Supporting Information

Studies of TiCl_4 promoted Baylis-Hillman reactions of Substituted 5-isoxazolecarboxaldehydes with Cycloalkenones

Arundhati.Patra,^a Sanjay Batra,^{a*} Bhawani S. Joshi,^b Raja Roy,^b Bijoy Kundu^a and

Amiya P.Bhaduri^a

Medicinal Chemistry and RSIC Division, Central Drug Research Institute, Lucknow, 226 001,
India

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Compounds **16a-d**^{35, 41, 60, 61} and **17c**⁵⁸ were identical to authentic samples by comparison of their spectral data. The compound **16c** was obtained as an oil as reported by Li et. al. (ref. no 41) and not solid as reported by Kataoka et. al. (ref. no. 35).

2a: 58% as colourless oil; IR (Neat) 1699, 3389 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.49-2.54 (m, 2H, CH_2), 2.69-2.71 (m, 2H, CH_2), 4.08 (brs, 1H, OH), 5.76 (s, 1H, CH), 6.63 (s, 1H, =CH), 7.43-7.46 (m, 3H, Ar-H), 7.63 (t, 1H, =CH), 7.77-7.82 (m, 2H, Ar-H); Mass (EI) m/z 255(M^+ , 13), 199 (25), 144(100). (Anal. calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_3$ C, 70.57, H, 5.13, N, 5.48. Found C, 70.32, H, 5.14, N, 5.22%).

2c: 50% as pale yellow oil; IR (Neat) 1699, 3388 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.50-2.55 (m, 2H, CH_2), 2.69-2.74 (m, 2H, CH_2), 4.02 (d, 1H, $J = 5.6$ Hz, OH), 5.78 (d, 1H, $J = 2.5$ Hz, CH), 6.77 (s, 1H, =CH), 7.33-7.47 (m, 3H, Ar-H), 7.64 (t, 1H, $J = 1.8$ Hz, =CH), 7.68-7.73 (m, 1H, Ar-H); Mass (EI) m/z 289(M^+ , 100), 285 (53), 240 (100). (Anal. calcd. for $\text{C}_{15}\text{H}_{12}\text{ClNO}_3$ C, 62.18, H, 4.17, N, 4.83. Found C, 61.97, H, 4.14, N, 4.99%).

2d: 65% as pale yellow solid, m.p. 80-82°C; IR (KBr) 1700, 3388 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.48-2.53 (m, 2H, CH_2), 2.68-2.70 (m, 2H, CH_2), 4.05 (d, 1H, $J = 6.2$ Hz, OH), 5.10 (s, 2H, $\text{C}_6\text{H}_5\text{CH}_2\text{O}$), 5.74 (d, 1H, $J = 5.4$ Hz, CH), 6.57 (s, 1H, =CH), 7.03 (d, 2H, $J = 8.7$ Hz, Ar-H), 7.30-7.42 (m, 5H, Ar-H), 7.61 (t, 1H, $J = 1.8$ Hz, =CH), 7.72 (d, 2H, $J = 8.7$ Hz, Ar-H); Mass (FAB+) m/z 362 ($\text{M}^+ + 1$). (Anal. calcd. for $\text{C}_{22}\text{H}_{19}\text{NO}_4$ C, 73.11, H, 5.29, N, 3.87. Found C, 73.01, H, 5.26, N, 4.05%).

3a: 7% as white solid, m.p. 140-141°C; ^1H NMR (CDCl_3) δ 2.35-2.59 (m, 3H, CH_2 and 1H of other CH_2), 2.77-2.90 (m, 1H, CH_2), 5.71 (d, 1H, $J = 6$ Hz, CHCl), 7.27 (bs, 1H, =CH), 7.48-

7.50 (m, 3H, Ar-H), 7.83-7.86 (m, 1H, Ar-H). Mass (ESMS) m/z 274.12 ($M^+ + 1$). (Anal. calcd. for $C_{15}H_{12}ClNO_2$ C; 65.82, H; 4.41, N; 5.11. Found C; 65.80, H; 4.47, N; 5.08%).

