C14-C15-C10	120.2(3)	C16'-C2'-C3'	108.9(3)
C14-C15-H15	119.1	C16'-C2'-C1'	109.6(3)
C10-C15-H15	120.7	C3'-C2'-C1'	111.2(3)
O17-C16-C18	119.7(3)	C16'-C2'-H2'	110.3
O17-C16-C2	118.6(3)	C3'-C2'-H2'	108.4
C18-C16-C2	121.7(3)	C1'-C2'-H2'	108.3
C23-C18-C19	119.1(3)	C4'-C3'-C24'	111.5(3)
C23-C18-C16	123.1(3)	C4'-C3'-C2'	110.8(3)
C19-C18-C16	117.8(3)	C24'-C3'-C2'	111.2(3)
C20-C19-C18	119.9(3)	C4'-C3'-H3'	107.5
C20-C19-H19	121.2	C24'-C3'-H3'	108.3
C18-C19-H19	118.9	C2'-C3'-H3'	107.4
C21-C20-C19	120.3(4)	C5'-C4'-C3'	112.0(3)
C21-C20-H20	119.9	C5'-C4'-H4'A	109.7
C19-C20-H20	119.8	C3'-C4'-H4'A	109.0
C20-C21-C22	119.8(3)	C5'-C4'-H4'B	109.3

