

# **Supporting Information**

## **The First Catalytic And Green Synthesis of Aryl-(Z)-Vinyl Chlorides and Its Plausible Addition-Elimination Mechanism**

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## I. General

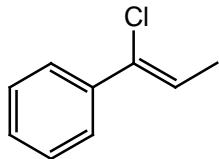
Starting materials and solvents were purchased from common commercial sources or prepared via common method without further purification.  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR and NOE spectra were recorded at VARIAN-400 using TMS as internal standard. IR spectra were recorded on AVATAR-370. GC analysis was performed on a GC-7890II instrument. Mass spectroscopy data of the products were collected on a MS-EI instrument (FINNIGAN Trace DSQ). Elemental Analysis was determined on a Carlo-Erba 1106 instrument. All reactions were monitored by TLC with GF254 silica gel coated plates.

## II. Experimental Section

**General procedure:** To a solution of ketones (5 mmol) and benzoyl chloride (0.25 mmol, 0.035 g) in ethyl acetate (2 mL),  $\text{Sc}(\text{OTf})_3$  (0.1 mmol, 0.049 g) was added successfully. The solution was heated to reflux. 10 min., and DMF (0.05 mmol) was added successively. Then BTC (2 mmol, 0.594 g in 5 mL of ethyl acetate) was added dropwise very carefully over 8 h at reflux. After completion (monitored by TLC) the mixture was treated with ammonia and extracted with ether. After dryness and condensation, the products vinyl chlorides were obtained by preparative TLC (petroleum ether/ethyl acetate).

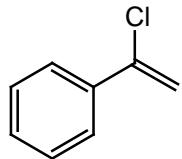
### III. Characterization of the products

**(Z)-(1-chloroprop-1-enyl)benzene (2a)**<sup>[1]</sup>.



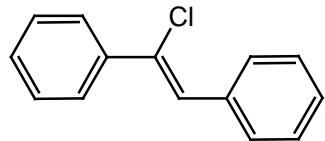
Prepared and purified according to the general procedure above to provide the clear oil (**2a**) in 77% yield. TLC: petroleum-ether:ethyl acetate (10:1)  $R_f$  0.65; IR ( $\text{cm}^{-1}$ ): 3089, 3016, 2986, 1617, 1538, 1436, 876, 796, 689.  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ ): 7.52-7.55 (2H, m), 7.26-7.32 (3H, m), 6.16 (1H, q,  $J=7.2\text{Hz}$ ), 1.92 (3H, d,  $J=7.2\text{Hz}$ ). MS (EI, m/z, %): 154 ( $M^++2$ , 32), 152 ( $M^+$ , 100).

**$\alpha$ -chlorostyrene (2b)**<sup>[2]</sup>.



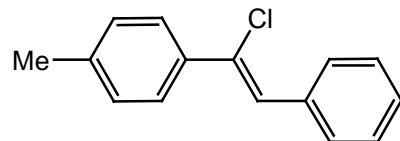
Prepared and purified according to the general procedure above to provide the clear oil (**2b**) in 31% yield. TLC: petroleum-ether:ethyl acetate (10:1)  $R_f$  0.69; IR ( $\text{cm}^{-1}$ ): 3080, 3026, 1611, 1532, 1456, 860, 776, 680.  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ ): 7.60-7.62 (2H, m), 7.31-7.34 (3H, m), 5.72 (1H, d,  $J=1.6\text{Hz}$ ), 5.49 (1H, d,  $J=1.6\text{Hz}$ ). MS (EI, m/z, %): 140 ( $M^++2$ , 34), 138 ( $M^+$ , 100).

**(Z)-(1-chloroethene-1,2-diyl)dibenzene (2c)**<sup>[3]</sup>.



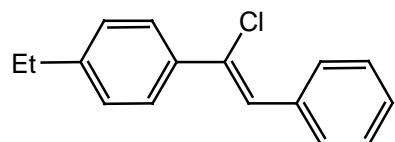
Prepared and purified according to the general procedure above to provide the white solid (**2c**) in 83% yield. TLC: petroleum-ether:ethyl acetate (8:1)  $R_f$  0.66; Mp 52.1-52.5°C, IR (cm<sup>-1</sup>): 3052, 3028, 1621, 1488, 1445, 930, 850, 756, 691. <sup>1</sup>HNMR (400MHz, CDCl<sub>3</sub>): 7.67-7.74 (4H, m), 7.30-7.40 (6H, m), 7.04 (1H, s). <sup>13</sup>CNMR (100MHz, CDCl<sub>3</sub>): 139.2, 135.2, 132.0, 129.4, 128.7, 128.4, 128.2, 128.0, 126.7, 126.1. MS (EI, m/z, %): 216 (M<sup>+</sup>+2, 31), 214 (M<sup>+</sup>, 100), 179 (54), 152 (8), 139 (2), 126 (1), 113 (1).

**(Z)-1-(1-chloro-2-phenylvinyl)-4-methylbenzene (2d)**<sup>[3]</sup>.



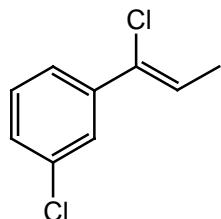
Prepared and purified according to the general procedure above to provide the clear oil (**2d**) in 79% yield. TLC: petroleum-ether:ethyl acetate (8:1)  $R_f$  0.65; IR (cm<sup>-1</sup>): 3048, 3022, 2978, 1629, 1481, 1449, 916, 860, 774, 698. <sup>1</sup>HNMR (400MHz, CDCl<sub>3</sub>): 7.71 (2H, d, J=8.0Hz), 7.57 (2H, d, J=8.0Hz), 7.35-7.39 (2H, m), 7.27-7.29 (1H, m), 7.16-7.18 (2H, m), 7.0 (1H, s), 2.36 (3H, s). <sup>13</sup>CNMR (100MHz, CDCl<sub>3</sub>): 138.8, 136.4, 135.4, 132.2, 129.4, 129.1, 128.2, 127.8, 126.6, 125.2, 21.1. MS (EI, m/z, %): 230 (M<sup>+</sup>+2, 39), 228 (M<sup>+</sup>, 100), 213 (9), 193 (24), 178 (8), 165 (4), 152 (1), 139 (3).

**(Z)-1-(1-chloro-2-phenylvinyl)-4-ethylbenzene (2e).**



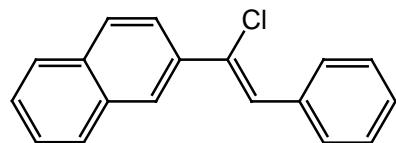
Prepared and purified according to the general procedure above to provide the clear oil (**2e**) in 81% yield. TLC: petroleum-ether:ethyl acetate (8:1)  $R_f$  0.65; IR ( $\text{cm}^{-1}$ ): 3054, 3012, 2978, 2879, 1620, 1475, 905, 845, 780, 696.  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ ): 7.68-7.71 (2H, m), 7.56-7.58 (2H, m), 7.31-7.35 (2H, m), 7.24-7.26 (1H, m), 7.15-7.17 (2H, m), 6.98 (1H, s), 2.61 (2H, q,  $J=7.6\text{Hz}$ ), 1.21 (3H, t,  $J=7.6\text{Hz}$ ).  $^{13}\text{C}$ NMR (100MHz,  $\text{CDCl}_3$ ): 145.0, 136.6, 135.3, 132.1, 129.4, 128.2, 127.8, 127.7, 126.6, 125.2, 28.5, 15.4. MS (EI, m/z, %): 244 ( $M^++2$ , 34), 242 ( $M^+$ , 100), 227 (8), 213 (9), 207 (10), 191 (15), 178 (15), 165 (5). Calcd. for  $C_{16}\text{H}_{15}\text{Cl}$ : C, 79.17; H, 6.23. Found: C, 79.27; H, 6.32.

**(Z)-1-chloro-3-(1-chloroprop-1-enyl)benzene (2g).**



Prepared and purified according to the general procedure above to provide the clear oil (**2g**) in 76% yield. TLC: petroleum-ether:ethyl acetate (10:1)  $R_f$  0.68; IR ( $\text{cm}^{-1}$ ): 3074, 3021, 2979, 1629, 1523, 1445, 870, 804, 675.  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ ): 7.53-7.54 (1H, m), 7.40-7.43 (1H, m), 7.24-7.25 (2H, m), 6.2 (1H, q,  $J=7.2\text{Hz}$ ), 1.93 (3H, d,  $J=7.2\text{Hz}$ ). MS (EI, m/z, %): 190 ( $M^++4$ , 11), 188 ( $M^++2$ , 64), 186 ( $M^+$ , 100).

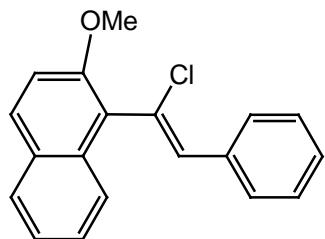
**(Z)-2-(1-chloro-2-phenylvinyl)naphthalene (2h)<sup>[4]</sup>.**



Prepared and purified according to the general procedure above to provide the white solid (**2h**) in 64% yield. TLC: petroleum-ether:ethyl acetate (8:1)  $R_f$  0.60; Mp 116.4-116.8°C (recrystallized from petroleum ether /  $\text{CH}_2\text{Cl}_2$ ), IR ( $\text{cm}^{-1}$ ): 3052, 3025, 1624, 1593, 1502,

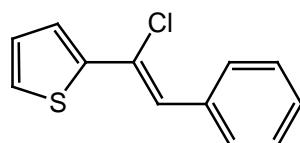
1444, 849, 816, 743, 692.  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ ): 8.16 (1H, d,  $J=1.6\text{Hz}$ ), 7.72-7.87 (6H, m), 7.28-7.51 (5H, m), 7.18 (1H, s).  $^{13}\text{C}$ NMR (100MHz,  $\text{CDCl}_3$ ): 136.4, 135.3, 133.3, 133.1, 132.1, 129.5, 128.5, 128.3, 128.0, 127.5, 126.7, 126.6, 126.4, 126.3, 124.1. MS (EI, m/z, %): 266 ( $M^++2$ , 34), 264 ( $M^+$ , 100), 229 (78), 202 (11), 189 (2), 176 (2).

**(Z)-1-(1-chloro-2-phenylvinyl)-2-methoxynaphthalene (2i).**



Prepared and purified according to the general procedure above to provide the white solid (**2i**) in 65% yield. TLC: petroleum-ether:ethyl acetate (8:1)  $R_f$  0.60; Mp 144.5-144.7°C (recrystallized from petroleum ether /  $\text{CH}_2\text{Cl}_2$ ), IR ( $\text{cm}^{-1}$ ): 3057, 3035, 2987, 1618, 1562, 1444, 1159, 853, 808, 697.  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ ): 8.12 (1H, s), 7.75-7.80 (5H, m), 7.40-7.44 (2H, t,  $J=7.6\text{Hz}$ ), 7.25-7.32 (1H, m), 7.14-7.20 (3H, m), 3.94 (3H, s).  $^{13}\text{C}$ NMR (100MHz,  $\text{CDCl}_3$ ): 158.3, 135.4, 134.5, 134.2, 132.3, 130.0, 129.5, 128.4, 128.3, 127.9, 126.8, 126.2, 125.6, 124.6, 119.4, 105.5, 55.3. MS (EI, m/z, %): 296 ( $M^++2$ , 27), 294 ( $M^+$ , 100), 259 (30), 244 (16), 228 (11), 215 (35), 202 (3), 189 (6), 108 (18). Calcd. for  $\text{C}_{19}\text{H}_{15}\text{ClO}$ : C, 77.42; H, 5.13. Found: C, 77.51; H, 5.20.

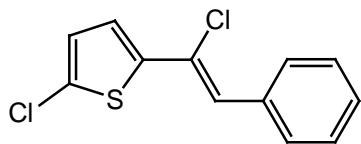
**(Z)-2-(1-chloro-2-phenylvinyl)thiophene (2j)<sup>[5]</sup>.**



Prepared and purified according to the general procedure above to provide the straw yellow oil (**2j**) in 82% yield. TLC: petroleum-ether:ethyl acetate (8:1)  $R_f$  0.64; IR ( $\text{cm}^{-1}$ ):

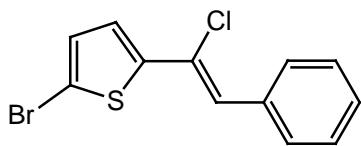
3081, 3023, 1613, 1530, 1440, 882, 789, 731, 691.  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ ): 7.68 (2H, d,  $J=7.2\text{Hz}$ ), 7.32-7.35 (3H, m), 7.24-7.27 (1H, m), 7.17-7.19 (1H, m), 7.05 (1H, s), 6.94-6.97 (1H, m).  $^{13}\text{C}$ NMR (100MHz,  $\text{CDCl}_3$ ): 143.4, 135.1, 129.8, 128.7, 128.4, 127.9, 126.5, 126.3, 125.7, 124.5. MS (EI, m/z, %): 222 ( $M^++2$ , 30), 220 ( $M^+$ , 100), 184 (39), 152 (11).

