# Direct Nucleophilic Substitution Reaction of Alcohols Mediated by a Zinc-based Ionic Liquid

Anlian Zhu, Lingjun Li, Jianji Wang*, Kelei Zhuo

School of Chemical and Environmental Sciences, Key Laboratory of Green Chemical
Media and Reactions, Ministry of Education, Henan Normal University,
Xinxiang, Henan 453007, P. R. China.
E-mail: Jwang@henannu.edu.cn

Contents

## 1. Materials and General Methods

2-Chloroethanlol and chlorobutane were purchased from alfa aesar and distilled before use. Zinc chloride, $CH_2Cl_2$, dioxane, 4-nitroaniline, benzoyl amide, 2,4-dinitrophenylhydrazine, tetrabutylammonium chloride, tetramethylammonium chloride were purchased from Beijing chemical Factory. 1-Methylimidazole, p-toluenesulfonamide, and alcohols were purchased from alfa aesar. The dicarbonate compounds were purchased from acrose organics. All of these reagents are AR grade and used without further purification. 1-Butyl-3-methylimidazolium chloride and 1-(2-hydroxy-ethyl)-3-methylimidazolium chloride were synthesized according to the procedures described in literatures.[1,2]

$^1H$ NMR data were recorded with Avance 400/DPX (Bruker) spectrometer from $CDCl_3$ solutions using the residual solvent signal as reference. Chemical shifts are reported in parts per million. All the values of chemical shift and coupling constants are quoted in ppm and Hz, respectively. Mass spectra were obtained on either VG-ZAB-HS or Bruker APEX. High-resolution MS were performed with Bruker BIFLEX III. Infrared spectra were recorded on a Bruker Vector 22 spectrometer in KBr with absorption in $cm^{-1}$. Elemental analyses were performed on Varian ELIII analyzer. The UV–vis spectroscopy was recorded using a TU-1021 UV–vis spectrometer (Beijing Instrument Company), and the wavelength accuracy is ±1.0 nm.

## 2. Preparation procedure of the $ZnCl_2$-based ionic liquids

The ILs were prepared according to the procedures reported in literature.[3] The quaternary ammonium salt was mixed with zinc chloride with a molar ratio of 1:2 and then heated to 150 $^oC$ in air with stirring until a clear homogeneous colorless liquid was obtained.

## 3. Characterization of compounds 3a-k

***N*-(4-nitrophenyl)-1,1'-diphenyl)-methyamine** (**3a**). The physical data shown below were comparable to those reported in literature.[4] Yellow solid, m.p. 194-195°C, reported m.p. 195°C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.07-8.03 (m, 2H), 7.40-7.31 (m, 10H), 6.54-6.51 (m, 2H), 5.66 (d, $J$ = 4 Hz, 1H), 5.02 (br, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$: 152.7, 141.3, 139.1, 129.7, 128.5, 127.7, 127.0, 112.7, 63.1.

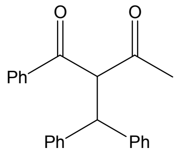
***N*-benzhydrylbenzamide (3b)**. The physical data shown below were comparable to those reported in literature. [5] White solid, m.p. 169-170 °C, reported m.p. 170°C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.85-7.44 (m, 5H), 7.39-7.29 (m, 10H), 6.72 (d, $J$ = 7.6 Hz, 1H), 6.48 (d, $J$ = 7.6 Hz, 1H), $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$: 166.5, 140.7, 133.2, 130.8, 128.1, 127.9, 127.7, 127.0, 126.6, 56.4.

***N*-benzhydryl-*p*-toluenesulfonamide (3c)**. The physical data shown below were comparable to those reported in literature. [4] White solid, m.p. 157-158 °C, reported m.p.157°C; $^1$H NMR (400 MHz, CDCl3) $\delta$: 7.56 (d, $J$ = 8.2 Hz, 2H), 7.21-7.07 (m, 12H), 5.61 (d, $J$ = 7.2 Hz, 1H), 5.21 (d, $J$ = 7.2 Hz, 1H), 2.5 (s, 3H); $^{13}$C NMR (100 MHz, CDCl3) $\delta$: 143.2, 142.6, 140.3, 132.5, 131.2, 130.5, 130.3, 130.1, 60.2, 23.1.

**N-Benzhydryl-N'-(2,4-dinitro-phenyl)-hydrazine (3d).** The physical data shown below were comparable to those reported in literature. [4] White solid, m.p. 165-166 °C, reported m.p. 165°C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 9.28 (s, 1H), 9.04 (d, $J$ = 2

Hz, 1H), 8.29 (dd, $J_1$ = 9 Hz, $J_2$ = 1 Hz), 7.95 (d, $J$ = 9 Hz, 1H), 7.45-7.31 (m, 10 H), 5.22 (d, $J$ = 5.2 Hz, 1H), 4.48 (d, $J$ = 6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 153.1, 140.5, 138.9, 134.5, 132.1, 130.1, 129.3, 128.8, 126.7, 120.8, 65.9.

**2-Benzhydryl-1-phenyl-butane-1,3-dione (3e).**



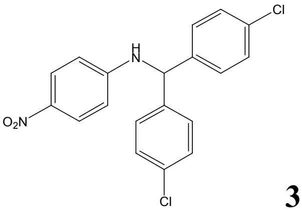
**3e**

White solid, m.p. 157-158 °C, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.97 (d, $J$ = 8 Hz, 2 H), 7.78-7.04 (m, 13 H), 5.63 (d, $J$ = 12 Hz, 1H), 5.12 (d, $J$ = 12 Hz, 1H), 2.06 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 202.1, 193.3, 140.8, 140.3, 136.0, 132.7, 128.0, 127.8, 127.7, 127.2, 126.8, 126.2, 125.8, 68.0, 50.5, 26.9. IR (KBr) $\nu$: 3436, 3060, 1715, 1675, 1589, 1442, 1266, 1242, 1201, 1144, 968, 772, 739, 690, 539. Element analysis ($C_{23}H_{20}O_2$): calculated C, 84.12; H, 6.14; Found C, 84.51; H, 6.17. HRMS (ESI): calculated 351.1361 for $C_{23}H_{20}O_2Na^+$, found 351.1359 (M+Na$^+$)

**3-Benzhydryl-pentane-2,4-dione (3f).** The physical data shown below were comparable to those reported in literature.[6] White solid, m.p. 113-114 °C, reported m.p.112-114°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.47-7.06 (m, 10 H), 4.82 (d, $J$ = 12 Hz, 1H), 7.74 (d, $J$ = 12 Hz, 1H), 2.01 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 202.9, 141.2, 128.9, 127.7, 127.0, 74.5, 51.2, 29.7.