C3'-C4'-H4'B	108.2	C13'-C14'-H14'	119.5
H4'A-C4'-H4'B	108.4	C15'-C14'-H14'	120.1
C4'-C5'-C6'	109.9(3)	C14'-C15'-C10'	120.3(3)
C4'-C5'-H5'A	109.3	C14'-C15'-H15'	120.8
C6'-C5'-H5'A	108.0	C10'-C15'-H15'	118.9
C4'-C5'-H5'B	110.9	O17'-C16'-C18'	118.6(3)
C6'-C5'-H5'B	110.3	O17'-C16'-C2'	118.3(3)
H5'A-C5'-H5'B	108.3	C18'-C16'-C2'	123.1(3)
C1'-C6'-C5'	112.2(3)	C19'-C18'-C23'	118.8(3)
C1'-C6'-H6'A	108.0	C19'-C18'-C16'	118.7(3)
C5'-C6'-H6'A	107.6	C23'-C18'-C16'	122.4(3)
C1'-C6'-H6'B	109.9	C20'-C19'-C18'	121.3(3)
C5'-C6'-H6'B	111.0	C20'-C19'-H19'	120.0
H6'A-C6'-H6'B	108.0	C18'-C19'-H19'	118.7
C8'-C7'-C1'	115.4(3)	C19'-C20'-C21'	119.5(4)
C8'-C7'-H7'A	109.1	C19'-C20'-H20'	119.9
C1'-C7'-H7'A	108.2	C21'-C20'-H20'	120.6
C8'-C7'-H7'B	108.3	C22'-C21'-C20'	120.6(3)
C1'-C7'-H7'B	108.0	C22'-C21'-H21'	119.8
H7'A-C7'-H7'B	107.6	C20'-C21'-H21'	119.6
O9'-C8'-C10'	119.7(3)	C21'-C22'-C23'	119.8(4)
O9'-C8'-C7'	121.3(3)	C21'-C22'-H22'	119.8
C10'-C8'-C7'	119.0(3)	C23'-C22'-H22'	120.4
C11'-C10'-C15'	118.9(3)	C18'-C23'-C22'	120.0(4)
C11'-C10'-C8'	119.2(3)	C18'-C23'-H23'	119.6
C15'-C10'-C8'	122.0(3)	C22'-C23'-H23'	120.4
C12'-C11'-C10'	120.3(3)	C3'-C24'-H24D	110.8
C12'-C11'-H11'	120.6	C3'-C24'-H24E	108.5
C10'-C11'-H11'	119.0	H24D-C24'-H24E	109.5
C11'-C12'-C13'	120.5(3)	C3'-C24'-H24F	109.1
C11'-C12'-H12'	119.1	H24D-C24'-H24F	109.5
C13'-C12'-H12'	120.4	H24E-C24'-H24F	109.5
C14'-C13'-C12'	119.6(4)		
C14'-C13'-H13'	120.0		
C12'-C13'-H13'	120.4		
C13'-C14'-C15'	120.4(4)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2e. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	24(2)	22(2)	23(2)	-1(1)	3(2)	-2(2)
C2	27(2)	24(2)	21(2)	3(2)	0(2)	-2(2)
C3	31(2)	24(2)	28(2)	0(2)	3(2)	-2(2)
C4	26(2)	30(2)	43(3)	-1(2)	5(2)	6(2)
C5	22(2)	39(2)	36(2)	2(2)	-2(2)	-1(2)
C6	30(2)	38(2)	29(2)	-2(2)	-2(2)	-3(2)
C7	29(2)	29(2)	23(2)	1(2)	1(2)	-3(2)
C8	32(2)	22(2)	25(2)	2(2)	-3(2)	3(2)
O9	39(2)	28(1)	40(2)	-5(1)	8(1)	-8(1)
C10	27(2)	22(2)	20(2)	3(2)	-1(2)	3(2)
C11	31(2)	32(2)	25(2)	-2(2)	-2(2)	1(2)
C12	36(2)	37(2)	28(2)	-4(2)	0(2)	7(2)
C13	32(2)	43(2)	25(2)	3(2)	2(2)	2(2)
C14	27(2)	37(2)	44(3)	0(2)	2(2)	2(2)
C15	33(2)	26(2)	31(2)	0(2)	1(2)	1(2)
C16	32(2)	21(2)	20(2)	-3(2)	3(2)	3(2)
O17	38(2)	32(2)	31(2)	7(1)	-1(1)	-1(1)
C18	24(2)	25(2)	25(2)	-2(2)	4(2)	4(2)
C19	34(2)	35(2)	26(2)	2(2)	-1(2)	-1(2)
C20	35(2)	39(2)	26(2)	-3(2)	-1(2)	3(2)
C21	26(2)	35(2)	32(2)	-4(2)	-4(2)	-2(2)
C22	34(2)	29(2)	37(2)	2(2)	-2(2)	-9(2)
C23	29(2)	32(2)	27(2)	0(2)	-2(2)	0(2)
C24	36(2)	29(2)	37(2)	-4(2)	3(2)	-1(2)
C1'	28(2)	23(2)	21(2)	-1(1)	0(2)	0(2)
C2'	22(2)	25(2)	24(2)	-2(2)	2(2)	2(2)
C3'	28(2)	27(2)	30(2)	0(2)	4(2)	-2(2)
C4'	30(2)	28(2)	36(2)	0(2)	-3(2)	0(2)
C5'	29(2)	31(2)	37(2)	1(2)	-8(2)	-2(2)
C6'	31(2)	29(2)	27(2)	3(2)	-6(2)	2(2)
C7'	24(2)	29(2)	22(2)	0(2)	-2(2)	0(2)
C8'	32(2)	23(2)	20(2)	-5(2)	1(2)	-1(2)
O9'	37(2)	31(1)	41(2)	2(1)	9(1)	8(1)

C10'	29(2)	23(2)	23(2)	-3(2)	-2(2)	-3(2)
C11'	34(2)	28(2)	24(2)	0(2)	-6(2)	1(2)
C12'	38(2)	35(2)	27(2)	3(2)	0(2)	-5(2)
C13'	33(2)	41(2)	32(2)	-1(2)	5(2)	-5(2)
C14'	31(2)	36(2)	37(3)	1(2)	8(2)	4(2)
C15'	34(2)	32(2)	29(2)	4(2)	4(2)	3(2)
C16'	28(2)	29(2)	20(2)	0(2)	6(2)	0(2)
O17'	40(2)	31(1)	34(2)	-9(1)	-5(1)	6(1)
C18'	31(2)	23(2)	21(2)	2(2)	1(2)	-2(2)
C19'	32(2)	35(2)	27(2)	2(2)	1(2)	-2(2)
C20'	31(2)	46(3)	31(3)	6(2)	-5(2)	0(2)
C21'	31(2)	42(2)	43(3)	16(2)	1(2)	4(2)
C22'	31(2)	31(2)	43(3)	-2(2)	3(2)	-3(2)
C23'	30(2)	30(2)	35(3)	-4(2)	-6(2)	1(2)
C24'	37(2)	39(2)	38(2)	9(2)	3(2)	-6(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 2e.

