Tandem 1,5-migration/Michael reactions to prepare adducts of pyrazolone derivatives: protecting group-directed rearrangement

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1 General information

NMR spectra were obtained on Bruker 300 or 400 MHz spectrometer in DMSO-d$_6$ or CDCl$_3$, and chemical shifts are reported in ppm using TMS as internal standard. IR and ESI-MS spectra were measured on Bruker Vector 22 as KBr pellets and Finnigan Mat TSQ 7000 instruments respectively. Microanalyses were obtained on Perkin-Elmer 240 instruments, and melting points (mp) were determined with a digital electrothermal apparatus without further correction.

2 General procedures for the synthesis of pyrazole

A vial charged with 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (10 mmol), acyl chloride (10 mmol) and DCM (25 mL) was stirred and cooled to -40 °C, The mixture was warmed to room temperature and continue to react for another 8 hours. The reaction mixture was filtered and evaporated to dryness. The residue was purified through chromatography on a silica gel column eluted with dichloromethane and methanol to give the corresponding products.

**Benzyl (3-methyl-1-phenyl-1H-pyrazol-5-yl) carbonate (1a)**

Yellow oil. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.36 (s, 3H), 5.24 (s, 2H), 6.16 (s, 1H), 7.28-7.45 (m, 8H), 7.58-7.60 (m, 2H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 14.6, 71.3, 95.5, 122.9, 127.2, 128.7, 128.8, 129.1, 129.2, 134.1, 137.9, 144.6, 148.9, 151.0. IR (KBr): $\nu$ = 3066, 3035, 1781, 1597, 1564, 1506, 1456, 1442, 1386, 1369, 1225, 1179, 1158, 1013, 905, 756, 695 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{18}$H$_{16}$N$_2$O$_3$Na: 331.1053, found: 331.1053.
Benzyl (1-(4-chlorophenyl)-3-methyl-1H-pyrazol-5-yl) carbonate (1b)

Yellow solid. M.p. 62-64 °C. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.34 (s, 3H), 5.25 (s, 2H), 6.15 (s, 1H), 7.35-7.42 (m, 7H), 7.50-7.53 (m, 2H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 14.5, 71.4, 95.6, 123.9, 128.7, 128.8, 129.2, 129.3, 132.7, 133.9, 136.4, 144.7, 149.2, 150.8. IR (KBr): $\nu$ = 3177, 1768, 1594, 1586, 1563, 1505, 1462, 1456, 1440, 1411, 1386, 1367, 1267, 1244, 1227, 1181, 1154, 1118, 1096, 1013, 955, 916, 835, 812, 779, 745, 699, 653, 503 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{18}$H$_{16}$N$_2$O$_3$Na: 365.0663, found: 365.0659.

Tert-butyl (3-methyl-1-phenyl-1H-pyrazol-5-yl) carbonate (2a)

Yellow oil. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 1.46 (s, 9H), 2.33 (s, 3H), 6.07 (s, 1H), 7.29-7.34 (m, 1H), 7.42-7.47 (m, 2H), 7.57-7.60 (m, 2H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 14.5, 27.4, 85.2, 95.5, 122.9, 127.0, 129.1, 138.1, 144.9, 148.8, 148.9. IR (KBr): $\nu$ = 2983, 2933, 1778, 1598, 1568, 1507, 1477, 1456, 1439, 1389, 1372, 1274, 1248, 1139, 1052, 1026, 878, 814, 775, 763, 694, 625 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{15}$H$_{18}$N$_2$O$_3$Na: 297.1210, found: 297.1207.
Tert-butyl (1-(4-chlorophenyl)-3-methyl-1H-pyrazol-5-yl) carbonates (2b)

Yellow oil. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 1.49 (s, 9H), 2.31 (s, 3H), 6.08 (s, 1H), 7.40-7.43 (m, 2H), 7.53-7.56 (m, 2H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 14.5, 27.4, 85.5, 95.7, 123.9, 129.2, 132.5, 136.6, 145.0, 148.7, 149.2. IR (KBr): $\nu$ = 2981, 1789, 1780, 1597, 1587, 1568, 1505, 1477, 1408, 1396, 1371, 1273, 1241, 1166, 1102, 1092, 1050, 1012, 991, 879, 836, 811, 784, 774, 622 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{15}$H$_{17}$N$_2$O$_3$ClNa: 331.0820, found: 331.0821.

Ethyl (3-methyl-1-phenyl-1H-pyrazol-5-yl) carbonates (2c)

Yellow oil. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 1.32 (t, J=7.0Hz, 3H), 2.34 (s, 3H), 4.29 (q, J=7.0Hz, 2H), 6.12 (s, 1H), 7.30-7.34 (m, 1H), 7.43-7.47 (m, 2H), 7.57-7.60 (m, 2H). $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 14.0, 14.5, 65.9, 95.3, 122.9, 127.1, 129.1, 137.9, 144.7, 148.9, 150.8. IR (KBr): $\nu$ = 3065, 2984, 2931, 1781, 1598, 1563, 1507, 1443, 1389, 1369, 1301, 1235, 1174, 1160, 1097, 1034, 1019, 983, 970, 892, 761, 693 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{13}$H$_{14}$N$_2$O$_3$Na: 269.0897, found: 269.0898.

