Diastereoselective Photocycloaddition using Memory Effect of Molecular Chirality Controlled by Crystallization

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Experimental

General. NMR spectra were recorded on $CDCl_3$ solutions on a BRUKER 300 operating 300 MHz, respectively, for ^1H- and ^{13}C-NMR spectroscopy. Chemical shifts are reported in parts per million (ppm) relative to TMS as internal standards. IR spectra were recorded on a JASCO FT/IR-230 spectrometers as KBr disks.

General procedure for the preparation of naphthamides 1a and 1b. Both naphthamides **1a-1b** were provided from the corresponding 2-alkoxynanthoic acids and proline methyl ester. A synthesis of **1a** was exemplified as follows. To a THF solution containing 1.11 g (5.5 mmol) of naphthoic acid and triethylamine 0.67g (6.6 mmol) was added 0.79 g (6.6 mmol) of thionyl chloride at 0°C. The reaction mixture was stirred for 0.5 h, and then a THF solution containing 1.68 g of proline methyl ester (13.0 mmol) was added dropwise. After the reaction mixture was stirred for 2 h, water and ethyl acetate were added, and the organic layer was extracted in the usual manner. After the organic solvent was evaporated in *vacuo*, the residual mixture was subjected to chromatography on silica gel and the naphthamide **1a** was separated. The structures of **1a** and **1b** were determined on the basis of spectral data, mass spectroscopy, and unequivocally X-ray single crystallographic analyses.

(*S*, a*R*) *N*-(2-Methoxy-1-naphthalencarbonyl)prolinecarboxilic acid methyl ester 1a

m.p. 109-112°C; IR (cm^{-1}, KBr) 1620, 1735; ^{1}H-NMR: (CDCl$_3$) δ 1.9-2.0 (m, 2H), 2.05-2.25 (m, 1H), 2.3-2.5 (m, 1H), 3.2-3.4 (m, 2H), 3.90 (s, 3H), 3.97 (s, 3H), 4.75-4.8 (m, 1H), 7.3-7.4 (m, 2H), 7.5-7.6 (m, 1H), 7.8 (d, *J*=8.2 Hz, 1H), 7.9-8.0 (m, 2H) , ^{13}C-NMR (CDCl$_3$) δ28.7, 33.9, 52.3, 56.3, 60.3, 62.9, 117.0, 123.6, 127.9, 128.5, 131.9, 132.2, 133.1, 135.0, 135.4, 156.9, 173.0, 177.1; EI-MS *m*/*z* (rel intensity): 313 (M$^+$, 10); HRMS (FABMS) *m*/*z* calcd for $C_{18}H_{19}N0_4$+H: 314.1392, found 314.1368.

(*S*, a*R*) *N*-(2-Ethoxy-1-naphthalencarbonyl)prolinecarboxilic acid methyl ester 1b

m.p. 133-135°C; IR (cm^{-1}, KBr) 1053, 1248, 1446, 1628, 1749, 2871, 2973; ^{1}H-NMR: (CDCl$_3$) δ 1.4 (t, *J*=7.0 Hz, 3H), 1.85-2.0 (m, 2H), 2.05-2.2 (m, 1H), 2.35-2.5 (m, 1H), 3.15-3.25 (m, 1H), 3.3-3.4 (m, 1H), 3.89 (s, 3H), 4.2-4.3 (m, 2H), 4.75-4.8 (m, 1H), 7.3-7.45 (m, 2H), 7.5 (dt, *J*=1.1 and 7.6 Hz, 1H), 7.8 (d, *J*=8.2 Hz, 1H), 7.8-8.0 (m, 2H), ^{13}C-NMR (CDCl$_3$) δ 19.0, ,28.8, 34.0, 52.3, 56.4, 62.8, 69.1, 118.2, 124.1, 128.0, 128.5, 131.9, 132.2, 133.1, 135.1, 135.3, 156.1, 173.0, 177.2; EI-MS *m*/*z* (rel intensity): 327 (M$^+$, 16); HRMS (FAB) *m*/*z* calcd for $C_{19}H_{21}N0_4$ +H 328.1549, found 328.1535.

General procedure for the photochemical reaction of naphthamide 1a-b with 9-cyanoanthracene using the chiral crystal.

Crystals of **1** were added to a cooled THF solution of 9-cyanoanthracene (0.025 M), and the solution was irradiated with a 350-W ultra-high pressure mercury lamp under argon atmosphere for 30 min. After removing the solvent in vacuo, the crude photolysate was subjected to chromatography on silica gel. The 4+4 cycloadduct **2** was obtained in 100% chemical yield accompanied by a small amount of a dimmer of 9-cyanoanthracene. The chemical yield of **2** was determined on the basis of the consumed naphthamide **1**.

Photoadduct of 1a with 9-cyanoanthracene 2a

Decomp. 103-105°C; IR (cm^{-1}, KBr) 1655, 1737; ^{1}H-NMR: (CDCl$_3$) δ 1.5-1.9 (m, 3H), 2.1-2.25 (m, 1H), 2.6-2.7 (m, 1H), 2.85-2.95 (m, 1H), 2.95 (s, 3H), 3.88 (s, 3H), 4.36 (d, *J*=7.6 Hz, 1H), 4.65-4.75 (m, 2H), 5.91 (s, 1H), 6.8-7.0 (m, 6H), 7.2-7.3 (m, 4H), 7.35-7.4 (m, 1H), 7.6-7.65 (m, 1H), ^{13}C-NMR (CDCl$_3$) δ 25.8, 29.2, 48.2, 52.7, 54.2, 54.5, 55.7, 56.0, 60.6, 64.7, 98.4, 122.0, 125.0, 125.3, 126.3, 126.9, 127.2, 127.3, 127.4, 128.7, 129.3, 139.3, 140.2, 140.6, 140.9, 142.0, 143.2, 164.3, 168.5, 173.7; FAB-MS *m/z* (rel intensiy) 517 (M^+ + 1, 11); HRMS (FAB-MS) *m/z* calcd for $C_{33}H_{28}N_20_4$ + H 517.2127, found 517.2007.