**2-Benzhydryl-3-oxo-butyric acid ethyl ester (3g).** The physical data shown below were comparable to those reported in literature.[7] White solid, m.p. 85-87°C, reported m.p. 84-86°C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.28-7.15 (m, 10 H), 4.77 (d, $J$ = 12 Hz, 1 H ), 4.55 (d, $J$ = 12 Hz, 1 H), 3.99 (q, $J$ = 7 Hz, 2 H), 2. 11 (s, 3 H), 1.01 (t, J = 7 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 201.7, 167.6, 141.5, 141.2, 128.8, 128.6, 127.8, 127.7, 126.9, 126.8, 65.2, 61.5, 50.9, 30.0, 13.7.

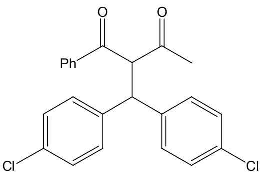
**[Bis-(4-chloro-phenyl)-methyl]-(4-nitro-phenyl)-amine (3h).**



**3h**

Yellow solid, m.p. 193-195 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.06 (m, 2H), 7.73-7.24 (m, 8H), 6.51 (d, $J$ = 8.8 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 150.6, 138.1, 133.2, 128.5, 127.8, 125.3, 111.4, 60.3. IR (KBr) ν: 3399, 1712, 1601, 1515, 1470, 1307, 1185, 1111, 1086, 1009, 825, 792, 747, 698, 530. Element analysis ($C_{19}H_{14}Cl_2N_2O_2$): calculated C, 61.14; H, 3.78; N, 7.51; found C, 61.05; H, 3.72; N, 7.49. HRMS (ESI): calculated 395.0330 for $C_{19}H_{14}Cl_2N_2O_2Na^+$, found 395.0318 (M+$Na^+$).

**2-[Bis-(4-chloro-phenyl)-methyl]-1-phenyl-butane-1,3-dione (3i).**

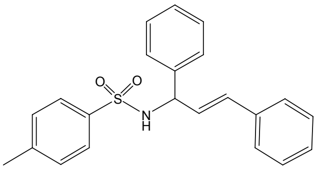


**3i**

White solid, m.p. 167-168 °C, $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.97 - 7.13 (m, 13 H), 5.53 (d, *J* = 12 Hz, 1H), 5.09 (d, *J* = 12 Hz, 1H), 2.06 (s, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) *δ*: 201.2, 192.7, 138.9, 138.3, 135.6, 133.1, 132.3, 131.8, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 67.7, 49.1, 27.0. IR (KBr) ν: 3432, 3060, 3023, 1716, 1670, 1593, 1495, 1446, 1352, 1262, 1246, 1205, 1148, 972, 768, 747, 702, 694, 547. Element analysis ($C_{23}H_{18}Cl_2O_2$): calculated C, 69.53; H, 4.57; found C, 69.42; H, 4.53. HRMS (ESI): calculated 419.0582 for $C_{23}H_{18}Cl_2O_2$ $Na^+$, found 419.0596 ($M+Na^+$).

**1-Phenyl-2-(1-phenyl-ethyl)-butane-1,3-dione (3j).** The physical data shown below were comparable to those reported in literature. [7] Oil, $^1$H NMR (400 MHz, $CDCl_3$) *δ*: 8.11-7.06 (m, 10 H), 4.92 (d, *J* = 11 Hz, 1H), 4.32 (d, *J* = 11 Hz, 1H), 3.91-3.83 (m, 2 H), 2.25 (s, 3 H), 1.92 (s, 3 H), 1.32 (d, *J* = 7 Hz, 3 H), 1.22 (d, *J* = 7 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) *δ*: 203.7, 203.2, 195.2, 143.4, 143.1, 137.2, 137.0, 133.8, 133.4, 128.9, 128.8, 128.6, 128.4, 127.5, 127.3, 127.0, 126.6, 71.5, 70.8, 40.9, 40.3, 27.9, 27.5, 21.6, 20.3. ESI-MS (m/z): 267.1 $(M+H)^+$.

**N-(1,3-Diphenyl-allyl)-4-methyl-benzenesulfonamide (3k).**



**3k**

White solid, m.p. 136-137 °C, $^1$H NMR (400 MHz, $CDCl_3$) *δ*: 7.70-7.68 (m, 2 H), 7.31-7.09 (m, 16 H (including the H of chloroform)), 6.41-6.37 (d, *J* = 16 Hz), 6.14-6.08 (dd, $J_1$ = 16 Hz, $J_2$ = 6.8 Hz), 5.16-5.13 (m, 1 H), 4.84-4.82 (d, *J* = 7.2 Hz), 2.37 (s, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$) *δ*: 137.6, 134.0, 132.0, 130.4, 126.5, 123.8, 123.1, 122.8, 122.5, 122.2, 122.2, 121.7, 121.4, 120.9, 54.1, 15.8. IR (KBr) ν: 3293, 3023, 1716, 1597, 1491, 1446, 1323, 1160, 1148, 1091, 1017, 968, 919, 817, 690, 666, 568, 543. Element analysis ($C_{22}H_{21}NO_2S$): calculated C, 72.70; H, 5.82; N, 3.85; found C, 72.58; H, 5.81; N, 3.79. HRMS (ESI): calculated 386.1191 for $C_{22}H_{21}NO_2S$ $Na^+$, found 386.1186 ($M+Na^+$)

## References

[1] A. Noda, M. Watanabe, Electrochim. Acta, 2000, **45**, 1265.

[2] J. F. Dubreuil, M. H. Famelart and J. P. Bazureau, Org. Proc. Res. Dev., 2002, **6**, 374.

[3] A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed, V. Tambyrajah, *Chem. Commun.*, 2001, 2010.

[4] V. Terrasson, S. Marque, M. Georgy, J. M. Campagne, D. Prim, *Adv. Synth. Catal.*, 2006, **348**, 2063.

[5] T. Maki, K. Ishihara, H. Yamamoto, *Org. Lett.*, 2006, **8**, 1431.

[6] K. Motokura, N. Nakagiri, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Org. Chem.*, 2007, **72**, 6006.

[7] R. Sanz, D. Miguel, A. Martı´nez, J. M. Álvarez-Gutiérrez, F. Rodríguez. *Org. Lett.*, 2007, **9**, 2027.