	x	y	z	U(eq)
H1	7583	4053	3695	28
H2	7348	-940	3607	29
H3	8468	1779	3224	33
H4A	9460	-315	3538	40
H4B	8815	-1672	3761	40
H5A	9058	3273	3811	39
H5B	9307	1492	4119	39
H6A	7963	560	4217	39
H6B	8103	3296	4276	39
H7A	6586	1234	4123	33
H7B	6261	2573	3782	33
H11	6028	8063	4696	36
H12	4862	8271	5048	40
H13	3892	5328	4987	40
H14	4051	2235	4555	43
H15	5202	1914	4218	36
H19	5952	1609	2648	38
H20	4862	-792	2473	40
H21	4533	-4206	2820	37
H22	5261	-5119	3349	40
H23	6344	-2770	3515	35
H24A	7986	-1406	2858	51
H24B	8885	-1754	2948	51
H24C	8244	-3206	3166	51
H1'	4415	8944	6259	29
H2'	4665	3976	6336	28
H3'	3542	6703	6723	34
H4'A	2553	4680	6410	37
H4'B	3189	3269	6188	37
H5'A	2959	8264	6130	39
H5'B	2706	6454	5826	39
H6'A	4034	5460	5737	35

H6'B	3932	8201	5669	35
H7'A	5454	6180	5827	30
H7'B	5749	7569	6169	30
H11'	5958	12983	5249	35
H12'	7117	13287	4900	40
H13'	8143	10459	4978	43
H14'	7964	7216	5375	41
H15'	6800	6922	5730	38
H19'	6104	6777	7279	37
H20'	7163	4412	7482	43
H21'	7489	875	7164	47
H22'	6762	-295	6650	42
H23'	5685	2095	6448	38
H24D	3129	3093	7000	58
H24E	3787	1727	6780	58
H24F	4023	3578	7085	58

Table 6. Torsion angles [°] for 2e.

C6-C1-C2-C16	-174.1(3)
C7-C1-C2-C16	62.4(4)
C6-C1-C2-C3	-53.2(4)
C7-C1-C2-C3	-176.7(3)
C16-C2-C3-C24	-59.9(4)
C1-C2-C3-C24	178.3(3)
C16-C2-C3-C4	175.8(3)
C1-C2-C3-C4	54.0(4)
C24-C3-C4-C5	179.7(3)
C2-C3-C4-C5	-55.7(4)
C3-C4-C5-C6	57.3(4)
C4-C5-C6-C1	-56.9(4)
C7-C1-C6-C5	177.3(3)
C2-C1-C6-C5	54.2(4)
C6-C1-C7-C8	70.0(4)
C2-C1-C7-C8	-167.1(3)
C1-C7-C8-O9	9.1(5)
C1-C7-C8-C10	-172.0(3)
O9-C8-C10-C15	172.2(3)
C7-C8-C10-C15	-6.8(5)
O9-C8-C10-C11	-7.3(5)
C7-C8-C10-C11	173.8(3)
C15-C10-C11-C12	0.7(5)
C8-C10-C11-C12	-179.8(3)
C10-C11-C12-C13	-0.2(6)
C11-C12-C13-C14	-0.9(6)
C12-C13-C14-C15	1.6(6)
C13-C14-C15-C10	-1.1(6)
C11-C10-C15-C14	-0.1(5)
C8-C10-C15-C14	-179.5(3)
C3-C2-C16-O17	-61.2(4)
C1-C2-C16-O17	62.1(4)
C3-C2-C16-C18	119.3(3)
C1-C2-C16-C18	-117.3(3)
O17-C16-C18-C23	-173.0(3)
C2-C16-C18-C23	6.5(5)
O17-C16-C18-C19	7.3(5)

