

SUPPORTING INFORMATION

Title: Generation and Reaction of Ammonium Ylides in Basic Two-Phase Systems

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(4-Cyanophenyl)-dimethylaminoacetonitrile (1c)

¹H NMR of crude product (400 MHz, CDCl₃) δ 2.29 (6H, s, N(CH₃)₂), 4.88 (1H, s, CHCN), 7.62-7.70 (4H, m, C₆H₄) and some minor signals of impurities at 1.30-2.80 ppm and 7.20-8.20 ppm.

2-Dimethylamino-4-methyl-pent-3-enenitrile (1g)

Yield 11.1 g (80%), bp 46-47°C/1.5 Torr,

Found: C, 69.5; H, 10.3; N, 20.2 Calc. for C₈H₁₄N₂ (138.21): C, 69.5; H, 10.2; N, 20.3%,

¹H NMR (200 MHz, CDCl₃) δ 1.69 (3H, bs, CH₃C=CH), 1.75 (3H, bs, CH₃C=CH), 2.29 (6H, s, N(CH₃)₂), 4.15 (1H, d, J 8.1, CHCN), 5.15-5.20 (1H, m, (CH₃)₂=CH).

Salts 2

N-(α-cyanobenzyl)-N,N,N-trimethylammonium methyl sulfate (2a1)

Yield 7.0 g (81%), mp 115-116°C (acetone),

Found: C, 50.0; H, 6.4; N, 9.7; Calc. for C₁₂H₁₈N₂O₄S (286.35): C, 50.3; H, 6.3; N, 9.8%,

¹H NMR (200 MHz, CDCl₃) δ 3.35 (9H, s, N⁺(CH₃)₃), 3.65 (3H, s, CH₃SO₄⁻), 6.60 (1H, s, CHCN), 7.45-7.60 (3H, m, C₆H₅), 7.65-7.75 (2H, m, C₆H₅),

¹³C NMR (50 MHz, CDCl₃) δ 51.45, 53.07, 66.33, 113.05, 124.80, 129.74, 131.88, 132.43.

N-(α-cyanobenzyl)-N-methylpyrrolidinium perchlorate (2a2)

Yield 7.7 g (85%), mp 127-128°C (MeOH),

Found: C, 51.9; H, 5.5; N, 9.2; Calc. for C₁₃H₁₇ClN₂O₄ (300.75): C, 51.9; H, 5.7; N, 9.3%,

¹H NMR (200 MHz, [D₆-DMSO]) δ 2.05-2.30 (4H, m, 2×CH₂), 3.04 (3H, s, N⁺(CH₃)₃), 3.30-3.45 (1H, m, N⁺CHH), 3.60-3.85 (3H, m, N⁺CHH and N⁺CH₂), 6.48 (1H, s, CHCN), 7.55-7.85 (5H, m, C₆H₅),

¹³C NMR (50 MHz, [D₆-DMSO]) δ 21.06, 46.32, 63.15, 64.12, 64.86, 113.89, 125.45, 129.67, 131.34, 132.15.

N-(α-cyanobenzyl)-N-methylmorpholinium methyl sulfate (2a3)

Yield 7.8 g (79%), mp 119-121°C (MeOH),

Found: C, 51.2; H, 6.2; N, 8.8; Calc. for $C_{14}H_{20}N_2O_5S$ (328.39): C, 51.2; H, 6.1; N, 8.5%,
 1H NMR (200 MHz, $[D_6-DMSO]$) δ 3.26 (3H, s, $CH_3SO_4^-$), 3.39 (3H, s, $N^+(CH_3)_3$), 3.55-3.80 (4H, m, $2 \times CH_2$), 3.85-4.10 (4H, m, $2 \times N^+CH_2$), 6.64 (1H, s, $CHCN$), 7.55-7.75 (3H, m, C_6H_5), 7.75-7.85 (2H, m, C_6H_5),
 ^{13}C NMR (50 MHz, $[D_6-DMSO]$) δ 42.54, 53.00, 58.09, 59.22, 59.91, 59.96, 68.13, 113.21, 123.56, 129.73, 132.41, 132.52.

N-[α -cyano-(4-methoxybenzyl)]-N,N,N-trimethylammonium methyl sulfate (2b)

Yield 7.4 g (78%), mp 143-145°C (MeOH),

Found: C, 49.5; H, 6.15; N, 8.85; Calc. for $C_{13}H_{20}N_2O_5S$ (316.38): C, 49.35; H, 6.4; N, 8.8%,
 1H NMR (400 MHz, $CDCl_3$) δ 3.36 (9H, s, $N^+(CH_3)_3$), 3.70 (3H, s, $CH_3SO_4^-$), 3.84 (3H, s, OCH_3), 6.52 (1H, s, $CHCN$), 6.99-7.04 (2H, m, C_6H_4), 7.65-7.71 (2H, m, C_6H_4).

N-[α -cyano-(4-cyanobenzyl)]-N,N,N-trimethylammonium methyl sulfate (2c)

Yield 5.8 g (62%) (calculated for aldehyde **1c**), mp 158-160°C (MeOH),

Found: C, 50.35; H, 5.4; N, 13.5; Calc. for $C_{13}H_{17}N_3O_4S$ (311.36): C, 50.15; H, 5.5; N, 13.5%,
 1H NMR (200 MHz, $CDCl_3$) δ 3.22 (9H, s, $N^+(CH_3)_3$), 3.37 (3H, s, $CH_3SO_4^-$), 6.54 (1H, s, $CHCN$), 7.92-7.95 (2H, m, C_6H_4), 8.12-8.15 (2H, m, C_6H_4).

N-[α -cyano-(naphthalen-1-yl-methylene)]-N,N,N-trimethylammonium methyl sulfate (2d)

Yield 9.6 g (95%), 156-158°C (acetone),

Found: C, 56.9; H, 6.1; N, 8.3; Calc. for $C_{16}H_{20}N_2O_4S$ (336.41): C, 57.1; H, 6.0; N, 8.3%
 1H NMR (200 MHz, $[D_6-DMSO]$) δ 3.28 (9H, s, $N^+(CH_3)_3$), 3.41 (3H, s, $CH_3SO_4^-$), 7.16 (1H, s, $CHCN$), 7.60-7.85 (3H, m, $C_{10}H_7$), 8.10-8.20 (2H, m, $C_{10}H_7$), 8.25-8.35 (1H, m, $C_{10}H_7$), 8.45-8.55 (1H, m, $C_{10}H_7$),
 ^{13}C NMR (50 MHz, $[D_6-DMSO]$) δ 51.77, 52.90, 62.81, 114.33, 121.20, 123.32, 125.46, 127.03, 128.37, 129.38, 131.66, 132.42, 133.59.

N-[α -cyano-(furan-2-yl-methylene)]-N,N,N-trimethylammonium perchlorate (2e)

Yield 6.9 g (87%), mp 168-170°C (dec.) (MeOH),

Found: C, 40.85; H, 4.9; N, 10.4; Calc. for $C_9H_{13}ClN_2O_5$ (264.67): C, 40.8; H, 4.95; N, 10.6%
 1H NMR (200 MHz, $[D_6-DMSO]$) δ 3.23 (9H, s, $N^+(CH_3)_3$), 6.73 (1H, s, $CHCN$), 6.78 (1H, dd, J 3.50, J 1.9, C_4H_3O), 7.21 (1H, dd, J 3.5, J 0.8, C_4H_3O), 8.08 (1H, dd, J 1.9, J 0.8, C_4H_3O),

^{13}C NMR (50 MHz, $[\text{D}_6\text{-DMSO}]$) δ 51.56, 60.05, 111.44, 112.27, 119.03, 137.91, 148.24.

N-[α -cyano-(thiophen-2-yl-methylene)]-N,N,N-trimethylammonium perchlorate (2f)

Yield 7.8 g (93%), mp 169-171°C (dec.) (MeOH),

Found: C, 38.5; H, 4.8; N, 9.9; Calc. for $\text{C}_9\text{H}_{13}\text{ClN}_2\text{O}_4\text{S}$ (280.73): C, 38.5; H, 4.7; N, 10.0%,

^1H NMR (200 MHz, $[\text{D}_6\text{-DMSO}]$) δ 3.23 (9H, s, $\text{N}^+(\text{CH}_3)_3$), 6.82 (1H, s, CHCN), 7.31 (1H, dd, J 5.2, J 3.7, $\text{C}_4\text{H}_3\text{S}$), 7.60 (1H, dd, J 3.7, J 1.2, $\text{C}_4\text{H}_3\text{S}$), 8.05 (1H, dd, J 5.2, J 1.2, $\text{C}_4\text{H}_3\text{S}$)

^{13}C NMR (50 MHz, $[\text{D}_6\text{-DMSO}]$) δ 51.13, 61.43, 113.05, 124.77, 128.45, 133.45, 135.70.

N-(1-cyano-3-methyl-2-butenyl)-N,N,N-trimethylammonium methyl sulfate (2g)

Yield 6.3 g (79%), mp 99-101°C (acetone),

Found: C, 45.5; H, 7.6; N, 10.6; Calc. for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$ (264.35): C, 45.4; H, 7.6; N, 10.6%,

^1H NMR (200 MHz, $[\text{D}_6\text{-DMSO}]$) δ 1.84 (3H, d, J 1.4, $\text{CH}_3\text{C}=\text{CH}$), 1.89 (3H, d, J 1.2,

$\text{CH}_3\text{C}=\text{CH}$), 3.18 (9H, s, $\text{N}^+(\text{CH}_3)_3$), 3.40 (3H, s, CH_3SO_4^-), 5.50-5.65 (1H, 2 $\times$ m,

$(\text{CH}_3)_2\text{C}=\text{CH}$), 5.75 (1H, d, J 10.6, CHCN),

^{13}C NMR (50 MHz, $[\text{D}_6\text{-DMSO}]$) δ 18.87, 25.77, 50.80, 52.91, 61.58, 108.94, 113.59, 152.45.

E-N-(1-cyano-3-phenyl-2-propenyl)-N-methylpiperidinium methyl sulfate (2h)

Yield 7.7 g (73%), mp 149-151°C (MeOH),

Found: C, 58.2; H, 6.6; N, 7.8; Calc. for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$ (352.46): C, 57.9; H, 6.7; N, 7.95%,

^1H NMR (200 MHz, $[\text{D}_6\text{-DMSO}]$) δ 1.40-1.65 (2H, m, CH_2), 1.70-2.05 (4H, m, 2 $\times$ CH_2),

3.30-3.70 (4H, m, 2 $\times$ N^+CH_2), 3.21 (3H, s, CH_3SO_4^-), 3.37 (3H, s, N^+CH_3), 6.09 (1H, d, J 8.4,

CHCN), 6.57 (1H, dd, J 15.6, J 8.4, $\text{C}_6\text{H}_5\text{CH}=\text{CH}$), 7.22 (1H, d, J 15.6, $\text{C}_6\text{H}_5\text{CH}=\text{CH}$), 7.40-

7.46 (3H, m, C_6H_5), 7.62-7.70 (2H, m, C_6H_5).

N-(α -ethoxycarbonylbenzyl)-N,N,N-trimethylammonium perchlorate (2i)

Yield 7.8 g (81%), mp 161-163°C (MeOH),

Found: C, 48.6; H, 6.3; N, 4.3; Calc. for $\text{C}_{13}\text{H}_{20}\text{ClNO}_6$ (321.76): C, 48.5; H, 6.3; N, 4.35%,

^1H NMR (200 MHz, $[\text{D}_6\text{-DMSO}]$) δ 1.13 (3H, t, J 7.1, $\text{CO}_2\text{CH}_2\text{CH}_3$), 3.18 (9H, s, $\text{N}^+(\text{CH}_3)_3$),

4.10-4.36 (2H, m, $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.73 (1H, s, $\text{CHCO}_2\text{CH}_2\text{CH}_3$), 7.59 (5H, s, C_6H_5).

Cyclopropanes 4

***Z,E*-1-phenylcyclopropane-1,2-carbonitrile (4aa)**^[16-18]

purified by distillation, yield 484 mg (96%) from salt **2a1** or 419 mg (83%) from salt **2a3**, bp 140-145°C/0.08 Torr (Kugel-Rohr),

Z-4aa: separated by column chromatography, yield 197 mg (39%), 73-74°C (hexane-EtOAc 10:1),

¹H NMR (500 MHz, CDCl₃) δ 2.01-2.07 (1H, m) and 2.15-2.21 (2H, m) (CH₂ and CHCN), 7.31-7.35 (2H, m, C₆H₅), 7.38-7.45 (3H, m, C₆H₅).

E-4aa: separated by column chromatography, yield 197 mg (39%), mp 76-77°C (hexane-EtOAc 10:1),

¹H NMR (500 MHz, CDCl₃) δ 2.12 (2H, d, J 8.0, CH₂), 2.54 (1H, t, J 8.0, CHCN), 7.44-7.48 (5H, m, C₆H₅).

***Z,E*-2-cyano-2-phenylcyclopropanecarboxylic acid, methyl ester (4ab)**^[20-21]

purified by distillation and short column chromatography, yield 549 mg (91%) in system A from salt **2a1** or 483 mg (80%) in system B from salt **2a1** or 471 mg (78%) in system A from salt **2a2**, bp 135-145°C/0.07 Torr (Kugel-Rohr),

¹H NMR (200 MHz, CDCl₃) δ 1.86 (*Z*, dd, J 8.3, J 5.4) and 1.92 (*E*, dd, J 8.7, J 5.8) (*Z+E*, 1H, CHH); 2.20 (*E*, dd, J 6.9, J 5.8) and 2.22 (*Z*, dd, J 7.1, J 5.4) (*Z+E*, 1H, CHH); 2.37 (*Z*, dd, J 8.3, J 7.1) and 2.72 (*E*, dd, J 8.7, J 6.9) (*Z+E*, 1H, CHCO₂CH₃); 3.44 (*E*) and 3.81 (*Z*) (*Z+E*, 2×s, CO₂CH₃); 7.30-7.35 (*Z+E*, m, 5H, C₆H₅).

***Z,E*-2-cyano-2-phenylcyclopropanecarboxylic acid, *t*-butyl ester (4ac)**^[16]

purified by distillation and short column chromatography, yield 664 mg (91%) from salt **2a1** or 526 mg (72%) from salt **2a2**, bp 120-125°C/0.1 Torr (Kugel-Rohr),

¹H NMR (200 MHz, CDCl₃) δ 1.13 (*E*) and 1.52 (*Z*) (*Z+E*, 9H, 2×s, CO₂C(CH₃)₃); 1.75 (*Z*, dd, J 8.1, J 5.2) and 1.83 (*E*, dd, J 8.6, J 5.8) (*Z+E*, 1H, CHH); 2.15 (*E*, dd, J 7.0, J 5.8) and 2.16 (*Z*, dd, J 7.1, J 5.2) (*Z+E*, 1H, CHH); 2.27 (*Z*, dd, J 8.1, J 7.1) and 2.61 (*E*, dd, J 8.6, J 7.0) (*Z+E*, 1H, CHCO₂(CH₃)₃); 7.30-7.35 (*Z+E*, m, 5H, C₆H₅).

***Z,E*-2-formyl-1-phenylcyclopropanecarbonitrile (4ad)**

purified by distillation and column chromatography, yield 236 mg (46%), bp 140-145°C/0.2 Torr (Kugel-Rohr),

Found: 171.06843 Calc. for C₁₁H₉NO (171.20): 171.06842,

^1H NMR (200 MHz, CDCl_3) δ 2.01 (Z, dd, J 8.5, J 5.8) and 2.09 (E, dd, J 8.9, J 6.1) (Z+E, 1H, CHH); 2.30 (Z, dd, J 6.9, J 5.8) and 2.34 (E, dd, J 6.7, J 6.1) (Z+E, 1H, CHH); 2.51 (Z, ddd, $J_{\text{H-CHO}}$ 4.6, J 8.5, J 6.9) and 2.77 (E, ddd, $J_{\text{H-CHO}}$ 5.0, J 8.9, J 6.7) (Z+E, 1H, CHCHO); 7.30-7.45 (Z+E, m, 5H, C_6H_5); 8.76 (E, d, J 5.0) and 9.52 (Z, d, J 4.6) (Z+E, 1H, CHO).