Photoadduct of 1b with 9-cyanoanthracene 2b

Decomp. 126-130°C; IR (cm^{-1}, KBr) 1174, 1413, 1635, 1747, 2237, 2979; ^{1}H-NMR: ($CDCl_3$) δ 1.0 (8, *J*=7.0 Hz, 3H), 1.45-1.6 (m, 1H), 1.45-1.85 (m, 2H), 2.1-2.3 (m, 1H), 2.55-2.7 (m, 2H), 2.9-3.0(m, 1H), 3.2-3.35(m, 1H), 3.87(s, 3H), 4.33 (d, *J*=7.6 Hz, 1H), 4.55-4.7 (m, 2H), 5.89 (s, 1H), 6.75-7.0 (m, 6H), 7.15-7.3 (m, 4H), 7.35-7.4 (m, 1H), 7.55-7.6 (m, 1H), ^{13}C=NMR ($CDCl_3$) δ 14.7, 25.9, 29.3, 48.2, 52.7, 54.3, 54.5, 55.7, 60.7, 64.4, 64.7, 98.3, 122.1, 124.9, 125.2, 126.3, 126.9, 127.0, 127.1, 127.2, 127.3, 127.4, 128.8, 129.4, 139.4, 140.2, 140.6, 140.9, 142.0, 143.3, 163.6, 168.5, 173.8; FAB-MS *m/z* (rel intensiy) 532 (M^+ + 1, 27); HRMS (FAB-MS) *m/z* calcd for $C_{34}H_{30}N_20_4$ + H 531.2284, found 531.2261.

Figure S1. ^{1}H NMR spectrum of **1a** before crystallization

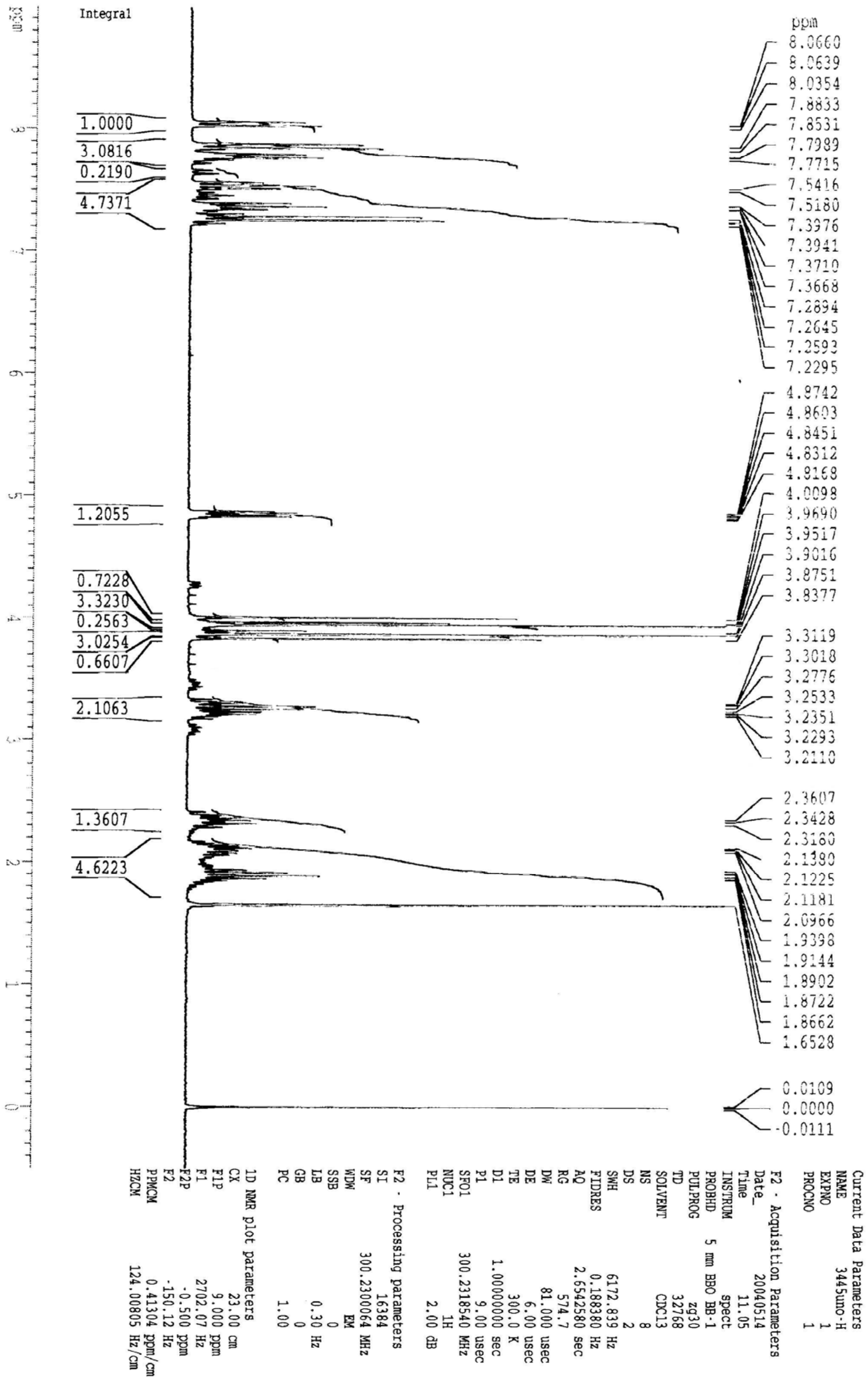


Figure S2. ^{1}H NMR spectrum of **1a** immediately after dissolving crystals in $CDCl_3$