C2-C16-C18-C19	-173.3(3)
C23-C18-C19-C20	-0.7(5)
C16-C18-C19-C20	179.1(3)
C18-C19-C20-C21	0.1(6)
C19-C20-C21-C22	0.1(6)
C20-C21-C22-C23	0.4(6)
C21-C22-C23-C18	-1.0(6)
C19-C18-C23-C22	1.1(5)
C16-C18-C23-C22	-178.6(3)
C6'-C1'-C2'-C16'	-173.9(3)
C7'-C1'-C2'-C16'	62.2(4)
C6'-C1'-C2'-C3'	-53.4(4)
C7'-C1'-C2'-C3'	-177.2(3)
C16'-C2'-C3'-C4'	174.6(3)
C1'-C2'-C3'-C4'	53.6(4)
C16'-C2'-C3'-C24'	-60.8(4)
C1'-C2'-C3'-C24'	178.2(3)
C24'-C3'-C4'-C5'	179.5(3)
C2'-C3'-C4'-C5'	-56.2(4)
C3'-C4'-C5'-C6'	57.3(4)
C7'-C1'-C6'-C5'	179.0(3)
C2'-C1'-C6'-C5'	55.6(4)
C4'-C5'-C6'-C1'	-57.1(4)
C6'-C1'-C7'-C8'	69.9(4)
C2'-C1'-C7'-C8'	-166.4(3)
C1'-C7'-C8'-O9'	8.4(5)
C1'-C7'-C8'-C10'	-171.8(3)
O9'-C8'-C10'-C11'	-7.7(5)
C7'-C8'-C10'-C11'	172.5(3)
O9'-C8'-C10'-C15'	172.3(3)
C7'-C8'-C10'-C15'	-7.4(5)
C15'-C10'-C11'-C12'	0.0(5)
C8'-C10'-C11'-C12'	-180.0(3)
C10'-C11'-C12'-C13'	-0.2(6)
C11'-C12'-C13'-C14'	0.6(6)
C12'-C13'-C14'-C15'	-0.9(6)
C13'-C14'-C15'-C10'	0.7(6)
C11'-C10'-C15'-C14'	-0.2(5)

C8'-C10'-C15'-C14'	179.8(4)
C3'-C2'-C16'-O17'	-59.4(4)
C1'-C2'-C16'-O17'	62.5(4)
C3'-C2'-C16'-C18'	119.9(3)
C1'-C2'-C16'-C18'	-118.2(3)
O17'-C16'-C18'-C19'	3.5(5)
C2'-C16'-C18'-C19'	-175.7(3)
O17'-C16'-C18'-C23'	-177.2(3)
C2'-C16'-C18'-C23'	3.5(5)
C23'-C18'-C19'-C20'	-1.5(6)
C16'-C18'-C19'-C20'	177.8(3)
C18'-C19'-C20'-C21'	0.7(6)
C19'-C20'-C21'-C22'	0.4(6)
C20'-C21'-C22'-C23'	-0.5(6)
C19'-C18'-C23'-C22'	1.3(5)
C16'-C18'-C23'-C22'	-178.0(3)
C21'-C22'-C23'-C18'	-0.3(6)

Figure 1. View of molecule 1 in **2e** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