3c: 12% as pale yellow oil; IR (Neat) 1705 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.46-2.58 (m, 3H, CH_2 and 1H of other CH_2), 2.75-2.95 (m, 1H, CH_2), 5.70 (d, 1H, $J = 6\text{ Hz}$, CHCl), 6.95 (s, 1H, $=\text{CH}$), 7.30-7.51 (m, 4H, $=\text{CH}$ and Ar-H), 7.75-7.77 (m, 1H, Ar-H); Mass (EI) m/z 308 (M^+ , 68). (Anal. calcd. for $C_{15}H_{11}Cl_2NO_2$ C, 58.46, H, 3.59, N, 4.57. Found C, 58.35, H, 3.48, N, 4.40%).

3d: 5% as white solid, m.p. $113\text{-}115^\circ\text{C}$; IR (KBr) 1700 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.44-2.59 (m, 3H, CH_2 and 1H of other CH_2), 2.77-2.90 (m, 1H, CH_2), 5.13 (s, 2H, OCH_2), 5.71 (d, 1H, $J = 6\text{ Hz}$, CHCl), 6.92 (s, 1H, $=\text{CH}$), 7.09 (d, 2H, $J = 9\text{ Hz}$, Ar-H), 7.32-7.46 (m, 6H, 5 Ar-H and $=\text{CH}$), 7.78 (d, 2H, $J = 9\text{ Hz}$, Ar-H); Mass (ESMS) m/z 401.93 ($M^+ + \text{Na}$). (Anal. calcd. for $C_{22}H_{18}ClNO_3$ C, 69.57, H, 4.78, N, 3.69. Found C, 69.23, H, 4.48, N, 3.82%).

4a: 35% as pale yellow solid, m.p. $92\text{-}94^\circ\text{C}$; IR (KBr) $1670, 3403\text{ cm}^{-1}$; ^1H NMR (CDCl_3) δ 2.05 (quintet, 2H, $J = 6.2\text{ Hz}$, CH_2), 2.44-2.53 (m, 4H, 2X CH_2), 5.57 (brs, 1H, CHOH), 6.61 (s, 1H, $=\text{CH}$), 7.02 (t, 1H, $J = 4.0\text{ Hz}$, $=\text{CH}$), 7.42-7.45 (m, 3H, Ar-H), 7.77-7.82 (m, 2H, Ar-H); Mass (EI) m/z 269 (M^+ , 11), 229 (100). (Anal. calcd. for $C_{16}H_{15}NO_3$ C, 71.36, H, 5.61, N, 5.20. Found C, 71.56, H, 5.39, N, 5.12%).

4c: 41% as yellow solid, m.p. $64\text{-}66^\circ\text{C}$; IR (KBr) $1668, 3367\text{ cm}^{-1}$; ^1H NMR (CDCl_3) δ 2.04 (quintet, 2H, $J = 6.0\text{ Hz}$, CH_2), 2.44-2.53 (m, 4H, 2X CH_2), 5.61 (s, 1H, CH), 6.74 (s, 1H, $=\text{CH}$), 7.05 (t, 1H, $J = 4.0\text{ Hz}$, $=\text{CH}$), 7.32-7.50 (m, 3H, Ar-H), 7.68-7.72 (m, 1H, Ar-H); Mass (EI) m/z 303 (M^+ , 18), 222 (6), 178 (73). (Anal. calcd. for $C_{16}H_{14}ClNO_3$ C, 63.26, H, 4.64, N, 4.61. Found C, 63.44, H, 4.67, N, 4.30%).

4d: 58% as pale yellow solid, m.p. 60-62°C; IR (KBr) 1670, 3389 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.04 (m, 2H, J = 6 Hz, CH_2), 2.36-2.52 (m, 4H, 2X CH_2), 5.10 (s, 2H, $\text{C}_6\text{H}_5\text{CH}_2\text{O}$), 5.56 (s, 1H, CH), 6.55 (s, 1H, =CH), 6.99-7.05 (m, 3H, =CH and Ar-H), 7.30-7.42 (m, 5H, Ar-H), 7.72 (d, 2H, J = 8.0 Hz, Ar-H); Mass (FAB+) m/z 376 ($\text{M}^+ + 1$). (Anal. calcd. for $\text{C}_{23}\text{H}_{21}\text{NO}_4$ C, 73.58, H, 5.63, N, 3.73. Found C, 73.43, H, 5.64, N, 3.79%).