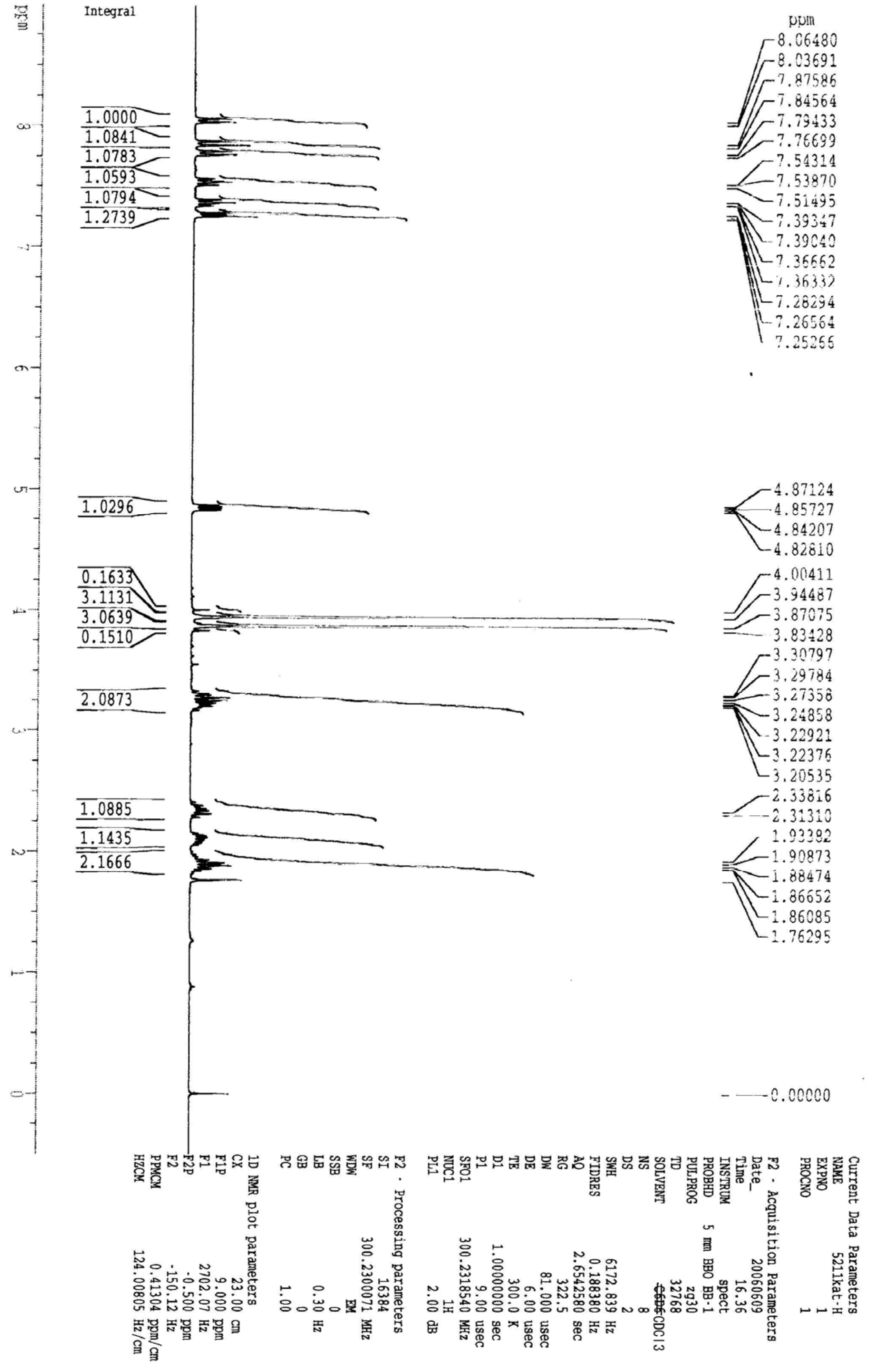
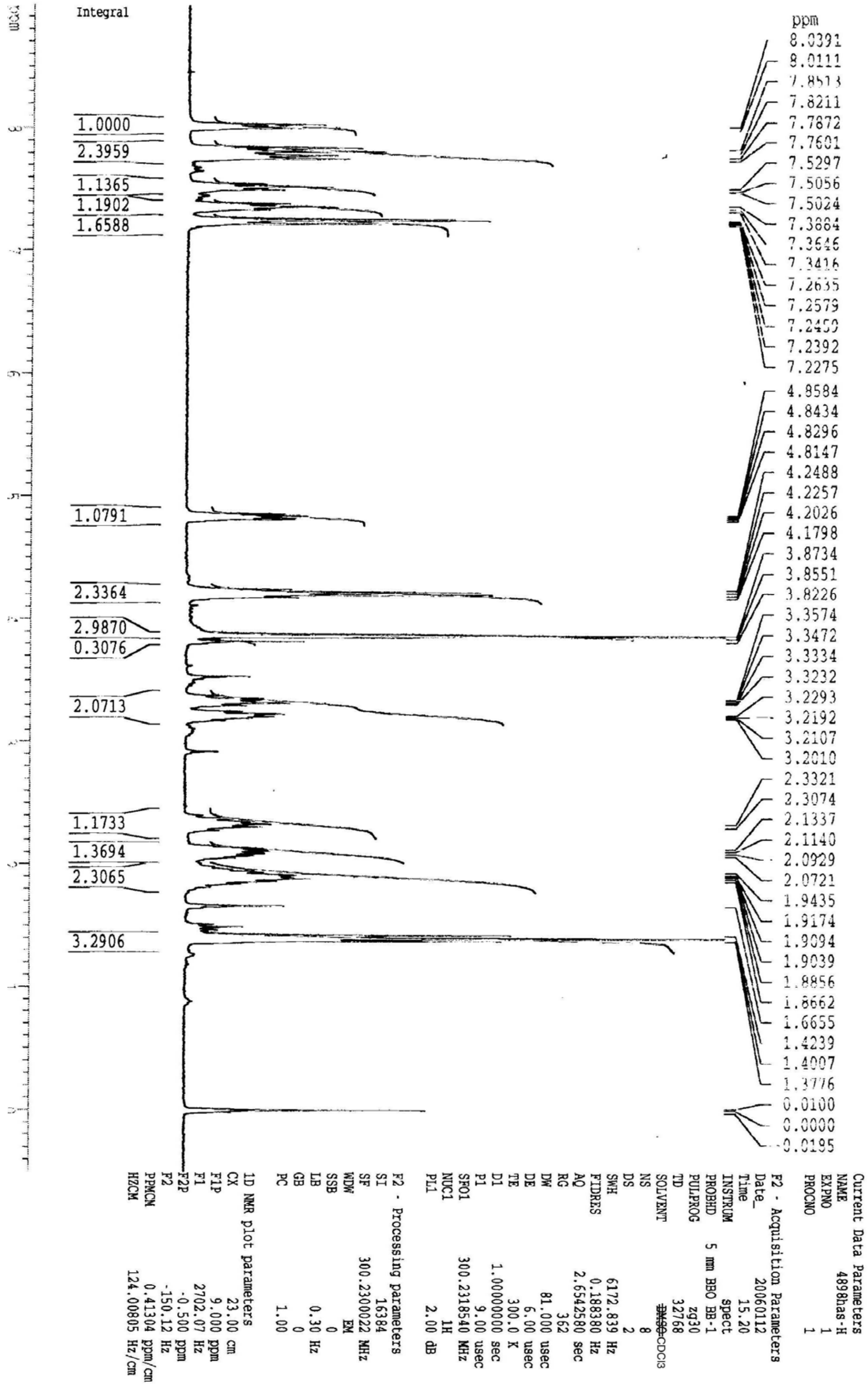


Figure S3. ^{1}H NMR spectrum of **1b** before crystallization



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PROCNO                     1

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PULPROG                 zg30
TD                     32768
SOLVENT           ~~DMSO~~CDCl3
NS                         8
DS                         2
SWH                 6172.839 Hz
FIDRES              0.188380 Hz
AQ                 2.6542580 sec
RG                       362
DW                    81.000 usec
DE                      6.00 usec
TE                     300.0 K
D1                1.00000000 sec
P1                      9.00 usec
SFO1             300.2318540 MHz
NUC1                      1H
PL1                     2.00 dB