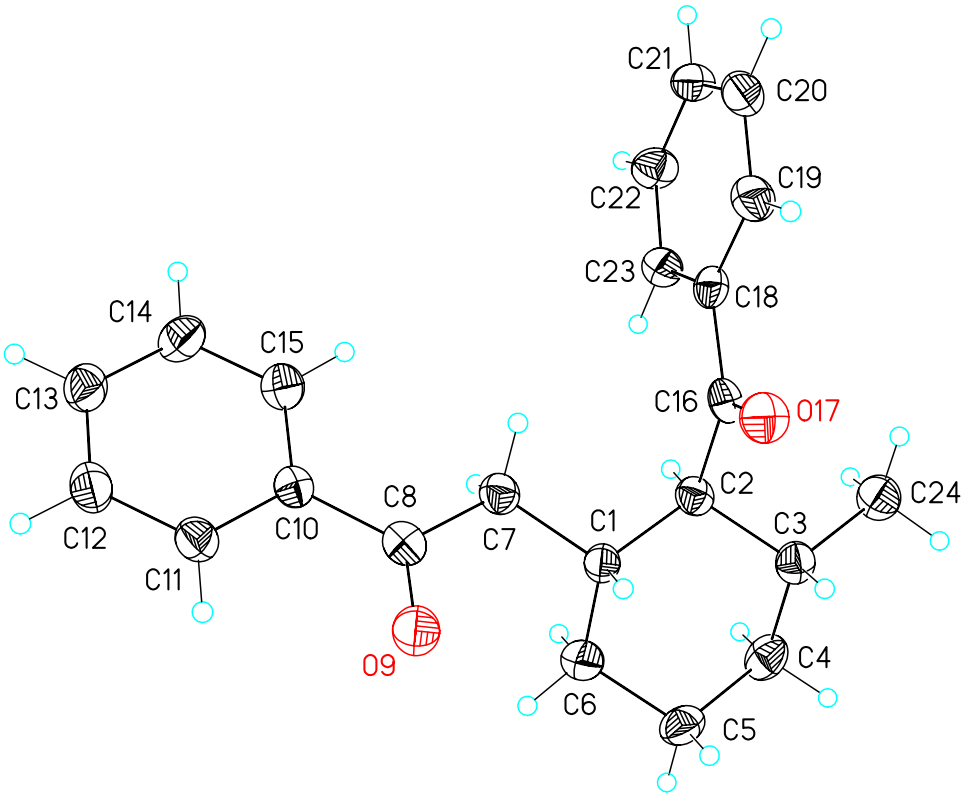


Figure 2. View of molecule 2 in **2e** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

