Supporting Information

for

Gold(I)-catalyzed hydroarylation reaction of aryl (3-iodoprop-2-yn-1-yl) ethers: synthesis of 3-iodo-2*H*-chromene derivatives

Pablo Morán-Poladura, Eduardo Rubio and José M. González*

Address: Departamento de Química Orgánica e Inorgánica and Instituto Universitario de Química Organometálica "Enrique Moles", Universidad de Oviedo, C/Julián Clavería 8, Oviedo, 33006, Spain

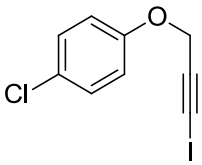
Email: José M. González* - jmgd@uniovi.es

*Corresponding author

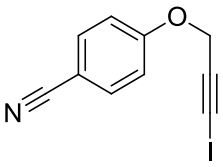
Characterization data for compounds 1a–j and 2a–j; ^{1}H and ^{13}C NMR spectra for compounds 1a–j and 2a–j; X-ray molecular structure for 2f; HPLC chromatograms for 1j and 2j and structural assignment for compounds 3

Summary

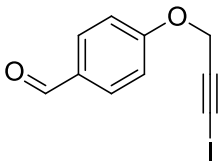
1.- Characterization data for compounds 1a–1j and 2a–2j



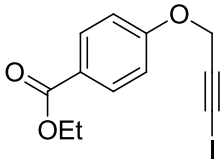
1-Chloro-4-[(3-iodoprop-2-yn-1-yl)oxy]benzene (1a)
White solid; mp 50-52 °C (lit.: 52-53 ºC [1]); Molecular formula: C_9H_6OClI; Purified by flash chromatography (Hex); HRMS (EI): calcd. for C_9H_6OClI: 291.9152, found: 291.9158; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.28 (d, *J* = 9.1 Hz, 2H), 6.92 (d, *J* = 9.1 Hz, 2H), 4.82 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 156.1 (C), 129.4 (CH), 126.6 (C), 116.2 (CH), 88.7 (C), 57.6 (CH_2), 5.3 (C).



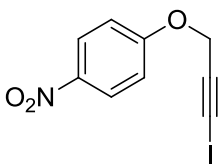
4-[(3-Iodoprop-2-yn-1-yl)oxy]benzonitrile (1b)
White solid; mp 160-161 °C (lit.: 161-162 ºC [1]); Molecular formula: $C_{10}H_6NOI$; Purified by flash chromatography (Hex:AcOEt, 20:1); HRMS (EI): calcd. for $C_{10}H_6NOI$: 282.9494, found: 282.9496; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.63 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 4.90 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 160.7 (C), 134.0 (CH), 119.0 (C), 115.6 (CH), 105.0 (C), 87.8 (C), 57.4 (CH_2), 6.5 (C).



4-[(3-Iodoprop-2-yn-1-yl)oxy]benzaldehyde (1c)
White solid; mp 154-155 °C; Molecular formula: $C_{10}H_7O_2I$; Purified by flash chromatography (Hex:AcOEt, 20:1); HRMS (EI): calcd. for $C_{10}H_7O_2I$: 285.9491, found: 285.9487; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 9.93 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 4.93 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 190.8 (CH), 162.3 (C), 131.9 (CH), 130.6 (C), 115.1 (CH), 88.1 (C), 57.4 (CH_2), 6.1 (C).

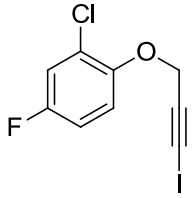


Ethyl 4-[(3-iodoprop-2-yn-1-yl)oxy]benzoate (1d)
White solid; mp 90-91 °C; Molecular formula: $C_{12}H_{11}O_3I$; Purified by flash chromatography (Hex:AcOEt, 40:1); HRMS (EI): calcd. for $C_{12}H_{11}O_3I$: 329.9753, found: 329.9756; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.02 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 4.89 (s, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 166.6 (C), 161.5 (C), 131.9 (CH), 124.2 (C), 114.8 (CH), 88.8 (C), 61.1 (CH_2), 57.7 (CH_2), 14.8 (CH_3), 6.1 (C).



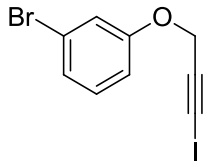
1-[(3-Iodoprop-2-yn-1-yl)oxy]-4-nitrobenzene (1e)
Yellow solid; decomp.: 187-189 °C (lit.: 184-185 ºC [1]); Molecular formula: $C_9H_6NO_3I$; Purified by flash chromatography (Hex:AcOEt, 10:1); HRMS (EI): calcd. for $C_9H_6NO_3I$: 302.9392, found: 302.9395; ^{1}H NMR

(300 MHz, DMSO-d_6), δ: 8.23 (d, J = 9.3 Hz, 2H), 7.18 (d, J = 9.3 Hz, 2H), 5.10 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6), δ: 162.8 (C), 141.8 (C), 126.3 (CH), 115.8 (CH), 87.8 (C), 58.3 (CH_2), 16.6 (C).



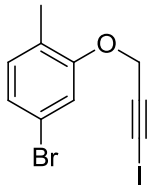
2-Chloro-4-fluoro-1-[(3-iodoprop-2-yn-1-yl)oxy]benzene (1f)

Pale yellow solid; mp 45-46 °C; Molecular formula: C_9H_5OFClI; Purified by flash chromatography (Hex); HRMS (EI): calcd. for C_9H_5OFClI: 309.9058, found: 309.9057; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.16 (dd, J = 8.0, 2.9 Hz, 1H), 7.06 (dd, J = 9.1, 4.9 Hz, 1H), 6.97 (ddd, J = 9.1, 7.7, 2.9 Hz, 1H), 4.90 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 157.3 (d, J = 243.6 Hz, C), 149.7 (d, J = 2.3 Hz, C), 124.3 (d, J = 10.6 Hz, C), 117.8 (d, J = 26.1 Hz, CH), 115.9 (d, J = 8.7 Hz, CH), 114.1 (d, J = 22.7 Hz, CH), 88.5 (s, C), 59.1 (s, CH_2), 6.0 (s, C); ^{19}F NMR (282 MHz, $CDCl_3$), δ: -119.8.



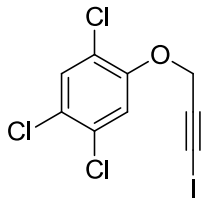
1-Bromo-3-[(3-iodoprop-2-yn-1-yl)oxy]benzene (1g)

Colourless oil; Molecular formula: C_9H_6OBrI; Purified by flash chromatography (Hex); HRMS (EI): calcd. for C_9H_6OBrI: 335.8647, found: 335.8649; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.23-7.12 (m, 3H), 6.92 (d, J = 7.5 Hz, 1H), 4.83 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 158.2 (C), 130.6 (CH), 124.8 (CH), 122.8 (C), 118.4 (CH), 113.7 (CH), 88.5 (C), 57.5 (CH_2), 5.6 (C).



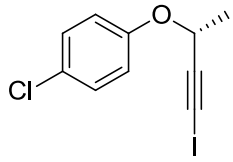
4-Bromo-2-[(3-iodoprop-2-yn-1-yl)oxy]-1-methylbenzene (1h)

White solid; mp 77-78 °C; Molecular formula: $C_{10}H_8OBrI$; Purified by flash chromatography (Hex); HRMS (EI): calcd. for $C_{10}H_8OBrI$: 349.8803, found: 349.8802; ^{1}H NMR (300 MHz, CD_2Cl_2), δ: 7.12-7.03 (m, 3H), 4.88 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2), δ: 156.8 (C), 132.3 (CH), 126.8 (C), 124.6 (CH), 119.6 (C), 115.5 (CH), 89.3 (C), 58.1 (CH_2), 16.0 (CH_3), 5.1 (C).



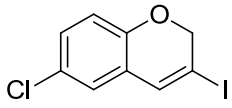
1,2,4-Trichloro-5-[(3-iodoprop-2-yn-1-yl)oxy]benzene (1i)

White solid; mp 114-115 °C (lit.: 114-115 ºC [1]); Molecular formula: $C_9H_4OCl_3I$; Purified by flash chromatography (Hex); HRMS (EI): calcd. for $C_9H_4OCl_3I$: 359.8372, found: 359.8374; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.49 (s, 1H), 7.16 (s, 1H), 4.91 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 152.5 (C), 131.6 (C), 131.5 (CH), 125.8 (C), 123.0 (C), 116.3 (CH), 87.9 (C), 59.2 (CH_2), 7.5 (C).



(*R*)-1-Chloro-4-[(4-iodobut-3-yn-2-yl)oxy]benzene (1j)

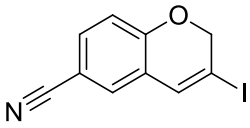
White solid; mp 79-80 °C; Molecular formula: $C_{10}H_8OClI$; Purified by flash chromatography (Hex); HRMS (EI): calcd. for $C_{10}H_8OClI$: 305.9308, found: 305.9300; Specific rotation (T =25,8 °C; c =0,0100 g/mL in CH_2Cl_2), $[\alpha]_D$= 201,40 deg·cm^3/g·dm ; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.27 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 4.93 (q, J = 6.6 Hz, 1H), 1.67 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), δ: 156.3 (C), 129.7 (CH), 126.8 (C), 117.5 (CH), 93.7 (C), 65.9 (CH), 22.7 (CH_3), 4.1 (C).



6-Chloro-3-iodo-2*H*-chromene (2a)

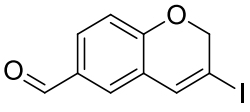
White solid; mp 79-80 °C; Molecular formula: C_9H_6OClI; Purified by flash chromatography (Hex); HRMS (EI): calcd. for C_9H_6OClI: 291.9152, found: 291,9153; ^{1}H NMR (401 MHz, CD_2Cl_2), δ: 7.11 (dd, J = 8.6, 2.5 Hz, 1H), 7.01 (bs, 1H), 6.92 (d, J = 2.5 Hz, 1H), 6.74 (d, J = 8.6 Hz, 1H), 4.90 (d, J = 1.7 Hz, 2H); ^{13}C NMR (75

MHz, CD_2Cl_2), δ: 150.9 (C), 132.7 (CH), 129.2 (CH), 126.2 (C), 125.2 (CH), 124.2 (C), 117.2 (CH), 89.7 (C), 73.8 (CH_2).



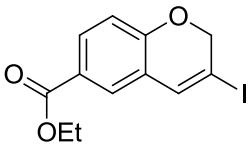
3-Iodo-2*H*-chromene-6-carbonitrile (2b)

White solid; mp 94-95 °C; Molecular formula: $C_{10}H_6NOI$; Purified by flash chromatography (Hex:AcOEt, 30:1); HRMS (EI): calcd. for $C_{10}H_6NOI$: 282.9494, found: 282.9493; ^{1}H NMR (300 MHz, CD_2Cl_2), δ: 7.46 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.05 (bs, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 5.02 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2), δ: 156.1 (C), 134.3 (CH), 132.3 (CH), 129.8 (CH), 123.5 (C), 119.0 (C), 117.2 (CH), 105.3 (C), 90.7 (C), 74.5 (CH_2).



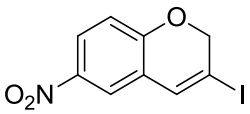
3-Iodo-2*H*-chromene-6-carbaldehyde (2c)

White solid; mp 120-121 °C; Molecular formula: $C_{10}H_7O_2I$; Purified by flash chromatography (Hex:AcOEt, 30:1); HRMS (EI): calcd. for $C_{10}H_7O_2I$: 285.9491, found: 285.9490; ^{1}H NMR (300 MHz, CD_2Cl_2), δ: 9.83 (s, 1H), 7.68 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.10 (bs, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 5.01 (d, *J* = 1.7 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2), δ: 190.6 (CH), 157.8 (C), 133.1 (CH), 132.6 (CH), 131.1 (C), 127.3 (CH), 123.1 (C), 116.8 (CH), 89.7 (C), 74.5 (CH_2).



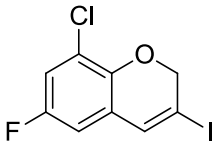
Ethyl 3-iodo-2*H*-chromene-6-carboxylate (2d)

White solid; mp 72-73 °C; Molecular formula: $C_{12}H_{11}O_3I$; Purified by flash chromatography (Hex); HRMS (EI): calcd. for $C_{12}H_{11}O_3I$: 329.9753, found: 329.9750; ^{1}H NMR (400 MHz, CD_2Cl_2), δ: 7.84 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.61 (d, *J* = 2.1 Hz, 1H), 7.08 (bs, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 4.98 (d, *J* = 1.7 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2), δ: 165.6 (C), 156.0 (C), 133.0 (CH), 131.4 (CH), 127.3 (CH), 124.0 (C), 122.3 (C), 115.7 (CH), 88.6 (C), 74.0 (CH_2), 60.8 (CH_2), 14.1 (CH_3).



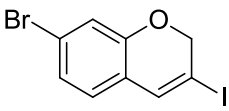
3-Iodo-6-nitro-2*H*-chromene (2e)

Yellow solid; mp 112-113 °C; Molecular formula: $C_9H_6NO_3I$; Purified by flash chromatography (Hex:AcOEt, 10:1); HRMS (EI): calcd. for $C_9H_6NO_3I$: 302.9392, found: 302.9394; ^{1}H NMR (300 MHz, DMSO), δ: 8.03 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.99 (d, *J* = 2.7 Hz, 1H), 7.36 (bs, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 5.08 (d, *J* = 1.7 Hz, 2H); ^{13}C NMR (75 MHz, DMSO), δ: 158.2 (C), 142.2 (C), 131.8 (CH), 126.4 (CH), 123.3 (C), 122.1 (CH), 117.2 (CH), 93.5 (C), 74.6 (CH_2).



8-Chloro-6-fluoro-3-iodo-2*H*-chromene (2f)

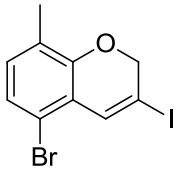
White solid; mp 129-130 °C; Molecular formula: C_9H_5OFClI; Purified by flash chromatography (Hex); HRMS (EI): calcd. for C_9H_5OFClI: 309.9058, found: 309.9053; ^{1}H NMR (300 MHz, CD_2Cl_2), δ: 7.04 (bs, 1H), 6.99 (dd, *J* = 8.3, 2.9 Hz, 1H), 6.64 (dd, *J* = 8.1, 2.9 Hz, 1H), 4.99 (d, *J* = 1.6 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2), δ: 156.8 (d, *J* = 242.4 Hz, C), 144.9 (d, *J* = 2.6 Hz, C), 132.9 (d, *J* = 2.0 Hz, CH), 125.0 (d, *J* = 9.2 Hz, C), 121.8 (d, *J* = 10.9 Hz, C), 117.1 (d, *J* = 26.3 Hz, CH), 111.2 (d, *J* = 24.0 Hz, CH), 91.3 (s, C), 74.6 (s, CH_2); ^{19}F NMR (282 MHz, CD_2Cl_2), δ: -121.2.



7-bromo-3-iodo-2*H*-chromene (2g)

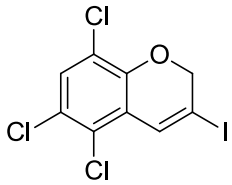
Unseparable regioisomeric mixture of **2g**-(7-bromo-3-iodo-2*H*-chromene) and **2g´**-(5-bromo-3-iodo-2*H*-chromene) (**2g**:**2g´**, 3:1); Molecular formula: C_9H_6OBrI; Purified by flash chromatography (Hex); HRMS (EI): calcd. for C_9H_6OBrI: 335.8647, found: 335.8630; ^{1}H NMR (300 MHz, CD_2Cl_2), δ: 7.41 (bs, 1H-**2g´**), 7.17 (dd, *J* = 8.0, 1.1 Hz, 1H-**2g´**), 7.10 – 6.95 (m, 3H-**2g**, 1H-**2g´**), 6.85 – 6.75 (m, 1H-**2g**, 1H-**2g´**), 4.91 (d, *J* = 1.7 Hz, 2H-**2g**), 4.89 (d, *J* = 1.6 Hz, 2H-**2g´**); ^{13}C NMR (75

MHz, CD_2Cl_2), δ: 153.55(C-**2g´**), 152.9 (C-**2g**), 133.0 (CH-**2g**), 132.5 (CH-**2g´**), 130.1 (CH-**2g´**), 126.7 (CH-**2g**), 125.6 (CH-**2g´**), 124.6 (CH-**2g**), 122.8 (C-**2g´**), 122.1 (C-**2g**), 121.9 (C-**2g**), 120.1 (C-**2g´**), 119.1 (CH-**2g**), 115.4 (CH-**2g´**), 89.9 (C-**2g´**), 88.2 (C-**2g**), 73.8 (CH_2-**2g**), 73. 7 (CH_2-**2g´**).



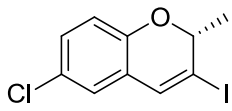
5-Bromo-3-iodo-8-methyl-2*H*-chromene (2h)

White solid; decomp.:160-162°C; Molecular formula: $C_{10}H_8OBrI$; Purified by flash chromatography (Hex); HRMS (EI) calcd. for $C_{10}H_8OBrI$: 349.8803, found: 349.8798; ^{1}H NMR (400 MHz), δ: 7.38 (t, *J* = 1.7 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 4.89 (d, *J* = 1.7 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2), δ: 151.5 (C), 132.8 (CH), 131.7 (CH), 125.1 (C), 124.8 (CH), 122.2 (C), 117.2 (C), 89.5 (C), 73.6 (CH_2), 15.1 (CH_3).



5,6,8-Trichloro-3-iodo-2*H*-chromene (2i)

White solid; m.p. =119-120°C; Molecular formula: $C_9H_4OCl_3I$; Purified by flash chromatography (Hex); HRMS (EI) calcd. for $C_9H_4OCl_3I$: 359.8372, found: 359.8370; ^{1}H NMR (300 MHz, CD_2Cl_2), δ: 7.46 (t, *J* = 1.7 Hz, 1H), 7.37 (s, 1H), 5.02 (d, *J* = 1.7 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2), δ: 147.6 (C), 129.9 (2 x CH), 126.7 (C), 125.2 (C), 123.1 (C), 120.4 (C), 91.8 (C), 73.9 (CH_2).



(*R*)-6-Chloro-3-iodo-2-methyl-2*H*-chromene (2j)

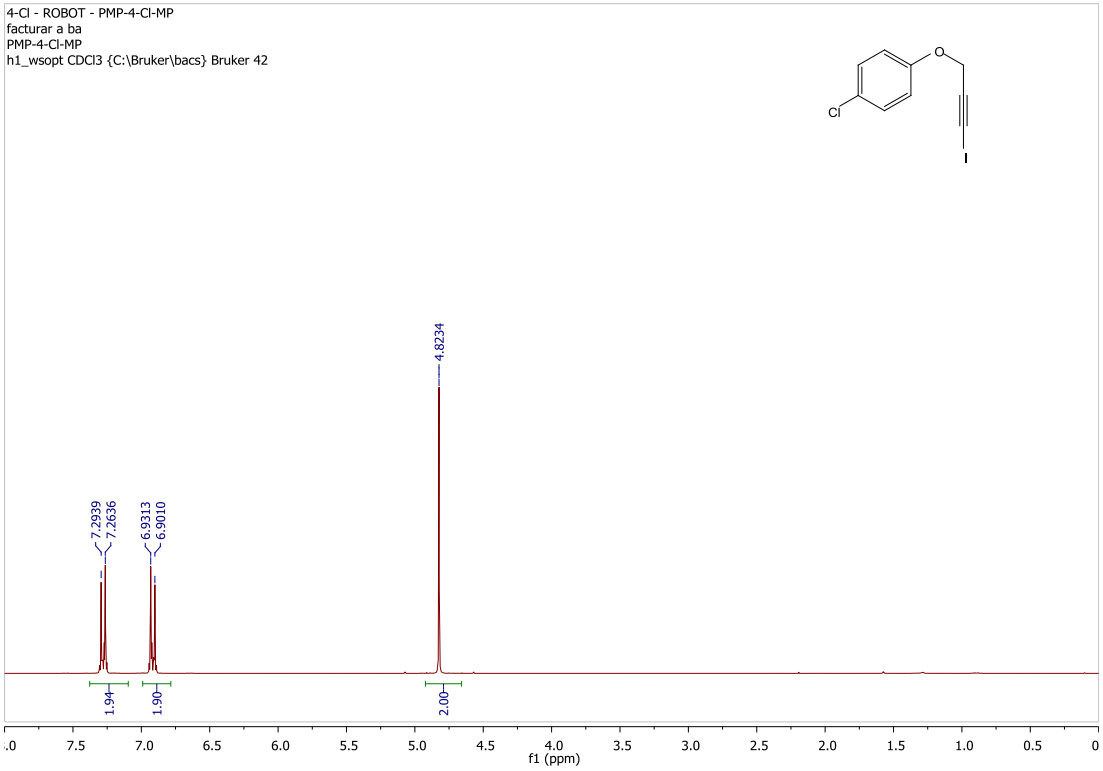
Pale yellow oil; Molecular formula: $C_{10}H_8OClI$; Purified by flash chromatography (Hex); HRMS (EI): calcd. for $C_{10}H_8OClI$: 305.9308, found: 305.9306; Specific rotation (T =25,8^{o}C; c =0,0108 g/mL in CH_2Cl_2), $[\alpha]_D$= -109,50 deg·cm^3/g·dm; ^{1}H NMR (300 MHz, CD_2Cl_2), δ: 7.13 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.99 (bs, 1H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 5.07 (qd, *J* = 6.6, 0.6 Hz, 1H), 1.48 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2), δ: 150.1 (C), 132.7 (CH), 129.6 (CH), 126.3 (C), 125.4 (CH), 124.4 (C), 118.3 (CH), 96.4 (C), 79.4 (CH), 19.1 (CH_3).