Z,E-2-acetyl-1-phenylcyclopropanecarbonitrile (4ae)

purified by distillation and short column chromatography, yield 500 mg (90%), bp 135-145°C/0.07 Torr (Kugel-Rohr),

Found: C, 78.0; H, 6.05; N, 7.5; Calc. for $\text{C}_{12}\text{H}_{11}\text{NO}$ (185.23): C, 77.8; H, 5.6; N, 7.6%,

^1H NMR (200 MHz, CDCl_3) δ 1.82 (Z, dd, J 8.1, J 5.3) and 2.15-2.25 (E, m) (Z+E, 1H, CHH); 2.13 (E) and 2.39 (Z) (Z+E, 2 $\times$ s, 3H, COCH_3) 2.22 (Z, dd, J 7.1, J 5.3) and 2.30-2.40 (E, m) (Z+E, 1H, CHH); 2.65 (Z, dd, J 8.1, J 7.1) and 2.99 (E, dd, J 8.4, J 7.0) (Z+E, 1H, CHCOCH_3); 7.20-7.40 (Z+E, m, 5H, C_6H_5).

Z-4ae: separated by column chromatography, yield 250 mg (45%), oil,

Found: 185.08303 Calc. for $\text{C}_{12}\text{H}_{11}\text{NO}$ (185.23): 185.08406,

^1H NMR (200 MHz, CDCl_3) δ 1.82 (1H, dd, J 8.1, J 5.3, CHH); 2.22 (1H, dd, J 7.1, J 5.3, CHH); 2.39 (s, 3H, COCH_3); 2.65 (1H, dd, J 8.1, J 7.1, CHCOCH_3); 7.30-7.45 (m, 5H, C_6H_5).

Z,E-2-benzoyl-1-phenylcyclopropanecarbonitrile (4af)

purified by distillation and short column chromatography, yield 445 mg (60%), bp 195-200°C/0.08 Torr (Kugel-Rohr),

Found: 247.09716 Calc. for $\text{C}_{17}\text{H}_{13}\text{NO}$ (247.30): 247.09972,

^1H NMR (500 MHz, CDCl_3) δ 2.01 (Z, dd, J 8.0, J 5.0) and 2.00-2.05 (E, m) (Z+E, 1H, CHH); 2.57 (Z, dd, J 7.5, J 5.0) and 2.59 (E, dd, J 7.5, J 5.5) (Z+E, 1H, CHH); 3.31 (Z, dd, J 8.0, J 7.5) and 3.65 (E, dd, J 8.5, J 7.5) (Z+E, 1H, CHCOC_6H_5); 7.21-7.28 (1H, m), 7.35-7.44 (4H, m), 7.46-7.52 (2H, m), 7.57-7.64 (1H, m) and 7.91-8.02 (2H, m) (Z+E, 10H, 5 $\times$ m, CC_6H_5 and COC_6H_5).

Z-4af: separated by crystallization, yield 208 mg (28%), mp 75-77°C (MeOH),

Found: C, 82.4; H, 5.2; N, 5.7; Calc. for $\text{C}_{17}\text{H}_{13}\text{NO}$ (247.30): C, 82.6; H, 5.3; N, 5.7%,

^1H NMR (200 MHz, CDCl_3) δ 2.02 (1H, dd, J 7.8, J 5.4, CHH); 2.58 (1H, dd, J 7.4, J 5.4, CHH); 3.30 (1H, dd, J 7.8, J 7.4, CHCOC_6H_5); 7.35-7.65 (8H, m, CC_6H_5 and COC_6H_5); 7.95-8.05 (2H, m, COC_6H_5),

^{13}C NMR (50 MHz, CDCl_3) δ 21.61, 24.84, 34.80, 118.30, 126.11, 128.45, 128.61, 128.91, 129.35, 133.88, 134.77, 136.70, 192.24.

***Z,E*-2-benzenesulfonyl-1-phenylcyclopropanecarbonitrile (4ag)**

purified by short column chromatography, yield 782 mg (92%), white solid,

Found: C, 67.9; H, 4.6; N, 4.9; Calc. for $C_{16}H_{13}NO_2S$ (283.35): C, 67.8; H, 4.6; N, 4.9%,

1H NMR (400 MHz, $CDCl_3$) δ 2.11 (Z, dd, J 8.8, J 6.4) and 2.19 (E, dd, J 9.2, J 6.4) (Z+E, 1H, CHH); 2.60 (Z, dd, J 7.2, J 6.4) and 2.65 (E, dd, J 6.8, J 6.4) (Z+E, 1H, CHH); 3.03 (Z, dd, J 8.8, J 7.2) and 3.42 (E, dd, J 9.2, J 6.8) (Z+E, 1H, $CHSO_2C_6H_5$); 7.05-7.13 (2H, m), 7.26-7.34 (3H, m), 7.60-7.77 (3H, m) and 8.08-8.14 (2H, m) (10H, 4×m, CC_6H_5 and $SO_2C_6H_5$).

Z-4ag: separated by crystallization, yield 638 mg (75%), mp 68-70°C (MeOH),

Found: C, 67.8; H, 4.6; N, 4.95; Calc. for $C_{16}H_{13}NO_2S$ (283.35): C, 67.8; H, 4.6; N, 4.9%,

1H NMR (200 MHz, $CDCl_3$) δ 2.12 (1H, dd, J 8.8, J 6.3, CHH); 2.61 (1H, dd, J 7.0, J 6.3, CHH); 3.03 (1H, dd, J 8.8, J 7.0, $CHSO_2C_6H_5$); 7.05-7.15 (2H, m, CC_6H_5); 7.25-7.35 (3H, m, CC_6H_5); 7.55-7.80 (3H, m, $SO_2C_6H_5$); 8.05-8.15 (2H, m, $SO_2C_6H_5$),

^{13}C NMR (50 MHz, $CDCl_3$) δ 19.25, 21.96, 46.97, 126.68, 128.21, 129.17, 129.40, 129.67, 133.10, 134.55, 139.02.

***Z,E*-1-(4-methoxyphenyl)cyclopropane-1,2-dicarbonitrile (4ba)**

purified column chromatography, yield 482 mg (81%), white solid,

Z-4ba: separated by column chromatography, yield 101 mg (17%), mp 77-79°C (MeOH),

Found: C, 72.65; H, 5.1; N, 14.2; Calc. for $C_{12}H_{10}N_2O$ (198.23): C, 72.7; H, 5.1; N, 14.1%,

1H NMR (400 MHz, $CDCl_3$) δ 1.97 (1H, dd, J 8.4, J 5.2, CHH), 2.09 (1H, dd, J 8.4, J 6.4, CHH), 2.14 (1H, dd, J 6.4, J 5.2, CHCN), 3.81 (3H, s, OCH_3), 6.87-6.93 (2H, m, C_6H_4), 7.23-7.28 (2H, m, C_6H_4),

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.75, 21.35, 22.10, 55.39, 114.76, 116.51, 118.01, 123.69, 128.18, 160.32.

E-4ba: separated by column chromatography, yield 202 mg (34%), mp 98-100°C (MeOH),

Found: C, 72.7; H, 5.1; N, 14.3; Calc. for $C_{12}H_{10}N_2O$ (198.23): C, 72.7; H, 5.1; N, 14.1%,

1H NMR (400 MHz, $CDCl_3$) δ 2.07 (1H, dd, J 6.8, J 6.0, CHH), 2.10 (1H, dd, J 9.6, J 6.0, CHH), 2.50 (1H, J 9.6, J 6.8, CHCN), 3.83 (3H, s, OCH_3), 6.94-6.99 (2H, m, C_6H_4), 7.35-7.40 (2H, m, C_6H_4),

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.69, 19.26, 20.55, 55.32, 114.80, 115.65, 119.50, 121.39, 129.89, 160.61.

***Z,E*-2-cyano-2-(4-methoxyphenyl)cyclopropanecarboxylic acid, methyl ester (4bb)**

purified by distillation, yield 583 mg (84%) in system A or 423 mg (61%) in system B, bp 180-185°C/0.04 Torr (Kugel-Rohr),

Found: C, 67.6; H, 5.9; N, 6.2; Calc. for C₁₃H₁₃NO₃ (231.25): C, 67.5; H, 5.7; N, 6.1%,

¹H NMR (400 MHz, CDCl₃) δ 1.80 (Z, dd, J 8.4, J 5.2) and 1.91 (E, dd, J 8.8, J 5.6) (Z+E, 1H, CHH); 2.16 (E, J 6.8, J 5.6) and 2.20 (Z, J 6.8, J 5.2) (Z+E, 1H, CHH); 2.31 (Z, J 8.4, J 6.8) and 2.69 (E, J 8.8, J 6.8) (Z+E, 1H, CHCO₂CH₃); 3.46 (E), 3.75 (E), 3.74 (Z) and 3.80 (Z) (2×3H, 4xs, OCH₃ and CO₂CH₃); 6.81-6.89 (Z+E, 2H, m, C₆H₄); 7.21-7.28 (Z+E, 2H, m, C₆H₄),

¹³C NMR (100 MHz, CDCl₃) δ 17.64, 20.91, 21.06, 21.79, 28.91, 30.13, 52.14, 52.46, 55.00, 55.14, 113.94, 114.23, 118.66, 121.25, 122.43, 126.08, 127.86, 127.96, 130.21, 159.49, 159.66, 167.20, 168.58.

Z,E-2-cyano-2-(4-methoxyphenyl)cyclopropanecarboxylic acid, *t*-butyl ester (4bc)

purified by distillation, yield 656 mg (80%), bp 175-180°C/0.04 Torr (Kugel-Rohr),

Found: C, 70.3; H, 7.0; N, 5.1; Calc. for C₁₆H₁₉NO₃ (273.34): C, 70.3; H, 7.0; N, 5.1%,

¹H NMR (400 MHz, CDCl₃) δ 1.18 (E) and 1.52 (Z) (Z+E, 9H, 2xs, CO₂C(CH₃)₃); 1.69 (Z, dd, J 8.0, J 5.2) and 1.80 (E, dd, J 8.4, J 5.6) (Z+E, 1H, CHH); 2.08 (E, dd, J 6.8, J 5.6) and 2.10 (Z, dd, J 7.2, J 5.2) (Z+E, 1H, CHH); 2.20 (Z, dd, J 8.0, J 7.2) and 2.57 (E, dd, J 8.4, J 6.8) (Z+E, 1H, CHC(CH₃)₃); 3.77 (E) and 3.78 (Z) (Z+E, 3H, 2xs, OCH₃); 6.83-6.89 (Z+E, 2H, m, C₆H₄); 7.22-7.30 (Z+E, 2H, m, C₆H₄).

¹³C NMR (100 MHz, CDCl₃) δ 17.30, 20.59, 21.08, 21.41, 27.51, 27.88, 30.29, 31.50, 55.16, 55.22, 82.01, 82.47, 113.90, 114.26, 118.83, 121.67, 122.83, 126.63, 127.76, 130.54, 159.46, 159.74, 165.64, 167.06.

Z,E-2-acetyl-1-(4-methoxyphenyl)cyclopropanecarbonitrile (4be)

purified by distillation, yield 542 mg (84%), bp 215-220°C/0.8 Torr (Kugel-Rohr),

Found: C, 72.5; H, 6.3; N, 6.3; Calc. for C₁₃H₁₃NO₂ (215.25): C, 72.5; H, 6.1; N, 6.5%,

¹H NMR (400 MHz, CDCl₃) δ 1.77 (Z, dd, J 8.0, J 5.2) and 1.82 (E, dd, J 8.4, J 5.6) (Z+E, 1H, CHH); 2.14 (E) and 2.40 (Z) (Z+E, 2xs, 3H, COCH₃); 2.20 (Z, dd, J 6.8, J 5.2) and 2.24 (E, dd, J 6.8, J 5.6) (Z+E, 1H, CHH); 2.57 (Z, dd, J 8.0, J 6.8) and 2.95 (E, dd, J 8.4, J 6.8) (Z+E, 1H, CHCOCH₃); 3.75 (E) and 3.78 (Z) (3H, 2xs, OCH₃); 6.80-6.90 (Z+E, 2H, m, C₆H₄); 7.18-7.28 (Z+E, 2H, m, C₆H₄),

^{13}C NMR (100 MHz, CDCl_3) δ 17.43, 21.65, 23.12, 23.70, 31.34, 31.46, 35.76, 37.39, 55.08, 55.25, 114.05, 114.34, 118.40, 121.68, 121.75, 126.41, 127.57, 130.16, 159.53, 159.66, 199.42, 200.55.

***Z,E*-2-benzoyl-1-(4-methoxyphenyl)cyclopropanecarbonitrile (4bf)**

purified by column chromatography, yield 574 mg (69%), white solid,

Found: C, 77.8; H, 5.6; N, 5.0; Calc. for $\text{C}_{18}\text{H}_{15}\text{NO}_2$ (277.33): C, 78.0; H, 5.45; N, 5.05%,

^1H NMR (400 MHz, CDCl_3) δ 1.97 (Z, dd, J 8.0, J 5.2) and 2.01 (E, dd, J 8.4, J 5.6) (Z+E, 1H, CHH); 2.53 (Z, dd, J 7.2, J 5.2) and 2.54 (E, dd, J 7.2, J 5.6) (Z+E, 1H, CHH); 3.24 (Z, dd, J 8.0, J 7.2) and 3.62 (E, dd, J 8.4, J 7.2) (Z+E, 1H, CHCOC_6H_5); 6.71-6.76 (E, m) and 6.91-6.96 (Z, m) (Z+E, 2×m, 2H, C_6H_4); 7.15-7.19 (E, m) and 7.32-7.37 (Z, m) (Z+E, 2×m, 2H, C_6H_4); 7.45-7.52 (m, 2H), 7.55-7.64 (m, 1H) and 7.91-8.02 (m, 2H) (Z+E, 5H, COC_6H_5).

Z-4bf: separated by crystallization, yield 324 mg (39%), mp 89-91°C (MeOH),

Found: C, 77.9; H, 5.4; N, 5.1; Calc. for $\text{C}_{18}\text{H}_{15}\text{NO}_2$ (277.33): C, 78.0; H, 5.45; N, 5.05%,

^1H NMR (400 MHz, CDCl_3) δ 1.97 (1H, dd, J 8.0, J 5.2, CHH), 2.55 (1H, dd, J 7.2, J 5.2, CHH), 3.23 (1H, dd, J 8.0, J 7.2, CHCOPh), 3.84 (3H, s, OCH_3), 6.92-6.97 (2H, m, C_6H_4), 7.33-7.38 (2H, m, C_6H_4), 7.45-7.53 (2H, m, COC_6H_5), 7.59-7.64 (1H, m, COC_6H_5), 7.97-8.02 (2H, m, COC_6H_5),

^{13}C NMR (100 MHz, CDCl_3) δ 21.29, 24.42, 34.59, 55.41, 114.63, 118.56, 126.67, 127.65, 128.37, 128.84, 133.77, 136.73, 159.74, 192.36.