**(Z)-2-chloro-5-(1-chloro-2-phenylvinyl)thiophene (2k).**



Prepared and purified according to the general procedure above to provide the straw yellow solid (**2k**) in 80% yield. TLC: petroleum-ether:ethyl acetate (8:1)  $R_f$  0.64; Mp 59.0-59.4°C (recrystallized from petroleum ether /  $\text{CH}_2\text{Cl}_2$ ), IR ( $\text{cm}^{-1}$ ): 3097, 3018, 1607, 1528, 1436, 871, 798, 758, 687.  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ ): 7.68-7.71 (2H, m), 7.36-7.41 (2H, m), 7.29-7.33 (1H, m), 7.16 (1H, d,  $J=4.4\text{Hz}$ ), 6.95 (1H, s), 6.85 (1H, d,  $J=4.4\text{Hz}$ ).  $^{13}\text{C}$ NMR (100MHz,  $\text{CDCl}_3$ ): 141.1, 134.4, 130.4, 129.5, 128.4, 128.3, 126.8, 125.3, 124.4, 124.2. MS (EI, m/z, %): 258 ( $M^++4$ , 13), 256 ( $M^++2$ , 63), 254 ( $M^+$ , 100), 219 (26), 184 (11), 152 (4), 139 (11). Calcd. for  $\text{C}_{12}\text{H}_8\text{Cl}_2\text{S}$ : C, 56.48; H, 3.16. Found: C, 56.56; H, 3.22.

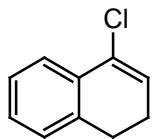
**(Z)-2-bromo-5-(1-chloro-2-phenylvinyl)thiophene (2l).**



Prepared and purified according to the general procedure above to provide the straw yellow solid (**2l**) in 79% yield. TLC: petroleum-ether:ethyl acetate (8:1)  $R_f$  0.64; Mp: 55.1-55.5°C (recrystallized from petroleum ether /  $\text{CH}_2\text{Cl}_2$ ), IR ( $\text{cm}^{-1}$ ): 3094, 3050, 1608, 1523, 1434, 870, 794, 747, 686.  $^1\text{H}$ NMR (400MHz,  $\text{CDCl}_3$ ): 7.69-7.71 (2H, m), 7.25-7.41

(3H, m), 7.13 (1H, d,  $J=4.0\text{Hz}$ ), 6.98-7.00 (2H, m),  $^{13}\text{CNMR}$  (100MHz,  $\text{CDCl}_3$ ): 144.1, 134.4, 130.5, 129.5, 128.8, 128.4, 128.3, 128.2, 124.5, 124.3, 112.9. MS (EI, m/z, %): 302 ( $M^++4$ , 28), 300 ( $M^++2$ , 94), 298 ( $M^+$ , 100), 263 (15), 184 (60), 152 (2), 139 (10). Calcd. for  $C_{12}\text{H}_8\text{BrClS}$ : C, 48.10; H, 2.69. Found: C, 48.16; H, 2.74.

**4-chloro-1,2-dihydronaphthalene (2m)**<sup>[6]</sup>.

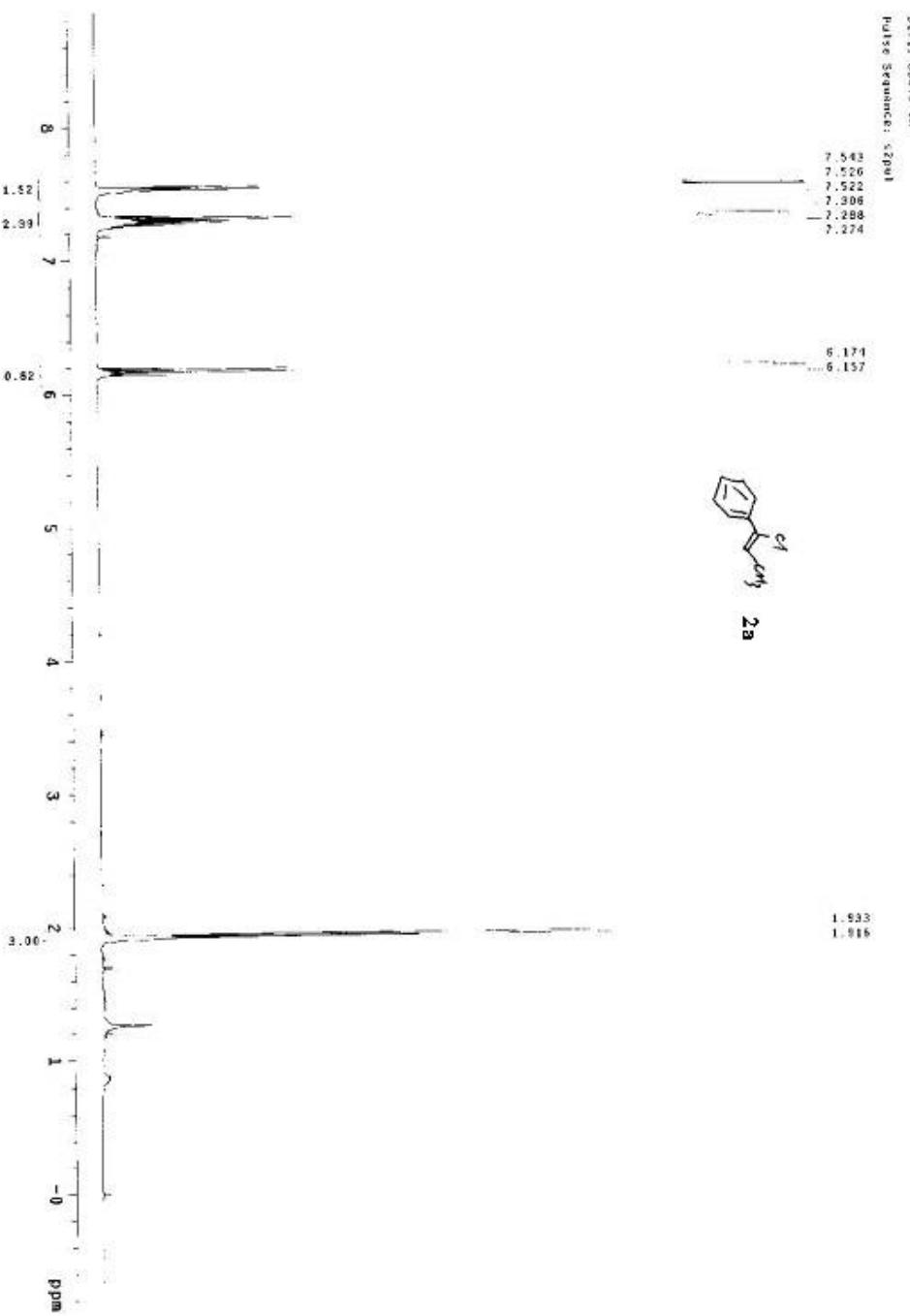


Prepared and purified according to the general procedure above to provide the clear oil (**2m**) in 74% yield. TLC: petroleum-ether:ethyl acetate (10:1)  $R_f$  0.60; IR ( $\text{cm}^{-1}$ ): 3099, 3046, 2990, 2897, 1622, 1521, 1450, 889, 789, 774, 674.  $^1\text{HNMR}$  (400MHz,  $\text{CDCl}_3$ ): 7.54 (1H, d,  $J=7.2\text{Hz}$ ), 7.12-7.21 (2H, m), 7.05 (1H, d,  $J=7.2\text{Hz}$ ), 6.1 (1H, t,  $J = 4.4 \text{ Hz}$ ), 2.75 (2H, t,  $J = 8.0\text{Hz}$ ), 2.27-2.33 (2H, m).  $^{13}\text{CNMR}$  (100MHz,  $\text{CDCl}_3$ ): 136.1, 132.2, 130.4, 128.1, 127.1, 126.5, 125.8, 123.9, 27.4, 24.0. MS (EI, m/z, %): 166 ( $M^++2$ , 36), 164 ( $M^+$ , 100).

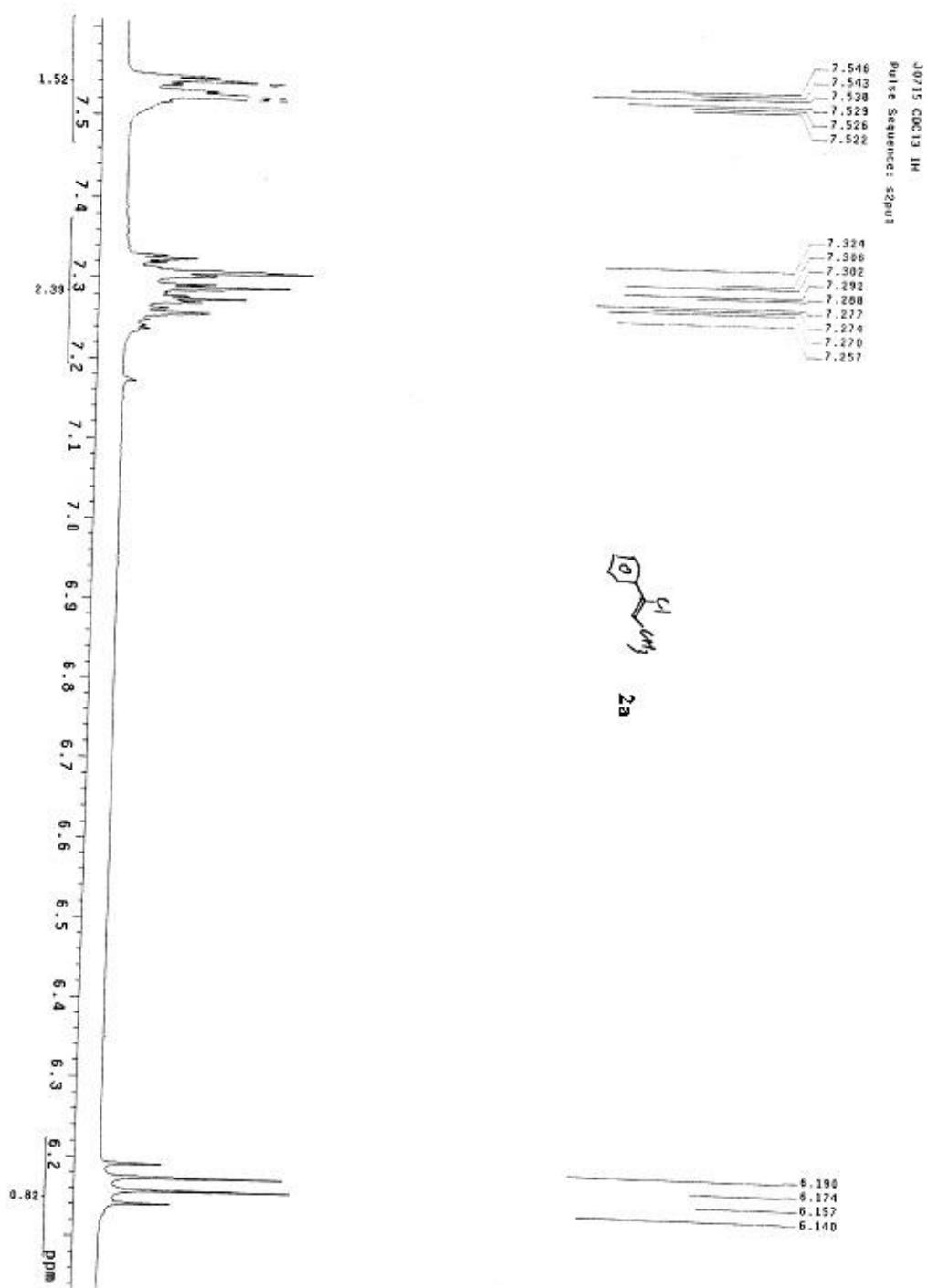
#### **IV. References**

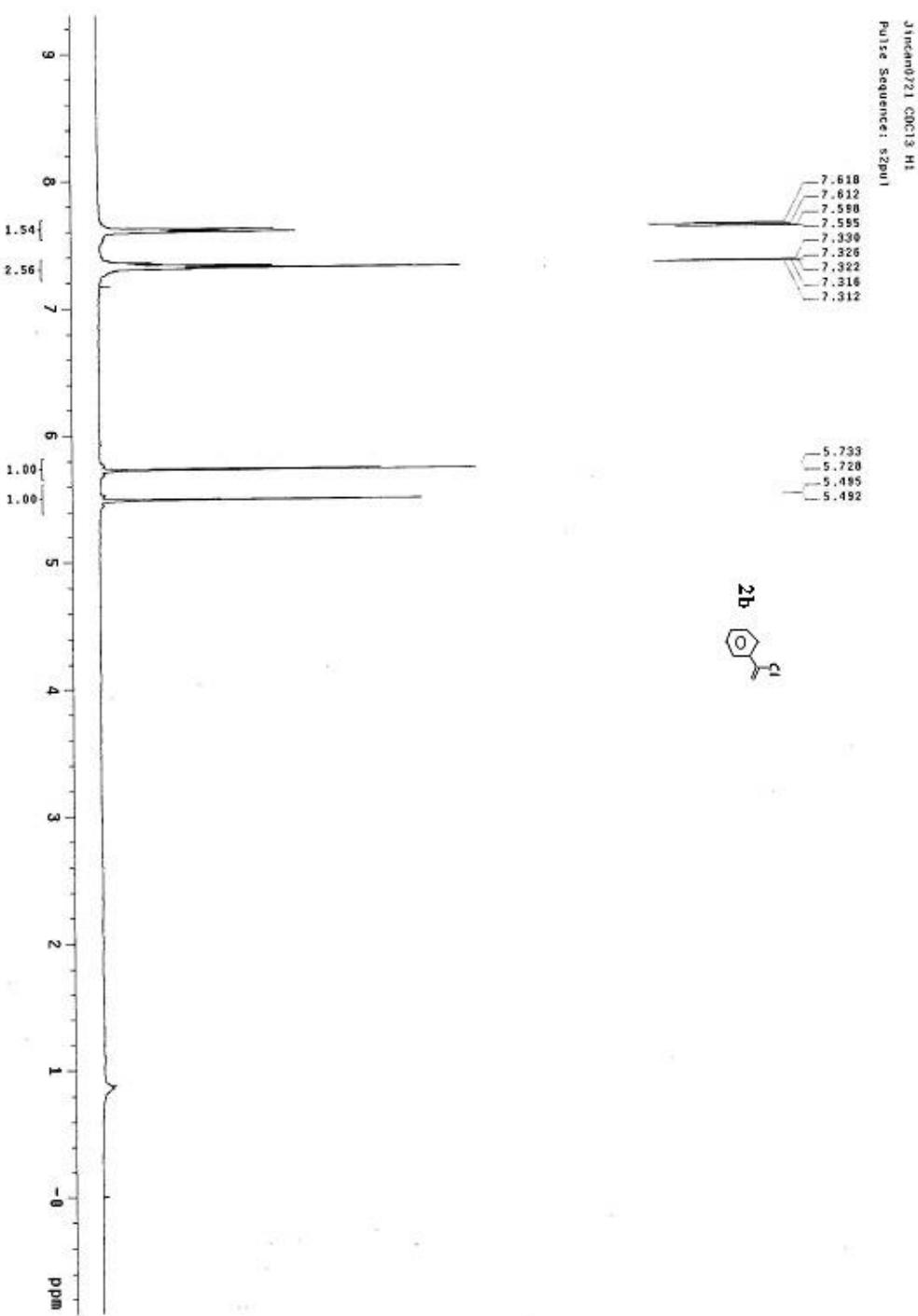
- [1] Shi, J. C.; Negishi, E. I. *J. Organomet. Chem.* **2003**, *687*, 518.
- [2] Massimo, C.; Francesco, E.; Carla, M. M.; Ornelio, R.; Monia, R. *Tetrahedron* **1999**, *55*, 6211.
- [3] Kodomari, M .; Nagaoka, T.; Furusawa, Y. *Tetrahedron Lett.* **2001**, *42*, 3105.
- [4] Ruggli, P.; Reinert, M. *Helv. Chim. Acta* **1926**, *9*, 67-79.
- [5] Minato, A.; Suzuki, K.; Tamao, K. *J. Am. Chem. Soc.* **1987**, *109*, 1257.
- [6] Moughamir, K.; Mezgueldi, B.; Atmani, A.; Mestdagh, H.; Rolando, C. *Tetrahedron Lett.* **1999**, *40*, 59.