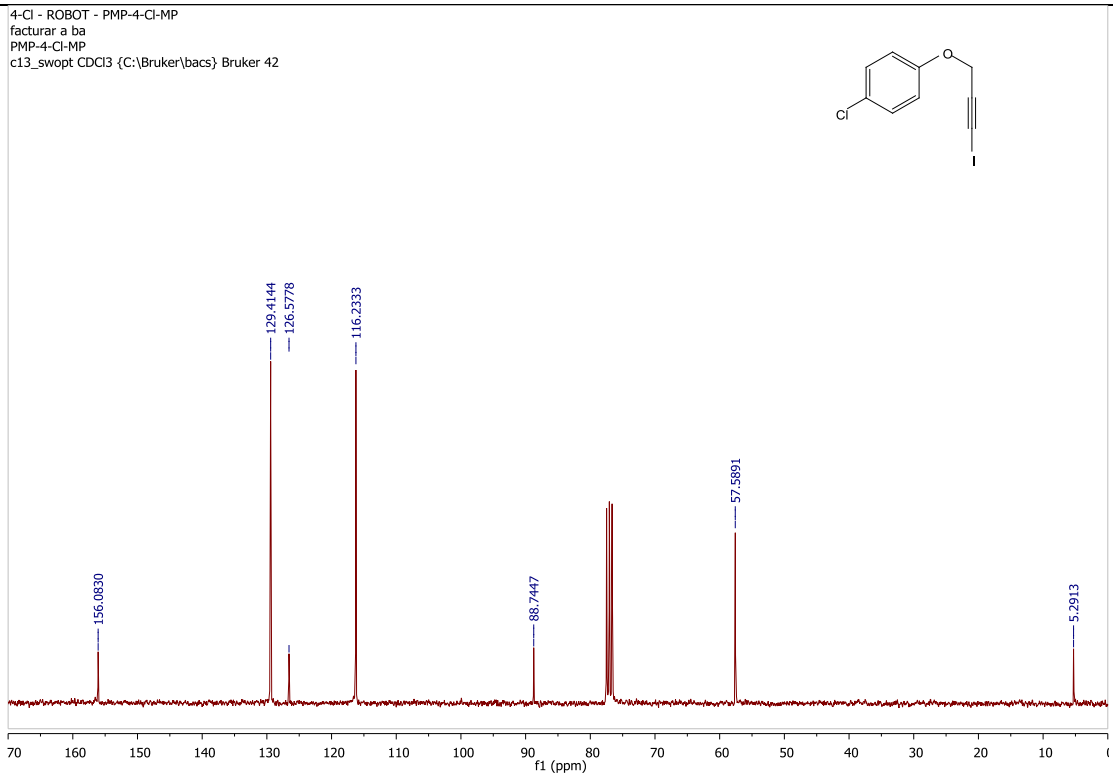
References

1. Seki, S. Nomiya, B. Owaga, H. Halopropargyl aryl ethers. JP Patent 39019791, Sep 12, 1964

2. ^{1}H and ^{13}C NMR spectra for compounds **1a**–**1j** and **2a**–**2j**

1a





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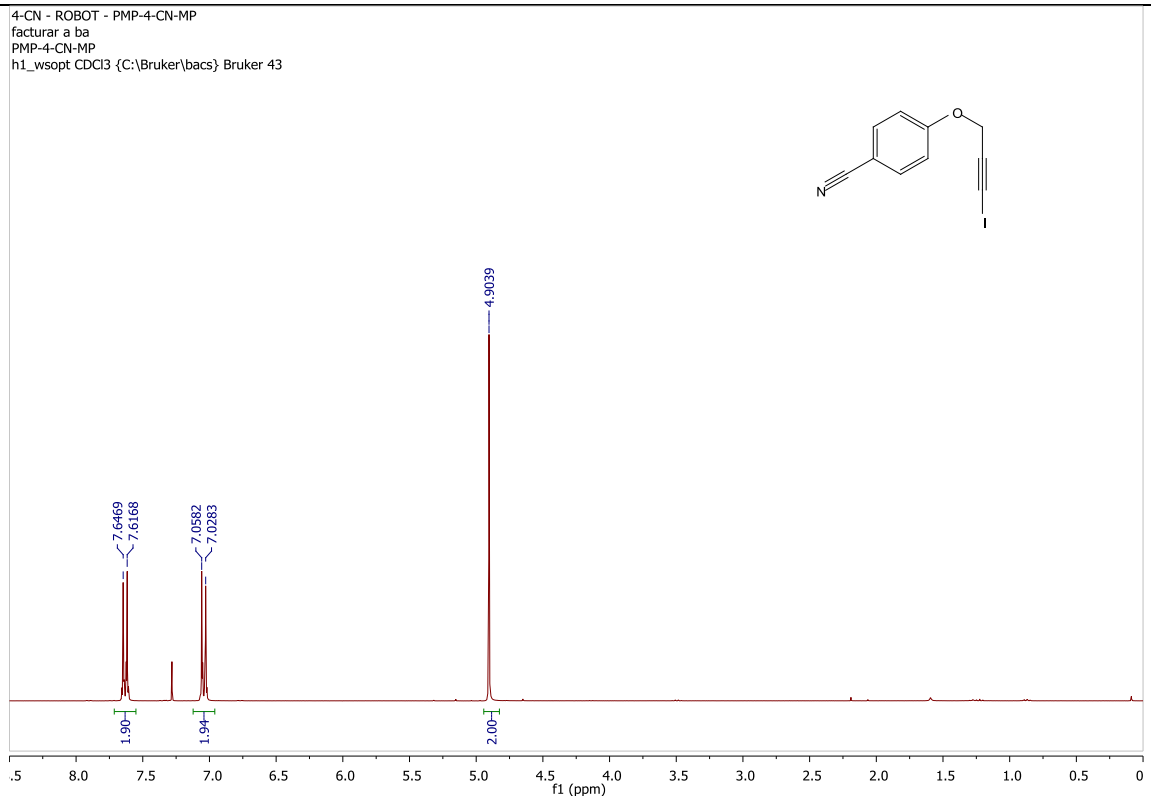
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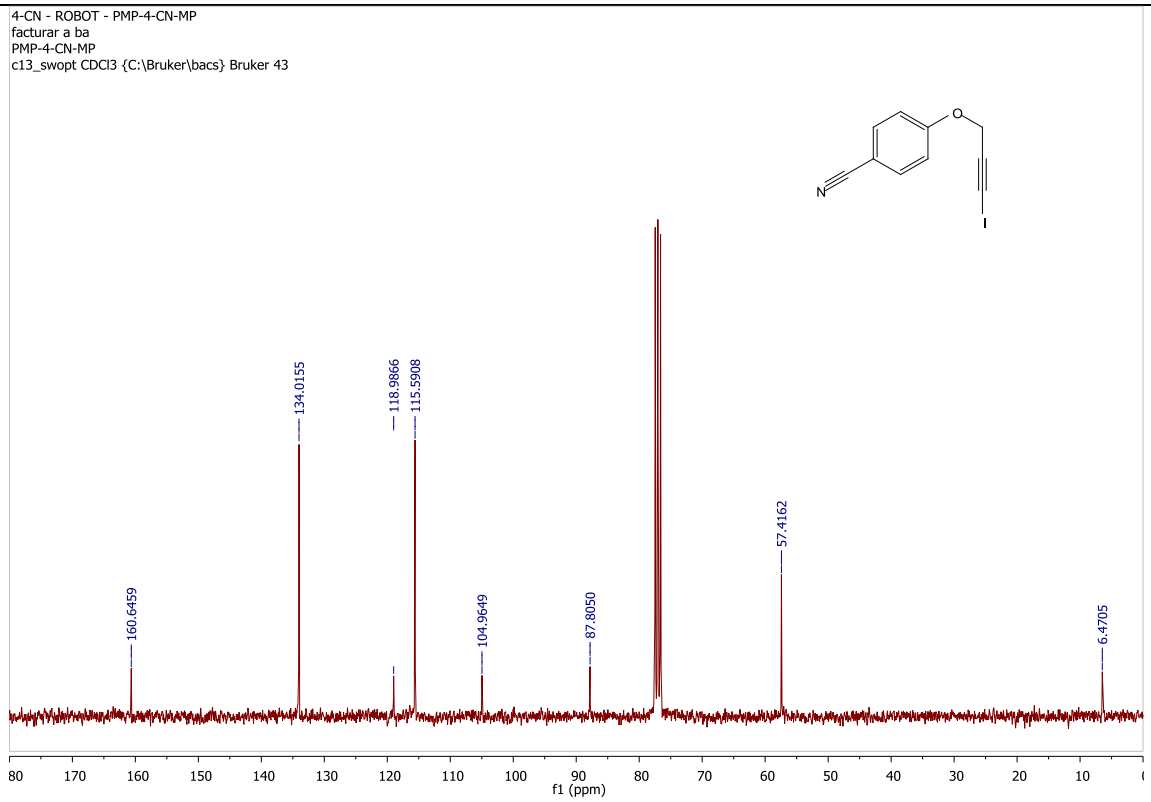
1.94
2.00
f1 (ppm)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PMP-4-CN-MP
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N
I
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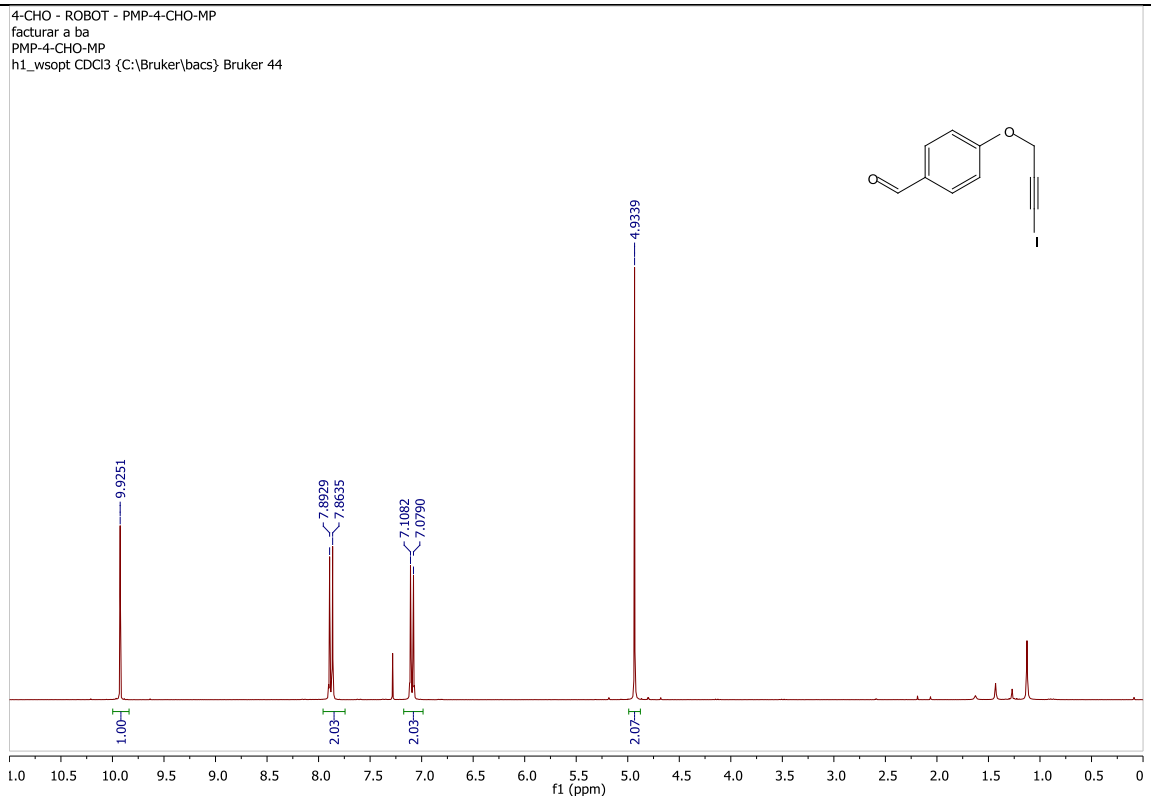
f1 (ppm)

1c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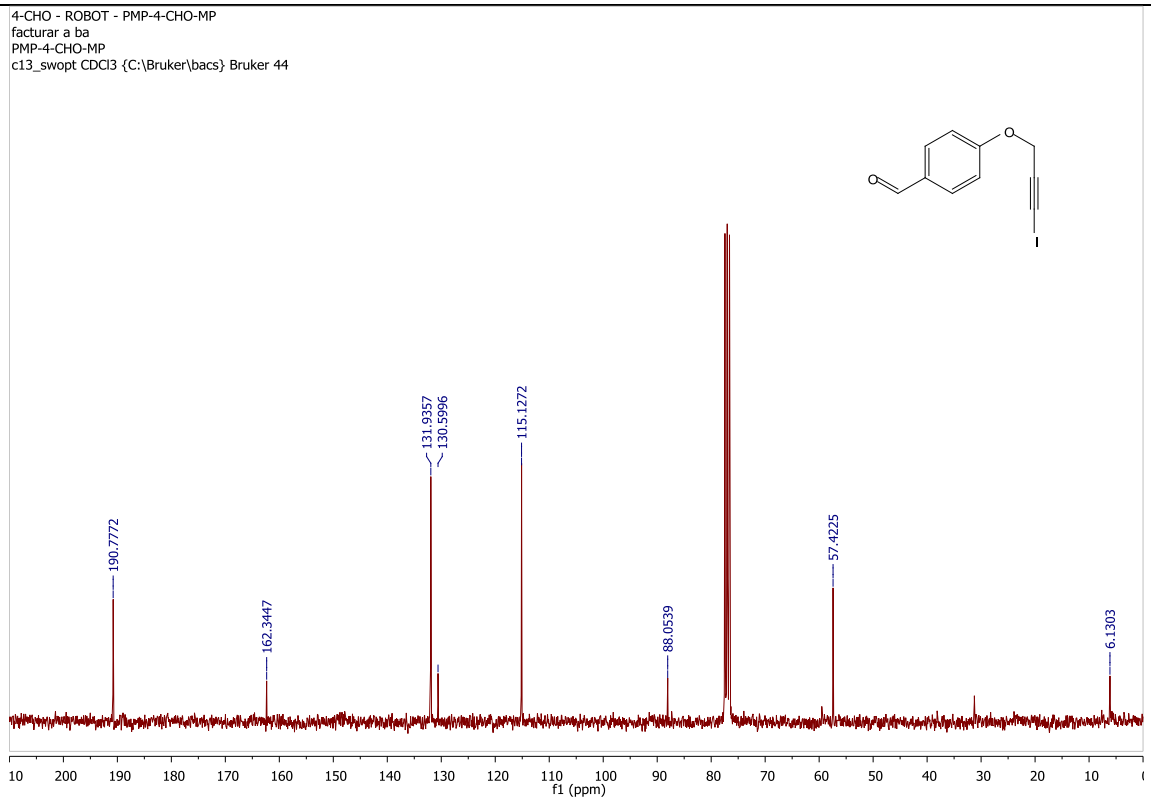
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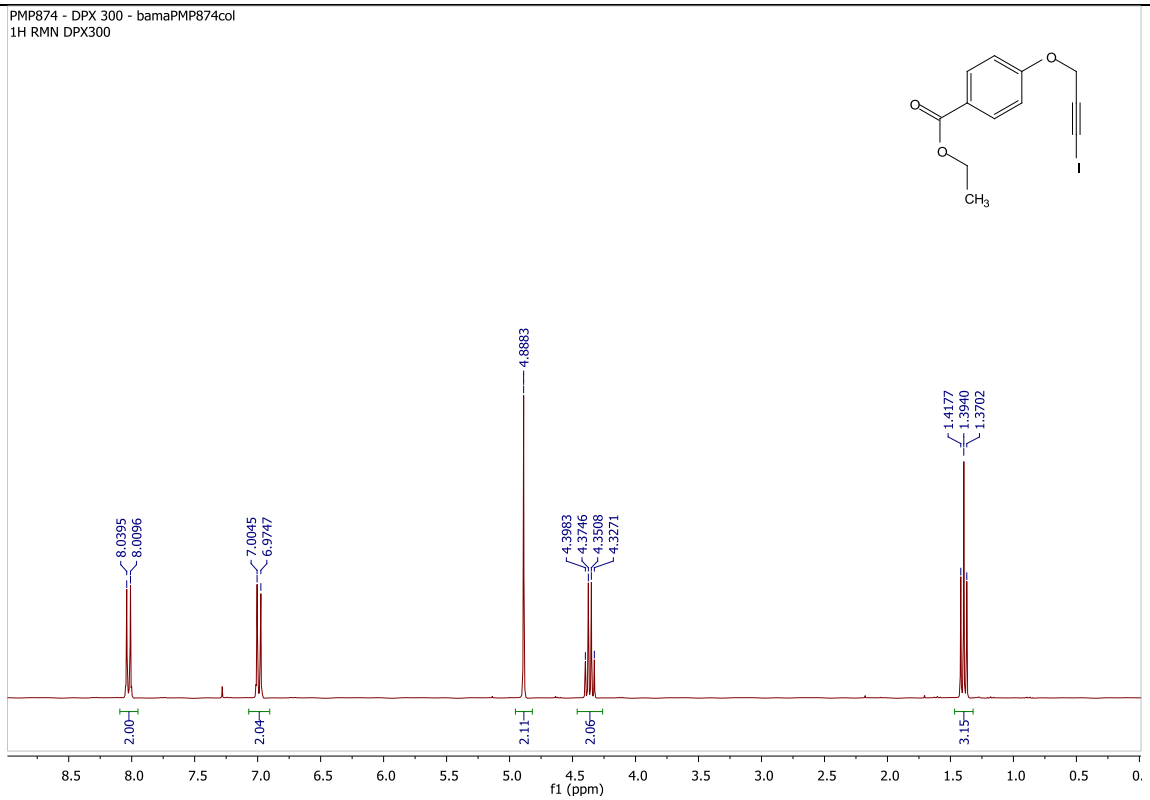
f1 (ppm)