***Z,E*-2-benzenesulfonyl-1-(4-methoxyphenyl)cyclopropanecarbonitrile (4bg)**

purified by column chromatography, yield 856 mg (91%), white solid,

Found: C, 65.4; H, 5.0; N, 4.5; Calc. for $\text{C}_{17}\text{H}_{15}\text{NO}_3\text{S}$ (313.38): C, 65.2; H, 4.8; N, 4.5%,

^1H NMR (400 MHz, CDCl_3) δ 2.05 (Z, dd, J 9.2, J 6.4) and 2.15 (E, J 9.2, J 6.4) (Z+E, 1H, CHH); 2.55 (Z, dd, J 6.8, J 6.4) and 2.58 (E, J 6.8, J 6.4) (Z+E, 1H, CHH); 2.96 (Z, dd, J 9.2, J 6.8) and 3.15 (E, J 9.2, J 6.8) (Z+E, 1H, $\text{CHSO}_2\text{C}_6\text{H}_5$); 6.76-6.86 (Z+E, 2H, m, C_6H_4); 6.96-7.24 (Z+E, 2H, m, C_6H_4); 7.60-7.66 (Z+E, 2H, m, $\text{SO}_2\text{C}_6\text{H}_5$); 7.70-7.80 (Z+E, 1H, m, $\text{SO}_2\text{C}_6\text{H}_5$); 8.08-8.14 (Z+E, 2H, m, $\text{SO}_2\text{C}_6\text{H}_5$).

Z-4bg: separated by crystallization, yield 583 mg (62%), mp 94-95°C (MeOH),

Found: C, 65.35; H, 4.6; N, 4.7; Calc. for $\text{C}_{17}\text{H}_{15}\text{NO}_3\text{S}$ (313.38): C, 65.2; H, 4.8; N, 4.5%,

^1H NMR (400 MHz, CDCl_3) δ 2.05 (1H, dd, J 8.8, J 6.4, CHH), 2.57 (1H, dd, J 6.8, J 6.4, CHH), 2.95 (1H, dd, J 8.8, J 6.8, $\text{CHSO}_2\text{C}_6\text{H}_5$), 6.77-6.82 (2H, m, C_6H_4), 6.98-7.02 (2H, m,

C₆H₄), 7.61-7.68 (2H, m, SO₂C₆H₅), 7.71-7.76 (1H, m, SO₂C₆H₅), 8.09-8.14 (2H, m, SO₂C₆H₅),
¹³C NMR (100 MHz, CDCl₃) δ 19.04, 21.40, 46.79, 55.35, 114.64, 117.38, 124.90, 128.08, 128.20, 129.58, 134.44, 139.03, 160.03.

***Z,E*-1-(4-cyanophenyl)cyclopropane-1,2-dicarbonitrile (4ca)**

Z-4ca: purified by column chromatography and crystalization, yield 122 mg (21%), mp 133-134°C (MeOH),

Found: C, 74.3; H, 3.7; N, 21.6; Calc. for C₁₂H₇N₃ (193.21): C, 74.6; H, 3.65; N, 21.75%,
¹H NMR (500 MHz, CDCl₃) δ 2.10 (1H, dd, J 9.0, J 6.0, CHH), 2.27 (1H, dd, J 9.0, J 7.0, CHCN), 2.33 (1H, dd, J 7.0, J 6.0, CHH), 7.45-7.48 (2H, m, C₆H₄), 7.72-7.76 (2H, m, C₆H₄),
¹³C NMR (100 MHz, CDCl₃) δ 16.06, 22.34, 22.49, 113.61, 115.65, 116.72, 117.57, 127.06, 133.27, 136.88.

E-4ca: purified by column chromatography and crystalization, yield 145 mg (25%), mp 95-97°C (MeOH),

Found: C, 74.6; H, 3.8; N, 21.7; Calc. for C₁₂H₇N₃ (193.21): C, 74.6; H, 3.65; N, 21.75%,
¹H NMR (500 MHz, CDCl₃) δ 2.19 (1H, dd, J 7.0, J 6.5, CHH), 2.26 (1H, dd, J 9.5, J 6.5, CHH), 2.67 (1H, dd, J 9.5, J 7.0, CHCN), 7.57-7.62 (2H, m, C₆H₄), 7.77-7.81 (2H, m, C₆H₄)
¹³C NMR (100 MHz, CDCl₃) δ 15.64, 19.63, 20.99, 114.11, 114.81, 117.63, 118.16, 129.00, 133.18, 134.58.

***Z,E*-2-cyano-2-(4-cyanophenyl)cyclopropanecarboxylic acid, methyl ester (4cb)**

purified by column chromatography, yield 597 mg (88%) in system A or 536 mg (79%) in system B, yellowish oil,

Found: C, 68.8; H, 4.65; N, 12.3; Calc. for C₁₃H₁₀N₂O₂ (226.24): C, 69.0; H, 4.5; N, 12.4%,
¹H NMR (400 MHz, CDCl₃) δ 1.91 (Z, dd, J 8.4, J 5.6) and 2.02 (E, dd, J 8.8, J 5.6) (Z+E, 1H, CHH); 2.22 (Z, dd, J 6.8, J 5.6) and 2.32 (E, dd, J 7.2, J 5.6) (Z+E, 1H, CHH); 2.42 (Z, J 8.4, J 7.2) and 2.79 (E, dd, J 8.8, J 6.8) (Z+E, 1H, CHCO₂CH₃); 3.48 (Z) and 3.81 (E) (Z+E, 3H, 2xs, CO₂CH₃); 7.42-7.51 (Z+E, 2H, m, C₆H₄), 7.61-7.68 (Z+E, 2H, m, C₆H₄).

Z-4cb: separated by crystalization, yield 163 mg (24%), mp 106-108°C (MeOH),

Found: C, 69.1; H, 4.4; N, 12.4; Calc. for C₁₃H₁₀N₂O₂ (226.24): C, 69.0; H, 4.5; N, 12.4%,

^1H NMR (400 MHz, CDCl_3) δ 1.91 (1H, dd, J 8.4, J 5.6, CHH), 2.37 (1H, dd, J 7.2, J 5.6, CHH), 2.43 (1H, dd, J 8.4, J 7.2, CHCO_2CH_3), 3.86 (3H, s, CO_2CH_3), 7.43-7.48 (2H, m, C_6H_4), 7.67-7.72 (2H, m, C_6H_4),
 ^{13}C NMR (100 MHz, CDCl_3) δ 22.22, 22.26, 31.44, 53.00, 112.57, 117.30, 117.83, 126.82, 132.89, 139.50, 167.79.

***Z,E*-2-cyano-2-(4-cyanophenyl)cyclopropanecarboxylic acid, *t*-butyl ester (4cc)**

purified by column chromatography, yield 523 mg (65%), yellowish oil,

Found: C, 71.4; H, 6.15; N, 10.3; Calc. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$ (268.32): C, 71.6; H, 6.0; N, 10.4%,

^1H NMR (400 MHz, CDCl_3) δ 1.18 (*E*) and 1.53 (*Z*) (*Z+E*, 9H, 2 $\times$ s, $\text{CO}_2\text{C}(\text{CH}_3)_3$); 1.82 (*Z*, dd, J 7.2, J 4.8) and 1.95 (*E*, dd, J 8.8, J 6.0) (*Z+E*, 1H, CHH); 2.18 (*E*, dd, J 7.2, J 6.0) and 2.30 (*Z*, dd, J 7.6, J 4.8) (*Z+E*, 1H, CHH); 2.31 (*Z*, dd, J 7.6, J 7.2) and 2.71 (*E*, dd, J 8.8, J 7.2) (*Z+E*, 1H, $\text{CHC}(\text{CH}_3)_3$); 7.42-7.53 (*Z+E*, 2H, m, C_6H_4); 7.63-7.70 (*Z+E*, 2H, m, C_6H_4),
 ^{13}C NMR (100 MHz, CDCl_3) δ 17.39, 21.05, 21.68, 22.16, 27.44, 27.76, 30.75, 32.63, 82.43, 83.09, 112.03, 112.58, 117.32, 117.79, 117.82, 121.86, 126.51, 130.08, 132.17, 132.19, 132.62, 132.65, 136.15, 139.82, 165.08, 166.04.

***Z,E*-2-acetyl-1-(4-cyanophenyl)cyclopropanecarbonitrile (4ce)**

purified by column chromatography, yield 404 mg (64%), yellowish oil,

Found: C, 74.1; H, 4.9; N, 13.4; Calc. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}$ (210.24): C, 74.3; H, 4.8; N, 13.3%,

^1H NMR (400 MHz, CDCl_3) δ 1.88 (*Z*, dd, J 8.4, J 5.6) and 1.96 (*E*, dd, J 8.4, J 5.6) (*Z+E*, 1H, CHH); 2.20 (*E*) and 2.44 (*Z*) (*Z+E*, 2 $\times$ s, 3H, COCH_3); 2.32 (*E*, dd, J 7.2, J 5.6) and 2.38 (*Z*, dd, J 7.2, J 5.6) (*Z+E*, 1H, CHH); 2.67 (*Z*, dd, J 8.4, J 7.2) and 3.08 (*E*, dd, J 8.4, J 7.2) (*Z+E*, 1H, CHCOCH_3); 7.41-7.48 (*Z+E*, 2H, m, C_6H_4); 7.60-7.67 (*Z+E*, 2H, m, C_6H_4),
 ^{13}C NMR (100 MHz, CDCl_3) δ 22.74, 23.83, 23.92, 31.51, 31.56, 31.86, 36.17, 38.24, 112.45, 112.91, 116.96, 117.85, 117.92, 120.44, 126.48, 129.87, 132.45, 132.88, 135.28, 139.83, 199.01, 199.38.

***Z*-4ce:** separated by crystallization, yield 139 mg (22%), mp 150-152°C (MeOH),

Found: C, 74.4; H, 4.7; N, 13.4; Calc. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}$ (210.24): C, 74.3; H, 4.8; N, 13.3%,

^1H NMR (400 MHz, CDCl_3) δ 1.89 (1H, dd, J 8.4, J 5.6, CHH), 2.41 (1H, dd, J 7.6, J 5.6, CHH), 2.45 (3H, s, CO_2CH_3), 2.67 (1H, dd, J 8.4, J 7.6, CHCO_2CH_3), 7.44-7.49 (2H, m, C_6H_4), 7.68-7.73 (2H, m, C_6H_4),
 ^{13}C NMR (100 MHz, CDCl_3) δ 22.73, 23.92, 31.53, 38.25, 112.47, 116.97, 117.86, 126.48, 132.91, 139.84, 199.37.

***Z,E*-2-benzoyl-1-(4-cyanophenyl)cyclopropanecarbonitrile (4cf)**

purified by column chromatography, yield 302 mg (37%), yellowish solid,

Found: C, 79.3; H, 4.6; N, 10.1; Calc. for $C_{18}H_{12}N_2O$ (272.31): C, 79.4; H, 4.4; N, 10.3%,

1H NMR (400 MHz, $CDCl_3$) δ 2.06 (*Z*, dd, *J* 8.4, *J* 5.6) and 2.15 (*E*, dd, *J* 8.4, *J* 5.6) (*Z+E*, 1H, *CHH*); 2.62 (*E*, dd, *J* 7.2, *J* 5.6) and 2.70 (*Z*, dd, *J* 7.2, *J* 5.6) (*Z+E*, 1H, *CHH*); 3.33 (*Z*, dd, *J* 8.4, *J* 7.2) and 3.74 (*E*, dd, *J* 8.4, *J* 7.2) (*Z+E*, 1H, *CHCOC* $_6H_5$); 7.38-7.43 (m), 7.47-7.58 (m), 7.61-7.66 (m), 7.73-7.77 (m) and 7.89-7.99 (m) (*Z+E*, 9H, 5×m, C_6H_4 and *COC* $_6H_5$).

Z-4cf: separated by crystalization, yield 82 mg (10%), mp 110-111°C (MeOH),

Found: C, 79.4; H, 4.7; N, 10.5; Calc. for $C_{18}H_{12}N_2O$ (272.31): C, 79.4; H, 4.4; N, 10.3%

1H NMR (400 MHz, $CDCl_3$) δ 2.06 (1H, dd, *J* 8.4, *J* 5.6, *CHH*), 2.69 (1H, dd, *J* 7.2, *J* 5.6, *CHH*), 3.34 (1H, dd, *J* 8.4, *J* 7.2, *CHCOPh*), 7.48-7.57 (m, 4H), 7.62-7.67 (m, 1H), 7.72-7.77 (m, 2H) and 7.94-7.99 (m, 2H) (9H, 4×m, C_6H_4 and *COC* $_6H_5$),

^{13}C NMR (100 MHz, $CDCl_3$) δ 22.31, 24.43, 35.24, 112.58, 117.14, 117.89, 126.52, 126.55, 128.40, 129.00, 133.05, 133.09, 134.18, 134.20, 136.29, 139.94, 191.28.

***Z,E*-2-benzenesulfonyl-1-(4-cyanophenyl)cyclopropanecarbonitrile (4cg)**

purified by column chromatography, yield 749 mg (81%), yellowish solid,

Found: C, 66.2; H, 3.9; N, 9.15; Calc. for $C_{17}H_{12}N_2O_2S$ (308.36): C, 66.2; H, 3.9; N, 9.1%,

1H NMR (400 MHz, $CDCl_3$) δ 2.14 (*Z*, dd, *J* 8.8, *J* 6.6) and 2.24 (*E*, *J* 9.2, *J* 6.6) (*Z+E*, 1H, *CHH*); 2.62 (*Z*, dd, *J* 7.0, *J* 6.6) and 2.70 (*E*, *J* 7.2, *J* 6.6) (*Z+E*, 1H, *CHH*); 3.04 (*Z*, dd, *J* 8.8, *J* 7.2) and 3.46 (*E*, *J* 9.2, *J* 7.0) (*Z+E*, 1H, *CHSO* $_2C_6H_5$); 7.46-7.76 (8H, m) and 8.06-8.12 (1H, m) (*Z+E*, 9H, 2×m, C_6H_4 and *SO* $_2C_6H_5$).

Z-4cg: separated by crystalization, yield 601 mg (65%), mp 155-157°C (MeOH),

Found: C, 66.1; H, 4.0; N, 9.2; Calc. for $C_{17}H_{12}N_2O_2S$ (308.36): C, 66.2; H, 3.9; N, 9.1%,

1H NMR (400 MHz, $CDCl_3$) δ 2.16 (1H, dd, *J* 8.8, *J* 6.4, *CHH*), 2.70 (1H, dd, *J* 7.2, *J* 6.4, *CHH*), 3.05 (1H, dd, *J* 8.8, *J* 7.2, *CHSO* $_2C_6H_5$), 7.21-7.27 (2H, m, C_6H_4), 7.60-7.68 (4H, m, C_6H_4 and *SO* $_2C_6H_5$), 7.73-7.80 (1H, m, *SO* $_2C_6H_5$), 8.06-8.11 (2H, m, *SO* $_2C_6H_5$).

1-naphtalen-1-yl-cyclopropane-1,2-dicarbonitrile (4da)

purified by column chromatography and crystallization, yield 268 mg (41%), mp 119-121°C (MeOH),

Found: C, 82.7; H, 4.7; N, 13.0; $C_{15}H_{10}N_2$ (218.26): C, 82.55; H, 4.8; N, 12.9%

^1H NMR (400 MHz, CDCl_3) δ 2.07 (1H, dd, J 9.2, J 5.6, CHH), 2.20 (1H, dd, J 9.2, J 6.4, CHH), 2.35 (1H, J 6.4, J 5.6, CHCN), 7.42-7.47 (2H, m, C_{10}H_7), 7.60-7.66 (1H, m, C_{10}H_7), 7.71-7.77 (1H, m, C_{10}H_7), 7.91-7.97 (2H, m, C_{10}H_7), 8.17-8.23 (1H, m, C_{10}H_7),
 ^{13}C NMR (100 MHz, CDCl_3) δ 13.66, 21.08, 30.89, 116.65, 117.80, 122.83, 125.04, 126.91, 127.40, 128.05, 128.10, 129.21, 130.98, 131.21, 133.80.