## V. Copies of $^1\text{H}$ , $^{13}\text{C}$ NMR and NOE spectra



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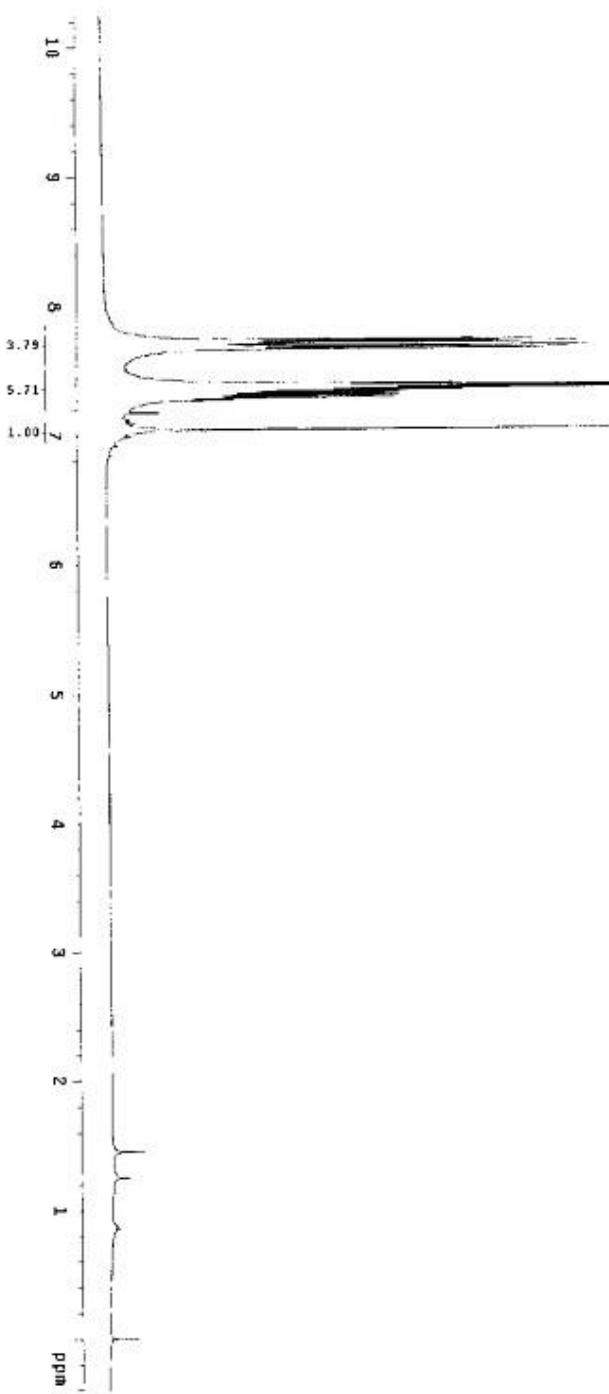
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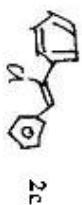
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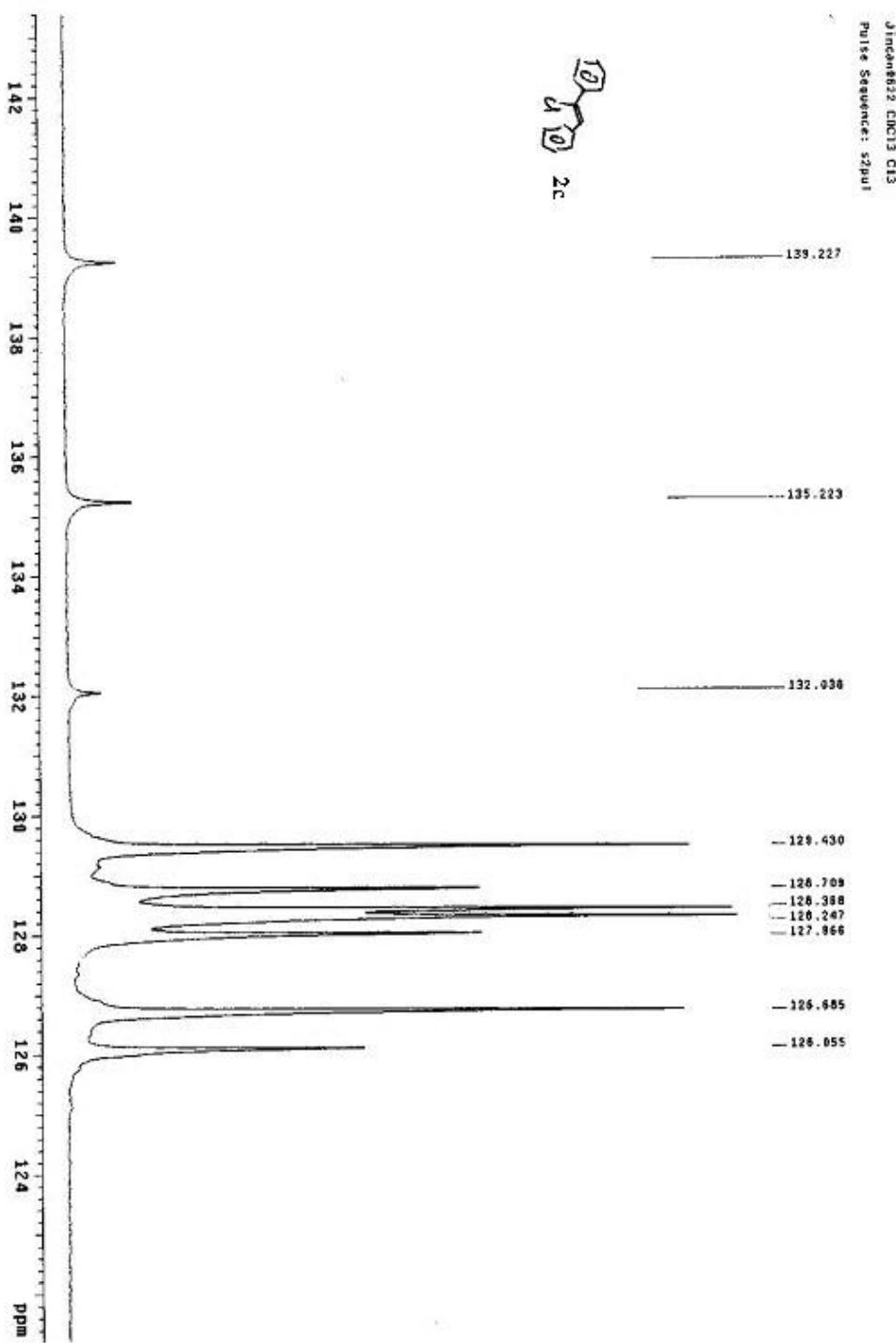


2c

— 131.227  
— 135.223  
— 132.036  
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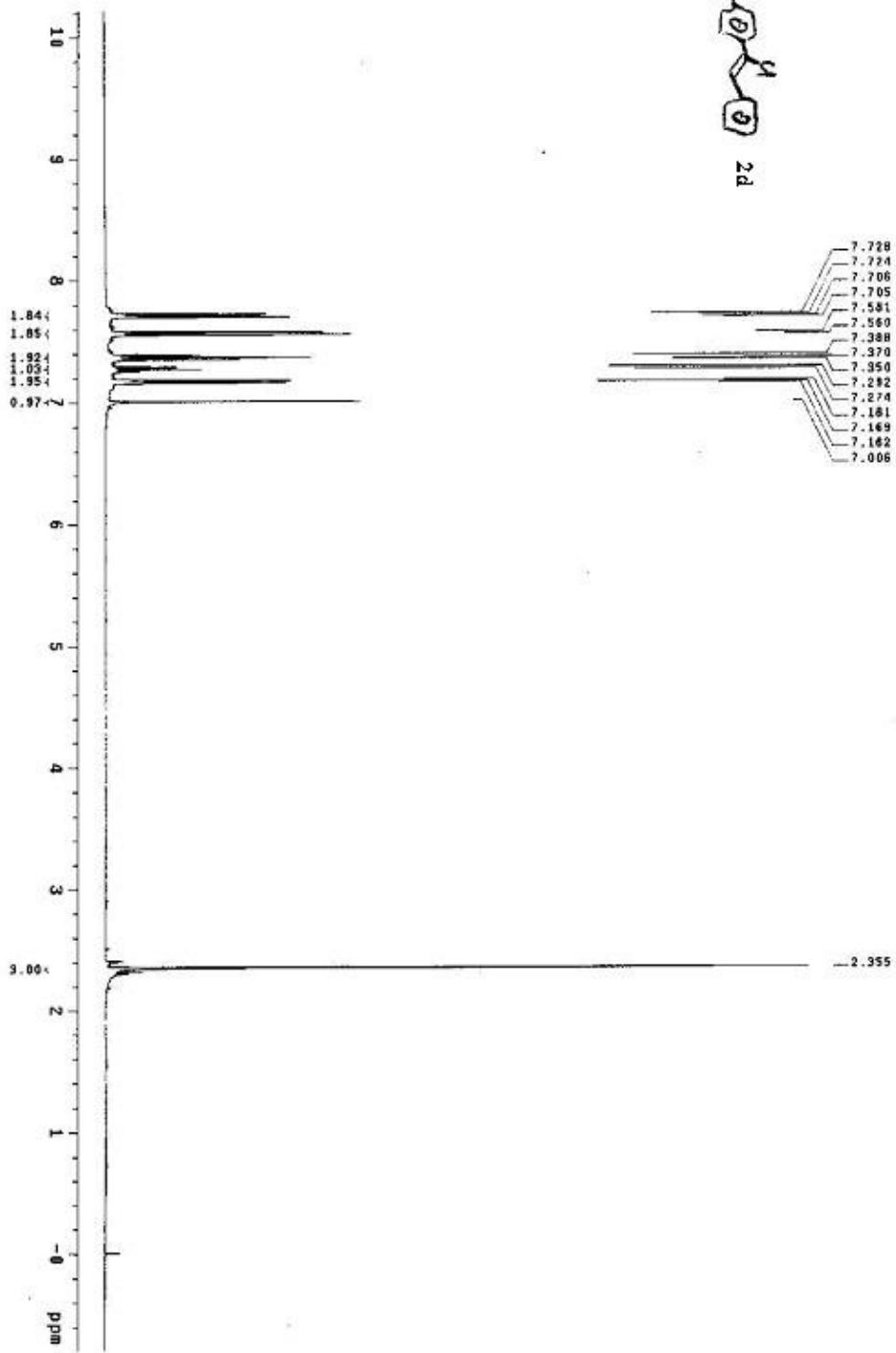