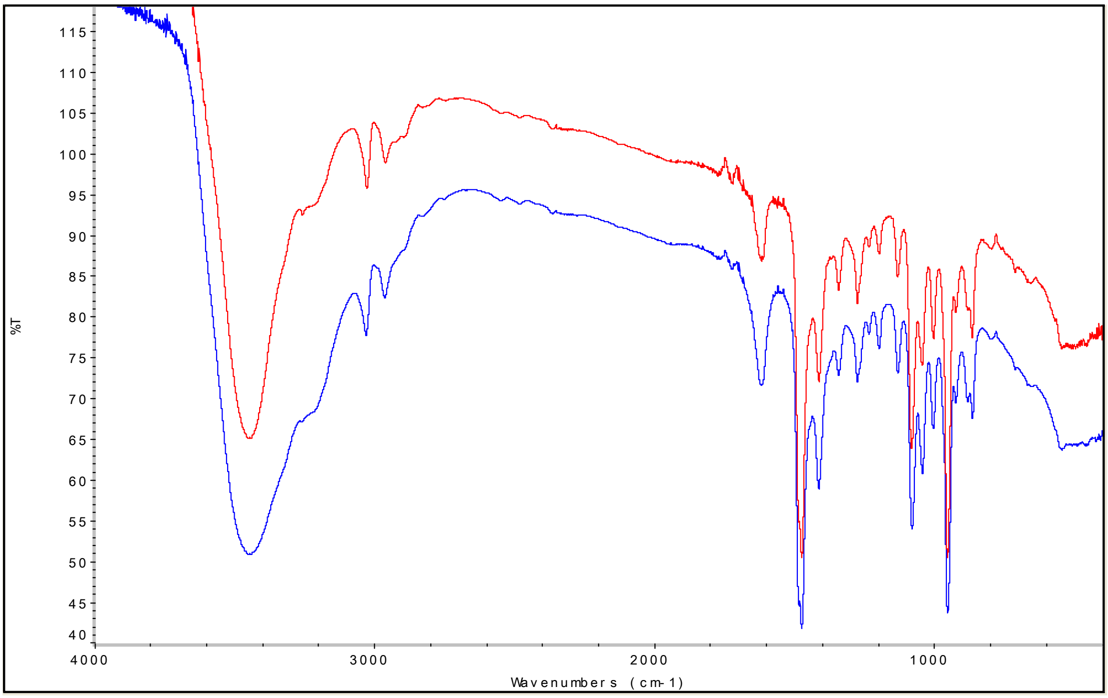
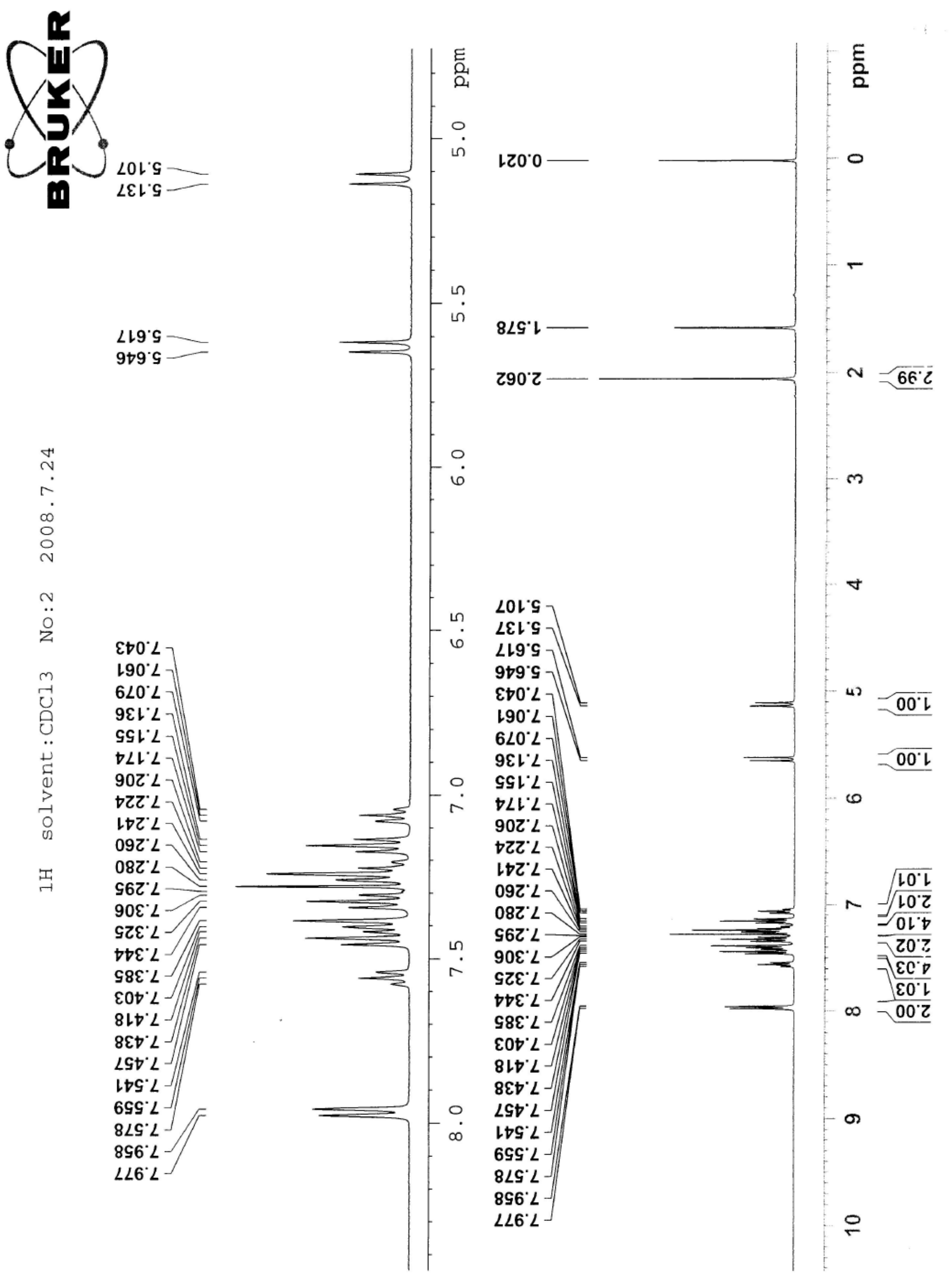
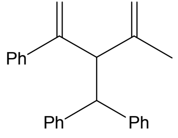
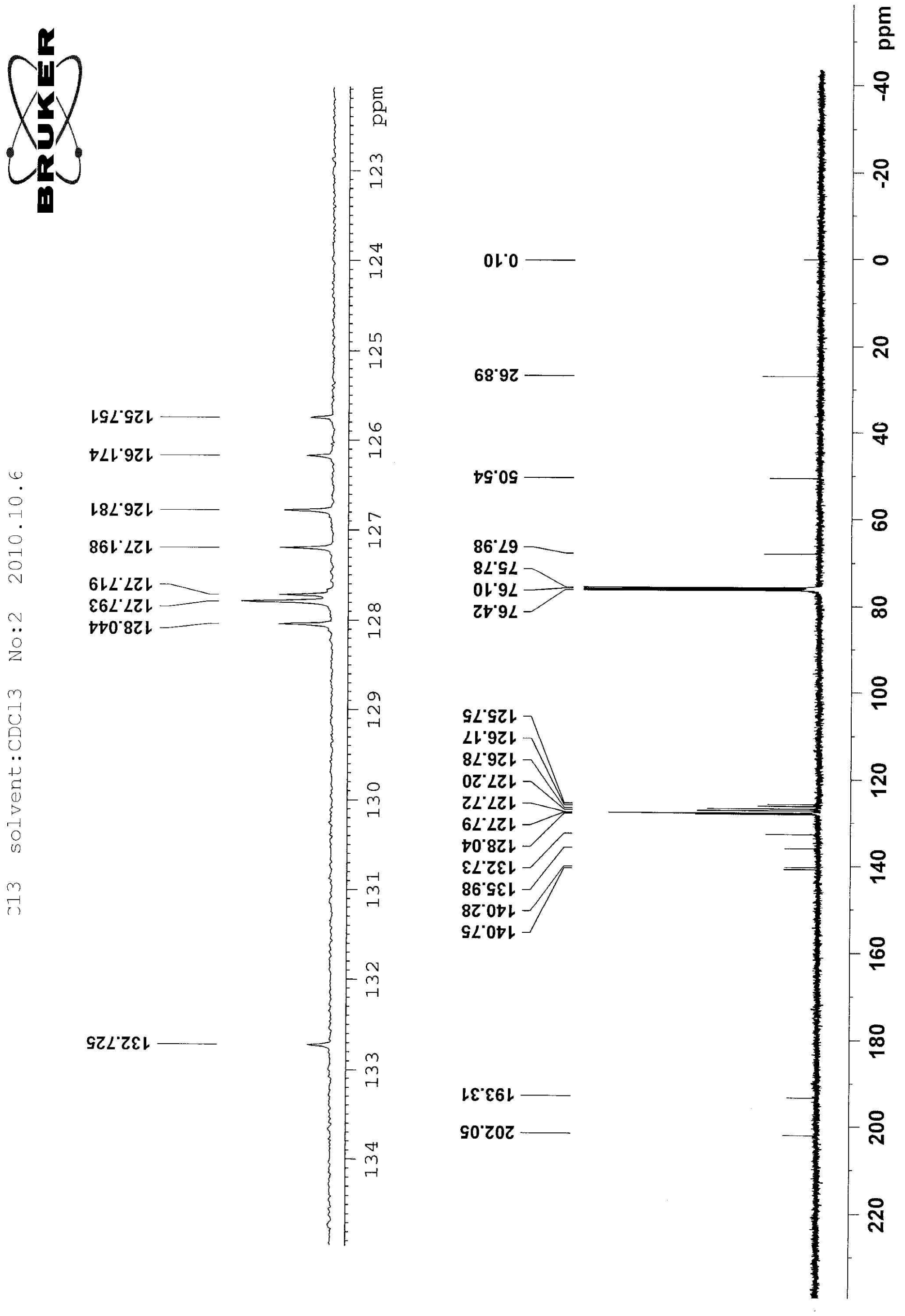
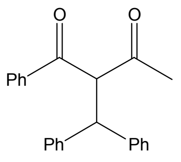