***Z,E*-2-cyano-1-naphtalen-1-yl-cyclopropanecarboxylic acid, methyl ester (4db)**

purified by column chromatography, yield 678 mg (90%), white solid,

Z-4db: separated by column chromatography and crystalization, yield 452 mg (60%), mp 93-94°C (MeOH),

Found: C, 76.4; H, 5.3; N, 5.7; Calc. for $\text{C}_{16}\text{H}_{13}\text{NO}_2$ (251.29): C, 76.5; H, 5.2; N, 5.6%,

^1H NMR (400 MHz, CDCl_3) δ 1.89 (1H, dd, J 8.4, J 4.8, CHH); 2.41 (1H, dd, J 6.8, J 4.8, CHH); 2.46 (1H, dd, J 8.4, J 6.8, CHCO_2CH_3); 3.94 (3H, s, CO_2CH_3); 7.41-7.70 (4H, m, C_{10}H_7), 7.86-7.94 (2H, m, C_{10}H_7), 8.21-8.27 (1H, m, C_{10}H_7).

^{13}C NMR (100 MHz, CDCl_3) δ 20.76, 20.83, 28.81, 52.90, 118.71, 123.32, 125.08, 126.53, 127.47, 127.52, 128.96, 130.19, 130.50, 131.41, 133.84, 169.00.

E-4db: separated by column chromatography and crystalization, yield 90 mg (12%), mp 151-153°C (MeOH),

Found: C, 76.4; H, 5.1; N, 5.5; Calc. for $\text{C}_{16}\text{H}_{13}\text{NO}_2$ (251.29): C, 76.5; H, 5.2; N, 5.6%,

^1H NMR (500 MHz, CDCl_3) δ 2.16 (1H, dd, J 8.8, J 5.4, CHH); 2.29 (1H, dd, J 6.8, J 5.4, CHH); 2.98 (1H, dd, J 8.8, J 6.8, CHCO_2CH_3); 3.23 (3H, s, CO_2CH_3); 7.46 (1H, dd, J 8.3, J 7.3, C_{10}H_7), 7.50-7.56 (2H, m, C_{10}H_7), 7.58-7.63 (1H, m, C_{10}H_7), 7.85-7.90 (2H, m, C_{10}H_7) and 8.23 (1H, dd, J 8.3, J 1.0, C_{10}H_7),

^{13}C NMR (50 MHz, CDCl_3) δ 19.17, 28.80, 52.20, 123.11, 125.21, 126.29, 126.99, 127.24, 128.81, 129.01, 130.11, 136.76.

2-cyano-1-naphtalen-1-yl-cyclopropanecarboxylic acid, *t*-butyl ester (4dc)

purified by column chromatography, yield 458 mg (52%), 95-96°C (MeOH),

Found: C, 77.7; H, 6.5; N, 4.8; Calc. for $\text{C}_{19}\text{H}_{19}\text{NO}_2$ (293.37): C, 77.8; H, 6.5; N, 4.8%,

^1H NMR (400 MHz, CDCl_3) δ 1.64 (9H, s, $\text{CO}_2\text{C}(\text{CH}_3)_3$), 1.78-1.86 (1H, m, CHH), 2.31-2.38 (2H, m CHH and $\text{CHCO}_2\text{C}(\text{CH}_3)_3$), 7.40-7.70 (4H, m, C_{10}H_7), 7.85-7.94 (2H, m, C_{10}H_7), 8.28-8.33 (1H, m, C_{10}H_7),

^{13}C NMR (100 MHz, CDCl_3) δ 20.19, 20.36, 28.13, 30.17, 82.86, 118.91, 123.57, 125.11, 126.48, 127.30, 127.45, 128.93, 130.05, 130.97, 131.57, 133.88, 167.42.

***Z,E*-2-acetyl-1-naphtalen-1-yl-cyclopropanecarbonitrile (4de)**

purified by distillation and column chromatography, yield 572 mg (81%), bp 175-195°C/0.1 Torr (Kugel-Rohr),

Found: C, 81.6; H, 5.75; N, 5.95; Calc. for $\text{C}_{16}\text{H}_{13}\text{NO}$ (235.29): C, 81.7; H, 5.6; N, 5.95%

^1H NMR (200 MHz, CDCl_3) δ 1.86 (*Z*, dd, *J* 8.3, *J* 4.9) and 2.07 (*E*, dd, *J* 8.6, *J* 5.2) (*Z+E*, 1H, *CHH*); 2.12 (*E*) and 2.55 (*Z*) (*Z+E*, 2 $\times$ s, 3H, COCH_3); 2.36 (*E*, dd, *J* 6.8, *J* 5.2) and 2.37 (*Z*, dd, *J* 6.8, *J* 4.9) (*Z+E*, 1H, *CHH*); 2.64 (*Z*, dd, *J* 8.3, *J* 6.8) and 3.22 (*E*, dd, *J* 8.6, *J* 6.8) (*Z+E*, 1H, CHCOCH_3); 7.36-7.70 (*Z+E*, 4H, m, C_{10}H_7), 7.79-7.95 (*Z+E*, 2H, m, C_{10}H_7) and 8.12-8.27 (*Z+E*, 1H, m, C_{10}H_7),

^{13}C NMR (50 MHz, CDCl_3) δ 19.34, 21.55, 22.78, 31.24, 31.61, 34.96, 35.37, 118.53, 122.99, 123.17, 125.25, 126.30, 126.61, 127.11, 127.43, 127.50, 129.21, 129.29, 130.13, 130.24, 130.86, 131.50, 133.97.

***Z,E*-2-benzoyl-1-naphtalen-1-yl-cyclopropanecarbonitrile (4df)**

purified by column chromatography, yield 740 mg (83%), colorless oil,

Found: 297.11536 Calc. for $\text{C}_{21}\text{H}_{15}\text{NO}$ (297.36): 297.11376,

^1H NMR (200 MHz, CDCl_3) δ 2.06 (*Z*, dd, *J* 8.2, *J* 4.8) and 2.26 (*E*, dd, *J* 8.5, *J* 5.1) (*Z+E*, 1H, *CHH*); 2.59 (*E*, dd, *J* 6.9, *J* 5.1) and 2.63 (*Z*, dd, *J* 6.8, *J* 4.8) (*Z+E*, 1H, *CHH*); 3.37 (*Z*, dd, *J* 8.2, *J* 6.8) and 3.95 (*E*, dd, *J* 8.5, *J* 6.9) (*Z+E*, 1H, CHCOC_6H_5); 7.40-7.70 (*Z+E*, 7H, m), 7.84-7.96 (*Z+E*, 2H, m) and 8.06-8.18 (*Z+E*, 3H, m) (12H, C_{10}H_7 and C_6H_5),

^{13}C NMR (50 MHz, CDCl_3) δ 20.08, 21.68, 23.62, 31.18, 31.77, 118.63, 123.37, 123.67, 125.17, 125.29, 126.11, 126.67, 127.29, 127.41, 128.31, 128.70, 128.96, 129.14, 129.40, 130.09, 130.27, 131.24, 131.57, 133.62, 134.04, 136.79, 193.04.

***Z*-2-benzenesulfonyl-1-naphtalen-1-yl-cyclopropanecarbonitrile (4dg)**

purified by crystallization, yield 800 mg (80%), 196-198°C (EtOAc),

Found: C, 71.7; H, 4.5; N, 4.05; Calc. for $\text{C}_{20}\text{H}_{15}\text{NO}_2\text{S}$ (333.41): C, 72.05; H, 4.5; N, 4.2%,

^1H NMR (500 MHz, CDCl_3) δ 2.20 (1H, dd, *J* 8.8, *J* 6.3, *CHH*); 2.75 (1H, dd, *J* 6.8, *J* 6.3, *CHH*); 3.04 (1H, dd, *J* 8.8, *J* 6.8, $\text{CHSO}_2\text{C}_6\text{H}_5$); 7.22-7.30 (3H, m), 7.34-7.40 (1H, m), 7.45-7.52 (2H, m), 7.70-7.75 (2H, m), 7.80-7.88 (3H, m) and 8.18-8.23 (1H, m) (12H, C_{10}H_7 and C_6H_5),

^{13}C NMR (50 MHz, CDCl_3) δ 18.67, 20.49, 45.58, 117.05, 122.77, 125.10, 126.60, 127.32, 127.44, 128.72, 129.04, 129.14, 129.88, 130.71, 130.94, 133.83, 134.70, 139.00.

***E,Z*-1-furan-2-yl-cyclopropane-1,2-dicarbonitrile (4ea)**

purified by distillation and short column chromatography, yield 337 mg (71%), bp 165-170°C/0.06 Torr (Kugel-Rohr),

Found: 158.047838 Calc. for $\text{C}_9\text{H}_6\text{N}_2\text{O}$ (158.16): 158.048012,

^1H NMR (200 MHz, CDCl_3) δ 2.05-2.20 (*E+Z*, m, 2H, CH_2); 2.35 (*E*, dd, J 9.4, J 6.9) and 2.54 (*Z*, dd, J 9.7, J 7.1) (*E+Z*, 1H, CHCN); 6.37 (*E*) and 6.41 (*Z*) (*E+Z*, 2×dd, J 3.4, J 1.9, 1H, $\text{C}_4\text{H}_3\text{O}$); 6.49 (*E*) and 6.55 (*Z*) (*E+Z*, 2×dd, J 3.4, J 0.8, 1H, $\text{C}_4\text{H}_3\text{O}$); 7.32 (*E*) and 7.44 (*Z*) (*E+Z*, 2×dd, J 1.9, J 0.8, 1H, $\text{C}_4\text{H}_3\text{O}$),

^{13}C NMR (50 MHz, CDCl_3) δ 14.26, 15.10, 15.81, 17.55, 19.41, 20.91, 109.71, 111.23, 111.32, 111.47, 115.22, 115.90, 117.14, 143.07, 143.41, 144.15, 144.43.

***E,Z*-2-cyano-2-furan-2-yl-cyclopropanecarboxylic acid, methyl ester (4eb)**

purified by distillation and short column chromatography, yield 367 mg (64%), bp 130-135°C/0.04 Torr (Kugel-Rohr),

Found: C, 62.8; H, 4.8; N, 7.4; Calc. for $\text{C}_{10}\text{H}_9\text{NO}_3$ (191.19): C, 62.8; H, 4.7; N, 7.3%,

^1H NMR (200 MHz, CDCl_3) δ 1.96 (*E*, dd, J 8.5, J 5.4) and 1.99 (*Z*, dd, J 8.8, J 5.3) (*E+Z*, 1H, CHH); 2.18 (*E*, dd, J 7.3, J 5.4) and 2.21 (*Z*, dd, J 7.3, J 5.3) (*E+Z*, 1H, CHH); 2.55 (*E*, dd, J 8.5, J 7.3) and 2.69 (*Z*, dd, J 8.8, J 7.3) (*E+Z*, 1H, CHCO_2CH_3); 3.58 (*Z*) and 3.80 (*E*) (*E+Z*, 2×s, 3H, CO_2CH_3); 6.33-6.41 (*E*, 2×*Z*, m) and 6.45 (*E*, dd, J 3.4, J 0.9) (2H, $\text{C}_4\text{H}_3\text{O}$); 7.32 (*E*) and 7.37 (*Z*) (*E+Z*, 2×dd, J 1.8, J 0.9, 1H, $\text{C}_4\text{H}_3\text{O}$),

^{13}C NMR (50 MHz, CDCl_3) δ 15.24, 17.42, 18.57, 20.48, 28.98, 29.08, 52.48, 52.67, 108.21, 110.81, 110.97, 111.04, 116.60, 118.88, 142.64, 143.33, 144.16, 146.65, 166.89, 168.08.

***E,Z*-2-cyano-2-furan-2-yl-cyclopropanecarboxylic acid, *t*-butyl ester (4ec)**

purified by distillation and short column chromatography, yield 567 mg (81%), bp 150-155°C/0.07 Torr (Kugel-Rohr),

Found: C, 66.9; H, 6.5; N, 6.1; Calc. for $\text{C}_{13}\text{H}_{15}\text{NO}_3$ (233.27): C, 66.9; H, 6.5; N, 6.0%,

^1H NMR (200 MHz, CDCl_3) δ 1.26 (*Z*) and 1.49 (*E*) (*E+Z*, 2×s, 9H, $\text{CO}_2(\text{CH}_3)_3$); 1.84 (*E*, dd, J 8.5, J 5.2) and 1.87 (*Z*, dd, J 8.7, J 5.6) (*E+Z*, 1H, CHH); 2.08 (*E*, dd, J 7.2, J 5.2) and 2.13 (*Z*, dd, J 7.4, J 5.6) (*E+Z*, 1H, CHH); 2.41 (*E*, dd, J 8.5, J 7.2) and 2.56 (*Z*, dd, J 8.7, J 7.4)

(*E*+*Z*, 1H, $\text{CHCO}_2(\text{CH}_3)_3$); 6.32 (*E*, dd, *J* 3.3, *J* 1.8), 6.41 (*E*, dd, *J* 3.3, *J* 0.9) and 6.30-6.42 (2×*Z*, 2×*m*) (2H, $\text{C}_4\text{H}_3\text{O}$); 7.28 (*E*) and 7.33 (*Z*) (*E*+*Z*, 1H, 2×dd, *J* 1.8, *J* 0.9, $\text{C}_4\text{H}_3\text{O}$), ^{13}C NMR (50 MHz, CDCl_3) δ 14.96, 17.23, 18.35, 20.47, 27.62, 28.01, 30.38, 30.67, 82.29, 83.00, 108.05, 110.91, 111.07, 111.13, 116.91, 119.37, 142.56, 143.19, 144.73, 147.23, 165.33, 166.61.

***E,Z*-2-formyl-1-furan-2-yl-cyclopropanecarbonitrile (4ed)**

purified by distillation and short column chromatography, yield 222 mg (46%), bp 120-130°C/0.2 Torr (Kugel-Rohr),

Found: 161.04735 Calc. for $\text{C}_9\text{H}_7\text{NO}_2$ (161.16): 161.04768,

^1H NMR (200 MHz, CDCl_3) δ 2.09 (*E*, dd, *J* 8.5, *J* 5.6) and 2.13 (*Z*, dd, *J* 8.9, *J* 6.0) (*Z*+*E*, 1H, *CHH*); 2.27 (*E*, dd, *J* 7.1, *J* 5.6) and 2.35 (*Z*, dd, *J* 7.2, *J* 6.0) (*Z*+*E*, 1H, *CHH*); 2.72 (*E*, ddd, $J_{\text{H-CHO}}$ 4.1, *J* 8.5, *J* 7.1) and 2.77 (*Z*, ddd, $J_{\text{H-CHO}}$ 4.8, *J* 8.9, *J* 7.2) (*Z*+*E*, 1H, *CHCHO*); 6.36 (*Z*) and 6.37 (*E*) (*Z*+*E*, 1H, 2×dd, *J* 3.4, *J* 1.9, $\text{C}_4\text{H}_3\text{O}$); 6.45 (*E*) and 6.46 (*Z*) (*Z*+*E*, 1H, 2×dd, *J* 3.4, *J* 0.9, $\text{C}_4\text{H}_3\text{O}$); 7.32 (*E*) and 7.37 (*Z*) (*Z*+*E*, 1H, 2×dd, *J* 1.9, *J* 0.9, $\text{C}_4\text{H}_3\text{O}$); 8.96 (*Z*, d, *J* 4.8) and 9.55 (*E*, d, *J* 4.1) (*Z*+*E*, 1H, *CHO*).