J1 mnmr616.CDC13.H  
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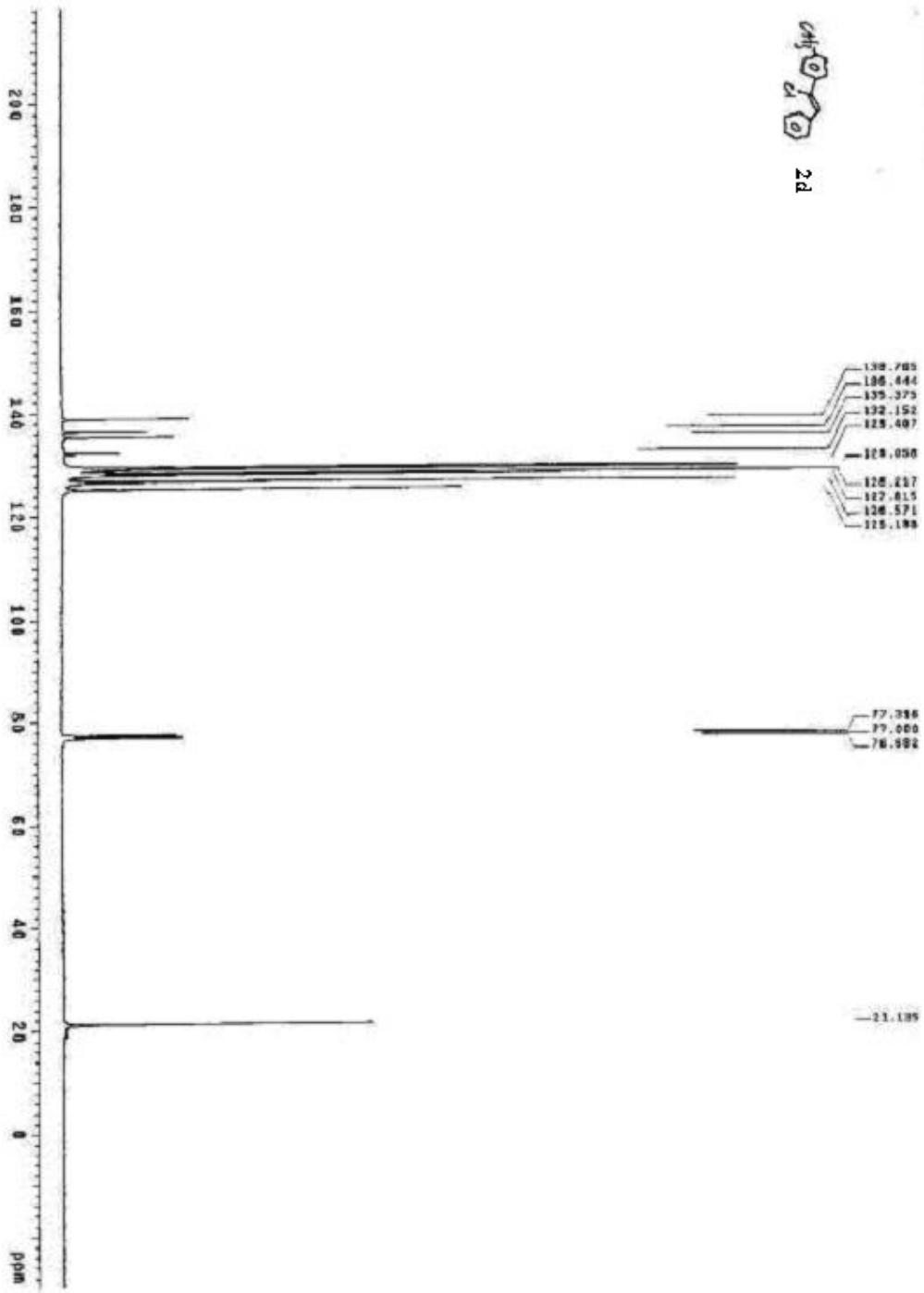


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J Infrared C COCl<sub>2</sub> H1  
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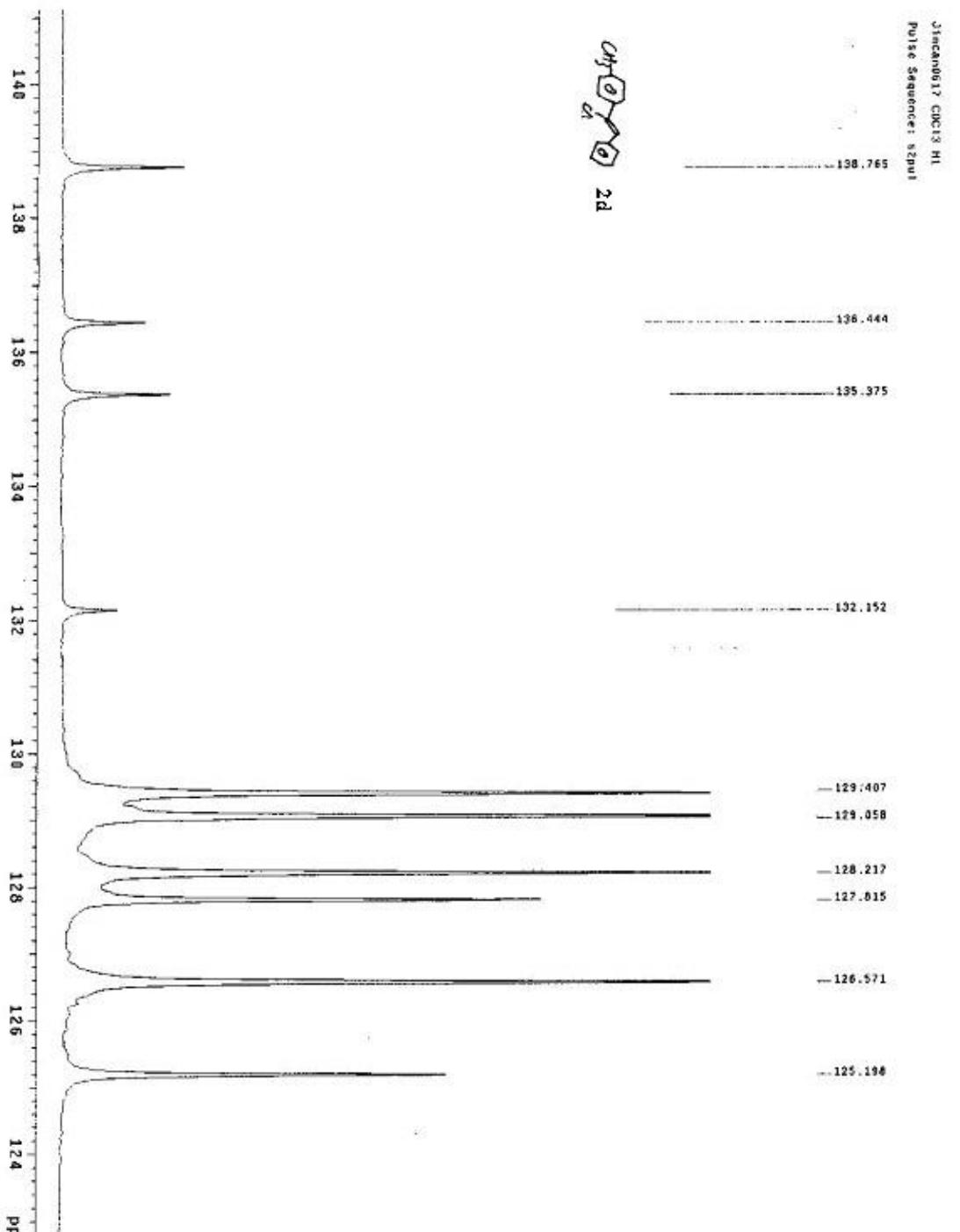
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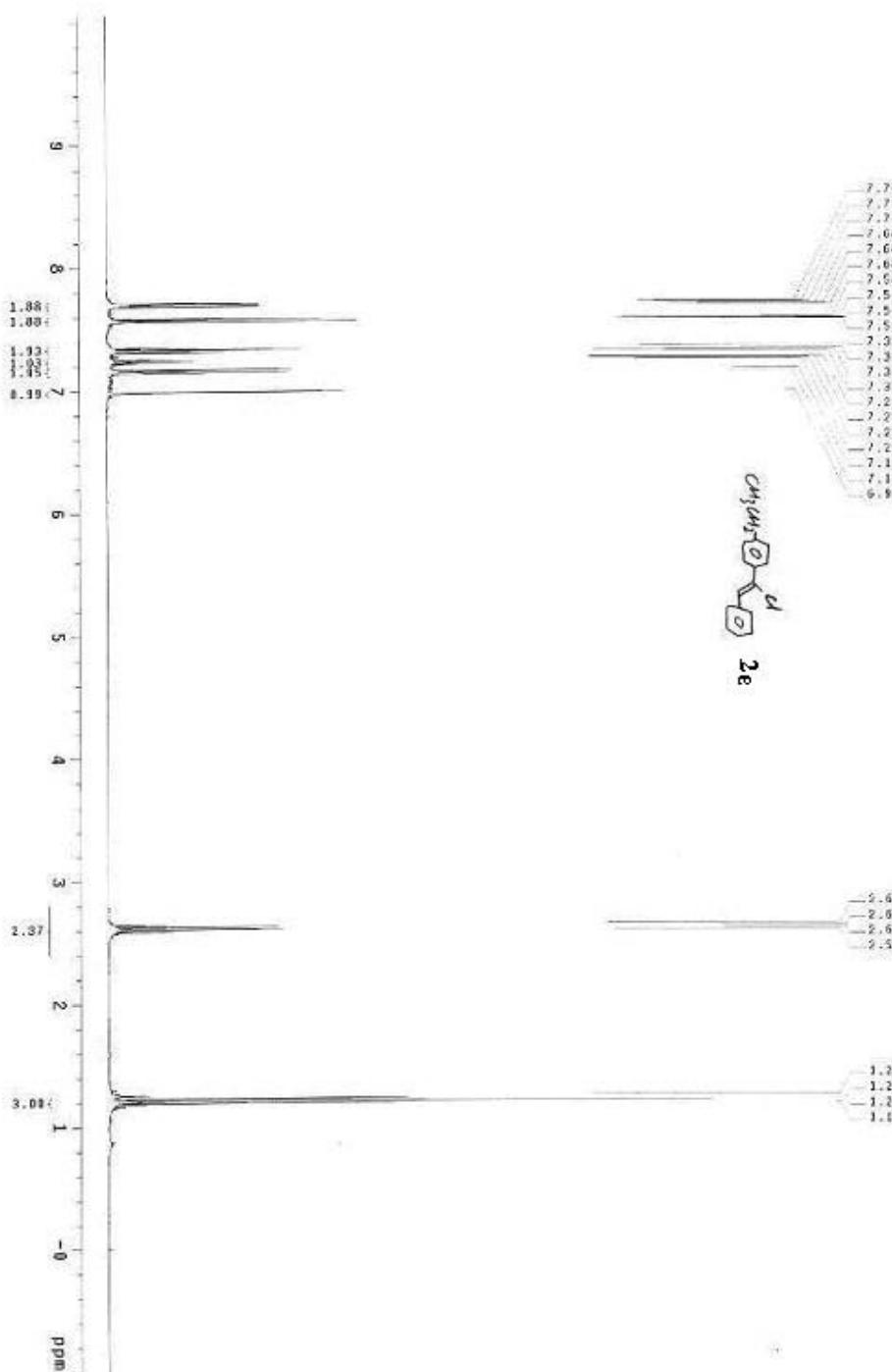


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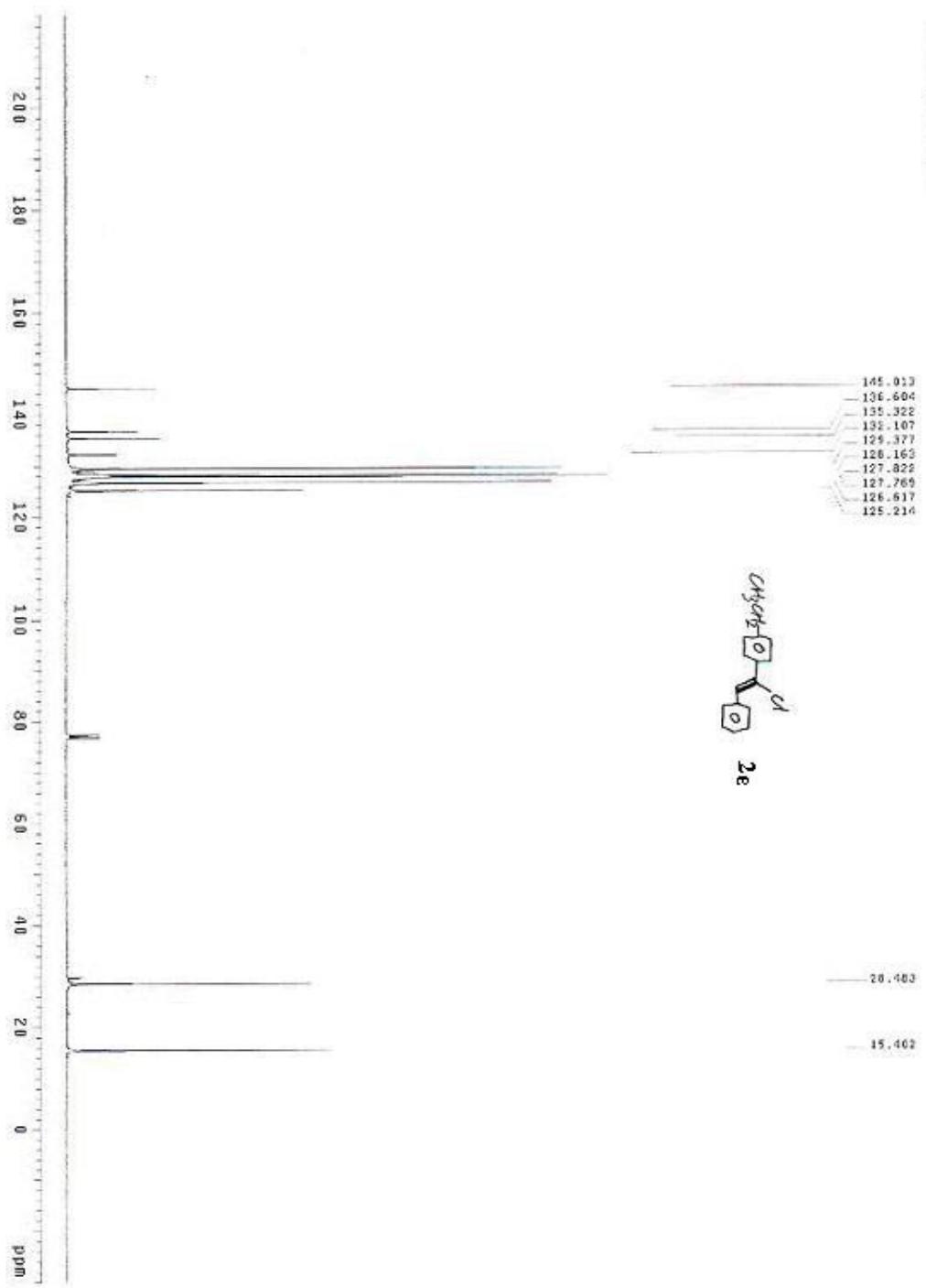