5a: 20% as pale yellow oil; IR (Neat) 3371 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.55-1.78 (m, 5H, 2X CH_2 and 1H of other CH_2), 1.97-2.09 (m, 3H, 1 CH_2 and 1H of other CH_2), 3.20 (t, 1H, J = 3 Hz, CH), 4.04 and 4.16 (2d, each 1H, J = 10 Hz, benzylic CH_2), 6.23 (s, 1H, =CH), 6.80 (t, 1H, J = 7.4 Hz, Ar-H), 6.96 (dd, 1H, J = 1.5, 6.4 Hz, Ar-H), 7.06 (dd, 1H, J = 1.5, 7.4 Hz, Ar-H), 7.39-7.42 (m, 3H, Ar-H), 7.72-7.76 (m, 2H, Ar-H); Mass (FAB+) m/z 348 ($\text{M}^+ + 1$). (Anal. calcd. for $\text{C}_{22}\text{H}_{21}\text{NO}_3$ C, 76.05, H, 6.09, N, 4.03. Found C, 76.41, H, 6.14, N, 3.84%).

5c: 21% as a pale yellow solid, m.p. 56-58°C; IR (KBr) 3400 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.54-1.77 (m, 5H, 2X CH_2 and 1H of other CH_2), 1.92-2.07 (m, 3H, CH_2 and 1H of other CH_2), 3.19 (t, 1H, J = 3 Hz, CH), 4.04 and 4.18 (2d, each 1H, J = 16 Hz, benzylic CH_2), 6.38 (s, 1H, =CH), 6.80 (t, 1H, J = 7.4 Hz, =CH), 6.95 (dd, 1H, J_1 = 1.5 Hz, J_2 = 7.4 Hz, Ar-H), 7.08 (dd, 1H, J_1 = 1.5 Hz, J_2 = 7.4 Hz, Ar-H), 7.30-7.47 (m, 3H, Ar-H), 7.67-7.71 (m, 1H, Ar-H); Mass (EI) m/z 382 ($\text{M}^+ + 1$, 85), 180 (100). (Anal. calcd. for $\text{C}_{22}\text{H}_{20}\text{ClNO}_3$ C, 69.19, H, 5.27, N, 3.66. Found C, 69.55, H, 5.24, N, 3.75%).

5d: 25% as pale yellow solid, m.p. 74-76°C; IR (KBr) 3389 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.50-1.70 (m, 5H, 2X CH_2 and 1H of other CH_2), 1.97-2.04 (m, 3H, CH_2 and 1H of other CH_2), 3.19 (t, 1H, J = 3.0 Hz, CH), 4.05 and 4.11 (2d, each 1H, J = 10 Hz, benzylic CH_2), 5.11 (s, 2H, $\text{C}_6\text{H}_5\text{CH}_2\text{O}$), 6.16 (s, 1H, =CH), 6.83 (t, 1H, J = 7.0 Hz, =CH), 6.93-7.07 (m, 4H, Ar-H), 7.31-

7.41 (m, 5H, Ar-H), 7.66 (d, 2H J = 8.0 Hz, Ar-H); Mass (FAB+) m/z 454 (M^+ +1). (Anal. calcd. for $C_{29}H_{27}NO_4$ C, 76.80, H, 5.99, N, 3.08. Found C, 76.81, H, 6.13, N, 3.19%).