1d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4.3508
4.3271
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1.3940
1.3702
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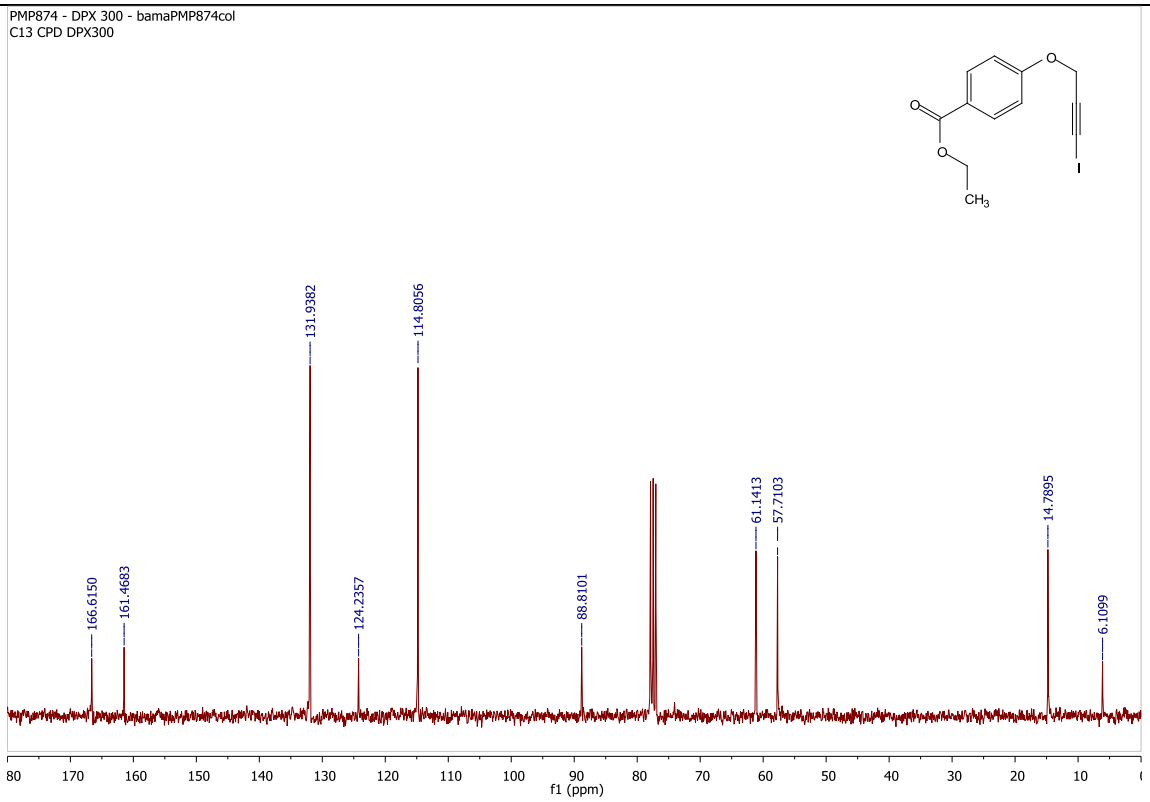
2.04
2.11
2.06
3.15
f1 (ppm)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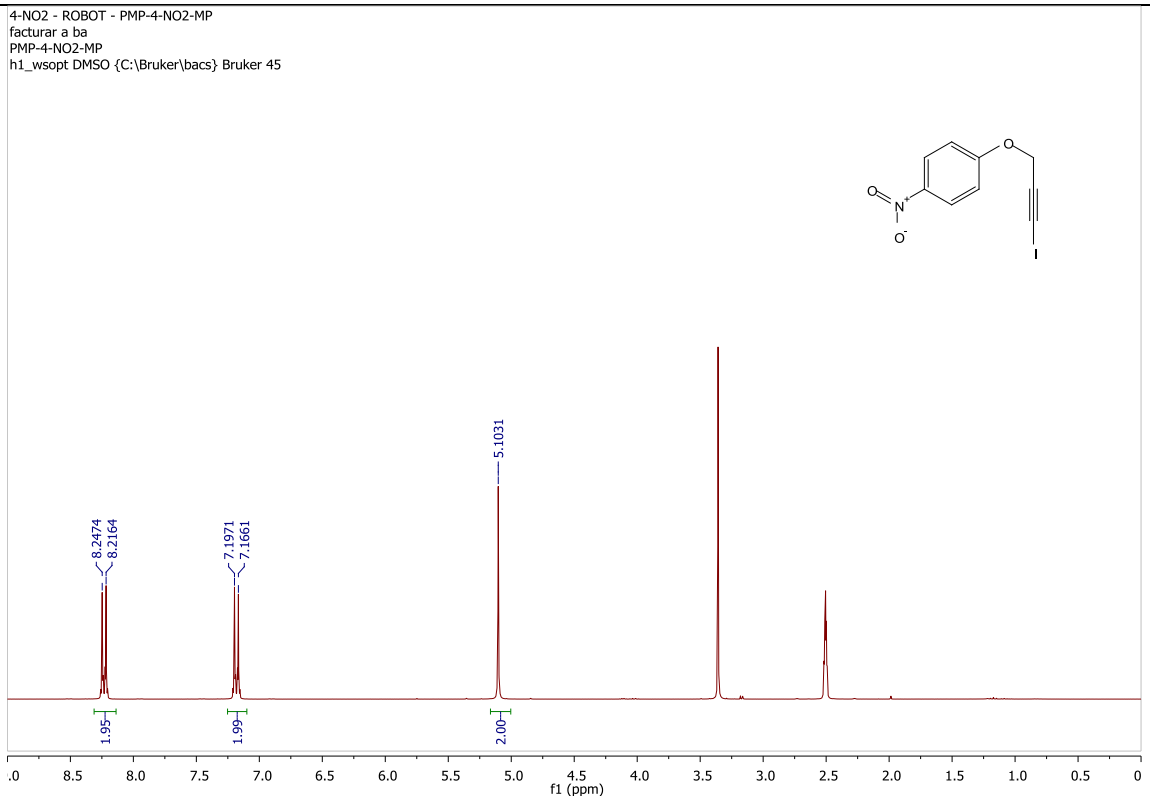
14.7895
6.1099
f1 (ppm)

1e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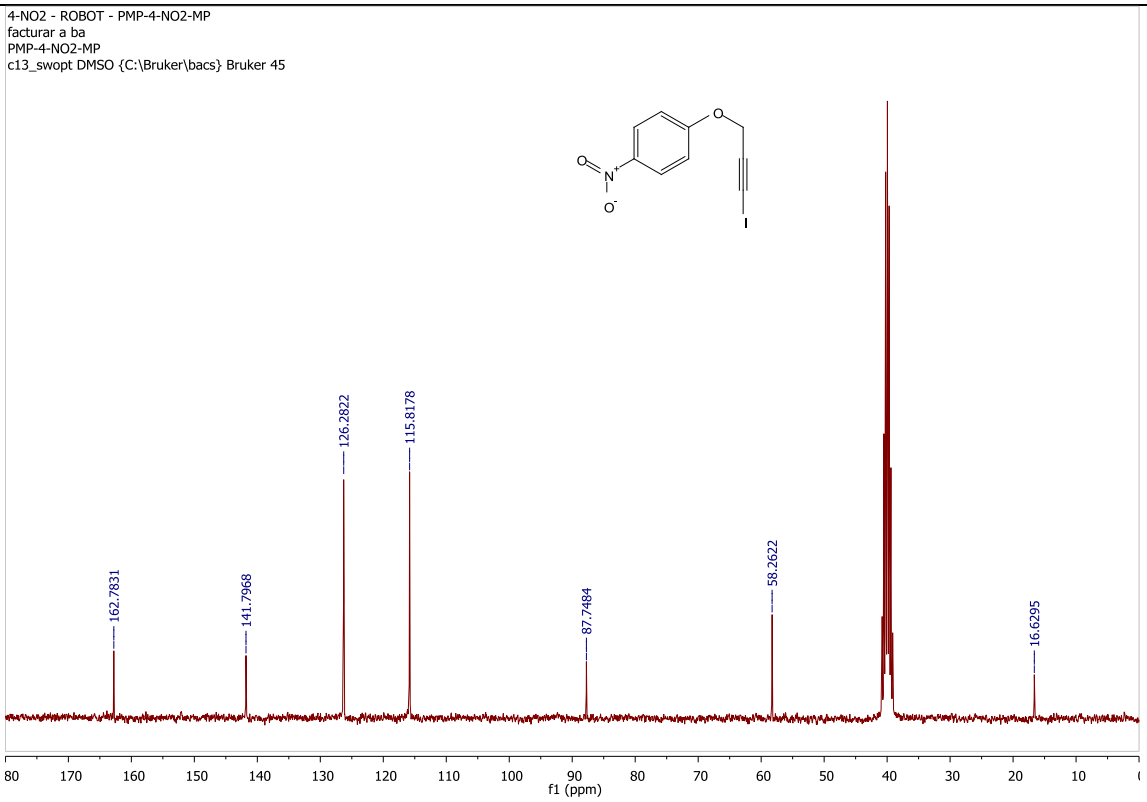
f1 (ppm)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PMP-4-NO2-MP
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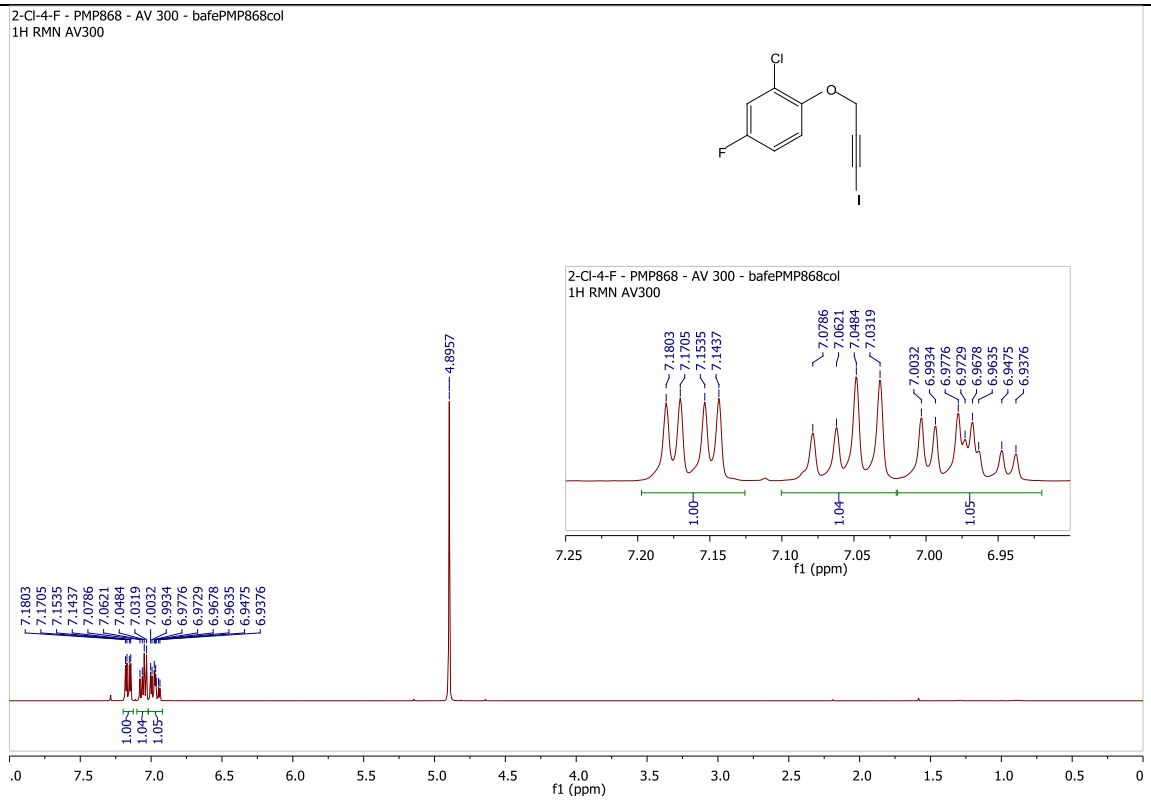
1f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7.1535
7.1437
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7.0484
7.0319
7.0032
6.9934
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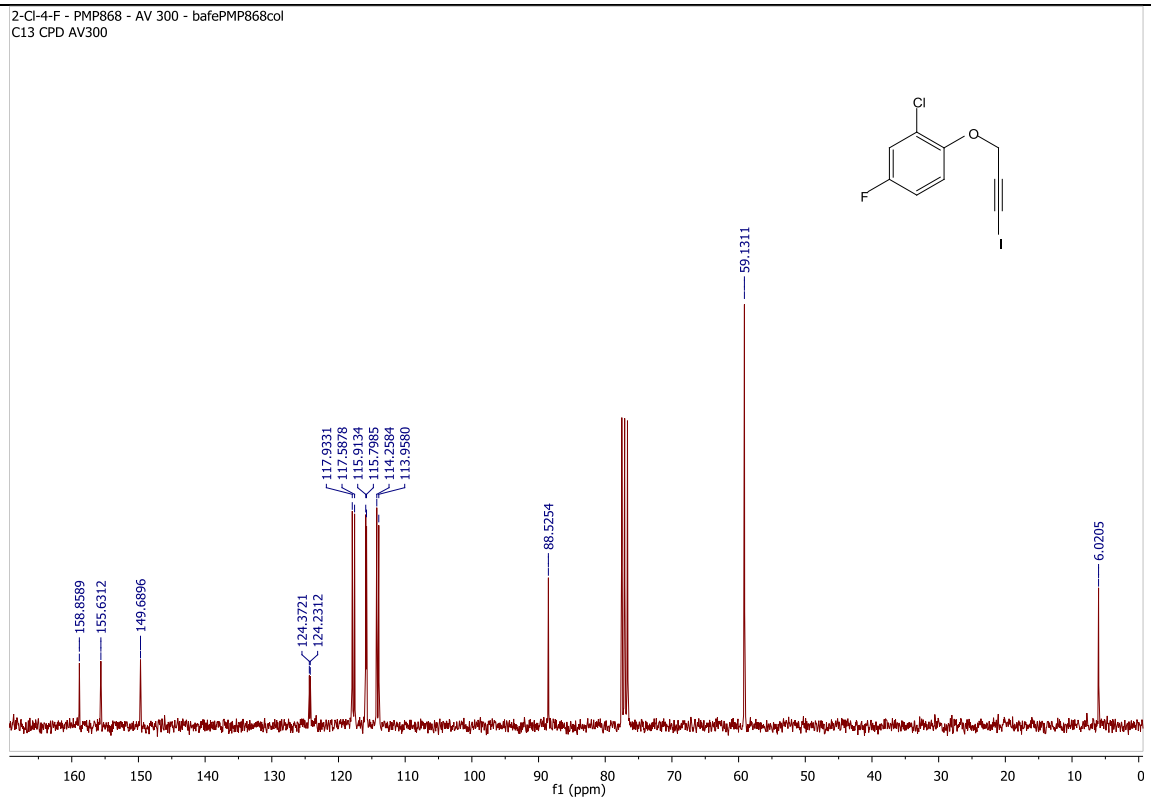
1.05
f1 (ppm)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O
F
I
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124.3721
124.2312
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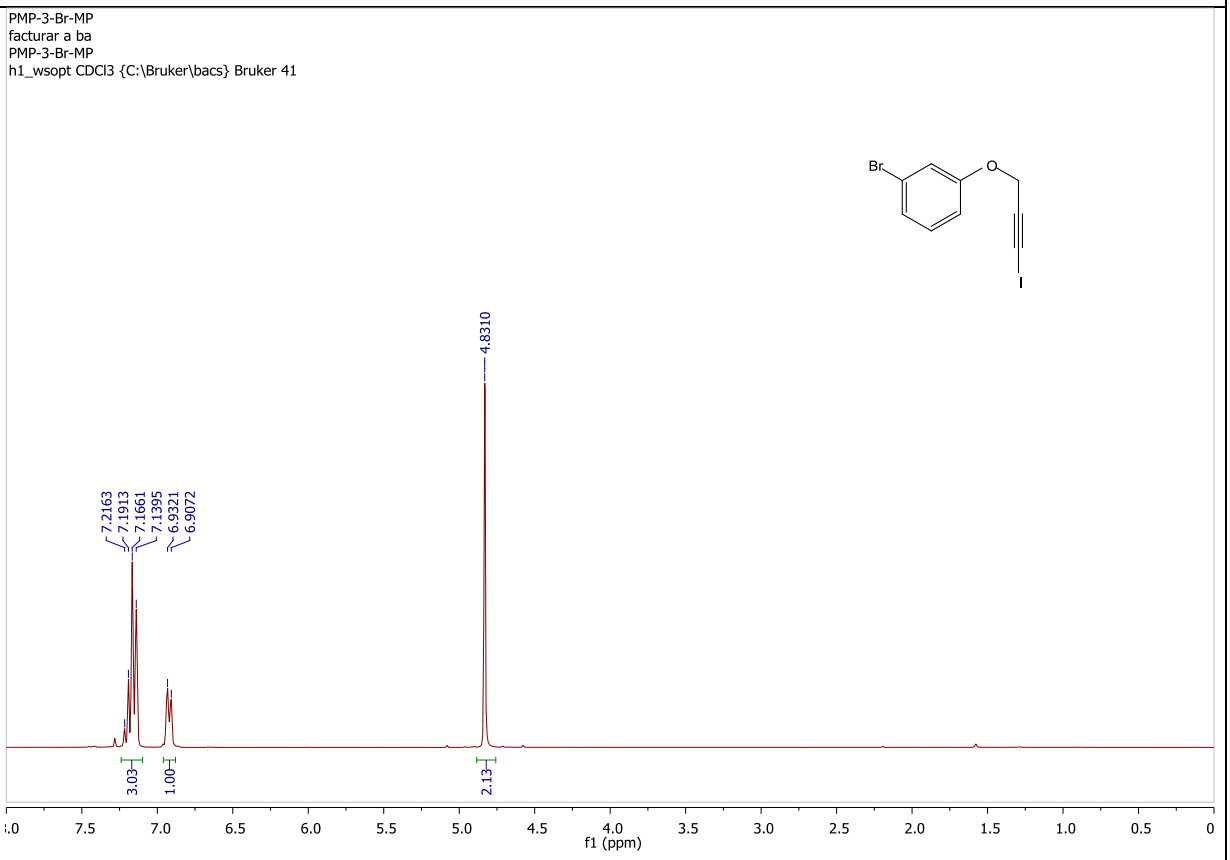
f1 (ppm)