3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3a)

Yellow oil. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.26 (s, 3H), 2.34 (s, 3H), 6.10 (s, 1H), 7.31-7.35 (m, 1H), 7.43-7.48 (m, 2H), 7.54-7.56 (m, 2H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 14.5, 20.7, 95.9, 123.0, 127.1, 129.1, 138.1, 144.3, 148.9, 166.1. IR (KBr): $\nu$ = 3066, 2928, 1790, 1596, 1561, 1505, 1439, 1387, 1369, 1186, 1144, 1044, 1024, 1008, 882, 807, 760, 694, 671 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{12}$H$_{12}$N$_2$O$_2$Na: 239.0791, found: 239.0793.
1-(4-chlorophenyl)-3-methyl-1H-pyrazol-5-yl acetate (3b)

Yellow oil. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 2.28 (s, 3H), 2.33 (s, 3H), 6.11 (s, 1H), 7.40-7.44 (m, 2H), 7.50-7.53 (m, 2H). $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 14.5, 20.8, 96.1, 124.1, 129.2, 132.7, 136.6, 144.4, 149.3, 165.9. IR (KBr): $\nu$ = 2928, 1793, 1597, 1586, 1560, 1501, 1473, 1441, 1408, 1387, 1369, 1185, 1143, 1094, 1038, 1014, 974, 881, 832, 808, 780, 686, 515 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{12}$H$_{11}$N$_2$O$_2$ClNa: 273.0401, found: 273.0410.

3 General Procedure for the addition of 1 and 2 to nitroolefins

A vial charged with benzyl (3-methyl-1-phenyl-1H-pyrazol-5-yl) carbonate (1a) (0.5 mmol), DMAP (0.005 mmol) and CH$_2$Cl$_2$ (2 mL) was stirred at room temperature, and then nitroolefins 4 (0.75 mmol) was added. The stirring was maintained for the indicated time. The reaction mixture was directly charged onto silica gel column eluted with hexane/ethyl acetate dichloromethane and methanol to give the corresponding products 5 or 6.

![Structure of Benzyl-5-methyl-4-(2-nitro-1-phenylethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate](structure.png)

Benzyl-5-methyl-4-(2-nitro-1-phenylethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate (5a)

Yellow oil, yield: 98 %. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.60 (s, 3H), 4.59-4.70 (m, 1H), 4.98-5.03 (m, 1H), 5.08-5.08 (m, 2H), 5.48-5.56 (m, 1H), 6.91-7.52 (m, 15H).
$^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.4, 40.1, 69.9, 76.2, 111.3, 122.7, 123.4, 127.0, 127.4, 127.9, 128.0, 128.4, 128.6, 128.8, 129.0, 129.3, 129.3, 133.5, 138.2, 138.3, 149.4, 151.4, 165.8. IR (KBr) $\nu$ 3459, 3064, 3032, 2921, 1876, 1279, 698 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{26}$H$_{23}$N$_3$O$_5$, 480.1530, found: 480.1533.

Benzyl-5-methyl-4-(2-nitro-1-p-tolylethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5b)

Yellow oil, yield: 92%. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.33 (s, 3H), 2.59 (s, 3H), 4.54-4.59 (m, 1H), 4.81-5.03 (m, 1H), 5.07-5.09 (m, 1H), 5.46-5.53 (m, 1H), 6.88-7.39 (m, 14H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.4, 21.1, 39.8, 69.9, 76.3, 111.6, 122.7, 123.3, 126.9, 127.2, 127.7, 128.4, 128.5, 128.8, 129.0, 129.3, 129.7, 129.9, 133.5, 135.2, 137.8, 138.3, 149.5, 151.2, 165.8. IR (KBr) $\nu$ 3064, 3033, 2955, 2933, 2860, 1278, 696 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{27}$H$_{25}$N$_3$O$_5$, 494.1686, found: 494.1689.

Benzyl 4-(1-(2-fluorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5c)

Yellow oil, yield: 92%. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.65 (s, 3H), 4.96-5.06 (m, 2H), 5.09 (s, 2H), 5.48-5.55 (m, 1H), 6.89-7.72 (m, 14H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$
13.4, 13.4, 31.4, 31.4, 70.0, 74.8, 110.0, 115.4, 115.7, 122.7, 123.3, 124.6, 124.8, 124.9, 124.9, 127.0, 128.5, 128.6, 128.8, 129.0, 129.3, 129.4, 129.5, 129.6, 133.5, 138.2, 149.4, 151.8, 158.2, 161.4, 165.7. IR (KBr) \( \nu \) 3066, 3035, 2961, 1750, 1683, 696 cm\(^{-1}\). HRMS [M+Na\(^+\)]: calcd for C\(_{26}\)H\(_{22}\)N\(_3\)O\(_5\)F, 498.1436, found: 498.1436.