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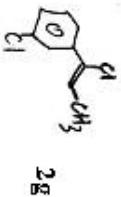
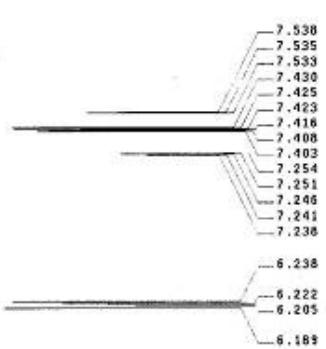


Customer: Z401400 Date: 12/12/2005  
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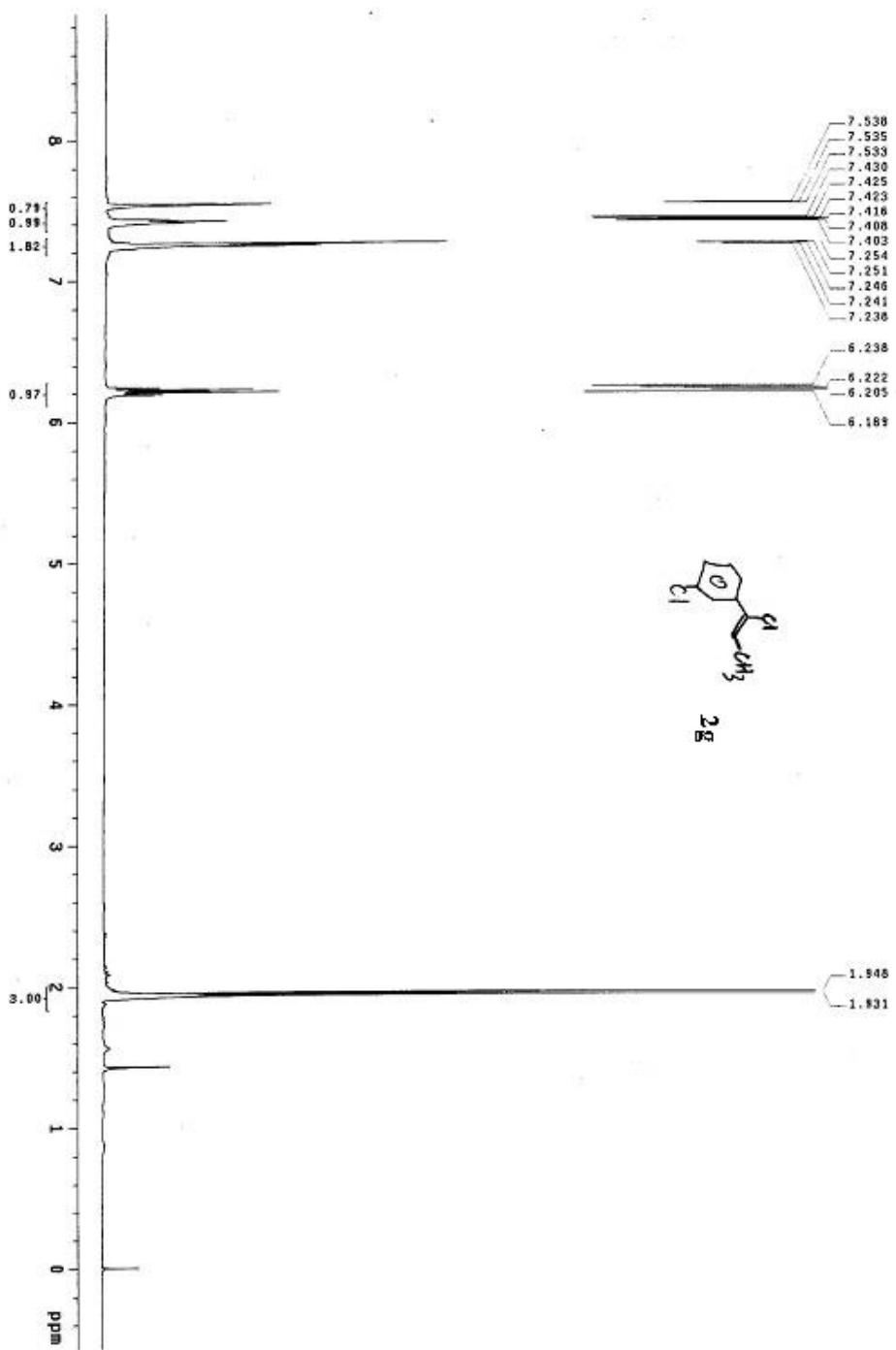
J\Cal0713 C1C13 C3  
puis Sequence: r2gul



J9919 CDCl<sub>3</sub> HI  
Pulse Sequence: 62 pu

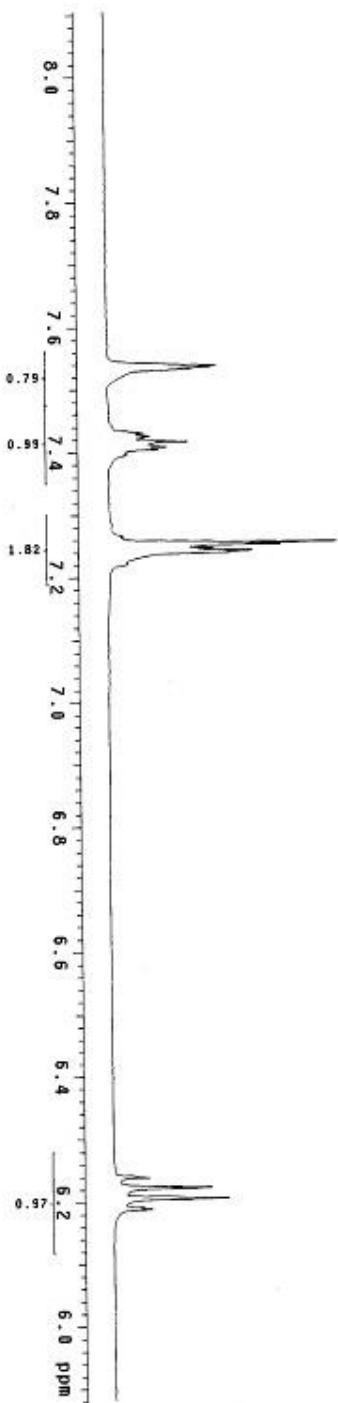
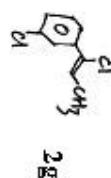
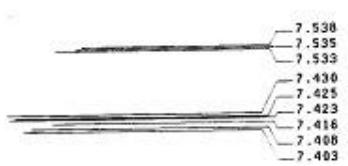