F2 - Processing parameters
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SF               300.2300022 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     23.00 cm
F1P                    9.000 ppm
F1                   2702.07 Hz
F2P                   -0.500 ppm
F2                   -150.12 Hz
PPMCM                0.41304 ppm/cm
HZCM               124.00805 Hz/cm
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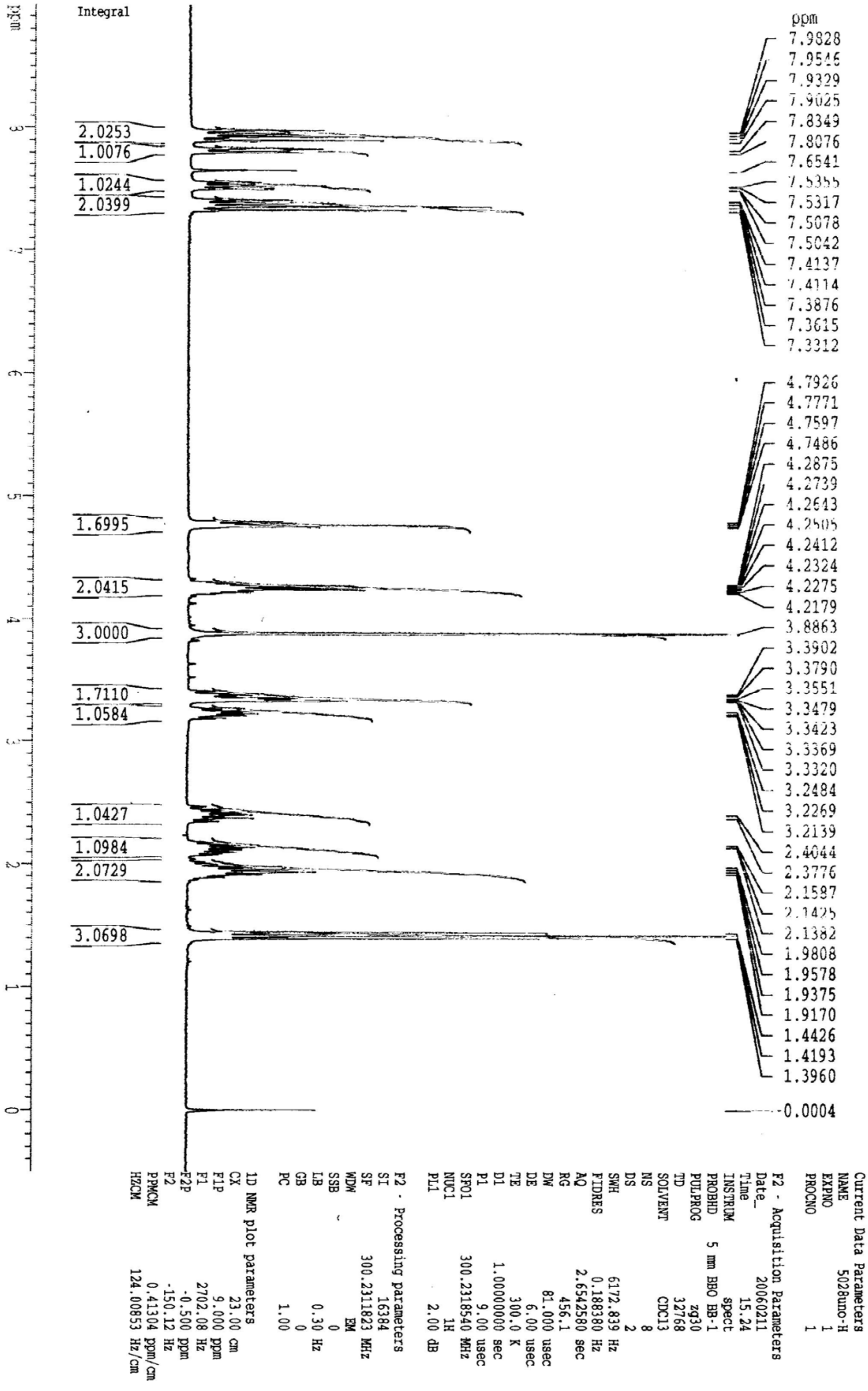
Figure S4.^{1}H NMR spectrum of **1b** immediately after dissolving crystals in $CDCl_3$



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EXPNO                     1
PROCNO                    1

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PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                2.6542580 sec
RG                    456.1
DW                   81.000 usec
DE                     6.00 usec
TE                    300.0 K
D1               1.00000000 sec
P1                     9.00 usec
SFO1            300.2318540 MHz
NUC1                     1H
PL1                    2.00 dB

F2 - Processing parameters
SI                    16384
SF              300.2311823 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    23.00 cm
F1P                   9.000 ppm
F1                  2702.08 Hz
F2P                  -0.500 ppm
F2                  -150.12 Hz
PPMCM               0.41304 ppm/cm
HZCM              124.00853 Hz/cm
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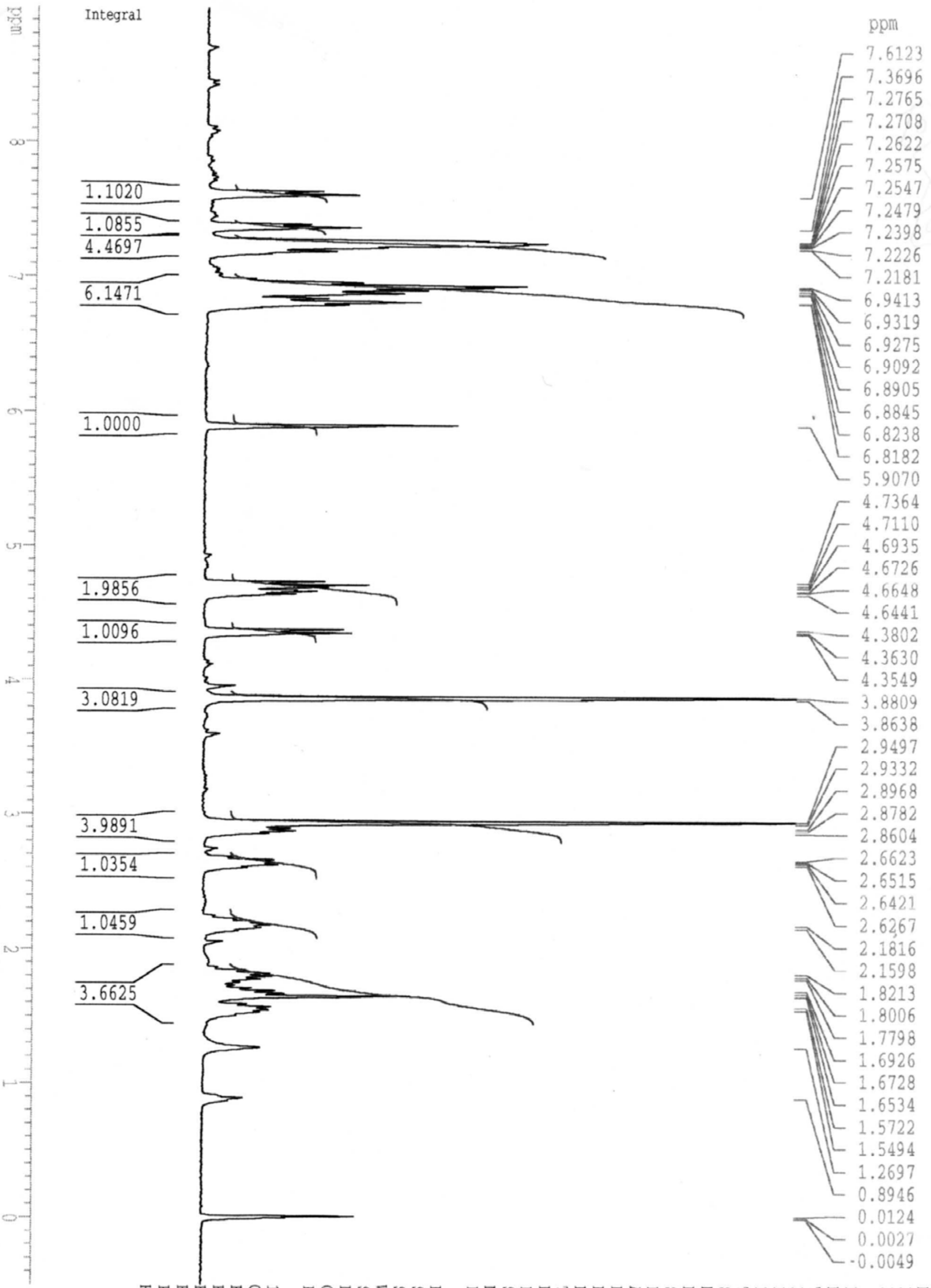
Figure S5. ^{1}H NMR spectrum of **2a**



