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Supplementary Information

Regioselective carboannulation of electron-deficient allenes with dialkyl (2-

formylphenyl)malonates leading to multisubstituted naphthalenes

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1	General procedure for the synthesis compounds 1 and 2	S1
2	Copies of ¹ H/ ¹³ C/ ³¹ P NMR Spectra	S2-S83

General procedure for the synthesis of carboxylic acid precursors to 1j and 1k:

Compounds 2-(1,3-diisopropoxy-1,3-dioxopropan-2-yl)benzoic acid and 2-(1,3-di-*tert*-butoxy-1,3-dioxopropan-2-yl)benzoic acid were prepared by a literature procedure.^{11b}



2-(1,3-Diisopropoxy-1,3-dioxopropan-2-yl)benzoic acid (precursor to 1j). Yield 1.5 g (using 6.66 mmol of 2,4-dimethylbenzoic acid), 67% (white solid): mp 150-152 0 C; IR (KBr, cm⁻¹) 2981, 1731, 1611, 1375, 1178, 1101, 1025, 833, 731; ¹H NMR (400 MHz, CDCl₃) δ 7.15 (s, 1H), 7.08 (s, 1H), 5.18-5.08 (m, 2H), 4.97 (s, 1H), 2.48 (s, 3H), 2.37 (s, 3H), 1.30 (d, *J* = 6.2 Hz, 6H), 1.27 (d, *J* = 6.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 172.2, 167.9, 140.8, 137.4, 131.9, 131.6, 129.1, 127.9, 69.6, 56.0, 21.6, 21.5, 21.3, 21.0; HRMS (ESI) Calcd. for C₁₈H₂₄O₆Na [M⁺+Na]: *m*/*z* 359.1471. Found: 359.1474.



2-(1,3-Di-tert-butoxy-1,3-dioxopropan-2-yl)benzoic acid (precursor to 1k). Yield 1.6 g (using 6.66 mmol of 2,4-dimethylbenzoic acid), 66% (white gummy solid): IR (neat, cm⁻¹) 2981, 1731, 1616, 1457, 1375, 1299, 1129, 1036, 855, 734; ¹H NMR (400 MHz, CDCl₃) δ 7.17 (s, 1H), 7.06 (s, 1H), 4.87 (s, 1H), 2.48 (s, 3H), 2.37 (s, 3H), 1.5 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 173.3, 167.8, 140.7, 137.4, 132.6, 131.4, 129.2, 127.7, 82.4, 57.6, 27.9, 21.4, 21.1; HRMS (ESI) Calcd. for C₂₀H₂₉O₆ [M⁺+H]: *m/z* 365.1964. Found: 365.1959.



Figure S2. ¹H NMR spectrum of compound 163



Figure S3. ¹³C NMR spectrum of compound 163



Figure S4. ¹H NMR spectrum of compound 164



Figure S5. ¹³C NMR spectrum of compound 164



Figure S6. ¹H NMR spectrum of compound 1b



Figure S7. ¹³C NMR spectrum of compound 1b







Figure S9. ¹³C NMR spectrum of compound 1c







Figure S11. ¹³C NMR spectrum of compound 1d



Figure S12. ¹H NMR spectrum of compound 1e



Figure S14. ¹³C NMR spectrum of compound 1f



Figure S15. ¹³C NMR spectrum of compound 1f



Figure S16. ¹³C NMR spectrum of compound 1g



Figure S17. ¹³C NMR spectrum of compound 1g



Figure S18. ¹HNMR spectrum of compound 1h



Figure S19. ¹³C NMR spectrum of compound 1h



Figure S20. ¹HNMR spectrum of compound 1i

Figure S22. ¹H NMR spectrum of compound 1j

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Figure S23. ¹³C NMR spectrum of compound 1j