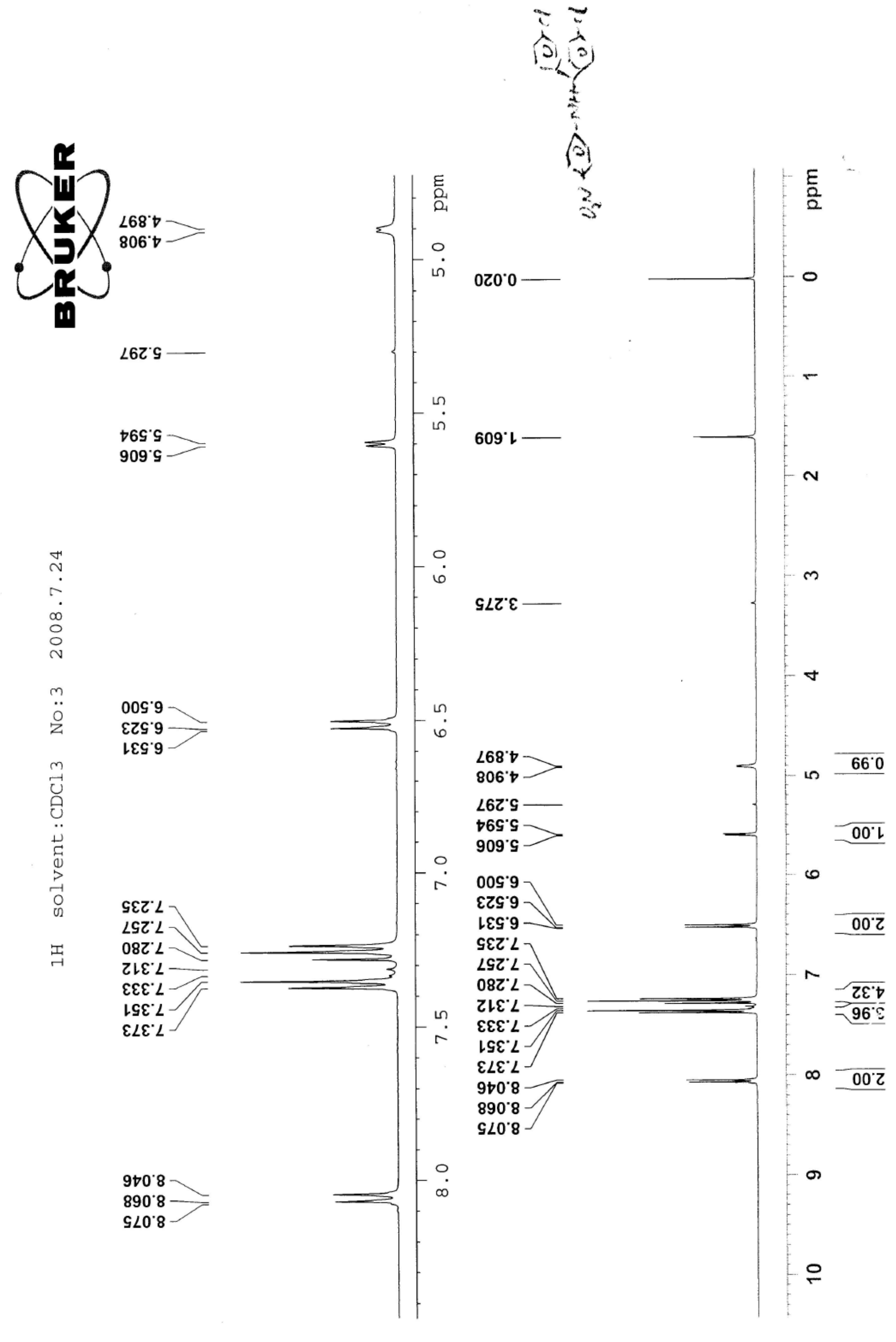
Fig. IR spectrum for the fresh and recovered ILs: bule, the fresh [CHCl][$ZnCl_2$]$_2$; red, the fifth recovered [CHCl][$ZnCl_2$]$_2$.