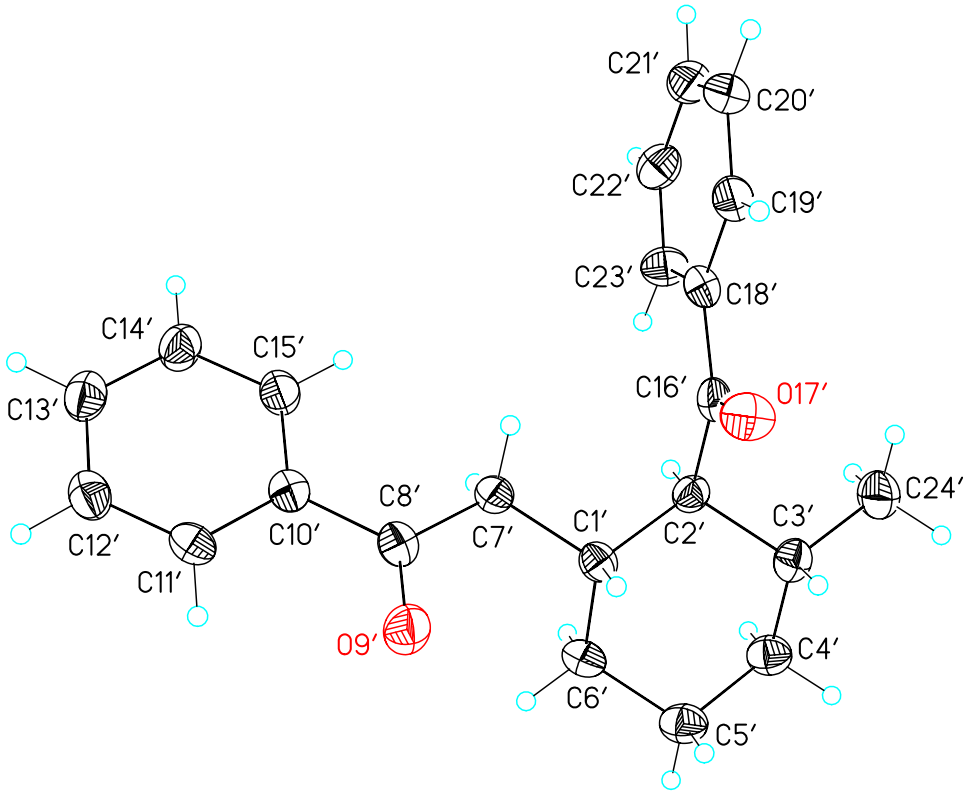


Figure 3. Fit by least-squares of selected atoms of molecule 1 (solid lines) onto the equivalent atoms of molecule 2 (dashed lines). The atoms of molecule 1 used in the fit are labeled.

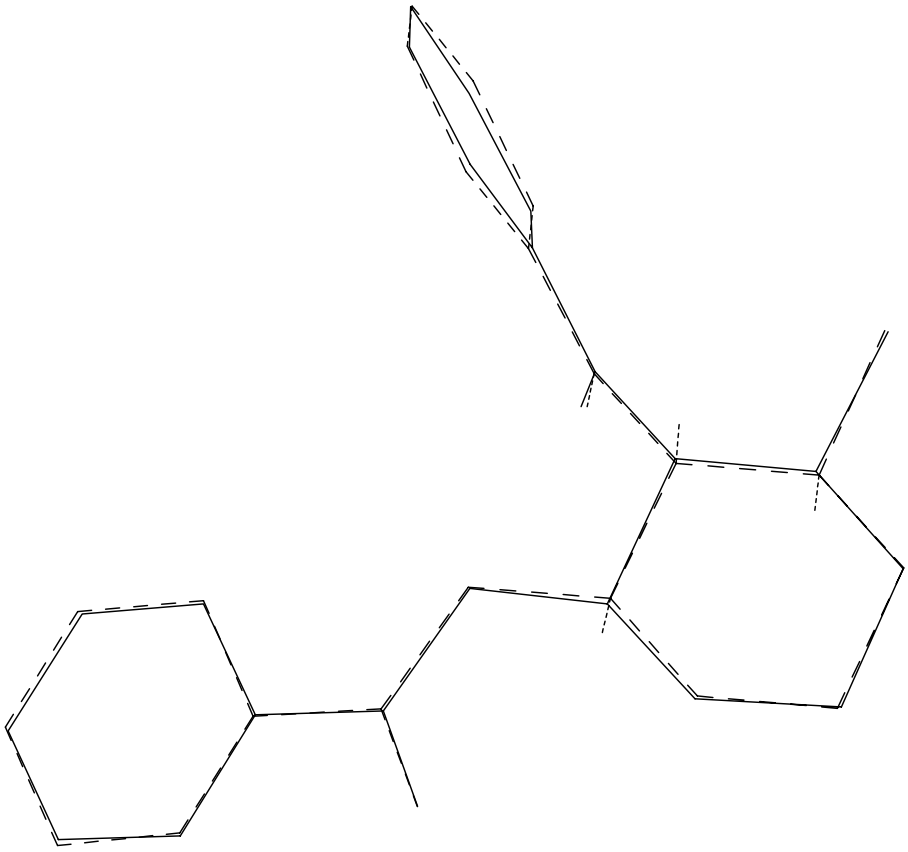


Figure 4. Unit cell packing diagram for **2e**. The view is approximately down the **b** axis. Molecules 1 are shown in ball-and-stick form while molecules 2 are in wire frame form.