Figure S24. ¹H NMR spectrum of compound 1k

Figure S25. ¹³C NMR spectrum of compound 1k

Figure S26. ¹H NMR spectrum of compound 3aa

Figure S27. ¹³C NMR spectrum of compound 3aa

Figure S28. ¹H NMR spectrum of compound 3ab

Figure S29. ¹³C NMR spectrum of compound 3ab

Figure S30. ¹H NMR spectrum of compound 3ac

Figure S31. ¹³C NMR spectrum of compound 3ac

Figure S32. ¹H NMR spectrum of compound 3ad

Figure S33. ¹³C NMR spectrum of compound 3ad

Figure S34. ¹H NMR spectrum of compound 3ba

Figure S35. ¹³C NMR spectrum of compound 3ba

Figure S36. ¹H NMR spectrum of compound 3ca

Figure S37. ¹³C NMR spectrum of compound 3ca

Figure S38. ¹H NMR spectrum of compound 3da

Figure S39. ¹³C NMR spectrum of compound 3da

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Figure S40. ¹H NMR spectrum of compound 3ea

Figure S41. ¹³C NMR spectrum of compound 3ea

Figure S42. ¹H NMR spectrum of compound 3fa

Figure S43. ¹³C NMR spectrum of compound 3fa

Figure S44. ¹H NMR spectrum of compound 3ga

Figure S45. ¹³C NMR spectrum of compound 3ga

Figure S46. ¹H NMR spectrum of compound 3ha

Figure S47. ¹³C NMR spectrum of compound 3ha

Figure S48. ¹H NMR spectrum of compound 3ic

Figure S49. ¹³C NMR spectrum of compound 3ic

Figure S50. ¹H NMR spectrum of compound 3jc

Figure S51. ¹³C NMR spectrum of compound 3jc

Figure S52. ¹H NMR spectrum of compound 3kc

Figure S54. ¹H NMR spectrum of compound 3ae

Figure S55. ¹³C NMR spectrum of compound 3ae

Figure S56. ³¹P NMR spectrum of compound 3ae

Figure S58. ¹³C NMR spectrum of compound 3af

Figure S60. ¹H NMR spectrum of compound 3ag

Figure S61. ¹³C NMR spectrum of compound 3ag

Figure S62. ³¹P NMR spectrum of compound 3ag

Figure S63. ¹H NMR spectrum of compound 3ah

Figure S64. ¹³C NMR spectrum of compound 3ah

Figure S65. ¹H NMR spectrum of compound 4ah

Figure S66. ¹³C NMR spectrum of compound 4ah

Figure S67. ¹H NMR spectrum of compound 3ai

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![](_page_35_Figure_3.jpeg)

Figure S68. ¹³C NMR spectrum of compound 3ai

![](_page_36_Figure_0.jpeg)

Figure S70. ¹³C NMR spectrum of compound 4ai

![](_page_37_Figure_0.jpeg)

![](_page_37_Figure_1.jpeg)

Figure S72. ¹³C NMR spectrum of compound 3aj

![](_page_38_Figure_0.jpeg)

Figure S73. ¹H NMR spectrum of compound 4aj

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![](_page_38_Figure_3.jpeg)

Figure S74. ¹³C NMR spectrum of compound 4aj

![](_page_39_Figure_0.jpeg)

Figure S76. ¹³C NMR spectrum of compound 3ak

![](_page_40_Figure_0.jpeg)

Figure S77. ¹H NMR spectrum of compound 4ak

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![](_page_40_Figure_3.jpeg)

Figure S78. ¹³C NMR spectrum of compound 4ak

![](_page_41_Figure_0.jpeg)

Figure S80. ¹³C NMR spectrum of compound 3ij

![](_page_42_Figure_0.jpeg)

Figure S81. ¹H NMR spectrum of compound 5

![](_page_42_Figure_2.jpeg)

Figure S82. ¹³C NMR spectrum of compound 5

![](_page_43_Figure_0.jpeg)

Figure S83. ³¹P NMR spectrum of compound 5