7a: 17% as white solid; m.p. 128-129°C; IR (KBr) 3214 cm^{-1} ; 1H NMR ($CDCl_3$) δ 4.14 (s, 2H, CH_2), 4.98 (s, 1H, OH), 6.24 (s, 1H, =CH), 6.79-6.82 (m, 1H, Ar-H), 6.92-6.96 (m, 1H, Ar-H), 7.13-7.18 (m, 2H, Ar-H), 7.39-7.47 (s, 3H, Ar-H), 7.73-7.77 (m, 2H, Ar-H); Mass (FAB+) m/z 252 (M^+ +1). (Anal. calcd. for $C_{16}H_{13}NO_2$ C, 76.47, H, 5.21, N, 5.57 Found C, 76.31, H, 5.19, N, 5.30%).

7c: 21% as white solid; m.p. 118-119°C; IR (KBr) 3210 cm^{-1} ; 1H NMR ($CDCl_3$) δ 4.17 (s, 2H, CH_2), 6.42 (s, 1H, =CH), 6.77-6.82 (m, 1H, Ar-H), 6.89-6.96 (m, 1H, Ar-H), 7.14-7.21 (m, 2H, Ar-H), 7.30-7.48 (m, 3H, Ar-H), 7.67-7.72 (m, 1H, Ar-H); Mass (FAB+) m/z 286 (M^+ +1). (Anal. calcd. for $C_{16}H_{12}ClNO_2$ C, 67.25, H, 4.23, N, 4.90. Found C, 67.47, H, 4.04, N, 5.03%).

7d: 13% as white solid; m.p. 145-147°C; IR (KBr) 3232 cm^{-1} ; 1H NMR ($CDCl_3$) δ 4.12 (s, 2H, CH_2), 5.09 (s, 1H, OCH_2), 6.18 (s, 1H, =CH), 6.79-6.81 (m, 1H, Ar-H), 6.90-6.95 (m, 1H, Ar-H), 7.00 (d, 2H, J = 8.0 Hz, Ar-H), 7.15-7.20 (m, 2H, Ar-H), 7.36-7.41 (m, 5H, Ar-H), 7.68 (d, 2H, J = 8Hz, Ar-H); Mass (ESMS) m/z 358.13 (M^+ +1). (Anal. calcd. for $C_{23}H_{19}NO_3$ C, 77.29, H, 5.35, N, 3.91. Found C, 76.91, H, 5.19, N, 4.30%).

16e: 59% as yellow oil; IR (Neat) 1708, 3310 cm^{-1} ; 1H NMR ($CDCl_3$) 1.97-2.06(m, 2H, CH_2), 2.38-2.48 (m, 4H, 2X CH_2), 5.57 (s, 1H, CHOH), 6.86 (t, 1H, J = 4.0 Hz, =CH), 7.26 (dd, 1H, J = 5.0, 7.5Hz, C-4 of pyridine ring), 7.71-7.76(m, 1H, C-5 of pyridine ring), 8.47 (dd, 1H, J = 1.5Hz, 4.8Hz, C-6 of pyridine ring), 8.54 (d, 1H, J = 2Hz, C-2 of pyridine ring); Mass (FAB+) m/z 286 (M^+ +1). (Anal. calcd. for $C_{12}H_{13}NO_2$ C, 70.91, H, 6.44, N, 6.89. Found C, 70.85, H, 6.39, N, 6.87%).

17a: 19% as yellow oil; IR (Neat) 3210 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.42-1.75 (m, 5H, 2X CH_2 , 1H of other CH_2), 1.93-2.04(m, 3H, CH_2 and 1H of another CH_2), 3.17 (t, 1H, $J=3.0\text{ Hz}$, CH), 3.90 (d, 1H, $J=15\text{ Hz}$, 1H of benzylic CH_2), 4.01 (d, 1H, $J=15\text{ Hz}$, 1H of benzylic CH_2), 6.74 (t, 1H, $J=7.3\text{ Hz}$, Ar-H), 6.86-6.94 (m, 2H, Ar-H), 7.10-7.33(m, 5H, Ar-H) Mass (FAB+) m/z 280 (M^+). (Anal. calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_2$ C, 81.39, H, 7.19. Found C, 81.09, H, 7.17%).