2g

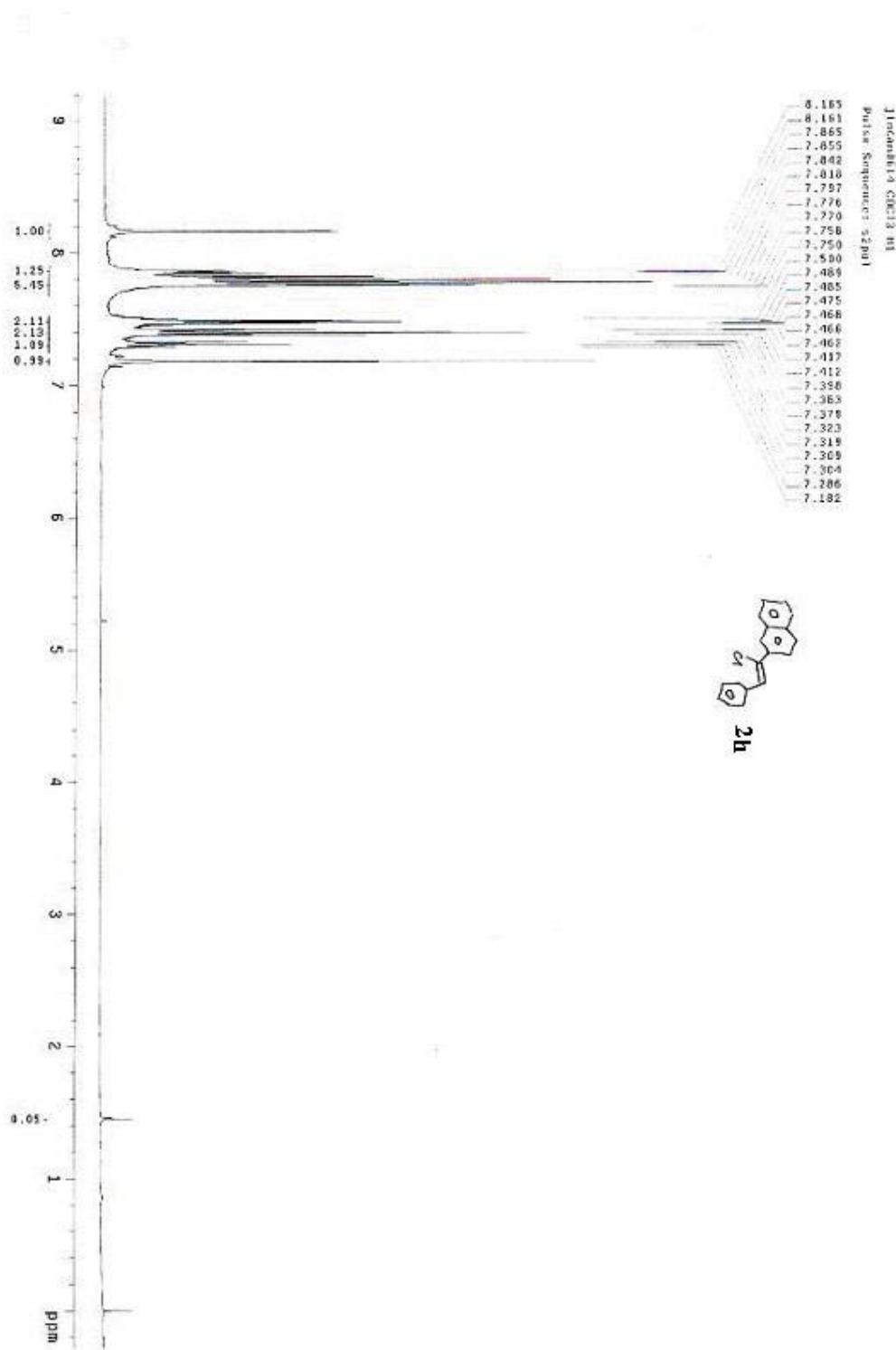


Customer: ZJUT400 Cont. SHI: 12192 Sep 20 2004  
Probe: ASW Ser. num: 6134 XWV

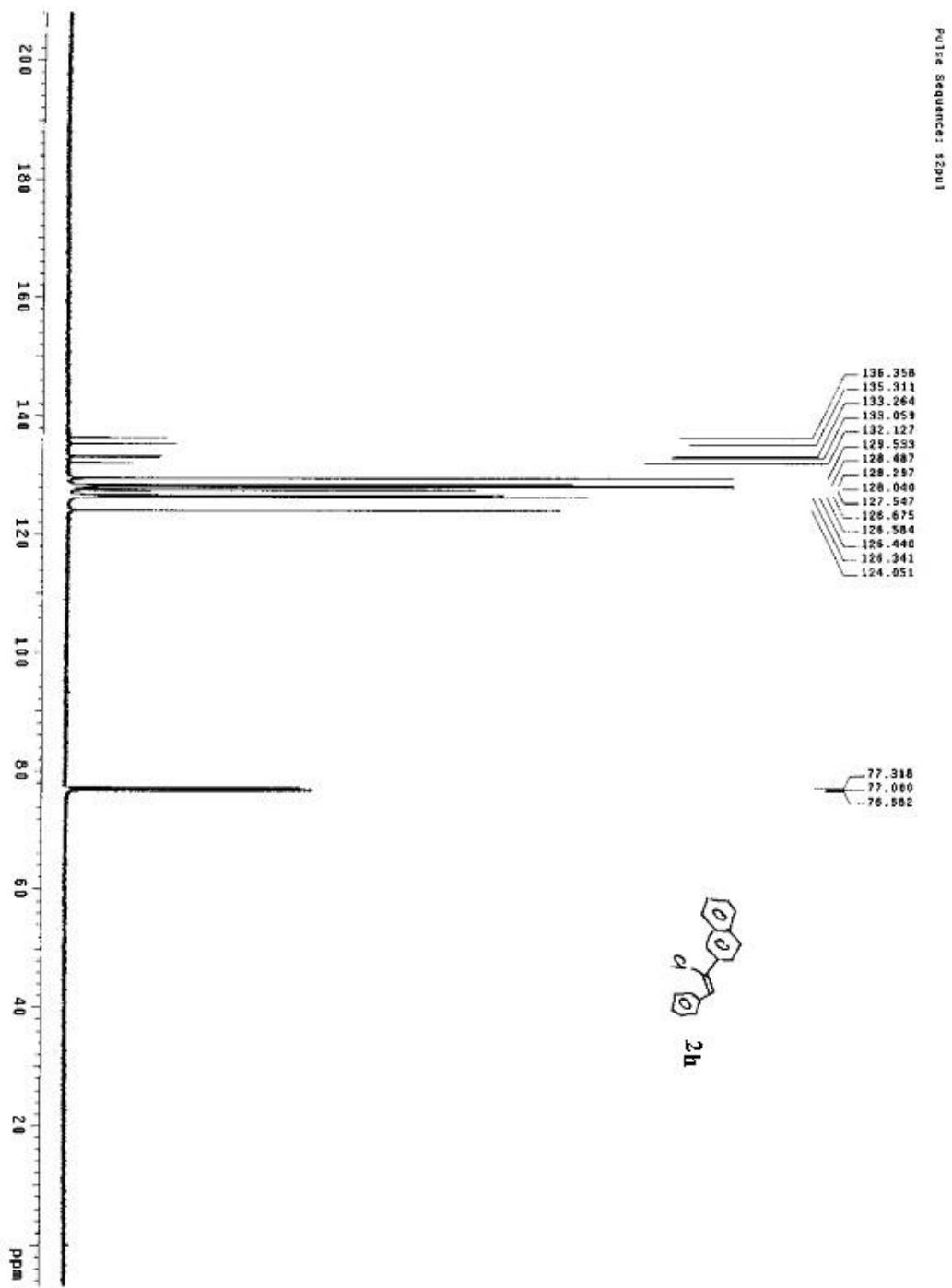
JES19 CDCL3 H3  
Pulse Sequence: S2pu1



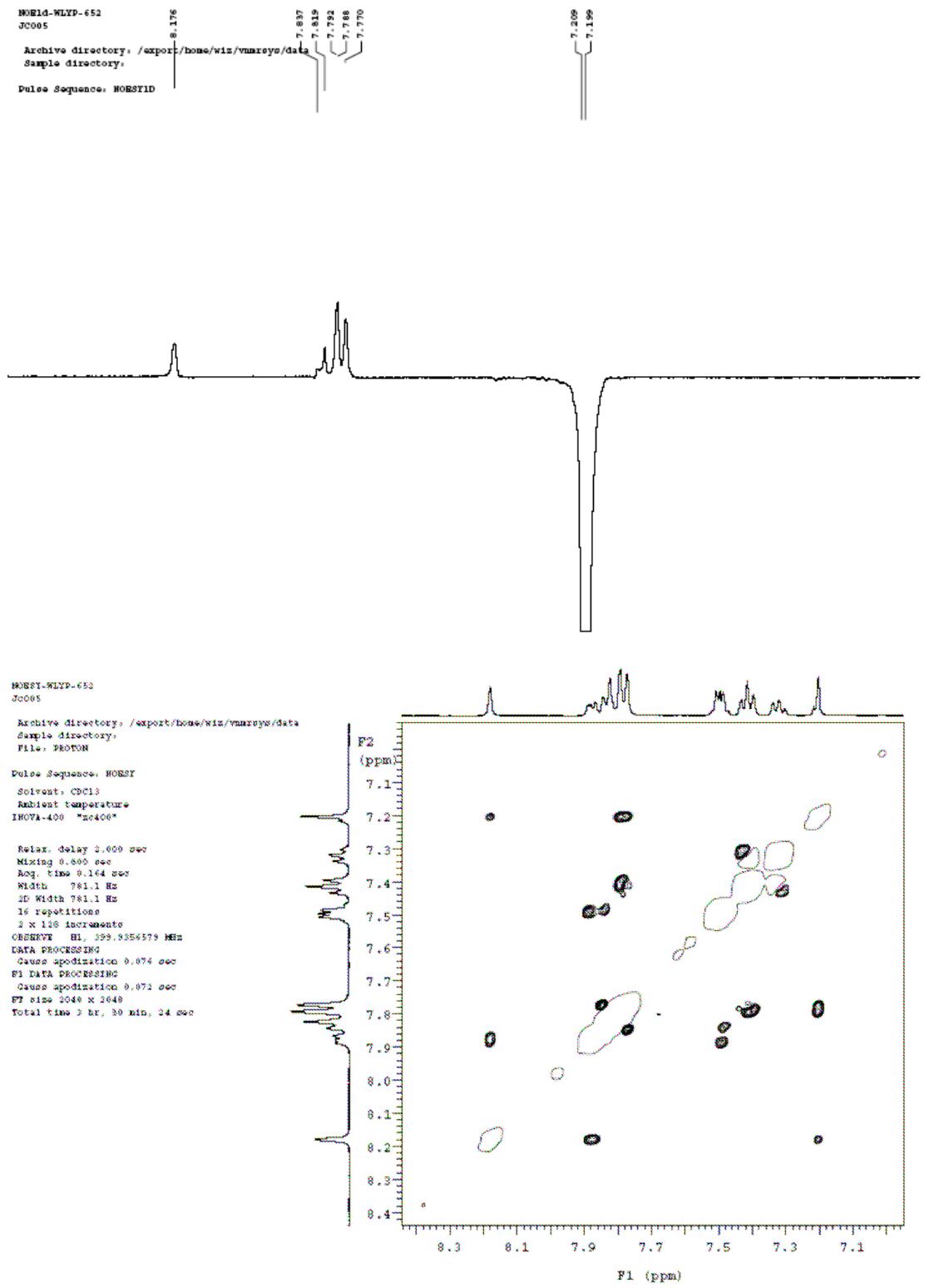
Customer: ZJUT400 Cons SN: 12182 Sep 20 2004  
Profile:ASW Ser num: 6134 KVV

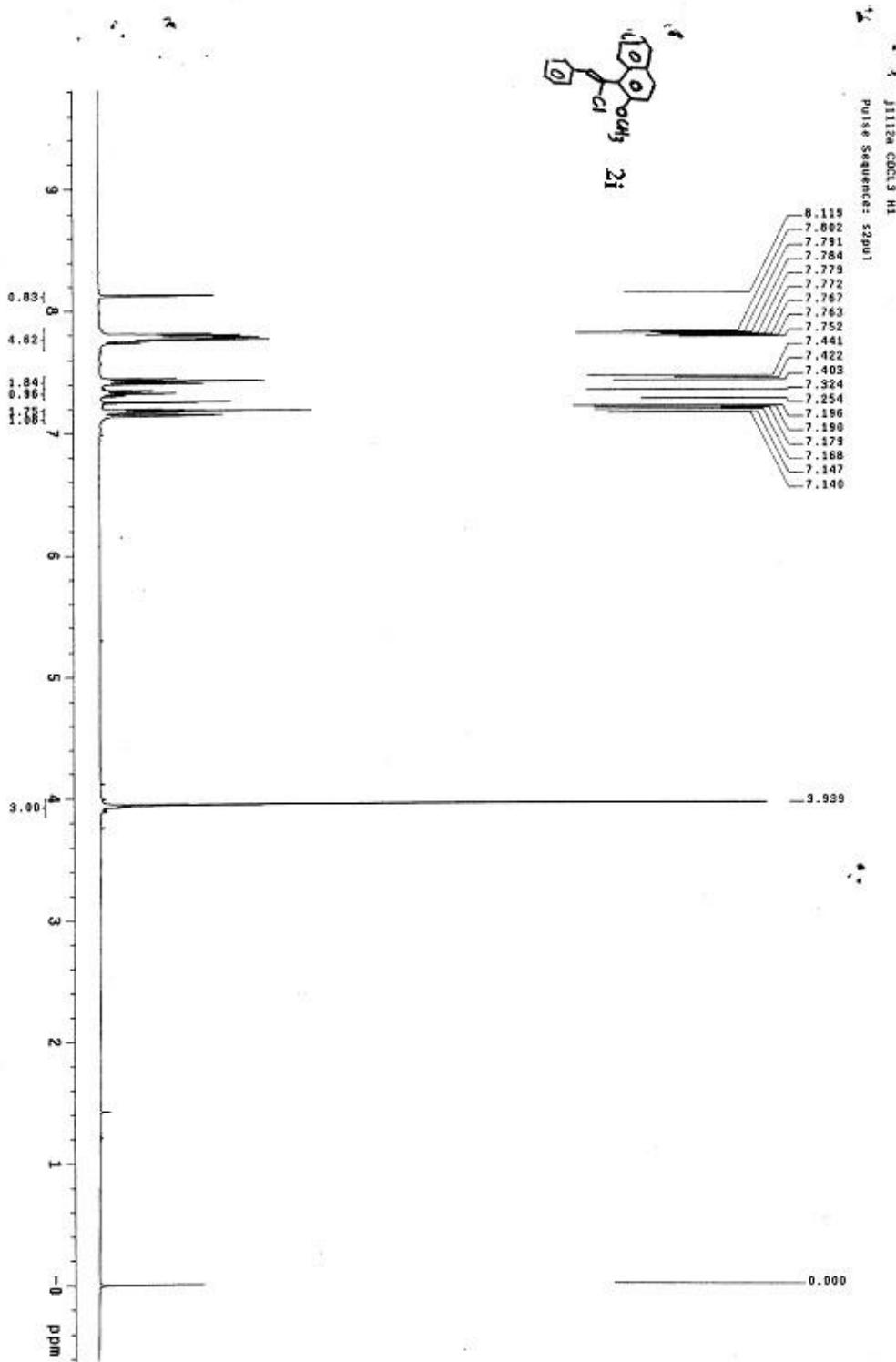


Customer: ZJUT440 Date: SN: 12142 Jun 14 2005  
Probe:ASW Spec num: 8134 NMR



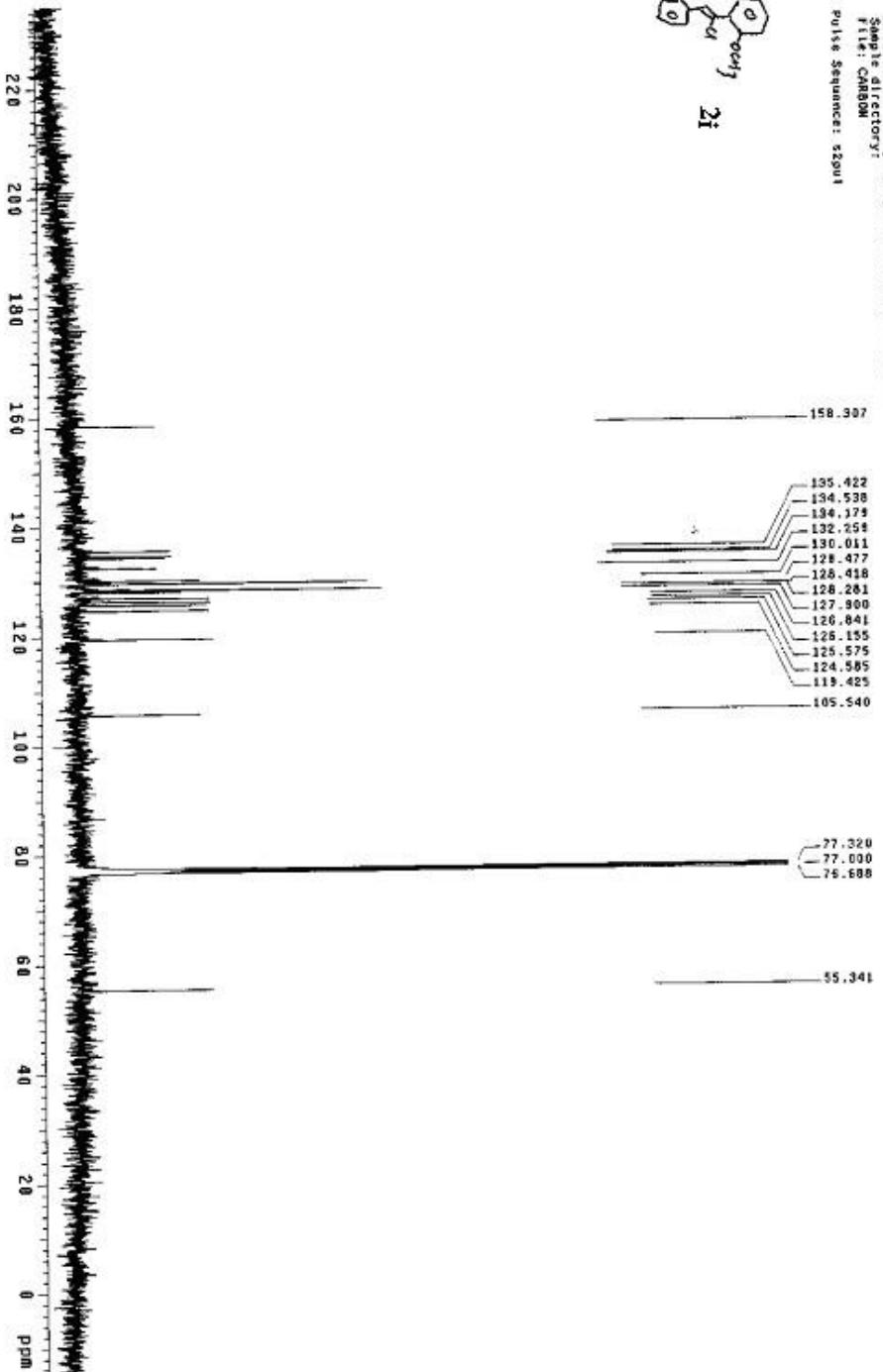
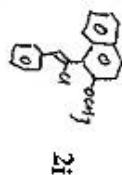
### NOE of **2h**