2a

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Current Data Parameters
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EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
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PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ            2.6542580 sec
RG                287.4
DW               81.000 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
P1                 9.00 usec
SFO1        300.2318540 MHz
NUC1                 1H
PL1                2.00 dB

F2 - Processing parameters
SI                16384
SF          300.2300012 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                23.00 cm
F1P               9.000 ppm
F1              2702.07 Hz
F2P              -0.500 ppm
F2              -150.12 Hz
PPMCM           0.41304 ppm/cm
HZCM          124.00805 Hz/cm
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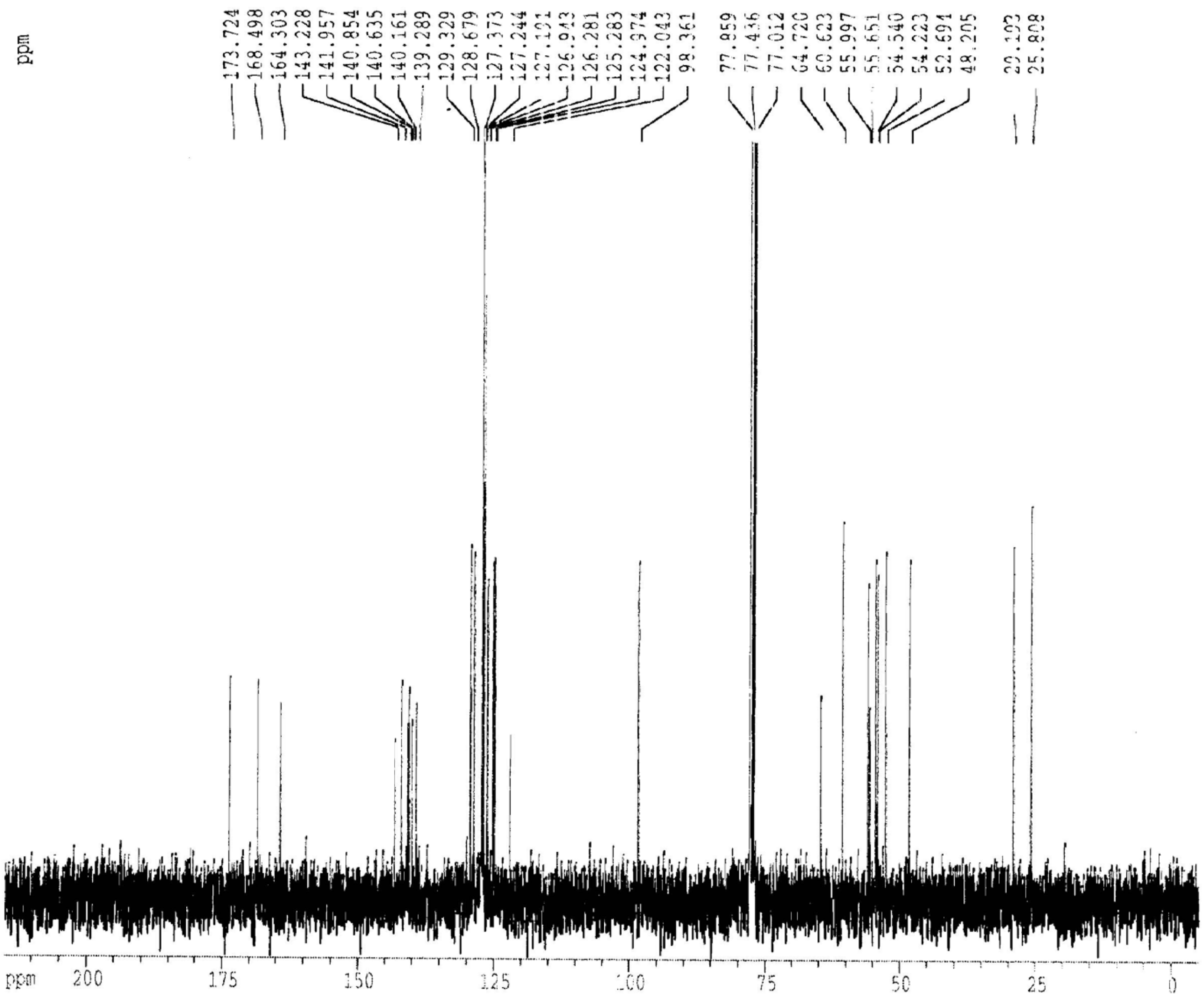
Figure S6. ^{13}C NMR spectrum of **2a**

2a



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EXPNO                   1
PROCNO                  1

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PULPROG           zgpg30
TD                 65536
SOLVENT            CDC13
NS                   256
DS                     2
SWH            23809.523 Hz
FIDRES          0.363304 Hz
AQ             1.3763061 sec
RG                  4096
DW                21.000 usec
DE                  6.00 usec
TE                 300.0 K
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d12           0.00002000 sec
PL13               25.00 dB
D1            2.00000000 sec
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PCPD2             100.00 usec
SFO2      300.2312009 MHz
NUC2                  1H
PL2                 2.00 dB
PL12               25.00 dB
P1                  8.00 usec
SFO1       75.5023983 MHz
NUC1                 13C
PL1                 3.00 dB