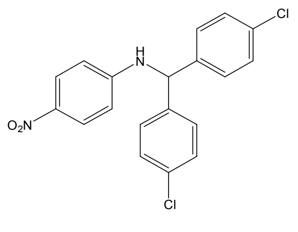

1H solvent:CDCl3 No:2 2008.7.24
5.107
5.137
5.617
5.646
7.043
7.061
7.079
7.136
7.155
7.174
7.206
7.224
7.241
7.260
7.280
7.295
7.306
7.325
7.344
7.385
7.403
7.418
7.438
7.457
7.541
7.559
7.578
7.958
7.977
0.021
1.578
2.062
2.99
1.00
1.00
1.01
2.01
4.10
2.02
4.03
1.03
2.00
ppm
5.0
5.5
6.0
6.5
7.0
7.5
8.0
0
1
2
3
4
5
6
7
8
9
10

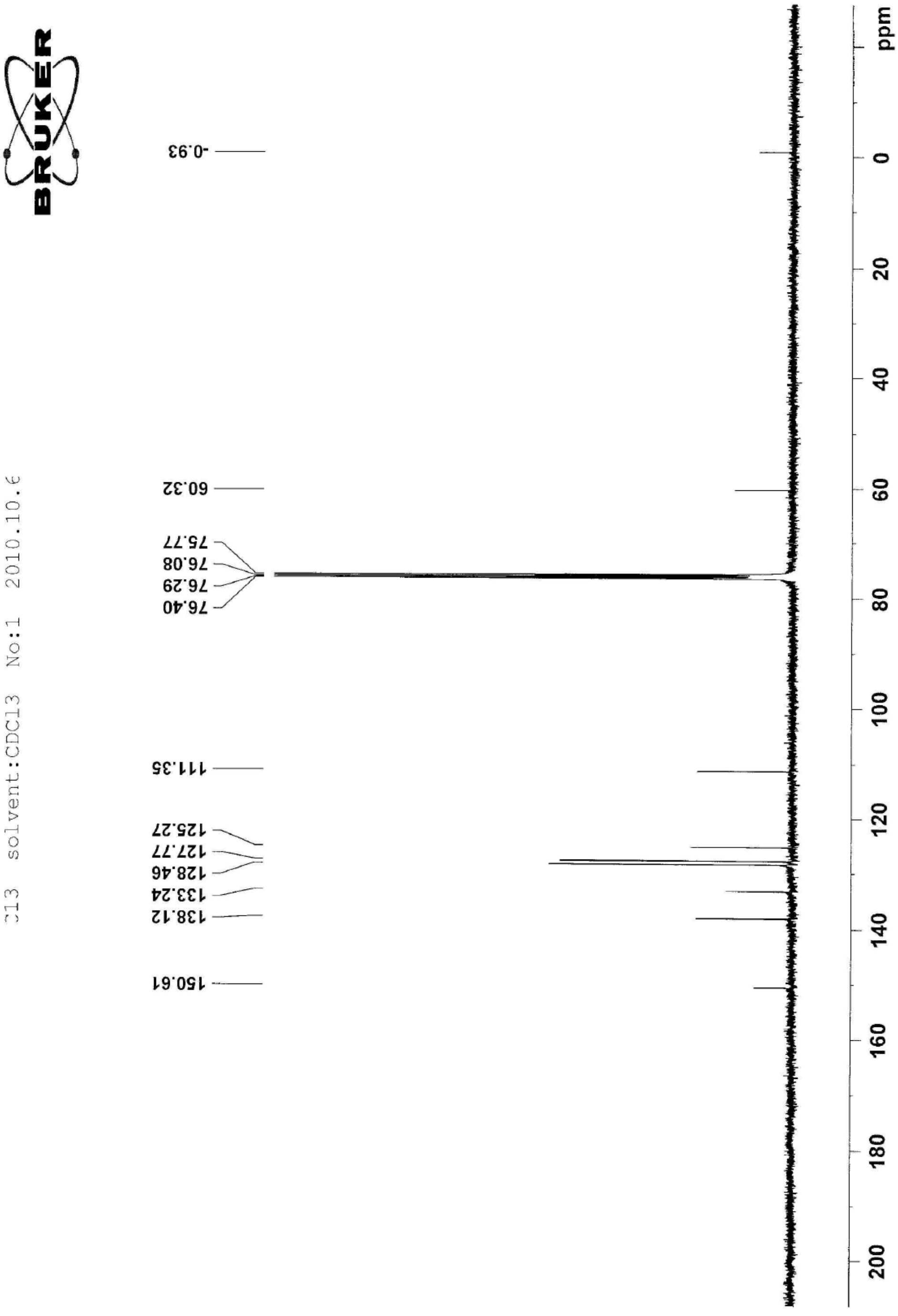

O
O
Ph
Ph
Ph

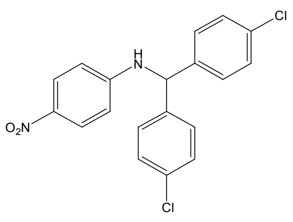

C13 solvent:CDCl3 No:2 2010.10.6
125.751
126.174
126.781
127.198
127.719
127.793
128.044
132.725
123 124 125 126 127 128 129 130 131 132 133 134 ppm
0.10
26.89
50.54
67.98
75.78
76.10
76.42
125.75
126.17
126.78
127.20
127.72
127.79
128.04
132.73
135.98
140.28
140.75
193.31
202.05
-40 -20 0 20 40 60 80 100 120 140 160 180 200 220 ppm