17b: 17% as yellow oil; IR (Neat) 3210 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.52-1.79 (m, 5H, 2X CH_2 , 1H each of other CH_2), 1.96-2.03 (m, 3H, CH_2 & 1H of another CH_2), 2.29 (s, 3H, Ar- CH_3), 3.16 (t, 1H, $J=3.0\text{ Hz}$, CH), 3.85 (d, 1 H, $J=15\text{ Hz}$, 1H of benzylic CH_2), 3.97 (d, 1H, $J=15\text{ Hz}$, 1H of benzylic CH_2), 6.72 (t, 1H, $J=7.3\text{ Hz}$, Ar-H), 6.84-6.91 (m, 2H, Ar-H), 7.05 (d, 2H, $J=8\text{ Hz}$, Ar-H), 7.12 (d, 2H, $J=8\text{ Hz}$, Ar-H) Mass (FAB+) m/z 295 (M^++1). (Anal. calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_3$ C, 81.59, H, 7.53. Found C, 81.44, H, 7.53%).

17d: 23% as yellow oil; IR (KBr) 3210 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.56-1.70 (m, 5H, 2X CH_2 , 1H of other CH_2), 1.93-2.04 (m, 3H, CH_2 and 1H of another CH_2), 3.18 (t, 1H, $J=3.0\text{ Hz}$, CH), 3.97 (d, 1 H, $J=15\text{ Hz}$, 1H of benzylic CH_2), 4.09 (d, 1H, $J=15\text{ Hz}$, 1H of benzylic CH_2), 6.74 (t, 1H, $J=7.3\text{ Hz}$, Ar-H), 6.84-6.91 (m, 2H, Ar-H), 7.04 (d, 2H, $J=8\text{ Hz}$, Ar-H), 7.12 (d, 2H, $J=8\text{ Hz}$, Ar-H) Mass (FAB+) m/z 349 (M^++1). (Anal. calcd. for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{O}_2$ C, 68.95, H, 5.49. Found C, 68.75, H, 5.52%).

Structure elucidation on the basis of HMQC and HMBC of compound **5b**

The ^1H NMR spectrum consists of two sets of ortho-coupled proton of the methyl substituted aromatic ring attached to the 3-position of the isoxazole and three sets of other aromatic ring attached to the methylene present at position 5 of isoxazole. The 3J correlation among these three sets of proton was confirmed by COSY spectrum. On the other hand ^{13}C NMR spectrum consist of 23 carbon signals. The spectral editing by DEPT experiment provided 1-methyl, 5-methylene, 9-methine and 8 quaternary carbons. The signals at 4.00 and 4.11 ppm of methylene and 6.20 ppm of methine in ^1H NMR and the signal at 99.6 ppm in ^{13}C NMR served as markers for the identification of hemiacetal. The complete structure of hemiacetal was however elucidated on the basis of the HMQC and HMBC spectra. In HMQC spectrum the crosspeak was observed between the proton signal at 4.00 and 4.11 ppm and carbon at 27.7 ppm while the proton at 6.20 ppm gave crosspeak with carbon at 99.6 ppm. In the HMBC spectrum the methylene proton at 4.00 and 4.11 showed contour peak with the carbon at 172.9 (C-5), 162.3 (C-3), 153.4 (C-7), 127.1 (C-5), 122.0 (C-6) and 99.6 (C-4). The methine proton at δ 6.20 showed contour peak with 153.4 (C-2), 98.9 (C-9) and 127.8 (C-5). These long-range correlations formed the basis of building up the structure of hemiacetal.

¹H-NMR spectrum of compound 2b

Current Data Parameters
 NAME May11-2001
 EXPNO 70
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20010511
 Time 9:59
 INSTRUM gpc200
 PROBHD 5 mm Dual 13
 PULPROG zg30
 TO 32768
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 4139.073 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 1625.5
 DW 120.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.00 usec
 PL1 -4.00 dB
 SF01 200.1312359 MHz

F2 - Processing parameters
 SI 16384
 SF 200.1300084 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

10. NMR plot parameters
 CX 20.00 cm
 F1P 11.030 ppm
 F1 2201.43 Hz
 F2P -1.000 ppm
 F2 -200.13 Hz
 PPMCH 0.60000 ppm/cm
 HZCM 120.07800 Hz/cm