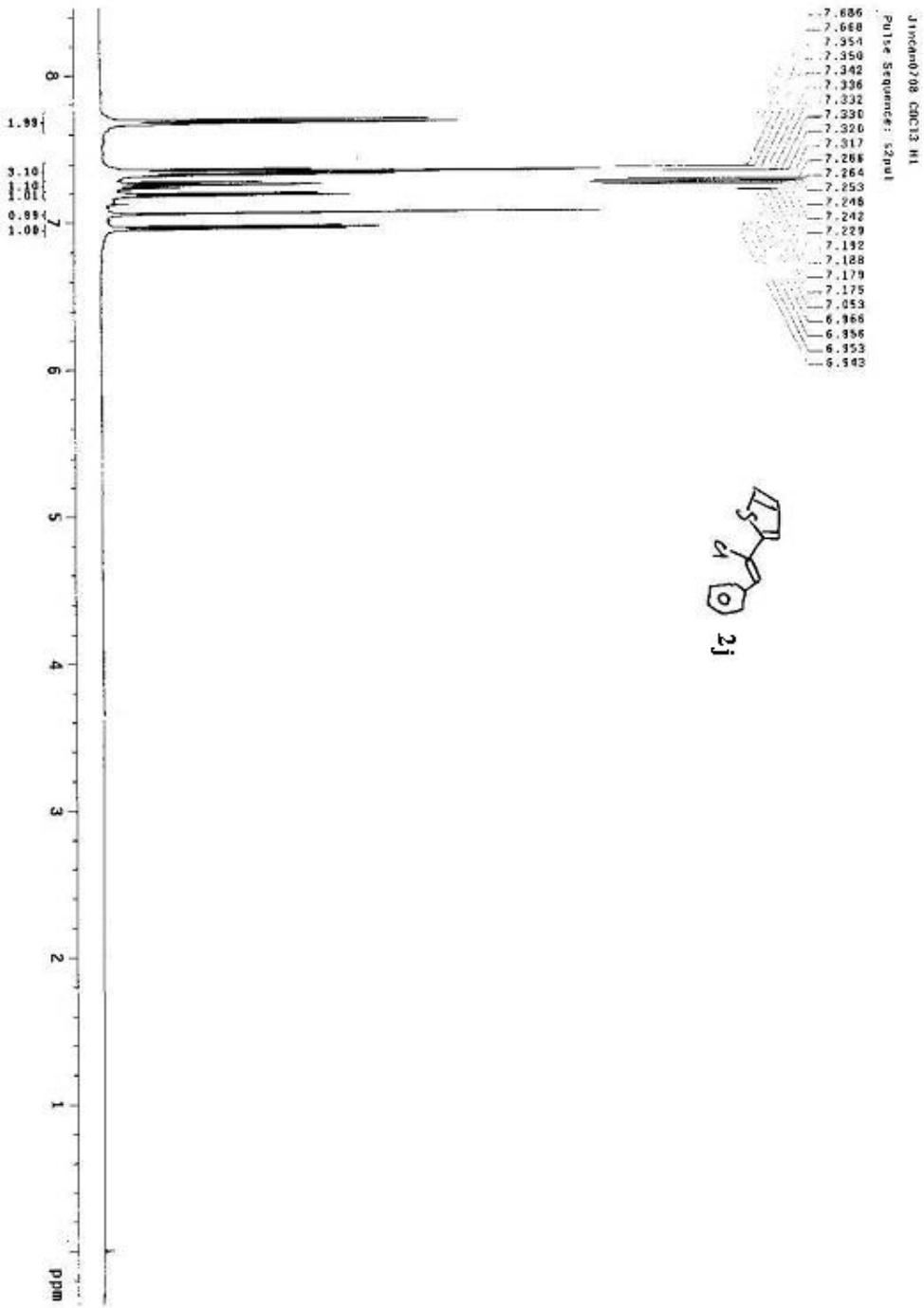


Customer: ZJUT400 Date: SN: 12132 Nov 15 2004  
 Probe: ASW Ser num: 6134 XWV

J1112c\_ddc13\_C13  
Archive directory: /export/home/xyy/vnmrfsys/data  
File: CARBON  
Pulse Sequence: s2001