1g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I
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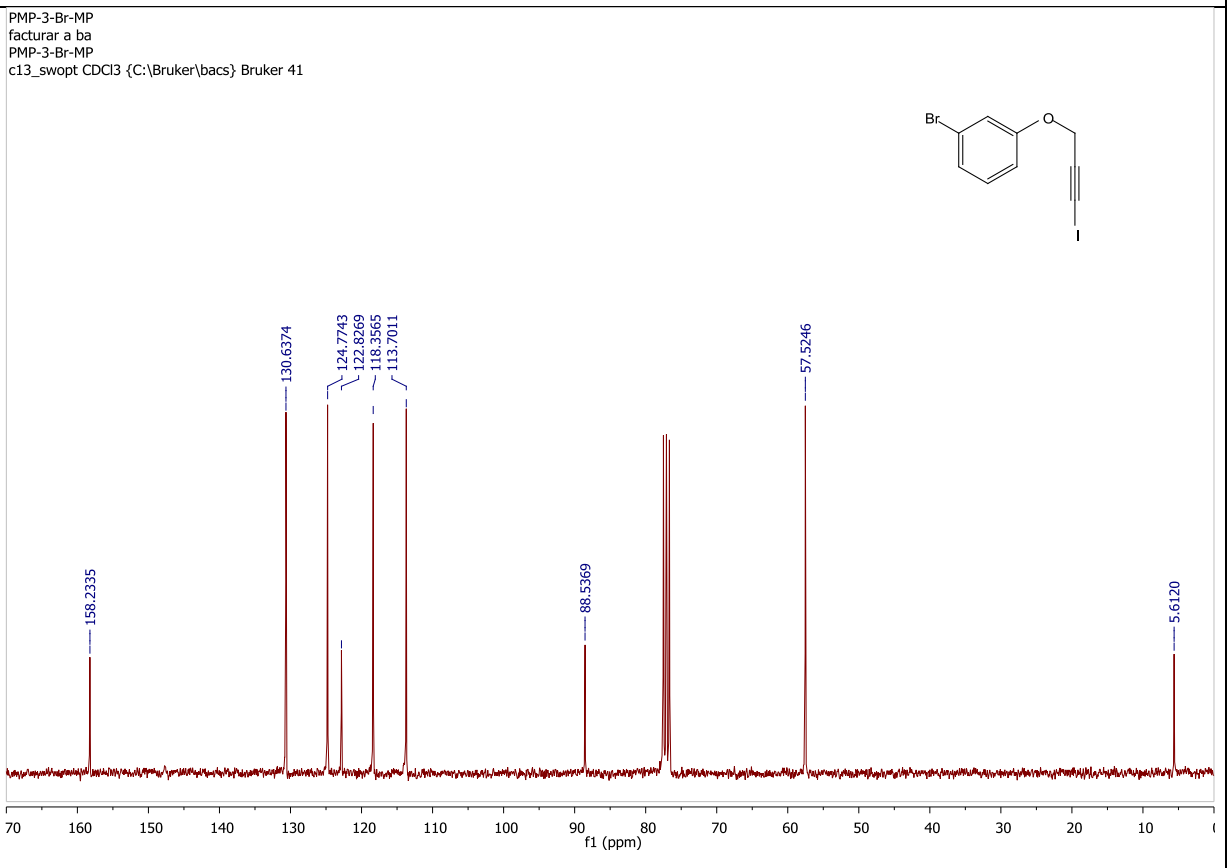
f1 (ppm)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Br
O
I
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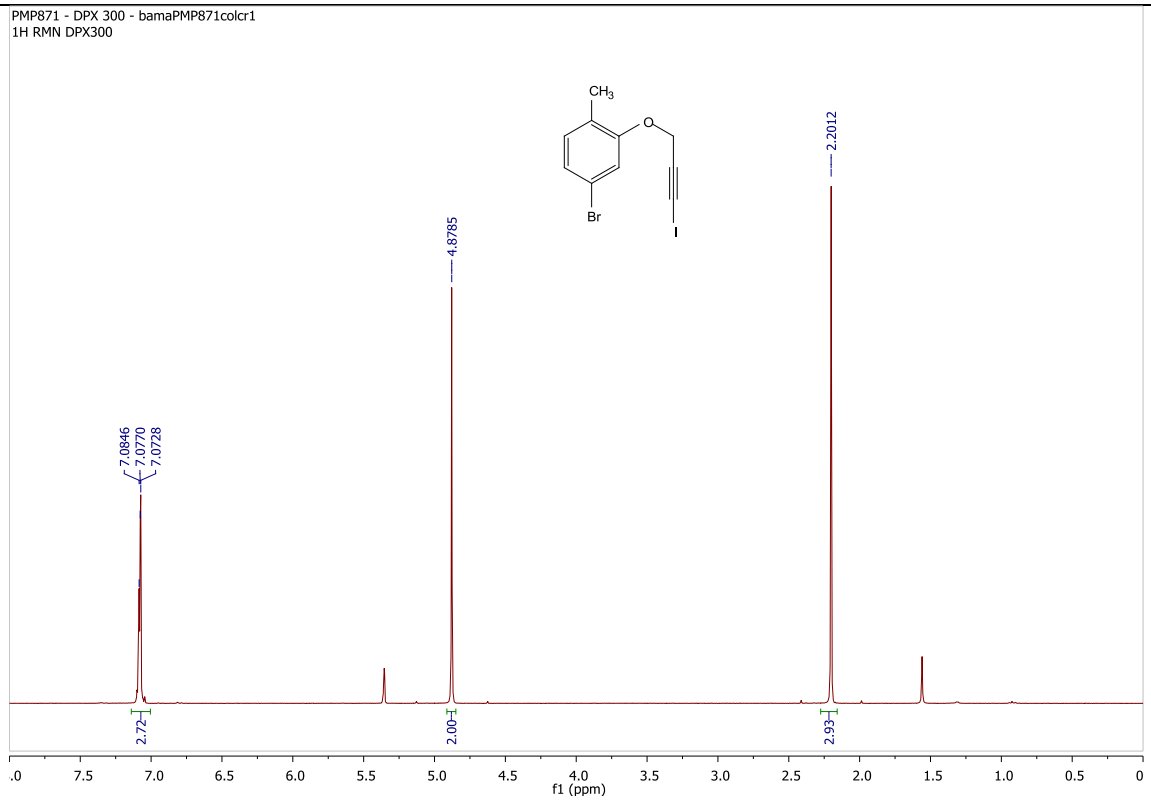
1h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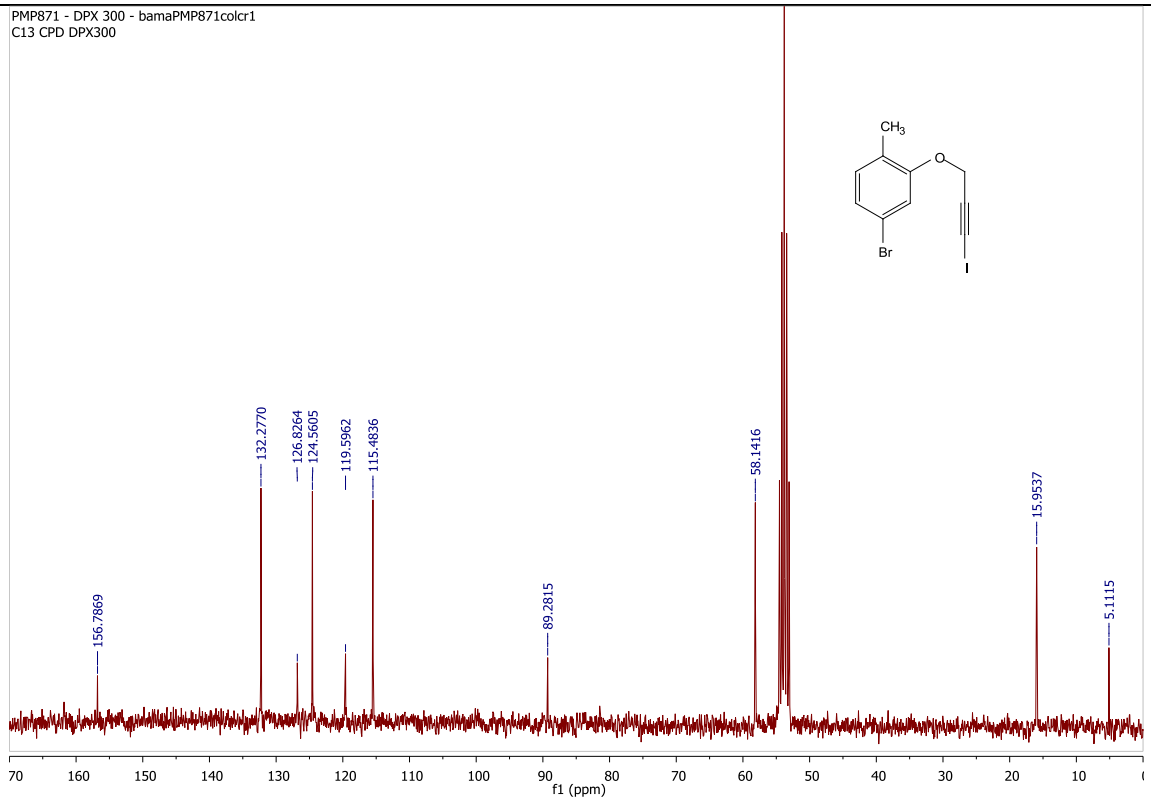
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O
Br
I
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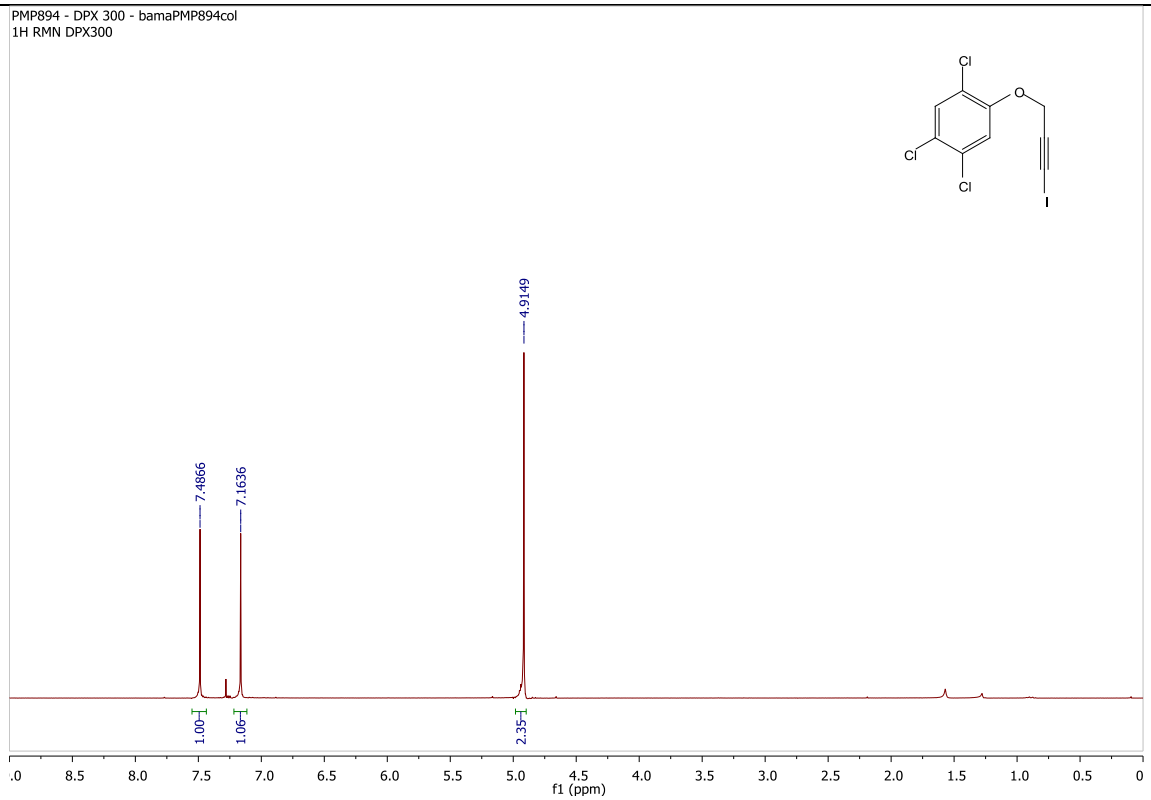
f1 (ppm)

1i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Cl
Cl
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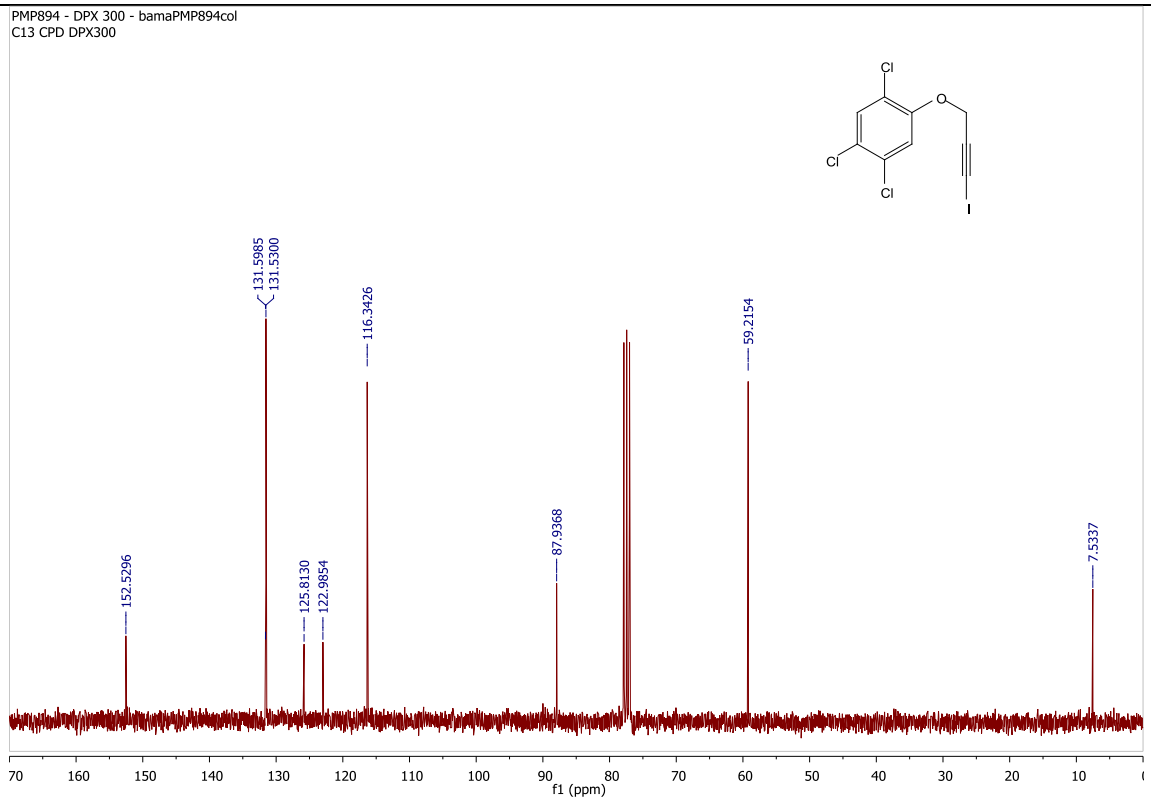
f1 (ppm)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Cl
Cl
I
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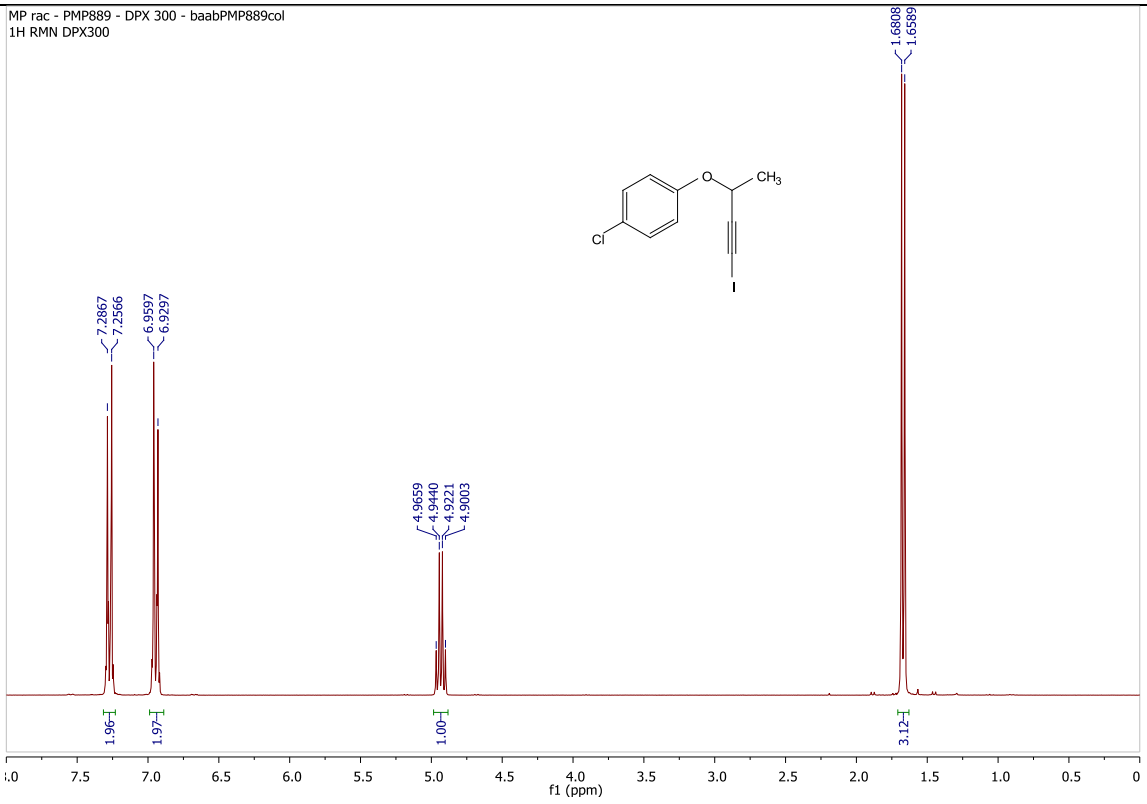
1j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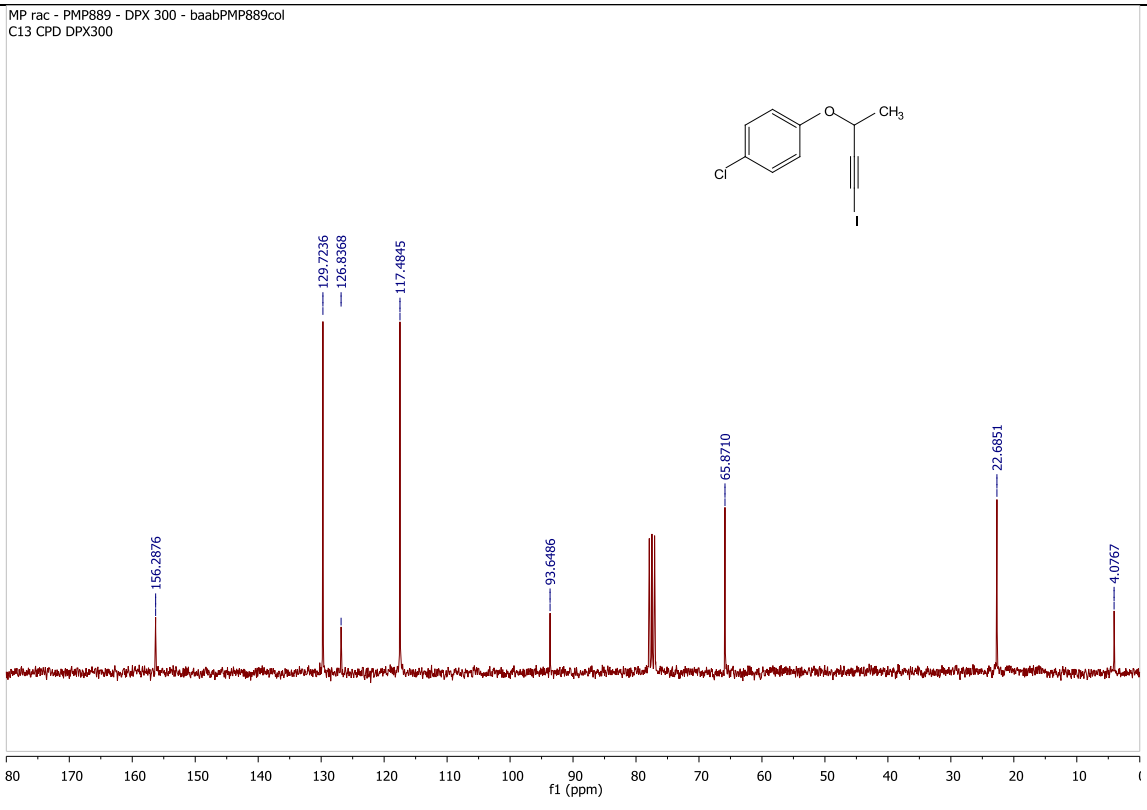
f1 (ppm)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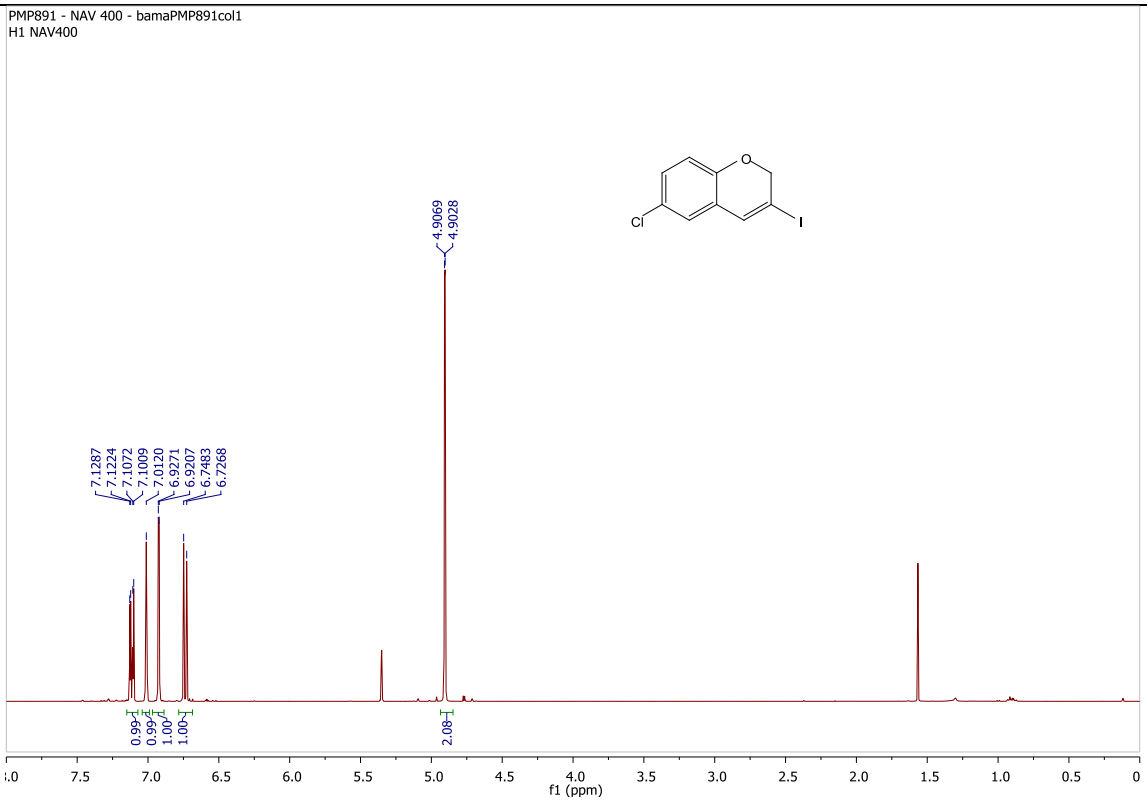
2a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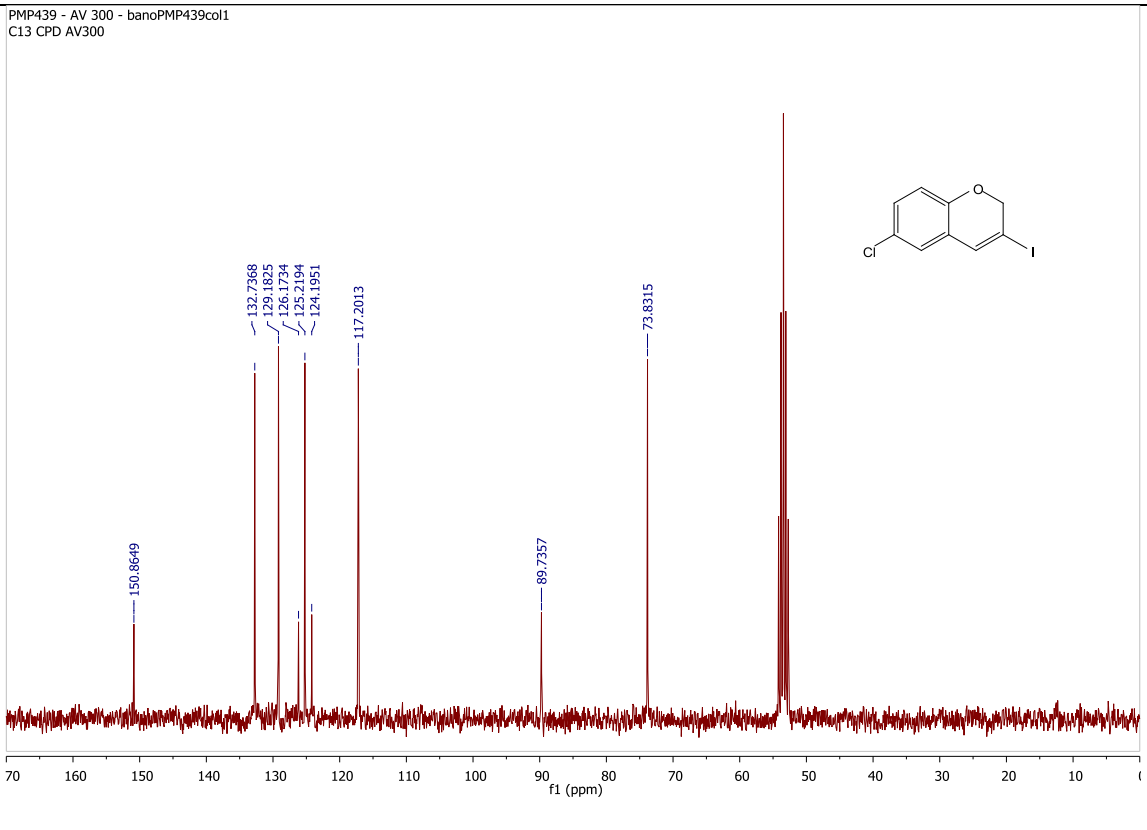
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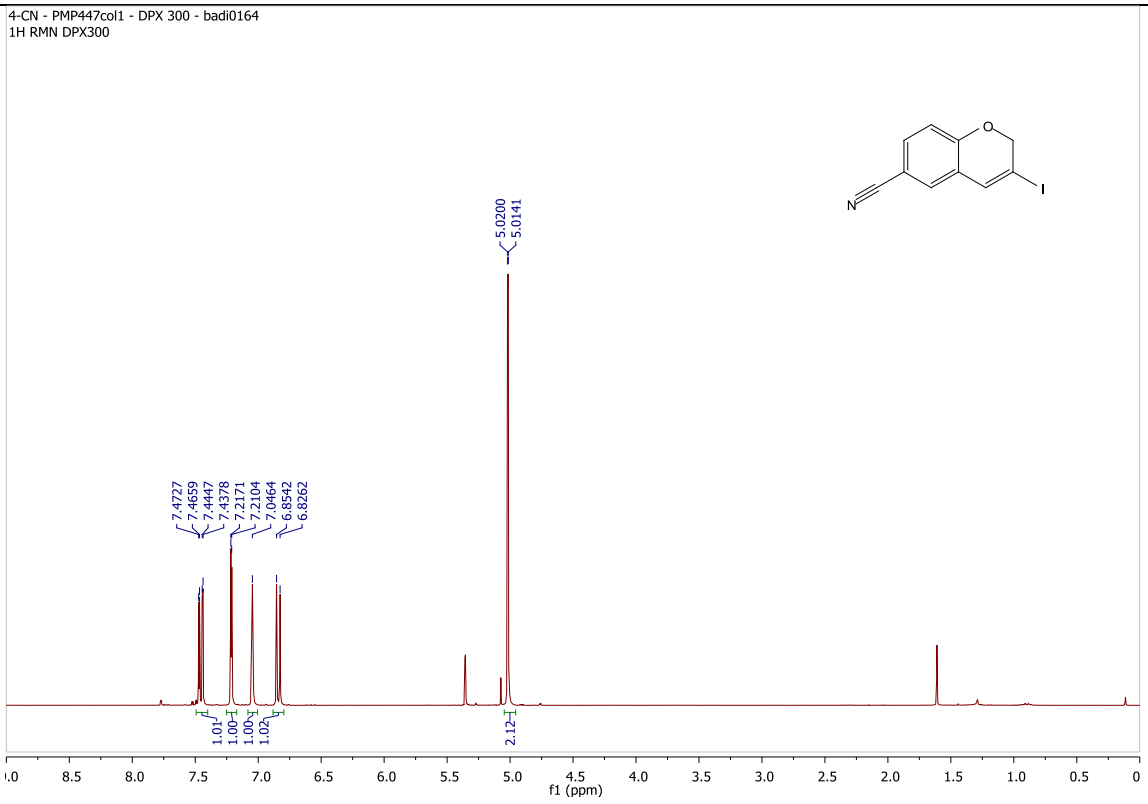
f1 (ppm)