F2 - Processing parameters
SI                 32768
SF            75.4928640 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              215.000 ppm
F1              16230.97 Hz
F2P               -5.000 ppm
F2               -377.46 Hz
PPMCM           11.00000 ppm/cm
HZCM           830.42151 Hz/cm
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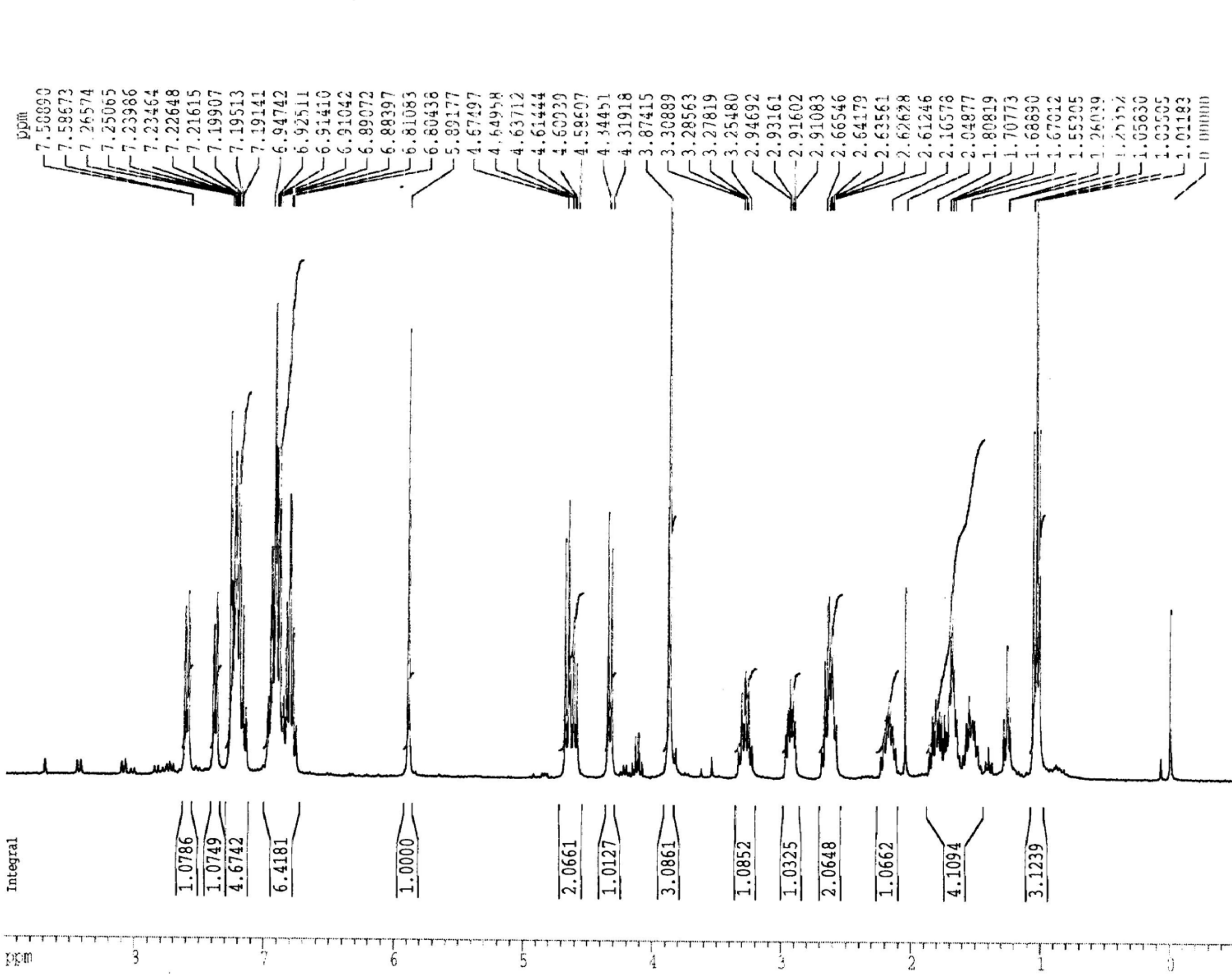
Figure S7. ^{1}H NMR spectrum of **2b**

2b



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Current Data Parameters
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EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
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Time                  11.54
INSTRUM               spect
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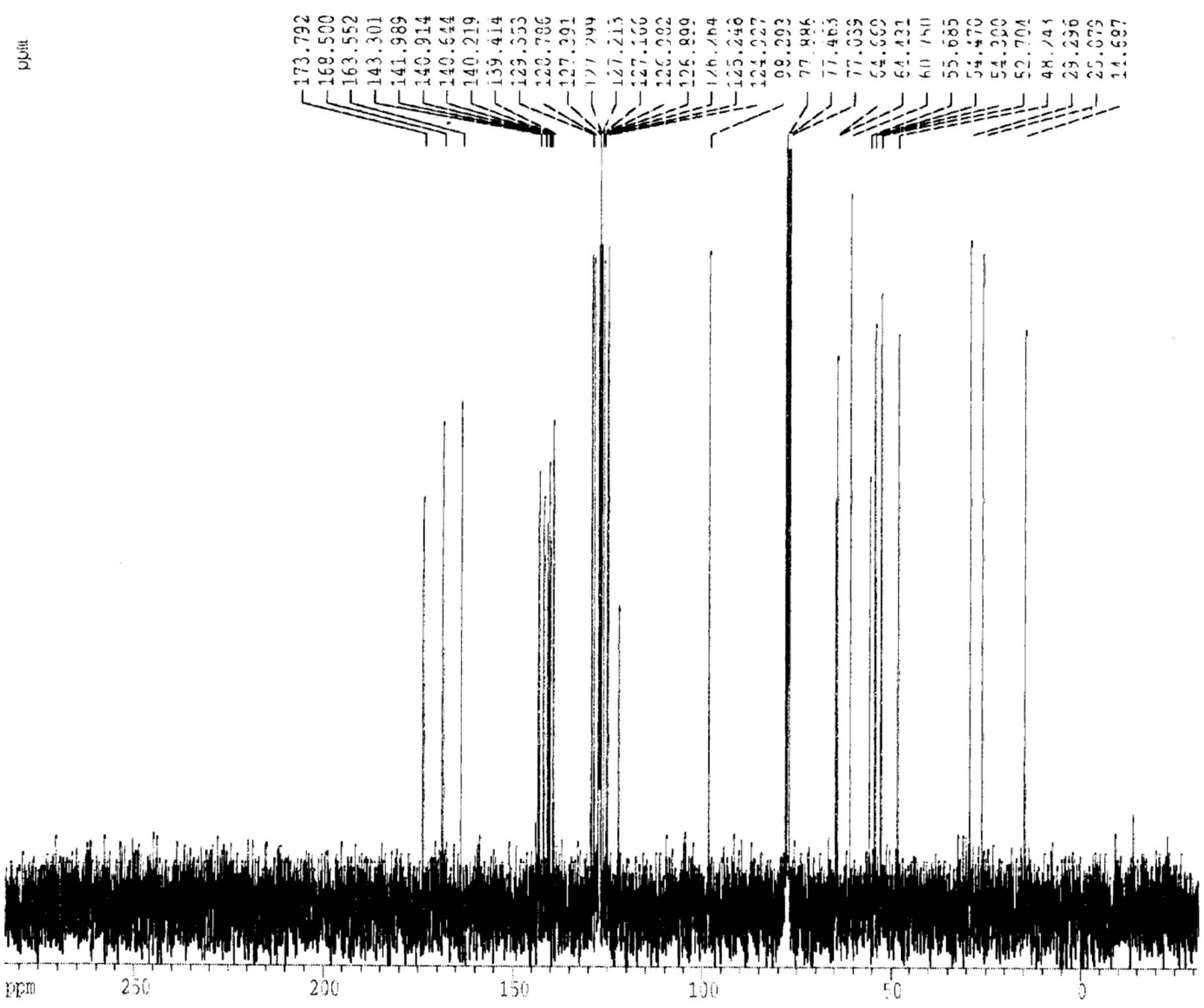
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                6172.839 Hz
FIDRES             0.188380 Hz
AQ                2.6542580 sec
RG                      256
DW                   81.000 usec
DE                     6.00 usec
TE                    300.0 K
D1               1.00000000 sec
P1                     9.00 usec
SFO1            300.2318540 MHz
NUC1                     1H
PL1                    2.00 dB