Benzyl 4-(1-(4-chlorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate (5d)

Yellow oil, yield: 95%, \(^1\)H NMR (300MHz, CDCl\(_3\)): \( \delta \) 2.59 (s, 3H), 4.55-4.60 (m, 1H), 4.98-5.08 (m, 1H), 5.08 (s, 2H), 5.39-5.46 (m, 1H), 6.89-7.72 (m, 14H). \(^1\)^\(^3\)C NMR (75MHz, CDCl\(_3\)): \( \delta \) 13.4, 39.4, 70.0, 74.8, 110.9, 122.7, 127.1, 128.4, 128.6, 128.8, 129.0, 129.3, 133.4, 133.9, 138.1, 138.7, 149.3, 151.3, 165.7. IR (KBr) \( \nu \) 3066, 3035, 2961, 1750, 1683, 696 cm\(^{-1}\). HRMS [M+Na\(^+\)]: calcd for C\(_{26}\)H\(_{22}\)N\(_3\)O\(_5\)Cl, 514.1140, found: 514.1142.

Benzyl 4-(1-(4-bromophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate (5e)
Yellow oil, yield: 95%. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.59 (s, 3H), 4.55-4.60 (m, 1H), 4.98-5.08 (m, 1H), 5.08 (s, 2H), 5.39-5.46 (m, 1H), 6.88-7.46 (m, 14H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.3, 39.5, 70.0, 71.9, 76.0, 110.8, 122.1, 122.7, 123.3, 127.1, 128.4, 128.6, 128.8, 128.8, 129.1, 129.3, 129.6, 132.3, 133.4, 137.2, 138.1, 149.3, 151.3, 165.6. IR (KBr) $\nu$ 3065, 3034, 2961, 1750, 1683, 695 cm$^{-1}$.

HRMS [M+Na$^+$]: calcd for C$_{26}$H$_{22}$N$_3$O$_5$Br, 558.0635, found: 558.0624.

Benzyl
4-(1-(4-methoxyphenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(5f)

Yellow oil, yield: 85%.$^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.58 (s, 3H), 3.79 (s, 3H), 4.53-4.70 (m, 1H), 4.95-5.02 (m, 1H), 5.07-5.07 (m, 2H), 5.31-5.50 (m, 1H), 6.85-7.43 (m, 14H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.4, 39.4, 55.2, 69.9, 76.4, 111.6, 122.7, 114.3, 114.5, 127.0, 128.4, `28.5, 128.8, 129.0, 129.0, 129.3, 130.2, 133.5, 138.3, 149.5, 151.1, 159.2, 165.8. IR (KBr) $\nu$ 3065, 3034, 2957, 2934, 1683, 695 cm$^{-1}$.

HRMS [M+Na$^+$]: calcd for C$_{27}$H$_{25}$N$_3$O$_6$, 510.1636, found: 510.1642.
Benzyl

4-(1-(3-methoxyphenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate (5g)

Yellow oil, yield: 95%, $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.59 (s, 3H), 3.79 (s, 3H), 4.55-4.60 (m, 1H), 4.98-5.05 (m, 1H), 5.07-5.09 (m, 2H), 5.48-5.54 (m, 1H), 6.82-7.46 (m, 14H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.5, 40.1, 55.3, 69.9, 76.1, 111.3, 113.2, 113.7, 120.0, 122.7, 123.3, 127.0, 127.6, 128.4, 128.5, 129.0, 129.3, 130.3, 133.5, 138.3, 139.7, 149.4, 151.4, 160.1, 165.8. IR (KBr) $\nu$: 3065, 3034, 2960, 2939, 1683, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{27}$H$_{25}$N$_3$O$_6$, 510.1636, found: 510.1637.

Benzyl

5-methyl-4-(1-(naphthalen-1-yl)-2-nitroethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate (5h)

Yellow oil, yield: 85%, $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.55 (s, 3H), 4.88-5.00 (m, 1H), 4.98-5.05 (m, 1H), 5.07 (s, 2H), 5.48-5.54 (m, 1H), 6.82-7.46 (m, 17H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.8, 35.1, 69.9, 75.6, 110.9, 121.9, 122.8, 123.5, 125.8, 126.0, 126.5, 127.0, 127.1, 127.2, 128.4, 128.5, 128.7, 128.7, 128.8, 129.1, 129.6, 130.5,
133.2, 133.5, 134.1, 138.9, 149.4, 152.0, 166.4. IR (KBr) ν 3063, 3037, 2961, 2921, 1683, 696 cm⁻¹. HRMS [M+Na⁺]: calcd for C₃₀H₂₅N₃O₅, 530.1686, found: 510.1683.

**Benzyl**

4-(1-(furan-2-yl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate (5i)

Yellow oil, yield: 83 %, ¹H NMR (300MHz, CDCl₃): δ 2.60 (s, 3H), 4.80-4.83 (m, 1H), 4.99-5.06 (m, 1H), 5.10-5.12 (m, 2H), 5.26-5.34 (m, 1H), 6.26-7.38 (m, 13H). ¹³C NMR (75 MHz, CDCl₃): δ 13.4, 33.4, 70.0, 76.6, 107.5, 108.9, 110.8, 126.9, 128.4, 128.6, 128.8, 129.0, 133.4, 138.2, 142.2, 149.4, 149.8, 152.0, 165.2. IR (KBr) ν 3147, 3177, 3065, 3035, 1693, 696 cm⁻¹. HRMS [M+Na⁺]: calcd for C₂₄H₂₁N₃O₆, 470.1323, found: 470.1322.