MY1512.LRP ADP-251B/MS A PATRA
Date run : 05-15-2001 Operator : PRAKASH/A.VOHRA/SUNIL

Scan : 8 RT= 0:53 No.ions= 223 Base=100.0ZF TIC=260070

CENTRAL DRUG RESEARCH INSTITUTE
05-15-2001

MY1512.LRP ADP-251B/MS A PATRA
Date run : 05-15-2001 Operator : PRAKASH/A.VOHRA/SUNIL

Scan : 9 RT= 0:53 No.ions= 12 Base=100.0ZF TIC=102079

MASS	%BASE
271	15.7
270	33.2
269	45.2
252	9.4
214	17.0
199	9.7
161	11.5
159	12.5
158	100.0
132	6.7
131	19.2
130	31.5

NAME 05130251a.f
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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Time 17 37
INSTRUM DRX300
PROBHD 5 mm Multinu
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.421029 sec
RG 228.1
CW 104.400 usec
DE 6.00 usec
TE 297.0 K
D1 1.0000000 sec

===== CHANNEL f1 =====
NUC1 ¹H
P1 6.28 usec
PL1 -3.00 dB
SF01 300.1318148 MHz

F2 - Processing parameters
SI 15384
SF 300.130063 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 0.90

1D NMR plot parameters
CX 20.00 cm
F1P 8.413 ppm
F1 2525.07 Hz
F2P -0.284 ppm
F2 -85.32 Hz
PRNCM 0.43488 ppm/cm
HZCM 130.51954 Hz/cm

FAB/MS spectrum of
compound 3b

MASS SPECTRUM Data File: 1IJN06S
Sample: ADP-251(A) MRS ARUNDHATI PATRA
RT: 0.12" FAB(Pos.) GC 1.4c BP: m/z 149.0000 Int. 52.8035 Lv 0.00
Scan# (1 to 3)

S-11

¹H-NMR spectrum of compound 4b

Current Data Parameters
NAME Apr27-2001
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010427
Time 15:42
INSTRUM dpx200
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4139.073 Hz
FIDRES 0.125314 Hz
AQ 3.9584243 sec
RG 2298.8
DM 120.800 usec
DE 5.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PL1 -4.00 dB
SF01 200.1312355 MHz

F2 - Processing parameters
SI 15384
SF 200.1300082 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
FIP 11.000 ppm
F1 2201.43 Hz
F2P -1.000 ppm
F2 -200.13 Hz
PPMCM 0.50000 ppm/cm
HZCM 120.07800 Hz/cm

¹³C-NMR spectrum of
Compound 4b

Current Data Parameters
NAME Apr27-2001
EXPNO 40
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010430
Time 10.49
INSTRUM ddx200
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 423
DS 4
SWH 12562.814 Hz
FIDRES 0.191693 Hz
AQ 2.6083827 sec
RG 128
DW 39.800 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 ¹³C
P1 6.00 usec
PL1 -6.00 dB
SFO1 50.3282440 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ¹H
P2 100.00 usec
PL2 -3.00 dB
PL12 18.00 dB
PL13 18.00 dB
SFO2 200.1305005 MHz

F2 - Processing parameters
SI 32768
SF 50.3227090 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40

ID NMR plot parameters
CX 20.00 cm
FIP 215.000 ppm
F1 10819.38 Hz
F2P -5.000 ppm
F2 -251.61 Hz
PPMCM 11.00000 ppm/cm
HZCM 553.54980 Hz/cm

के. डी. र. सं.
C. D. R. I.