***E,Z*-2-acetyl-1-furan-2-yl-cyclopropanecarbonitrile (4ee)**

purified by distillation and short column chromatography, yield 468 mg (89%) in system C or 168 mg (32%) in system B, bp 135-145°C/0.15 Torr (Kugel-Rohr),

Found: C, 68.55; H, 5.3; N, 7.9; Calc. for $\text{C}_{10}\text{H}_9\text{NO}_2$ (175.19): C, 68.6; H, 5.2; N, 7.8%,

^1H NMR (200 MHz, CDCl_3) δ 1.85 (*Z*, dd, *J* 8.2, *J* 5.4) and 1.87 (*E*, dd, *J* 8.2, *J* 5.0) (*E*+*Z*, 1H, *CHH*); 2.15 (*E*, dd, *J* 7.2, *J* 5.0) and 2.16 (*Z*, dd, *J* 7.4, *J* 5.4) (*E*+*Z*, 1H, *CHH*); 2.22 (*Z*) and 2.37 (*E*) (*E*+*Z*, 2×*s*, 3H, COCH_3); 2.79 (*E*, dd, *J* 8.2, *J* 7.2) and 2.92 (*Z*, dd, *J* 8.2, *J* 7.4) (*E*+*Z*, 1H, *CHCOCH}_3); 6.29 (*Z*) and 6.32 (*E*) (*E*+*Z*, 1H, 2×dd, *J* 3.3, *J* 1.8, $\text{C}_4\text{H}_3\text{O}$); 6.39 (*E*+*Z*, 1H, 2×dd, *J* 3.3, *J* 0.8, $\text{C}_4\text{H}_3\text{O}$); 7.28 (*E*+*Z*, 1H, 2×dd, *J* 1.8, *J* 0.8, $\text{C}_4\text{H}_3\text{O}$),*

^{13}C NMR (50 MHz, CDCl_3) δ 16.69, 18.14, 19.08, 20.90, 30.96, 31.34, 35.28, 35.44, 108.05, 110.71, 111.07, 111.20, 116.37, 119.14, 142.55, 143.49, 143.92, 147.00, 198.67, 200.10.

***E,Z*-2-benzoyl-1-furan-2-yl-cyclopropanecarbonitrile (4ef)**

purified by distillation and short column chromatography, yield 420 mg (59%), bp 170-175°C/0.15 Torr (Kugel-Rohr),

Found: 237.07932 Calc. for $\text{C}_{15}\text{H}_{11}\text{NO}_2$ (237.26): 237.07898,

¹H NMR (200 MHz, CDCl₃) δ 2.06 (Z, dd, J 8.6, J 5.4) and 2.07 (E, dd, J 8.4, J 5.0) (E+Z, 1H, CHH); 2.51 (E, dd, J 7.2, J 5.0) and 2.52 (Z, dd, J 7.4, J 5.4) (E+Z, 1H, CHH); 3.51 (E, dd, J 8.4, J 7.2) and 3.57 (Z, dd, J 8.6, J 7.4) (E+Z, 1H, CHCOC₆H₅); 6.23 (Z) and 6.41 (E) (E+Z, 1H, 2×dd, J 3.4, J 1.8, C₄H₃O); 6.27 (Z) and 6.52 (E) (E+Z, 1H, 2×dd, J 3.4, J 0.8, C₄H₃O); 7.21 (Z) and 7.38 (E) (E+Z, 1H, 2×dd, J 1.8, J 0.8, C₄H₃O); 7.44-7.56 (E+Z, 3H, m, C₆H₅); 7.57-7.68 (E+Z, 2H, m, C₆H₅).

E-4ef: separated by crystallization, yield 171 mg (24%), mp 90-92°C (MeOH),

Found: C, 75.9; H, 4.7; N, 5.9; Calc. for C₁₅H₁₁NO₂ (237.26): C, 75.9; H, 4.7; N, 5.9%,

¹H NMR (200 MHz, CDCl₃) δ 2.06 (dd, J 8.0, J 5.0, 1H, CHH); 2.51 (dd, 1H, J 7.4, J 5.0, 1H, CHH); 3.51 (dd, J 8.0, J 7.4, 1H, CHCOC₆H₅); 6.42 (dd, J 3.4, J 2.0, 1H, C₄H₃O); 6.52 (dd, J 3.4, J 0.8, 1H, C₄H₃O); 7.38 (dd, J 2.0, J 0.8, 1H, C₄H₃O); 7.44-7.68 (m, 3H, C₆H₅); 7.98-8.05 (m, 2H, C₆H₅).

E,Z-1-benzenesulfonyl-1-furan-2-yl-cyclopropanecarbonitrile (4eg)

purified by distillation and column chromatography, yield 435 mg (53%) in system A or 156 mg (19%) in system C, bp 180-200°C/0.03 Torr (Kugel-Rohr),

Found: 273.045951 Calc. for C₁₄H₁₁NO₃S (273.31): 273.045962,

¹H NMR (200 MHz, CDCl₃) δ 2.13 (E, dd, J 8.8, J 6.3) and 2.23 (Z, dd, J 9.2, J 6.5) (Z+E, 1H, CHH); 2.53 (E, dd, J 7.2, J 6.3) and 2.58 (Z, dd, J 7.2, J 6.5) (Z+E, 1H, CHH); 3.24 (E, dd, J 8.8, J 7.2) and 3.41 (Z, dd, J 9.2, J 7.2) (Z+E, 1H, CHSO₂C₆H₅); 6.25-6.40 (Z+E, 1H, m, C₄H₃O); 7.20-7.35 (Z+E, 1H, 2×m, C₄H₃O); 7.40-7.70 (Z+E, 5H, m, C₄H₃O and C₆H₅); 8.00-8.05 (Z+E, 1H, m, C₆H₅).

E,Z-1-thiophen-2-yl-cyclopropane-1,2-dicarbonitrile (4fa)

purified by distillation and short column chromatography, yield 423 mg (81%), bp 170-175°C/0.08 Torr (Kugel-Rohr),

Found: C, 61.85; H, 3.5; N, 16.1; Calc. for C₉H₆N₂S (174.23): C, 62.05; H, 3.5; N, 16.1%

¹H NMR (200 MHz, CDCl₃) δ 1.95-2.30 and 2.55-2.65 (E+Z, 3H, 2×m, CH₂ and CHCN); 6.97 and 7.03 (E+Z, 1H, 2×dd, J 5.2, J 3.7, C₄H₃S); 7.12 and 7.20 (E+Z, 1H, 2×dd, J 3.7, J 1.3, C₄H₃S); 7.29 and 7.37 (E+Z, 1H, 2×dd, J 5.2, J 1.3, C₄H₃S),

¹³C NMR (50 MHz, CDCl₃) δ 16.39, 16.56, 18.63, 18.78, 21.48, 23.26, 115.33, 116.05, 117.13, 118.45, 126.85, 127.69, 127.71, 127.88, 128.02, 129.28, 132.58, 135.10.

***E,Z*-2-cyano-2-thiophen-2-yl-cyclopropanecarboxylic acid, methyl ester (4fb)**

purified by distillation and short column chromatography, yield 560 mg (90%), bp 170-180°C/0.09 Torr (Kugel-Rohr),

Found: C, 58.1; H, 4.4; N, 6.7; Calc. for C₁₀H₉NO₂S (207.25): C, 57.95; H, 4.4; N, 6.8%,

¹H NMR (200 MHz, CDCl₃) δ 1.86 (*E*, dd, J 8.4, J 5.4) and 2.03 (*Z*, dd, J 8.7, J 5.7) (*E*+*Z*, 1H, CHH); 2.22 (*Z*, dd, J 7.2, J 5.7) and 2.27 (*E*, dd, J 7.1, J 5.4) (*E*+*Z*, 1H, CHH); 2.44 (*E*, dd, J 8.4, J 7.1) and 2.75 (*Z*, dd, J 8.7, J 7.2) (*E*+*Z*, 1H, CHCO₂CH₃); 3.55 (*Z*) and 3.82 (*E*) (*E*+*Z*, 3H, 2×s, CO₂CH₃); 6.93 (*Z*) and 6.95 (*E*) (*E*+*Z*, 1H, 2×dd, J 5.2, J 3.6, C₄H₃S); 7.06 (*Z*) and 7.12 (*E*) (*E*+*Z*, 1H, 2×dd, J 3.6, J 1.3, C₄H₃S); 7.23 (*E*) and 7.27 (*Z*) (*E*+*Z*, 1H, 2×dd, J 5.2, J 1.3, C₄H₃S),

¹³C NMR (50 MHz, CDCl₃) δ 16.37, 18.51, 19.98, 23.22, 30.29, 31.91, 52.43, 52.68, 117.67, 120.11, 125.57, 126.78, 126.93, 127.24, 129.11, 133.41, 138.09, 166.64, 167.98.

***E,Z*-2-cyano-2-thiophen-2-yl-cyclopropanecarboxylic acid, *t*-butyl ester (4fc)**

purified by distillation and short column chromatography, yield 449 mg (60%), bp 170-180°C/0.15 Torr (Kugel-Rohr),

Found: C, 62.4; H, 5.95; N, 5.8; Calc. for C₁₃H₁₅NO₂S (249.33): C, 62.6; H, 6.1; N, 5.6%,

¹H NMR (200 MHz, CDCl₃) δ 1.23 (*Z*) and 1.52 (*E*) (*E*+*Z*, 2×s, 9H, CO₂(CH₃)₃); 1.76 (*E*, dd, J 8.2, J 5.2) and 1.94 (*Z*, dd, J 8.7, J 5.7) (*E*+*Z*, 1H, CHH); 2.17 (*Z*, dd, J 7.2, J 5.7) and 2.21 (*E*, dd, J 7.3, J 5.2) (*E*+*Z*, 1H, CHH); 2.34 (*E*, dd, J 8.2, J 7.3) and 2.64 (*Z*, J 8.7, J 7.2) (*E*+*Z*, 1H, CHCO₂(CH₃)₃); 6.93 (*Z*) and 6.95 (*E*) (*E*+*Z*, 1H, 2×dd, J 5.2, J 3.6, C₄H₃S); 7.06 (*Z*) and 7.12 (*E*) (*E*+*Z*, 1H, 2×dd, J 3.6, J 1.3, C₄H₃S); 7.22 (*E*) and 7.26 (*Z*) (*E*+*Z*, 1H, 2×dd, J 5.2, J 1.3, C₄H₃S),

¹³C NMR (50 MHz, CDCl₃) δ 16.09, 18.25, 19.62, 23.29, 27.53, 27.90, 31.69, 33.29, 82.16, 82.88, 117.85, 120.51, 125.27, 126.54, 126.65, 126.87, 127.24, 129.07, 132.58, 138.77, 165.01, 166.38.

***E,Z*-2-acetyl-1-thiophen-2-yl-cyclopropanecarbonitrile (4fe)**

purified by distillation and short column chromatography, yield 511 mg (89%) in system C or 230 mg (40%) in system B, bp 105-115°C/0.5 Torr (Kugel-Rohr),

Found: C, 63.0; H, 4.9; N, 7.2; Calc. for C₁₀H₉NOS (191.25): C, 62.8; H, 4.7; N, 7.3%

¹H NMR (200 MHz, CDCl₃) δ 1.83 (*E*, dd, J 8.0, J 5.2) and 1.96 (*Z*, dd, J 8.4, J 5.6) (*E*+*Z*, 1H, CHH); 2.24 (*Z*) and 2.45 (*E*) (*E*+*Z*, 2×s, 3H, COCH₃); 2.32 (*Z*, dd, J 7.2, J 5.6) and 2.34 (*E*, dd, J 7.4, J 5.2) (*E*+*Z*, 1H, CHH); 2.70 (*E*, dd, J 8.0, J 7.4) and 3.01 (*Z*, dd, J 8.4, J 7.2) (*E*+*Z*,

1H, CHCOCH_3); 6.93 (Z) and 6.97 (E) (E+Z, 1H, 2×dd, J 5.1, J 3.7, $\text{C}_4\text{H}_3\text{S}$); 7.01 (Z) and 7.14 (E) (E+Z, 1H, 2×dd, J 3.7, J 1.3, $\text{C}_4\text{H}_3\text{S}$); 7.22 (E) and 7.24 (Z) (E+Z, 1H, dd, J 5.1, J 1.3, $\text{C}_4\text{H}_3\text{S}$).

***E,Z*-2-benzoyl-1-thiophen-2-yl-cyclopropanecarbonitrile (4ff)**

purified by distillation and short column chromatography, yield 600 mg (79%), bp 130-140°C/0.15 Torr (Kugel-Rohr),

Found: 253.05674 Calc. for $\text{C}_{15}\text{H}_{11}\text{NOS}$ (253.32): 253.05614,

^1H NMR (200 MHz, CDCl_3) δ 1.98 (E, dd, J 8.0, J 5.4) and 2.12 (Z, dd, J 8.3, J 5.5) (E+Z, 1H, CHH); 2.57 (Z, dd, J 7.3, J 5.5) and 2.62 (E, dd, J 7.0, J 5.4) (E+Z, 1H, CHH); 3.37 (E, dd, J 8.0, J 7.0) and 3.65 (Z, dd, J 8.3, J 7.3) (E+Z, 1H, CHCOC_6H_5); 6.83 (Z, dd, J 5.2, J 3.8) and 7.01 (E, dd, J 5.2, J 3.6) (E+Z, 1H, $\text{C}_4\text{H}_3\text{S}$); 6.94 (Z, dd, J 3.8, J 1.2) and 7.20 (E, dd, J 3.6, J 1.2) (E+Z, 1H, $\text{C}_4\text{H}_3\text{S}$); 7.14 (Z) and 7.28 (E) (E+Z, 1H, 2×dd, J 5.2 Hz, J 1.2 Hz, $\text{C}_4\text{H}_3\text{S}$); 7.46-7.68 (E+Z, 3H, m, C_6H_5); 7.92-8.06 (E+Z, 2H, m, C_6H_5).

E-4ff: separated by crystallization, yield 258 mg (34%), mp 76-78°C (MeOH),

Found: C, 71.1; H, 4.4; N, 5.5; Calc. for $\text{C}_{15}\text{H}_{11}\text{NOS}$ (253.32): C, 71.1; H, 4.4; N, 5.5%,

^1H NMR (200 MHz, CDCl_3) δ 1.98 (1H, dd, J 8.1, J 5.1, CHH); 2.63 (1H, dd, J 7.3, J 5.1, CHH); 3.37 (1H, dd, J 8.1, J 7.3, CHCOC_6H_5); 7.02 (1H, dd, J 5.2, J 3.8, $\text{C}_4\text{H}_3\text{S}$); 7.21 (1H, dd, J 3.8, J 1.2, $\text{C}_4\text{H}_3\text{S}$); 7.28 (1H, dd, J 5.2, J 1.2, $\text{C}_4\text{H}_3\text{S}$); 7.46-7.70 (3H, m, C_6H_5); 7.98-8.06 (2H, m, C_6H_5),

^{13}C NMR (50 MHz, CDCl_3) δ 21.06, 23.50, 36.02, 117.65, 125.58, 126.89, 127.69, 128.53, 128.97, 134.03, 136.59, 138.93.