2b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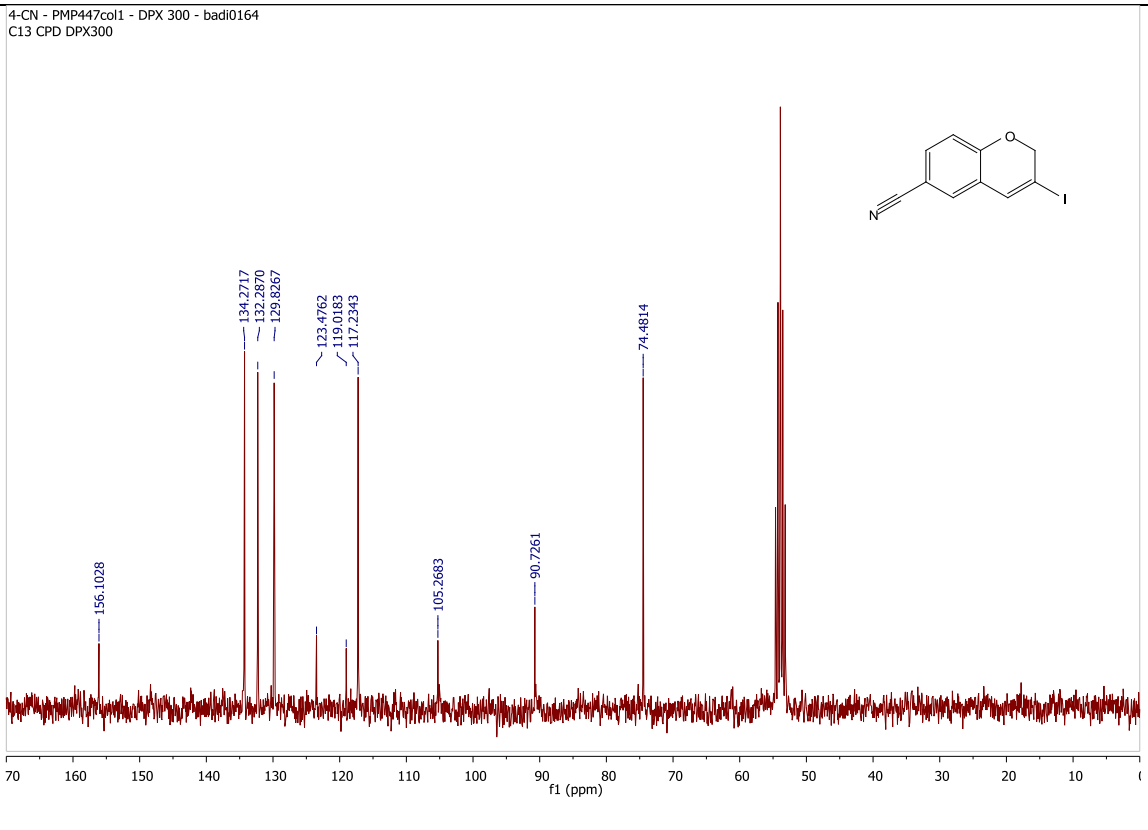
f1 (ppm)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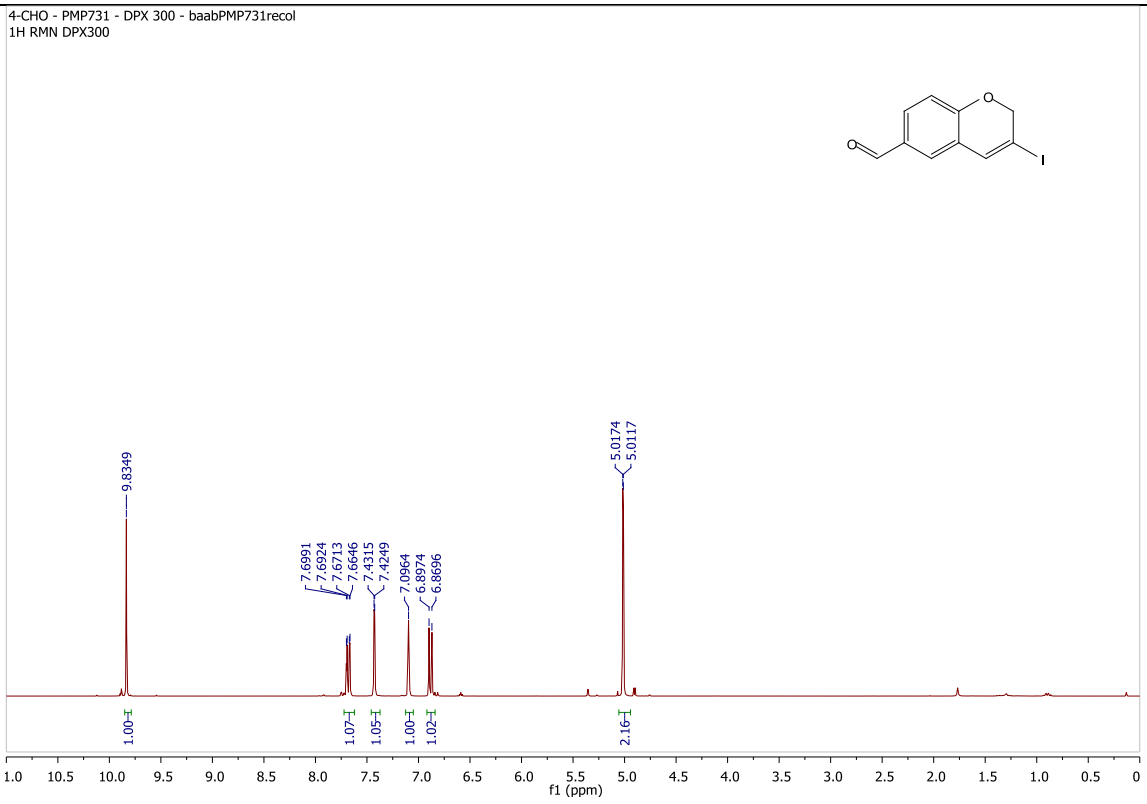
2c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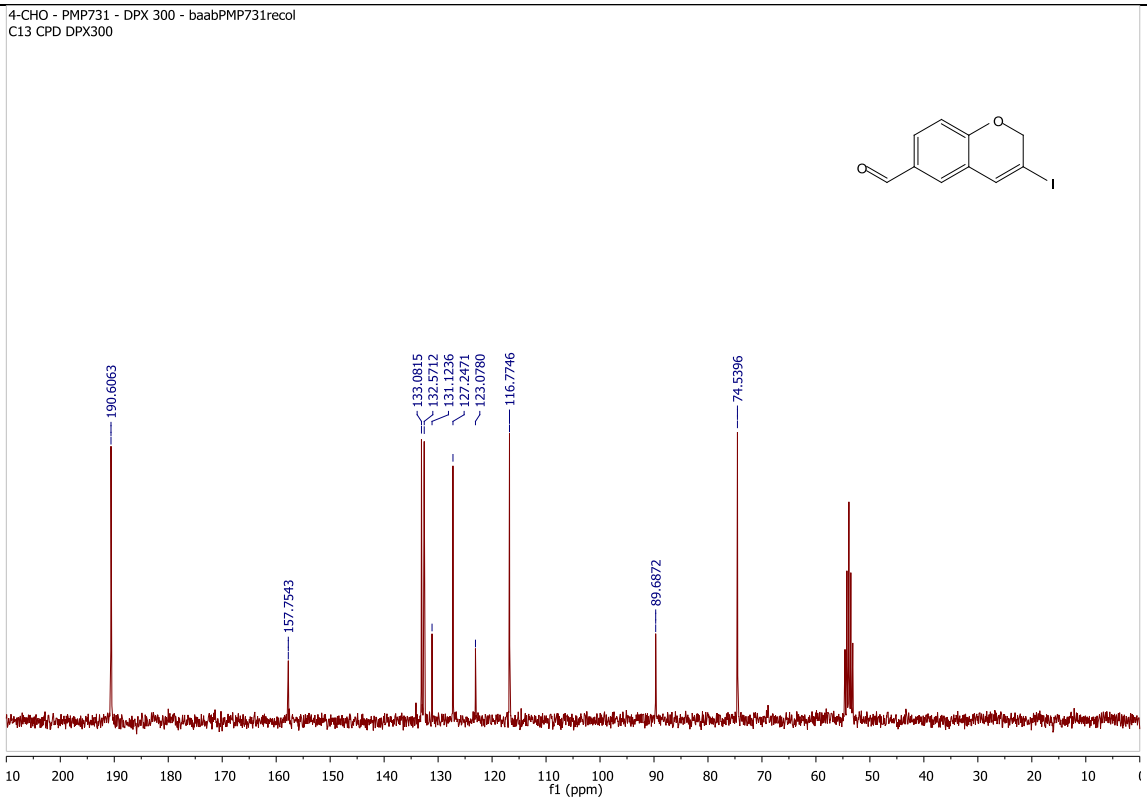
f1 (ppm)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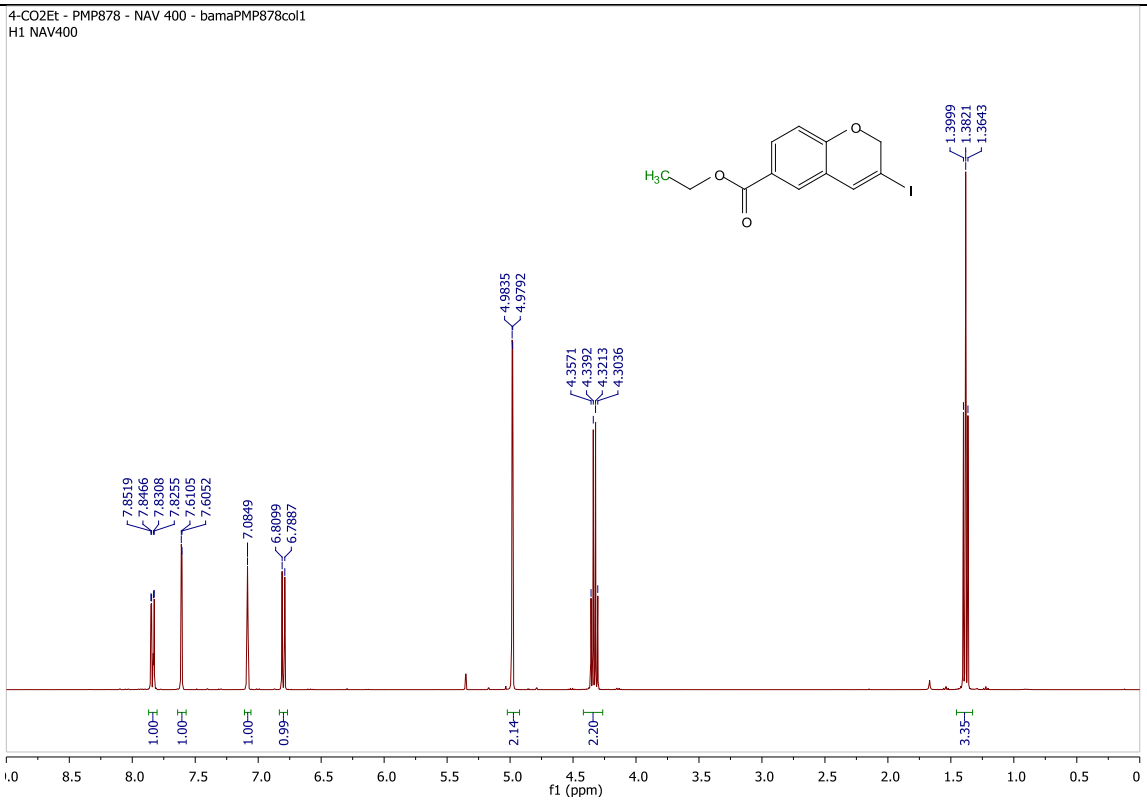
f1 (ppm)