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-248B 04-26-2001

AP2615.LRP ADP-248B/MR R ARORA

Date run : 04-26-2001

Operator : PRAKASH/A.VOHRA/SUNIL

Scan : 6 RT= 0:38 No.ions= 254 Base= 68.2%F TIC=449940

EIMS spectrum of
compound 4b

CENTRAL DRUG RESEARCH INSTITUTE

248B 04-26-2001

AP2615.LRP ADP-248B/MR R ARORA

Date run : 04-26-2001

Operator : PRAKASH/A.VOHRA/SUNIL

Scan : 6 RT= 0:38 No.ions= 26 Base= 68.2%F TIC=153008

MASS %BASE

284	31.8
283	43.9
282	15.3
266	17.4
256	9.2
255	43.6
254	16.4
237	17.9
228	17.1
227	40.9
226	9.0
221	11.1
220	9.6
212	20.5
210	10.8
200	12.9
199	79.9
198	10.5
185	11.8
166	12.2
160	72.8
159	14.2
158	100.0
138	18.8
132	16.3

¹H-NMR spectrum of compound 5b

ADP-248 (A)

Current Data Parameters
NAME Oct03-2001
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20011003
Time 15.44
INSTRUM dxt200
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4139.073 Hz
FIDRES 0.126314 Hz
AQ 3.3584243 sec
RG 574.7
DM 120.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

Channel f1
NUC: 1H
P1 9.00 usec
PL1 -4.00 dB
SFO: 200.1312359 MHz

F2 - Processing parameters
SI 16384
SF 200.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

10 NMR plot parameters
CX 20.00 cm
F1 11.000 ppm
F2 2201.43 Hz
F3 -1.000 ppm
F4 -200.13 Hz
PPM0 0.50000 ppm/c
HZ0 120.07800 Hz/cm

S-15

¹³C-NMR spectrum
of compound 5b.

S-16

Current Data Parameters
NAME 0316003-5b.f
EXP 1
PROCNO 1

DEPT spectrum
of compound 5b

F2 - Acquisition Parameters

Date_ 20110516
Time 5:27
INSTRUM QNP300
PROBHD 5 mm Nucleus
PULPROG zgpg30
TD 65536
FID 32768
SOLVENT CDCl3
VS 207
DS 0
SWH 18932.393 Hz
FIDRES 0.5719 Hz
AQ 0.570404 sec
RG 11500
JM 25.550 MHz
DE 1.00 MHz
TE 300.0 K
CNST2 145.6306000
Q1 2.0000000 sec
Q2 0.0034625 sec
Q12 0.0002000 sec
DELTA 0.0001273 sec

===== CHANNEL f1 =====

NUC1 13C
P1 10.00 sec
PL1 0.00 dB
PL2 0.00 dB
SF01 75.162190 MHz

===== CHANNEL f2 =====

CPDPRG2 zgpg30
NUC2 1H
P2 0.99 sec
PL2 0.00 dB
PL12 0.00 dB
SF02 300.131475 MHz

F2 - Processing Parameters

SI 1.12384
SF 75.162190 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.50

F2 NMR plot parameters

AX 20.00 cm
F1P 125.338 MHz
F1 125.338 MHz
F2P 400.146 MHz
F2 400.146 MHz
DPMCH 0.00000000
PCN 0.00000000

S-17

HMBC
spectr
of com
5b.

S-18

20311

spect

of cent
55

FABMS spectrum of
Compound 5b

4-OCT- 1 16:13

Data File: 110T042

MASS SPECTRUM

Sample: ADP-248[A] MRS A PATRA

RT 0.00 GC 1.4c BP: m/z 362.1141 Int. 16.0094 Lv 0.00

FAB(Pos.)

Scan# (1 to 2)

S-20

¹H-NMR spectrum of compound 7b.

Current Data Parameters
 NAME Nov24-2001
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20011124
 Time 10:17
 INSTRUM dd200
 PROBO 5 mm Dual 13
 PULPROG zg30
 TO 32768
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 4135.073 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 574.7
 CW 120.800 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.0000000 sec

***** CHANNEL f1 *****
 NUC1 1H
 P1 9.00 usec
 PL1 -4.00 dB
 SFO1 200.1312359 MHz

F2 - Processing parameters
 SI 16384
 SF 200.1300235 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.30 cm
 F1P 11.000 ppm
 F1 2201.43 Hz
 F2P -1.000 ppm
 F2 -200.13 Hz
 PPMCM 0.60000 ppm/cm
 HZCM 120.07801 Hz/cm