***E,Z*-2-benzenesulfonyl-1-thiophen-2-yl-cyclopropanecarbonitrile (4fg)**

purified by column chromatography, yield 616 mg (71%), yellow oil,

Found: C, 58.1; H, 3.8; N, 4.75; Calc. for $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{S}_2$ (289.38): C, 58.1; H, 3.8; N, 4.8%,

^1H NMR (400 MHz, CDCl_3) δ 2.12 (E, dd, J 8.9, J 6.4) and 2.22-2.30 (Z, dd, J 9.2, J 6.4) (E+Z, 1H, CHH); 2.66 (E, dd, J 7.1, J 6.4) and 2.55-2.65 (Z, m) (E+Z, 1H, CHH); 3.11 (E, dd, J 8.9, J 7.1) and 3.36-3.44 (Z, m) (E+Z, 1H, $\text{CHSO}_2\text{C}_6\text{H}_5$); 6.80-7.10 (E+Z, 2H, m), 7.15-7.25 (E+Z, 1H, m), 7.45-7.80 (E+Z, 3H, m) and 8.00-8.15 (E+Z, 2H, m) (8H, $\text{C}_4\text{H}_3\text{S}$ and C_6H_5).

E-4fg: separated by crystallization, yield 382 mg (44%), mp 77-79°C (MeOH),

Found: C, 58.3; H, 3.9; N, 4.7; Calc. for $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{S}_2$ (289.38): C, 58.1; H, 3.8; N, 4.8%,

^1H NMR (500 MHz, CDCl_3) δ 2.12 (1H, dd, J 8.8, J 6.4, CHH); 2.66 (1H, dd, J 7.3, J 6.4, CHH); 3.11 (1H, dd, J 8.8, J 7.3, $\text{CHSO}_2\text{C}_6\text{H}_5$); 6.90 (1H, dd, J 5.4, J 3.9, $\text{C}_4\text{H}_3\text{S}$); 6.93 (1H,

dd, J 3.9, J 1.0, C_4H_3S); 7.21 (1H, dd, J 5.4, J 1.0, C_4H_3S); 7.63-7.68 (m, 2H, C_6H_5); 7.73-7.78 (m, 2H, C_6H_5); 8.09-8.13 (m, 2H, C_6H_5),
 ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.04, 21.39, 48.13, 116.36, 126.43, 127.35, 127.56, 128.14, 129.68, 134.61, 136.47, 138.84.

***E,Z*-1-(2-methyl-1-propenyl)cyclopropane-1,2-dicarbonitrile (4ga)**

purified by distillation and short column chromatography, yield 360 mg (82%), bp 125-130°C/0.01 Torr (Kugel-Rohr),

Found: 146.08436 Calc. for $C_9H_{10}N_2$ (146.19): 146.084398,

1H NMR (200 MHz, $CDCl_3$) δ 1.49 (*E*, dd, J 6.6, J 5.4) and 1.54 (*Z*, dd, J 8.7, J 5.2) (*E+Z*, 1H, *CHH*); 1.76 (*Z*, d, J 1.2), 1.85 (*E*, d, J 1.2), 1.91 (*Z*, d, J 1.0) and 1.95 (*E*, d, J 1.0) (*E+Z*, 6H, $(CH_3)_2C=C$); 1.80-2.05 (*E*, 2×*Z*, m) and 2.33 (*E*, dd, J 9.4, J 6.6) (*E+Z*, 2H, *CHH* and *CHCN*); 5.07-5.10 (*Z*) and 5.19-5.22 (*E*) (*E+Z*, 1H, 2×m, *CH=C*),

^{13}C NMR (50 MHz, $CDCl_3$) δ 13.69, 14.11, 14.34, 16.61, 19.50, 19.67, 21.98, 22.44, 25.14, 25.32, 114.00, 116.05, 116.80, 117.94, 119.16, 146.48, 147.81.

***E,Z*-2-cyano-2-(2-methyl-1-propenyl)cyclopropanecarboxylic acid, methyl ester (4gb)**

purified by distillation and short column chromatography, yield 328 mg (61%), bp 120-125°C/0.03 Torr (Kugel-Rohr),

Found: C, 66.8; H, 7.4; N, 7.6; Calc. for $C_{10}H_{13}NO_2$ (179.22): C, 67.0; H, 7.3; N, 7.8%,

1H NMR (200 MHz, $CDCl_3$) δ 1.33 (*Z*, dd, J 7.5, J 4.2) and 1.56 (*E*, dd, J 7.0, J 5.1) (*E+Z*, 1H, *CHH*); 1.73 (*E*, dd, J 8.8, J 5.1) and 1.85-2.05 (*Z*, m) (*E+Z*, 1H, *CHH*); 1.75 (bs), 1.85 (d, J 1.0) and 1.88 (d, J 1.0) (6H, $(CH_3)_2C=C$); 1.85-2.05 (*Z*, m) and 2.46 (*E*, dd, J 8.8, J 7.0) (*E+Z*, 1H, $CHCO_2CH_3$); 3.64 (*E*) and 3.74 (*Z*) (*E+Z*, 2×s, 3H, CO_2CH_3); 4.93-4.97 (*E*) and 5.06-5.09 (*Z*) (*E+Z*, 1H, 2×m, *CH=C*),

^{13}C NMR (50 MHz, $CDCl_3$) δ 15.37, 16.65, 19.20, 19.27, 20.83, 22.13, 25.14, 25.28, 28.78, 29.65, 52.37, 52.61, 114.83, 118.38, 118.81, 121.05, 144.33, 144.40, 168.25, 169.19.

***E,Z*-2-cyano-2-(2-methyl-1-propenyl)cyclopropanecarboxylic acid, *t*-butyl ester (4gc)**

purified by distillation, yield 544 mg (82%), bp 130-135°C/0.03 Torr (Kugel-Rohr),

Found: C, 70.85; H, 8.7; N, 6.6; Calc. for $C_{13}H_{19}NO_2$ (221.30): C, 70.6; H, 8.65; N, 6.3%,

1H NMR (200 MHz, $CDCl_3$) δ 1.24-1.36, 1.38-1.46, 1.57-1.62, 1.66-1.76, 1.88-1.94 (2×*E*, 3×*Z*, 5×m) and 2.43 (*E*, dd, J 8.8, J 7.1) (3H, CH_2 and $CHCO_2(CH_3)_3$); 1.42 (*E*) and 1.51 (*Z*)

(*E*+*Z*, 2×s, 9H, CO₂(CH₃)₃); 1.73 (bs) and 1.88 (d, *J* 1.2) (6H, (CH₃)₂C=C); 4.99-5.02 (*E*) and 5.10-5.14 (*Z*) (*E*+*Z*, 1H, 2×m, CH=C),

¹³C NMR (50 MHz, CDCl₃) δ 14.83, 16.17, 19.15, 19.38, 20.37, 21.67, 25.10, 25.25, 27.93, 28.04, 30.20, 30.90, 81.90, 82.38, 115.32, 118.76, 121.32, 143.93, 144.03, 166.67, 167.66.

***E,Z*-2-acetyl-1-(2-methyl-1-propenyl)cyclopropanecarbonitrile (4ge)**

purified by distillation, yield 450 mg (92%), bp 95-105°C/0.2 Torr (Kugel-Rohr),

Found: C, 73.4; H, 8.1; N, 8.5; Calc. for C₁₀H₁₃NO (163.22): C, 73.6; H, 8.0; N, 8.6%,

¹H NMR (200 MHz, CDCl₃) δ 1.30 (*Z*, dd, *J* 7.8, *J* 4.6) and 1.56-1.64 (*E*, m) (*Z*+*E*, 1H, CHH); 1.65-1.72 (*E*, m) and 1.94 (*Z*, dd, *J* 6.7, *J* 4.6) (*Z*+*E*, 1H, CHH); 1.66 (*E*, d, *J* 1.5), 1.68 (*Z*, d, *J* 1.5), 1.77 (*E*, d, *J* 1.3) and 1.81 (*Z*, d, *J* 1.3) (*Z*+*E*, 6H, (CH₃)₂C=C); 2.26 (*E*) and 2.34 (*Z*) (*Z*+*E*, 2×s, 3H, COCH₃); 2.28 (*Z*, dd, *J* 7.8, *J* 6.7) and 2.74 (*E*, dd, *J* 8.3, *J* 7.1) (*Z*+*E*, 1H, CHCOCH₃); 4.82-4.86 (*E*) and 5.05-5.09 (*Z*) (*Z*+*E*, 1H, 2×m, CH=C),

¹³C NMR (50 MHz, CDCl₃) δ 17.47, 18.57, 19.25, 19.32, 21.23, 22.89, 25.17, 25.29, 31.35, 31.66, 35.13, 36.27, 114.72, 118.55, 118.85, 121.34, 143.86, 143.95, 200.65, 201.26.

***E,Z*-2-benzenesulfonyl-1-(2-methyl-1-propenyl)cyclopropanecarbonitrile (4gg)**

purified by crystallization, yield 721 mg (92%), white solid,

***E*-4gg**: separated by column chromatography and crystallization, yield 486 mg (62%), mp 102-104°C, (MeOH),

Found: C, 64.4; H, 5.8; N, 5.3; Calc. for C₁₄H₁₅NO₂S (261.35): C, 64.3; H, 5.8; N, 5.4%,

¹H NMR (500 MHz, CDCl₃) δ 1.57 (3H, d, *J* 1.5, CH₃C=C); 1.78 (3H, d, *J* 1.5, CH₃C=C); 2.03 (2H, d, *J* 7.8, CH₂); 3.20 (1H, t, *J* 7.8, CHSO₂C₆H₅); 5.18-5.21 (1H, m, CH=C); 7.57-7.62 (*E*+*Z*, 2H, m, C₆H₅); 7.68-7.72 (*E*+*Z*, 1H, m, C₆H₅); 7.85-7.88 (*E*+*Z*, 2H, m, C₆H₅),

¹³C NMR (50 MHz, CDCl₃) δ 16.21, 19.12, 20.32, 25.54, 44.55, 112.92, 119.35, 127.82, 129.30, 134.12, 139.48, 145.01.

***Z*-4gg**: separated by column chromatography and crystallization, yield 86 mg (11%), mp 139-141°C (MeOH),

Found: C, 64.2; H, 5.7; N, 5.45; Calc. for C₁₄H₁₅NO₂S (261.35): C, 64.3; H, 5.8; N, 5.4%,

¹H NMR (200 MHz, CDCl₃) δ 1.41 (3H, d, *J* 1.3, CH₃C=C); 1.60 (1H, dd, *J* 8.6, *J* 5.8, CHH); 1.63 (3H, d, *J* 1.4, CH₃C=C); 2.37 (1H, dd, *J* 6.6, *J* 5.8, CHH); 2.73 (1H, dd, *J* 8.6, *J* 6.6, CHSO₂C₆H₅); 4.93-4.97 (1H, m, CH=C); 7.55-7.75 (3H, m, C₆H₅); 8.00-8.10 (2H, m, C₆H₅),

^{13}C NMR (50 MHz, CDCl_3) δ 15.90, 18.42, 20.07, 25.13, 46.38, 117.00, 117.19, 128.35, 129.55, 134.41, 139.04, 145.43.

***Z,E*-2-cyano-2-phenylethenyl-cyclopropanecarboxylic acid, methyl ester (4hb)**

purified by distillation and short column chromatography, yield 198 mg (29%), bp 150-160°C/0.06 Torr (Kugel-Rohr),

Found: 227.09458 Calc. for $\text{C}_{14}\text{H}_{13}\text{NO}_2$ (227.27): 227.09463,

^1H NMR (200 MHz, CDCl_3) δ 1.62 (dd, J 8.0, J 5.0), 1.86 (dd, J 7.4, J 5.4), 1.97 (dd, J 8.8, J 5.4), 2.17 (dd, J 7.0, J 5.0), 2.27 (dd, J 8.0, J 7.0) and 2.67 (dd, J 8.8, J 7.4) (3H, CH_2 and CHCO_2CH_3); 3.75 and 3.83(2xs, 3H, CO_2CH_3); 5.56 and 6.04 (2xd, J 16.0, $\text{C}_6\text{H}_5\text{CH}=\text{CH}$); 6.93 and 6.97 (2xd, J 16.0, $\text{C}_6\text{H}_5\text{CH}=\text{CH}$); 7.26-7.40 (m, 5H, C_6H_5).

***Z,E*-2-cyano-1-phenylcyclopropanecarboxylic acid, ethyl ester (4ia)^[21]**

purified by distillation and short column chromatography, yield 232 mg (36%), bp 150-160°C/0.2 Torr (Kugel-Rohr),

^1H NMR (200 MHz, CDCl_3) δ 1.17 (*E*) and 1.24 (*Z*) (*Z+E*, 2xt, J 7.0, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$); 1.71 (*Z*, dd, J 9.0, J 4.8), 1.85 (*E*, dd, J 6.4, J 4.8), 2.02 (*E*, dd, J 9.2, J 4.6), 2.07 (*Z*, dd, J 9.0, J 6.6), 2.27 (*Z*, dd, J 6.6, J 4.8) and 2.53 (*E*, dd, J 9.2, J 6.4) (*Z+E*, 3H, CH_2 and CHCN); 4.12 (*E*, dq, J 7.0, J 3.4) and 4.22 (*Z*, dq, J 7.0, J 2.0) (*Z+E*, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$); 7.30-7.40 (*Z+E*, m, C_6H_5).

***Z,E*-1-phenylcyclopropane-1,2-dicarboxylic acid, 1-ethyl ester 2-methyl ester (4ib)^[21]**

purified by distillation and short column chromatography, yield 380 mg (51%) in system A or 298 mg (40%) in system D, bp 140-145°C/0.03 Torr (Kugel-Rohr),

^1H NMR (200 MHz, CDCl_3) δ 1.19 (*Z+E*, t, J 7.2, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$); 1.52 (*Z*, dd, J 8.4, J 4.8) and 1.87 (*E*, dd, J 8.4, J 4.4) (*Z+E*, 1H, CHH); 2.00 (*E*, dd, J 6.6, J 4.4) and 2.10 (*Z*, dd, J 6.4, J 4.8) (*Z+E*, 1H, CHH); 2.24 (*Z*, dd, J 8.4, J 6.4) and 2.75 (*E*, dd, J 8.4, J 6.6) (*Z+E*, 1H, CHCO_2CH_3); 3.42 (*E*) and 3.73 (*Z*) (*Z+E*, 2xs, 3H, CO_2CH_3); 4.00-4.15 (*Z+E*, m, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$); 7.25-7.45 (*Z+E*, m, 5H, C_6H_5).

***Z,E*-1-phenylcyclopropane-1,2-dicarboxylic acid, 1-*t*-butyl ester 2-ethyl ester (4ic)**

purified by distillation and short column chromatography, yield 235 mg (27%), bp 140-145°C/0.15 Torr (Kugel-Rohr),

Found: C, 70.25; H, 7.5; Calc. for $\text{C}_{17}\text{H}_{22}\text{O}_4$ (290.36): C, 70.3; H, 7.6%,

^1H NMR (200 MHz, CDCl_3) δ 1.16 (*E*) and 1.48 (*Z*) (*Z+E*, 2 $\times$ s, 9H, $\text{CO}_2(\text{CH}_3)_3$); 1.17 (*E*) and 1.20 (*Z*) (*Z+E*, 2 $\times$ t, J 7.2, 3H, $\text{CO}_2\text{CH}_2\text{CH}_3$); 1.43 (*Z*, dd, J 8.2, J 4.6) and 1.80 (*E*, dd, J 8.4, J 4.4) (*Z+E*, 1H, *CHH*); 1.95 (*E*, dd, J 6.6, J 4.4) and 2.04 (*Z*, dd, J 6.4, J 4.6) (*Z+E*, 1H, *CHH*); 2.17 (*Z*, dd, J 8.2, J 6.4) and 2.64 (*E*, dd, J 8.4, J 6.6) (*Z+E*, 1H, $\text{CHCO}_2(\text{CH}_3)_3$); 4.09 (*E*, dq, J 7.2, J 1.2) and 4.11 (*Z*, dq, J 7.2, J 0.6) (*Z+E*, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$); 7.27-7.35 (*Z+E*, 3H, m, C_6H_5); 7.40-7.46 (*Z+E*, 2H, m, C_6H_5).