F2 - Processing parameters
SI                    16384
SF              300.2300070 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    23.00 cm
F1P                   9.000 ppm
F1                  2702.07 Hz
F2P                  -0.500 ppm
F2                  -150.12 Hz
PPMCM               0.41304 ppm/cm
HZCM              124.00805 Hz/cm
```

Figure S8. ^{13}C NMR spectrum of **2b**



2b

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Current Data Parameters
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EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060228
Time                12.10
INSTRUM             spect
PROBHD     5 mm BBO BB-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     2
SWH            23809.523 Hz
FIDRES          0.363304 Hz
AQ             1.3763061 sec
RG                  1024
DW                21.000 usec
DE                  6.00 usec
TE                 300.0 K
d11           0.03000000 sec
d12           0.00002000 sec
PL13               25.00 dB
D1            2.00000000 sec
CPDPRG2          waltz16
PCPD2             100.00 usec
SFO2        300.2312009 MHz
NUC2                  1H
PL2                 2.00 dB
PL12               25.00 dB
P1                  8.00 usec
SFO1          75.5023983 MHz
NUC1                 13C
PL1                 3.00 dB

F2 - Processing parameters
SI                 32768
SF            75.4928640 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              283.988 ppm
F1              21439.04 Hz
F2P              -31.400 ppm
F2              -2370.48 Hz
PPMCM           15.76939 ppm/cm
HZCM          1190.47620 Hz/cm
```

Crystal data for ***1a*** (recrystallized from a mixture of $CHCl_3$ and hexane); $C_{18}H_{19}NO_4$, $Mr = 313.34$, monoclinic, space group $P2_1$, $a = 11.0267(17)$ Å, $b = 6.9804(11)$ Å, $c = 11.2114(17)$ Å, $\beta = 116.392(2)°$, $V = 773.0(2)$ Å^3, $Z = 2$, $\rho = 1.346$ Mgm^{-3}; in the final least-square refinement cycles on F^2, the model converged an $R_1 = 0.0352$, $wR_2 = 0.0884$ for 4315 reflections.

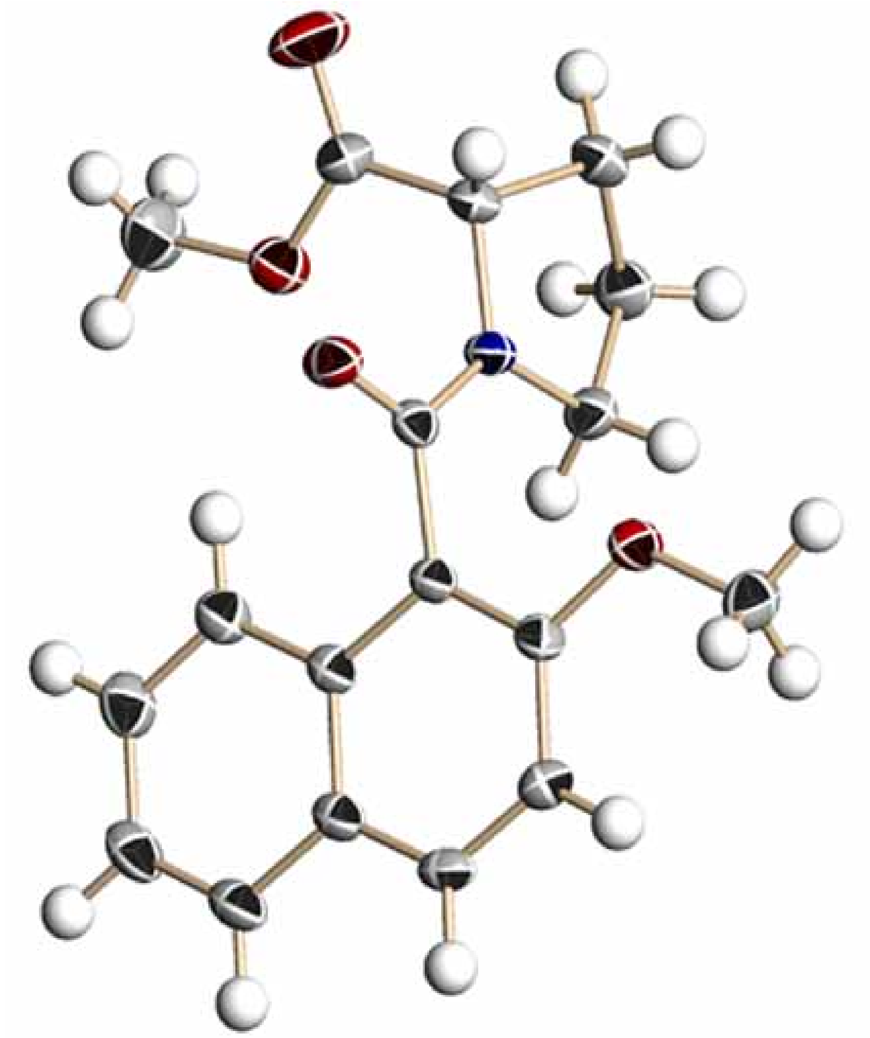

Figure S9. View of **1a** showing the atoms and thermal ellipsoids at 40% probability.