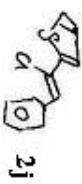


Customer: ZJUT408 Cons SN: 12192 Nov 15 2004  
probe: ASW Ser num: 6134 XYY

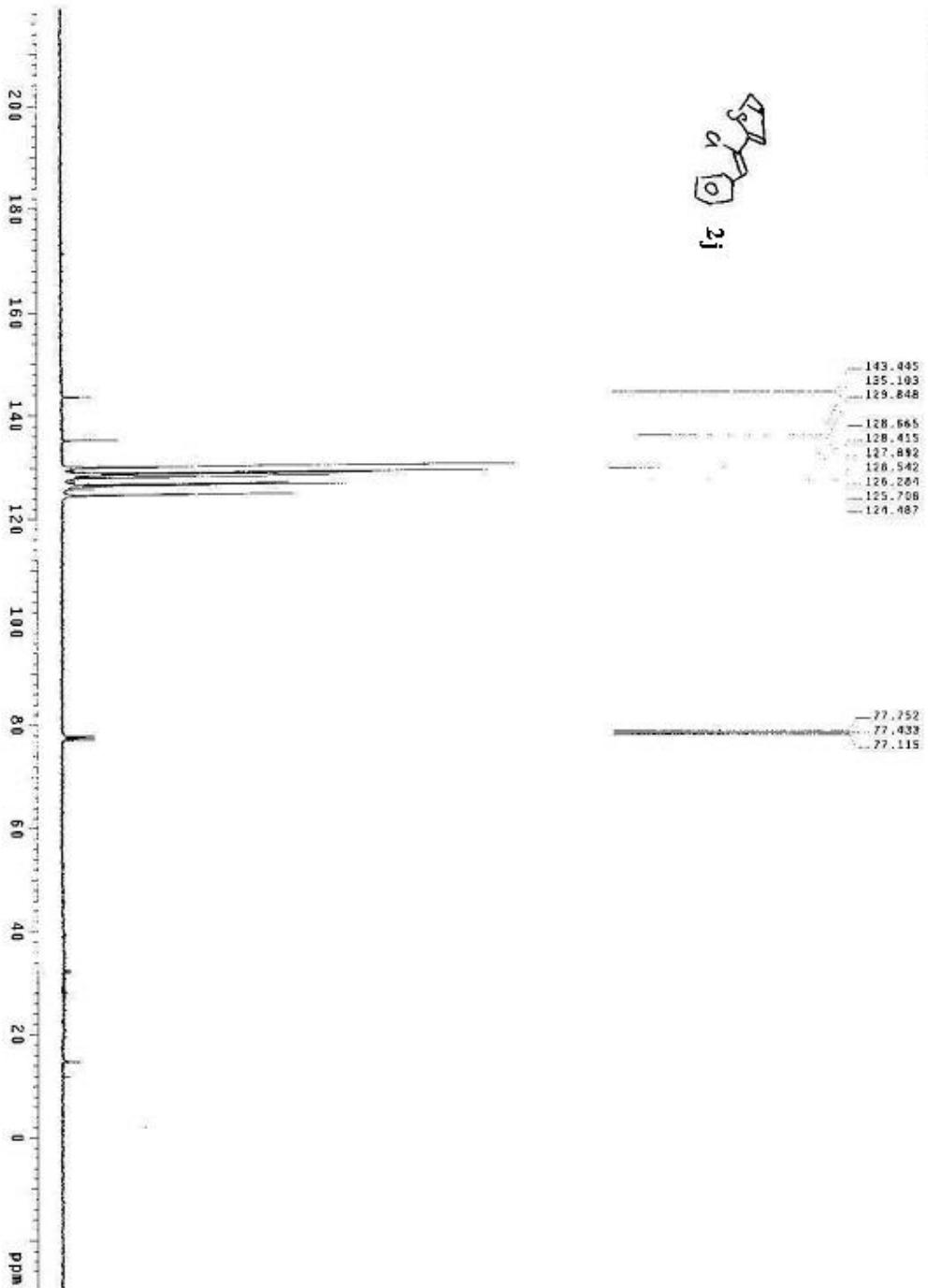


Customer: ZAUUR400 Cents SN: 12192 Jul 7 2005  
File#: RSM Ser num: 613n xxv

J Inclurop 85 (2003) 219  
Pulse Sequence: 13Cpu

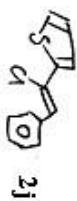


2j



J:\ncano\0708\CDCl<sub>3</sub>.C13  
Pulse Sequence: s2pul1

143.445



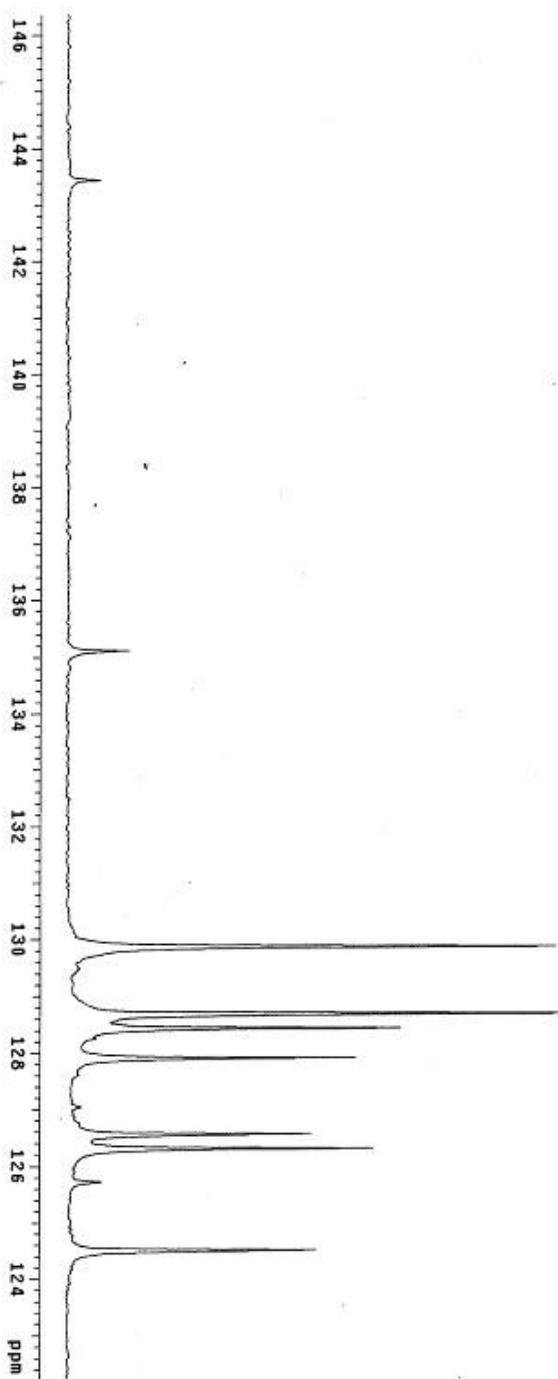
135.103

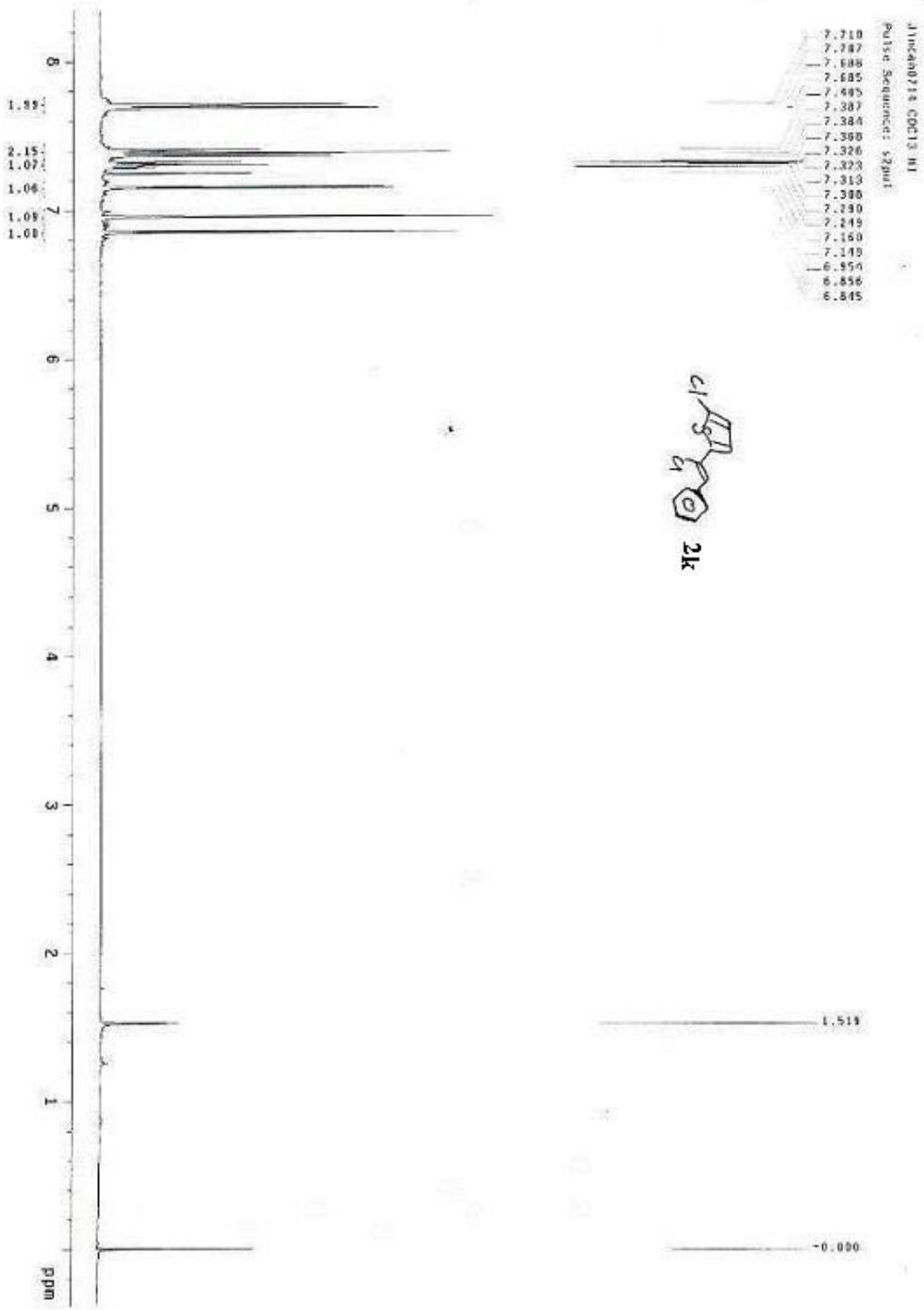
129.848

128.665  
128.415  
127.852

126.542  
126.284  
125.708

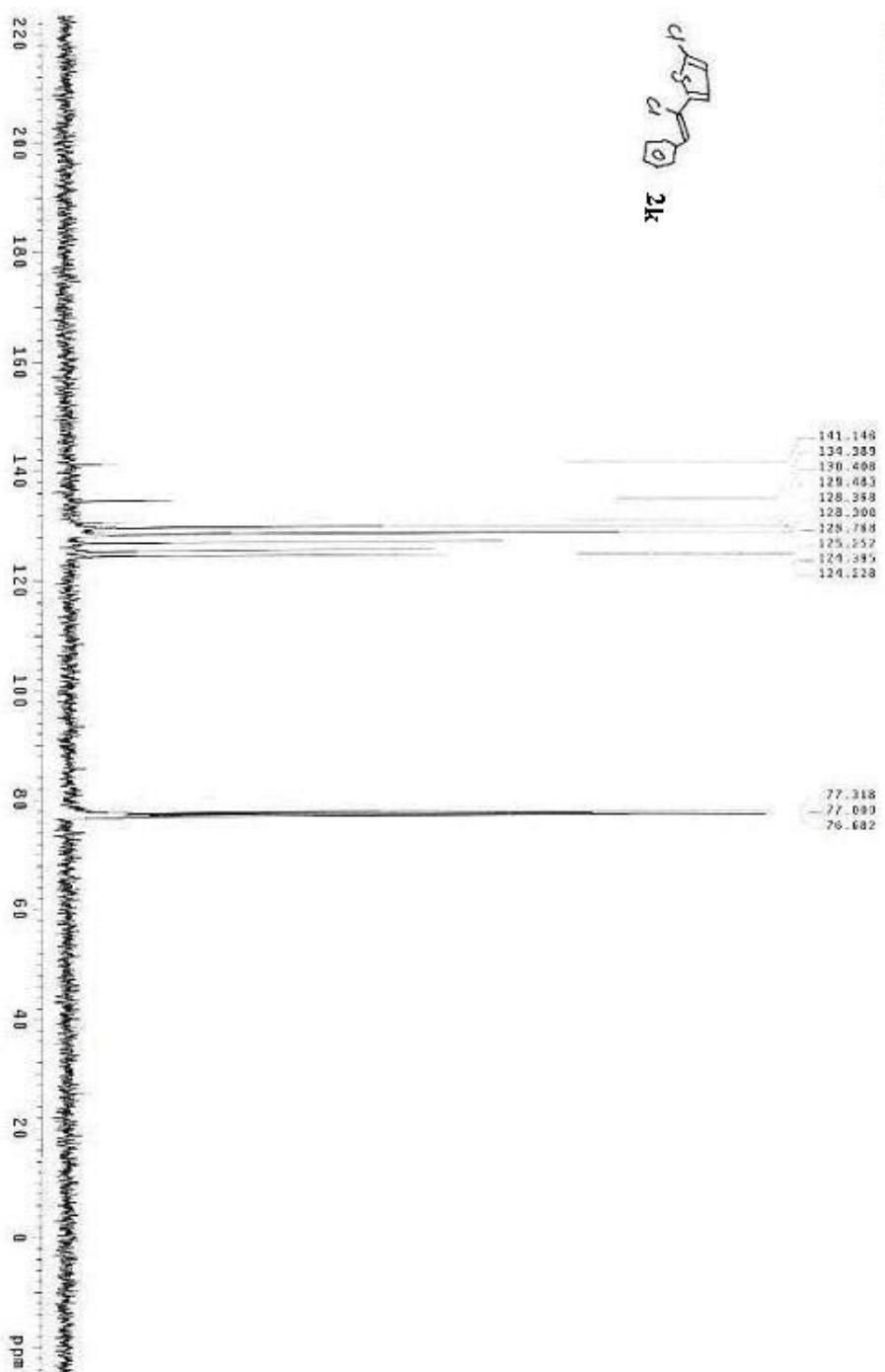
124.487



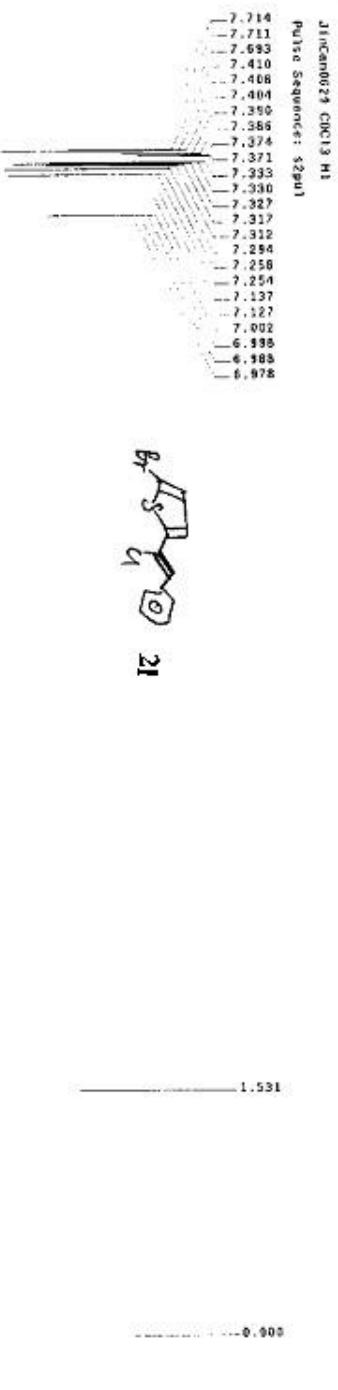


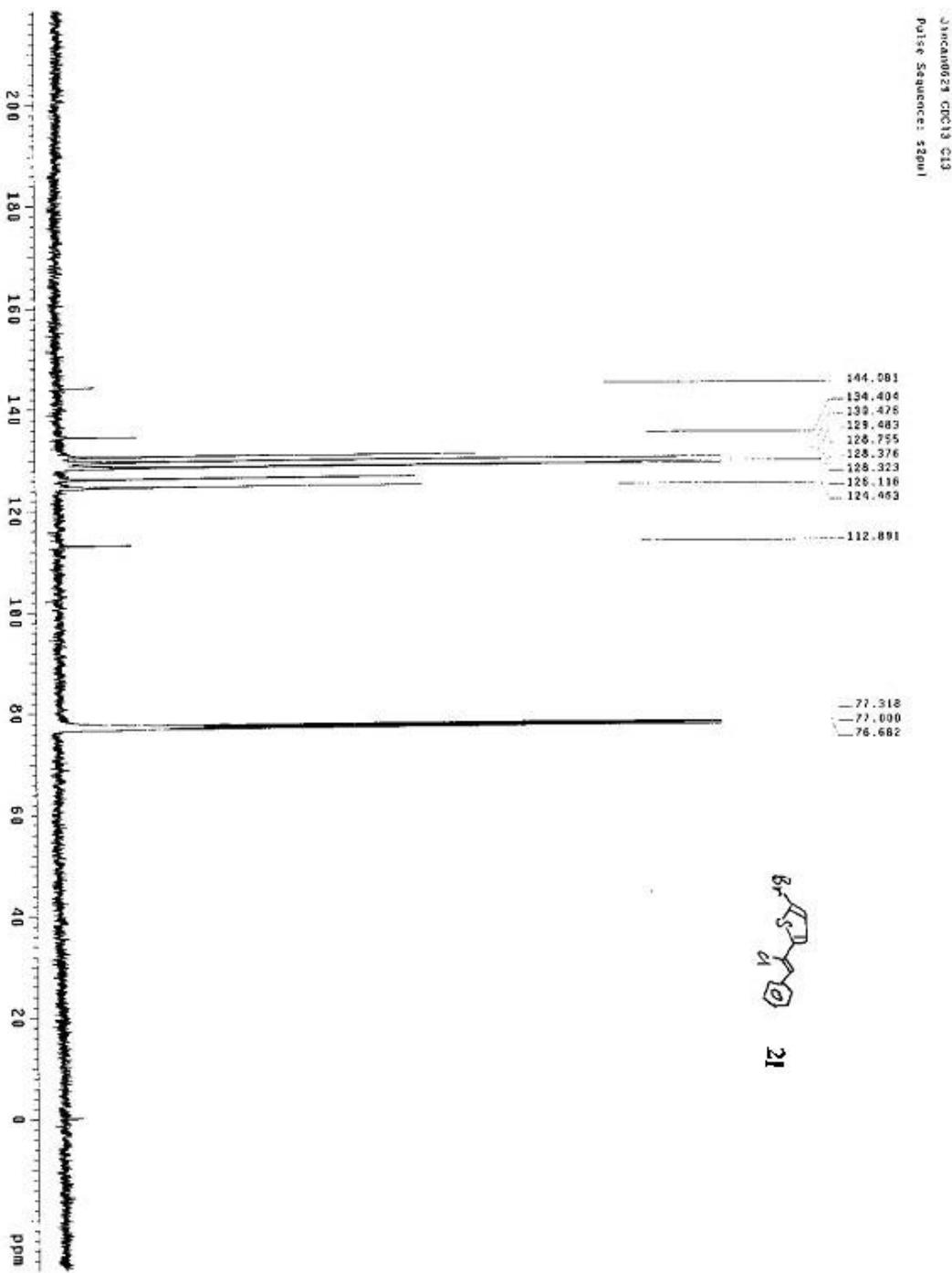
Customer: ZHENG Dong S/N: 12192 Jul 14 2005  
 Probe/MSP: Ser num: 6131 Rev

JeanMarie/14 CDCl<sub>3</sub> G13  
Pulse Sequence: 32pwi



Customer: ZJUTK0 Cons Sh: 12142 Jul 14 2005  
Probe: ASK Ser num: 6134 xwv

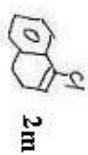




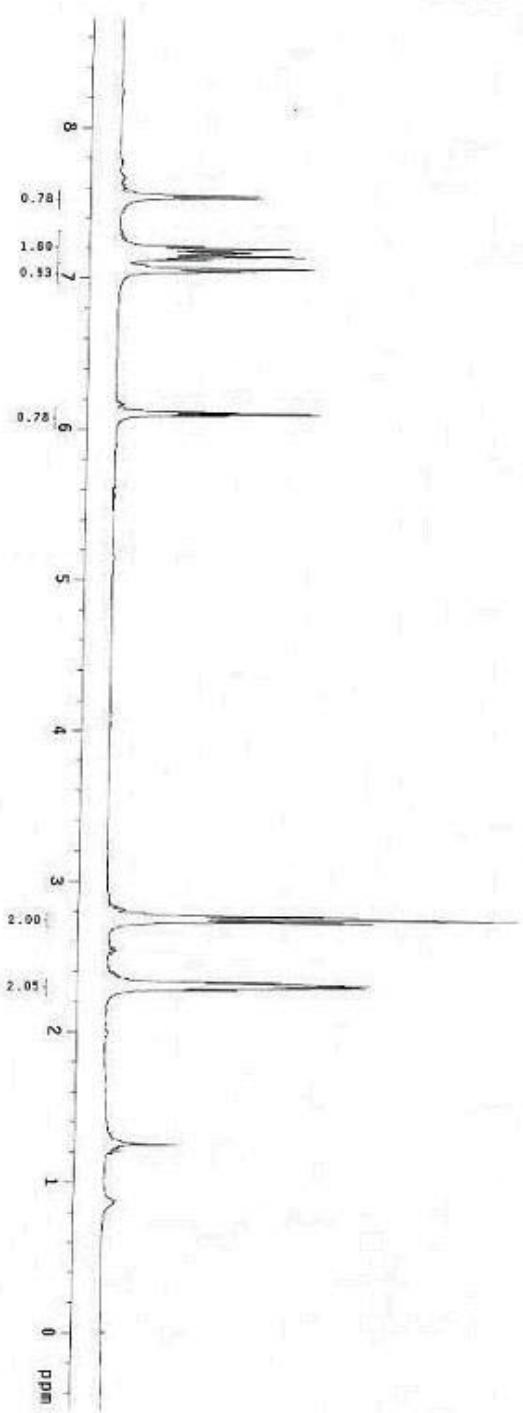
J:\Invent\215\GCC13.H1  
Palsc Sequence: szmu1

7.551  
7.533  
7.209  
7.110  
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7.157  
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7.001

6.112  
6.100  
6.059



2.766  
2.745  
2.725  
2.326  
2.313  
2.308  
2.301  
2.295  
2.288  
2.276  
2.274



Customer: ZJU1460 Cons SN: 12132 Jul 14 2005  
probe: f5v Ser mm: 6134 xxv

J:\ncarb0719\CD713.C13  
Pulse Sequence: zgppr1