2d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7.0849
6.8099
6.7887
4.9835
4.9792
4.3571
4.3392
4.3213
4.3036
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1.00
1.00
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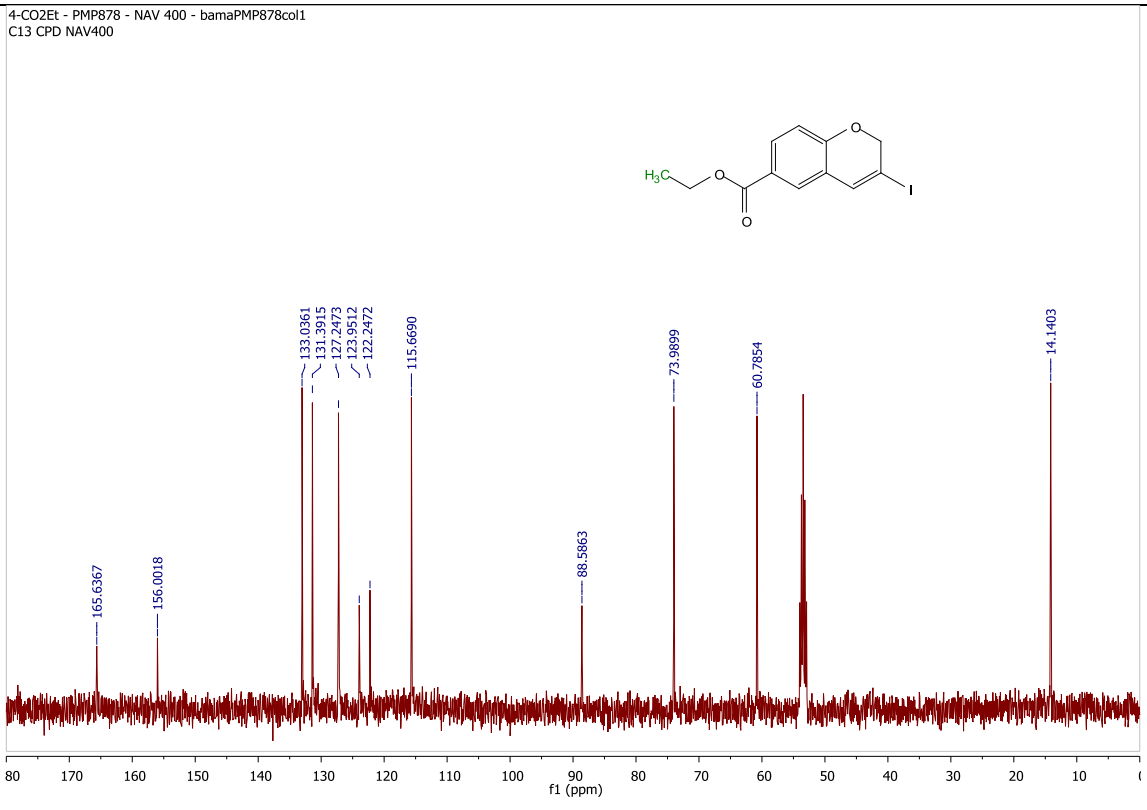
2.14
2.20
3.35
f1 (ppm)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60.7854
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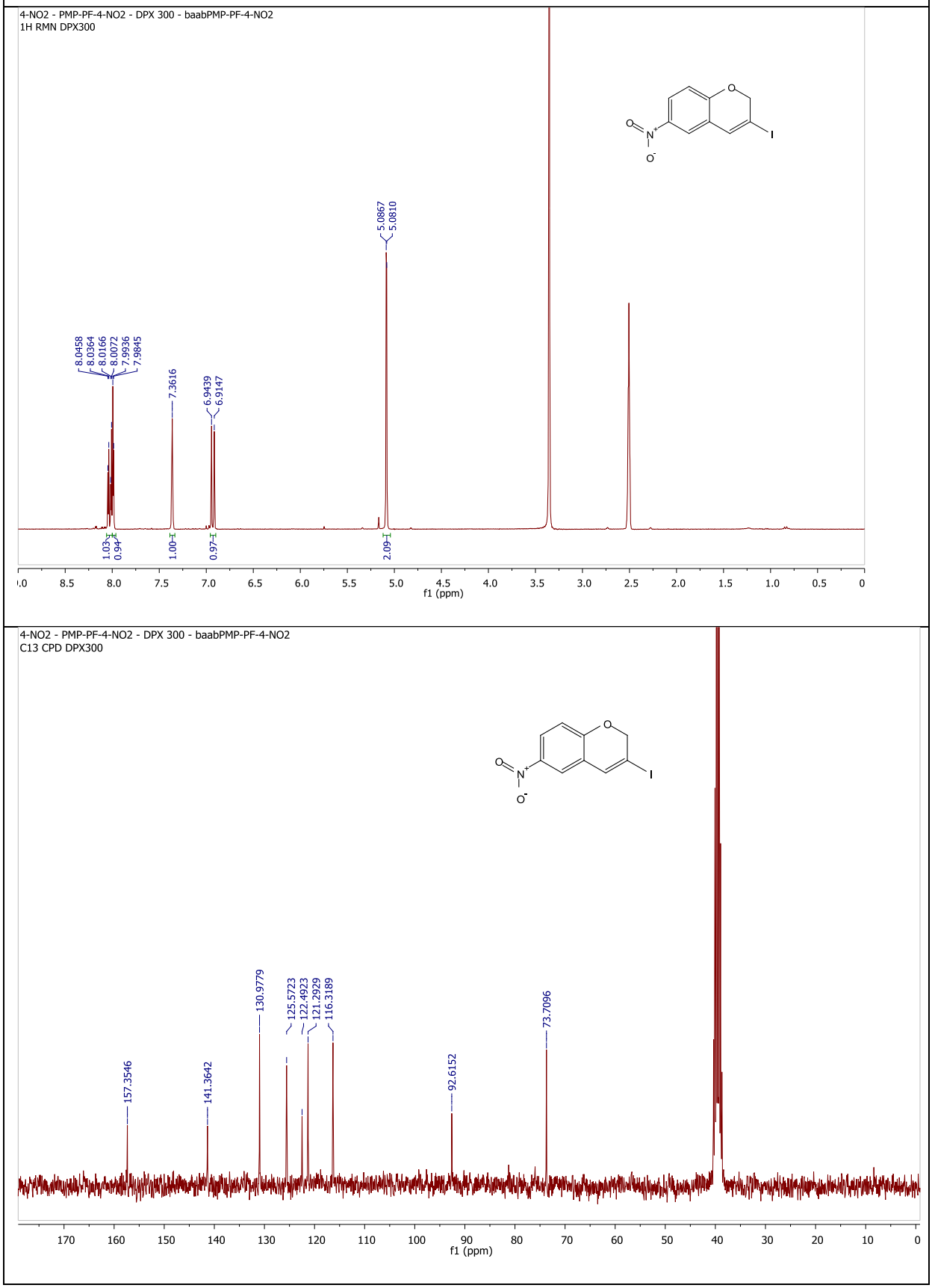
f1 (ppm)

2e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8.0166
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7.9845
7.3616
6.9439
6.9147
5.0867
5.0810
1.03
0.94
1.00
0.97
2.09
f1 (ppm)
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C13 CPD DPX300
157.3546
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121.2929
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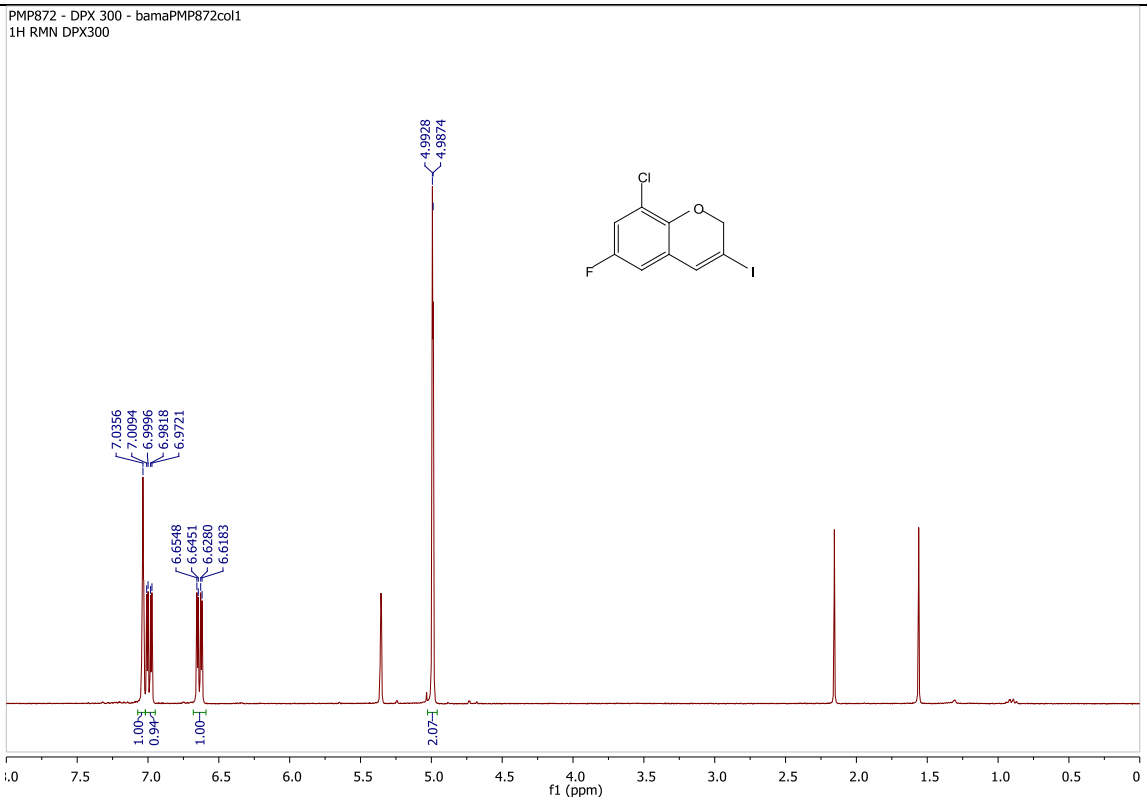
73.7096
f1 (ppm)

2f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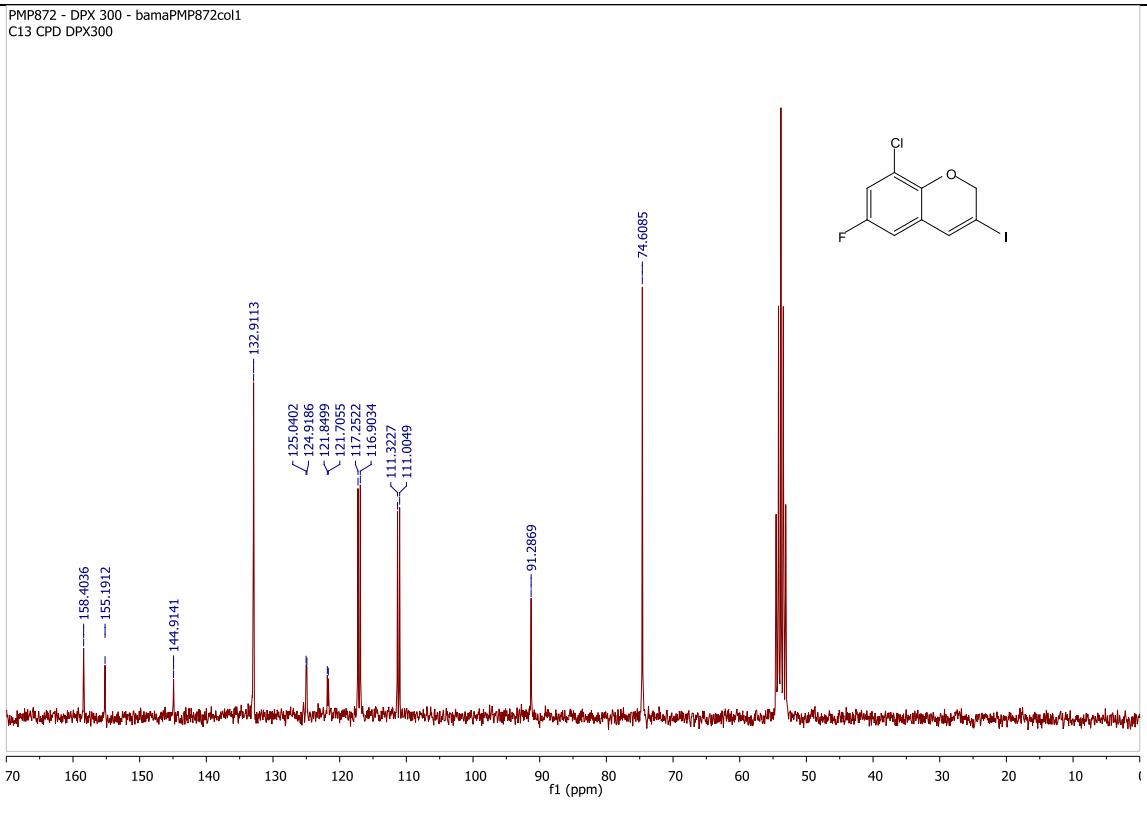
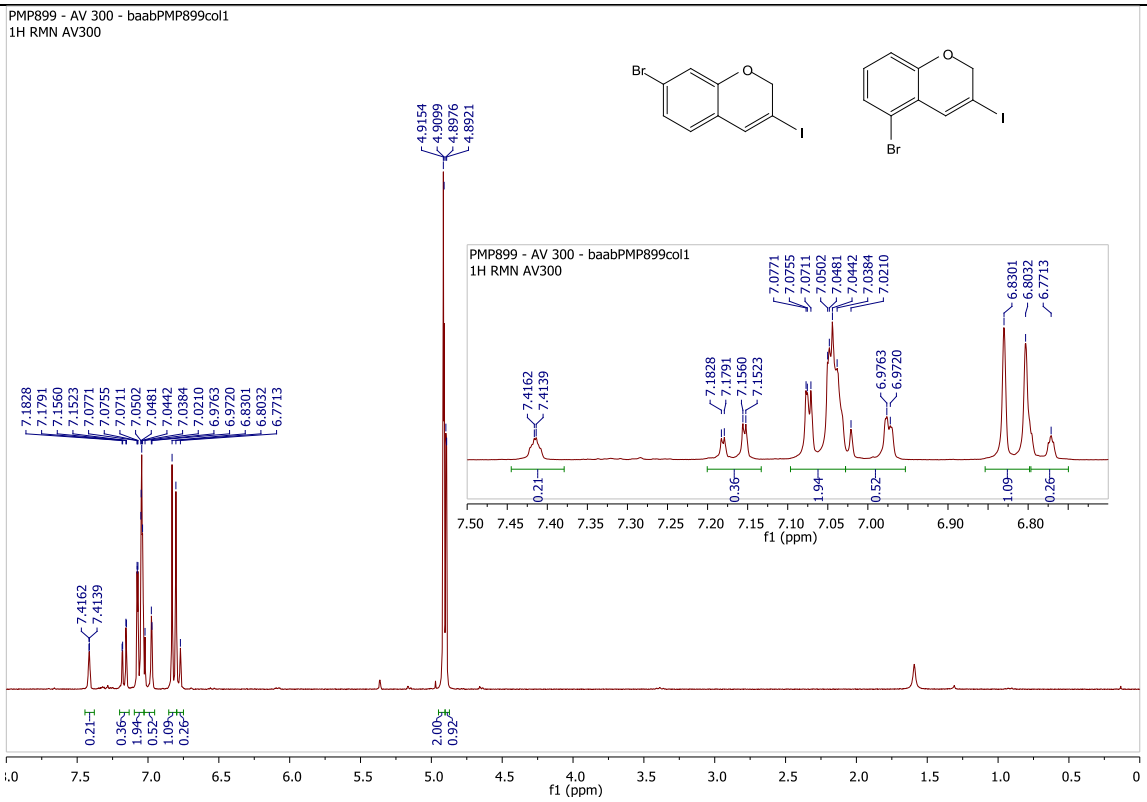
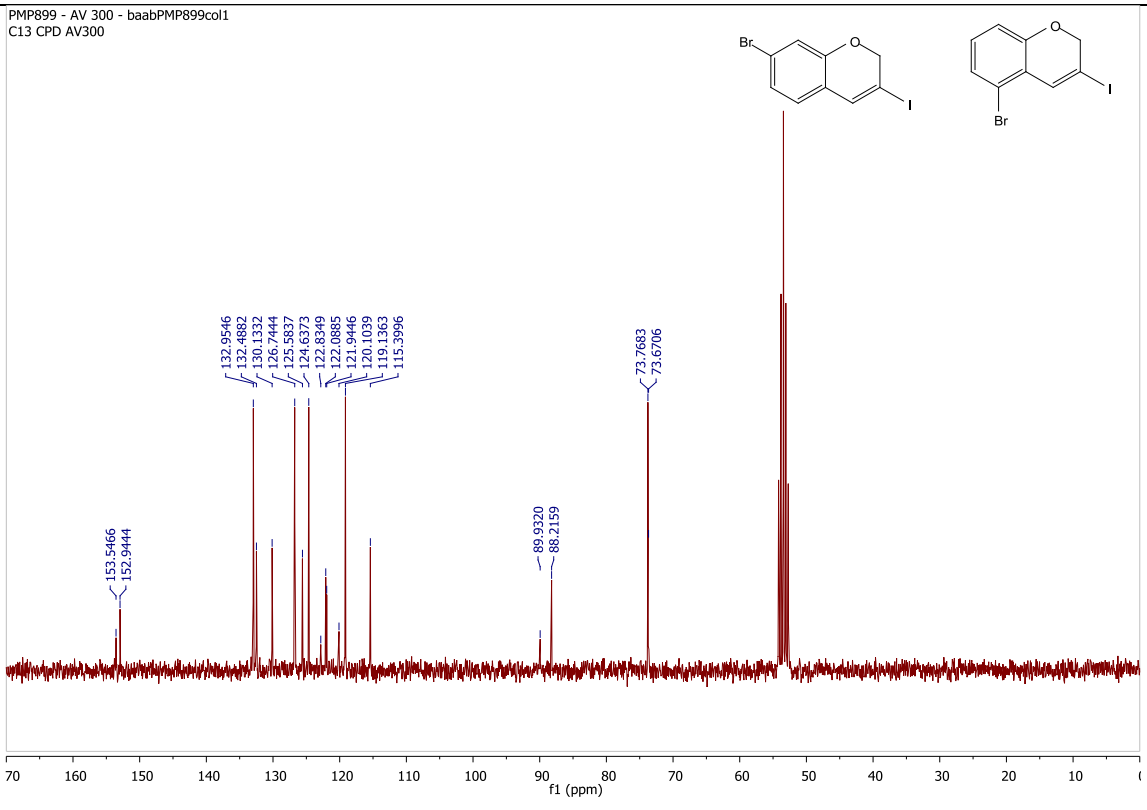
6.9818
6.9721
6.6548
6.6451
6.6280
6.6183
1.00
0.94
1.00
2.07
Cl
O
F
I
f1 (ppm)