1-methyl-2-phenylcyclopropane-1,2-dicarbonitrile (6)^[22]

yield 246 mg (27%), mp 96-98°C (MeOH),

Found: 182.083441 Calc. for $\text{C}_{12}\text{H}_{10}\text{N}_2$ (182.23): 182.084398,

^1H NMR (200 MHz, CDCl_3) δ 1.80 and 2.28 (2H, Ab q, J 6.5, CH_2), 1.85 (3H, s, CH_3), 7.40-7.45 (5H, m, C_6H_5)

Alkenes 8

2-phenyl-penta-2,4-dienenitrile (8aa)^[29]

purified by column chromatography and distillation, yield 359 mg (77%) from salt **2a3** or 349 mg (75%) from salt **2a1**, bp 140-145°C/0.1 Torr (Kugel-Rohr),

Found: 155.073696 Calc. for $\text{C}_{11}\text{H}_9\text{N}$ (155.20): 155.073499,

^1H NMR (200 MHz, CDCl_3) δ 5.54 (minor isomer, ddd, J 10.0, J 1.3, J 0.7), 5.65 (main isomer, ddd, J 10.0, J 1.2, J 0.6), 5.69 (minor isomer, ddd, J 16.7, J 1.3, J 0.7) and 5.74 (main isomer, ddd, J 16.5, J 1.2, J 0.6) (1H, $\text{CH}=\text{CH}_2$); 6.69 (minor isomer, ddd, J 16.7, J 11.3, J 10.0) and 6.98 (main isomer, ddd, J 16.5, J 11.1, J 10.0) (1H, $\text{CH}=\text{CH}_2$); 7.23 (main isomer, d, J 11.1) and 7.32-7.62 (both isomers, m) (together, 6H, C_6H_5 and $\text{C}_6\text{H}_5\text{C}=\text{CH}$).

5-methyl-2-phenyl-hexa-2,4-dienenitrile (8ab)

purified by crystallization, yield 517 mg (94%), mp 63-65°C (hexane),

Found: 183.10458 Calc. for $\text{C}_{13}\text{H}_{13}\text{N}$ (183.26): 183.1048,

^1H NMR (200 MHz, CDCl_3) δ 1.97 (3H, bs, $\text{CH}_3\text{C}=\text{CH}$), 1.99 (3H, bs, $\text{CH}_3\text{C}=\text{CH}$), 6.48-6.58 (1H, m, $(\text{CH}_3)_2\text{C}=\text{CH}$), 7.30-7.70 (6H, m, C_6H_5 and $\text{C}_6\text{H}_5\text{C}=\text{CH}$),

^{13}C NMR (50 MHz, CDCl_3) δ 19.39, 26.88, 123.19, 125.52, 128.61, 128.98, 138.14, 147.94.

2,5-diphenyl-penta-2,4-dienenitrile (8ac)^[30]

purified by crystallization, yield 375 mg (54%), mp 119-120°C (MeOH),

¹H NMR (400 MHz, CDCl₃) δ 6.98-7.07 (1H, m), 7.32-7.45 (8H, m), 7.53-7.58 (2H, m), 7.61-7.65 (2H, m).

¹³C NMR (50 MHz, CDCl₃) δ 112.97, 116.90, 124.98, 125.48, 127.43, 128.83, 128.96, 129.47, 133.07, 135.61, 141.16, 141.49.

Z-2,3-diphenylpropenenitrile (8ad)^[31]

purified by crystallization, yield 505 mg (82%) from salt **2a2** or 493 mg (80%) from salt **2a1**, mp 87-88°C (MeOH),

¹H NMR (200 MHz, CDCl₃) δ 7.35-7.52 (6H, m, C₆H₅), 7.55 (1H, s, C=CH), 7.65-7.75 (2H, m, C₆H₅), 7.85-7.95 (2H, m, C₆H₅).

2-(4-methoxyphenyl)-penta-2,4-dienenitrile (8ba)

purified by column chromatography and distillation, yield 472 mg (85%), bp 150-155°C/0.1 Torr (Kugel-Rohr),

Found: C, 77.9; H, 6.1; N, 7.5; Calc. for C₁₂H₁₁NO (185.23): C, 77.8; H, 6.0; N, 7.6%,

¹H NMR (400 MHz, CDCl₃) δ 3.82 (main isomer, s) and 3.82 (minor isomer, s) (3H, OCH₃); 5.51 (minor isomer, ddd, J 10.0, J 1.2, J 0.8), 5.57 (main isomer, ddd, J 10.0, J 1.2, J 0.8), 5.65 (minor isomer, ddd, J 16.8, J 1.2, J 0.8) and 5.67 (main isomer, ddd, J 16.8, J 1.2, J 0.8) (2H, C=CH₂); 6.71 (minor isomer, ddd, J 16.8, J 11.2, J 10.0) and 6.93 (main isomer, ddd, J 16.8, J 11.2, J 10.0) (1H, CH₂=CH); 6.87-6.94 (both isomers, m) and 7.12 (main isomer, d, J 11.2) (3H, C(CN)=CH and C₆H₄); 7.31-7.36 (minor isomer, m) and 7.50-7.55 (main isomer, m) (2H, C₆H₄).

Z-2-(4-methoxyphenyl)-3-phenylpropenenitrile (8bd)^[32]

purified by crystallization, yield 501 mg (71%), mp 92-94°C (MeOH),

¹H NMR (400 MHz, CDCl₃) δ 3.86 (3H, s, OCH₃), 6.94-6.99 (2H, m, C₆H₄), 7.39-7.49 (3H, m, C=CH and C₆H₅), 7.59-7.64 (2H, m, C₆H₄), 7.84-7.89 (m, 2H, C₆H₄).

2-(2-methyl-1-propenyl)-penta-2,4-dienenitrile (8ga)

purified by column chromatography and distillation, yield 300 mg (75%), bp 70-75°C/0.03 Torr (Kugel-Rohr),

Found: 133.089066 Calc. for $C_9H_{11}N$ (133.20): 133.089149,

1H NMR (200 MHz, $CDCl_3$) δ 1.83 (main isomer, bs), 1.85 (minor isomer, bs), 1.88 (minor isomer, bs) and 2.02 (main isomer, bs) (6H, $(CH_3)_2C=CH$); 5.40-5.60 (both isomers, m, 2H, $CH=CH_2$); 5.65-5.70 (main isomer, m) and 5.79-5.83 (minor isomer, m) (1H, $(CH_3)_2C=CH$); 6.52-6.66 (both isomers) and 6.82 (main isomer, ddd, J 16.5, J 11.3, J 9.9) (together 2H, $C(CN)=CH$ and $CH=CH_2$).

2-(2-methyl-1-propenyl)-5-phenyl-penta-2,4-dienitrile (8gc)

purified by column chromatography and distillation, yield 446 mg (71%), bp 170-180°C/0.03 Torr (Kugel-Rohr),

Found: 209.120576 Calc. for $C_{15}H_{15}N$ (209.29): 209.12045,

1H NMR (500 MHz, $CDCl_3$) δ 1.86 (main isomer, bs), 1.92 (minor isomer, d, J=1.0 Hz), 1.95 (minor isomer, d, J=1.0 Hz) and 2.07 (main isomer, bs) (6H, $(CH_3)_2C=CH$); 5.72-5.76 (main isomer, m) and 5.92-5.96 (minor isomer, m) (1H, $(CH_3)_2C=CH$); 6.75-6.85 (m), 6.98-7.06 (m), 7.22-7.40 (m), 7.43-7.51 (m) (both isomers, 8H, $C=CH$ and C_6H_5).

2-benzylidene-4-methyl-pent-3-enitrile (8gd)^[33]

purified by column chromatography and distillation, yield 473 mg (86%), bp 125-130°C/0.03 Torr (Kugel-Rohr),

1H NMR (200 MHz, $CDCl_3$) δ 1.88 (main isomer, bs), 1.89 (minor isomer, bs), 1.98 (minor isomer, bs) and 2.06 (main isomer, bs) (6H, $(CH_3)_2C=CH$); 5.81-5.86 (main isomer, m) and 5.87-5.91 (minor isomer, m) (1H, $(CH_3)_2C=CH$); 6.94 (main isomer, s) and 7.09 (minor isomer, s) (1H, CHC_6H_5); 7.30-7.45 (both isomers, 3H, m, C_6H_5); 7.70-7.80 (both isomers, 2H, m, C_6H_5),

4-methyl-2-thiophen-2-yl-methylene-pent-3-enitrile (8ge)

purified by column chromatography and distillation, yield 432 mg (76%), 145-155°C/0.5 Torr (Kugel-Rohr),

Found: C, 69.7; H, 6.0; N, 7.45; Calc. for $C_{11}H_{11}NS$ (189.28): C, 69.8; H, 5.9; N, 7.4%,

1H NMR (500 MHz, $CDCl_3$) δ 1.86 (main isomer, bs), 1.92 (minor isomer, bs), 1.94 (minor isomer, bs) and 2.04 (main isomer, bs) (6H, $(CH_3)_2C=CH$); 5.75-5.77 (main isomer, m) and 5.90-5.93 (minor isomer, m) (1H, $(CH_3)_2C=CH$); 7.05 (main isomer, s, CHC_4H_3S); 7.07 (main isomer) and 7.08 (minor isomer) (2×dd, J 2.0, J 1.6, 1H, C_4H_3S); 7.22-7.26 (m) and 7.43-7.51 (m) (both isomers, 2H, C_4H_3S).

^{13}C NMR (50 MHz, CDCl_3) δ 18.89, 19.69, 26.27, 27.46, 105.34, 106.77, 116.50, 118.61, 119.80, 120.26, 127.26, 127.48, 128.94, 130.93, 131.11, 132.36, 136.07, 136.51, 137.74, 137.85, 139.74, 143.88.

Compounds 9

2-(2-cyano-2-phenylethenyl)-1-phenylcyclopropanecarbonitrile (9a)

yield 852 mg (70%), mp 98-99°C (hexane/ethyl acetate 5/1),

Found: C, 84.7, H, 5.3; N, 10.3; Calc. for $\text{C}_{19}\text{H}_{14}\text{N}_2$ (270.34): C, 84.4; H, 5.2; N, 10.4%,

^1H NMR (400 MHz, CDCl_3) δ 1.99 (1H, dd, J 6.8, J 6.4, CHH), 2.17 (1H, dd, J 8.8, J 6.4, CHH), 2.85 (1H, ddd, $J_{\text{C}=\text{CH}-\text{CH}}$ 10.4, J 8.8, J 6.8, CHCH=CC $_6\text{H}_5$), 6.66 (1H, d, J 10.4, CH=CC $_6\text{H}_5$), 7.30-7.45 (8H, m, C $_6\text{H}_5$), 7.55-7.65 (2H, m, C $_6\text{H}_5$).

^{13}C NMR (50 MHz, CDCl_3) δ 23.66, 24.51, 31.88, 116.36, 118.60, 119.69, 125.74, 126.14, 128.57, 129.12, 129.27, 129.69, , 132.17, 133.85, 141.49.

2-[2-cyano-2-(4-methoxyphenyl)ethenyl]-1-(4-methoxyphenyl)cyclopropanecarbonitrile (9b)

yield 847 mg (57%), mp 99-100°C (hexane/ethyl acetate 10/1),

Found: C, 76.4, H, 5.5; N, 8.55; Calc. for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_2$ (330.29): C, 76.3; H, 5.5; N, 8.5%,

^1H NMR (400 MHz, CDCl_3) δ 1.90 (1H, dd, J 6.8, J 6.0, CHH), 2.07 (1H, dd, J 8.6, J 6.0, CHH), 2.75 (1H, dd, $J_{\text{C}=\text{CH}-\text{CH}}$ 10.0, J 8.6, J 6.8, CHCH=CC $_6\text{H}_4$), 3.82 (3H, s, OCH $_3$), 3.84 (3H, s, OCH $_3$), 6.50 (1H, d, J 10.0, CH=CC $_6\text{H}_4$), 6.87-7.00 (4H, m, C $_6\text{H}_4$), 7.25-7.34 (2H, m, C $_6\text{H}_4$), 7.47-7.56 (2H, m, C $_6\text{H}_4$).

^{13}C NMR (100 MHz, CDCl_3) δ 22.98, 24.15, 31.45, 55.43, 114.48, 114.64, 116.65, 117.91, 120.17, 124.90, 126.05, 126.87, 127.15, 127.97, 130.81, 139.30, 159.76, 160.72.

Compounds 10

2,3-dipheny-but-2-enedinitrile (10a)^[34]

yield 500 mg (62%), mp 161-162°C (MeOH).

2,3-bis(4-methoxyphenyl)but-2-enedinitrile (10b)^[52]

yield 417 mg (41%), mp 188-189°C (MeOH),

^1H NMR (200 MHz, CDCl_3) δ 3.88 (6H, s, OCH_3), 6.99-7.04 (4H, m, C_6H_4), 7.77-7.82 (4H, m, C_6H_4).

2,3-dithiophen-2-yl-but-2-enedinitrile (10f)

yield 594 mg (70%), mp 212-213°C (MeOH),

Found: C, 59.2, H, 2.5; N, 11.55; Calc. for $\text{C}_{12}\text{H}_6\text{N}_2\text{S}_2$ (242.32): C, 59.5; H, 2.5; N, 11.6%,

^1H NMR (200 MHz, CDCl_3) δ 7.19 (1H, dd, J 5.1, J 3.9, $\text{C}_4\text{H}_3\text{S}$), 7.62 (1H, dd, J 5.1, J 1.1, $\text{C}_4\text{H}_3\text{S}$), 7.87 (1H, dd, J 3.9, J 1.1, $\text{C}_4\text{H}_3\text{S}$).

^{13}C NMR (50 MHz, CDCl_3) δ 116.30, 128.19, 131.34, 133.05, 135.11.

Oxiranes 12

Z-2,3-diphenyl-oxirane-2-carbonitrile (12aa)^[16]

purified by crystallization, yield 759 mg (49%), mp 69-70°C (MeOH),

^1H NMR (200 MHz, CDCl_3) δ 4.20 (1H, s, CHC_6H_5), 7.40-7.55 (10H, m, $2\times\text{C}_6\text{H}_5$).

Z-3-(2-chlorophenyl)-2-phenyl-oxirane-2-carbonitrile (12ab)^[50]

purified by crystallization, yield 859 mg (48%), mp 92-93°C (MeOH),

Found: C, 70.3; H, 3.75; N, 5.2; Calc. for $\text{C}_{15}\text{H}_{10}\text{ClNO}$ (255.71): C, 70.5; H, 3.9; N, 5.5%,

^1H NMR (200 MHz, CDCl_3) δ 4.44 (1H, s, CHC_6H_4), 7.35-7.62 (9H, m, C_6H_5 and C_6H_4).

Z-3-(4-chlorophenyl)-2-phenyl-oxirane-2-carbonitrile (12ac)^[16]

purified by crystallization, yield 841 mg (47%), mp 112-113°C (MeOH),

^1H NMR (200 MHz, CDCl_3) δ 4.16 (1H, s, CHC_6H_4), 7.40-7.55 (9H, m, C_6H_5 and C_6H_4).

Z-2-(4-methylphenyl)-3-phenyl-oxirane-2-carbonitrile (12ad)^[51]

purified by crystallization, yield 758 mg (46%), mp 79-80°C (MeOH),

^1H NMR (200 MHz, CDCl_3) δ 2.39 (3H, s, CH_3), 4.14 (1H, s, CHC_6H_4), 7.22-7.56 (9H, m, C_6H_5 and C_6H_4).