*Crystal data for **1b*** (recrystallized from a mixture of $CHCl_3$ and hexane); $C_{19}H_{21}NO_4$, *Mr* = 327.37, Monoclinic, space group $P2_1$, a = 7.6617(7) Å, b = 12.7932(12) Å, c = 9.0838(8) Å, β = 99.4840(10)°, V = 878.20(14) Å^3, Z = 2, ρ = 1.238 Mgm^{-3}; in the final least-square refinement cycles on F2, the model converged an R_1 = 0.0462, wR_2 = 0.0834 for 3567 reflections.

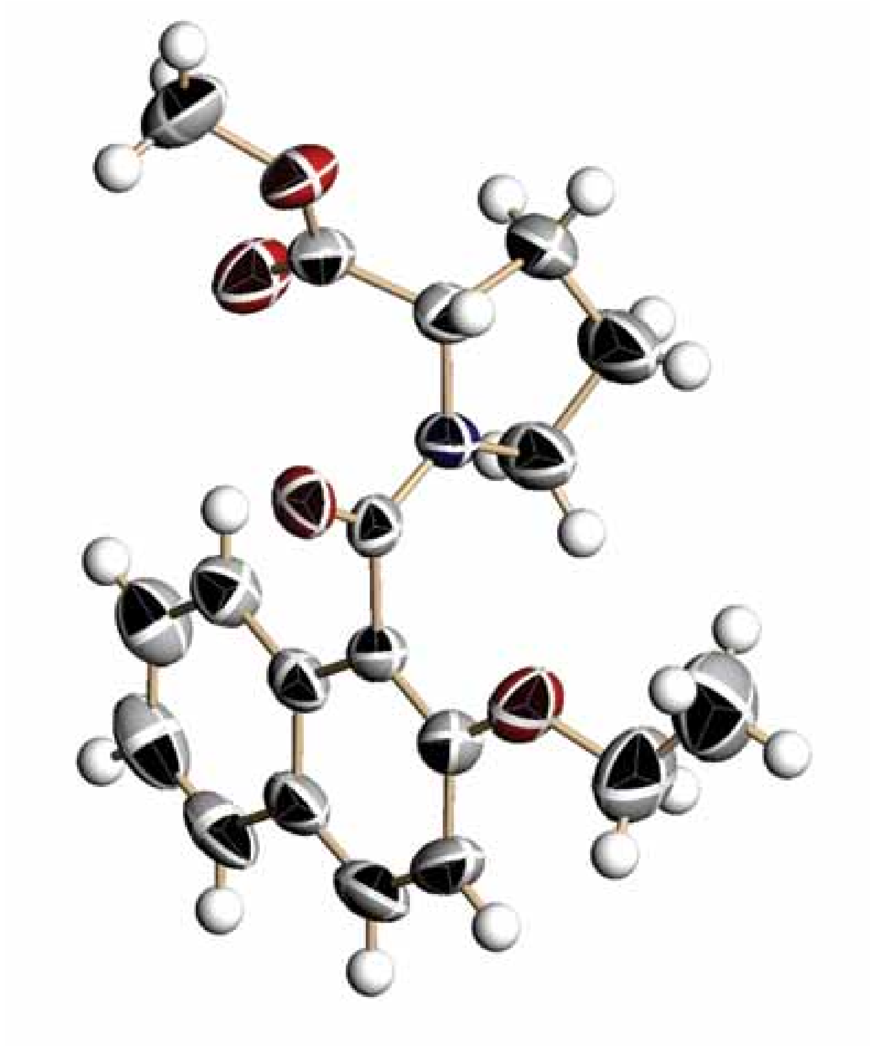

Figure S10. View of **1b** showing the atoms and thermal ellipsoids at 40% probability.

*Crystal data for **2b*** (recrystallized from a mixture of $CHCl_3$ and hexane); $C_{34}H_{30}N_2O_4$, *Mr* = 530.60, Orthorhombic, space group $P2_12_12_1$, *a* = 10.1985(5) Å, *b* = 12.5024(6) Å, *c* = 21.8216(10) Å, *V* = 2782.4(2) Å^3, *Z* = 4, ρ = 1.267 Mgm^{-3}; in the final least-square refinement cycles on F2, the model converged an R_1 = 0.0443, wR_2 = 0.1204 for 6395 reflections.

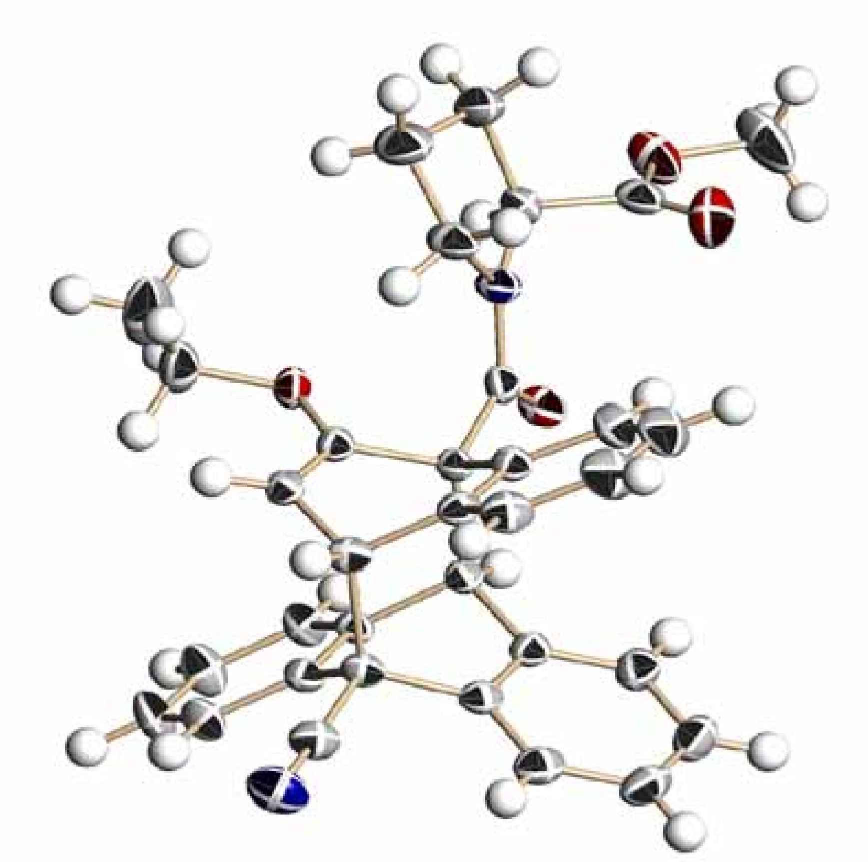

Figure S11. View of **2b** showing the atoms and thermal ellipsoids at 40% probability.