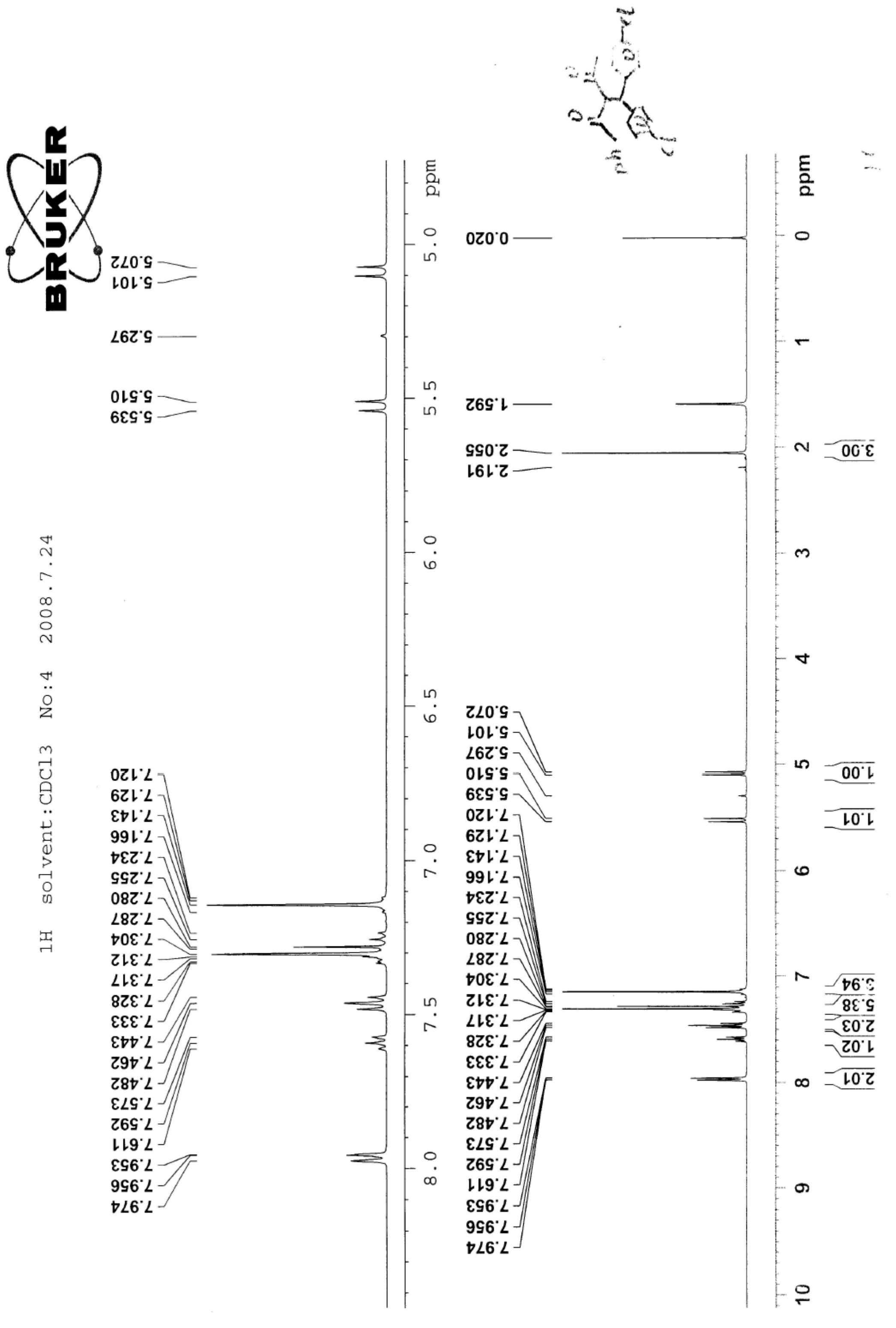

O
O
Ph
Ph
Ph

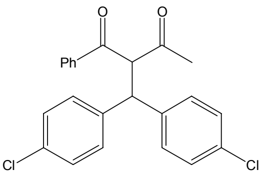

1H solvent:CDCl3 No:3 2008.7.24
BRUKER
4.897
4.908
5.297
5.594
5.606
6.500
6.523
6.531
7.235
7.257
7.280
7.312
7.333
7.351
7.373
8.046
8.068
8.075
5.0
5.5
6.0
6.5
7.0
7.5
8.0
ppm
0.020
1.609
3.275
0.99
1.00
2.00
4.32
3.96
2.00
0
1
2
3
4
5
6
7
8
9
10
ppm