Z-3-(4-fluorophenyl)-2-phenyl-oxirane-2-carbonitrile (12ae)

purified by crystallization, yield 754 mg (45%), mp 102-103°C (MeOH),

Found: C, 75.0; H, 4.1; N, 5.6; Calc. for $C_{15}H_{10}FNO$ (239.25): C, 75.3; H, 4.2; N, 5.85%,
 1H NMR (200 MHz, $CDCl_3$) δ 4.17 (s, 1H, CHC_6H_4), 7.10-7.26 (2H, m, C_6H_4), 7.43-7.56 (7H, m, C_6H_5 and C_6H_4).

***Z*-2-(4-methoxyphenyl)-3-phenyl-oxirane-2-carbonitrile (12ba)^[16]**

purified by crystallization, yield 616 mg (35%), mp 113-115°C (EtOH),

1H NMR (400 MHz, $CDCl_3$) δ 3.85 (3H, s, OCH_3), 4.17 (1H, s, CHC_6H_5), 6.97-6.99 (7H, m, C_6H_5 and C_6H_4), 7.39-7.51 (2H, m, C_6H_5 and C_6H_4).

***Z*-3-(4-chlorophenyl)-2-(4-methoxyphenyl)-oxirane-2-carbonitrile (12bc)**

purified by crystallization, yield 640 mg (32%), mp 128-130°C (EtOH),

Found: C, 67.15; H, 4.1; N, 4.8; Calc. for $C_{16}H_{12}ClNO_2$ (285.73): C, 67.3; H, 4.2; N, 4.9%,
 1H NMR (400 MHz, $CDCl_3$) δ 3.85 (3H, s, OCH_3), 4.14 (1H, s, CHC_6H_5), 6.94-6.99 (7H, m, C_6H_5 and C_6H_4), 7.45-7.47 (2H, m, C_6H_5 and C_6H_4).

***Z,E*-2-(2-methyl-1-propenyl)-3-phenyl-oxirane-2-carbonitrile (12ga)**

purified by column chromatography and distillation, yield 725 mg (52%), bp 110-115°C/0.05 Torr (Kugel-Rohr),

Found: C, 78.5; H, 6.5; N, 7.1; Calc. for $C_{13}H_{13}NO$ (199.25): C, 78.4; H, 6.6; N, 7.0%,
 1H NMR (200 MHz, $CDCl_3$) δ 1.67 (*E*), 1.79 (*E*), 1.83 (*Z*) and 1.94 (*Z*) (*Z+E*, 6H, 4×d, J 1.2, $(CH_3)_2C=CH$); 4.09 (*Z*) and 4.50 (*E*) (*Z+E*, 1H, 2×s, CHC_6H_5); 4.91-4.96 (*E*) and 5.39-5.46 (*Z*) (*Z+E*, 1H, 2×m, $(CH_3)_2C=CH$); 7.30-7.45 (*Z+E*, 5H, m, C_6H_5).

***Z*-12ga**: separated by crystallization, yield 265 mg (19%), mp 60-62°C (MeOH),

Found: C, 78.2; H, 6.6; N, 7.1; Calc. for $C_{13}H_{13}NO$ (199.25): C, 78.4; H, 6.6; N, 7.0%,
 1H NMR (200 MHz, $CDCl_3$) δ 1.83 (3H, d, J 1.1, $CH_3C=CH$), 1.94 (3H, d, J 1.3, $CH_3C=CH$), 4.09 (1H, s, CHC_6H_5), 5.39-5.43 (1H, m, $(CH_3)_2C=CH$), 7.43 (5H, s, C_6H_5).

***Z,E*-3-(4-chlorophenyl)-2-(2-methyl-1-propenyl)-oxirane-2-carbonitrile (12gc)**

purified by column chromatography and distillation, yield 523 mg (32%), bp 125-130°C/0.1 Torr (Kugel-Rohr),

Found: C, 66.7; H, 5.1; N, 6.1; Calc. for $C_{13}H_{12}ClNO$ (233.70): C, 66.8; H, 5.2; N, 6.0%,

^1H NMR (200 MHz, CDCl_3) δ 1.68 (*E*, d, *J* 1.2), 1.78 (*E*, d, *J* 0.8), 1.83 (*Z*, d, *J* 1.4) and 1.93 (*Z*, d, *J* 1.0) (*Z+E*, 6H, $(\text{CH}_3)_2\text{C}=\text{CH}$); 4.06 (*Z*) and 4.47 (*E*) (*Z+E*, 1H, 2 $\times$ s, CHC_6H_4); 4.90-4.95 (*E*) and 5.36-5.41 (*Z*) (*Z+E*, 1H, 2 $\times$ m, $(\text{CH}_3)_2\text{C}=\text{CH}$); 7.26-7.45 (*Z+E*, 4H, m, C_6H_4).

1-(2-cyanoethyl)-2-naphtalen-1-yl-cyclopropane-1,2-dicarbonitrile (13)

yield 236 mg (29%), mp 196-198°C (MeOH),

Found: C, 79.5, H, 4.8; N, 15.2; Calc. for $\text{C}_{18}\text{H}_{13}\text{N}_3$ (271.33): C, 79.7; H, 4.8; N, 15.5%,

^1H NMR (200 MHz, CDCl_3) δ 0.84 (1H, ddd, *J* 14.8, *J* 10.0 Hz, *J* 7.6), 1.90-2.05 (1H, m), 2.25 (1H, d, *J* 6.6 Hz), 2.42-2.52 (1H, m), 2.54-2.68 (2H, m) 7.38-7.42 (1H, m, C_{10}H_7), 7.46-7.53 (1H, m, C_{10}H_7), 7.61-7.68 (1H, m, C_{10}H_7), 7.72-7.79 (1H, m, C_{10}H_7), 7.95-8.02 (2H, m, C_{10}H_7), 8.09-8.14 (1H, m, C_{10}H_7).

^{13}C NMR (100 MHz, CDCl_3) δ 15.10, 23.62, 24.71, 25.00, 26.63, 117.22, 117.53, 117.95, 122.70, 125.06, 125.38, 127.26, 128.48, 128.57, 129.50, 131.28, 131.49, 133.95.

Stereochemistry of the products prepared

Cyclopropanes

^1H NMR spectra of products **4aa–4ag** are quite similar. Reported ^1H NMR spectral data for *Z*-**4ab** and *E*-**4ab** show lower values for $\delta_{Z\text{-CHY}}$ than $\delta_{E\text{-CHY}}$.^[21] Considering this information, *Z* stereochemistry to all major isomers of **4ab–4ag** was assigned and in the case of **4ab** and **4ac** it was additionally confirmed by NOE experiments. Irradiation of aromatic protons at $\delta = 7.35$ ppm and $\delta = 7.34$ ppm of *Z* and *E* isomers mixtures of **4ab** or **4ac** respectively, resulted in signal enhancement of only one *CHY* proton. This indicates that the enhanced proton is located in close proximity to the phenyl group and must be on the same side of cyclopropane ring (*Z* isomers) (Fig. 3).

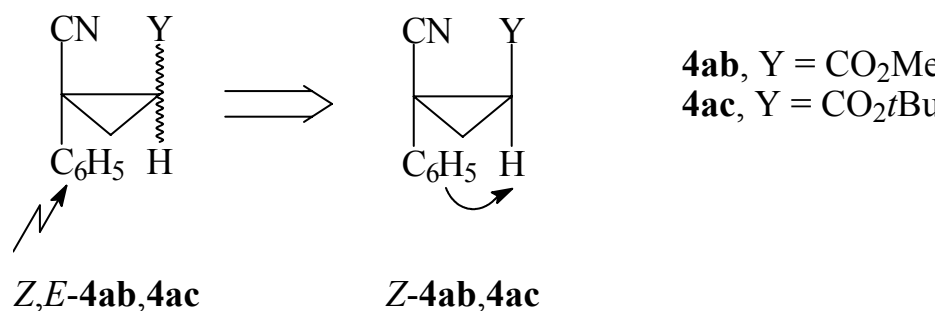


Fig. 3. Stereochemistry of cyclopropanes **Z,E-4ab,4ac** using NOE

Stereochemistry of cyclopropanes **4aa** was unequivocally determined by crystal structure (Fig. 1).

Assuming that other aromatic groups such as: 4-methoxyphenyl, 4-cyanophenyl, naphthyl, furyl and thienyl, behave like phenyl group we attempted to assign *Z,E*-stereochemistry on the basis of different values of δ_{CHY} in both isomers of all cyclopropanes.

Comparing chemical shifts of *CHY* in ¹H NMR spectra of mixtures of isomers of cyclopropanes **4aa–4ag**, **4ba–4bg** and **4ca–4cg** we determined the ratio of *Z/E* isomers in cyclopropanes **4ba–4bg** and **4ca–4cg**.

In the case of naphthyl substituted cyclopropanes **4db**, **4de** and **4df**, which were isolated as mixture of isomers, *Z* stereochemistry was always assigned to the major isomers of these products. The *Z* stereochemistry was also suggested for cyclopropane **4dg**, substituted with bulky benzenesulphonyl group which was formed as the single isomer. In the case of cyclopropanes **4da** and **4dc**, which were also isolated as single isomers, the stereochemistry was not suggested as the products were isolated from quite complicated mixtures of products.

Some difficulties were encountered during determination of stereochemistry of cyclopropanes **4ea–4eg**, substituted with 2-furyl group. The chemical shift values (δ_{CHY}) in cyclopropanes **4ea**, **4eb**, **4ec** and **4ee** suggested *E* stereochemistry for the major isomers. Stereochemistry of **4ec** was confirmed by NOE experiments. Irradiation of furyl ring proton at $\delta = 6.41$ ppm caused intensity enhancement of proton signal at $\delta = 2.41$ ppm, which is located *cis* to furyl ring (*E* isomer) (Fig. 4).

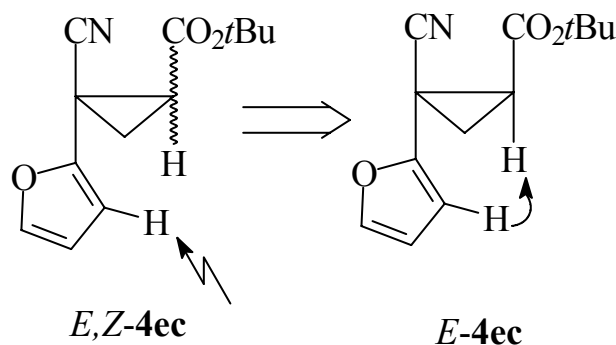


Fig. 4. Stereochemistry of cyclopropanes *Z,E-4ec* using NOE

In the case of cyclopropanes **4ed**, **4ef** and **4eg** the analysis of chemical shift of *CHY* protons (δ_{CHY}) as well as coupling constants between *CHH-CHY* protons ($J_{CHH-CHY}$) did not allow for unequivocal stereochemistry assignment of these products.

In case of cyclopropanes **4fb–4fg**, substituted with 2-thienyl group, the analysis of the isomer mixture by ^1H NMR spectroscopy allowed for determination of *E,Z*-stereochemistry. The *E*-configuration of major isomers of **4fe** was confirmed by NOE (Fig. 5). Irradiation of thiophene ring proton at $\delta = 7.14$ ppm of *E,Z-4fe* mixture resulted in signal enhancement at $\delta = 2.70$ ppm assigned to *CHCOMe* proton. The stereochemistry of **4fa** was not elucidated due to complexity observed in ^1H NMR spectrum.

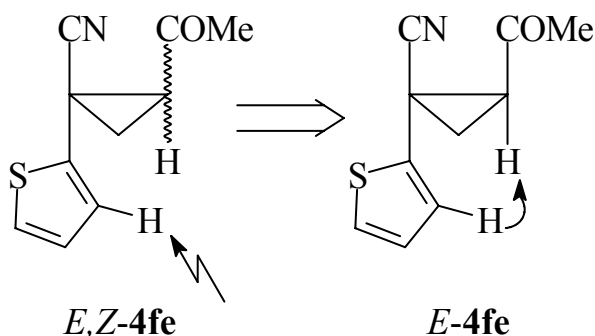


Fig. 5. Stereochemistry of cyclopropanes *E,Z-4fe* using NOE

All cyclopropanes derived from salt **2g** were isolated as mixtures of *Z,E* isomers. Stereochemistry of *E-4gg* was unequivocally determined by crystal structure analysis (Fig. 2).

Stereochemistry of cyclopropanes **4ga–4gc** and **4ge** was proposed based on δ_{CHY} values. This stereochemistry assignment could not be confirmed, however, in the case of **4gc** using NOE experiment, as the irradiation of neither *CHCO₂tBu* proton ($\delta = 2.43$ ppm) of

major isomer nor $HC=C$ proton in major (at $\delta = 4.99$ ppm) or minor (at $\delta = 5.11$ ppm) isomer resulted in noticeable enhancement of $HC=C$ or $CHCO_2tBu$ signals, respectively (Fig. 6).

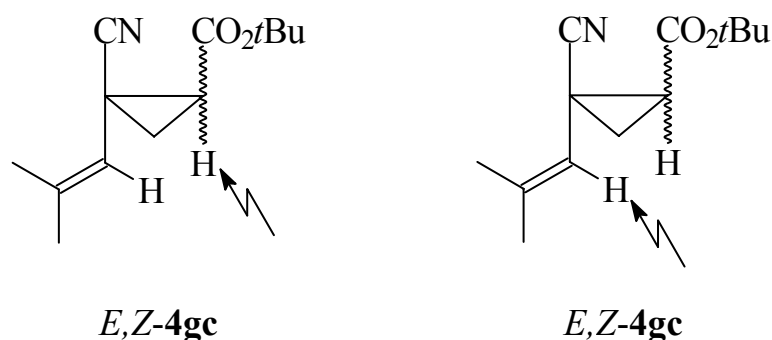


Fig. 6. Stereochemistry of cyclopropanes *E,Z*-4gc using NOE

Stereochemistry of **4hb** was not determined, while *Z* configuration was assigned to a major isomer of **4ic** on the basis of literature data for derivatives **4ia–4ib**.^[21]

Oxiranes

Oxiranes prepared from salts **2a** and **2b** were isolated as single isomers, while mixtures of isomers were obtained from salt **2g**. Literature data^[16, 50-51] suggest *Z* configuration for all oxiranes **12a** and **12b**. To determine the stereochemistry of **12ga** oxirane protons at $\delta = 4.09$ ppm (major isomer) and $\delta = 4.50$ ppm (minor isomer) were irradiated. The NOE enhancement was observed during irradiation of $HC=C$ proton ($\delta = 5.39$ - 5.46 ppm) of the major isomer which is consistent with *cis* arrangement of dimethylvinyl group and oxirane proton (*Z* stereochemistry) (Fig. 7).

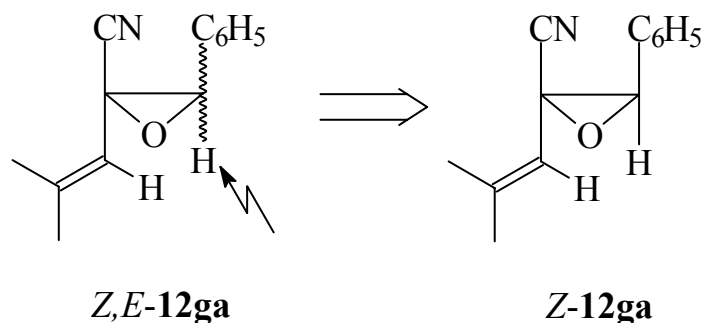


Fig. 7. Stereochemistry of oxiranes *Z,E*-12ga using NOE

Due to similarities of **12ga** and **12gc** in their ^1H NMR spectra, the same stereochemistry was assigned to the latter product.