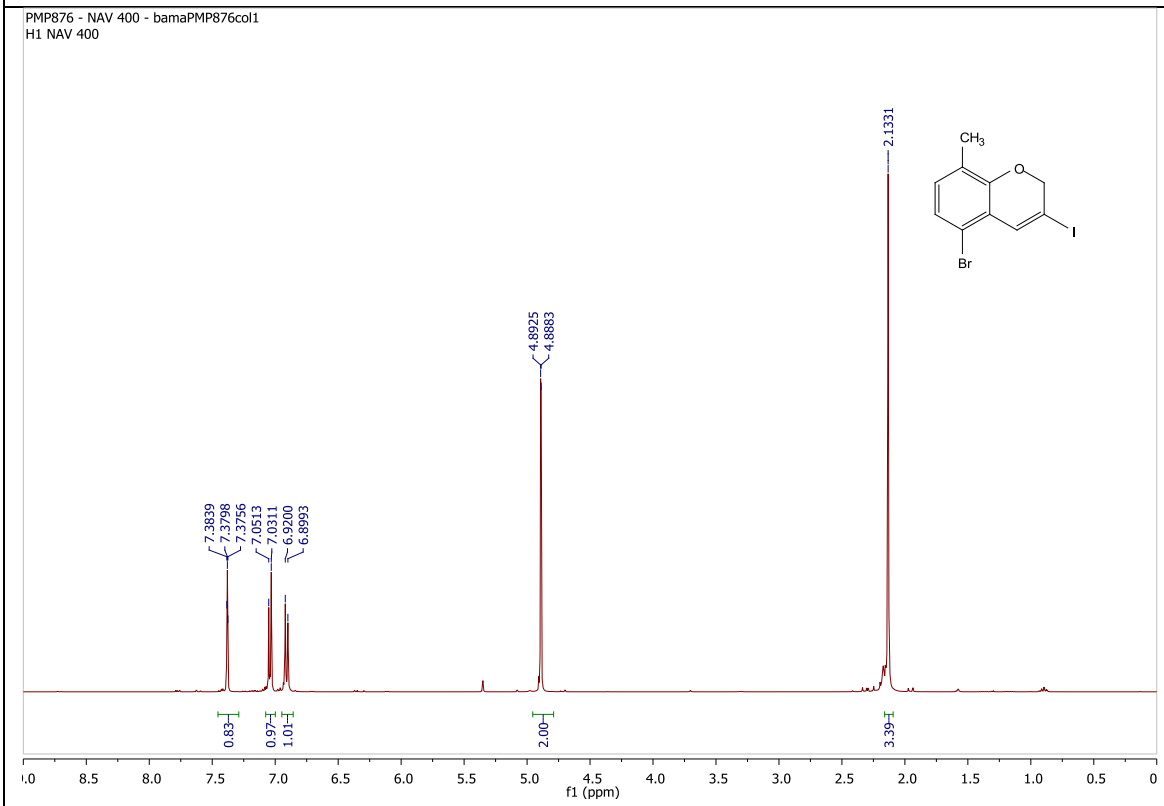

PMP872 - DPX 300 - bamaPMP872col1
C13 CPD DPX300
158.4036
155.1912
144.9141
132.9113
125.0402
124.9186
121.8499
121.7055
117.2522
116.9034
111.3227
111.0049
91.2869
74.6085
Cl
O
F
I
f1 (ppm)

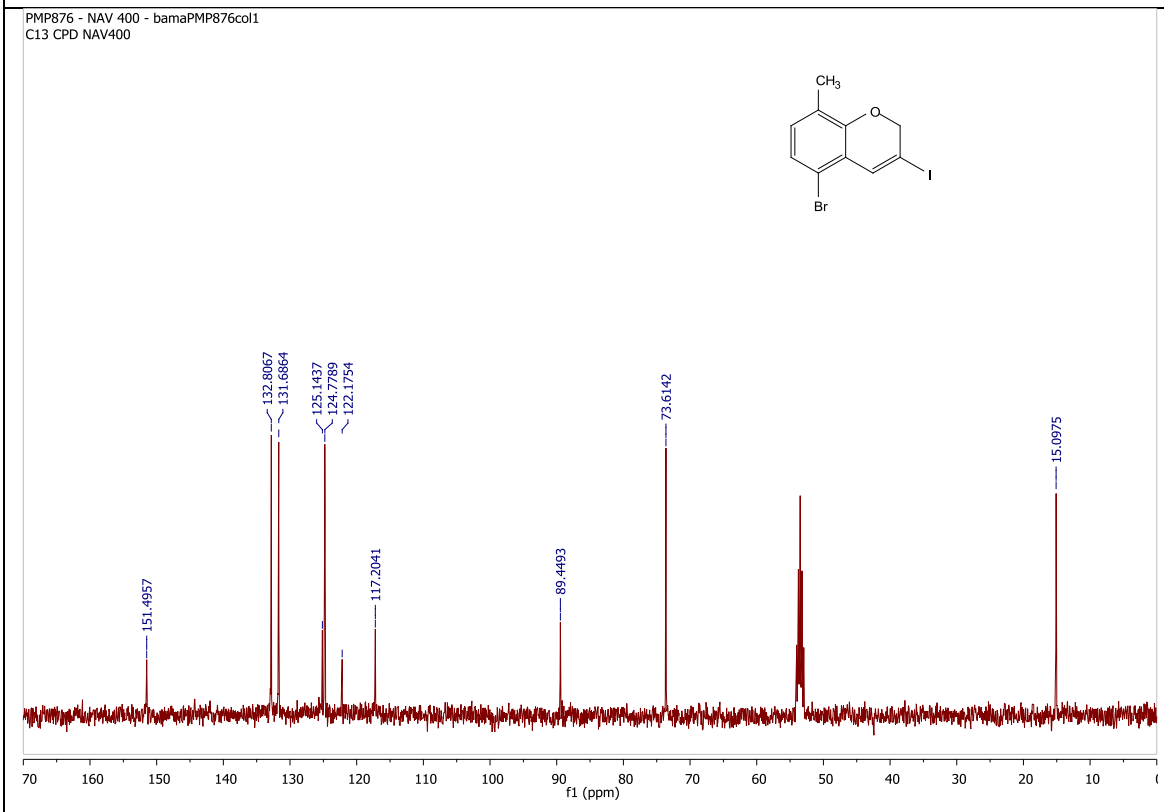
2g + 2g’


PMP899 - AV 300 - baabPMP899col1
1H RMN AV300
Br
O
I
Br
4.9154
4.9099
4.8976
4.8921
7.1828
7.1791
7.1560
7.1523
7.0771
7.0755
7.0711
7.0502
7.0481
7.0442
7.0384
7.0210
6.9763
6.9720
6.8301
6.8032
6.7713
7.4162
7.4139
0.21
0.36
1.94
0.52
1.09
0.26
2.00
0.92
f1 (ppm)
PMP899 - AV 300 - baabPMP899col1
1H RMN AV300
f1 (ppm)

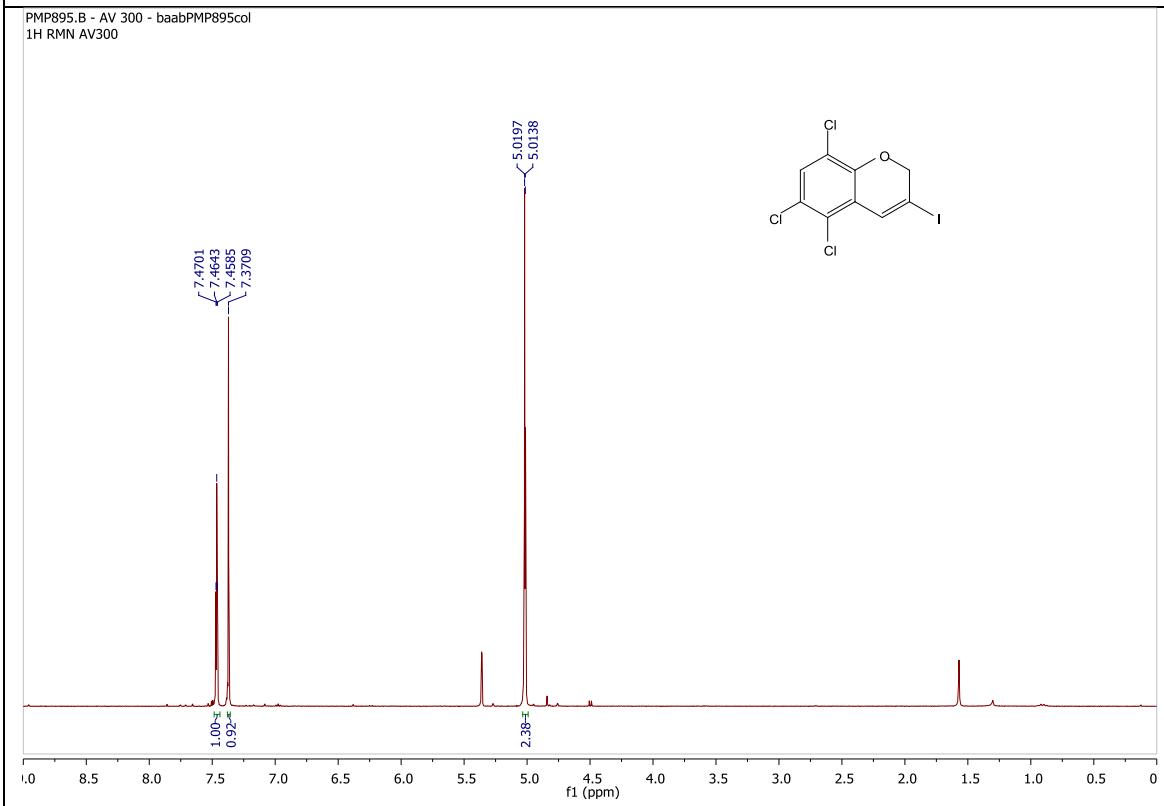

PMP899 - AV 300 - baabPMP899col1
C13 CPD AV300
Br
O
I
Br
132.9546
132.4882
130.1332
126.7444
125.5837
124.6373
122.8349
122.0885
121.9446
120.1039
119.1363
115.3996
153.5466
152.9444
89.9320
88.2159
73.7683
73.6706
f1 (ppm)

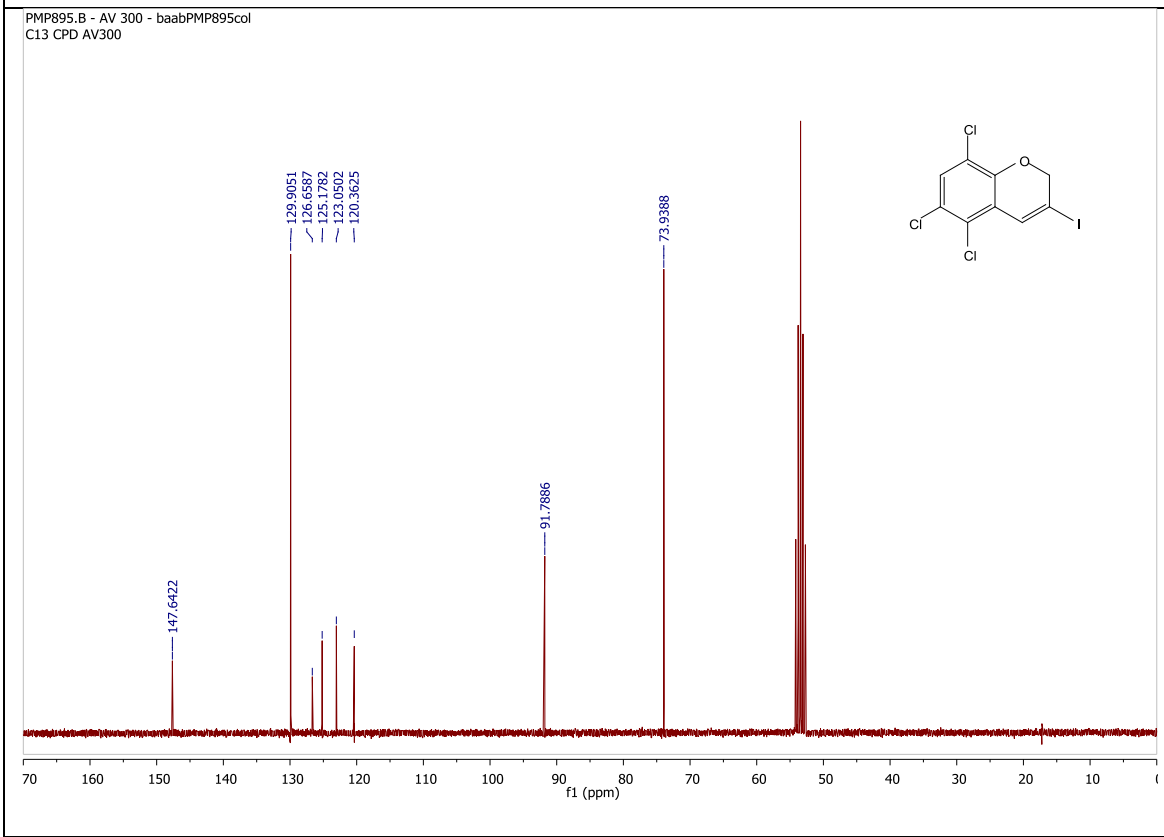
2h


PMP876 - NAV 400 - bamaPMP876col1
H1 NAV 400
2.1331
4.8925
4.8883
7.3839
7.3798
7.3756
7.0513
7.0311
6.9200
6.8993
0.83
0.97
1.01
2.00
3.39
f1 (ppm)

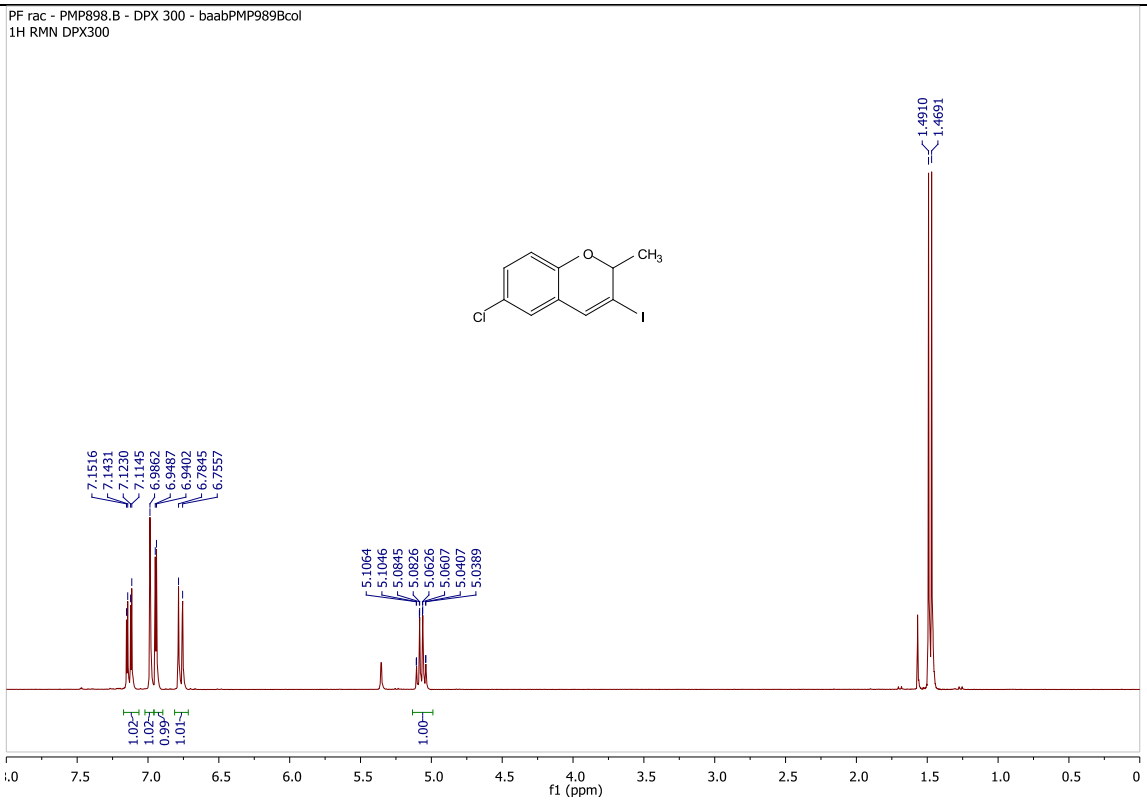

PMP876 - NAV 400 - bamaPMP876col1
C13 CPD NAV400
132.8067
131.6864
125.1437
124.7789
122.1754
117.2041
89.4493
73.6142
15.0975
151.4957
f1 (ppm)

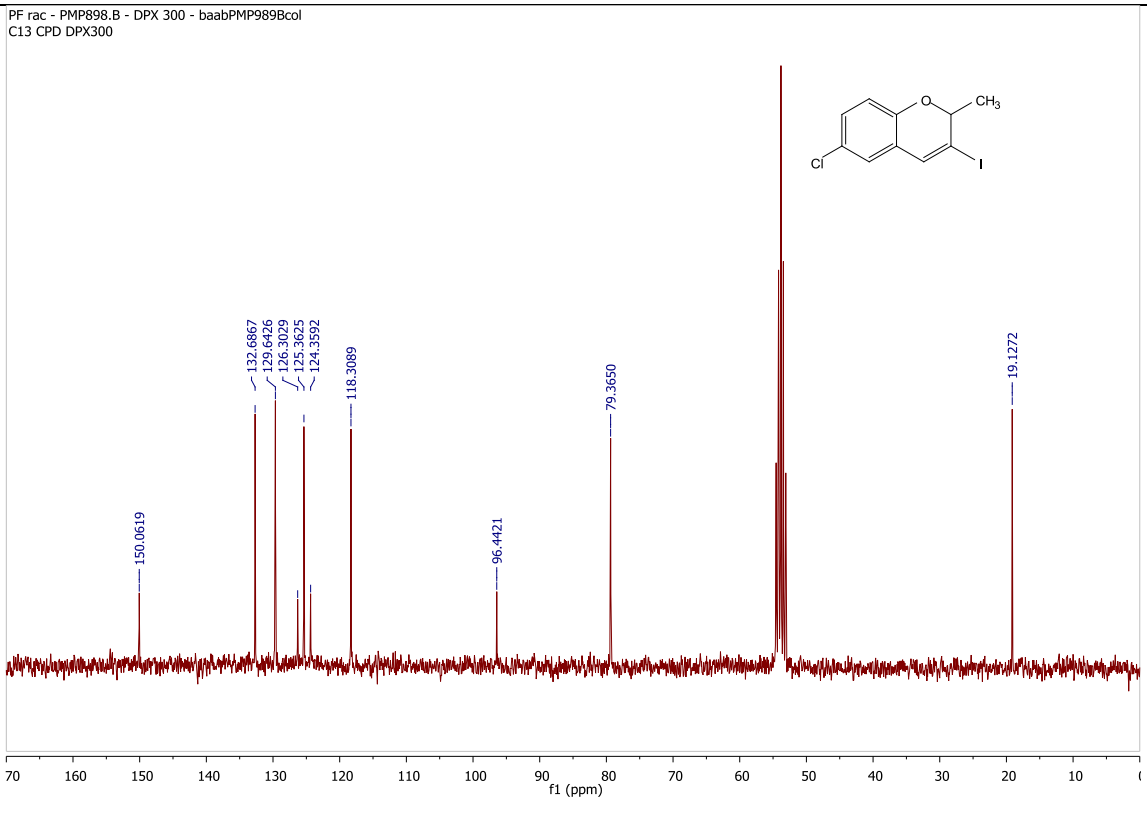
2i


PMP895.B - AV 300 - baabPMP895col
1H RMN AV300
5.0197
5.0138
7.4701
7.4643
7.4585
7.3709
Cl
O
Cl
I
Cl
1.00
0.92
2.38
f1 (ppm)


PMP895.B - AV 300 - baabPMP895col
C13 CPD AV300
129.9051
126.6587
125.1782
123.0502
120.3625
147.6422
91.7886
73.9388
Cl
O
Cl
I
Cl
f1 (ppm)

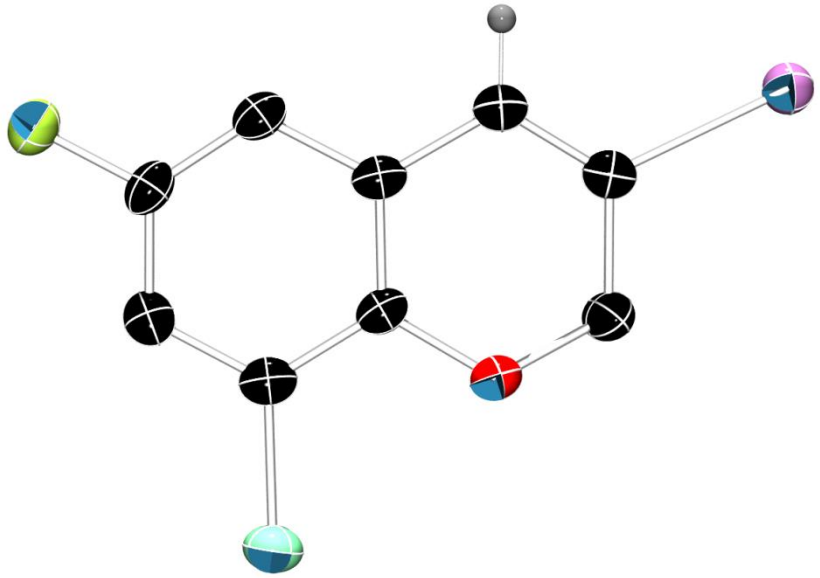
2j


PF rac - PMP898.B - DPX 300 - baabPMP989Bcol
1H RMN DPX300
O
CH3
Cl
I
7.1516
7.1431
7.1230
7.1145
6.9862
6.9487
6.9402
6.7845
6.7557
5.1064
5.1046
5.0845
5.0826
5.0626
5.0607
5.0407
5.0389
1.4910
1.4691
1.02
1.02
0.99
1.01
1.00
f1 (ppm)