**Benzyl**

5-methyl-4-(2-nitro-1-(thiophen-2-yl)ethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate (5j)

Yellow oil, yield: 76 %, ¹H NMR (300MHz, CDCl₃): δ 2.61 (s, 3H), 4.89-5.03 (m, 2H), 5.09-5.11 (m, 2H), 5.43-5.50 (m, 1H), 6.89-7.41 (m, 13H). ¹³C NMR (75 MHz, CDCl₃): δ 13.4, 34.8, 70.0, 76.2, 110.9, 122.7, 123.3, 125.1, 126.0, 127.0, 127.4, 128.4, 128.6, 128.8, 129.0, 133.4, 138.2, 139.6, 149.4, 151.3, 165.3. IR (KBr) ν
3090, 3067, 3035, 2959, 1683, 698 cm\(^{-1}\). HRMS [M+Na\(^+\)]: calcd for C\(_{24}H_{21}N_3O_5S\), 486.1094, found: 486.1096.

![Chemical structure](image1)

**Benzyl**

\(2-(4\text{-chlorophenyl})-5\text{-methyl}-4\text{-}(2\text{-nitro-1-phenylethyl})-3\text{-oxo-2,3-dihydropyrazole-1-carboxylate}(5k)\)

Yellow oil, yield: 92\%, \(^1H\) NMR (300MHz, CDCl\(_3\)): \(\delta\) 2.60 (s, 3H), 4.58-4.69 (m, 1H), 4.94-5.00 (m, 1H), 5.09-5.14 (m, 2H), 5.48-5.56 (m, 1H), 6.94-7.49 (m, 14H). \(^{13}\)C NMR (75MHz, CDCl\(_3\)): \(\delta\) 13.5, 40.1, 65.3, 76.1, 111.4, 124.6, 127.0, 127.8, 128.1, 128.6, 129.0, 129.1, 129.3, 129.3, 132.6, 133.3, 136.7, 138.0, 149.3, 151.8, 165.7. IR (KBr) \(\nu\) 3090, 3064, 2961, 1751, 699 cm\(^{-1}\). HRMS [M+Na\(^+\)]: calcd for C\(_{26}H_{22}N_3O_5Cl\), 514.1140, found: 514.1129.

![Chemical structure](image2)

**Benzyl**

\(2-(4\text{-chlorophenyl})-4\text{-}(1\text{-}(2\text{-fluorophenyl})-2\text{-nitroethyl})-5\text{-methyl-3-oxo-2,3-dihydropyrazole-1-carboxylate}(5l)\)

Yellow oil, yield: 93\%, \(^1H\) NMR (300MHz, CDCl\(_3\)): \(\delta\) 2.64 (s, 3H), 4.91-5.06 (m, 2H), 5.10-5.10 (m, 2H), 5.17-5.22 (m, 1H), 5.48-5.55 (m, 1H), 6.94-7.65 (m, 13H). \(^{13}\)C
NMR (75MHz, CDCl₃): δ 13.4, 13.4, 31.4, 31.4, 70.1, 74.7, 110.0, 115.5, 115.8, 124.5, 124.9, 127.0, 128.6, 128.6, 128.7, 129.0, 129.1, 129.2, 129.3, 129.5, 129.8, 132.6, 133.3, 136.6, 149.2, 152.2, 152.6, 161.4, 165.5. IR (KBr) ν 3091, 3066, 2958, 1750, 698 cm⁻¹. HRMS [M+Na⁺]: calcd for C₂₆H₂₁N₃O₅ClF, 532.1046, found: 532.1046.

Benzyl

2-(4-chlorophenyl)-4-(1-(2-chlorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2,3-dihydropyrazole-1-carboxylate(5m)

Yellow oil, yield: 92%. ¹H NMR (300MHz, CDCl₃): δ 2.66 (s, 3H), 4.80-4.86 (m, 1H), 5.10-5.10 (m, 2H), 5.17-5.22 (m, 1H), 5.49-5.57 (m, 1H), 6.93-7.40 (m, 13H). ¹³C NMR (75MHz, CDCl₃): δ 14.0, 35.7, 70.1, 74.9, 110.9, 124.6, 127.0, 127.7, 128.6, 128.7, 129.0, 129.1, 129.3, 129.4, 129.9, 132.7, 133.0, 133.3, 134.9, 136.6, 149.2, 152.7, 165.7. IR (KBr) ν 3092, 3064, 2956, 1750, 698 cm⁻¹. HRMS [M+Na⁺]: calcd for C₂₆H₂₁N₃O₅Cl₂, 548.0750, found: 548.0742.

Tert-butyl-5-methyl-4-(2-nitro-1-phenylethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6a)

Yellow oil, yield: 90%. ¹H NMR (300MHz, CDCl₃): 1.21-1.28 (m, 9H), 2.59 (s, 3H),
4.58-4.63 (m, 1H), 5.00-5.06 (m, 1H), 5.50-5.57 (m, 1H), 7.30-7.54 (m, 10H). \(^{13}\)C NMR (75MHz, CDCl\(_3\)): \(\delta\) 13.5, 27.5, 40.1, 76.2, 86.4, 110.6, 124.5, 127.9, 128.0, 129.0, 129.3, 132.3, 137.0, 138.3, 147.5, 151.6, 165.2. IR (KBr) \(\nu\) 3071, 2980, 2933, 1749, 699 cm\(^{-1}\). HRMS [M+Na\(^{+}\)]: calcd for C\(_{23}\)H\(_{25}\)N\(_3\)O\(_5\), 446.1486, found: 446.1687.