S-21

Current: Data Parameters
 NAME .ds1acd259a.rr
 EXPNO 5
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20011202
 Time 21:55
 INSTRUM DRX300
 PROBHD 5 mm NulTnu
 PULPROG zgpg30
 TO 32768
 SOLVENT COC13
 NS 10500
 DS 0
 SWH 19960.080 Hz
 FIDRES 0.609133 Hz
 AQ 0.8208884 sec
 RG 8192
 CW 25.050 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec

***** CHANNEL f1 *****
 NUC1 13C
 P1 10.00 usec
 PL1 -3.00 dB
 SFO1 75.4767751 MHz

***** CHANNEL f2 *****
 CPOPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 -3.00 dB
 PL12 20.00 dB
 SFO2 300.1319935 MHz

F2 - Processing parameters
 SI 16384
 SF 75.4677503 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 0.90

1D NMR plot parameters
 CX 20.00 cm
 FIP 206.103 ppm
 F1 15554.12 Hz
 F2P -9.669 ppm
 F2 -729.69 Hz
 PRMCM 10.78859 ppm/cm
 HZCM 814.19080 Hz/cm

S-22

FAB MS spectrum of
Compound 7b

24-NOV- 1 14:58

Data File: 1INV24T

MASS SPECTRUM

Sample: ADP-269 MRS A PATRA

RT 0.12" BP: m/z 154.0000 Int. 49.0692 Lv 0.00

FAB(Pos.) GC

Scan# (1 to 3)

FAB/MS spectrum of
compound 14b

3-JAN- 2 10:55

DATA FILE: 2IJN03A

MASS SPECTRUM

Sample: ADP-286 MRS A PATRA

RT: 0.00 min FAB(Pos.) GC

Scan# (1 to 2)

BP: 154.0000 Int. 41.7480 Lv 0.00

¹H-NMR spectrum of compound 16e

S-26

FABMS spectrum of
Compound 16c

MASS SPECTRUM Data File: 110T12Y
Sample: ADP-264[B] MRS A PATRA
RT 0.12" FAB(Pos.) GC 1.4c BP: m/z 135.9820 Int. 41.4022 Lv 0.00
Scan# (1 to 3)

12-OCT- 1 14:52

S-27

¹H-NMR spectrum of
Compound 17b

Current Data Parameters
NAME Oct09-2001
EXPNO 180
PROCNO 1

F2 - Acquisition Parameters
Date_ 20011009
Time 13.31
INSTRUM dpx200
PROBHD 5 mm QNP 13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4139.073 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 574.7
DM 120.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PL1 -4.00 dB
SFO1 200.1312359 MHz

F2 - Processing parameters
SI 16384
SF 200.1300088 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 11.000 ppm
F1 2201.43 Hz
F2P -1.000 ppm
F2 -200.13 Hz
PPMV 0.60000 ppm/cm
HZCM 120.07500 Hz/cm

CENTRAL DRUG RESEARCH INSTITUTE
10-12-2001

OT1213.LRP ADP-268B/MRA A PATRA

Date run : 10-12-2001

Operator : PRAKASH/A.SONI/SUNIL

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C.D.R.I. Scan : 5 RT= 0:35 No.ions= 267 Base= 14.3% TIC=100555

EIMS spectrum
of compound 17

CENTRAL DRUG RESEARCH INSTITUTE
10-12-2001

OT1213.LRP ADP-268B/MRA A PATRA

Date run : 10-12-2001

Operator : PRAKASH/A.SONI/SUNIL

Scan : 5 RT= 0:35 No.ions= 40 Base= 14.3% TIC= 41402

MASS	%BASE
298	12.3
297	31.4
296	52.3
295	100.0
280	10.2
280	14.6
279	15.6
278	30.9
277	40.6
276	40.0
266	11.6
265	17.1
264	26.3
263	38.6
262	40.4
258	10.2
257	10.3
253	23.4
252	35.5
250	16.3
249	20.1
236	10.1
225	14.6
224	15.7
210	13.3
203	10.7
203	15.7

190 13.0

189 14.3

186 15.0

S-29