PF rac - PMP898.B - DPX 300 - baabPMP989Bcol
C13 CPD DPX300
O
CH3
Cl
I
150.0619
132.6867
129.6426
126.3029
125.3625
124.3592
118.3089
96.4421
79.3650
19.1272
f1 (ppm)

3. X-ray molecular structure for **2f**

CCDC 939930 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.cam.ac.uk/data_request/cif.
The most relevant crystal and refinement data for *8-chloro-6-fluoro-3-iodo-2H-chromene* is as follows:



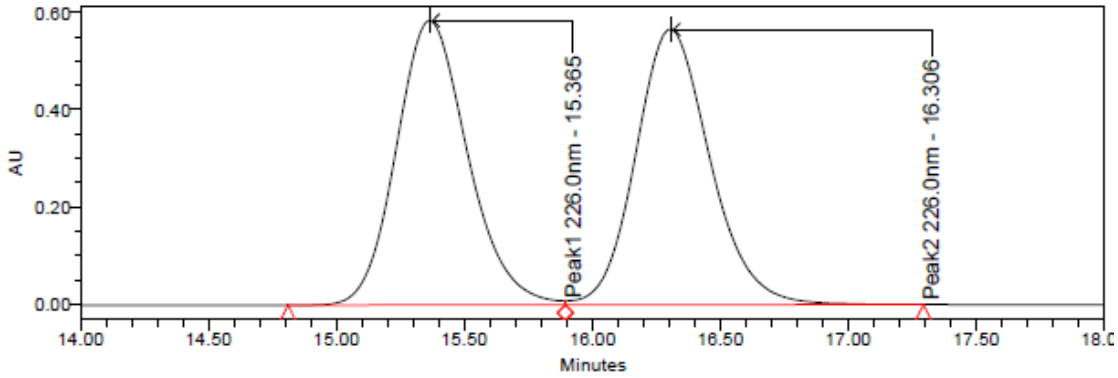
Empirical formula C_9H_5ClFIO, M_r = 310.49, T = 173 (2) K, λ =0.71073 Å, crystal system, space group: triclinic, 'P -1', unit cell dimensions: *a* = 4.3434 (3), *b* = 9.8103 (9), *c* = 11.5211 (10) Å, α = 111.092 (3), β = 91.559 (5), γ = 93.498 (5) °, V = 456.53 (7) Å, Z = 2, ρ_{calcd} = 2.259 gcm^{-1}, μ = 3.767 mm^{-1}, *F*(000) = 292 crystal si : 0.45 x 0.30 x 0.10 mm, θrange data collection : 4.17 – 27.48 °, index ranges: -5≤h≤5 , -12≤k≤11 , -0≤l≤14, reflections collected/unique = 2071/2071 [R_{int} = 0.0000], completeness to 2θ = 27.48 (98.4 %), absorption correction: semi-empirical from equivalents, max. and min. transmission = 0.7103 and 0.1494 , refinement method: full matrix least-squares on F^2 , data/restraints/parameters = 2071/0/118, goodness-of-fit on F^2 = 1.058, final *R* indices [$I>2\sigma(I)$]: R_1 = 0.0336, wR_2 = 0.0855, R indices (all data): R_1 = 0.0389, wR_2 = 0.0879; largest difference peak and hole = 0.896 and -1.021 e $Å^{-3}$.

4. HPLC chromatograms for **1j** and **2j**

The compound (*R*)-**1j** was obtained from commercially available (*S*)-3-butyn-2-ol using standard Mitsunobu-type chemistry, which is known to yield the desired aryl-substituted ether arising from clean inversion of configuration.

HPLC Chromatogram for (*R*)-1-chloro-4-((4-iodobut-3-yn-2-yl)oxy)benzene

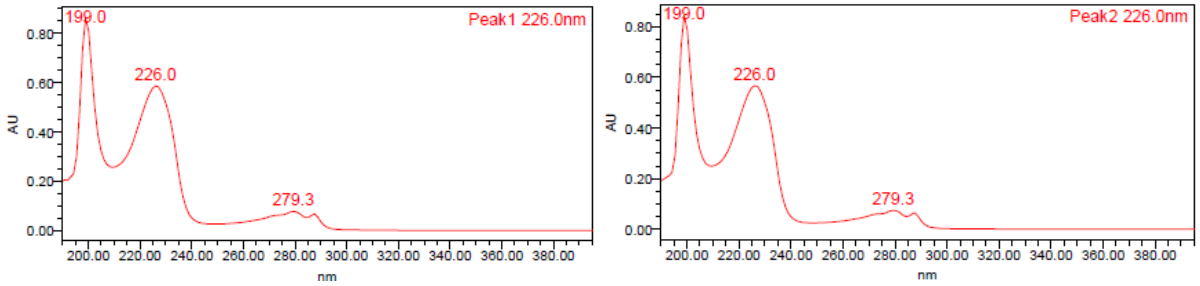
CHIRALCEL OD-H: *n*-Hexane: Isopropanol; 99:1; Flow 0.4 ml/min; λ = 226.0 nm



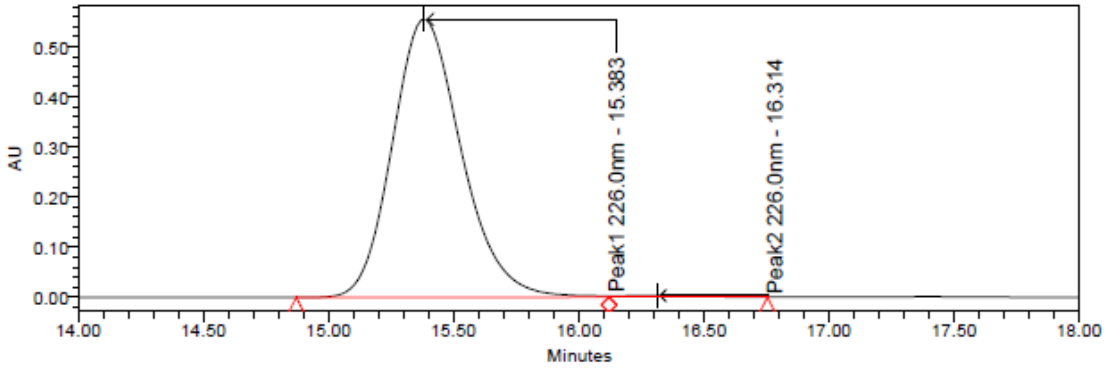
Peak Results

	Name	RT	Area	Height	% Area
1	Peak1 226.0nm	15.365	11381765	586015	49.82
2	Peak2 226.0nm	16.306	11462488	567378	50.18

Chromatogram for racemic **1j** and peak results



UV spectra at retention times 15,365 and 16,306 respectively



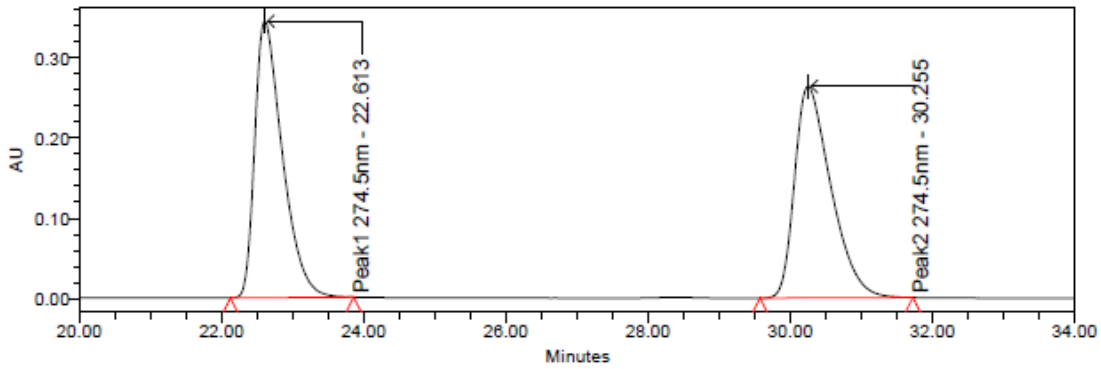
Peak Results

	Name	RT	Area	Height	% Area
1	Peak1 226.0nm	15.383	10666512	555485	99.37
2	Peak2 226.0nm	16.314	67968	3173	0.63

Chromatogram for (*R*)-**1j** and peak results

HPLC Chromatogram for (*R*)-6-chloro-3-iodo-2-methyl-2*H*-chromene (2j)

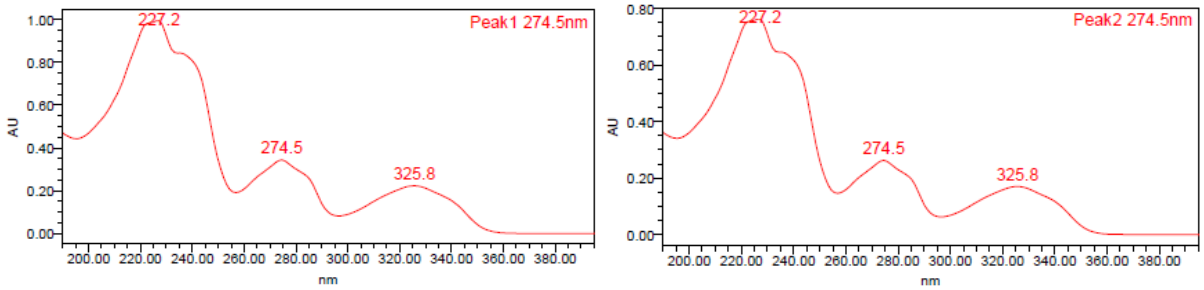
CHIRALCEL OD-H: *n*-Hexane; 100; Flow 0.6 ml/min; λ = 274.5 nm



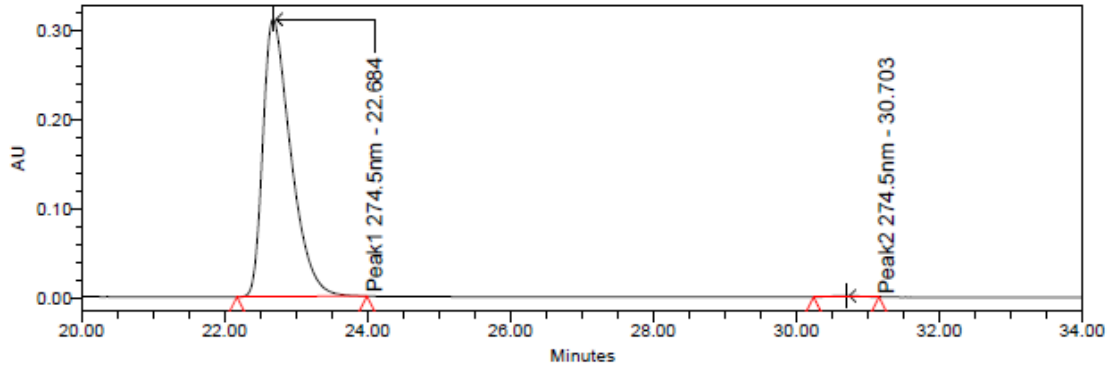
Peak Results

	Name	RT	Area	Height	% Area
1	Peak1 274.5nm	22.613	9288718	343388	49.88
2	Peak2 274.5nm	30.255	9334772	262805	50.12

Chromatogram for racemic **2j** and peak results



UV spectra at retention times 22,613 and 30,255 respectively



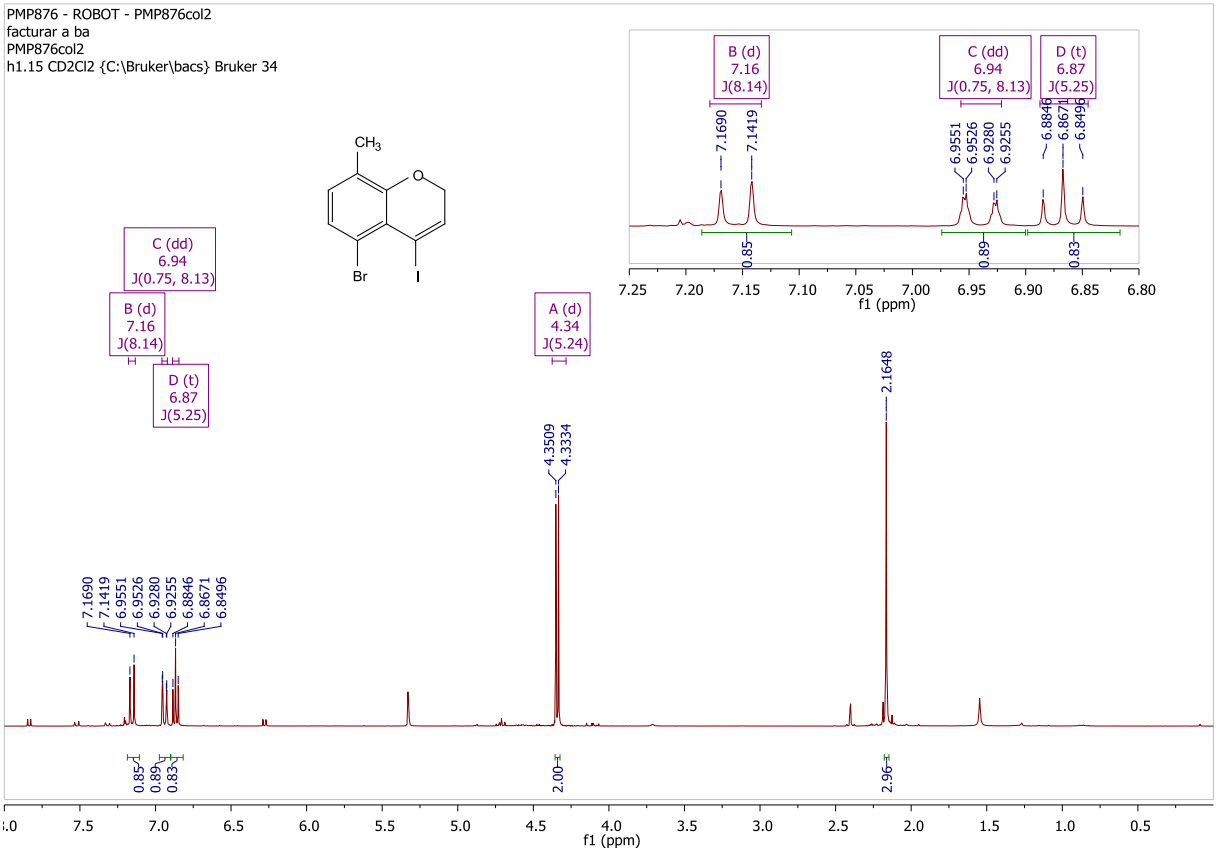
Peak Results

	Name	RT	Area	Height	% Area
1	Peak1 274.5nm	22.684	8421813	311024	99.56
2	Peak2 274.5nm	30.703	37201	1307	0.44

Chromatogram for (*R*)-**2j** and peak results

5. Structural assignment for compounds **3**

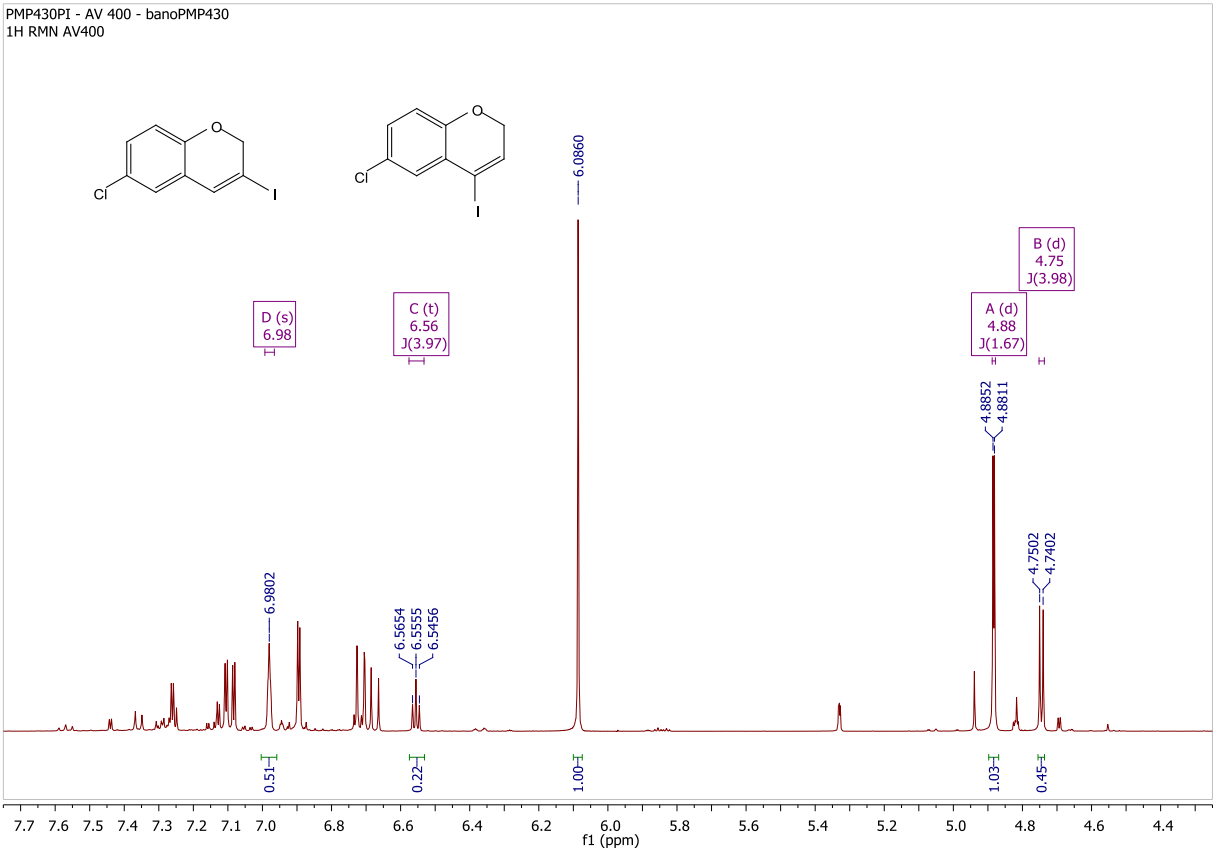
The products **3** are formed as minor components from the gold-catalyzed cyclization reactions of the starting **1**. Although in general compounds **3** were not isolated from crude reaction mixtures containing compounds **2** as the major regioisomers, some of them were isolated. Thus, below is shown the ^{1}H NMR spectrum for compound **3h**, which was separable from **2h**.



The signals at δ: 4.34 and 6.87 ppm are characteristic for the presence of compounds **3**. They always show coupling constants in the range of 4.5 Hz (higher values than those associated to compounds **2**) and lower chemical shifts than the corresponding signals in compounds **2**.

On this basis, regioisomeric ratios were determined from crude reaction mixtures upon inspection by ^{1}H NMR. A representative case is discussed in the next paragraph.

The given ^{1}H NMR corresponds to the reaction depicted in Table 1 for entry 9. It is possible to clearly distinguish and assign the signals for the allylic hydrogens of **2a** (δ = 4.88 ppm; *J* = 1.67 Hz) and **3a** (δ = 4.75 ppm; *J* = 3.98 Hz); and also for the vinylic hydrogen of **2a** (δ = 6.98 ppm; broad singlet) and **3a** (δ = 6.56 ppm; *J* = 3.97 Hz).


PMP430PI - AV 400 - banoPMP430
1H RMN AV400
Cl
I
O
Cl
I
O
6.0860
B (d)
4.75
J(3.98)
D (s)
6.98
C (t)
6.56
J(3.97)
A (d)
4.88
J(1.67)
4.8852
4.8811
4.7502
4.7402
6.9802
6.5654
6.5555
6.5456
0.51
0.22
1.00
1.03
0.45
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4
f1 (ppm)