**Tert-butyl**

4-(1-(4-fluorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6b)

Yellow oil, yield: 92 %. \(^1\)H NMR (300MHz, CDCl\(_3\)): \(\delta\) 1.21-1.29 (m, 9H), 2.58 (s, 3H), 4.56-4.61 (m, 1H), 5.00-5.07 (m, 1H), 5.41-5.48 (m, 1H), 7.15-7.45 (m, 9H). \(^{13}\)C NMR (75MHz, CDCl\(_3\)): \(\delta\) 13.2, 27.4, 39.4, 76.4, 86.1, 110.3, 115.9, 116.3, 123.4, 126.9, 129.6, 129.7, 134.2, 134.3, 138.3, 147.5, 150.9, 160.6, 163.9, 165.1. IR (KBr) \(\nu\) 3071, 2980, 2933, 1749, 699 cm\(^{-1}\). HRMS [M+Na\(^{+}\)]: calcd for C\(_{23}\)H\(_{24}\)N\(_3\)O\(_5\)F, 464.1592, found: 464.1597.

**Tert-butyl**

4-(1-(4-chlorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6c)

Yellow oil, yield: 94%. \(^1\)H NMR (300MHz, CDCl\(_3\)): \(\delta\) 1.21-1.28 (m, 9H), 2.58 (s, 3H),
4.55-4.60 (m, 1H), 5.01-5.07 (m, 1H), 5.40-5.48 (m, 1H), 7.27-7.49 (m, 8H). $^{13}$C NMR (75MHz, CDCl$_3$): δ 13.3, 27.4, 29.7, 39.5, 76.2, 86.2, 110.0, 123.4, 126.9, 128.8, 129.3, 133.9, 137.0, 138.3, 147.5, 151.0, 165.1. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{23}$H$_{24}$N$_3$O$_5$Cl, 480.1297, found: 480.1305.

Tert-butyl

4-(1-(4-bromophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6d)

Yellow oil, yield: 98%, $^1$H NMR (300MHz, CDCl$_3$): δ 1.21-1.29 (m, 9H), 2.58 (s, 3H), 4.53-4.59 (m, 1H), 5.01-5.07 (m, 1H), 5.40-5.48 (m, 1H), 7.17-7.51 (m, 9H). $^{13}$C NMR (75MHz, CDCl$_3$): δ 13.3, 27.1, 27.4, 29.7, 39.6, 76.1, 86.2, 109.9, 122.0, 122.8, 123.4, 126.9, 128.8, 129.2, 129.3, 129.6, 132.3, 137.5, 138.2, 147.5, 151.0, 165.1. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{24}$H$_{27}$N$_3$O$_6$, 476.1792, found: 476.1789.

Tert-butyl

4-(1-(4-methoxyphenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6e)
Yellow oil, yield: 98%, $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 1.27-1.27 (m, 9H), 2.58 (s, 3H), 3.82 (s, 3H), 4.54-4.59 (m, 1H), 4.96-5.04 (m, 1H), 5.41-5.48 (m, 1H), 7.22-7.46 (m, 8H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.3, 27.4, 39.5, 55.3, 77.2, 86.0, 110.7, 114.5, 123.3, 126.8, 128.2, 128.8, 129.0, 130.5, 138.4, 147.6, 150.8, 159.2, 165.3. IR (KBr) $\nu$ 3071, 2980, 2933, 1749, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{23}$H$_{24}$N$_3$O$_5$Br, 526.0775, found: 526.0765.

Tert-butyl

4-(1-(2-chlorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6f)

Yellow oil, yield: 96%, $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 1.22-1.24 (m, 9H), 2.65 (s, 3H), 4.84-4.90 (m, 1H), 5.20-5.24 (m, 1H), 5.52-5.60 (m, 1H), 7.22-7.86 (m, 8H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.8, 27.4, 35.8, 75.1, 86.1, 108.9, 123.4, 126.8, 127.7, 128.8, 129.1, 129.8, 130.1, 130.3, 132.9, 135.4, 138.4, 147.4, 151.9, 165.4. IR (KBr) $\nu$ 3071, 2980, 2933, 1749, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{23}$H$_{24}$N$_3$O$_5$Cl, 480.1297, found: 480.1302.

Tert-butyl

5-methyl-4-(1-(naphthalen-1-yl)-2-nitroethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole
**e-1-carboxylate(6g)**

Yield oil, yield: 82%. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 1.21-1.28 (m, 9H), 2.55 (s, 3H), 4.89-4.95 (m, 1H), 5.52-5.57 (m, 1H), 5.76-5.83 (m, 1H), 7.32-8.27 (m, 12H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.7, 27.4, 35.0, 75.8, 86.0, 109.9, 122.0, 123.5, 125.8, 125.9, 126.6, 126.9, 127.1, 128.6, 128.8, 129.3, 129.5, 130.6, 133.5, 134.1, 138.5, 151.6, 165.8. IR (KBr) $\nu$ 3071, 2980, 2933, 1749, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{27}$H$_{27}$N$_3$O$_5$, 496.1843, found: 496.1839.