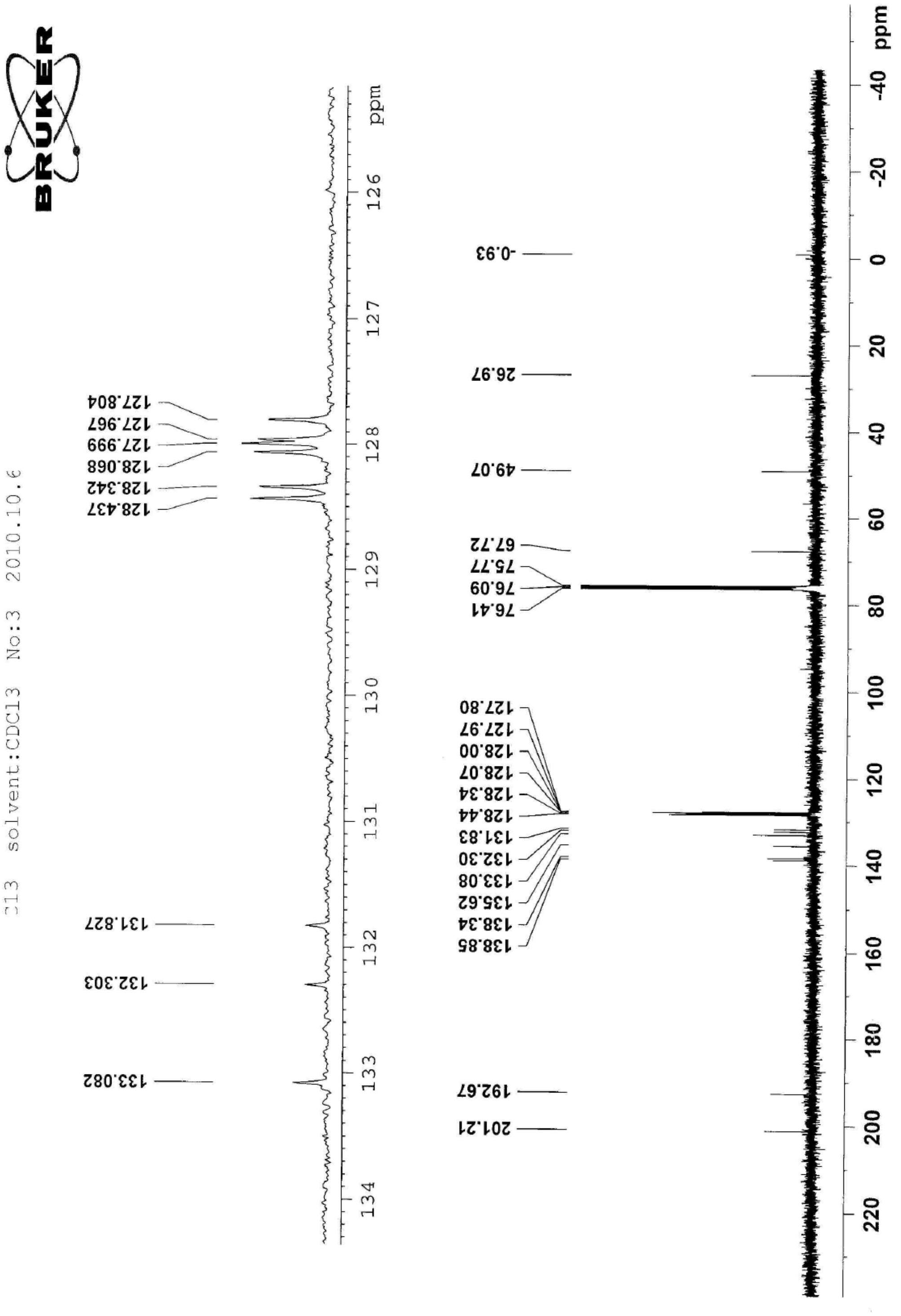

H
N
O2N
Cl
Cl

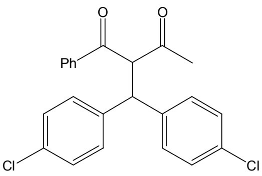

C13 solvent:CDCl3 No:1 2010.10.6
-0.93
60.32
75.77
76.08
76.29
76.40
111.35
125.27
127.77
128.46
133.24
138.12
150.61
ppm
0
20
40
60
80
100
120
140
160
180
200