![Chemical structure](image)

**Tert-butyl**

4-(1-(furan-2-yl)-2-nitroethyl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate(6h)

Yellow oil, yield: 65%. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 1.23-1.27 (m, 9H), 2.59 (s, 3H), 4.79-4.84 (m, 1H), 5.01-5.08 (m, 1H), 5.28-5.36 (m, 1H), 6.29-7.49 (m, 7H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.3, 27.4, 33.4, 74.3, 86.9, 107.4, 107.9, 110.8, 123.2, 126.8, 128.8, 138.4, 142.1, 147.6, 150.1, 151.6, 164.7. IR (KBr) $\nu$ 3071, 2980, 2933, 1749, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{21}$H$_{23}$N$_3$O$_6$, 436.1479, found: 436.1471.

![Chemical structure](image)

**Tert-butyl**

5-methyl-4-(2-nitro-1-(thiophen-2-yl)ethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-
1-carboxylate(6i)

Yellow oil, yield: 70%. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 1.22-1.28 (m, 9H), 2.60 (s, 3H), 4.89-5.04 (m, 2H), 5.44-5.51 (m, 1H), 6.95-7.45 (m, 8H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.2, 27.4, 34.8, 76.4, 86.1, 109.9, 123.3, 124.9, 126.8, 127.4, 128.8, 138.4, 139.9, 147.6, 151.0, 164.7. HRMS [M+Na$^+$]: calcd for C$_{21}$H$_{23}$N$_3$O$_5$S, 452.1251, found: 436.1247.

![Diagram](image)

Tert-butyl

2-(4-chlorophenyl)-5-methyl-4-(2-nitro-1-phenylethyl)-3-oxo-2,3-dihydropyrazole-1-carboxylate(6j)

White solid, yield: 94%. m.p. 114-115 °C. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 1.27-1.28 (m, 9H), 2.58 (s, 3H), 4.57-4.62 (m, 1H), 4.96-5.03 (m, 1H), 5.50-5.57 (m, 1H), 7.23-7.52 (m, 9H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.4, 27.5, 40.1, 76.2, 86.3, 110.6, 124.5, 127.8, 128.0, 128.9, 129.2, 132.3, 138.3, 139.0, 147.5, 151.6, 165.3. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{23}$H$_{24}$N$_3$O$_5$Cl, 480.1297, found: 480.1302.

![Diagram](image)

Tert-butyl

2-(4-chlorophenyl)-4-(1-(4-chlorophenyl)-2-nitroethyl)-5-methyl-3-oxo-2,3-dihydropyrazole
ropyrzole-1-carboxylate(6k)

Yellow solid. Yield: 95%. M.p. 122-123 °C. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 1.27-1.27 (m, 9H), 2.58 (s, 3H), 4.58-4.59 (m, 1H), 4.96-5.04 (m, 1H), 5.41-5.48 (m, 1H), 7.22-7.46 (m, 8H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.2, 27.4, 34.8, 76.4, 86.1, 109.9, 123.3, 124.9, 126.0, 126.8, 127.4, 128.8, 138.4, 139.9, 147.6, 151.0, 164.7. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{23}$H$_{23}$N$_3$O$_5$Cl$_2$, 514.0907, found: 514.0909.

![nitrile](image1.png)

Tert-butyl

4-(1-(4-bromophenyl)-2-nitroethyl)-2-(4-chlorophenyl)-5-methyl-3-oxo-2,3-dihydropyrzole-1-carboxylate(6l)

Yellow solid, yield: 92%, M.p. 128-129 °C. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 1.26-1.34 (m, 9H), 2.57 (s, 3H), 4.53-4.58 (m, 1H), 4.97-5.03 (m, 1H), 5.40-5.49 (m, 1H), 7.22-7.49 (m, 8H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.3, 27.4, 40.2, 76.3, 86.0, 110.4, 123.4, 126.8, 127.9, 127.9, 128.8, 129.0, 129.2, 129.3, 138.4, 138.5, 147.6, 151.0, 165.2. IR (KBr) ν 3071, 2980, 2933, 1749, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{23}$H$_{23}$N$_3$O$_5$ClBr, 558.0402, found: 558.0384.

![nitrile](image2.png)

Ethyl
5-methyl-4-(2-nitro-1-phenylethyl)-3-oxo-2-phenyl-2,3-dihydropyrazole-1-carboxylate (6m)

Yellow oil, yield: 98%, $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 0.96-1.01 (m, 3H), 2.60 (s, 3H), 4.09-4.16 (m, 2H), 4.53-4.63 (m, 1H), 4.98-5.05 (m, 1H), 5.51-5.59 (m, 1H), 7.32-7.59 (m, 10H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.3, 13.5, 39.6, 64.4, 76.0, 110.6, 122.1, 123.4, 127.1, 128.9, 129.6, 132.3, 137.3, 138.1, 149.3, 151.1, 165.5. IR (KBr) $\nu$ 3071, 2980, 2933, 1749, 699 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{21}$H$_{21}$N$_3$O$_5$, 418.1373, found: 418.1376.