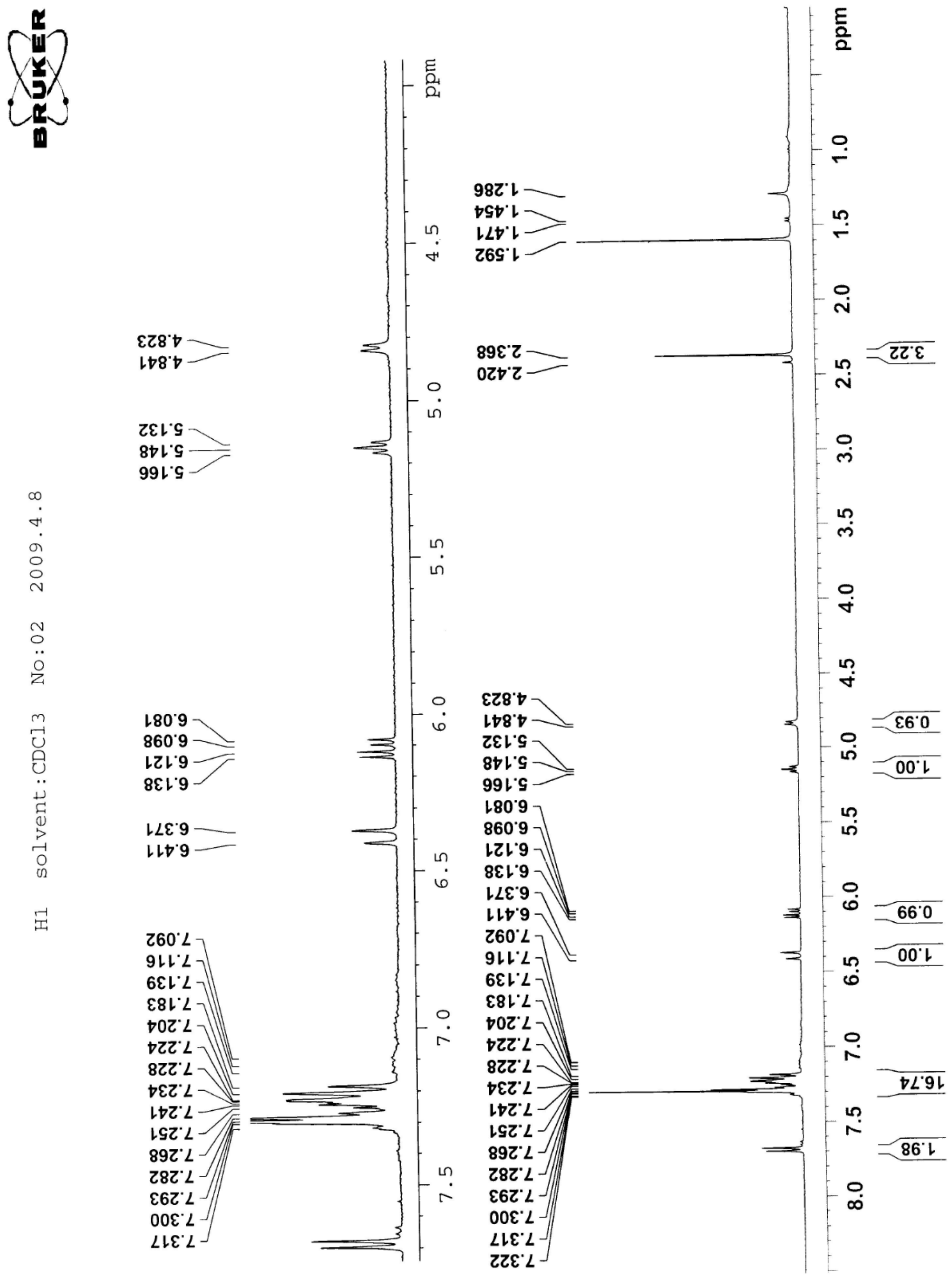

H
N
Cl
Cl
O2N

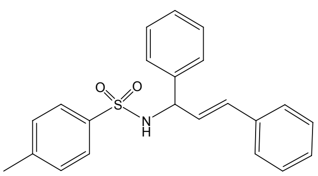

1H solvent:CDCl3 No:4 2008.7.24
5.072
5.101
5.297
5.510
5.539
7.120
7.129
7.143
7.166
7.234
7.255
7.280
7.287
7.304
7.312
7.317
7.328
7.333
7.443
7.462
7.482
7.573
7.592
7.611
7.953
7.956
7.974
0.020
1.592
2.055
2.191
ppm
5.0
5.5
6.0
6.5
7.0
7.5
8.0
0
1
2
3
4
5
6
7
8
9
10
3.00
1.00
1.01
3.94
5.38
2.03
1.02
2.01

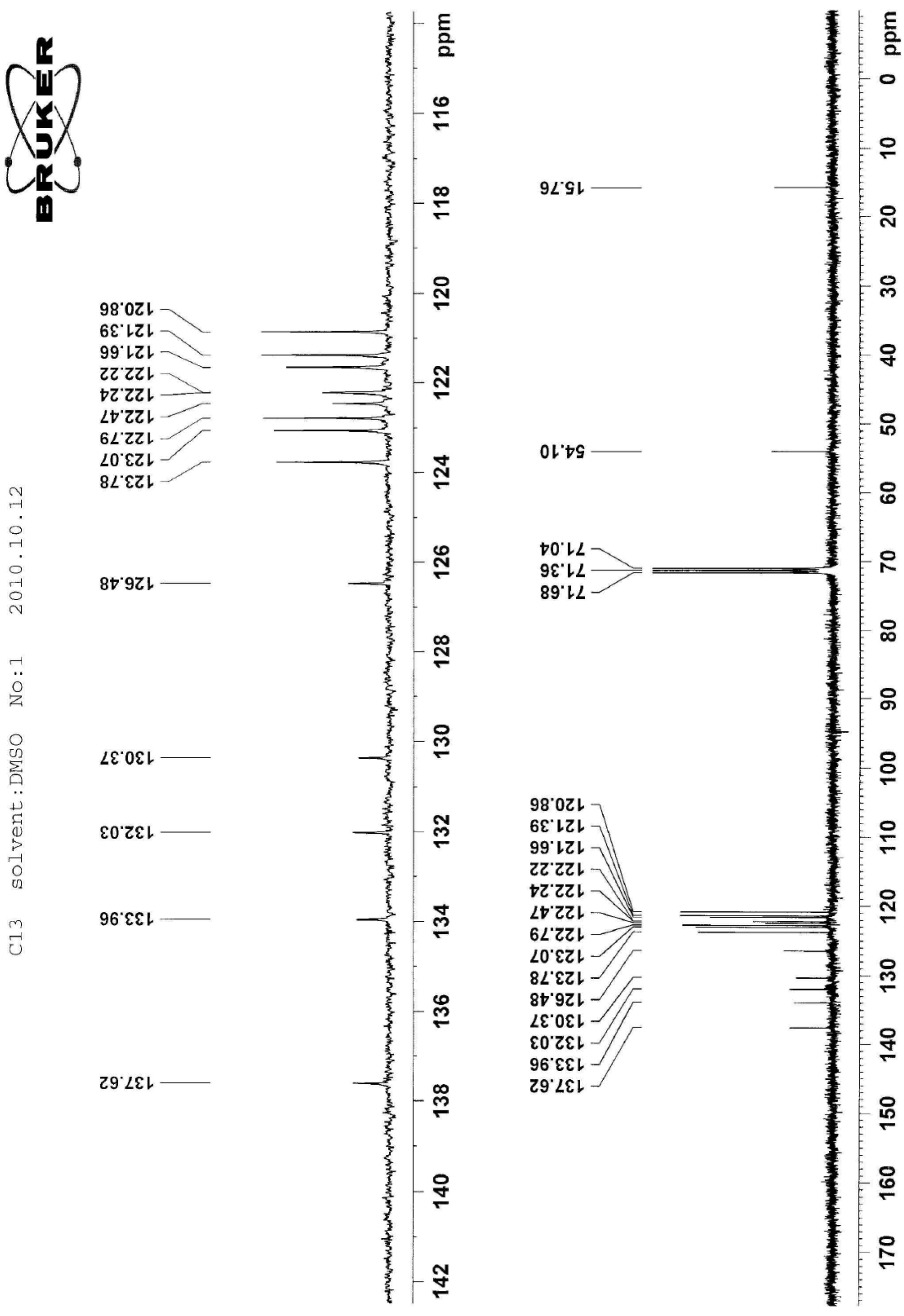

O
O
Ph
Cl
Cl

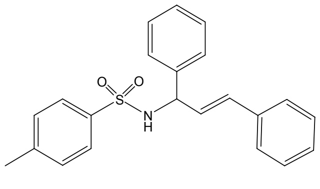

C13 solvent:CDCl3 No:3 2010.10.6
127.804
127.967
127.999
128.068
128.342
128.437
131.827
132.303
133.082
126
127
128
129
130
131
132
133
134
ppm
-0.93
26.97
49.07
67.72
75.77
76.09
76.41
127.80
127.97
128.00
128.07
128.34
128.44
131.83
132.30
133.08
135.62
138.34
138.85
192.67
201.21
-40
-20
0
20
40
60
80
100
120
140
160
180
200
220
ppm


O
O
Ph
Cl
Cl


H1 solvent:CDCl3 No:02 2009.4.8
ppm
7.317
7.300
7.293
7.282
7.268
7.251
7.241
7.234
7.228
7.224
7.204
7.183
7.139
7.116
7.092
6.411
6.371
6.138
6.121
6.098
6.081
5.166
5.148
5.132
4.841
4.823
7.322
1.286
1.454
1.471
1.592
2.368
2.420
3.22
0.93
1.00
0.99
1.00
16.74
1.98
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0


O
O
S
N
H


C13 solvent:DMSO No:1 2010.10.12
120.86
121.39
121.66
122.22
122.24
122.47
122.79
123.07
123.78
126.48
130.37
132.03
133.96
137.62
15.76
54.10
71.04
71.36
71.68
ppm
116
118
120
122
124
126
128
130
132
134
136
138
140
142
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170


O
O
S
N
H