4 General procedure for the addition of 3 to nitroolefins

A vial charged with benzyl 3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3a) (0.5 mmol), DMAP (0.005 mmol) and CH$_2$Cl$_2$ (2 mL) was stirred at room temperature, and then nitroolefins 4 (0.75 mmol) was added. The stirring was maintained for the indicated time. The reaction mixture was directly charged onto silica gel column eluted with hexane/ethyl acetate to give the corresponding products 7.

![Chemical structure](attachment:image.png)

3-methyl-4-(2-nitro-1-phenylethyl)-1-phenyl-1H-pyrazol-5-yl acetate (7a)

Yellow solid, yield 95 %. M.p. 110-112 °C. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.12 (s, 3H), 2.19 (s, 3H), 4.84-4.91 (m, 2H), 4.99-5.05 (m, 1H), 7.28-7.38 (m, 6H), 7.42-7.48 (m, 4H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.4, 20.2, 38.6, 77.2, 106.7, 123.0, 127.4, 127.7, 129.0, 129.3, 137.6, 141.8, 147.5, 167.3. IR (KBr): $\nu$ = 3063, 2922, 1792, 1596, 1554, 1502, 1453, 1374, 1168, 757, 697 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{20}$H$_{19}$N$_3$O$_4$Na: 388.1268, found: 388.1270.
4-(1-(2-chlorophenyl)-2-nitroethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (7b)

Yellow oil, yield 92 %. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.08 (s, 3H), 2.24 (s, 3H), 4.81-4.88 (m, 1H), 4.96-5.03 (m, 1H), 5.23-5.30 (m, 1H), 7.23-7.49 (m, 9H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.3, 20.3, 36.0, 75.5, 105.0, 123.1, 127.1, 127.7, 127.9, 129.1, 129.2, 130.4, 134.1, 134.8, 137.6, 142.0, 147.8, 167.3. IR (KBr): $\nu$ = 3065, 2924, 1792, 1597, 1555, 1505, 1475, 1375, 1168, 1040, 758, 737, 695 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{20}$H$_{18}$ClN$_3$O$_4$Na: 422.0878, found: 422.0876.

4-(1-(4-chlorophenyl)-2-nitroethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (7c)

Yellow oil, yield 94 %. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.15 (s, 3H), 2.17 (s, 3H), 4.79-4.89 (m, 2H), 4.93-5.02 (m, 1H), 7.21-7.46 (m, 9H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.4, 20.3, 38.2, 77.0, 106.3, 123.0, 127.8, 128.8, 129.1, 129.3, 133.6, 136.2, 137.5, 141.8, 147.3, 167.4. IR (KBr): $\nu$ = 3066, 2925, 1792, 1721, 1597, 1556, 1505, 1494, 1435, 1375, 1168, 1093, 1014, 911, 886, 824, 760, 734, 695 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{20}$H$_{18}$ClN$_3$O$_4$Na: 422.0878, found: 422.0876.
3-methyl-4-(2-nitro-1-p-tolylethyl)-1-phenyl-1H-pyrazol-5-yl acetate (7d)

Yellow oil, yield 73 %. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.13 (s, 3H), 2.19 (s, 3H), 2.34 (s, 3H), 4.78-4.89 (m, 2H), 4.94-5.03 (m, 1H), 7.13-7.19 (brs, 4H), 7.40-7.48 (m, 5H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.4, 20.3, 21.0, 38.4, 77.3, 106.8, 123.0, 127.2, 127.6, 129.2, 129.6, 134.6, 137.3, 137.7, 141.7, 147.5, 167.3. IR (KBr): $\nu$ = 3027, 2923, 1792, 1598, 1555, 1434, 1375, 1323, 1168, 1072, 1006, 886, 814, 759, 696 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{21}$H$_{21}$N$_3$O$_4$Na: 402.1424, found: 402.1427.

4-(1-(2-fluorophenyl)-2-nitroethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (7e)

Yellow oil, yield 82 %. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.13 (s, 3H), 2.28 (s, 3H), 4.88-4.95 (m, 1H), 5.02-5.12 (m, 2H), 7.06-7.46 (m, 9H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.2, 20.2, 33.0, 75.8, 105.3, 116.0, 116.3, 123.0, 124.4, 124.5, 127.7, 128.3, 128.4, 129.2, 129.5, 129.6, 137.6, 141.9, 147.4, 158.9, 162.2, 167.1. IR (KBr): $\nu$ = 3067, 2925, 1793, 1724, 1597, 1585, 1557, 1505, 1493, 1456, 1435, 1376, 1234, 1168, 1108, 1046, 1006, 912, 885, 808, 759, 735, 695 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{20}$H$_{18}$FN$_3$O$_4$Na: 406.1174, found: 406.1176.
4-(1-(3-fluorophenyl)-2-nitroethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (7f)

Yellow oil, yield 88 %. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.14 (s, 3H), 2.18 (s, 3H), 4.81-4.89 (m, 2H), 4.95-5.03 (m, 1H), 6.97-7.08 (m, 5H); 7.28-7.47 (m, 4H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.3, 20.2, 38.4, 76.9, 106.2, 114.5, 114.6, 114.8, 114.9, 123.1, 127.8, 129.0, 129.3, 130.5, 130.6, 137.5, 140.2, 140.3, 141.8, 147.3, 161.4, 164.6, 167.3. IR (KBr): $\nu$ = 3066, 2925, 1792, 1613, 1595, 1555, 1505, 1491, 1375, 1257, 1168, 1047, 1006, 883, 786, 759, 696 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{20}$H$_{18}$FN$_3$O$_4$Na: 406.1174, found: 406.1179.

4-(1-(4-fluorophenyl)-2-nitroethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (7g)

Yellow oil, yield 83 %. $^1$H NMR (300MHz, CDCl$_3$): $\delta$ 2.14 (s, 3H), 2.16 (s, 3H), 4.79-4.89 (m, 2H), 4.92-5.01 (m, 1H), 7.01-7.07 (m, 2H), 7.23-7.36 (m, 2H), 7.40-7.49 (m, 5H). $^{13}$C NMR (75MHz, CDCl$_3$): $\delta$ 13.4, 20.3, 38.1, 77.2, 106.6, 115.7, 116.0, 123.0, 127.8, 129.0, 129.3, 133.4, 133.5, 137.6, 141.7, 160.4, 163.7, 167.4. IR (KBr): $\nu$ = 3070, 2925, 1792, 1598, 1555, 1507, 1475, 1434, 1375, 1228, 1167, 1136, 1046, 1006, 912, 886, 836, 804, 760, 733, 696 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{20}$H$_{18}$FN$_3$O$_4$Na: 406.1174, found: 406.1175.
4-(1-(4-bromophenyl)-2-nitropropyl)-1-(4-chlorophenyl)-3-methyl-1H-pyrazol-5-yl acetate(7h)

White solid, yield 90 %. M.p. 135-136 °C. \( ^1 \)H NMR (300MHz, CDCl\(_3\)): \( \delta \) 1.52-1.54 (m, 3H), 2.22 (s, 3H), 2.28 (s, 3H), 4.32-4.37 (m, 1H), 5.24-5.28 (m, 1H), 7.14-7.17 (m, 2H), 7.40 (s, 4H), 7.49-7.52 (m, 2H). \( ^{13} \)C NMR (75MHz, CDCl\(_3\)): \( \delta \) 13.5, 19.7, 20.5, 45.4, 84.2, 107.2, 121.8, 124.3, 129.5, 130.0, 132.3, 133.4, 136.9, 147.8, 166.8.

IR (KBr): \( \nu = \) 3097, 3027, 2954, 2924, 2860, 1793, 1730, 1686, 1597, 1579, 1555, 1502, 1467, 1438, 1407, 1374, 1319, 1288, 1166, 1093, 1044, 1012, 910, 886, 833, 733, 691, 649, 503 cm\(^{-1}\). HRMS [M+Na\(^{+}\)]: calcd for C\(_{21}\)H\(_{20}\)ClN\(_3\)O\(_4\)Na: 436.1035, found: 436.1037.

5 X-ray analysis

2a CCDC: 874014
**6j** CCDC: 861353

**7h** CCDC: 874398
Electronic Supplementary Material (ESI) for RSC Advances
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6 NMR Spectra of 1–3 and 5–7

$^1$H and $^{13}$C of 1a
$^1\text{H}$ and $^{13}\text{C}$ of 1b
$^1$H and $^{13}$C of 2a
$^1$H and $^{13}$C of 2b
$^1$H and $^{13}$C of 2c
$^1$H and $^{13}$C of 3a
$^1$H and $^{13}$C of 3b
$^1$H and $^{13}$C of 5a
$^1$H and $^{13}$C of 5b
\( ^1H \) and \( ^{13}C \) of 5c
$^1$H and $^{13}$C of 5d
$^{1}H$ and $^{13}C$ of 5e
$^{1}H$ and $^{13}C$ of 5f
$^1$H and $^{13}$C of 5g

Electronic Supplementary Material (ESI) for RSC Advances
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$^1$H and $^{13}$C of 5h
$^{1}H$ and $^{13}C$ of 5i
$^1$H and $^{13}$C of 5j
$^1$H and $^{13}$C of 5k
$^1$H and $^{13}$C of 5l
$^1$H and $^{13}$C of 5m
$^1$H and $^{13}$C of 6a
$^1$H and $^{13}$C of 6b
$^1$H and $^{13}$C of 6c
$^1$H and $^{13}$C of 6d
$^1$H and $^{13}$C of 6f
$^1$H and $^{13}$C of 6g
$^1$H and $^{13}$C of 6h
$^1$H and $^{13}$C of 6i
$^1$H and $^{13}$C of 6j
$^1\text{H}$ and $^{13}\text{C}$ of 6k
$^1$H and $^{13}$C of 6l
$^1$H and $^{13}$C of 6m
$^1$H and $^{13}$C of 7a
$^1\text{H}$ and $^{13}\text{C}$ of 7b
$^1$H and $^{13}$C of 7c
$^1$H and $^{13}$C of 7d
$^1$H and $^{13}$C of 7e
$^1$H and $^{13}$C of 7f
$^1$H and $^{13}$C of 7g
$^1\text{H}$ and $^{13}\text{C}$ of 7h